# Studies in the chemistry of the nitrogen-halogen bond

N. D. Cowan

Cowan, N. D. (1977) Studies in the chemistry of the nitrogen-halogen bond. Doctoral thesis, Durham University.

# ABSTRACT

The reactions of dimethylchloramine with a variety of different substrates has been studied.

With basic substrates such as hydrazine and the alkyl substituted hydrazines, dimethylchloramine acts as an oxidising agent, but with ammonia and the methylamines contrast was found with the corresponding $NH_2Cl$ reactions. Simple nucleophillic attack of the amine on the dimethylchloramine nitrogen explains the products found in the reactions with $CH_3NH_2$ and $NH_3$, whilst dehydrohalegonation reaction accounts for the observed products. With dimethylamine a complex reaction occurs which is most probably intimately associated with the decomposition of $(CH_3)_2NCl$ itself.

Dimethylchloramine reacts in two different ways with methyl esters of certain acids. On the one hand, esters typified by $CH_3OSO_2F$, and including $CH_3OClO_3$, yielding a cationic species identified as $(CH_3)_3\overset{+}{N}Cl$.

In this cation, the nitrogen chlorine bond possesses a slight dipole, the positive end of which is directed towards the chlorine atom, in accord with the $^{35}Cl$ NQR absorption frequency of 56.09 MHz, found in the $ClO_4^-$, $(CH_3)_3\overset{+}{N}Cl\ ClO_4^-$, being in excess of that found for $Cl_2$. The application of standard approximate methods to the observed coupling constants for the $ClO_4^-$ and $BF_4^-$ indicate that the bonding between the nitrogen and chlorine atoms in the cation involves an almost pure chlorine p orbital.

The ion, $(CH_3)_3\overset{+}{N}Cl$, is precipitable from aqueous solutions of the chlorine trimethylamine complex, $(CH_3)_3NCl_2$, by $ClO_4^-$ and $BF_4^-$ ions.

With the methyl halides, dimethylchloramine reacts to yield, with methyl bromide, the addition complex of trimethylamine, $(CH_3)_3NBrCl$, the infra red spectrum of which fits well with the trends observed for other $(CH_3)_3N$ (Halogen)$_2$ addition complexes, whilst with methyl iodide, a novel tetramethylammonium pseudopolyhalide, $(CH_3)_4\overset{+}{N}[(CH_3)_2N(ICl)_2]^-$, forms.

Dimethyl bromamine, $(CH_3)_2NBr$, reacts in a similar way to $(CH_3)_2NCl$, with alkylating agents, the unstable $(CH_3)_3\overset{+}{N}Br\ OSO_2F^-$ forms with $CH_3OSO_2F$ and $(CH_3)_3\overset{+}{N}Br\ ClO_4^-$ can be precipitated from aqueous solutions of the fluorosulphate by $ClO_4^-$ ions. With $CH_3I$, $(CH_3)_2NBr$ yields, in a similar way to $(CH_3)_2NCl$, $(CH_3)_4\overset{+}{N}[(CH_3)_2N(IBr)_2]^-$.

# STUDIES IN THE CHEMISTRY

# OF THE

# NITROGEN-HALOGEN BOND

A THESIS PRESENTED BY

N. D. COWAN

FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

OF THE UNIVERSITY OF DURHAM

DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF DURHAM,
DECEMBER, 1977.

TO MY MOTHER AND FATHER

# ACKNOWLEDGEMENTS

The Author would like to thank Professor T. C. Waddington, and Dr. J. C. Ludman of the Chemistry Department, University of Durham, for their help and guidance during the completion of this work.

I would also like to thank Dr. N. W. Alcock and his team at Warwick University for the crystallographic work carried out on the compound described in Chapter Five.

Acknowledgement is also due to my wife, for assistance in preparing the diagrams and Miss S. C. Wayman for typing the manuscript.

This work was carried out under a research studentship from the Science Research Council.

# CONTENTS

# CHAPTER ONE

## INTRODUCTION

# INTRODUCTION

The study of N-Halamines covers a very broad area of chemistry, from the use of $NCl_3$ as a bleaching agent for flour, through their use as precursors to hydrazines, important in rocket propellants to reactions involving alkylamino steriods.

N-Halamines, as a class of halogen derivatives of nitrogen, have been discussed by Mellor (1) and Gmelin (2), and much early work on $NCl_3$ has been reviewed by Sneldes (3). Almost certainly the best described member of the Halamine class, chloramine, $NH_2Cl$, has been reviewed by Drago (4) and Colton and Jones (5). An important area of N-Halamine chemistry, that of water treatment and bacterial activity, was discussed by Berliner (6) in the early 30's. A comprehensive treatise on the chemistry of N-Halamines has been undertaken by Kovacic (7).

In the chemistry of N-Halo compounds, both the halogen and the nitrogen act as reaction sites, and as a consequence their chemistry is very varied. The nitrogen can act as both a cation and an anion, as in certain bicyclic rearrangement reactions and in hydrazine formation, and can also act as a base in nucleophillic substituion, a radical cation in the Hoffman-Loffler reaction and as a radical in photolytic and addition reactions.

The halogen, in many instances, can act as a cation in halogenation reactions and as an anion in Grignard reactions and hence N-Halamines can serve as useful starting materials for a host of organic compounds.

The Halamines vary in toxicity and explosiveness, serious injury has been caused by $NCl_3$ to some early workers in this field, indeed P. L. Dulong lost three fingers and an eye, as Mellor (1) states. The toxicity of $NCl_3$ quickly stopped further use as a bleaching agent for flour.(8).

The reactions of the Halamines can be split into five classes' Dealkylation, Dehydrohalogenation, Halogenation, Ammination, and Rearrangements.

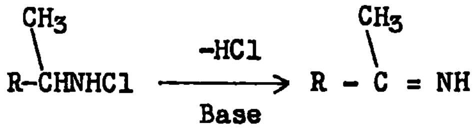
Dealkylation reactions are typified by the non radical disproportionation of n-$(C_4H_9)_2N^+HCl$, the di-n-butylchlorammonium cation, to n$(C_4H_9)NHCl$, mono-n-butylchloramine, in acid solution (9),

$$(C_4H_9)_2N^+HCl + H_2O \longrightarrow (C_4H_9)NHCl + H_3{}^+O + C_4 \text{ fragment}$$

$$(C_4H_9)NHCl + H^+ \rightleftharpoons (C_4H_9)N^+H_2Cl$$

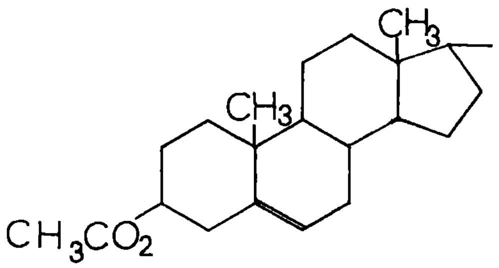
$$(C_4H_9)NHCl + (C_4H_9)_2N^+HCl \longrightarrow (C_4H_9)NCl_2 + (C_4H_9)_2N^+H_2$$

whereas an example of dehydrohalogenation is found in the conversion of the N-chloro derivative of 3β-acetoxy-20-amino-5-pregene; a steroid, to the corresponding immine (10).



$$\overset{CH_3}{\text{R-CHNHCl}} \xrightarrow[\text{Base}]{\text{-HCl}} \text{R} - \overset{CH_3}{\text{C}} = \text{NH}$$

where R =



This reaction is usually followed by hydrolysis to form the corresponding carbonyl compound, as exemplified in the conversion of N-chloroisopropylamine to acetone and ammonia, via a postulated isopropylimine structure:

$$(CH_3)_2CHNHCl \xrightarrow{-HCl} (CH_3)_2C = NH \xrightarrow{H_2O} (CH_3)_2C = O + NH_3$$

and N,N dihalamines containing at least β carbon atoms produce nitriles when subjected to Caesium fluoride (11)

$$RCH_2NCl_2 \xrightarrow{CsF} RC \equiv N$$

and specifically

$$n\text{-}(C_4H_9)NCl_2 \xrightarrow{CsF} (C_3H_7)C \equiv N \text{ (90\% yield)}$$

N-Halamines are well known to act as halogenating agents of aliphatic and aromatic compounds. Alkanes, esters, alkyl halides and ethers were found to be susceptible to chlorination by $(CH_3)_2NCl$ (12, 13, 14, 15, 16, 17), in sulphuric acid solution, usually with Fe(II) compounds or light as the initiator. The reaction involves a radical cation generated from the protonated alkyl chloramine (12).

$$(CH_3)_2N^+HCl \xrightarrow[-HCl]{} (CH_3)_2\dot{N}^+$$

The amino radical cation then abstracts a hydrogen atom from an alkane, RH, forming the dimethylammonium cation and the radical R•

$$(CH_3)_2\dot{N}H^+ + RH \longrightarrow (CH_3)_2N^+H_2 + R\cdot$$

which then interacts with the protonated dimethylchloramine to form an alkyl halide and further dimethylamino radical cations:

$$R\cdot + (CH_3)_2N^+HCl \longrightarrow RCl + (CH_3)_2\dot{N}^+H$$

In the case of methyl heptanoate, halogenation occurred predominantly at the second carbon atom in the alkyl chain:

$$CH_3O_2CCH_2CH_2CH_2CH_2CH_2CH_3 \xrightarrow[Fe(II)]{(CH_3)_2NCl} CH_3O_2CCH_2CH_2CH_2CH_2CHClCH_3$$

however an alternative mechanism (18) based on evidence from the isomer distributions obtained in the chlorination of 1-chloropropane, suggested that the chlorine atom was the chain propagating species, and not the dialkylamino radical cation, since the orientation and isomer distributions were identical with different N-chloramines and also with photochlorinations which definitely involves Cl•.

$$R_2N^+H + HCl \longrightarrow Cl_2 + R_2N^+H_2$$ /Cl

$$R^\bullet + X_2 \longrightarrow RX + X^\bullet$$

$$X^\bullet + RH \longrightarrow HX + R^\bullet$$

Recent work by Ingold (19) on the N-Halamine halogenation of 1-chlorobutane indicated that along with the radical cation mechanism, a concurrent chlorine atom process could occur resulting from impurities in the N-Halamine ($Cl_2$, HCl or $Cl^-$).

Chloramines may also act as halogenation agents towards olefins, $NH_2Cl$ and cyclohexene produce low yields of the 1-2 dichlorocyclohexane (20), whereas $NCl_3$ has been shown to form, in high (90-97%) yields, vic-dichlorides of certain olefins (21)

$$3RCH = CH_2 + 2NCl_3 \longrightarrow 3RCCHClCH_2Cl + N_2\uparrow$$

or specifically, 1,2-dichlorohexane from 1-hexene.

$$CH_3(CH_2)_3CH = CH_2 \xrightarrow[CH_2Cl_2\ 0^\circ C]{NCl_3} CH_3(CH_2)_3CClCH_2Cl + N_2\uparrow$$

The interaction of N-chloramines with primary and secondary amines result in an exchange process (22)

$$(CH_3)_2NH + (CH_3)_2NCl \rightleftharpoons (CH_3)_2NCl + (CH_3)_2NH$$

and with tertiary amines there is some doubt (7, 23). ?

Ammination reactions with $NCl_3$ and $AlCl_3$ apparently sparked off a great deal of work in studying the interaction of N-Halamines with saturated functionalities (24, 25, 7), such as alkanes. The reaction is postulated to proceed via an hydride abstraction process, presumably by $Cl^+$ followed by addition of the dichloroamide ion; to yield a N,N-dichloramine,

$$Cl_3N + AlCl_3 \rightleftharpoons \overset{\delta+}{Cl}\ (NCl_2AlCl_3)^{\delta-}$$

$$R\text{-}CH_2CH_3 \xrightarrow{Cl^+} R\text{-}\underset{+}{C}H\text{-}CH_3 \xrightarrow{NCl_2^-} R\text{-}CH(NCl_2)CH_3$$

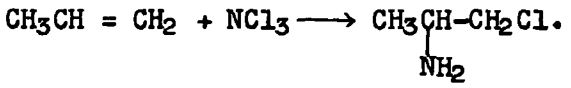
followed by reduction to the corresponding amine. In the case of cyclohexane, N,N-dichlorocyclohexylamine was isolated (26) indicating probable involvement of the nucleophile, $^-NCl_2$, the dichloroamide ion. A similar reaction occurs with alkyl halides such as t-butyl chloride, $(CH_3)_3CCl$, producing t-butylamine in 90% yield on treatment with $NCl_3$, $AlCl_3$ followed by reduction of the N,N-dichloro intermediate, which was isolated (27).

$$(CH_3)_3CCl \xrightarrow{AlCl_3} (CH_3)_3C^+ \xrightarrow{NCl_2^-} (CH_3)_3CNCl_2 \xrightarrow{+H^+} (CH_3)_3CNH_2$$

With unsaturated compounds such as olefins, acetylenes, $\alpha$, $\beta$ unsaturated ketones, acids and ketenes, ammination occurs by addition to the multiple bond. $NCl_3$ addition, followed by reduction of the N,N-dichloro derivative, yielded $\beta$ chloroalkylamines with the olefins, ethylene, propylene isobutylene and cyclohexene (27, 28, 29) as exemplified by the reaction with ethylene as shown below:

$$CH_2 = CH_2 + NCl_3 \longrightarrow ClCH_2NH_2NCl_2 \xrightarrow{HCl} ClCH_2CH_2NH^+_3Cl^-$$

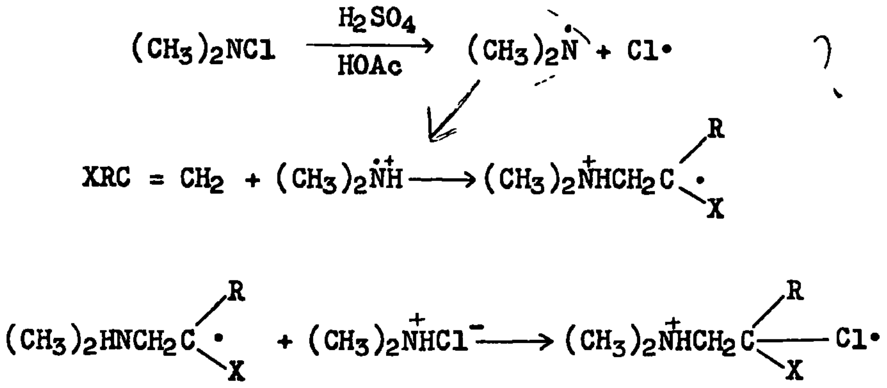
and with propylene, showing that Markovnikov addition occurs:



$$CH_3CH = CH_2 + NCl_3 \longrightarrow CH_3\underset{NH_2}{CH}-CH_2Cl.$$

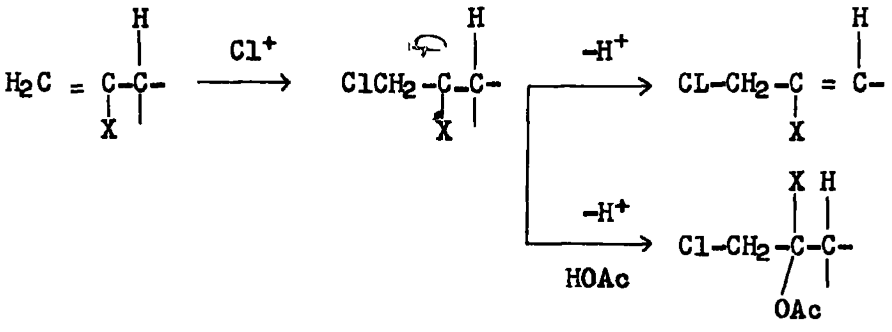
however the substituted ethylenes, 1,1 diphenyl; 1,1,2 trimethyl; 1,1,2 triphenyl; and tetraphenyl, gave no organic amine products on treatment with the $NCl_3$, $AlCl_3$ system.

With dialkyl-N-chloramines radical additions were found to occur with terminal olefins (30)



$(X = F, Cl, Br, Si(CH_3)_3)$

However, concurrent with the radical cation process, a competing reaction scheme involving $Cl^+$ occurred:



With N-chlorodiethylamine good yields of β chlorinated amines were obtained from 4M $H_2SO_4/HOAc$ mixtures of the olefin and chloramine at 30°C, for example (30):

$$CH_2 = CHCH_3 \xrightarrow[H_2SO_4/HOAc]{(C_2H_5)_2NCl} (C_2H_5)_2NCH_2CHClCH_3 \quad (42\%)$$

$$CH_2 = CHF \longrightarrow (C_2H_5)_2NCH_2CHClF \quad (80\%)$$

$$CH_2 = CHCH_2Cl \longrightarrow (C_2H_5)_2NCH_2CHClCH_2Cl \quad (83\%)$$

It was found also (31, 32, 33, 34) that N-chloroalkylamines added to olefins by a radical process in redox systems.

$$R_2NCl + M^+ \longrightarrow R_2N\cdot + MCl^+$$

$$R_2N\cdot + CH_3CH_2CH_2CH_2CH = CH_2 \longrightarrow CH_3(CH_2)_3CHNR_2CH_2\cdot$$

$$CH_3(CH_2)_3CHNR_2CH_2\cdot + MCl^+ \longrightarrow CH_3(CH_2)_3CHNR_2CH_2Cl + M^+$$

$$M = Cu,\ Fe.$$

Modification of the system to include sulphuric acid, altered the attacking species from the pure radical to the protonated radical ion $R_2\dot{N}H^+$ (35).

Depending on the Grignard reagent chosen, N-Halamines can produce primary, secondary and tertiary amines. $NH_2X$, (X = Cl, Br), form primary amines with $(n\text{-}C_4H_9)MgX$ (36) whereas $NHBr_2$ and $NCl_3$ produce both primary and secondary amines (37, 38). Alkyl substituted halamines produced 1°, 2° and 3° amines if the halamine was $N(Hal)_2$ substituted, whilst only 2° and 3° amines resulted if the halamine was $N(dialkyl)_2$ substituted (39).

Coleman (36) presented the equations:

$$RMgX + NH_2Cl \longrightarrow RNH_2 + MgXCl$$

$$RMgX + NH_2Cl \longrightarrow RCl + MgXNH_2$$

to account for the variety of products obtained when investigating $NH_2Cl$ reactions with various Grignard reagents, illustrating the dual nature of halogen in the N-Halamines, amine production shows Cl as the leaving entity through Sn2 attack whilst, when alkyl halides are obtained, the amino group is displaced. The nature of R determined the major pathway, both reactions were shown to be interdependent since $NH_3$ production was found to be inversely proportional to amine formation. With other organometallic compounds, chloramine forms primary amines (39):

$$RM + NH_2Cl \longrightarrow RNH_2 + MCl$$

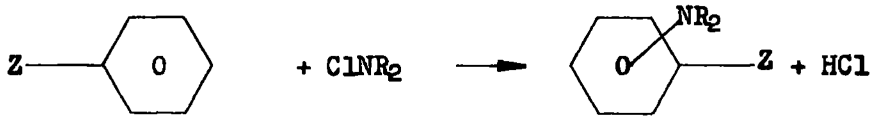
$$M = Li,\ Zn$$

and with $NCl_3$, $R_2Zn$ produces 1° and 2° amines. Whilst with dialkylhalamines, hydrazine and 3° amine formation occurs with alkylpotassium complexes (40).

$$((CH_3)_2CH)K + ((CH_3)_2CH)_2NCl \longrightarrow ((CH_3)_2CH)_3N;\ ((CH_3)_2CH)_2NN((CH_3)_2CH)_2$$

however the yields (3% amine; 4.5% hydrazine) were low.

Ammination involving aromatic compounds has received considerable attention in the past, Bock and Kompa, Minisci et. al. and Kovacic et. al. are probably the three leading groups in this field. With toluene and a variety of other monosubstituted arenes, amminations occurred in 96% sulphuric acid media.

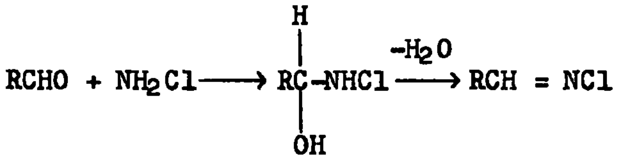


with toluene, the distribution of products between -o-m,-p substituted toluidines was found to favour m- substitution (9:53:38; o:m:p) (41). A similar product distribution was noted when $R_2NCl$, $H_2SO_4$, $CH_3{\cdot}C_6H_6$ was photolysed (9:53:38), (42), whilst when toluene was reacted with dimethylchloramine and aluminium trichloride in a nitroalkane solvent p- substitution was the predominant mode of ammination, the distribution 14:27:59 (o:m:p) being found (43).

With toluene and dimethylchloramine in redox systems, ammination again occured in the ration 9:53:38 (o:m:p) (44) which is contrasted by the almost equal o- and p- content of the result of ammination of toluene with aminosulphuric acid, $NH_2OSO_3H$.

With $NCl_3$, $AlCl_3$ amminating systems, 100% m- toluidine was formed from toluene, in 42% yield (45) and with other alkyl arenes similar orientations were found (46), however with NN dialkylhalamines, although m- specificity was noted, the high m- orientated yields with $NCl_3$ were not reproduced. (47). The decrease in m- orientated product yield was attributed to electrophillic ammination or free radical reactions competing with the o- substitution reaction.

Aldehydes and ketones react with chloramine to produce ald-chlorimines and ketochlorimines by a Schiffs base reaction:



$$\mathrm{RCHO} + \mathrm{NH_2Cl} \longrightarrow \mathrm{R}\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}\mathrm{{-}NHCl} \xrightarrow{-\mathrm{H_2O}} \mathrm{RCH = NCl}$$

and primary amines are afforded by reduction (48,49).

With nitrogenous substitutes, much work has been carried out in the synthesis of hydrazines from amines. A discussion of the literature concerning the reactions of chloramine and substituted alkyl chloramines with amines can be found in chapter 3.

With phosphorous compounds N-Halamines react in a variety of different ways. Aryl phosphites act as Lewis bases towards dialkylchloramines forming an adduct:

$$(C_6H_5O)_3P + Et_2NCl \longrightarrow (C_6H_5O)_3P(N(Et)_2)Cl$$

whereas with alkyl phosphites further reaction occurs (50).

$$(EtO)_3P + (Et)_2NCl \longrightarrow (Et)_2N\text{-}PO(OEt)_2 + EtCl$$

With phosphines, chloramine yields 4° amino phosphonium chlorides in high yield (51).

$$R_3P + NH_2Cl \longrightarrow [R_3PNH_2]^+Cl^-$$

but these salts are often difficult to isolate because of hydrolysis:

$$[R_3PNH_2]^+Cl^- + H_2O \longrightarrow R_3P = O + NH_4Cl$$

With aryl phosphines, P-P bonds form with $(CH_3)_2NCl$, forming tetraphenylphosphetane from phenyl phosphine, and tetraphenylbisphosphine from diphenylphosphine (52).

$$4C_6H_5PH_2 + 4(CH_3)_2NCl \longrightarrow (C_6H_5P)_4 + 4(CH_3)_2NH_2Cl$$

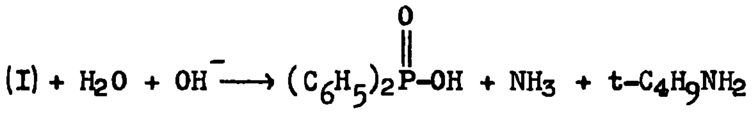
and:

$$2(C_6H_5)_2PH + (CH_3)_2NCl \longrightarrow (C_6H_5)_2PP(C_6H_5)_2 + (CH_3)_2NH_2Cl$$

Whilst with phosphine, oxidation by dimethylchloramine yielded elemental phosphorous.

$$PH_3 + 3(CH_3)_2NCl \longrightarrow 2P + 3(CH_3)_2NH_2Cl$$

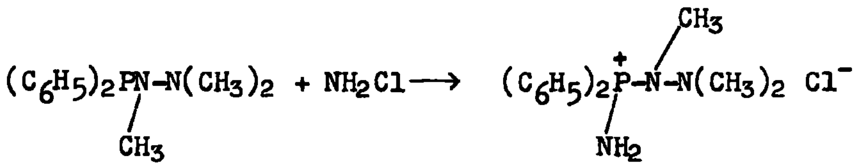
With amino phosphines, ammination always occurs at the phosphorous site yielding further P-N bonds rather than at the nitrogen site yielding hydrazines (53, 54). This was shown by the hydrolysis of the phosphonium salt $H_2N - P^+(C_6H_5)_2)(tC_4H_9NH)\ Cl^-$, amino-t-butylaminodiphenylphosphonium chloride, (I), formed from a chloramine interaction with di-t-butylaminodiphenylphosphine. Hydrolysis of I yielded t-butylamine and ammonia as the nitrogenous substances:



$$(I) + H_2O + OH^- \longrightarrow (C_6H_5)_2\overset{\overset{O}{\|}}{P}{-}OH + NH_3 + t{-}C_4H_9NH_2$$

whereas if ammination of the aminophosphine had occurred at the nitrogen, then t-butylhydrazine would have been formed on hydrolysis.

The phosphorous preference in ammination is also shown in reactions with hydrazinophosphines (55).



$$(C_6H_5)_2P\underset{\underset{CH_3}{/}}{N}{-}N(CH_3)_2 + NH_2Cl \longrightarrow (C_6H_5)_2\underset{\underset{NH_2}{/}}{\overset{+}{P}}{-}\overset{\overset{CH_3}{/}}{N}{-}N(CH_3)_2\ Cl^-$$

thus demonstrating the enhanced phosphorous electron density when bonded to an amino group.

Analogous behaviour of chloramine towards phenyl substituted phosphines is noted in the equivalent arsenic compounds, aminoarsonium halides being formed (56).

$$(C_6H_5)_3As \xrightarrow{NH_2Cl} (C_6H_5)_3As^+NH_2\ Cl^-$$

With aliphatic arsines, dimethylchloramine yields arsenic, diarsines, and tetrasubstituted cyclopolyarsines (57) as shown below.

| Arsine | Products | Yield (as cpd) |
|---|---|---|
| $AsH_3$ | As, $(CH_3)_2NH_2Cl$ | 66% |
| $CH_3AsH_2$ | $(CH_3As)_5$; $(CH_3)_2NH_2Cl$ | 85% |
| $(CH_3)_2AsH$ | $(CH_3)_2AsAs(CH_3)_2$; $(CH_3)_2NH_2Cl$ | 45% |

Stibanes chloraminated with $NH_2Cl$ yield aminoalkylchlorostibanes:

$$R_3Sb + NH_2Cl \longrightarrow R_3Sb(NH_2)Cl$$

which condense to form the iminobis-trialkylchlorostibane which are readily hydrolysable to the anhydrides and ammonia (58). With silyl, germyl and stannylamines, $NH_2Cl$ gave products resulting from the cleavage of the Si-, Ge- or Sn-N bond (59), and no stable addition compounds were formed analogously to the phosphine case.

Dimethyl(trialkyl silyl, germyl, stannyl)amines reacted with chloramine to yield, for example, the trialkylgermyl halide, dimethylamine, ammonia and nitrogen:

$$3R_3MN(CH_3)_2 + 3NH_2Cl \longrightarrow 3R_3MCl + 3(CH_3)_2NH + NH_3 + N_2$$

$$M = Si,\ Ge,\ Sn$$

and in the case of bis-(trialkyl, germyl or stannyl)amine, similar products were noted:

$$3(R_3M)_2NH + 6MH_2Cl \longrightarrow 6R_3MCl + 5NH_3 + 2N_2$$

$$(M = Ge,\ Sn).$$

There has been little work in the behaviour of sulphur compounds towards halamines. Most commonly, reactions appear to proceed via nucleophillic substitution on the halamine nitrogen by the sulphur compound. Dialkyl sulphides, when treated with an etherial solution of chloramine, precipitate the aminodialkylsulphonium salt (60).

$$R_2S + NH_2Cl \longrightarrow R_2S^{+}NH_2\ Cl^{-}$$

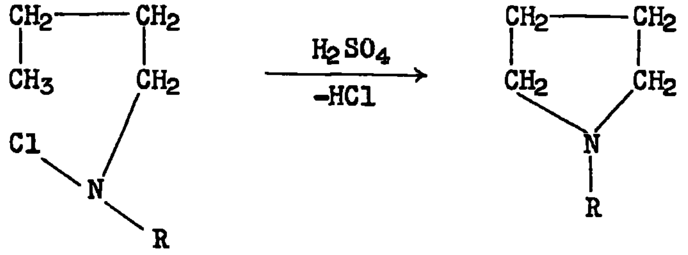
A new N-halo compound, N,N-dihalo-S,S-dimethylsulphurdiimmide, was formed by halogenation of the dimethylsulphurdiimmide with the halogen in aqueous solution (61).

$$(CH_3)_2S(=NH)_2 + X_2 \longrightarrow (CH_3)_2S(=NX)_2$$

These N-halo compounds reacted with $R_2S$ compounds yielding S-N unsaturated salts by nucleophillic substitution.

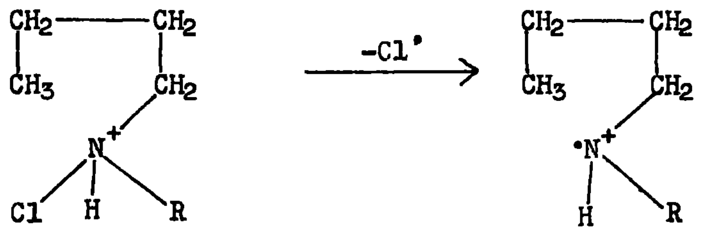
$$R_2S + (CH_3)_2S(=NX)_2 \longrightarrow (CH_3)_2S(=N^{+}SR_2)_2\ 2X^{-}$$

Of the rearrangement reactions undergone by substances involving N-halamines, the best known is probably the Hoffman-Loffler reaction, for the synthesis of certain cyclic amines from N-halogeno compounds. The reaction can be exemplified by the formation of N-alkylpyrollidine from N-chloro-(alkyl)-n-butylamine:

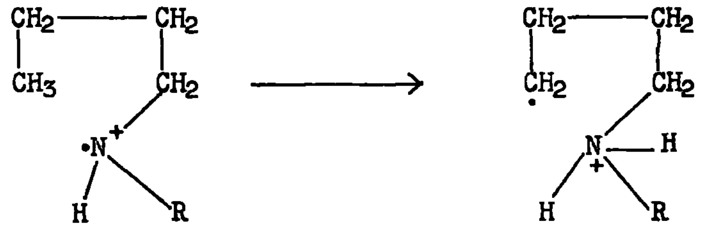


The above transformation appears to be a straightforward dehydrohalogenation reaction, but the isolation of 4-chlorodibutylamine from N chlorodibutylamine (62) shows that a different mechanism is involved.

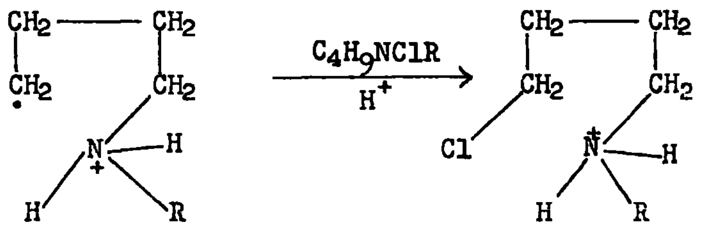
It is thought that the initially protonated N-chloramine is homolytically cleaved under the influence of some initiatory influence, (heat or light), to yield amminium radicals.



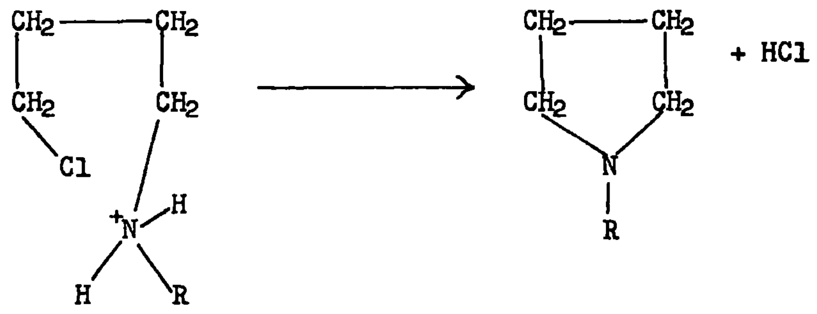
The amminium radicals then abstracts a sterically favourable proton to yield an alkyl radical:



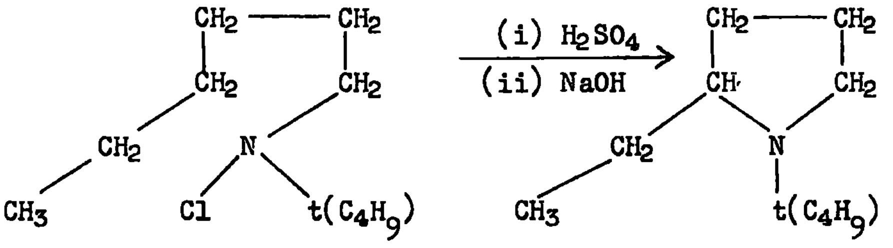
The alkyl radical then abstracts chlorine intermolecularly in a chain reaction:



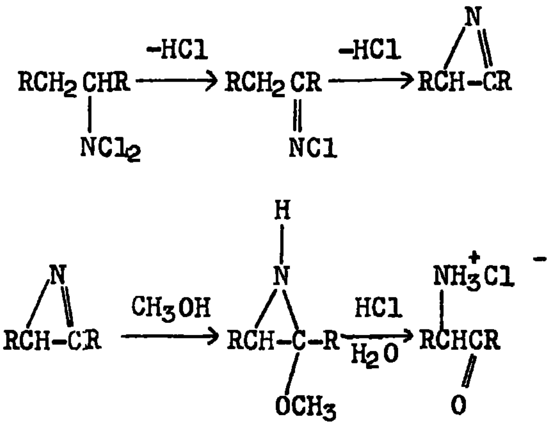
The, (isolable), 4-chlorobutylammonium salt is then converted, by alkaline hydrolysis, into the cyclic tertiary amine:



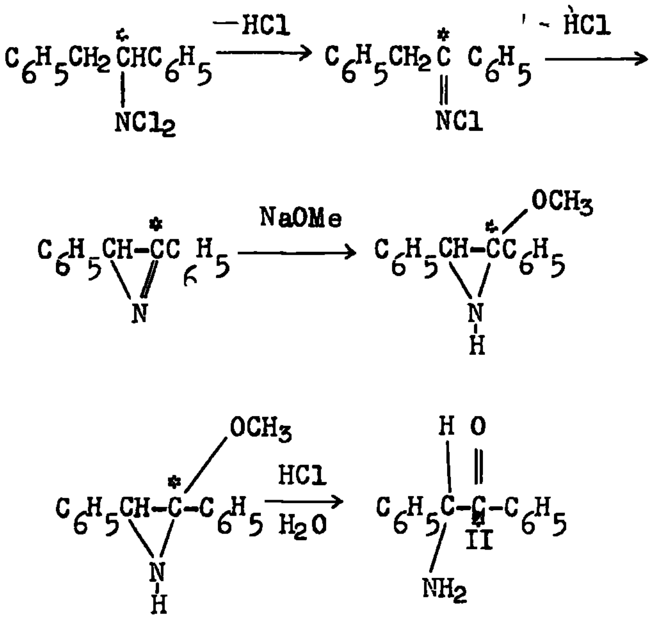
An interesting feature, shown in further investigations of the mechanism of this reaction, is that selectivity for hydrogen abstraction is at $C_4$ by preference (63). N-chloro-N-t-butylhexylamine yielded products which were concomitant with $C_4$ hydrogen abstraction:



A quite different type of rearrangement was found in the conversion of N,N-dichloro-sec-alkylamines to α aminoketones (64). The N-Halamine is successively treated with sodium methoxide and HCl:

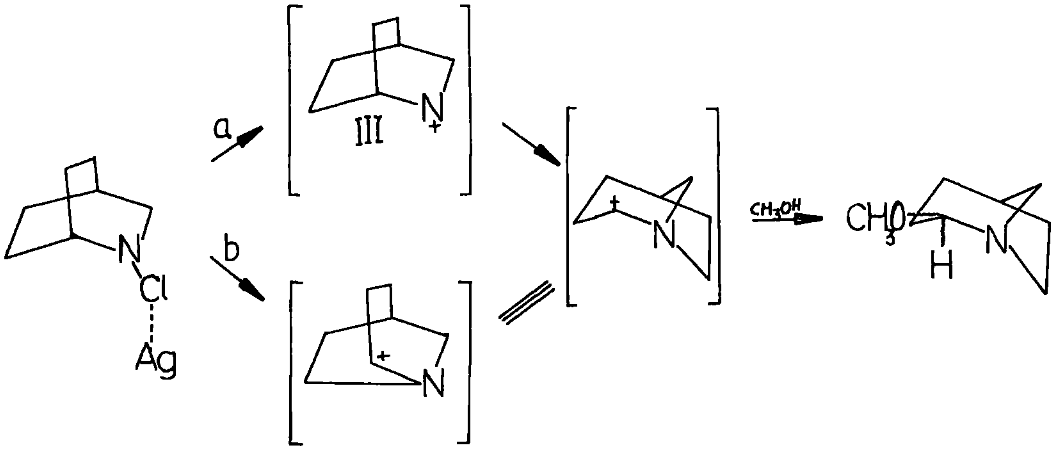


The above scheme accounted for, for example, the rearrangement of N,N-dichloro-sec-cyclohexylamine to 2-aminocyclohexane in 72% yield (65, 66). The N chlorimine, $RCH_2C(=NCl)R$, was isolated and subsequently transformed to the α amino ketone (67). Further support for this mode of rearrangement was obtained in a $^{14}C$ labelled N,N dichloro-1, 2 diphenylethylamine-1-$^{14}C$ transformation, the $^{14}C$ being found almost exclusively in the carbinyl group (68).



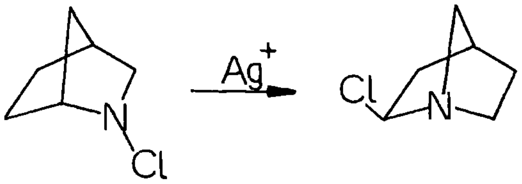
after degrative procedures were carried out on the product, II, the labelled C* atom was found in the ketonic material.

One type of N halamine rearrangement is thought to proceed via a nitrenium ion intermediate. From an investigation of the solvolysis of N-chloroisoquinuclidine with $CH_3OH$ in the presence of $AgNO_3$, (69, 70) 60% yield of 2-methoxy-1-azabicyclo (3.2.1) octane indicated an alkyl migration. There are two conceivable pathways leading to this product, each involving an alkyl migration:



pathway (a) involving the formation of a nitrenium ion as a discrete intermediate (III) and subsequent rearrangement by alkyl migration, whereas pathway (b) suggests a concerted process where Cl loss occurs at the same time as alkyl migration.

A further example of this type of rearrangement is (71):



Supporting mechanistic evidence to the nitrenium ions' discrete existence was obtained from kinetic studies. Methanolysis of several 2-chloro-2-azabicyclo (2.2.1) heptane derivatives gave thermodynamic parameters in accord with those expected for a process involving ions (72).

This brief review of the chemistry of N-Halamines shows how versatile the compounds can be and of what value they are to the synthetic chemist.

In this work, the reactions of one of the members of the halo amine class, dimethyl chloramine, will be investigated. Its reactions with basic substrates such as the amines and hydrazines show differing behaviour to that of the simple chloramine $NH_2Cl$. The reactions of dimethyl chloramine with alkylating agents is also presented, and in this area evidence is gained for the existance of the chlorammonium cation $(CH_3)_3N^+Cl$, and its considerably less stable bromo analogue $(CH_3)_3N^+Br$.

The cation $(CH_3)_3NCl^+$ is investigated with many spectroscopic techniques including NQR spectroscopy where it is found that the chlorine is the more electropositive atom in the N-Cl bond, showing that $(CH_3)_3N^+Cl$ is certainly a more effective chlorinating agent than molecular chlorine.

The work on the cation $(CH_3)_3NCl^+$ indicates that past considerations of the structure of the halogen trimethylamine addition compounds, $(CH_3)_3NX_2$, X = Cl, Br, I, in terms of structures such as $(CH_3)_3N^+X\ X^-$, is perhaps incorrect in the solid phase for all, with the possible exception of $(CH_3)_3NCl_2$, where although the ion $(CH_3)_3N^+Cl$ is formed in aqueous solution, evidence for Cl-Cl interaction has been found in the solid phase.

The alkylations of $(CH_3)_2NCl$ and $(CH_3)_2NBr$ with less powerful alkylating agents than, for example $CH_3OClO_3$, $CH_3OSO_3F$, provide an interesting contrast. In the case of $CH_3I$, dimethylchloramine yielded the unexepcted tetramethylammonium salt of a pseudo-polyhalide anion, $(CH_3)_4N^+\quad (CH_3)_2N(JCl)_2{}^-$. When dimethyl bromamine is reacted with methyl iodide, the corresponding bromo compound is produced, formulated as $(CH_3)_2N^+\ (CH_3)_2N(IBr)_2{}^-$, but the interaction of dimethylchloramine with methyl bromide gives the known compound, $(CH_3)_3NBrCl$. In complete contrast, when methyl chloride is used as the alkylating agent, only decomposition products of the chloramine are obtained.

# CHAPTER TWO

## EXPERIMENTAL METHODS

# EXPERIMENTAL METHODS

The study of the reactions of Halo amines with acid and basic species required the use of a variety of manipulative techniques. Although the majority of reagents used were not particularly volatile, a vacuum line allowed quantitative transferences of materials to be made under anhydrous conditions. The vacuum line also allowed investigations of reaction products which were volatile, for example methane, which would otherwise have been lost if conventional "bench" techniques had been used.

In order to maintain anhydrous conditions throughout a series of reactions, a dry box was used.

This Chapter will describe the vacuum and dry box systems and give details of the equipment associated with them. The methods employed to purify or prepare and purify all the reactants used in the study are also explained and discussed.

## 1. The Vacuum Line

The vacuum line was of general purpose design, as shown diagrammatically in Figure 1. It can be split into four sections, comprising of a pumping section (P), a general working section (W), a storage section (S), and a fractionating section (F).

The pumping section comprised of a Jencons mercury diffusion pump, D, backed by an Edwards two-stage rotary oil pump.

The diffusion pump was rated at better than 30 litre per second pumping

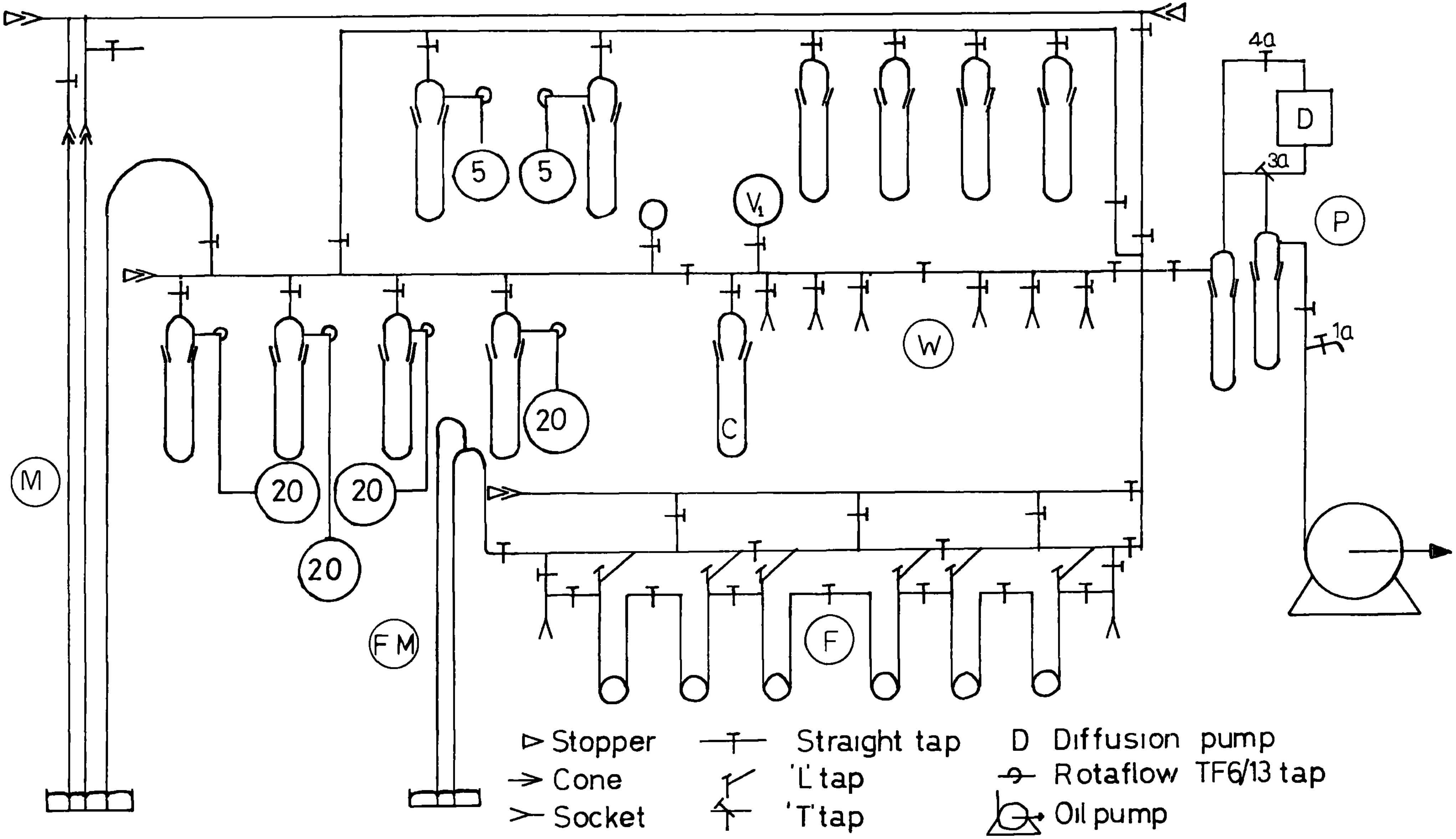

M
5
5
V1
P
D
4a
3a
1a
W
C
20
20
20
20
20
FM
F
Stopper
Cone
Socket
Straight tap
'L' tap
'T' tap
D Diffusion pump
Rotaflow TF6/13 tap
Oil pump

fig 1

capacity at $10^{-3}$ to $10^{-5}$ mm Hg., and could attain an ultimate vacuum of $3 \times 10^{-7}$ mm Hg. The pump was heated electrically using a 320 Watt wrap round heating element. The critical backing pressure of 0.2 mm Hg. was easily obtained using the two-stage rotary oil pump which was an Edwards "Speedivac" model 2SC20A, powered by a 0.25 horsepower motor, providing a pumping speed of 22 litre per minute and an ultimate vacuum of better than $10^{-3}$ mm Hg.

The diffusion pump was situated between two cold traps, it being isolable from the rest of the line by a large three-way tap 3a (Figure 1) and tap 4a, thus ensuring that if chemicals reactive to hot mercury, e.g. $Cl_2$, were being handled in this section no contamination could occur.

An air bleed was provided via tap 1a to prevent oil suck back when the oil pump was switched off. The connections between rotary pump and diffusion pump and the rest of the line were as large as possible.

The general working section consisted of an array of six taps terminating in B14 sockets to allow attachment of various pieces of apparatus such as infra red gas cells or reaction vessels. It was found more convenient to have B14 sockets rather than B14 cones on this section as reactions were carried out which often required the making and breaking of connections to this part of the line, for example weight analysis cell work, where the cleaning of vacuum grease from the demounted apparatus was facilitated by having a cone and not a socket. This section of the line was also equipped with a standard volume $V_1$ and a cold finger, C.

The storage section provided a total capacity of 90 litres in the form of four 20 litre bulbs and two 5 litre bulbs. The storage bulbs were connected to the vacuum line via Rotaflow taps, which were found to be more satisfactory than greased ground glass taps for this particular purpose, since the seal provided was found to be, in general, more durable than that offered by a greased tap. The merits of this type of vacuum tap are discussed later.

For the investigation of volatile reaction products, or the purification of volatile reactants, the fractionation section was used. This consisted of six individually isolable fractionation bulbs, of diameter such that they made a close fit in the mouth of a "Thermos" dewar.

The fractionation section was demountable, for ease of cleaning, and was equipped with its own monometer, FM, Figure 1, so that slow distillations could be carried out whilst leaving the rest of the vacuum line free for other work. Access to this section was via B14 sockets.

Cold baths necessary for distillations were made up using organic liquids of suitable melting point, and liquid nitrogen (never liquid air). The temperatures of such baths are given in Table 1.

Table 1: Temperatures of Liquid Nitrogen Slush Baths

| Cold bath component | Temperature (°C) |
|---|---|
| Melting $CCl_4$ | -23 |
| Melting $C_6H_5Cl$ | -45 |
| Melting $CHCl_3$ | -64 |
| Melting $C_2H_5CO_2CH_3$ | -78 |
| Solid $CO_2$ $(CH_3)_2CO$ | -84 |
| Melting $C_6H_5CH_3$ | -98 |

The cold traps used in the pumping section contained liquid nitrogen. The dewars used with the vacuum line were either "Thermos" refills fitted, most conveniently, into empty one pint oil cans supported on cork rings, or standard quart "Thermos" flasks. The latter were used predominantly for freezing purified products on the fractionation train when such products could not be stored elsewhere, for example dimethyl chloramine, since nitrogen evaporation losses were minimised by the narrow neck of the flask, and cottonwool. The other dewars were used for holding the cold baths.

All parts of the line were connected, via various manifolds, either directly or indirectly to the main manometers M, (Figure 1), which were direct reading and fabricated from 8 mm bore tubing. Pressures were recorded using a cathetometer yielding pressure readings to 0.01 mm.

The standard volume situated in the working section of the line was calibrated using an external known volume, whose volume was found by weight measurements full and empty of mercury, and the standard P, V, and T relationships.

For vacuum checking, when the vacuum was observed to be better than 0.01 mm from the manometer, a Tesla coil was used which indicated, by the discharge colour inside the vacuum line, when the pressure had fallen below approximately $10^{-5}$ mm Hg., (a black vacuum) and this condition was considered satisfactory when pumping out reaction vessels or joints between the line and demountable pieces of apparatus. The use of the Tesla coil could induce the formation of "F" centres in alkali halide infra red plates (a blue coloration), and also cause the decomposition of some reactants (such as $(CH_3)_2NCl$), thus care was exercised in its use. It did however prove extremely useful in the detection of pinholes in the glass tubing of the vacuum line but could also cause pinholes if insufficient care was taken when checking thin walled containers such as molecular weight bulbs.

In all cases Apiezon M grease was used for joints which were broken, such as cones and sockets, Apiezon L grease was used for taps within the vacuum line as this grade proved more convenient, especially when the ambient temperature was low, since it remained more fluid than M grease at lower temperatures. Black Picein wax was used for the connections at the diffusion pump since this was considerably more permanent than either Apiezon L and M grease and would also withstand the temperatures at this area.

For experiments involving substances reactive towards Apiezon greases, such as chlorine, Kel-F 90, a fully fluorinated grease was used.

Examples of different apparati used with the vacuum line are shown in Figures 2-8. Infra red gas cells, storage ampoules and some weight analysis cells were equipped with the "Rotaflow" stopcock. This stopcock is shown in section in Figure 9 and consists of a PTFE plug attached to a plastic knurled knob, the whole fitting into a specifically designed glass tube. When the stopcock is closed the PTFE plug is clamped tightly onto the valve seat formed in the glass tube, thus sealing the contents of the enclosed vessel off from the atmosphere. The seal at the other side of the stop cock is formed by expanding the PTFE plug along about 1 cm of its length by means of a resilient insert inside the PTFE plug.

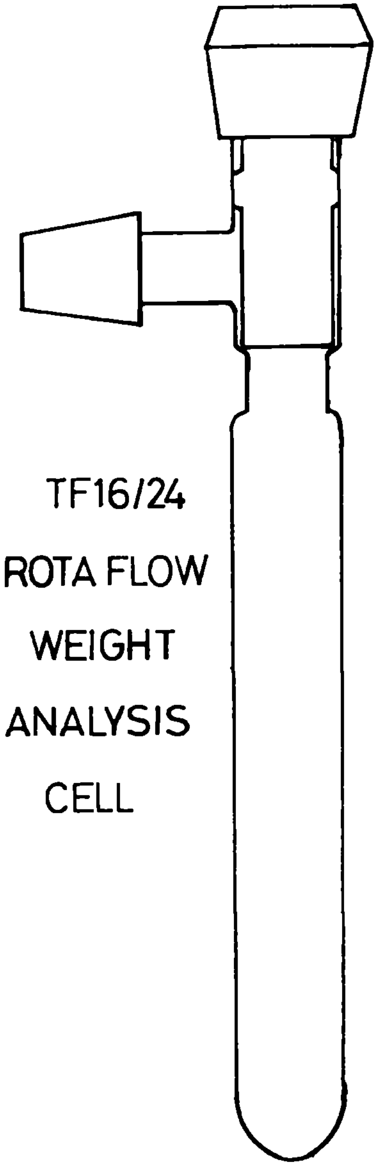


fig 2

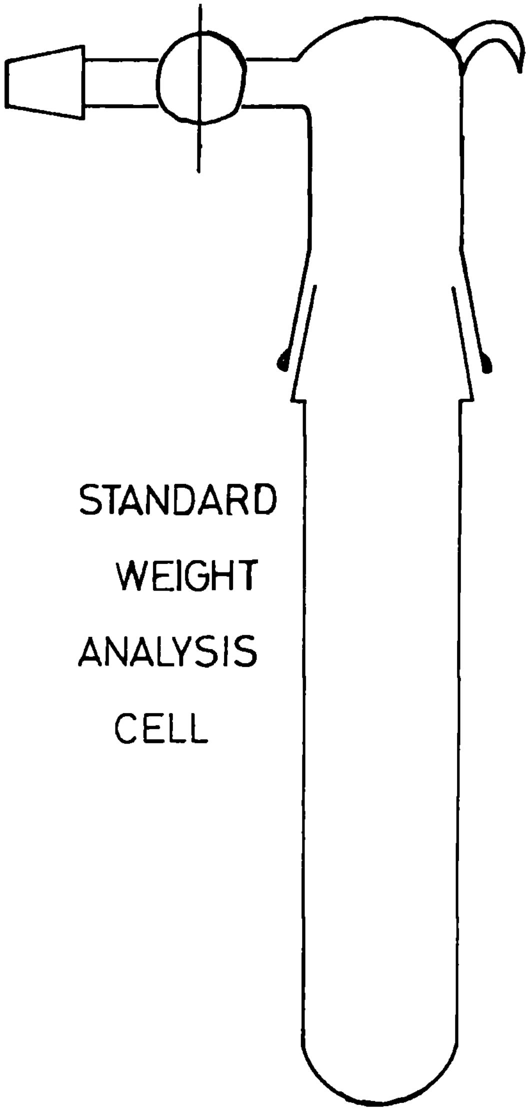


fig.3

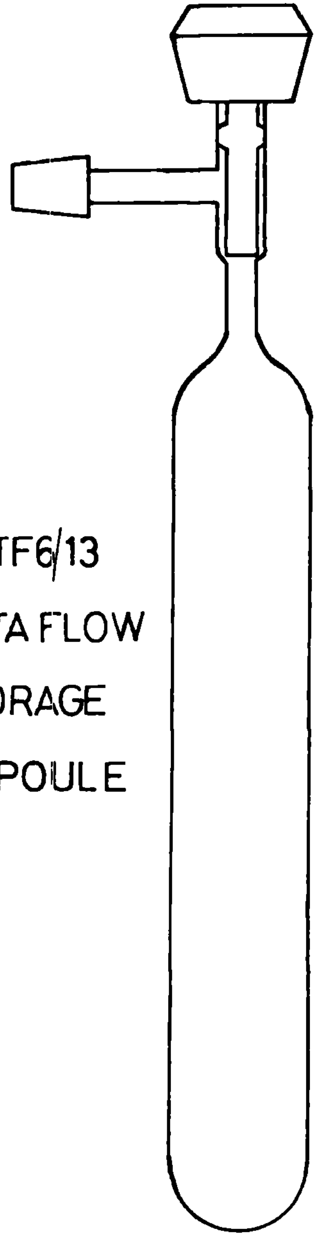
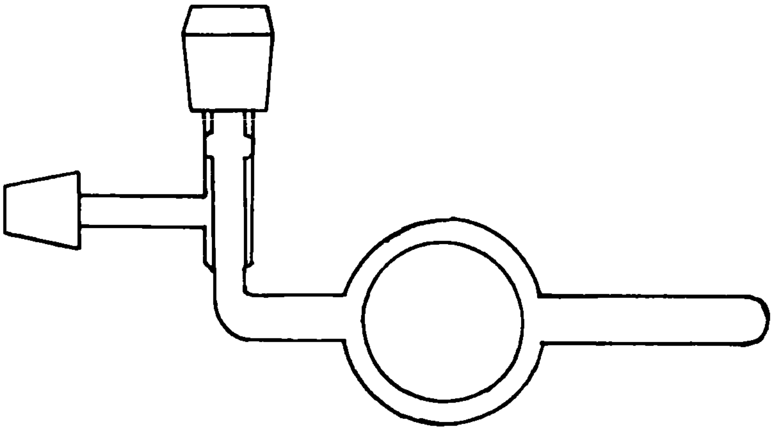
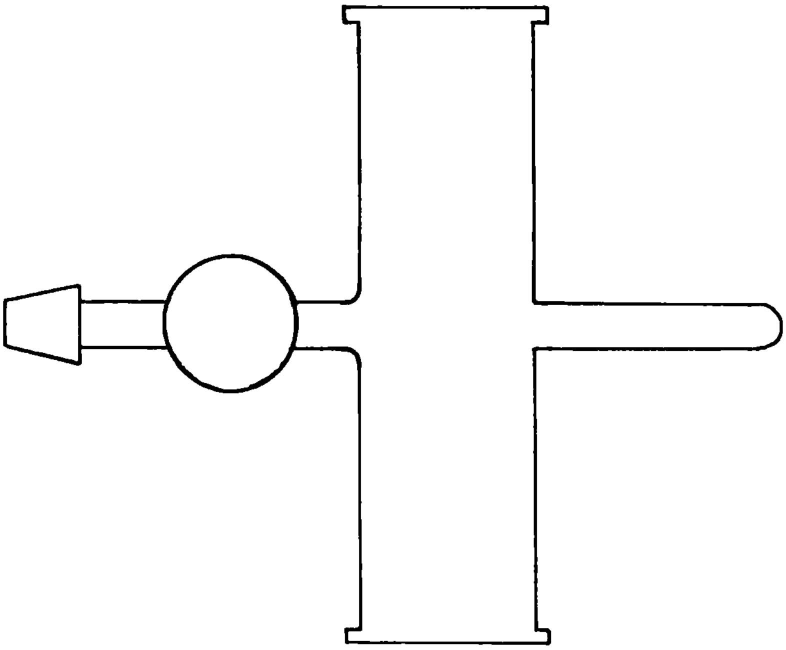


fig 4

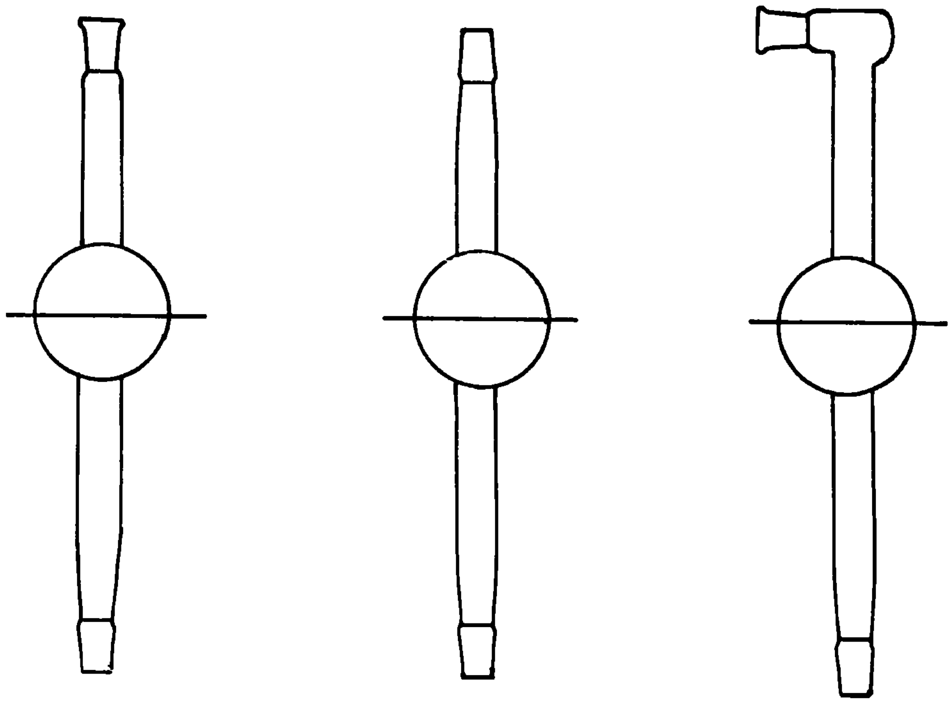


INFRA RED GAS CELL,(SIDE VEIW)



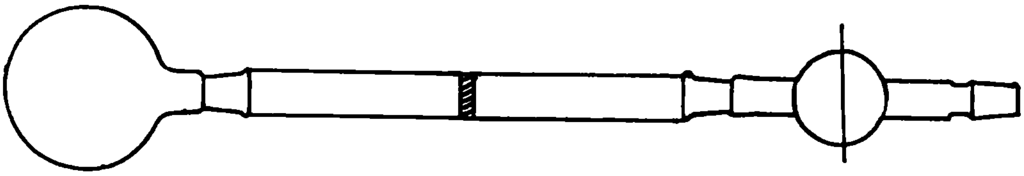
INFRA RED GAS CELL,(PLAN)

fig 5



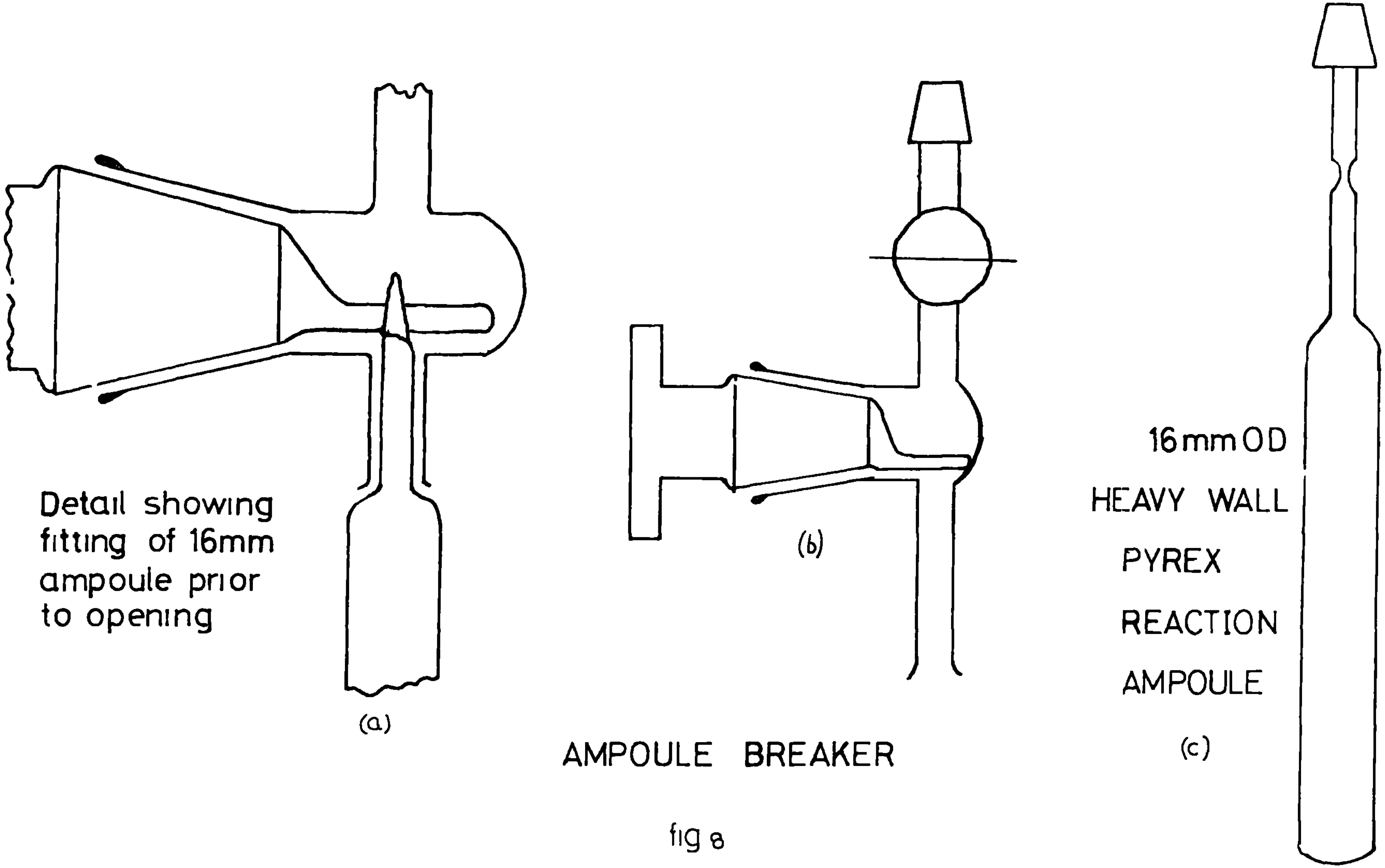
A SELECTION OF TAP CONE CONNECTORS

fig 6



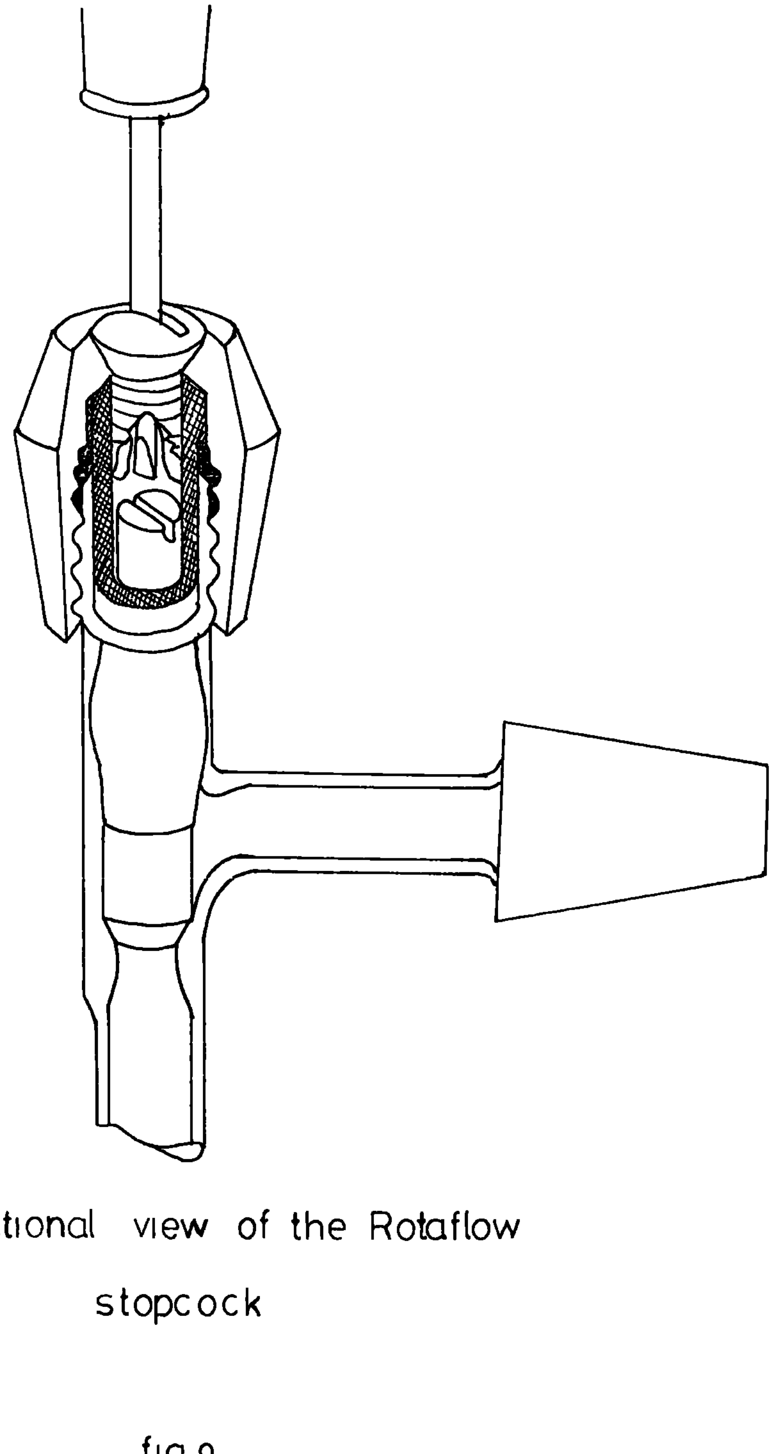
APPARATUS USED IN THE PREPARATION OF $(CH_3)_3NCl_2$

fig 7



AMPOULE BREAKER

fig 8



Sectional view of the Rotaflow stopcock

fig 9

Conditions of a good seal were obtained when both PTFE/glass contact areas appeared "wetted" by the PTFE. It was found important to ensure that no dust particles or pieces of fibre adhered to the valve seat or the valve stem as this could cause leakage.
The use of a Tesla spark coil, for vacuum testing, could degrade the PTFE around the valve seat area if care was not taken.
It was found that this type of stopcock had several advantages over the more standard greased, ground glass tap, in that it could be used quantitatively after long periods of time in contact with, for example $BCl_3$ whereas a conventional greased tap would have deteriorated.
Indeed for weight analysis experiments where the reaction studies involved materials whose boiling point was less than room temperature, the Rotaflow system offered ease of manipulation, reproducibility and safety.
It was found however that although a seal may be satisfactory at room temperature, this may not be so at say -23°C, in a freezer, for example, when the PTFE plug contracts, but this does not represent a serious drawback since the contraction can be compensated for by pre adjustment.

The use of the stopcock when formed into a storage ampoule is shown in Figure 4. Clearly the convenience of this method over a sealed pyrex ampoule need not be emphasised.

Figure 5 shows two views of the infra red gas cell which was fabricated from 25 mm diameter tubing and had a path length of approximately 10 cm. The cell was equipped with a short, approximately 3 cm, cold finger for the collection of small quantities of volatile materials, and was sealable by means of a Rotaflow stopcock. Normally KBr infra red plates were affixed to the ground glass ends by means of Piceine wax, care being taken during the application of the plates to prevent cracking under the heat of an infra red lamp used to melt the black Piceine sealing wax. In some cases CsI plates were affixed in a similar way.

Figure 3 shows a standard weight analysis cell formed from a B24 cone and socket. The socket part of the cell contained a ground glass tap whereas the container part was formed from a cone. This was so that, with careful greasing, materials could be weighed into the cell without coming in contact with the grease around the cone and socket joint. The standard cell was only practicable for dealing with reactions involving volatile products or reactants where the temperature did not exceed the boiling point of the most volatile component. For weight analyses involving higher temperatures, the Rotaflow system was used (Figure 2) which consisted of a TF16/24 stopcock fused to a wider bore tube rounded at the end. This size of stopcock allowed quantitative transferences to be made by completely removing the PTFE plug.

For the opening of 16 mm O.D. heavy walled pyrex reaction ampoules (Figure 8c) an ampoule breaker was used, which is shown in Figure 8b and in use in Figure 8a. The ampoule breaker was used by initially deeply scoring the sealed end of the ampoule to be opened, with a glass knife, near to the tip but below the fused end, and coating the neck of the ampoule with Piceine wax. Whilst the wax was still soft, the open end of the ampoule breaker was slid onto the ampoule so that the scored end was close to the heavy operating lever of the ampoule breaker tap, and the whole allowed to cool. Visual inspection usually revealed if the seal was adequate since the wax "wetted" the inside of the breaker tube. The complete breaker and ampoule was then affixed to the vacuum line via the B14 cone, shown in Figure 8b, and the whole evacuated. The ampoule to be opened was usually frozen in liquid nitrogen before opening, and the tip of the ampoule cracked off by carefully turning the large tap thus bringing the operating lever in an arc across the tip of the ampoule.

A selection of tap cone connectors, consisting of a ground glass tap fused to either a B14 cone or socket are shown in Figure 6. These were used to connect standard quickfit flasks to the vacuum line.

Figure 7 shows an extremely useful addition to the tap cone connector, exemplified in Figure 7, as the apparatus used in the preparation of $(CH_3)_3NCl_2$. The apparatus consisted of a standard tap cone connector joined to a standard quickfit flask by means of a sintered glass filter stick, of porosity 4, which had a B14 cone fused to each end. The reason for employing the filter stick was to prevent fine powdered product from, typically, the $(CH_3)_3N$, $Cl_2$, Freon 11, reaction entering the vacuum line when the solvent, Freon 11, was pumped away, since in the latter stages of solvent removal, bumping can occur. The sintered glass filter allowing reactants and volatile products to pass but not the solid residues. The use of this addition increased the time taken to pump out flasks attached to it.

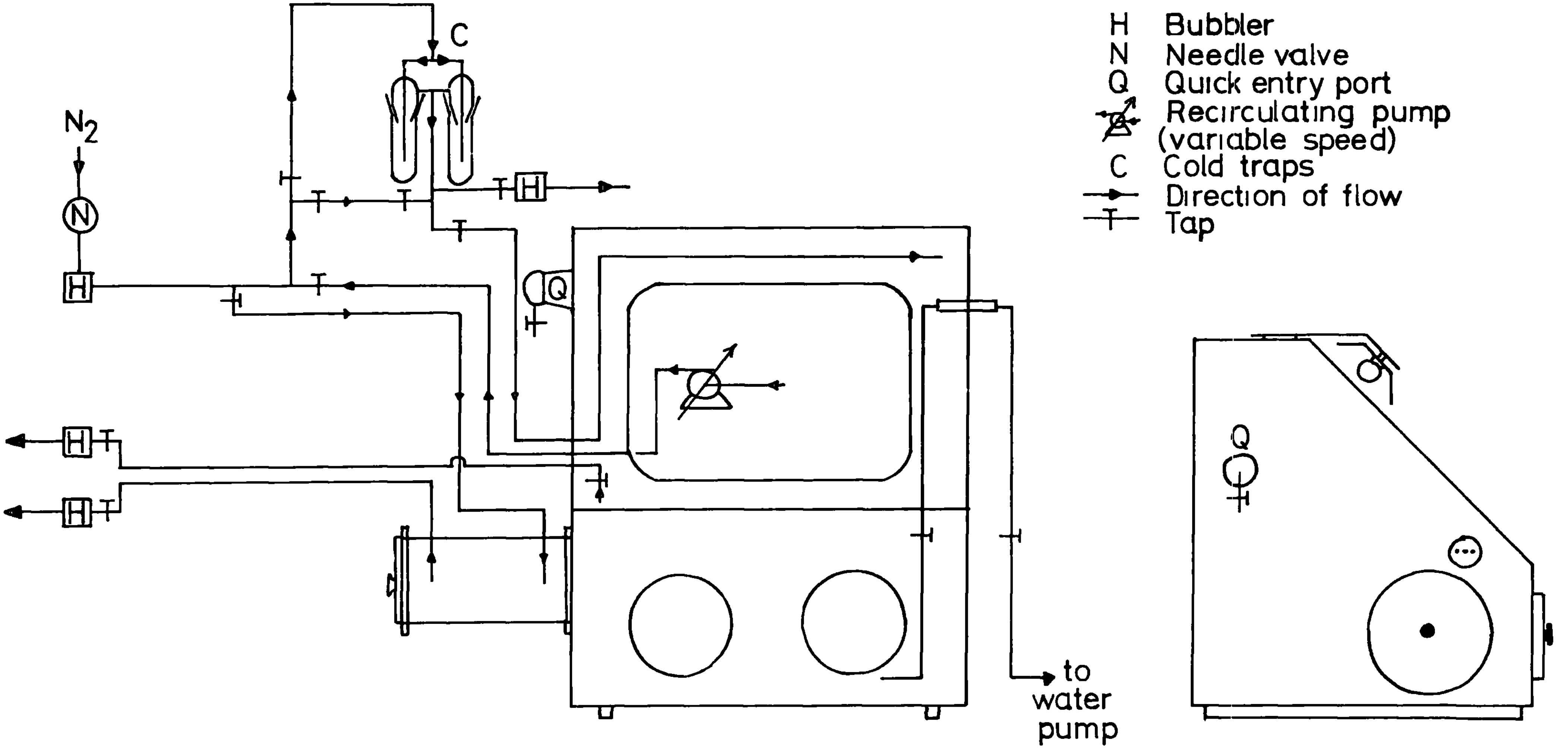
The storage ampoules and tube work of the vacuum line were dried and degassed before use by gently playing a gas flame over the outside surface whilst pumping at black vacuum.

## 2. The Dry Box

The dry box was a standard glass box of approximately 30 litres capacity and is shown, along with the associated humidity control equipment, in Figure 10.

The glove box was manufactured in 1970 at the Science Site Central Workshops at Durham, from an original drawing from Warwick University, from $^1/_8$ inch mild steel, all joints were welded. A tubular spanner was welded into the base to take an infra red press.
An enclosed variable speed recirculating pump, P positioned inside the glove box, passed the box atmosphere, approximately once every seven minutes, through two cold traps, C, fitted in parallel. The box was maintained, at all times when not in use, under a positive pressure of nitrogen, such that the gloves were inflated. The nitrogen used for the make-up of the box atmosphere was drawn off the central liquid nitrogen storage cylinder and was rated at less than 6 ppm $H_2O$.

The box itself was kept dry with dishes of phosphoric oxide, or with sodium potassium alloy, placed in strategic positions around the box floor. The adequacy of the dessication can be seen from spectra of extremely moisture sensitive compounds such as $BCl_4^-$ (Figure 30, Chapter 4).



THE DRY BOX GENERAL LAYOUT

SIDE VIEW

fig 10

The entry and exit to and from the box was, for large objects, via the main port, A, which was purged with nitrogen for between 30 and 45 minutes depending on the item(s) being taken into the box. For small items, such as infra red cells or analytical samples, the quick entry and exit port, Q, was used. This consisted of two brass B55 cones bolted back to back on the main port side of the box. B55 glass sockets equipped with Rotaflow taps, were fitted over the cones and the whole could be evacuated to water pump vacuum within minutes.

The box was also fitted with an electrical connection via a gland in the sidewall terminating in a 13 amp socket, thus enabling the use of a magnetic stirrer or hot plate. Facilities for filtration were also provided via a tube passing through the sidewall, which terminated in a three-way tap within the box, so that vacuum control could be made conveniently. Care was taken to ensure an adequate inflow of nitrogen during filtration operations.

All non welded joints, such as at the large plastic window, were sealed with silicoset silicone rubber, and before commissioning, the box was purged with nitrogen for at least two weeks, and before use was set to recirculate the box atmosphere through the cold traps, which were immersed in dewars of liquid air, for at least four hours. Liquid air was used in this instance because, with the positive nitrogen pressure in the box it was possible to liquify the box atmosphere if liquid nitrogen was used.

To facilitate the handling of fine powders within the box, under such dry conditions, a radioactive source was employed. This consisted of a 20 cm aluminium rod which had a thin strip of tin plate bolted to its end. The tin plate was coated with Americium nitrate ($^{95}Am_{243}$). The nuclide decays by $\alpha$ emission and has a half life $7.95 \times 10^3$ years. This proved satisfactory in reducing the electrostatic conditions inside the box.

## 3. Preparation and Purification of Reactants

### (a) The alkyl halides, $CH_3X$, X = F, Cl, Br, I

Methyl chloride, bromide and iodide were readily available reagent grade materials. Methyl fluoride was prepared from dimethyl sulphate and potassium fluoride.

Methyl iodide was dried over phosphoric oxide and distilled into a Rotaflow storage ampoule surrounded by aluminium foil to prevent photolytic decomposition reactions occurring.

Methyl bromide was received in 100 ml ampoules which were cooled in ice water then opened, the contents poured quickly into a chilled flask containing phosphoric oxide, degassed on the vacuum line by freezing in liquid nitrogen, pumping out then allowing the contents of the flask to melt then refreezing and re-evacuating. This procedure was repeated until, when frozen at 77K, no discharge could be obtained with a Tesla spark coil. The methyl bromide was then distilled into a Rotaflow storage ampoule.

Methyl chloride was introduced, from a commercial cylinder, into the fractionation section of the vacuum line and distilled through two baths at -84 (acetone, solid $CO_2$) and condensed at 77K in liquid nitrogen. The methyl chloride was stored in a pre-evacuated 20 litre bulb on the vacuum line.

Methyl fluoride was prepared by the method of Yates (73) from dimethyl sulphate and potassium fluoride according to the reaction:

$$(CH_3)_2OSO_3 + 2KF = 2CH_3F + K_2SO_4$$

In a typical preparation, 25 gm (0.43 mole) of potassium fluoride, previously dried at 120°C for twelve hours, was introduced into a 250 ml three-necked flask fitted with a condenser, thermometer and nitrogen inlet. 25 ml (0.26 mole) dimethyl sulphate was added and the flask purged with nitrogen, the effluent nitrogen from the top of the condenser was passed through a trap and thence to the atmosphere through a bubbler.

The contents of the flask were heated to 160°C for three hours with only a trickle of nitrogen flowing. As the heating commenced, the effluent trap was immersed, slowly, in liquid air contained in a dewar.

After the heating period the trap was isolated and transferred, frozen, to the vacuum line and pumped out. On warming the trap, the contents were allowed to distill through a bath at -131°C (melting n-pentane) into a liquid nitrogen trap. The thus prepared gas was checked for purity and stored in a demountable 2 litre bulb.

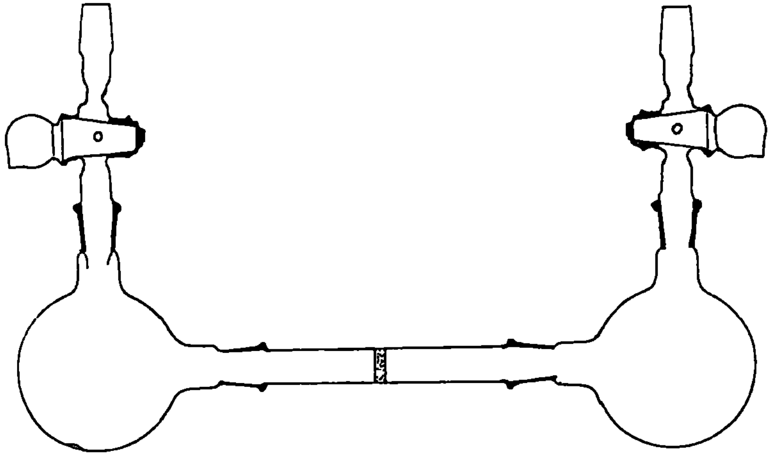


fig 11

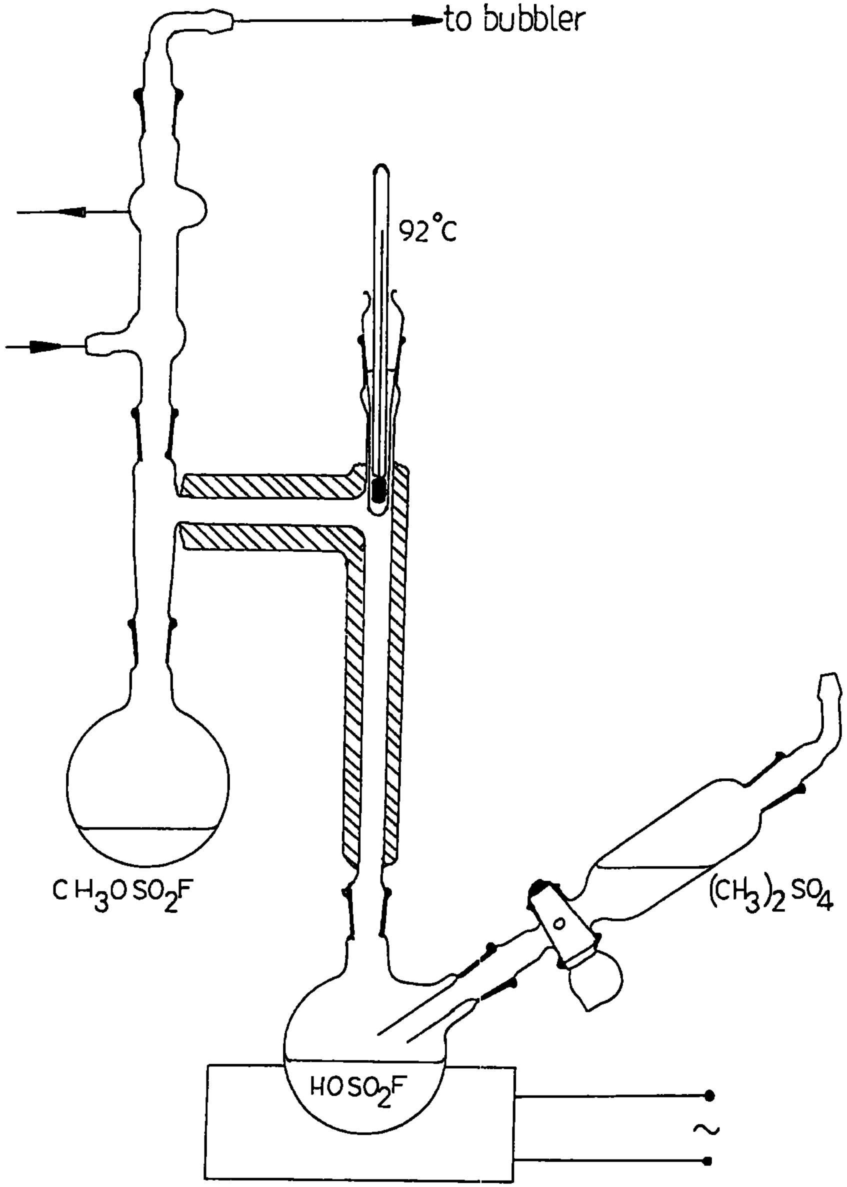


fig 12

Infra red spectra on all the alkyl halides obtained were checked with published spectra.

(b) Other Alkylating Agents

Methyl perchlorate, $CH_3ClO_4$, due to its high instability in the pure state, was prepared in solution, according to the method of Hammond (74), by mixing silver perchlorate and methyl iodide, in carbon tetrachloride solution, but modified to ensure no methyl iodide was present in the resulting solution.

In the dry box 2.0 gm (9.65 m mole) $AgClO_4$, finely ground, was introduced into a 100 ml two-necked B14 quickfit flask, and 25 ml dry $CCl_4$ added. To this, 0.5 ml (1.14 g, 8.01 m mole) $CH_3I$ was added, the flask stoppered, covered in aluminium foil and removed from the dry box, placed on a flask shaker and agitated for 24 hours. The flask was returned to the dry box and after the, now, yellow solid had settled, an aliquot of the solution was investigated by infra red spectroscopy and found to show no absorptions due to $CH_3I$. The flask was then attached to the apparatus shown in Figure 11, consisting of a filter stick joining the reaction flask to a second two-necked 100 ml flask equipped with a tap cone connector.

The complete apparatus was then transferred to the vacuum line where the empty flask was partially evacuated causing the solution in the reaction flask to pass through the filter, after which the whole was returned to the dry box and the filtrate stoppered in its flask. The residue was treated, out of the dry box, with distilled water and dried in an oven at 120°C, and weighed yielding 1.8845 gm AgI.

$^1H$ NMR of an aliquot of the solution showed only one peak at $\tau$ 5.8 from external TMS, infra red spectroscopy showed the presence of the characteristic perchlorate bands at 1460 $cm^{-1}$ and it was concluded that the solution contained 0.9172 g (8.01 m mole) $CH_3ClO_4$ representing the complete conversion of the methyl iodide.

Methyl fluorosulphate, $CH_3OSO_2F$, was prepared from fluorosulphuric acid and dimethyl sulphate in the apparatus shown in Figure 12.

60 ml (1 mole) fluorosulphuric acid was placed in a 250 ml two-necked round bottomed flask containing some pieces of porous pot. A lagged 12 inch column, with side arm, was connected with a condenser and receiving flask.

150 ml (1.5 mole) dimethyl sulphate was run into the reaction flask and the whole heated to boiling. The fraction boiling at 92°C was collected, treated with anhydrous $Na_2CO_3$ and distilled on the vacuum line into a Rotaflow storage ampoule.

Dimethyl sulphate was treated with anhydrous sodium carbonate, decanted, and used without further purification.

### (c) Ammonia and the Methyl Amines

Ammonia, $NH_3$, was introduced from a cylinder into a trap frozen in liquid air, containing some small pieces of clean sodium metal.

The trap was allowed to warm up, producing the characteristic blue-gold coloration, and the ammonia distilled into the fractionation section of the vacuum line, through two traps at -84°C (acetone, solid $CO_2$) and finally frozen at -196°C in liquid nitrogen. The dry ammonia was then transferred to the cold finger of a previously evacuated 20 litre storage bulb, into which it was allowed to expand.

Infra red spectroscopy showed that the material was free from other amines or contaminants.

Methylamine, $CH_3NH_2$, was obtained from a 40% w/v aqueous solution by distillation from the solution into the fractionation section of the vacuum line, the solution being exposed, with care, to the pump via two baths at -84°C (acetone, solid $CO_2$) and a trap at -196°C.

The majority of the product collected at -84°C, along with some water and some ammonia. A second distillation through a -84°C bath, collected methylamine and ammonia. The separation of the $NH_3$ from $CH_3NH_2$ proved to be difficult but some five distillations through a -84°C bath, and frequent monitoring of the infra red spectrum of the first and subsequent volatiles at -84°C, indicated that after five distillations the residual methylamine at -84°C was ammonia free. The amine was stored in a Rotaflow storage ampoule.

Anhydrous dimethylamine, $(CH_3)_2NH$, was obtained in 500 ml ampoules as reagent grade chemical. The ampoule was cooled in an ice/NaCl mixture and opened in the fume hood, the contents being poured briskly into a cooled flask fitted with a tap cone connector. After degassing on the vacuum line the amine was distilled through a -64°C bath (melting chloroform) and collected in a trap, at -196°C, in liquid nitrogen. Infra red spectroscopy revealed the major contaminant to be tetramethylmethylenediamine, ($(CH_3)_2NCH_2N(CH_3)_2$), which was retained at -64°C (Bpt 98°C, 760 mm). The purified amine was stored in a large Rotaflow storage ampoule.

Trimethylamine, $(CH_3)_3N$, was obtained as the anhydrous reagent grade material in 500 ml ampoules. The purification procedures for this amine were the same as that used for dimethylamine, and the resultant pure dry amine was stored in a large Rotaflow storage ampoule. Purity was checked by infra red spectroscopy on samples of the vapour at various pressures, comparisons being made with published data. In no cases were there any absorptions not accountable for by the pure amine.

### (d) The Hydrazines

Hydrazine, $N_2H_4$, can be prepared as the anhydrous compound, from a hydrazinium salt and liquid ammonia, requiring fairly large volumes of liquid ammonia and some none too simple manipulative techniques such as filtering solutions of liquid ammonia in a dry atmosphere. A simpler method was to start with the hydrate, $N_2H_4.H_2O$ and dehydrate with calcium hydride, $CaH_2$, in the dry box. In a typical preparation, ca 20 ml hydrazine hydrate was treated with excess calcium hydride in the dry box, in a two-necked flask. The hydrazine hydrate, calcium hydride slurry was then removed from the dry box and quickly fitted to a condenser set for reflux with a nitrogen purge. The purged flask was heated and the mixture allowed to reflux for an hour, and then distilled. Final infra red check and melting point (1.5°C) showed pure anhydrous hydrazine (hydrate melting point is -40°C).

The methyl and dimethyl hydrazines, $CH_3NHNH_2$, $(CH_3)_2NNH_2$, were obtained as anhydrous reagents, and purified by treating with calcium hydride and distilling on the vacuum line. N,N dimethylhydrazine was distilled four times through a -84°C bath (acetone, solid $CO_2$) removing $NH_3$. No evidence of oxidation of the final sample of $CH_3NHNH_2$ was found, no methane apparent in the infra red spectrum, methyl hydrazine vapour is prone to oxidation in the air, by a first order process yielding methane and nitrogen (101)

These products were stored in Rotaflow ampoules.

Trimethylhydrazine, $(CH_3)_2NNHCH_3$, was prepared from N,N dimethylhydrazine following the method of Class (75) by converting N,N dimethylhydrazine into N,N dimethylmethyleneimmine and subsequently reducing to trimethylhydrazine, according to the reaction sequence below.

$$(CH_3)_2NNH_2 + CH_2O \longrightarrow (CH_3)_2NN = CH_2 + H_2O$$

$$(CH_3)_2NN = CH_2 \xrightarrow{LiAlH_4} (CH_3)_2NNHCH_3$$

The method of Class was followed until the final stages where the free hydrazine was distilled from a caustic soda solution of its hydrochloride on the vacuum line, collecting in a Rotaflow ampoule part filled with calcium hydride. The hydrazine was shaken with the drying agent for approximately one hour and then distilled into a Rotaflow storage ampoule.

Infra red spectroscopy showed the product to be free of any $(CH_3)_2NN = CH_2$ which can result from oxidation of the hydrazine (76).

### (e) The Halogens $Cl_2$, $Br_2$, $I_2$

Chlorine was obtained from a cylinder and introduced into the fractionation section of the vacuum line through two traps at -84°C (acetone, solid $CO_2$) and collected at -196°C. Infra red spectroscopy in a gas cell with NaCl plates showed no HCl at pressures up to 500 mm Hg, but some $CO_2$ which was removed by holding the chlorine at -84°C, and carefully pumping. The halogen was stored in two 5 litre storage bulbs on the vacuum line for immediate use and as a liquid in a heavy walled pyrex ampoule, and in a heavy walled Rotaflow storage ampoule, in the refrigerator.

Bromine was purified by shaking with anhydrous sodium carbonate, decanting and drying over phosphoric oxide and finally distilling into a Rotaflow storage ampoule.

Iodine was sublimed, under vacuum, transferred to the dry box and bottled in the dry box.

The sections of the vacuum line used for handling these halogens were greased with Kel-F 90, a fully fluorinated grease, to minimise absorption and deterioration. After the purification procedures all relevant sections were regreased with Apiezon L and M grease.

### (f) Other Chemicals

Boron trichloride, $BCl_3$, was obtained in 50 ml ampoules which were cooled in ice/salt mixture, opened and transferred to a purged flask equipped with a tap cone connector and introduced, after degassing, into the fractionation section of the vacuum line, where it was distilled through a trap at -95°C (melting toluene), a trap at -116°C (melting diethyl ether), and into a trap at -196°C. The compound was liquid at -95°C and solid at -116°C. HCl, which was apparent in the crude material was removed completely at -116°C (HCl vapour pressure is approximately 100 mm Hg. at this temperature). A small quantity of the purified product was condensed into a Rotaflow storage ampoule, the ampoule sealed, allowed to warm to room temperature and the $BCl_3$ swished around the inside. The ampoule was then returned to the line and pumped out, and the remaining bulk of the $BCl_3$ distilled in. This procedure was adopted to make sure of the dryness of the inner surface of the storage ampoule.

Sulphur dioxide, $SO_2$, was obtained in pressurised cans from which the liquid was poured onto an excess of phosphoric oxide in a round bottomed flask equipped with a tap cone connector. After degassing the compound was distilled from the phosphoric oxide through a -84°C bath (acetone, solid $CO_2$) and collected at -196°C. Infra red spectroscopy indicated the purity of the sample, and it was stored in a Rotaflow storage ampoule.

Antimony pentachloride, $SbCl_5$, and antimony pentafluoride, $SbF_5$, were used as obtained, as satisfactory analytical figures were found. ($SbCl_5$, Found %, Sb, 40.51; Cl, 58.63; required %, Sb, 40.71; Cl, 59.29. $SbF_5$, Found %, Sb, 55.72; F, 42.31; required %, Sb, 56.81; F, 43.83.)

### (g) N-Halamines

There are many varied methods, in the literature, for preparing N-halamines. Classically, $(CH_3)_2NCl$, is prepared from a solution of dimethylammonium chloride and sodium hypochlorite, but chloramines have been formed from t-Butyl hypochlorite and an amine, and from the cleavage of trimethylsilylamines with chlorine gas (77).

A convenient method of formation of simple alkyl halamines was found to be that of Ruschig (78) where dialkylamines were treated with N—chlorosuccinimide. The succinimide reaction was found to be most convenient, and provides better yields than with the use of dimethylammonium chloride and sodium hypochlorite.

In a typical preparation of dimethylchloramine, 7 gm (52.4 m mole) N-chlorosuccinimide was placed in a Rotaflow weight analysis cell and after degassing on the vacuum line, 2.2206 gm (49.35 m mole) dimethylamine was condensed in. The Rotaflow was sealed and placed in a freezer at -23°C for 24 hours, after which time the cell was returned to the vacuum line and the volatile material distilled out. Infra red spectroscopy showed no strong C-N vibrations of $(CH_3)_2NH$ at approximately 780 $cm^{-1}$, and the presence of a weaker absorption at 600 $cm^{-1}$ was noted (N-Cl vibration). The total volatiles recovered weighed 3.7814 gm representing a conversion of 96.4%.

Dimethylchloramine was stored on the vacuum line in one of the traps on the fractionation train, frozen at -196°C, because of its instability at elevated temperatures.
The infra red spectrum of $(CH_3)_2NCl$ was recorded in the vapour phase and the spectrum is shown in Figure 14. Figure 15 shows the infra red spectrum of $(CH_3)_2NCl$ at -196°C in a low temperature cell. The bands at 590, 910, 1005, 1160, 1190, 1210 $cm^{-1}$ correspond to the values 592, 912, 1004, 1149, 1684, 1209 $cm^{-1}$, Heasley V. L. quotes for the chloramine in solution (47).

Dimethylbromamine, $(CH_3)_2NBr$, can be prepared utilising similar techniques to that for $(CH_3)_2NCl$. The most satisfactory method of preparation was found in the reaction of N-bromosuccinimide with dimethylamine.
The bromamine is much less stable than the equivalent chloramine, preparations resulting in the pure material often resulted in rapid decomposition to, $CH_4$, $NH_3$, $(CH_3)_3N$, $(CH_3)_2NH$ and $Br_2$ as shown in Figure 16, recorded after a sealed tube of $(CH_3)_2NBr$ turned from the characteristic greenish yellow colour to a dark reddish-brown mass. It was found more convenient to prepare the compound in a solvent, thus increasing its stability.

In a typical preparation of the anhydrous material, 1.9 g (10.7 m mole) N-bromosuccinimide was weighed into a 100 ml round

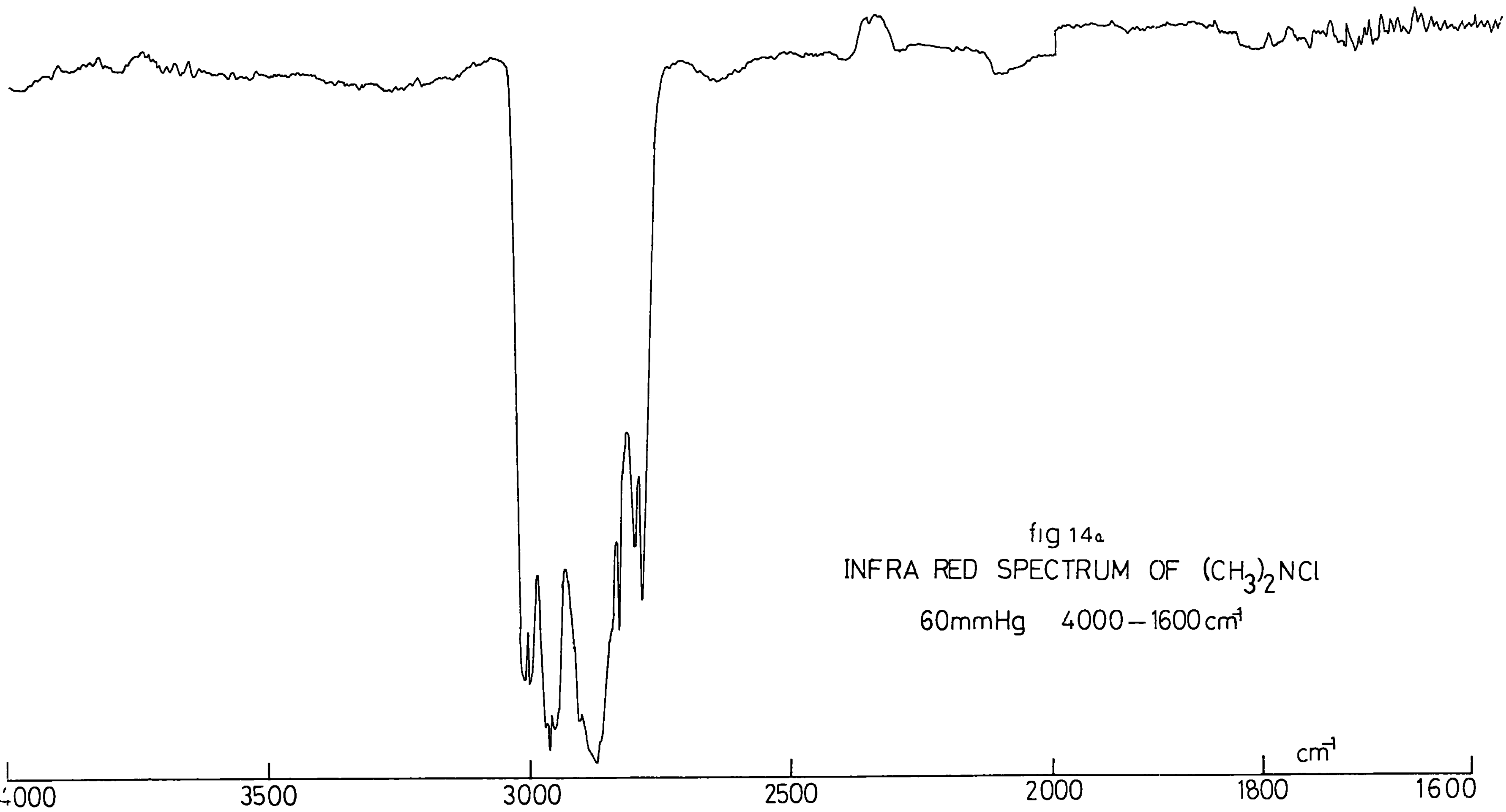
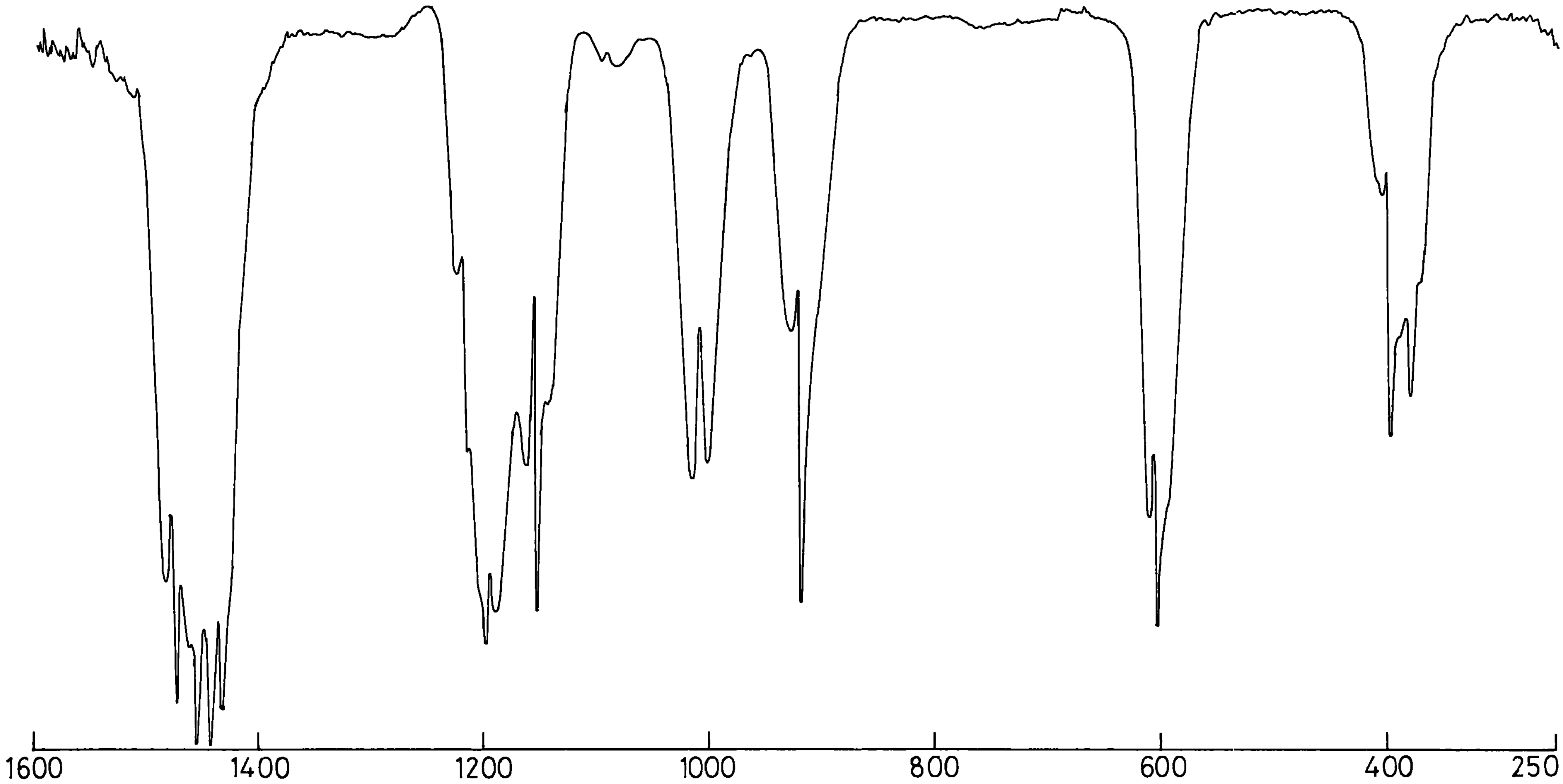


fig 14a

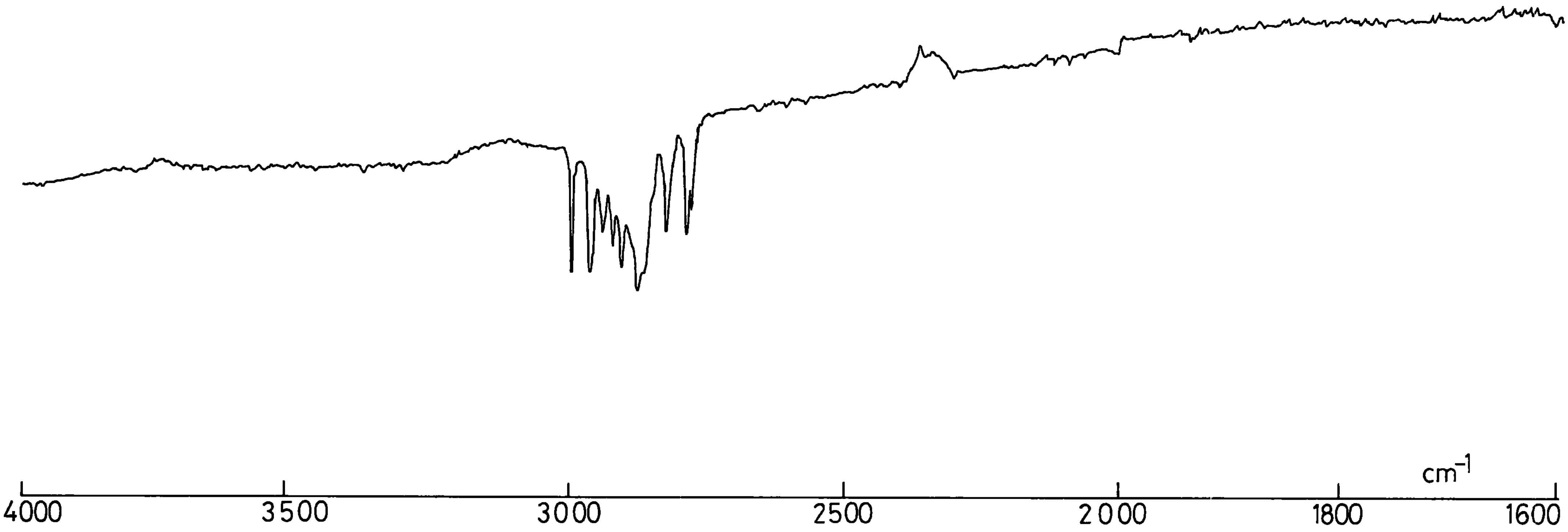
INFRA RED SPECTRUM OF $(CH_3)_2NCl$

60mmHg 4000 – 1600 $cm^{-1}$



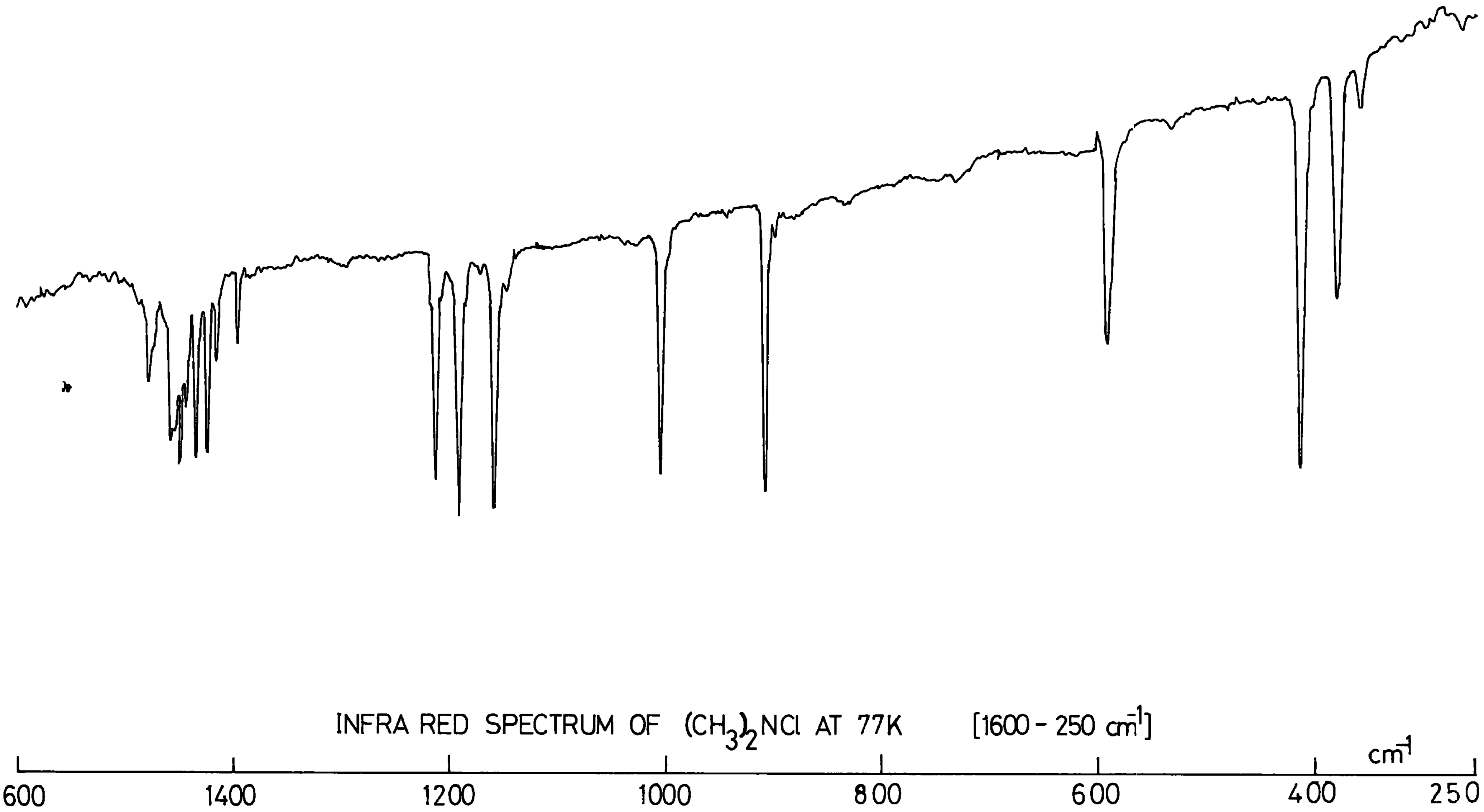
INFRA RED SPECTRUM OF $(CH_3)_2NCl$, 60mmHg, [1600-250 $cm^{-1}$]

fig 14b



INFRA RED SPECTRUM OF $(CH_3)_2NCl$ AT 77K. [4000—1600 cm$^{-1}$]

fig 15a



INFRA RED SPECTRUM OF $(CH_3)_2NCl$ AT 77K [1600 - 250 cm$^{-1}$]

fig 15b

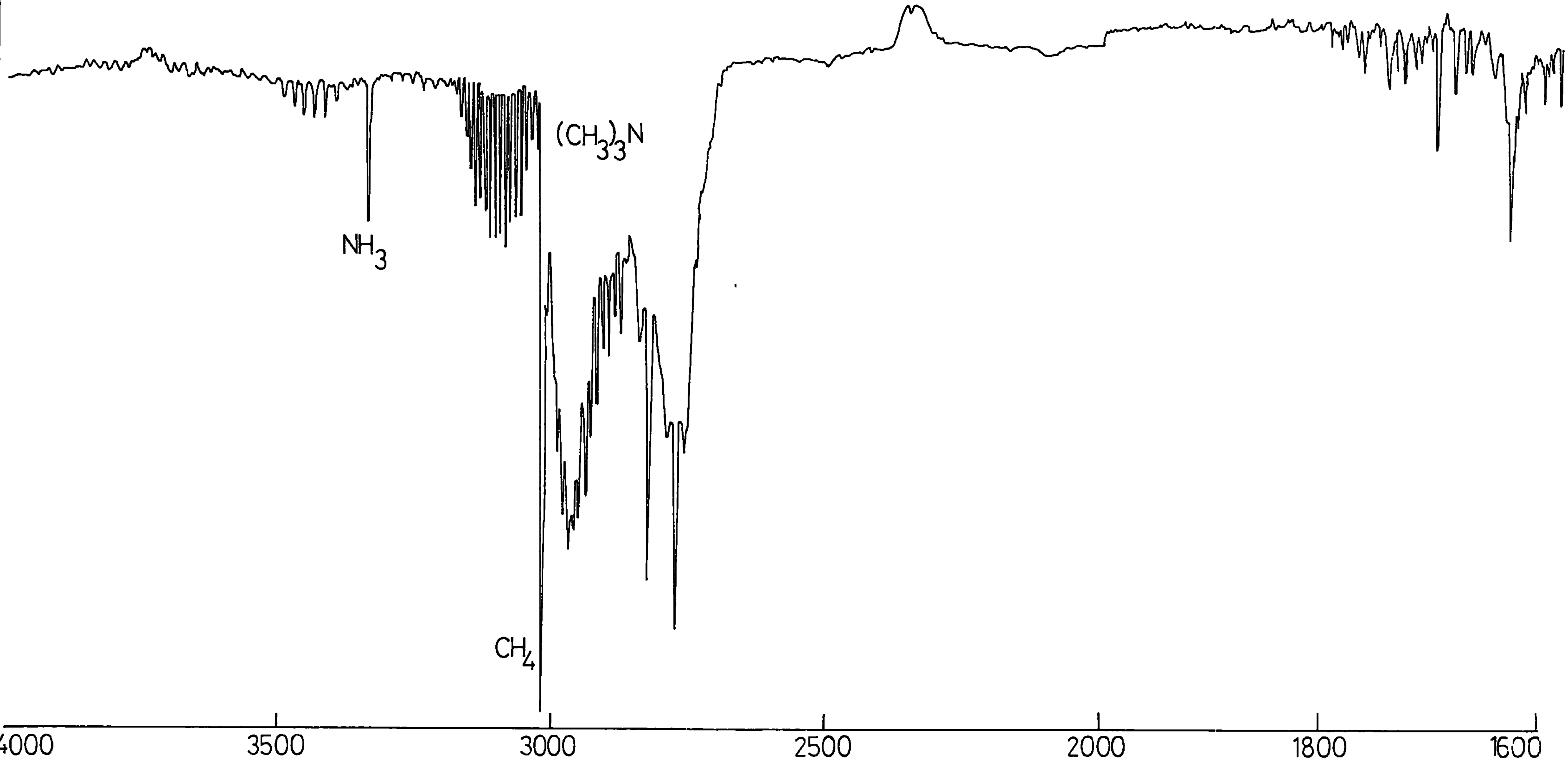


fig 16a INFRA RED SPECTRUM OF THE PRODUCTS OF $(CH_3)_2NBr$ DECOMPOSITION AT -84°C
[4000 — 1600 cm$^{-1}$]

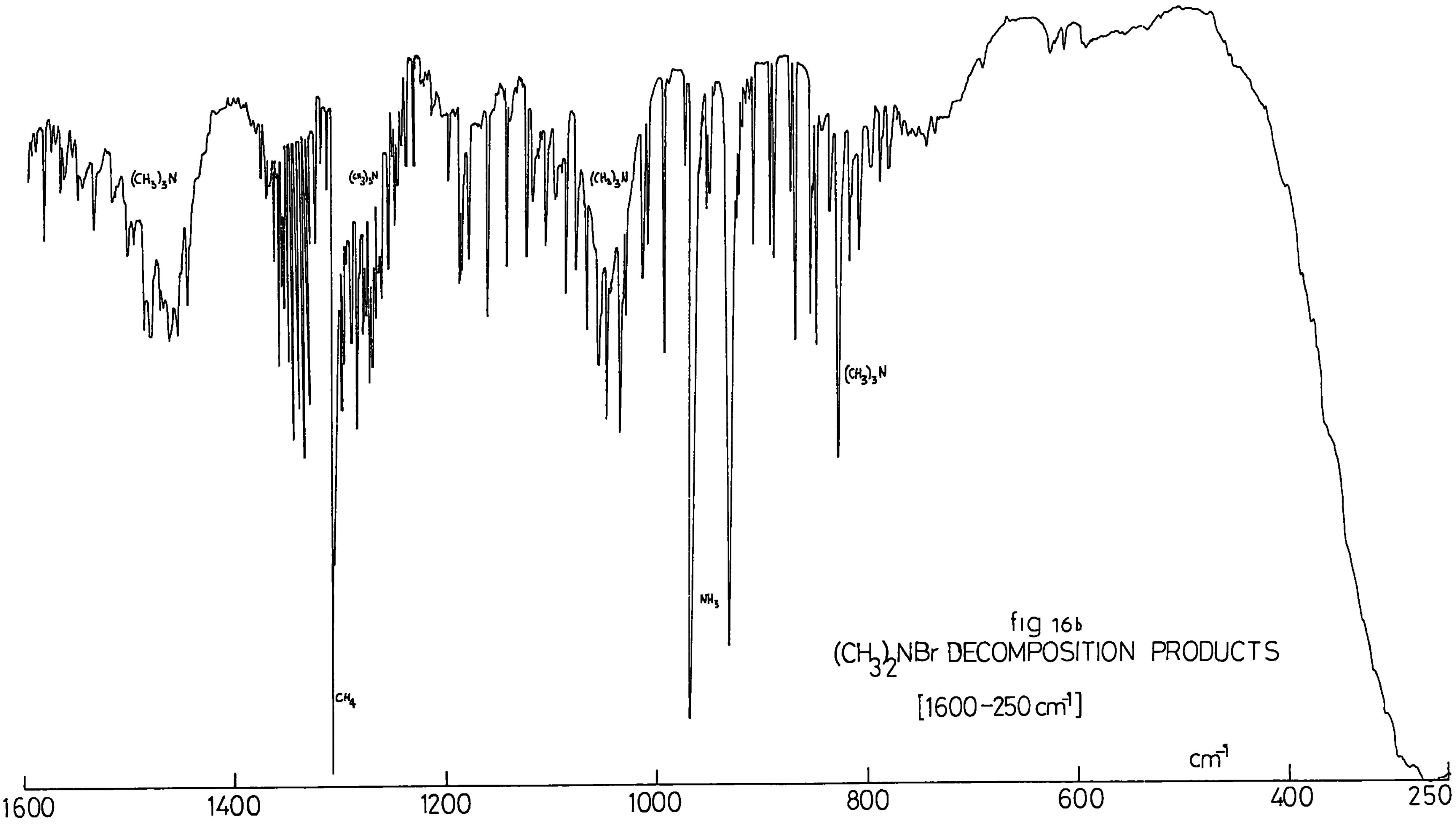


fig 16b

(CH$_3$)$_2$NBr DECOMPOSITION PRODUCTS

[1600–250 cm$^{-1}$]

bottomed flask equipped with a tap cone connector. The flask was placed on the vacuum line and degassed. 0.4147 g (9.2 m mole) $(CH_3)_2NH$ was then condensed onto the bromosuccinimide and the flask isolated from the vacuum line and allowed to warm up to -23°C (melting $CCl_4$), where over a period of fifteen minutes, the yellow colour of the N-bromosuccinimide was observed to fade leaving a partially white residue. At this stage the volatile contents of the flask were distilled into a calibrated test tube on the vacuum line, resulting in the collection of 0.75 ml of a bright greenish-yellow liquid, which was then distilled over as short a distance as possible into a second cold finger containing approximately 0.1 gm N-bromosuccinimide where it was stored frozen at -196°C.

In a typical solvent based preparation, 1.8 g (10.1 m mole) N-bromosuccinimide was ground to a fine powder and placed in a 100 ml beaker to which 40 ml distilled water was added, along with a stirrer bar, and the whole gently stirred to disperse the fine particles of N-bromosuccinimide. To this dispersion 1.50 ml of a 26% w/v aqueous solution of dimethylamine, prepared by condensing 26 gm $(CH_3)_2NH$ into 100 ml distilled water frozen on the vacuum line and allowing to warm to room temperature, was added. The yellow solid gradually disappeared leaving a clear faintly yellow solution. 10 ml $CCl_4$ was then added and the whole transferred to a separating funnel, where the yellow product extracted into the $CCl_4$ layer was transferred to a 100 ml conical flask containing anhydrous $MgCl_2$ and the contents were shaken and then treated with a second quantity of $MgCl_2$. The $MgCl_2$ was allowed to settle leaving a clear yellow solution.

An aliquot of the solution was placed in a UV cell and the absorption spectrum recorded over the range 200-450 nm, showing two absorptions at 262 and 320 nm, which compares with 259 and 320 nm given in the literature (47).

The infra red spectrum was recorded in 0.1 mm path liquid cell and the bands obtained compared with those given by Heasley.

(Heasley) 1201 1172 1148 1001 900 525

(Found) 1205 1175 1145 1000 900 530

All the absorptions were accounted for.

Figures 17 and 18 show the UV and IR spectra of the compound.

### (h) Solvents

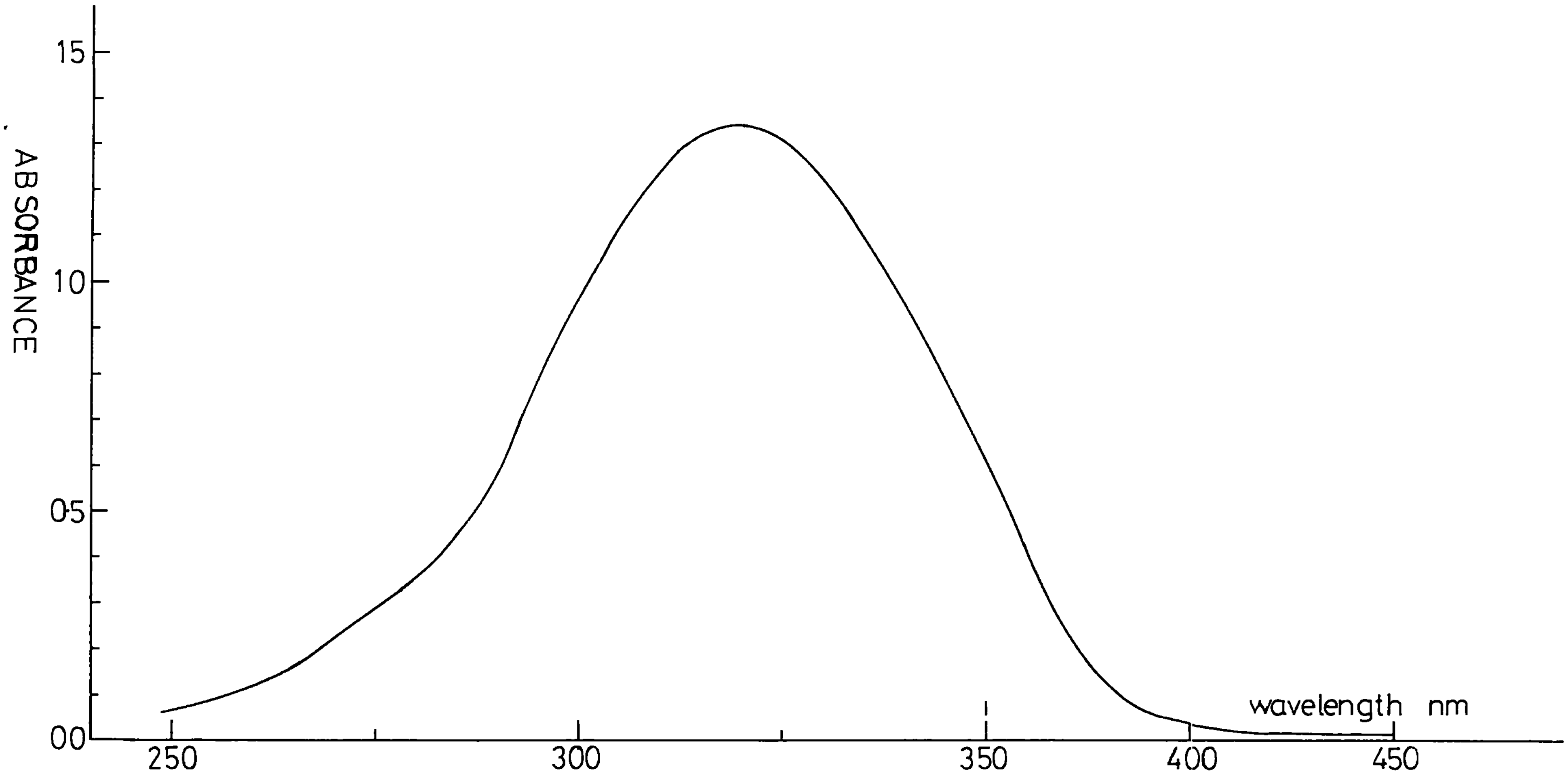
The majority of solvents or reaction media used were either over phosphoric oxide or sodium metal. $CCl_4$ and $CH_2Cl_2$ were refluxed over $P_2O_5$ for approximately half an hour and then distilled into a large flask containing fresh $P_2O_5$.

Chloroform, $CHCl_3$ was washed with sulphuric acid and then water and distilled, under nitrogen, from $P_2O_5$ onto $P_2O_5$ and stored under nitrogen to prevent oxidation to $COCl_2$. Infra red spectroscopy did not reveal any $COCl_2$ when the solvent was handled in this manner.

Diethyl ether and hexane were dried over fine sodium wire, whilst freon 11, trichlorofluoromethane, $CCl_3F$, was distilled in vacuo from $P_2O_5$ into a Rotaflow storage ampoule.

Acetonitrile, $CH_3CN$, was refluxed with phosphoric oxide for approximately half an hour, and then distilled into a receiving flask containing phosphoric oxide.

In all cases, dried solvents were kept in either stoppered 1 litre round bottomed flasks, or for convenience in vacuum line use, in large Rotaflow storage ampoules.



UV SPECTRUM OF $(CH_3)_2NBr$ IN $CCl_4$ SOLUTION

fig 17

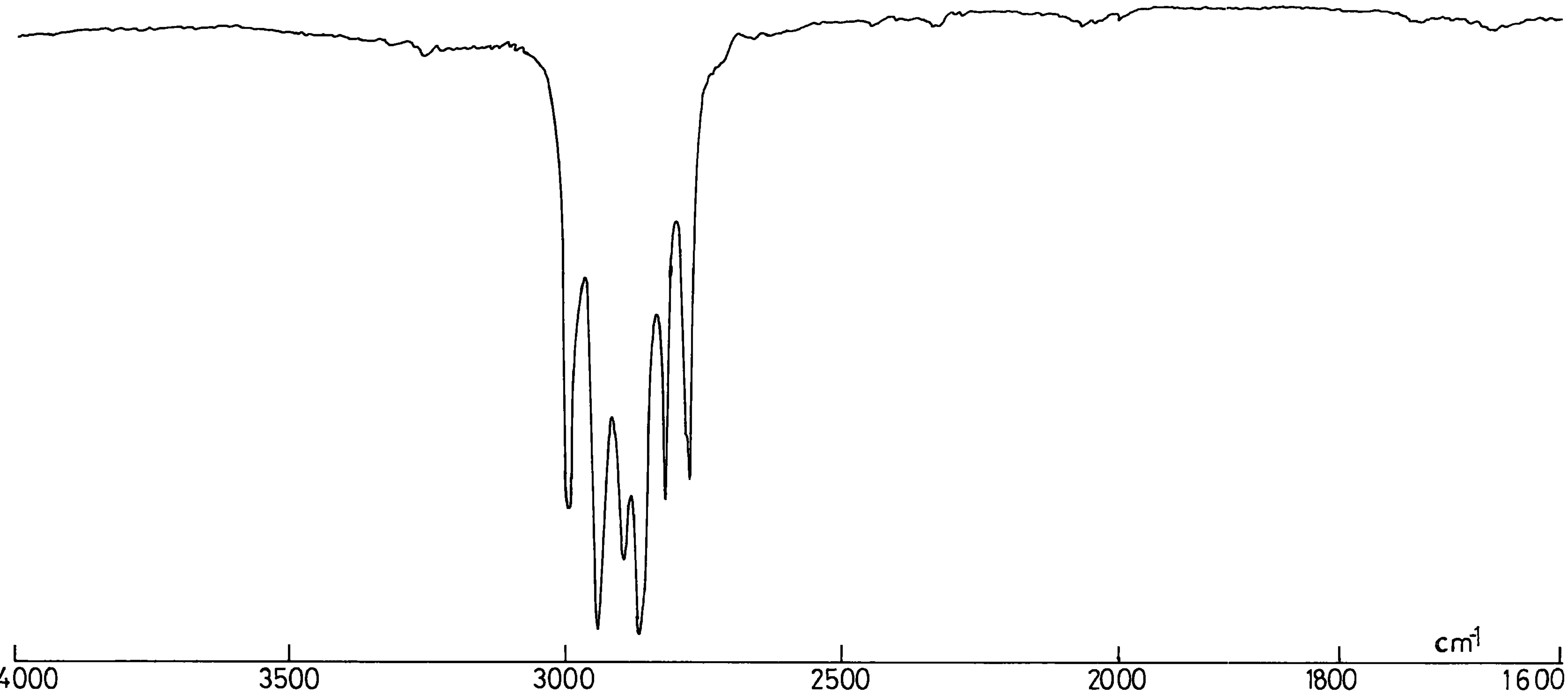


fig 18a INFRA RED SPECTRUM OF $(CH_3)_2NBr$ ($CCl_4$ sol) [4000–1600 cm$^{-1}$]

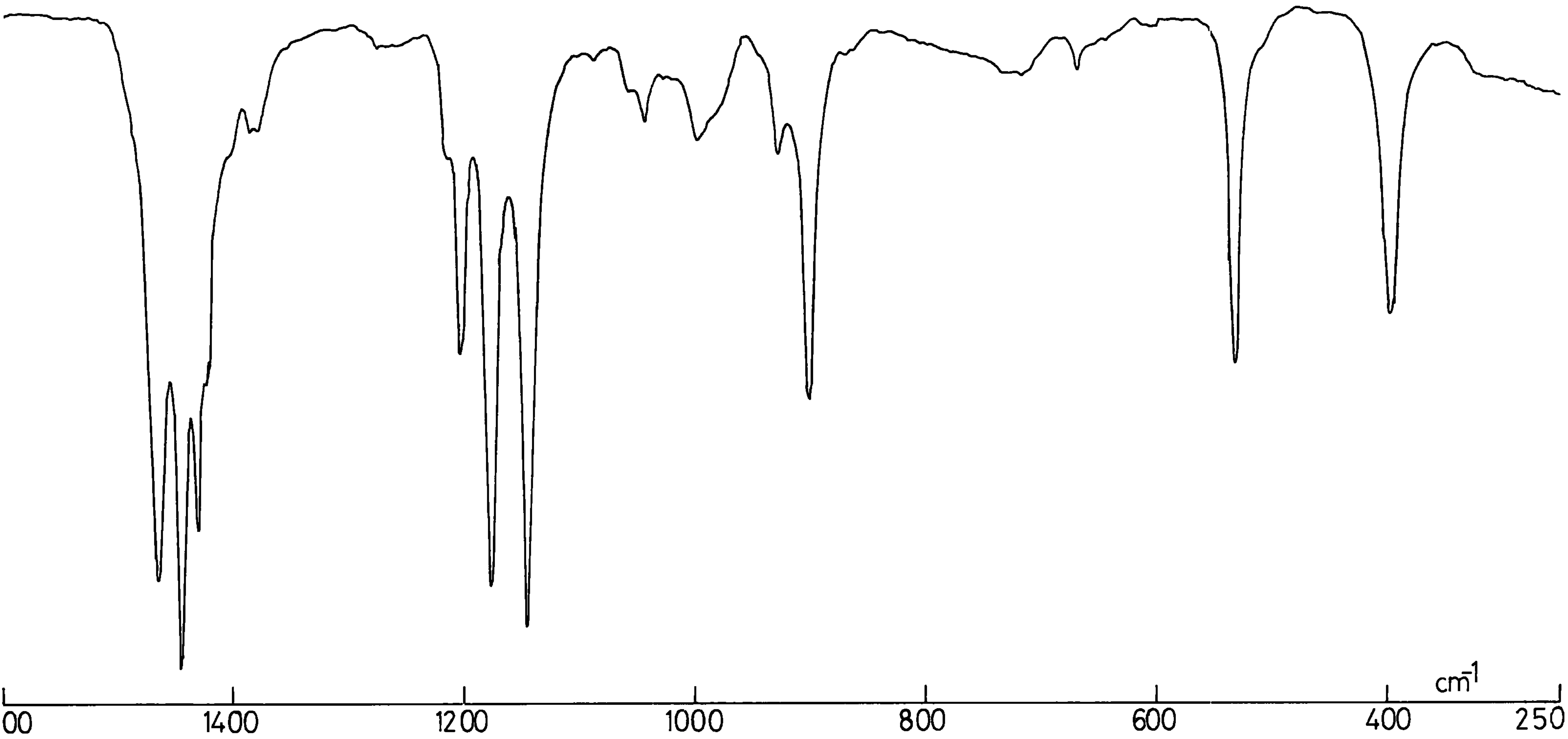


fig 18b INFRA RED SPECTRUM OF $(CH_3)_2NBr$, ($CCl_4$ sol) [1600—250 cm$^{-1}$]

# CHAPTER THREE

## THE REACTIONS OF DIMETHYLCHLORAMINE WITH SIMPLE ALIPHATIC AMINES AND HYDRAZINES

## Introduction

The reactions of chloramine with nitrogenous substrates has been mostly confined to the synthesis of hydrazines, and the reactions in which hydrazines form are detailed below, from the review by Drago (79).

$$NH_2Cl + 2NH_3 \rightarrow (NH_2)_2 + NH_4Cl$$

$$NH_2Cl + 2RNH_2 \rightarrow RNHNH_2 + RNH_3Cl$$

$$NH_2Cl + 2R_2NH \rightarrow R_2NNH_2 + R_2NH_2Cl$$

$$NH_2Cl + R_3N \rightarrow (R_3NNH_2)^+Cl^-$$

$$NH_2Cl + 2NH_3(aq) \rightarrow N_2H_4 + 2NH_4Cl$$

$$NH_2Cl + NH_3(aq) + OH^- \rightarrow N_2H_4 + Cl^- + H_2O$$

$$NH_2Cl + RNH_2(aq) + OH^- \rightarrow RNHNH_2 + Cl^- + H_2O$$

$$NH_2Cl + R_2NH(aq) + OH^- \rightarrow R_2NNH_2 + Cl^- + H_2O$$

$NH_2NH_2$ has also been formed from $NH_2Br$ and $KNH_2$ in liquid ammonia (80).

The reaction between chloramine and ammonia in liquid ammonia was shown by Sisler (81) to be pseudo first order, whilst in aqueous solutions the reaction is first order in both $NH_2Cl$ and $NH_3$ from pH 10-14, and follows a base independant path (82). Nucleophillic substitution of chloramine by ammonia is used to explain the base independant pathway, and substitution of alkyl groups for hydrogen on $NH_3$ increases the reaction rate constant as would be expected for an Sn2 type of reaction. At high alkalinities (up to 9M KOH) the reaction is base catalysed and the reaction is formulated along the lines of a rapid pre-equilibrium formation of the chloramide ion which is subsequently attacked by ammonia:

$$OH^- + NH_2Cl \rightarrow NHCl^- + H_2O$$

$$NH_3 + NHCl^- \rightarrow N_2H_4 + Cl^-$$

The reaction between chloramine and alkyl substituted ammonias is believed to follow a similar pathway at pH up to 14, and indeed the reaction product from the $R_3N$, $NH_2Cl$ interaction is similar to that proposed for the intermediate in the Sn2 reaction of $NH_2Cl$ and $NH_3$:

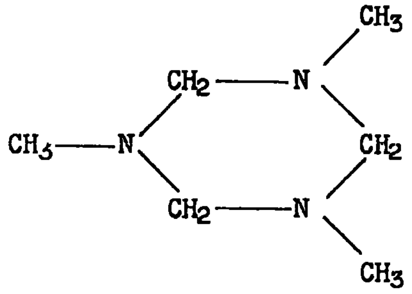
$$NH_3 + NH_2Cl \longrightarrow [H_3\overset{+}{N}\text{-}NH_2Cl^-] \longrightarrow N_2H_4 + Cl^-$$

$$R_3N + NH_2Cl \longrightarrow [R_3\overset{+}{N}NH_2\ Cl^-]$$

The quest for hydrazines led Klages (99) to the reaction between dialkylchloramines and copper bronze, but found the reaction

$$(CH_3)_2NCl \overset{\text{CuBronze}}{\not\longrightarrow} ((CH_3)_2N)_2$$

did not yield tetramethylhydrazine but formed, amongst other products, tetramethylmethylenediamine, $(CH_3)_2NCH_2N(CH_3)_2$ and trimethyltriamine:

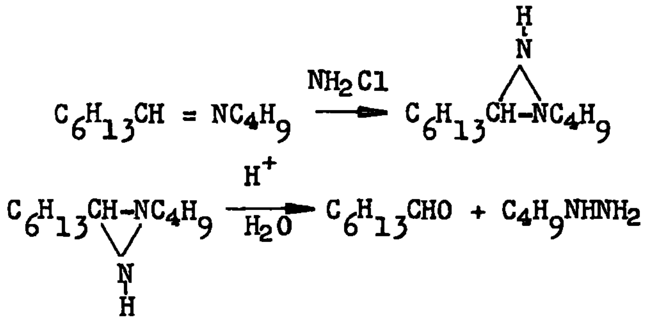


Both products being indicative of dealkylation of the chloramine. With higher alkyl amines, reduction to the parent amine occurred:

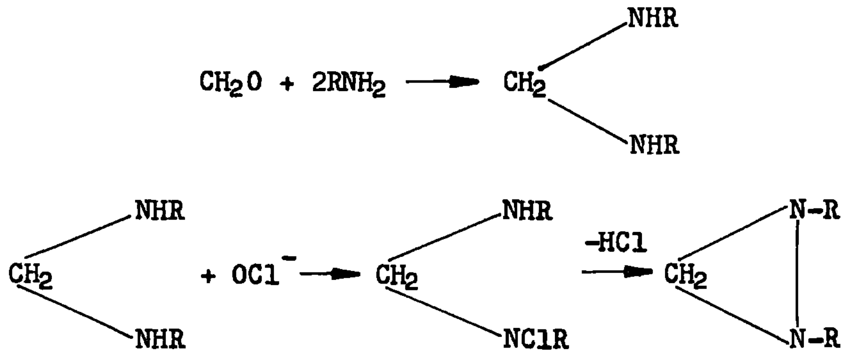
$$t(C_4H_9)_2NCl \xrightarrow{\text{CuBronze}} t(C_4H_9)_2NH$$

and reactions involving dialkylamino magnesium halides also failed to yield tetramethylhydrazine.

Schiff's bases however yield ultimately alkyl hydrazines when the initially formed diaziridine is treated with dilute acid (83)



and diaziridines are also formed from the interaction of $OCl^-$ with alkylamines and formaldehyde in 2N NaOH (84). The reaction proceeding via N-chlorination of the formaldehyde - amine addition product and subsequent dehydrohalegonation:



yields of 72% have been reported for R = n-Butyl (84).

With Hydrazines, chloramine reacts to form triazanium salts (85)

$$R_2NNH_2 + NH_2Cl \longrightarrow [H_2NNR_2NH_2]^+Cl^-$$

The triazanium ion $NH_2NH_2NH_2^+$ was suggested by Sisler (81) to be the probable intermediate in the decomposition of hydrazine by chloramine in liquid ammonia:

$$NH_2NH_2 + NH_2Cl \longrightarrow NH_2NH_2NH_2^+Cl^-$$

and,

$$2NH_2\overset{+}{N}H_2NH_2Cl^- \longrightarrow 2NH_4Cl + N_2H_4 + N_2$$

yielding an overall reaction:

$$N_2H_4 + 2NH_2Cl \longrightarrow 2NH_4Cl + N_2$$

On closer inspection, the reaction between $NH_2Cl$ and 1,1 dimethylhydrazine was found to yield, along with the expected 2,2 dimethyltriazanium chloride, tetramethyl-2-tetrazene, $(CH_3)_2NN = NN(CH_3)_2$, (86). Sisler (86) found that the presence of ammonia in the $NH_2Cl$, increased the yield of 2,2 dimethyltriazanium chloride whilst decreased the amount of tetramethyl-2-tetrazene, and concluded that the mode of attack of 1,1 dimethylhydrazine with chloramine is uncertain, but involves either direct attachment on the $(CH_3)_2N-$ moety to yield directly $(CH_3)_2N(NH_2)_2\ Cl^-$, or a hydrogen abstraction reaction yielding either $(CH_3)_2N\overset{|}{N}H$ or $(CH_3)_2NN\!<$ groups as reactive intermediates. The presence of $NH_3$ which was found to decrease the yield of $((CH_3)_2NN)_2$, was considered to reform $(CH_3)_2NNH_2$ from the radicals produced from hydrogen abstraction of the hydrazine:

$$(CH_3)_2NNH_2 \xrightarrow{NH_2Cl} (CH_3)_2N\dot{N}H$$

$$(CH_3)_2N\dot{N}H + NH_3 \longrightarrow \dot{N}H_2 + (CH_3)_2NNH_2$$

Thus effectively removing hydrazine radicals from the sphere of reaction and consequently reducing the extent to which $((CH_3)_2NN)_2$ forms according to the reaction:

$$2(CH_3)_2N\dot{N}H \longrightarrow (CH_3)_2NNHNHN(CH_3)_2$$

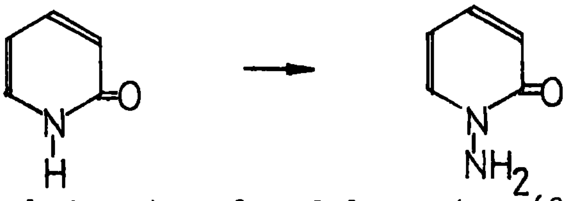
$$(CH_3)_2NNHNHN(CH_3)_2 \xrightarrow{NH_2Cl} (CH_3)_2NN = NN(CH_3)_2$$

and

$$2(CH_3)_2NN\!: \longrightarrow (CH_3)_2NN = NN(CH_3)_2$$

Chloramination of $(CH_3)_2NNHCH_3$ and $(CH_3)_2NN = CH_2$ are also reported to yield $(CH_3)_2N(NH_2)_2Cl$ (85).

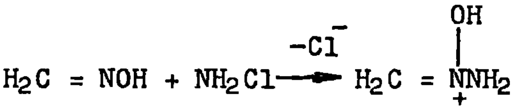
Chloramine will react with heterocyclic bases to yield the corresponding hydrazine in low yield (87), for example from α pyridone:



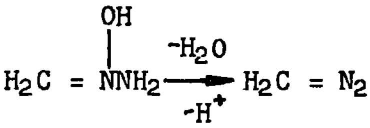
and diazo compounds have been formed from oximes (88).

The diazo compounds from the oximes of acetophenone, benzophenone and benzaldehyde were prepared in this way.

Purely aliphatic oximes yield aliphatic diazo compounds as shown by the 75% yield of diazomethane from formaldehyde oxime and chloramine (89), and Gassman (88) considered that a sequence of steps initiated by nucleophillic displacement at the chloramine nitrogen was most likely:

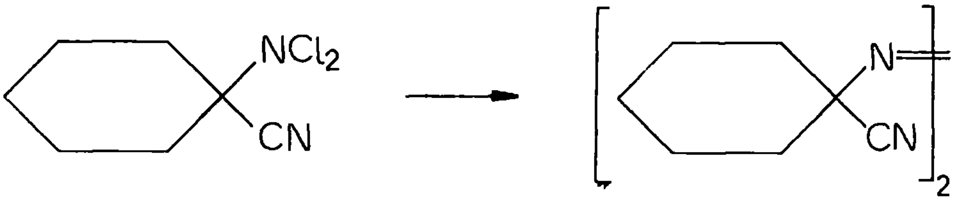


$$H_2C = NOH + NH_2Cl \xrightarrow{-Cl^-} H_2C = \overset{\overset{OH}{|}}{\underset{+}{N}}NH_2$$



$$H_2C = \overset{\overset{OH}{|}}{N}NH_2 \xrightarrow[-H^+]{-H_2O} H_2C = N_2$$

Symmetrical Azo compounds can be prepared by coupling 2 mole N,N-dichloramine (90) in methanol solution with 50% NaOH at low temperature.



and in general NCRRCN = NCRRCN forms by this method, where R and R are low molecular weight alkyl groups; or RR is a cycloalkyl group as shown in the example.

Bock (91) investigated nucleophillic substitution reaction in N-chloramines with the anions $N_3^-$ and $SCN^-$, finding that with $LiN_3$ in THF, azidotetrahydrofuran was produced, but with $NaN_3$, the first dialkylamino azide was prepared:

$$(CH_3)_2NCl + NaN_3 \xrightarrow{CH_2Cl_2} (CH_3)_2NN_3 + NaCl \quad (25\% \text{ yield})$$

and with $NH_4SCN$, a dialkylamino thiocyanate was produced:

$$NH_4SCN + (CH_3)_2NCl \xrightarrow[\text{R.T. 5 hours}]{CH_3CN} (CH_3)_2NSCN + NH_4Cl$$

with other anions, $NH_2Cl$ reacts with $OH^-$ to form hydroxylamine by a Sn2 mechanism (92):

$$NH_2Cl + OH^- \longrightarrow NH_2OH$$

whilst in strongly basic conditions (93)

$$NH_2Cl + OH^- \longrightarrow NH_3 + OCl^-$$

With $CN^-$, $NH_2Cl$ yields an amino cyanide which can further react to yield a disubstituted cyanide (94)

$$2NH_2Cl + 2KCN \xrightarrow{0°C} 2NH_2CN + 2KCl$$

$$2NH_2CN \longrightarrow NH(CN)_2 + NH_3$$

but Markwald (95) reported KCNO as a product and, Raschig (96) reported CNCl as a product.

Alkoxides yield $RONH_2$ compounds when treated with $NH_2Cl$ in ROH (97, 98)

$$RO^- + NH_2Cl \xrightarrow{ROH} RONH_2 + Cl^-$$

In this Chapter the reactions of $(CH_3)_2NCl$ with nitrogen bases such as the methyl substituted ammonias and hydrazines are presented, and the results discussed by comparing and contrasting with the corresponding $NH_2Cl$ reactions.

## Results and Discussion

The results of the investigations into the reactions of dimethyl chloramine with nitrogenous substrates are summarised in Table 2 below. An equation indicates where the stoichiometry has been established. All reactants were anhydrous unless otherwise stated.

TABLE 2: REACTIONS OF $(CH_3)_2NCl$ WITH SOME AMINES AND HYDRAZINES

| Reactant | Identified Products |
|---|---|
| $(CH_3)_2NCl$ | $(CH_3)_2NH;((CH_3)_2N)_2CH_2;(CH_3)_2NH_2Cl$ |
| $NH_3$ | $(CH_3)_2NCl+2NH_3 \rightarrow (CH_3)_2NNH_2+NH_4Cl$ |
| $CH_3NH_2$ | $2CH_3NH_3+2(CH_3)_2NCl \rightarrow (CH_3)_2NN{=}CH_2+(CH_3)_2NH_2Cl+CH_2NH_3Cl$ |
| $(CH_3)_2NH$ | $CH_4;((CH_3)_2N)_2CH_2;(CH_3)_2NH_2Cl$ |
| $(CH_3)_3N$ | $(CH_3)_2NCl+2(CH_3)_3N \rightarrow ((CH_3)_2N)_2CH_2+(CH_3)_3NHCl$ |
| $N_2H_4$($CCl_3F$ sol) | $(CH_3)_2NH;N_2;(CH_3)_2NH_2Cl;N_2H_5Cl$ |
| $CH_3NHNH_2$($Et_2O$ sol) | $(CH_3)_2NCl+(CH_3)NHNH_2 \rightarrow CH_4+N_2+(CH_3)_2NH+(CH_3NHNH_3Cl$ |
| $(CH_3)_2NNH_2$ | $(CH_3)_2NH;N_2;CH_4;(CH_3)_2NNH_3Cl;(CH_3)_2NH_2Cl$ |
| $(CH_3)_2NNH_2$($Et_2O$ sol) | $(CH_3)_2NH_2Cl;(CH_3)_2NNNN(CH_3)_2$ |
| $CH_3NHN(CH_3)_2$ | $(CH_3)_2NCl+CH_3NHN(CH_3)_2 \rightarrow (CH_3)_2NN = CH_2+(CH_3)_2NH_2Cl$ |

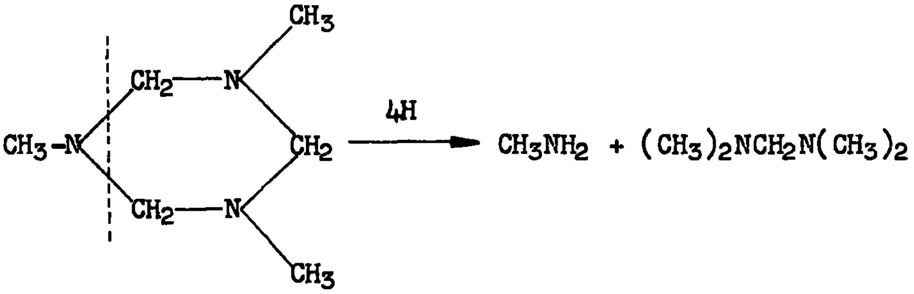
In any considerations of the reactions of $(CH_3)_2NCl$, its inherent instability must be considered, and although the stoichiometry of the decomposition reaction was not established, the products in most abundance were dimethylammonium chloride and tetramethylmethylenediamine, however although the mass balance was satisfactory in the decomposition studied, the molar quantities are in poor agreement.

The amine, $((CH_3)_2N)_2CH_2$ indicates that alkylation has occurred since the C/N ratio of chloramine to the amine was increased from 2:1 to 2.5:1. Klages (99) found tetramethylmethylenediamine in the reaction of dimethylchloramine and copper bronze, also finding the cyclic trimer of N-methylmethyleneimmine ($(CH_3-N = CH_2)_3$), but did not discuss the formation of the diamine.

The formation of the trimer $(CH_3-N = CH_2)_3$ or 1,3,5 trimethyl 1,3,5 hexahydrotriazine, can be easily explained by considering the self dehydrohalegonation of a chloramine molecule

$$(CH_3)_2NCl \longrightarrow CH_3N = CH_2 + HCl$$

and the rapid trimerisation of the so formed immine. It is well known that this trimer is susceptible to aqueous acid decomposition, yielding its usual starting materials, formaldehyde and methylamine, however under anhydrous conditions the pathway of decomposition may be different. It can be envisaged that $(CH_3)_2NCH_2N(CH_3)_2$ forms from the trimer, as indicated by the equation



but such an equation indicates that as much methylamine is formed as tetramethylmethylenediamine, and no methylamine was detected in the decomposition of dimethylchloramine, and further, it is unlikely that the trimer would be reduced in the presence of dimethylchloramine which is an oxidising agent. No evidence of large quantities of $(CH_3-N = CH_2)_3$ was found in the $(CH_3)_2NCl$ decomposition.

Another source of $(CH_3)_2NCH_2N(CH_3)_2$ would be the reaction of a dimethylchloramine molecule with a molecule of trimethylamine:

$$(CH_3)_2NCl + (CH_3)_3N \longrightarrow (CH_3)_2NCH_2N(CH_3)_2 + HCl$$

and this reaction has been studied, as shown in Table 2, and found to yield 100% $(CH_3)_2NCH_2N(CH_3)_2$.

Trimethylamine could form in a disproportionation reaction of the type

$$2(CH_3)_2NCl \longrightarrow (CH_3)_3N + CH_3NCl_2$$

and although no evidence for methyl dichloramine was found in the decomposition of $(CH_3)_2NCl$, $(CH_3)_3N$ was observed amongst the decomposition products of $(CH_3)_2NBr$, however $(CH_3)_2NCH_2N(CH_3)_2$ was not detected from the $(CH_3)_2NBr$ decomposition, which is consistant with $(CH_3)_3N$ being present, since all the $(CH_3)_2NBr$ had decomposed.

Dimethylchloramine reacted with the methyl amines and ammonia, on the whole cleanly, with the exception of dimethylamine.

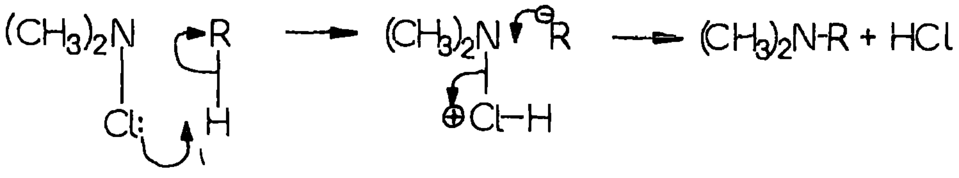
With ammonia and methylamine, hydrazine formation occurred, while with trimethylamine C-N bond formation predominated. Simple nucleophillic attack by ammonia and methylamine on dimethylchloramine would account for N-N bond formation:

R = H, $CH_3$

The polarisation of the N-Cl bond $\overset{\delta+}{N}$-$\overset{\delta-}{Cl}$ assisting $Cl^-$ formation as the N-N bond is established. Subsequent oxidation of the hydrazine $(CH_3)_2NNHCH_3$ with further dimethylchloramine, in the case of the methylamine reaction, yielded the product detected, $(CH_3)_2NN = CH_2$.

In the case of trimethylamine, nucleophillic attack by the amine would not account for the observed products, since by this process the hydrazinium salt $(CH_3)_3\overset{+}{N}N(CH_3)_2Cl^-$, would be expected:

An alternative mechanism, which would indeed account for the products observed in the reactions with $NH_3$, $CH_3NH_2$ and $(CH_3)_3N$ involves the chlorine in $(CH_3)_2NCl$ acting as a nucleophile towards a proton on the amine substrate:



where R = $-NH_2$ in ammonia, $-NHCH_3$ in methylamine and $-CH_2N(CH_3)_2$ in trimethylamine.

It would seem more likely that the actual situation is a compromise between these extremes, the greater basic strength of methylamine (pKb 3.36) over that of trimethylamine (4.20) tending to force the methylamine reaction along the N-nucleophile pathway whilst stearic reasons and a higher pKb tend to guide the trimethylamine reaction along the $Cl^-$ nucleophile pathway. In the case of ammonia, it would seem likely that either the N-nucleophile pathway is favoured because of low stearic hinderance of the nitrogen line pair, or that the Cl-nucleophile pathway is favoured because of the lower basic strength of ammonia (4.75) over methylamine.

It is interesting to note that in the case of methylamine the ultimate product of the reaction was a result of the oxidation of presumably, the initially formed trimethylhydrazine, whilst in the case of ammonia the dimethylhydrazine formed was not attacked, although, as described later, dimethylchloramine does react with dimethylhydrazine. This is perhaps suggestive of two differing mechanisms.

With dimethylamine, the situation is far less clear. Amongst the products detected was the amine tetramethylmethylenediamine. This amine was found in both $(CH_3)_2NCl$ decomposition and in the $(CH_3)_3N$ reaction. In the case of $(CH_3)_3N$ its formation is simply explicable, but with $(CH_3)_2NH$ it is suggestive of $(CH_3)_2NCl$ decomposition since no simple mechanism can yield this product.

The ratio of $(CH_3)_2NCl$ to $((CH_3)_2N)_2CH_2$ found in the decomposition of $(CH_3)_2NCl$ differs from that found in the reaction of $(CH_3)_2NH$ with $(CH_3)_2NCl$, which suggests that the amine is not merely acting as a medium for the chloramine decomposition.

Methane wasfound in both the methylamine and dimethylamine reactions, but not with any other amines studied, perhaps this is related to the order of magnitude greater basic strength of these two amines over that of ammonia and trimethylamine.

With the hydrazines, dimethylchloramine acted as an oxidising agent. $N_2H_4$, $CH_3NHNH_2$, and $(CH_3)_2NNHCH_3$ reacted stoichiometrically yielding $N_2$

in the case of $N_2H_4$, $N_2$ and $CH_4$ with $CH_3NHNH_2$, and the immine, $(CH_3)_2NN = CH_2$, with $(CH_3)_2NNHCH_3$.

With N,N dimethylhydrazine, $(CH_3)_2NNH_2$, the reaction products indicate that although oxidation had taken place, the reaction was by no means straightforward. Products including $CH_4$, $N_2$, and $NH_3$ were detected as was the result of oxidative coupling of two hydrazine molecules, tetramethyl-2-tetrazane, $(CH_3)_2NN = NN(CH_3)_2$.

The hydrazine reactions can be rationalised by considering the initial step to be the formation of a trizanium structure which then breaks down to yield the products found.

In the case of hydrazine itself, the following scheme accounts for the observed stoichiometry, and is in accord with known (100) hydrazine oxidations:

$$2(CH_3)_2NCl + 2N_2H_4 \longrightarrow 2(CH_3)_2NNH_2NH_2{}^+Cl^-$$

$$2(CH_3)_2NNH_2NH_2{}^+Cl^- \longrightarrow 2(CH_3)_2NH + 2NHNH + 2HCl$$

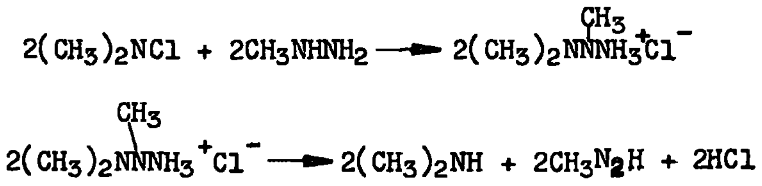
$$2NHNH \longrightarrow N_4H_4$$

$$N_4H_4 \longrightarrow N_2 + N_2H_4$$

yielding an overall reaction:

$$2(CH_3)_2NCl + NH_2NH_2 \longrightarrow 2(CH_3)_2NH_2Cl + N_2$$

By a similar process, monomethylhydrazine yields methane and nitrogen:



$$2(CH_3)_2NCl + 2CH_3NHNH_2 \longrightarrow 2(CH_3)_2N\overset{CH_3}{N}NH_3{}^+Cl^-$$

$$2(CH_3)_2N\overset{CH_3}{N}NH_3{}^+Cl^- \longrightarrow 2(CH_3)_2NH + 2CH_3N_2H + 2HCl$$

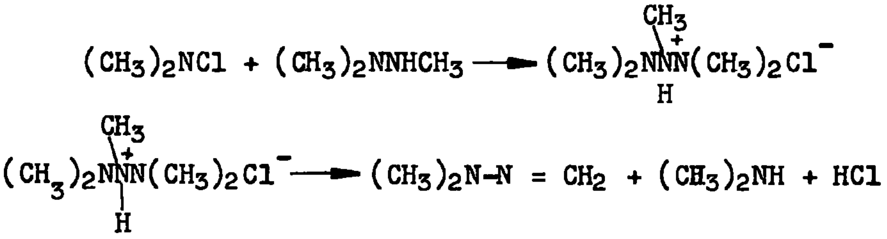
$$2CH_3N_2H \longrightarrow CH_3NHN = NNHCH_3$$

$$CH_3NHN = NNHCH_3 \longrightarrow 2N_2 + 2CH_4$$

overall:

$$(CH_3)_2NCl + CH_3NHNH_2 \longrightarrow CH_4 + N_2 + (CH_3)_2NH_2Cl$$

In the case of trimethylhydrazine, $(CH_3)_2NNCH_3H$, the following scheme accounts for the immine formation:



$$(CH_3)_2NCl + (CH_3)_2NNHCH_3 \longrightarrow (CH_3)_2N\underset{H}{\overset{CH_3}{\overset{+}{N}}}N(CH_3)_2Cl^-$$

$$(CH_3)_2N\underset{H}{\overset{CH_3}{\overset{+}{N}}}N(CH_3)_2Cl^- \longrightarrow (CH_3)_2N\text{-}N = CH_2 + (CH_3)_2NH + HCl$$

and overall:

$$(CH_3)_2NCl + CH_3NNHCH_3 \longrightarrow (CH_3)_2N\text{-}N = CH_2 + (CH_3)_2NH_2Cl$$

In the case of dimethylhydrazine, $(CH_3)_2NNH_2$, the product complexity is difficult to explain along the above lines. It would seem reasonable that initial triazanium salt formation does occur:

$$(CH_3)_2NCl + (CH_3)_2NNH_2 \longrightarrow (CH_3)_2N\text{-}\overset{+}{N}H_2\text{-}N(CH_3)_2Cl^-$$

which can yield the immine:

$$(CH_3)_2N\overset{+}{N}H_2N(CH_3)_2Cl^- \longrightarrow (CH_3)_2\overset{+}{N} = NH + (CH_3)_2NH + Cl^-$$

and this further reacts:

$$2(CH_3)_2\overset{+}{N} = NHCl^- \longrightarrow (CH_3)_2NN = NN(CH_3)_2 + 2HCl$$

which on an overall basis would yield:

$$2(CH_3)_2NCl + 2\,(CH_3)_2NNH_2 \longrightarrow (CH_3)_2NN = NN(CH_3)_2 + 2(CH_3)_2NH_2Cl$$

The formation of tetramethyl-2-tetrazane, $(CH_3)_2NN = NN(CH_3)_2$ was indeed observed, but in quantities far less than that indicated by the equation. The N,N dimethyldiazanium compound $(CH_3)_2N = NHCl^-$, from above, could rearrange to yield methane and a diazonium salt:

$$(CH_3)_2N = NHCl^- \longrightarrow CH_4 + CH_3N \equiv \overset{+}{N}Cl^-$$

which would account for the observed methane, and the subsequent decomposition of this diazonium salt would lead to nitrogen formation, also observed. In this instance methyl chloride would also be expected to form, which was not observed:

$$CH_3\overset{+}{N} \equiv NCl^{-} \longrightarrow CH_3Cl + N_2$$

This mode of reaction would tend to reduce the yield of HCl formed in the initial triazonium decomposition, resulting in the presence of free $(CH_3)_2NH$, which was also observed. It is unclear why $(CH_3)_2NNH_2$ should react in a different manner to the other hydrazines with dimethylchloramine.

## Discussion

A comparison of the reactions of $(CH_3)_2NCl$ and $NH_2Cl$ with the alkylamines and hydrazines is shown in Table 3.

TABLE 3

REACTIONS OF $(CH_3)_2NCl$ AND $NH_2Cl$ WITH SOME AMINES AND HYDRAZINES

| Reactant | Products | | |
|---|---|---|---|
| | $(CH_3)_2NCl$ (this work) | $NH_2Cl$ | (ref) |
| $NH_3$ | $(CH_3)_2NNH_2$ | $N_2H_4$ | 79 |
| $CH_3NH_2$ | $(CH_3)_2NN = CH_2$ | $CH_3NHNH_2$ | 79 |
| $(CH_3)_2NH$ | $CH_4$, $((CH_3)_2N)_2CH_2$ | $(CH_3)_2NNH_2$ | 79 |
| $(CH_3)_3N$ | $((CH_3)_2N)_2CH_2$ | $(CH_3)_3NNH_2Cl$ | 79 |
| $N_2H_4$ | $N_2$ | $N_2$ | 81 |
| $CH_3NHNH_2$ | $CH_4$, $N_2$ | - | |
| $(CH_3)_2NNH_2$ | $CH_4$, $N_2$, $((CH_3)_2N)_2N_2$ | $(CH_3)_2\overset{+}{N}(NH_2)_2Cl^{-}$,<br>$((CH_3)_2N)_2N_2$ | 86 |
| $(CH_3)_2NN(CH_3)H$ | $(CH_3)_2NN = CH_2$ | $(CH_3)_2\overset{+}{N}(NH_2)_2Cl^{-}$ | 85 |

From Table 3, it can be seen that there are several differences between the reactions of $(CH_3)_2NCl$ and $NH_2Cl$ with amines and hydrazines. Most, if not all, $NH_2Cl$ reactions with ammonia, methyl amines and methyl hydrazines, can be rationalised by nucleophillic attack of the substrate nitrogen lone pair on the chloramine nitrogen, since in all the cases above N-N bond formation occurs, whilst in the case of $(CH_3)_2NCl$ this is not entirely so, certainly with trimethylamine C-N bond formation resulted however with ammonia and the hydrazines, a nucleophillic attack mechanism accounts, ultimately, for the products of the reactions.

It is unclear why $(CH_3)_2NH$ does not react with $(CH_3)_2NCl$ in the same way as either $NH_3$ or $(CH_3)_3N$ does, certainly $(CH_3)_2NH$ is more basic in water than either trimethylamine or ammonia, as reflected in the pKb value, and if steric reasons prohibit close enough approach of the attacking nucleophile to $(CH_3)_2NCl$, then C-N bond formation, as in the case of $(CH_3)_3N$, should occur.

Oxidations of hydrazines with N-chloro compounds are known, and most of the simple alkyl hydrazines are easily oxidised. Both $CH_3NHNH_2$ and $(CH_3)_2NNCH_3H$ are oxidisable by air, yielding $CH_4$ and $N_2$ and $(CH_3)_2NN = CH_2$ respectively (101, 102) and of course hydrazine itself is oxidised to nitrogen by $NH_2Cl$.

The reaction between $NH_2Cl$ and the alkyl hydrazines show differences between corresponding $(CH_3)_2NCl$ reactions, especially in the case of trimethylhydrazine, $(CH_3)_2NNHCH_3$, where the triazanium complex was found by Sisler (85). Indeed Sisler found that the oxidation product of trimethylhydrazine, $(CH_3)_2NN = CH_2$ was reduced by $NH_2Cl$ to the triazanium complex.

The oxidation of hydrazine to nitrogen only, by dimethylchloramine, shows that the chloramine is a two electron oxidant, for example (100):

$$M^{n+} + N_2H_4 \longrightarrow N_2H_2 + M^{(n-2)+} + 2H^+$$

$$2N_2H_2 \longrightarrow N_4H_4$$

$$N_4H_4 \begin{array}{l} \nearrow N_2 + N_2H_4 \\ \\ \searrow NH_3 + HN_3 \end{array}$$

and not a one electron oxidant, for example:

$$M^{n+} + N_2H_4 \longrightarrow M^{(n-1)+} + N_2H_3 + H^+$$

$$2N_2H_3 \longrightarrow N_4H_6$$

$$N_4H_6 \longrightarrow N_2 + 2NH_3$$

Diimmide involvement in the two electron case has been shown in the oxidation of hydrazine by aqueous Mo(VI), as $MoO_4^{2-}$ at low pH (100).

$$N_2H_5^+ + Mo(VI) \longrightarrow N_2H_2 + 3H^+ + Mo(IV)$$

$$2N_2H_2 + H^+ \longrightarrow N_2 + N_2H_5^+$$

$$Mo(VI) + Mo(IV) \longrightarrow 2Mo(V) \rightleftharpoons [Mo(V)]_2$$

The $N_2H_2$ was observed mass spectrometrically and also trapped with cis-1,2-cyclohexanedicarboxylic acid.

Methylhydrazine oxidation by the one equivalent oxidant Mn(III), has been studied in aqueous acid perchlorate media, (100), and the reactions:

$$4Mn(III) + 2CH_3NHNH_3^+ \longrightarrow CH_3NH_2N = NNH_2CH_3 + 4Mn(II) + 4H^+$$

$$2Mn(III) + 2(CH_3)_2NNH_3^+ \longrightarrow (CH_3)_2NHNHNHNH(CH_3)_2 + 2Mn(II) + 2H^+$$

$$2Mn(III) + 2(CH_3)_2NNH_2CH_3^+ \longrightarrow (CH_3)_2NHN(CH_3)N(CH_3)NH(CH_3)_2 + 2Mn(II) + 2H^+$$

which contrasts with the oxidation products found when $(CH_3)_2NCl$ is used as oxidant. The Mn(III) reaction with hydrazine shows the one equivalent nature:

$$2Mn(III) + 2N_2H_5^+ \longrightarrow N_3H_5 + NH_4 + 2Mn(II) + H^+$$

and not

$$2Mn(III) + N_2H_5^+ \longrightarrow N_2 + 2Mn(II) + 5H^+$$

which would be expected in a two equivalent case.

Reactions of $(CH_3)_2NCl$ with the silver salts and sodium metal and indicative of little $\overset{\delta+}{N}-\overset{\delta-}{Cl}$ polarisation, certainly less than is present in $\overset{\delta+}{C}-\overset{\delta-}{Cl}$ , which is supported by the $^{35}Cl$ NQR result of 43.67 MHz for $(CH_3)_2NCl$ at -196°C. Most, if not all the reactions in this section support the view that the N-Cl bond is polarised $\overset{\delta+}{N}-\overset{\delta-}{Cl}$ which is in accord with the NQR result being less than that of molecular chlorine.

## Experimental

### 1. Decomposition of $(CH_3)_2NCl$

5.1094 g (64.27 m mole) $(CH_3)_2NCl$ was condensed into a Rotaflow ampoule and left for approximately two weeks in a cupboard at room temperature. It was observed that a quantity of off-white solid had formed. The Rotaflow was connected to the fractionation section of the vacuum line and all volatile material distilled into a trap at -196°C. The Rotaflow was then removed and weighed, yielding 1.5321 g of a yellowish white solid. The Rotaflow was taken into the dry box where the solid was investigated. The infra red spectrum was recorded and

and indicated $(CH_3)_2NH_2Cl$ to be the major component, as shown in Figure 19, the accompanying contaminants were not identified.

1.2132 g of the solid material, which analysed as, %, C, 33.48; H, 9.06; N, 18.35; Cl, 39.3; was placed in a two-necked round bottomed flask, as shown in Figure 20, and approximately 5 $cm^3$ distilled water added. The small bulb was charged with approximately 5 g KOH pellets and carefully attached to the flask, which, when equipped with a tap cone connector, was connected to the fractionation section of the vacuum line.

The KOH pellets were shaken into the solution and the contents of the flask were exposed to the vacuum pump via traps at -64°C, -84°C, and -196°C, the air being pumped away and the volatile contents separating in the fractionation train. The contents of the traps were fractionated and found to contain 0.6413 g $(CH_3)_2NH$ and 0.0113 g $(CH_3)_2NCH_2N(CH_3)_2$. A trace of $NH_3$ was also observed in the spectrum of the more volatile components.

The original volatiles from the Rotaflow were distilled in vacuo and found to contain 2.7133 g (27.83 m mole) $(CH_3)_2NCl$ and 0.8639 g (8.47 m mole) $(CH_3)_2NCH_2N(CH_3)_2$, and no other products were observed.

In the dark, dimethylchloramine decomposed to yield $(CH_3)_2NCH_2N(CH_3)_2$ and $(CH_3)_2NH_2Cl$. The stoichiometry of this decomposition reaction is not clear, however, 30.14 m mole $(CH_3)_2NCl$ yielded 8.47 m mole $(CH_3)_2NCH_2N(CH_3)_2$, and a solid residue of whose analytical figures suggest the empirical formula $C_{25}H_{28}N_{12}Cl$, of which, by infra red spectroscopy, $(CH_3)_2NH_2Cl$ is a major component, and indeed, from the

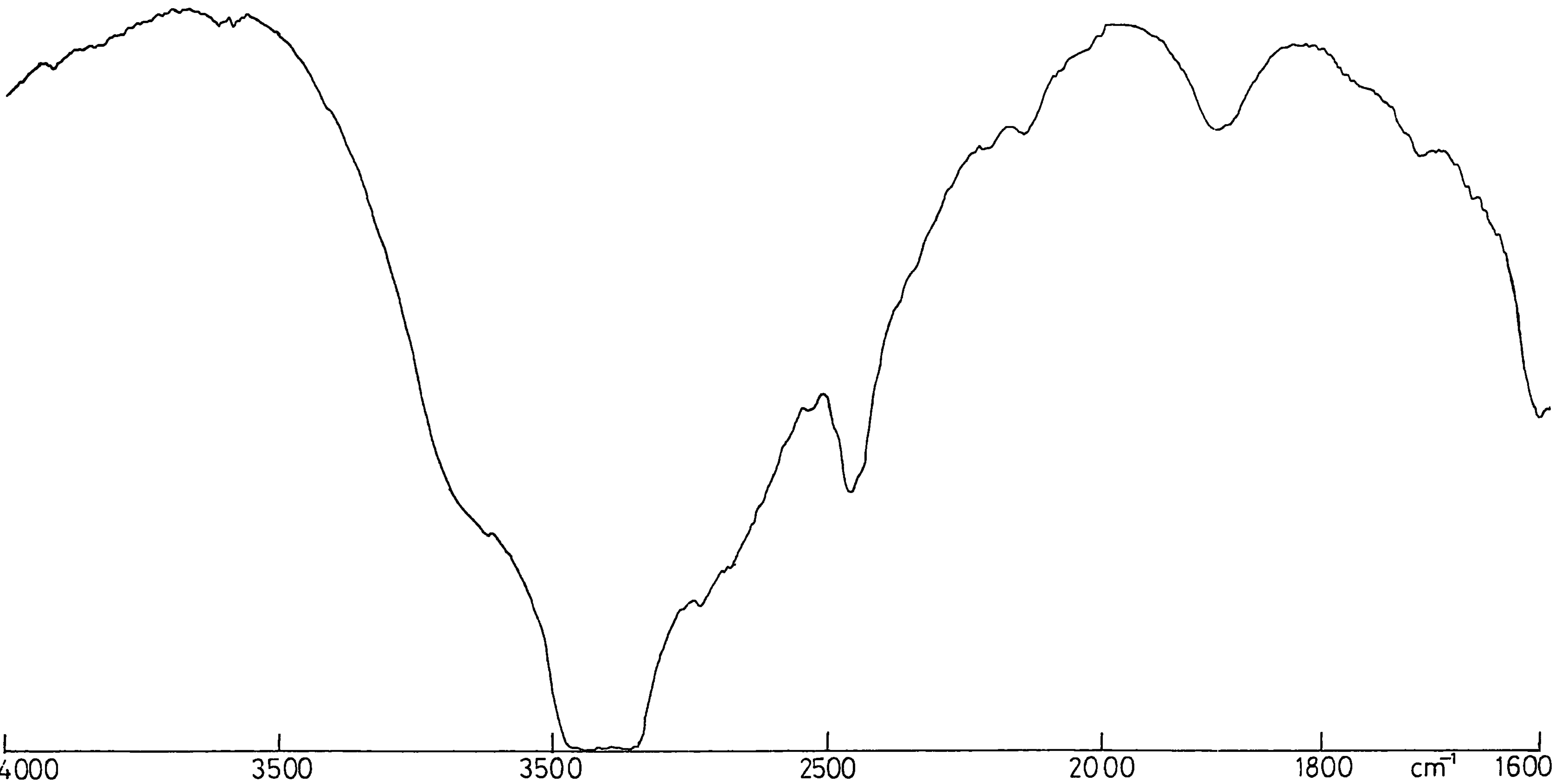


fig 19a INFRA RED SPECTRUM OF THE RESIDUE FROM THE DECOMPOSITION OF $(CH_3)_2NCl$ [4000 - 1600cm$^{-1}$]

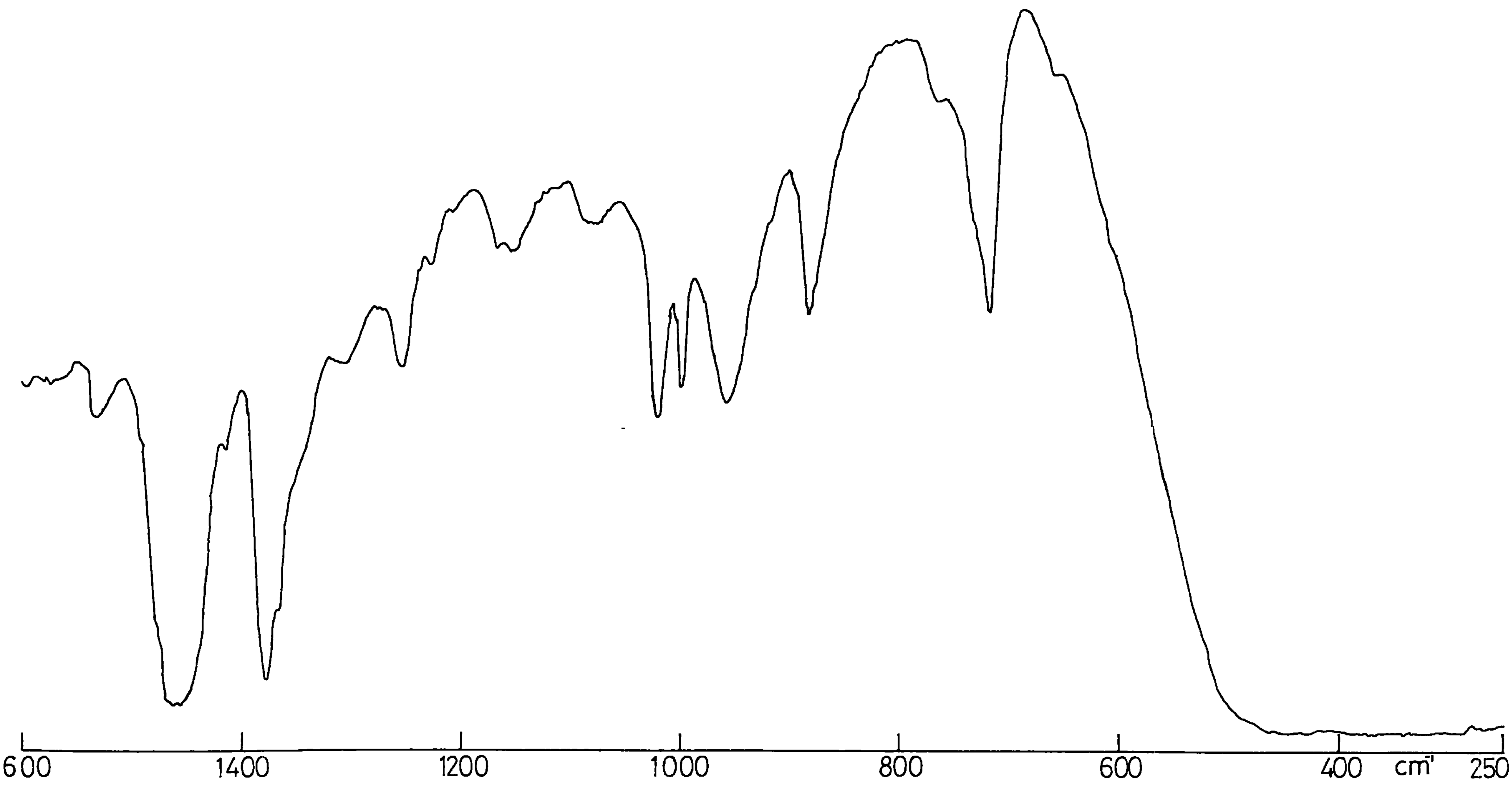


fig19b INFRA RED SPECTRUM OF THE RESIDUE FROM THE DECOMPOSITION OF $(CH_3)_2NCl$ [1600–250cm$^{-1}$]

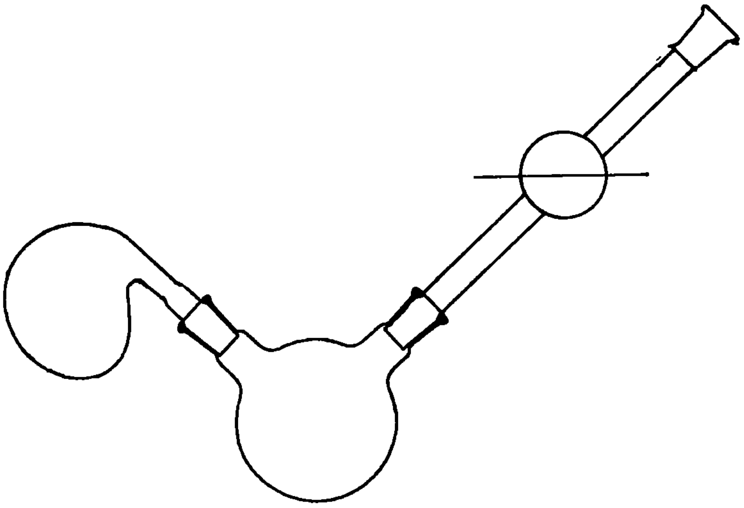


fig 20 APPARATUS USED IN THE REACTIONS OF NaOH WITH AMINE SALTS

treatment of this solid with KOH, the amount of dimethylamine evolved indicates that 95.7% of the solid is dimethylammonium chloride, which on this basis indicates that 18 m moles of the amine salt was formed.

The decomposition of $(CH_3)_2NBr$ was studied at -84°C by holding freshly prepared $(CH_3)_2NBr$ in a Rotaflow in an acetone, solid $CO_2$ slurry until the reaction had commenced and then frozen at -196°C.

The decomposition reaction, which is violent even at -84°C, proceeds within seconds, and subsequent examination of the volatile fraction of the product remaining after the reaction had taken place, revealed $NH_3$, $CH_4$,$(CH_3)_3N$ and a trace of $(CH_3)_2NH$. The solid material which was a dark involatile red brown tar was not investigated.

### 2. The Reactions of $(CH_3)_2NCl$ With The Anhydrous Amines $NH_3$,$CH_3NH_2$, $(CH_3)_2NH$ and $(CH_3)_3N$

#### (a) $NH_3$

A 16 mm OD heavy walled pyrex reaction ampoule was attached to the vacuum line, into which approximately 6 $cm^3$ (7.9512 g, 446.78 m mole) $NH_3$ was condensed, followed by 0.3215 g (4.04 m mole) $(CH_3)_2NCl$. The tube was sealed and allowed to warm to room temperature where the contents formed a clear homogeneous solution. The ampoule was placed in a cupboard where, after three months, no solid material had separated.

The ampoule was fitted to the ampoule breaker, as shown in Figure 8, Chapter 2, and attached to the fractionation section of the vacuum line, and frozen at -196°C. The ampoule was carefully opened to the manometers and no noticeable depression was recorded indicating the absence of any non condensable material. The volatile material was distilled into the fractionation train, via traps at -64°C, -84°C and -196°C, by allowing the ampoule to slowly warm to room temperature.

The bulk of the ammonia collected as a liquid at -84°C, whilst some was solidified at -196°C. Subsequent fractionation at -84°C separated a single component, and the ammonia collected at -196°C. The identity of the component collected at -84°C was found to be the hydrazine $(CH_3)_2NNH_2$, of which there was 0.2308 g.

The ampoule was weighed and transferred to the dry box where it was carefully broken open and the white solid isolated. By careful washing and drying, the pieces of ampoule and breaker were reweighed and the mass of white solid was found to be 0.2113 g, the identity of which was $NH_4Cl$, shown by infra red spectroscopy and confirmed by elemental analysis found (%) H, 7.05; N, 26.33; Cl, 65.94; $NH_4Cl$ requires (%) H, 7.47; N, 26.16; Cl, 66.35. The reaction is summarised in Table 4.

TABLE 4: SUMMARY OF REACTION OF ANHYDROUS $NH_3$ WITH $(CH_3)_2NCl$

| Reactants | Products |
|---|---|
| $NH_3$, 7.9512 g (466.77 m mole) | $(CH_3)_2NNH_2$, 0.2308 g (3.84 m mole) |
| $(CH_3)_2NCl$, 0.3215 g (4.04 m mole) | $NH_4Cl$, 0.2113 g (3.95 m mole) |
|  | $NH_3$, 7.8306 g (460.62 m mole) (by difference) |

Hence 4.04 m mole $(CH_3)_2NCl$ reacted with excess ammonia to yield 3.84 m mole $(CH_3)_2NNH_2$, N,N dimethylhydrazine, and 3.95 m mole ammonium chloride, and the reaction can be expressed by the equation:

$$(CH_3)_2NCl + 2NH_3 \longrightarrow (CH_3)_2NNH_2 + NH_4Cl$$

(b) <u>$CH_3NH_2$</u>

0.2035 g (2.56 m mole) $(CH_3)_2NCl$ was condensed into a 16 mm heavy walled pyrex reaction ampoule, as shown in Figure 8, Chapter 2, followed by 1.4747 (47.58 m mole) anhydrous methylamine. The ampoule was stored at room temperature in a cupboard. After nine months the contents of the ampoule had remained homogeneous.

The ampoule was fitted to the ampoule breaker in the manner described in the previous section, and the whole fitted to the fractionation section of the vacuum line and the ampoule opened whilst frozen at -196°C. The non condensable material filled a pre-calibrated volume attached to the fractionation section and a pressure of 5 mm Hg was recorded. The infra red spectrum of the non-condensable material was found to consist of $CH_4$. From the volume and pressure measurements, the quantity of the $CH_4$ was estimated at 0.00112 g (0.07 m mole).

The ampoule was isolated from the vacuum line and the methane pumped away. The ampoule, still frozen, was again exposed to the standard volume and no noticeable change in pressure was recorded. The ampoule was then allowed to warm up, and the volatile contents distilled through a trap at -84°C and into a trap at -196°C. As the distillation proceeded a white solid was noted in the ampoule, which remained when the ampoule was held at -23°C (melting $CCl_4$).

The contents of the trap at -196°C was investigated by infra red spectroscopy and found to contain $NH_3$ and $CH_3NH_2$. The contents of this trap were distilled through a trap at - 96°C (melting toluene), but the mixture was found not easily separable. The mixture of methylamine and ammonia was then returned to a trap at -196°C and redistilled through a trap at -117°C (melting diethyl ether), where methylamine and ammonia was found in the first volatiles through the trap, but after the distillation was approximately three quarters complete the residue was found to consist of only methylamine. The mixture was then redistilled into the trap at -196°C and the relative amounts of $NH_3$ and $CH_3NH_2$ determined by infra red spectroscopy. The absorbance of the 1045 $cm^{-1}$ band in the $CH_3NH_2$ spectrum was used at the analytical peak, and its extinction coefficient measured by plotting a graph of absorbance against pressure for the amine on its own, and is shown in Figure 21. The pressures were determined by manometer and cathetometer.

In order to analyse the mixture, a second standard volume was attached to the vacuum line at the fractionation section, and the total amount of mixture was expanded into this volume, which included an infra red gas cell, in three aliquots of total pressure approximately 33 mm Hg. The infra red spectrum of each aliquot was recorded over the range 1150 $cm^{-1}$ to 900 $cm^{-1}$ and the absorbance read off the spectra.

The infra red spectrometer was not adjusted in any way, except for 100% control, during the determination of the calibration curve and the recording of the unknown spectra. Since the spectra are displayed, on this instrument, in the transmittance mode the peaks appear less intense as the base line is reduced to zero transmittance. In order to correct observed transmittances to true transmittances, a correlation factor was determined (103), which was accomplished by recording the spectrum of a fixed pressure of $POF_3$ at different base line transmittance, t, against the extrapolated base line value at the peak position, t . The true transmittance T can be obtained from the empirical expression:

$$T = \frac{100(t - 2.5)}{t} + 2.5$$

and the absorbance A determined from the transmittance T. The results of this determination are given below:

Calibration of 1045 $cm^{-1}$ absorption:

| Pmm | 5.18 | 9.70 | 16.29 | 31.19 |
|---|---|---|---|---|
| A | 0.061 | 0.089 | 0.152 | 0.284 |

Extinction coefficient of this absorption = 9.89 x 10   mm Hg mm

Calculated Pressure of $CH_3NH_2$ in Mixtures

| | | | |
|---|---|---|---|
| Total pressure, mm Hg | 30.90 | 31.34 | 34.35 |
| Calculated $CH_3NH_2$ mm Hg | 28.32 | 31.05 | 34.21 |
| M moles $CH_3NH_2$ | 3.98 | 4.33 | 4.77 |
| M moles $NH_3$ | 0.36 | 0.04 | 0.02 |

giving a total quantity of 13.08 m moles $CH_3NH_2$ (0.4055 g) and the amount of $NH_3$, by difference, 0.42 m moles (0.0071 g). The remaining

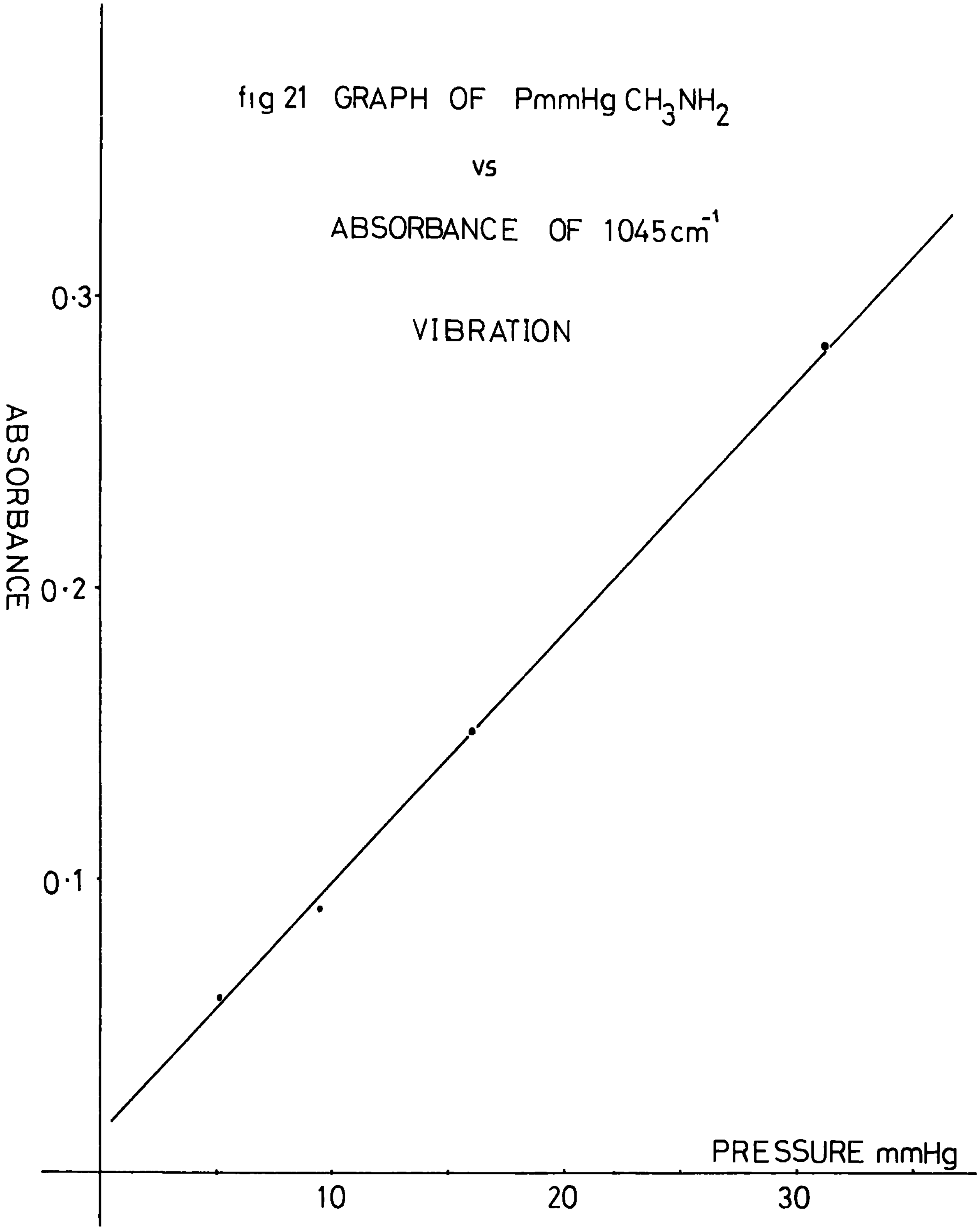


fig 21 GRAPH OF PmmHg $CH_3NH_2$

vs

ABSORBANCE OF 1045 $cm^{-1}$

VIBRATION

$CH_3NH_2$ was distilled into a Rotaflow and weighed, yielding 0.9036 g, thus the total amount of $CH_3NH_2$ recovered from the mixture was 1.3091 g (42.23 m mole), indicating that 0.0846 g $CH_3NH_2$ had been consumed.

The trap at -84°C was found to contain a small quantity of a fairly involatile substance, whose molecular weight was found to be 74.12, determined by expanding the trap contents at a known pressure, into a bulb of known mass and volume and weighing. The compound was identified as methylenedimethylhydrazine, $(CH_3)_2NN = CH_2$, by comparison of infra red spectra with an authentic sample of $(CH_3)_2NN = CH_2$ prepared from $(CH_3)_2NNH_2$ and aqueous $CH_2O$ solution, and detailed under part d, of this section.
It was found that there was 0.0903 g of this compound in the reaction product, which corresponds to 1.25 m mole.

The ampoule was isolated from the vacuum line, weighed, and transferred to the glove box where it was broken open by scoring the sidewall and carefully breaking over a piece of polyethylene film to collect any pieces of broken glass. This precaution was found unnecessary, as the ampoule broke cleanly into two parts. The solid was scooped out, and the pieces of ampoule and breaker were removed from the dry box, carefully washed with water and acetone, taking extreme care not to dissolve any of the black Piceine wax sealing the neck of the ampoule into the breaker, and allowed to dry in a vacuum dessicator. Subsequent weighings showed that 0.1892 g solid residue was formed in the reaction.

The solid, which analysed as, %, C, 23.41; H, 9.62; N, 18.73; Cl, 48.14; was treated with KOH in the apparatus shown in Figure 20, and the resulting volatile components examined on the vacuum line. It was found that $CH_3NH_2$ and $(CH_3)_2NH$ were both present, accompanied by a trace of $NH_3$.

The infra red spectrum of the solid was recorded and found to consist of both $(CH_3)_2NH_2Cl$ and $CH_3NH_3Cl$. The analytical figures are consistant with an almost 50:50 mixture of $(CH_3)_2NH_2Cl$ and $CH_3NH_3Cl$.

In the reaction between $(CH_3)_2NCl$ and $CH_3NH_2$, 0.0846 g, 2.18 m mole $CH_3NH_2$ reacted with 0.2035 g $(CH_3)_2NCl$, to yield 0,0903 g $(CH_3)_2NN = CH_2$ and 0.1892 g of a 50% mixture of $(CH_3)_2NH_2Cl$ and $CH_3NH_3Cl$. Also formed were a small amount of $CH_4$ and $NH_3$. These results can be summarised by the equation:

$$2CH_3NH_2 + 2(CH_3)_2NCl \longrightarrow (CH_3)_2NN = CH_2 + (CH_3)_2NH_2Cl + CH_3NH_3Cl.$$

(c) <u>$(CH_3)_2NH$</u>

1.4242 g (31.59 m mole) dimethylamine was condensed into a heavy walled 16 mm pyrex reaction ampoule, as shown in Figure 8, Chapter 2, followed by 0.1735 g (2.1814 m mole) $(CH_3)_2NCl$. The ampoule was sealed and allowed to warm to room temperature, where a homogeneous solution formed. After approximately six months in a dark cupboard, the solution had deposited a quantity of white crystals.

The ampoule was fitted to the ampoule breaker as detailed previously, attached to the fractionation section of the vacuum line and frozen at 196°C. The ampoule was carefully opened to the manometer and a pressure of 1.34 mm Hg was recorded using a cathetometer. Infra red spectroscopy showed that the non condensable material was methane, $CH_4$, and subsequent volume calibration of the pertinent section of the vacuum line revealed that this pressure corresponded to 0.0186 m mole $CH_4$.

The non condensables were pumped away with the ampoule isolated from the vacuum line and again the ampoule was opened to the manometer, where no noticeable change in pressure occurred. The volatile contents of the ampoule were then distilled through a trap at -84°C and collected at -196°C. Subsequent refractionation at -84°C yielded 0.1489 g (1.46 m mole) $((CH_3)_2N)_2CH_2$, tetramethylmethylenediamine, characterised by infra red spectroscopy and 1.2825 g (28.5 m mole) $(CH_3)_2NH$, dimethylamine, which collected at -196°C. Further fractionation of the $(CH_3)_2NH$ fraction revealed no other amines.

The ampoule and breaker were isolated from the vacuum line, weighed and transferred to the dry box where after careful breaking of the ampoule, the solid residue was removed. With great care the pieces of ampoule and breaker were washed with distilled water, rinsed in acetone and dried in a vacuum dessicator, after which weighings showed that 0.1630 g of solid material had been formed. The solid was analysed and found to contain, (%), C, 29.57; H, 11.20; N, 17.18; Cl, 44.10; $(CH_3)_2NH_2Cl$ requires, (%), C, 29.31; H, 9.81; N, 17.15; Cl, 43.40, and infra red spectroscopy confirmed that the solid was $(CH_3)_2NH_2Cl$.

The reaction is summarised below:

| **Reactants** | | **Products** | |
|---|---|---|---|
| $(CH_3)_2NH$ | 1.4242 g (31.59 m mole) | $CH_4$ | 0.0007 g (0.019 m mole) |
| $(CH_3)_2NCl$ | 0.1735 g (2.18 m mole) | $((CH_3)_2N)_2CH_2$ | 0.1489 g (1.46 m mole) |
| | | $(CH_3)_2NH$ | 1.2825 g (28.5 m mole) |
| | | $(CH_3)_2NH_2Cl$ | 0.1630 g (2.0 m mole) |
| Total mass = 1.5977 g | | Total mass = 1.5957 g | |

Thus 0.1417 g (3.15 m mole) $(CH_3)_2NH$ reacted with 0.1735 g (2.18 m mole) $(CH_3)_2NCl$ to form 0.1489 g (1.46 m mole) $((CH_3)_2N)_2CH_2$; 0.1630 g (2.0 m mole) $(CH_3)_2NH_2Cl$ and 0.0007 g (0.019 m mole) $CH_4$.

### (d) $(CH_3)_3N$

4.4095 g (74.61 m mole $(CH_3)_3N$, trimethylamine, was condensed into a previously weighted TF6/24 Rotaflow weight analysis cell as shown in Figure , Chapter 2, followed by 1.1748 g (14.77 m mole) $(CH_3)_2NCl$. The Rotaflow tap was closed, and the weight analysis cell allowed to warm to room temperature, where a homogeneous solution formed. The reaction was allowed to proceed in a cupboard for approximately eight months, after which time the solution had deposited a white crystalline solid.

The Rotaflow was attached to the fractionation section of the vacuum line frozen at -196°C, and opened to the manometers where no change in pressure was recorded. The volatile contents were then distilled through a tap at -84°C and collected at -196°C, by allowing the Rotaflow to warm slowly to room temperature. The distillation was continued until no further mass change was found on successive weighings of the Rotaflow weight analysis cell. The volatile components were fractionated and found to contain only two substances, $(CH_3)_3N$, isolated at -196°C, and $((CH_3)_2N)_2CH_2$, tetramethylmethylenediamine, isolated at -84°C, both identified by infra red spectroscopy.

From these fractionations, 1.4724 g tetramethylmethylenediamine was recovered.

The solid material in the Rotaflow weight analysis cell, of which there was 1.4113 g, was transferred to the dry box and found to be $(CH_3)_3NHCl$, trimethylammonium chloride, by infra red spectroscopy. The C, H, N, and Cl microanalysis confirmed the identity of the solid, the analytical figures found being, (%), C, 37.60; H, 9.81; N, 15.24; Cl, 37.31, and $(CH_3)_3NHCl$ requires, (%), C, 37.68; H, 10.55; N, 14.66; Cl, 37.10.

The reaction is summarised below:

| Reactants | | Products | |
|---|---|---|---|
| $(CH_3)_3N$, | 4.4095 g (74.61 m mole) | $((CH_3)_2N)_2CH_2$, | 1.4724 g (14.41 m mole) |
| $(CH_3)_2NCl$, | 1.1748 g (14.77 m mole) | $(CH_3)_3NHCl$, | 1.4724 g (14.77 m mole) |
| | | $(CH_3)_3N$ (by difference), | 2.7006 g (45.77 m mole) |

Hence 1.7089 g (28.96 m mole) $(CH_3)_3N$ reacted with 1.1748 g (14.77 m mole) $(CH_3)_2NCl$ to form 1.4724 g (14.41 m mole) $((CH_3)_2N)_2CH_2$ and 1.4724 (14.77 m mole) $(CH_3)_3NHCl$, and the reaction can be represented by the equation:

$$2(CH_3)_3N + (CH_3)_2NCl = (CH_3)_2NCH_2N(CH_3)_2 + (CH_3)_3NHCl$$

## 3. The Reactions of $(CH_3)_2NCl$ With The Hydrazines $N_2H_4$, $CH_3NHNH_2$, $(CH_3)_2NNH_2$ and $(CH_3)_2NNHCH_3$

### (a) $N_2H_4$

0.4094 g (5.15 m mole $(CH_3)_2NCl$ was condensed into a 16 mm heavy walled pyrex reaction ampoule, followed by 1.7942 g (55.98 m mole) anhydrous hydrazine, $N_2H_4$. 8.1195 g Freon 11, $(CCl_3F)$ was then added by distillation, to act as a moderator for the reaction, and the tube sealed. After the ampoule had warmed up to room temperature, bubbles were observed in the solution, and the reaction, was allowed to continue at room temperature behind a brick screen as a safety precaution. After two weeks the ampoule was fitted to the ampoule breaker and frozen at -196°C when attached to the fractionation section of the vacuum line. A standard volume was also attached at this point on the vacuum line, and with the ampoule frozen, the neck carefully broken off and the contents exposed to the standard volume and manometer, where a pressure of 18.24 mm Hg was recorded using a cathetometer.

The infra red spectrum of the non condensables showed no absorptions in the region 4,000 $cm^{-1}$ to 250 $cm^{-1}$, and it was concluded that the gas was nitrogen. A pressure of 18.24 mm Hg. in the total volume 2.5569 litre, indicated 2.55 m moles of $N_2$ to be present.

The non condensables were pumped away and the remaining volatiles distilled into the fractionation section via traps at -23°C, -84°C and -196°C. As the liquid level in the ampoule decreased, a white solid was deposited, and towards the end of the distillation the ampoule was left for 24 hours exposed to a trap at -196°C, in order to remove the last traces of $N_2H_4$ from the solid.

The contents of this trap were distilled through -23°C and -84°C combining the most volatile fraction with that obtained in the initial distillation. The least volatile fraction was found to contain only $N_2H_4$, identified by infra red spectroscopy, of which there was 1.5614 (48.72 m mole).
The most volatile fraction contained only $CCl_3F$ and $(CH_3)_2NH$ identified again by infra red spectroscopy, and this mixture was found to be inseparable. The mixture was weighed and the amount of $(CH_3)_2NH$ estimated, assuming $CCl_3F$ to be inert, yielding 0,2114 g (4.69 m mole) $(CH_3)_2NH$.

The ampoule was transferred to the dry box and the solid material isolated. Infra red spectroscopy showed the solid to be a mixture, predominantly $N_2H_5Cl$, but absorptions due to $(CH_3)_2NH_2Cl$ were also present. The elemental analysis confirmed the presence of carbon in the sample, found (%), C, 0.92; H, 9.70; N, 44.52; Cl, 44.86, and the melting range was found to be 85-93°C, $(CH_3)_2NH_2Cl$, mpt 170°C; $N_2H_5Cl$, 89°C.
The reaction is summarised below.

| Reactants | | Products | |
|---|---|---|---|
| $N_2H_4$, | 1.7942 g (55.98 m mole) | $N_2$, | 0.0714 g (2.55 m mole) |
| $(CH_3)_2NCl$, | 0.4094 g (5.15 m mole) | $(CH_3)_2NH$, | 0.2114 g (4.70 m mole) |
| | | $N_2H_4$, | 1.5612 g (48.79 m mole) |
| | | Residue | 0.3566 g (By difference) |

Thus in this reaction 0.2330 g (7.28 m mole ) $N_2H_4$ have been consumed by 5.15 m mole $(CH_3)_2NCl$, producing 2.55 m mole $N_2$.

Now for this amount of dimethyl chloramine and nitrogen, the reaction

$$2(CH_3)_2NCl + N_2H_4 = 2(CH_3)_2NH_2Cl + N_2$$

requires a chloramine to nitrogen molar ratio of 2:1, which compares with the 2.02:1 ratio found. The reaction also requires 0.0824 $N_2H_4$ for 0.4094 g $(CH_3)_2NCl$.

A second reaction that presumably takes place, since $(CH_3)_2NH$ was found as a product, is:

$$(CH_3)_2NH_2Cl + N_2H_4 \longrightarrow (CH_3)_2NH + N_2H_5Cl$$

and adding this to the equation above, the overall reaction is:

$$2(CH_3)_2NCl + 3N_2H_4 \longrightarrow 2N_2H_5Cl + 2(CH_3)_2NH + N_2$$

The figures obtained indicate that the second of these reactions has not gone to completion, and thus the reaction is best represented as

$$(CH_3)_2NCl + (1 + X)N_2H_4 = (2 - X)(CH_3)_2NH_2Cl + X(CH_3)_2NH + XN_2H_5Cl + N_2$$

and this equation and the figures obtained for $(CH_3)_2NH$ production and $(CH_3)_2NCl$ consumption, allow X to be evaluated, since 0.4094 g $(CH_3)_2NCl$ will yield 0.1159X g $(CH_3)_2NH$, and since 0.2144 g $(CH_3)_2NH$ was found, X becomes 1.85.

By a similar means, a value of 1.83 for X is obtained from the consumption of $N_2H_4$ and $(CH_3)_2NCl$.

Thus the final equation representing the reaction between $N_2H_4$ and $(CH_3)_2NCl$ is:

$$2'CH_3)_2NCl + 2.84N_2H_4 = 0.16(CH_3)_2NH_2Cl + 1.84(CH_3)_2NH + 1.84N_2H_5Cl + N_2$$

(b) $CH_3NHNH_2$

7.4298 g (approximately 10 $cm^3$) sodium dried diethyl ether, $(C_2H_5)_2O$, was introduced into a TF6/24 Rotaflow weight analysis cell and degassed on the vacuum line and reweighed. To the frozen ether in the Rotaflow, 0.4065 g (5.11 m mole) $(CH_3)_2NCl$ was added by condensation, and the whole allowed to warm up until a homogeneous solution had formed.

On refreezing at -196°C, 0.9078 g (19.68 m mole) methylhydrazine, $CH_3NHNH_2$, was added, and the Rotaflow isolated from the vacuum line and allowed to slowly warm to room temperature.
Small bubbles were observed in the homogeneous solution soon after room temperature had been attained, and a small quantity of white solid had precipitated. After two days at room temperature, behind a brick screen for safety, no further bubbles were observed, and the Rotaflow was transferred to the vacuum line and frozen at -196°C. The Rotaflow was carefully opened to the manometers and a pressure of 36.92 mm Hg was recorded, which by infra red spectroscopy, was found to contain methane, $CH_4$, but the spectrum was not as intense as expected from such a pressure, and since no other absorptions could be found in the infra red spectrum it was concluded that the non condensable gas was a mixture of $CH_4$ and either $N_2$ or $H_2$.

The Rotaflow was isolated from the vacuum line and the non condensable gases pumped away. Subsequent opening to the manometer revealed further quantities of non condensable gas, and it was

concluded that there was a saturated vapour of $CH_4$ present ($CH_4$, vapour pressure at -196°C is 10 mm Hg).
The Rotaflow was held at -196°C and all non condensables were pumped away until a constant mass remained, resulting in a mass loss of 0.2281 g.

The Rotaflow was then allowed to warm to room temperature as the contents distilled through a trap at -84°C and -196°C. Infra red spectroscopy showed that $(C_2H_5)_2O$ and $(CH_3)_2NH$ collected at -196°C, and $CH_3NHNH_2$ at -84°C. 0.4314 g $CH_3NHNH_2$ was recovered, and the mass of the more volatile components was 7.4298 g. The Rotaflow and contents were transferred to the dry box, where 0.4262 g of a white solid was isolated, which was identified as $CH_3NHNH_3Cl$, by infra red spectroscopy and elemental analysis. Found, (%), C14.82; H, 8.82; N, 33.64; Cl, 42.91. $CH_3NHNH_3Cl$ requires, (%), C, 14.55; H, 8.55; N, 33.94; Cl, 42.96.

The equation:

$$(CH_3)_2NCl + 2CH_3NHNH_2 = CH_3NHNH_3Cl + CH_4 + N_2 + (CH_3)_2NH$$

requires, at -196°C, a total mass loss of 0.2252 g, calculated from the starting amount of $(CH_3)_2NCl$, and since the mass loss after pumping at -196°C was found to be 0.2281 g, it was concluded that the non condensable gases were $CH_4$ and $N_2$.

From the mass of $CH_3NHNH_2$ recovered, 0.4764 g (10.36 m mole) had reacted with 0.4065 g (5.11 m mole) $(CH_3)_2NCl$. Assuming the diethyl ether had not entered the reaction, and indeed no evidence was found for chlorinated hydrocarbons or other C-O or C=O compounds then from the total mass of the $(C_2H_5)_2O$, $(CH_3)_2NH$ mixture, 0.2305 g

(5.12 m mole) $(CH_3)_2NH$ was recovered from the reaction.

The reaction is summarised below.

| Reactants | Products |
|---|---|
| $(CH_3)_2NCl$, 0.4065 g (5.11 m mole) | $CH_4 + N_2$ |
| $CH_3NHNH_2$, 0,9078 g (19.68 m mole) | $(CH_3)_2NH$, 0,2305 g (5.12 m mole) |
| | $CH_3NHNH_2$, 0.4314 g (9.36 m mole) |
| | $CH_3NHNH_3Cl$, 0.4262 g (5.17 m mole) |

Thus 5.11 m mole $(CH_3)_2NCl$ has reacted with 10.36 m mole $(CH_3)NHNH_2$ to yield $CH_4$ and $N_2$, 5.12 m mole $(CH_3)_2NH$ and 5.17 m mole $CH_3NHNH_3Cl$ which is consistant with the equation:

$$(CH_3)_2NCl + NCl + 2CH_3NHNH_2 \longrightarrow CH_4 + N_2 + (CH_3)_2NH + CH_3NHNH_3Cl$$

### (c) $(CH_3)_2NNH_2$

0.7191 g (9.05 m mole) $(CH_3)_2NCl$ was condensed into a heavy walled 16 mm pyrex reaction ampoule, followed by 2.8487 g (47.48 m mole) anhydrous $(CH_3)_2NNH_2$, and the ampoule sealed. As the ampoule warmed to room temperature fine bubbles were observed, and after 24 hours at -23°C in a freezer, fine white needles had precipitated. The ampoule was left for approximately one week, after which time the supernatent solution had a distinct yellowish tinge.

The ampoule was fitted to the ampoule breaker and frozen at -196°C, after which the ampoule was carefull opened to the manometers and approximately 18.5 mm of non condensable gas was observed. Infra red spectroscopy showed this to be $CH_4$ along with another non condensable substance, probably either $N_2$ or $H_2$.

The non condensables were pumped away and the remaining volatile material distilled through a trap at -84°C and collected at -196°C.

The residue in the ampoule had a yellowish colour, and the ampoule was isolated, removed from the vacuum line and weighed, and from the mass of materials put into the ampoule, 0.8392 g of solid residue was recovered.

The volatiles were fractionated to separate 1.9726 g $(CH_3)_2NNH_2$ by passing through traps at -64°C and -78°C until, after four such distillations, no trace of the more volatile $(CH_3)_2NH$ or $NH_3$ could be found by infra red spectroscopy.
The ampoule was taken into the dry box and opened where the solid residue was found coated with an involatile yellowish oil. The infra red spectrum revealed absorptions due to $(CH_3)_2NH_2Cl$ and $(CH_3)_2NNH_3Cl$, amongst other unidentifiable peaks. Thus in this reaction, 0.7191 g $(CH_3)_2NCl$ had reacted with 0.8761g $(CH_3)_2NNH_2$, to yield 0.8392 g of solid residue composed of, in part, $(CH_3)_2NH_2Cl$ and $(CH_3)_2NNH_3Cl$. 0.7560 g of a mixture of $NH_3$,$(CH_3)_2NH$ and non condensable $CH_4$ and $N_2$ or $H_2$ accounted for the most volatile material.

The experiment was repeated, and in this instance, 2.0871 g (34.78 m mole) $(CH_3)_2NNH_2$ was condensed into a Rotaflow weight analysis cell, followed by 0.353 g (4.45 m mole) $(CH_3)_2NCl$. The Rotaflow was isolated from the vacuum line, and, still frozen, transferred to the fractionation section and affixed to part of the vacuum line which had a previously calibrated standard demountable, volume attached. This section of the vacuum line is shown diagrammatically in Figure 22.

When the Rotaflow was attached to this section of the vacuum line, the joints were pumped down to black vacuum and the section sealed from the rest of the line by means of tap $T_1$ (Figure 22). The Rotaflow was isolated from the vacuum section be means of tap $T_r$, and the Rotaflow ampoule allowed to warm to room temperature. Bubbles started to form whilst part of the contents were still frozen, and began to effervesce vigorously shortly after. The Rotaflow was quickly cooled at this point, and it was noticed that the liquid had taken on a yellow colour. After approximately ten minutes at -196°C the Rotaflow was opened to the standard volume and manometer by means of tap $T_r$, and a pressure of 21.99 mm Hg was recorded. The procedure was repeated three times, and no change in manometer reading was obtained.

The infra red spectrum of the non condensable gas revealed that methane was present, and since the total pressure was in excess of the saturated vapour pressure of $CH_4$ at -196°C, it was concluded that other non condensable materials were present.

The amount of $CH_4$ present in the mixture was estimated by observing the relationship between the pressure and the infra red absorbance of the C-H vibration at approximately 3010 $cm^{-1}$. In order to accomplish this, natural gas, which contains 94% $CH_4$, (104), was passed through two traps at -196°C, whilst both traps were open to the vacuum pump. The material that collected in the second trap was found to contain only $CH_4$ by infra red spectroscopy, other alkanes and thiols being isolated in the first trap. The infra red spectra of aliquots of $CH_4$, at known pressures, were recorded and a graph plotted of absorbance against pressure for this

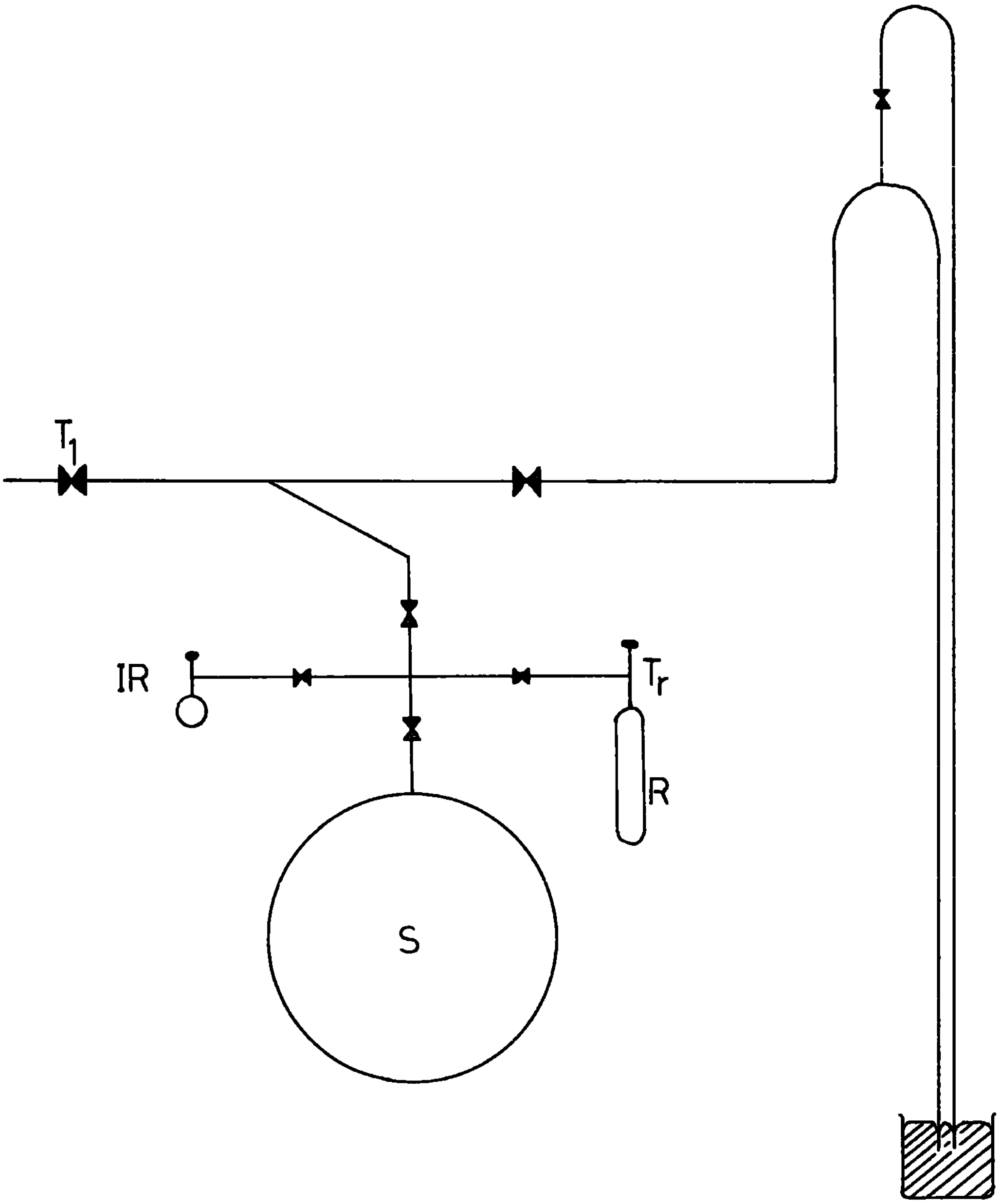


fig 22 SECTION OF VACUUM LINE USED IN $(CH_3)_2NNH_2$ REACTION

vibration, and is shown in Figure 23. The absorbances were were corrected for base line error of the instrument in the manner described in the section dealing with $CH_3NH_2$ reactions (section 1b).

The values of absorbance and pressure found are given below.

| Absorbance: | 0.045 | 0.053 | 0.067 | 0.084 | 0.106 |
|---|---|---|---|---|---|
| Pressure (mm Hg): | 1.90 | 3.05 | 4.17 | 6.67 | 7.90 |

and from the graph it can be seen that this absorption does not obey the Beer-Lambert relation at these pressures, but over the pressure range 2-8 mm Hg $CH_4$ the relation is linear.

From the spectrum of the non condensable mixture, the absorbance of the $CH_4$ vibration at 3010 $cm^{-1}$ was found to be 0.0916, which from the calibration graph, corresponds to a partial pressure of 6.95 mm Hg. Thus from the total pressure of 21.99 mm Hg, 15.04 mm Hg corresponds to the other non condensable material. 6.95 mm Hg of $CH_4$ in the total volume of 2.5569 litre corresponds to 0.995 m mole, and 15.04 mm Hg of the other non condensable corresponds to 2.06 m mole.

The Rotaflow was frozen at -196°C and all non condensables pumped away, isolated at $T_r$ (Figure 22), removed from the vacuum line and allowed to warm to room temperature behind a brick screen. The solution was distinctly yellow in colour. The Rotaflow was reweighed and a mass loss of 0,0756 g found. After two days at room temperature the Rotaflow was again returned to the vacuum line and attached to the standard volume system shown in Figure 22, with

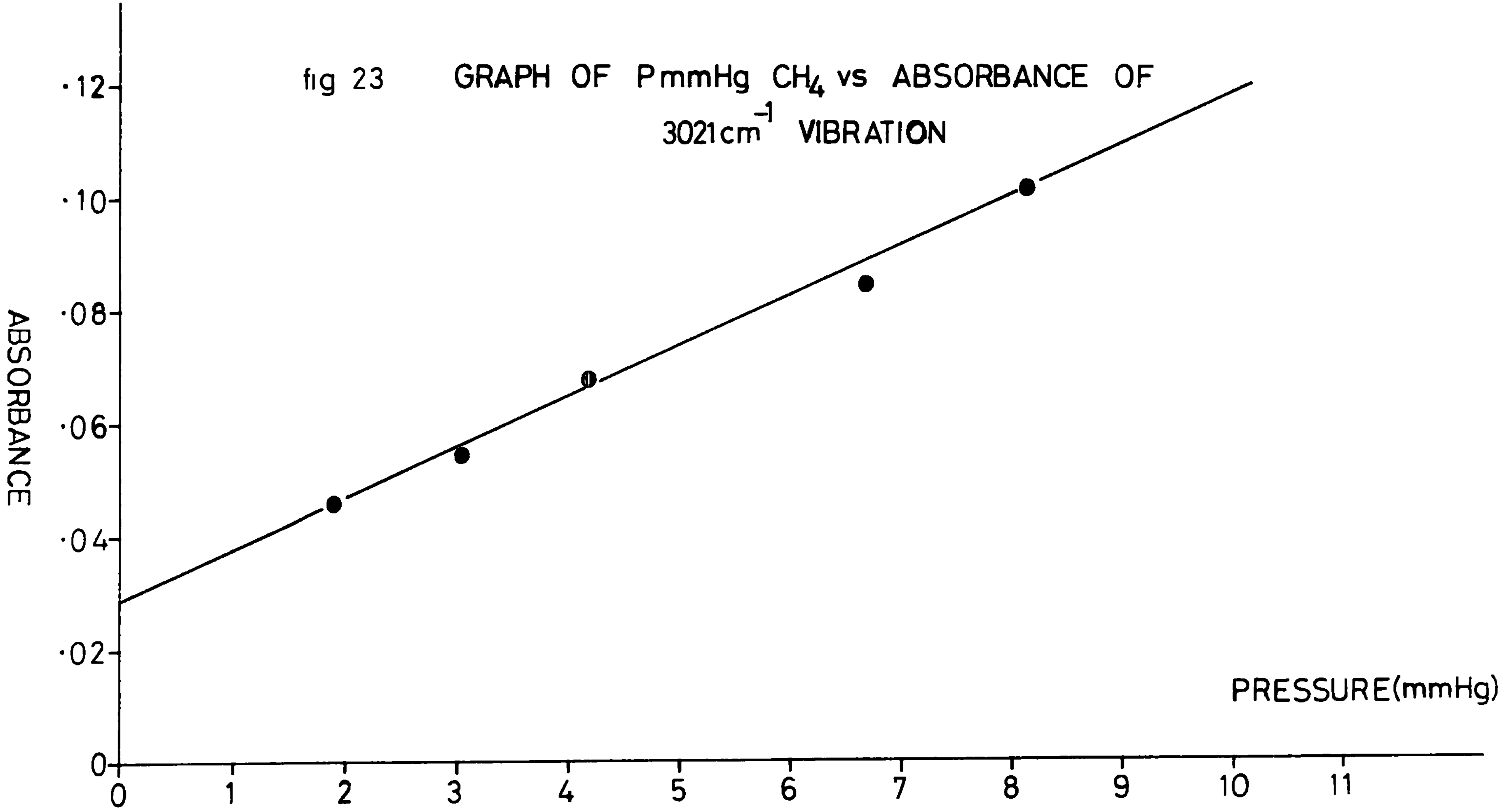


fig 23 GRAPH OF P mmHg $CH_4$ vs ABSORBANCE OF $3021 cm^{-1}$ VIBRATION

the exception of the large volume S. The Rotaflow was frozen at -196°C and opened to the manometers, where 12.18 mm Hg of non condensables were obtained. By a similar process this quantity of gas corresponded to 0.036 m mole $CH_4$ and 0.077 m mole of other non condensables.
The entire process was repeated a third time but no further non condensables were found.

From the mass loss figure, an approximate molecular weight of the non condensable gases was obtained, since 0.0756 g of gas occupied a volume of 2.5569 litre at a total pressure of 21.99 mm Hg. The resulting molecular weight of 25.07 indicated that the mixture contains only $N_2$ and $CH_4$ since the molecular weight of a 2.16:1 molar ratio of $N_4$ and $CH_4$ is 24.2.

The Rotaflow was then allowed to warm to room temperature and the volatile materials distilled into the vacuum line where again $NH_3$ and $(CH_3)_2NH$ were observed in the most volatile fraction.

In a third experiment a solvent was used as a moderator for the vigorous reaction.
A 150 ml round bottomed flask containing approximately 25 $cm^3$ dry diethyl ether and a teflon stirrer bar, was degassed on the vacuum line and 2.0154 g $(CH_3)_2NNH_2$ added by condensation. The flask was isolated from the vacuum line and the contents allowed to warm up and mix. After refreezing at -196°C, 1.7159 g (21.58 m mole) $(CH_3)_2NCl$ was introduced and the flask isolated from the vacuum line, placed on a magnetic stirrer, and allowed to warm to room temperature with stirring.

After twelve hours a good deal of white solid had formed and this was separated in the dry box using a filter stick and a two-necked 150 ml round bottomed flask. The now clear, but yellow, solution was returned to the stirrer and agitated for a further 24 hours when more solid had appeared. The solid was again collected in the dry box and the solution returned to the stirrer for a further two days, after which time it was completely clear but yellow in colour. A total of 1.5427 g of solid was isolated, which was identified as a mixture of $(CH_3)_2NH_2Cl$ and $(CH_3)_2NNH_3Cl$, by infra red spectroscopy, with $(CH_3)_2NH_2Cl$ being the most predominant component.

The yellow solution was poured into a 25 ml quickfit three-necked semi-micro pear shaped flask and the diethyl ether was distilled off conventionally at atmospheric pressure, the temperature remaining between 35 and 38°C. As the temperature of distillation started to rise above 40°C, the heating was stopped and the residue in the distillation flask, of which there was approximately 2 ml, was transferred to the vacuum line and all the remaining diethyl ether distilled off at room temperature, leaving a small quantity of a yellow oily involatile liquid, of which there was 0.0185 g. A quantity was distilled into the cold finger of the infra red cell, by gentle warming, and the infra red spectrum showed the substance to be tetramethyl-2-tetrazene, $(CH_3)_2NN{=}NN(CH_3)_2$, which was confirmed by the preparation of an authentic sample by the oxidation of $(CH_3)_2NNH_2$ with HgO (105), and the comparison of the two spectra.

The results from these experiments indicate that $(CH_3)_2NCl$ reacts vigorously with $(CH_3)_2NNH_2$ to yield $CH_4$, $N_2$, $NH_3$, $(CH_3)_2NH$ and $(CH_3)_2NN{=}NN(CH_3)_2$, and the indicated stoichiometry is that 2 moles of $(CH_3)_2NCl$ react with 3 moles $(CH_3)_2NNH_2$. The ratio of nitrogen to methane is approximately 2:1 and the halogen is present in the products as the halide ion. Tetramethyl-2-tetrazene is formed in very small quantities.

(d) $(CH_3)_2NNHCH_3$

Trimethylhydrazine, 1.136 g (15.33 m mole) was condensed into a 16 mm heavy walled pyrex reaction ampoule followed by dimethylchloramine, 0.3279 g (4.12 m mole). The ampoule was sealed and removed from the vacuum line to warm to room temperature behind a brick screen. After approximately 20 minutes at room temperature a white solid had formed over the surface of the ampoule in contact with the originally homogeneous solution.

After two weeks at room temperature the ampoule was fitted to an ampoule breaker and attached to the fractionation section of the vacuum line. With the ampoule frozen at -196°C, the tip was carefully broken off and the contents opened to the manometers, where no measurable depression was noted: the ampoule was allowed to warm slowly to room temperature, the contents being distilled through traps at -45°C (melting chlorobenzene), -84°C and -196°C. The majority of the volatile material collected at -45°C with some at -84°C and very little at -196°C. Infra red spectroscopy showed that all fractions contained $(CH_3)_2NNHCH_3$ and an unknown substance.

The volatiles were all combined at -196°C and then warmed to -45°C where infra red spectroscopy showed that the unknown substance was methylenedimethylhydrazine, $(CH_3)_2NN{=}CH_2$, identifiable by the characteristic $=CH_2$ vibrations at approximately 3080 $cm^{-1}$ in the infra red.

The entire volatiles were transferred to a preweighed Rotaflow ampoule, yielding 1.1186 g.

The composition of the mixture was estimated by utilising the 600 $cm^{-1}$ absorption of $(CH_3)_2NN{=}CH_2$. An authentic sample was prepared from $(CH_3)_2NNH_2$ and aqueous $CH_2O$ solution (106).

$^1H$ NMR spectroscopy showed only two absorptions for the prepared sample $(CH_3)_2NN{=}CH_2$ at $\tau$ 2.15, 5.42, from external TMS, and had an integrated ratio of 3.03:1, indicating the $=CH_2$ protons absorbed at $\tau$ 5.42 and the methyl protons at $\tau$ 2.15.

Infra red spectra of various pressures of $(CH_3)_2NN{=}CH_2$ were recorded and the absorbance of the 600 $cm^{-1}$ band measured and corrected for base line error as described previously.

A graph was plotted of the pressure and corrected absorbance values, as shown below and in Figure 24.

| Pmm Hg | 6.05 | 18.33 | 36.99 | 46.50 | 56.11 |
|---|---|---|---|---|---|
| Absorbance | 0.077 | 0.198 | 0.307 | 0.367 | 0.643 |

The extinction coefficient was found to be $7.43 \times 10^{-5}$ (mm)(mm Hg)$^{-1}$.

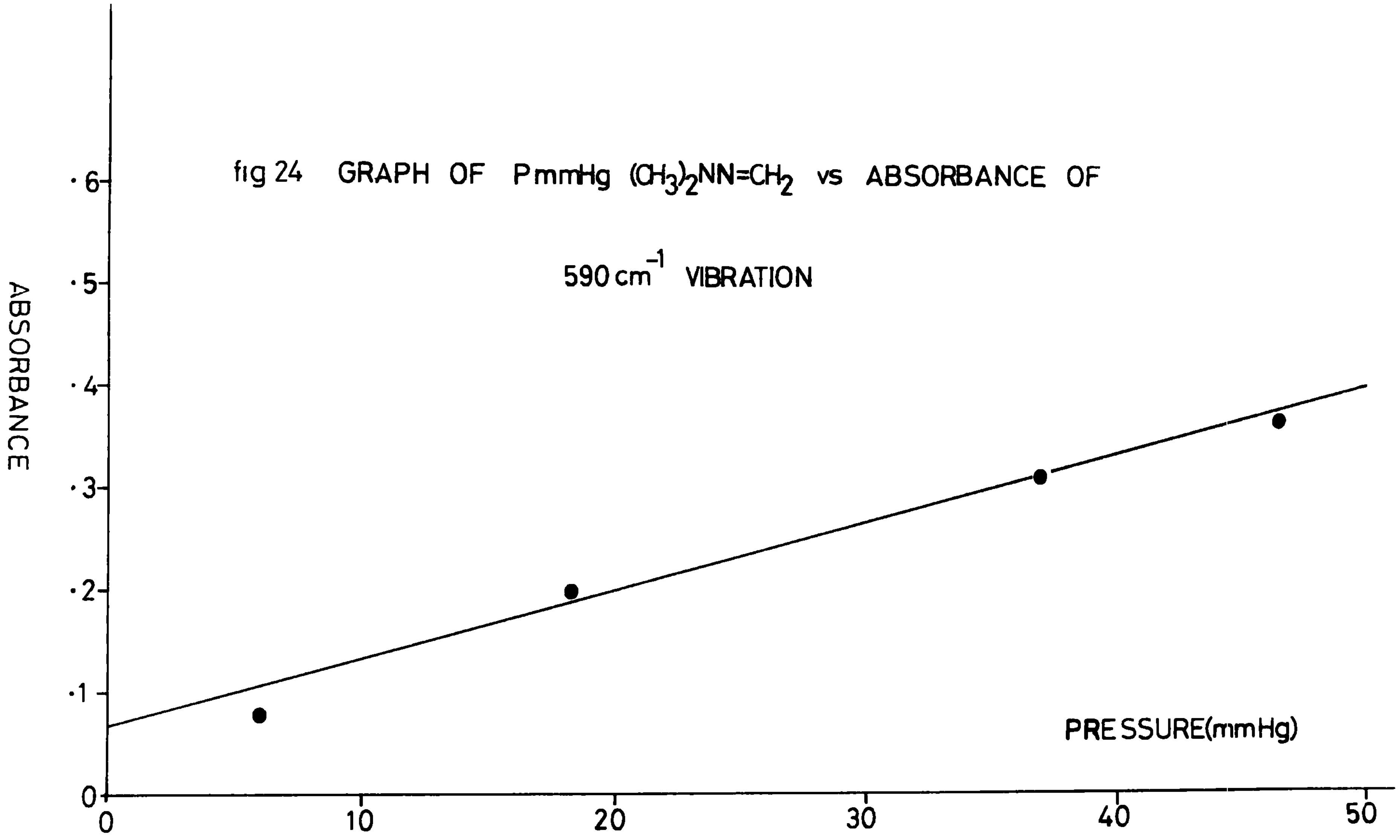


fig 24 GRAPH OF P mmHg $(CH_3)_2NN{=}CH_2$ vs ABSORBANCE OF 590 cm$^{-1}$ VIBRATION

The mixed hydrazines in the Rotaflow were connected to the vacuum line as shown in Figure 22, and the contents allowed to expand against the manometer at room temperature. When the pressure had stabilised, after ten minutes, the infra red spectrum of the vapour phase was recorded and from the absorbance measurements made on the 600 cm$^{-1}$ band, 4.345 m moles $(CH_3)_2NN{=}CH_2$ was found.

The white residue in the reaction ampoule, of which there was 0.3461 g, was isolated in the dry box and identified as $(CH_3)_2NH_2Cl$ by infra red spectroscopy, and elemental analysis, $(CH_3)_2NH_2Cl$ requires, (%), C, 29.31; H, 9.81; N, 17.15; Cl, 43.40; Found, (%), C, 29.59; H, 9.64; N, 17.23; Cl, 4.10.

In the reaction between $(CH_3)_2NCl$ and $(CH_3)_2NNHCH_3$, 4.12 m mole $(CH_3)_2NCl$ reacts with excess $(CH_3)_2NNHCH_3$ to yield 4.34 m mole methylenedimethylhydrazine, $(CH_3)_2NN{=}CH_2$, and 4.24 m mole dimethylammonium chloride, $(CH_3)_2NH_2Cl$, and the stoichiometry indicated by these figures is illustrated by the equation:

$$(CH_3)_2NCl + (CH_3)_2NNHCH_3 = (CH_3)_2NN{=}CH_2 + (CH_3)_2NH_2Cl$$

## 4. Miscellaneous $(CH_3)_2NCl$ Reactions

### (a) With Silver Compounds

The silver compounds, $Ag_2O$ (dry and moist), Ag (oxalate), $Ag_2CO_3$, $AgNO_3$, and $Ag_2(N_2O_2)$, were used in weight analysis experiments with dimethylchloramine.

In a typical experiment, approximately 0.1 g of the dry silver compound was weighed into a Rotaflow weight analysis cell followed by degassing on the vacuum line and the introduction of an excess of $(CH_3)_2NCl$. The Rotaflow was sealed and shaken at room temperature for approximately ten minutes and then returned to the fractionation section of the vacuum line where all the volatiles were removed and the Rotaflow reweighed.

In each case no mass change was observed and infra red spectroscopy revealed only $(CH_3)_2NCl$ in the liquid phase. With moist silver oxide, a small quantity ( 0.1 g) was placed in a test tube and shaken with an excess ( 5 ml) pure dimethylchloramine, and no change was noted in the supernatent liquid, nor in the colour of the silver oxide.

(b) $\underline{Li_2O}$

Approximately 0.1 g $Li_2O$ was placed in a weighed Rotaflow weight analysis cell in the dry box, and transferred to the vacuum line where an excess of $(CH_3)_2NCl$ (~1 g) was introduced. The weight analysis cell was sealed, removed from the vacuum line and warmed to room temperature with shaking.

After approximately ten minutes at room temperature, where no change was noted in the Rotaflow contents, the dimethylchloramine was distilled out, and subsequent weighings indicated no mass change.

### (c) Na Metal

A small piece of sodium was cut from a stick in the dry box, washed with dry diethyl ether, loaded into a previously weighed Rotaflow weight analysis cell, and attached to the vacuum line. The cell was pumped out leaving the small cube of sodium metal, bright, in its base. Approximately 5 ml dimethylchloramine was condensed on top of the sodium and the Rotaflow sealed and allowed to warm to room temperature, where after ten minutes, no change in the bright metallic surface was noted. On returning to the vacuum line no significant mass change was recorded on distilling out the dimethylchoramine.

# CHAPTER FOUR

# REACTIONS OF DIMETHYLHALAMINES LEADING TO THE FORMATION OF TRIMETHYLHALAMMONIUM CATIONS

## Introduction

In the study of the addition compounds of the halogens, $Cl_2$, $Br_2$, and $I_2$, with simple aliphatic tertiary amines, such as trimethylamine, $(CH_3)_3N$, the existance of discrete halotrialkylammonium cations have been suggested, but never satisfactorily isolated as cations with anions other than halides.

Hantzch (107) studied the reaction between aqueous trimethylamine and hypochlorite, finding the products included dimethylchloramine and methanol and suggested the formation of the ion $(CH_3)_3NCl$, as an intermediate, accounted for the products, according to the reaction:

$$(CH_3)_3N + HOCl \longrightarrow (CH_3)_3NClOH \longrightarrow (CH_3)_2NCl + CH_3OH$$

Bohme and Krause (108), considered the best representation of addition compounds such as $(CH_3)_3N\ Br_2$ was $(CH_3)_3NBr\ Br$, the cation being responsible for the sixteen-fold increase in conductivity of a solution of trimethylamine and bromine in $SO_2/CCl_4$ at -20°C, over that of the individual reactants, concluding that all known addition compounds of the halogens Cl, Br, I with trimethylamine were best represented as $(CH_3)_3NX\ X$, however some ionisation would be expected in $SO_2$ solution because of the possibility of halide ion acceptance by $SO_2$:

$$(CH_3)_3NX_2 + SO_2 \rightleftharpoons (CH_3)_3\overset{+}{N}X + X\overset{-}{SO_2}$$

Bohme and Boll (109), formed a compound which they claimed contained the chlorotrimethylammonium cation, $(CH_3)_3NCl$, when equimolar mixtures of $(CH_3)_3N$, $SbCl_5$, $Cl_2$, in carbon tetrachloride were allowed to react, the solid product which was isolated indeed gave a reaction to KI solution, releasing $I_2$, but on drying in a vacuum dessicator for 24 hours, chlorine was lost according to the reaction:

$$(CH_3)_3\overset{+}{N}Cl\ SbCl_6^- \xrightarrow{-Cl_2} (CH_3)_3NSbCl_5$$

Ellis (110) showed, from kinetic and spectroscopic evidence, that the species responsible for the ultimate formation of $(CH_3)_2NCl$ from $(CH_3)_3N$ and HOCl was an ionic intermediate similar to that suggested by Hantzch, namely $(CH_3)_3NCl$.

The UV spectrum of an aqueous solution of the chlorine, trimethylamine complex, $(CH_3)_3NCl_2$, showed the presence of bands attributable to $(CH_3)_2NCl$ almost immediately, but in acid solution the formation of the chloramine could be suppressed, and a curve obtained for an intermediate, which was neither $^-OCl$ nor $Cl_2$. The freezing point of a solution of $(CH_3)_3NCl_2$ in 0.01N $H_2SO_4$ was consistent with $(CH_3)_3NCl\ Cl$.formulation. On mixing aqueous trimethylamine with aqueous $^-OCl$ at pH 2.6, an UV absorption identical to that found for acid solutions of $(CH_3)_3NCl_2$, indicating that a similar species is formed in both cases.

The HOCl, $(CH_3)_3N$ reaction was studied kinetically and it was found that at constant amine concentration the initial rate was a function of the HOCl concentration, passing through a maximum at a $(CH_3)_3N/HOCl$ ratio of approximately 1:0.5, at a constant pH of 3.4. At constant HOCl concentration the reaction velocity was found to be proportional to the concentration excess of $(CH_3)_3N$ over HOCl.

The reaction was formulated according to the scheme below:

$$(CH_3)_3N + HOCl \xrightarrow{\text{fast}} (CH_3)_3\overset{+}{N}Cl,\ OH^-$$

$$(CH_3)_3\overset{+}{N}Cl + (CH_3)_3N \xrightarrow{\text{slow}} [\text{PRODUCTS}] \xrightarrow{H_2O} (CH_3)_3\overset{+}{N}H,\ (CH_3)_2NH,\ CH_2O$$

$$(CH_3)_3\overset{+}{N}Cl + (CH_3)_2NH \longrightarrow (CH_3)_3\overset{+}{N}H + (CH_3)_2NCl$$

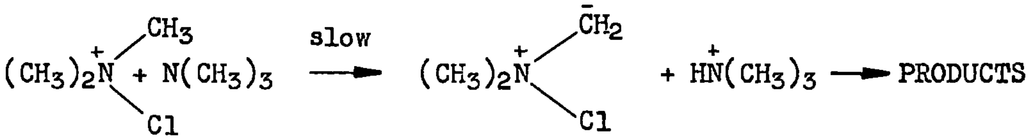
where initial rapidly formed $(CH_3)_3\overset{+}{N}Cl$ cations act as an efficient chlorinating agent, yielding products with probably C-Cl bonds. C-chlorination has been shown to be responsible for the formation of secondary amines and aldehydes when tertiary amines react with sources of "positive chlorine" (114), α carbon chlorination occurring. Thus the nature of the [PRODUCTS] , not isolated by Ellis, above are presumably compounds of the type $CH_2ClN(CH_3)_2$, or $(CH_2Cl)(CH_3)_2NH$, hydrolysing to $(CH_3)_2NH$ and the aldehyde $CH_2O$.
$(CH_3)_3\overset{+}{N}Cl$ then chlorinates the so formed dimethylamine to give $(CH_3)_2NCl$.

Another explanation for the resultant products and the rates at which they are formed, was put forward by Ellis, based on the Bohme and Krause formulation:

$$[(CH_3)_2Cl\overset{+}{N}CH_3]\,Cl^- \xrightarrow{-HCl} \underset{(IV)}{(CH_3)_2\overset{+}{N}Cl\overset{-}{C}H_2}$$

$$(CH_3)_2\overset{+}{N}Cl\overset{-}{C}H_2 \longrightarrow (CH_3)_2N\text{-}CH_2Cl \xrightarrow{H_2O} (CH_3)_2\overset{+}{N}H_2 + Cl^- + CH_2O$$

where the associated halide ion abstracting a proton from a nitrogen methyl group forming an intermediate, (IV), which rearranges to an α chloroamine which then hydrolyses to a secondary amine and formaldehyde.
The dependence of the rate of the reaction on the free amine concentration may thus be due to its ability as a proton acceptor, removing the proton from an α carbon atom on the chlorotrimethylammonium cation:



$$(CH_3)_2\overset{+}{N}(CH_3)(Cl) + N(CH_3)_3 \xrightarrow{slow} (CH_3)_2\overset{+}{N}(\overset{-}{C}H_2)(Cl) + H\overset{+}{N}(CH_3)_3 \longrightarrow PRODUCTS$$

On examination of the rate of formation of the ion $(CH_3)_3\overset{+}{N}Cl$ from $(CH_3)_3N$ and HOCl in the presence of $Cl^-$ ions, it was found by Ellis, that the rate decreased as the $Cl^-$ concentration increased, UV measurements showing increasing formation of $Cl_2$ with increasing $Cl^-$ addition, indicating that the $(CH_3)_3\overset{+}{N}Cl$ cation is more effective in chlorinating power than molecular chlorine.

In conclusion it would appear that the ion $(CH_3)_3\overset{+}{N}Cl$ is present in aqueous solutions of $(CH_3)_3NCl_2$, but to then go on and consider that in the solid phase, all trimethylamine, halogen addition compounds are $(CH_3)_3\overset{+}{N}\text{-Hal}\ \text{Hal}^-$, is clearly misleading. No simple compounds containing the halotrimethylammonium cation have been isolated and shown to contain such cations in the solid phase.

The remainder of this section will be devoted to how, and under what circumstances, the cation $(CH_3)_3\overset{+}{N}Cl$ may be prepared and isolated. The spectroscopic techniques employed in the investigation of the charge distribution in the cation are discussed in Chapter 6.

## The Formation Of The Cation $(CH_3)_3\overset{+}{N}Cl$

There are three methods which can provide the cation $(CH_3)_3\overset{+}{N}Cl$, two of which start with the trimethylamine, chlorine complex and the third, starting from dimethylchloramine.

### (a) $(CH_3)_3\overset{+}{N}Cl$ Formation From Aqueous $(CH_3)_3NCl_2$

The work of Ellis (110) has shown that in aqueous acid solutions of $(CH_3)_3NCl_2$, the cation $(CH_3)_3\overset{+}{N}Cl$ is present, so that addition of a large stabilising anion such as $ClO_4^-$ or $BF_4^-$ can be used to precipitate salts such as $(CH_3)_3\overset{+}{N}Cl\ ClO_4^-$, $(CH_3)_3\overset{+}{N}Cl\ BF_4^-$.

(b) $(CH_3)_3\overset{+}{N}Cl$ Formation From $(CH_3)_3NCl_2$ And A Lewis Acid

The work of Boll and Bohme (109), suggested that when mixtures of $(CH_3)_3N$, $Cl_2$, and $SbCl_5$ were allowed to react, a complex $(CH_3)_3\overset{+}{N}Cl\ Sb\overset{-}{Cl_6}$ formed. By utilising this technique, $(CH_3)_3\overset{+}{N}Cl\ B\overset{-}{Cl_4}$ can be obtained by reacting $(CH_3)_3NCl_2$ with $BCl_3$ in a sealed tube.

(c) $(CH_3)_3\overset{+}{N}Cl$ Formation From $(CH_3)_2NCl$

It is well known that trialkylamines when treated with alkylating agents, form tetraalkylammonium salts according to the reaction below:

$$(CH_3)_3N + CH_3I = (CH_3)_4\overset{+}{N}I^-$$

By careful choice of alkylating agent, bearing in mind the low basicity of $(CH_3)_2NCl$, (pkb = 13.6, (115)), salts can be prepared as shown in the following reaction:

$$(CH_3)_2NCl + CH_3X = (CH_3)_3NClX$$

This method can be used to prepare salts where X is $OSO_3CH_3$, $OSO_2F$, $ClO_4$.

The Preparation Of $(CH_3)_3NCl_2$

The trimethylamine chlorine complex was prepared from $(CH_3)_3N$ and $Cl_2$ in Freon 11, rather than $CCl_4$ as used by other workers, to allow a lower reaction temperature (-84°C), and ease of handling on the vacuum line. The reaction between trimethylamine and chlorine can be explosively violent, even at -84°C, if no solvent is used, strong solutions of chlorine and trimethylamine can also explode at room temperature, on mixing, thus a liberal excess of solvent is particularly recommended.

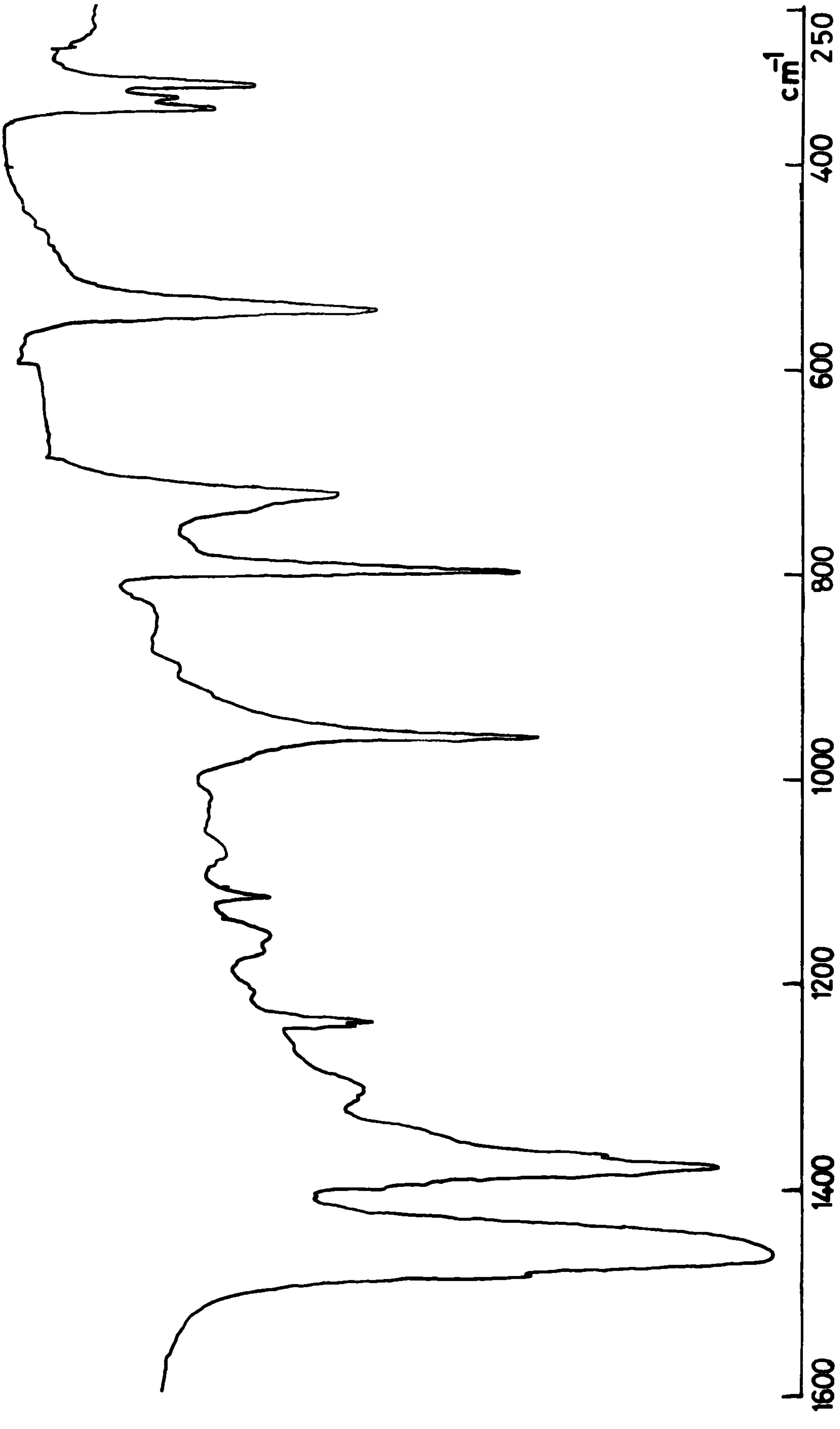
In a typical preparation, $(CH_3)_3N$ (1 ml, 13.13 m mole) was condensed into a 50 ml round bottomed flask separated from a tap cone connector by a short filter stick as shown in Figure 7, Chapter 2, on the vacuum line. Approximately 7 ml Freon 11 was condensed in, and the whole allowed to warm up until solution occurred, (approximately -23°C). The flask and contents were then refrozen in liquid nitrogen, and chlorine, (0.5 ml, 12.2 m mole) condensed in, followed by a further 5 ml Freon 11. The flask was isolated from the vacuum line and the liquid nitrogen dewar replaced by one containing an acetone, solid $CO_2$ slurry, at -84°C, and left for approximately 15 minutes, after which time the tap to the vacuum line was opened and the flask pumped dry, the filter stick preventing the finely divided white solid remaining, from passing into the vacuum line.

When the flask and contents had warmed to room temperature, it was transferred to the dry box where the solid was removed from the flask, bottled and weighed. The solid was used as soon as possible after preparation 1.58 g of product was isolated in this way, representing 100% yield, which was found to be $C_3H_9NCl_2$ by analysis: Required for $C_3H_9NCl_2$, (%), C, 27.71; H, 6.98; N, 10.77; Cl, 54.54; Found, (%), C, 28.26; H, 6.34; N, 10.87; Cl, 54.96.

The infra red spectrum was recorded, shown in Figure 25, and no evidence for $(CH_3)_3\overset{+}{N}H$ could be found, equally there were no absorptions attributable to C-Cl structures.
A small sample was dissolved in 0.01N $H_2SO_4$ and the UV spectrum recorded, as shown in Figure 26, which agreed directly with that found by Ellis (110).

## Reaction Of $(CH_3)_3NCl_2$ With Aqueous Anions

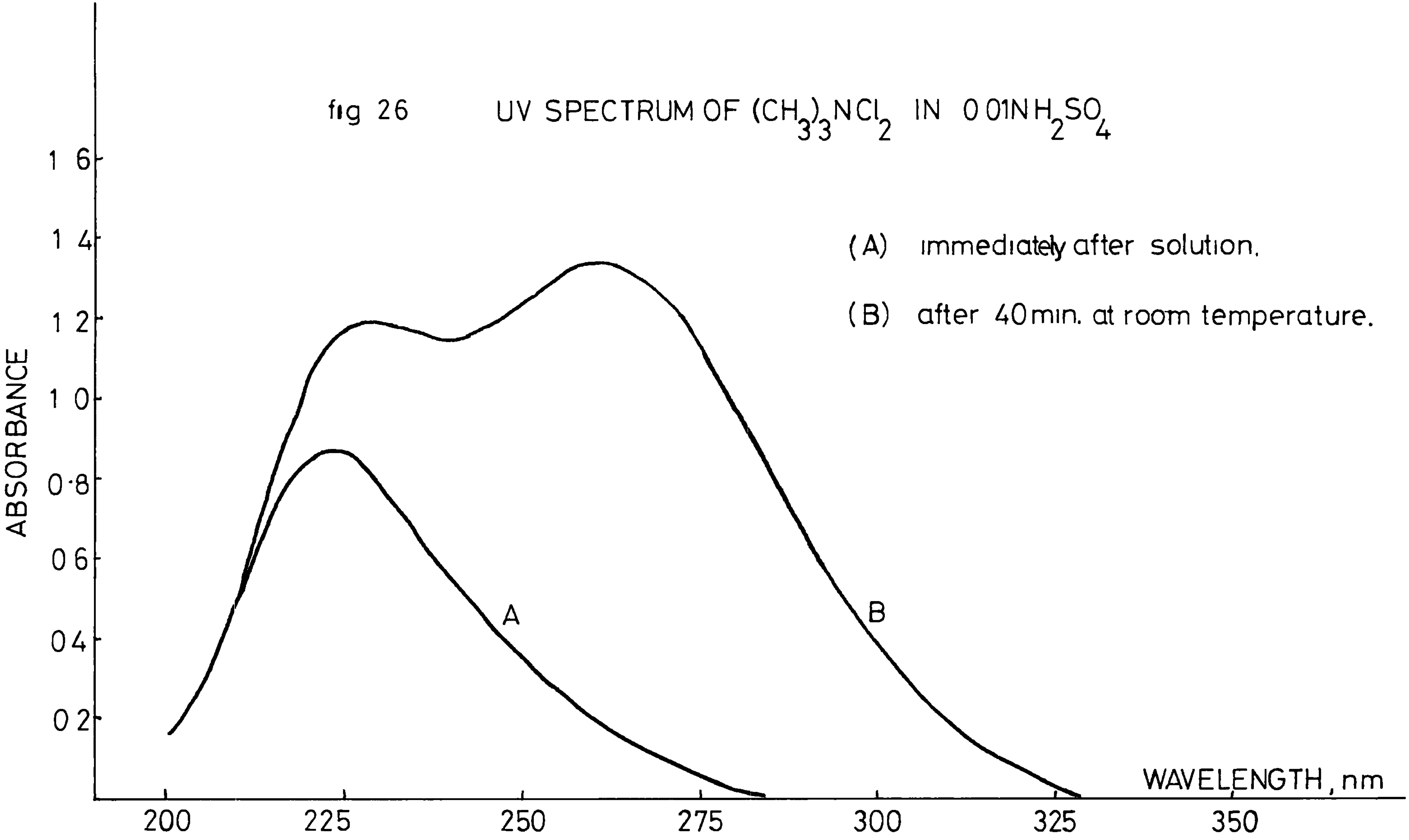
Saturated solutions, in distilled water, of $NaClO_4$, $NaBF_4$, $LiPF_6$ $NaN_3$ and NaNCS, were made up and added to a strong solution (1 g/5 ml, 200 g/litre) of $(CH_3)_3NCl_2$ in distilled water, a freshly prepared solution



INFRA RED SPECTRUM OF $(CH_3)_3NCl_2$

Fig 25

fig 26 UV SPECTRUM OF $(CH_3)_3NCl_2$ IN 0 01N $H_2SO_4$



of $(CH_3)_3NCl_2$ being used for each anion. Only $ClO_4^-$ and $BF_4^-$ produced precipitates of fine white microcrystals.

$(CH_3)_3\overset{+}{N}Cl\ ClO_4^-$ and $(CH_3)_3\overset{+}{N}Cl\ BF_4^-$ were prepared by dissolving 1 g (7.69 m mole) freshly prepared $(CH_3)_3NCl_2$ in 5 ml distilled water in a 50 ml beaker. To this solution a saturated solution of either sodium perchlorate or sodium tetrafluoroborate was added and the product, which formed within seconds, isolated by suction on a sintered glass filter. The product was washed with a few drops of dry hexane and allowed to dry on the sinter to a free flowing white powder. 0.3 g (20% yield) $(CH_3)_3\overset{+}{N}Cl\ ClO_4^-$ and 0.4 g (28.7% yield) $(CH_3)_3\overset{+}{N}Cl\ \overset{-}{BF_4}$ were isolated in this way, and analysis confirmed the formation of, $C_3H_9NCl_2O_4$ (Requires, (%), C, 18.55; H, 4.64; N, 7.22; Cl, 36.59, Found (%), C, 18.39; H, 4.44; N, 7.95; C, 36.2) and of $C_3H_9NClBF_4$ (Requires, (%), C, 19.85; H, 4.96; N, 7.72; Cl, 19.58; B, 5.96; F, 41.92, Found, (%), 19.45; H, 5.10; N, 7.61; Cl, 19.4; B, 5.87; F, 41.51).

Infra red spectra of each of these two products were recorded as nujol mulls on CsI polyethylene protected plates, and shown in Figures 27, 28.

A sample of $(CH_3)_3\overset{+}{N}Cl\ ClO_4^-$ was dissolved in 0.01N $H_2SO_4$ and the UV spectrum recorded, shown in Figure 29. This is comparable with Figure 26, showing the spectrum obtained for a solution of $(CH_3)_3NCl_2$ in $H_2SO_4$, and shows that in solution both species give rise to a compound which is in all probability $(CH_3)_3\overset{+}{N}Cl$.

Specimens of these two compounds were examined by NQR spectroscopy, the results of which are discussed in Chapter 6.

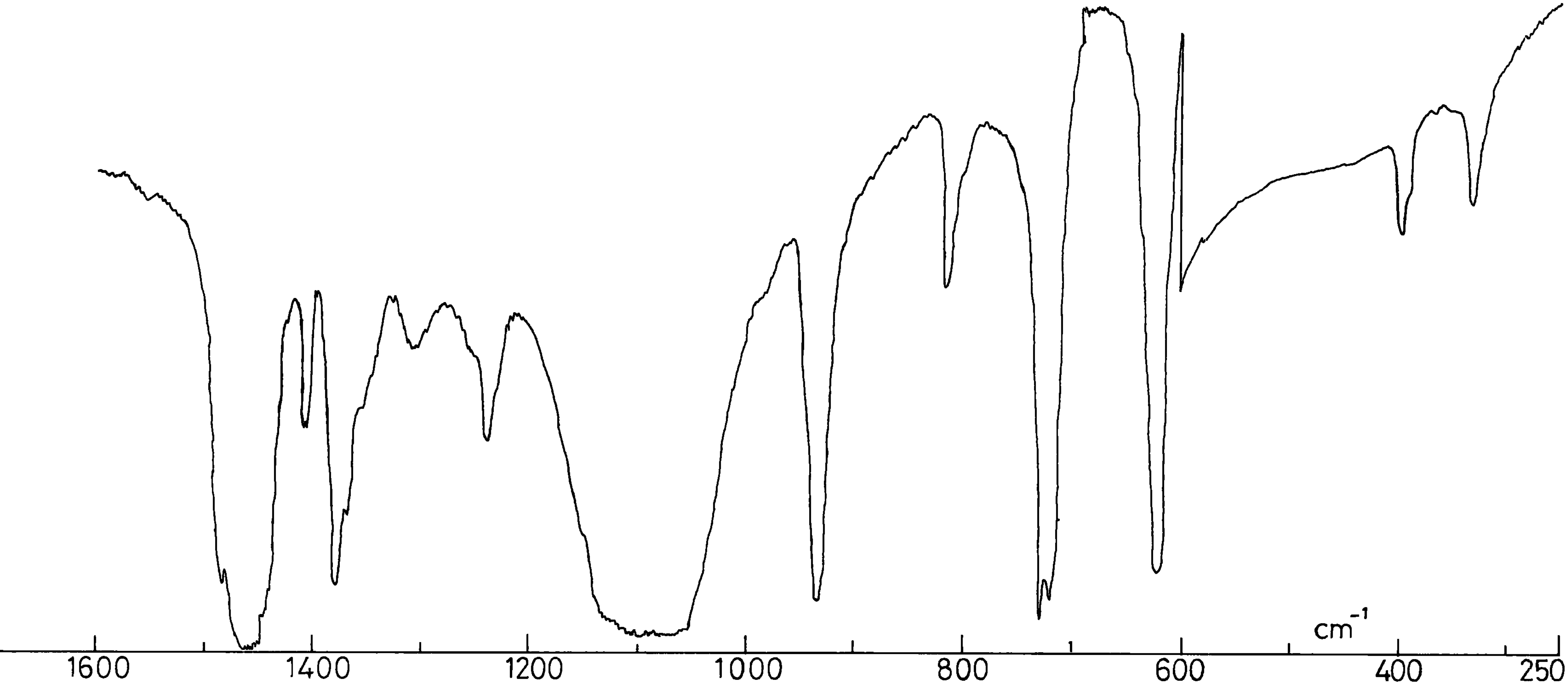


fig 27 INFRA RED SPECTRUM OF

$(CH_3)_3NCl^+ \; ClO_4^-$

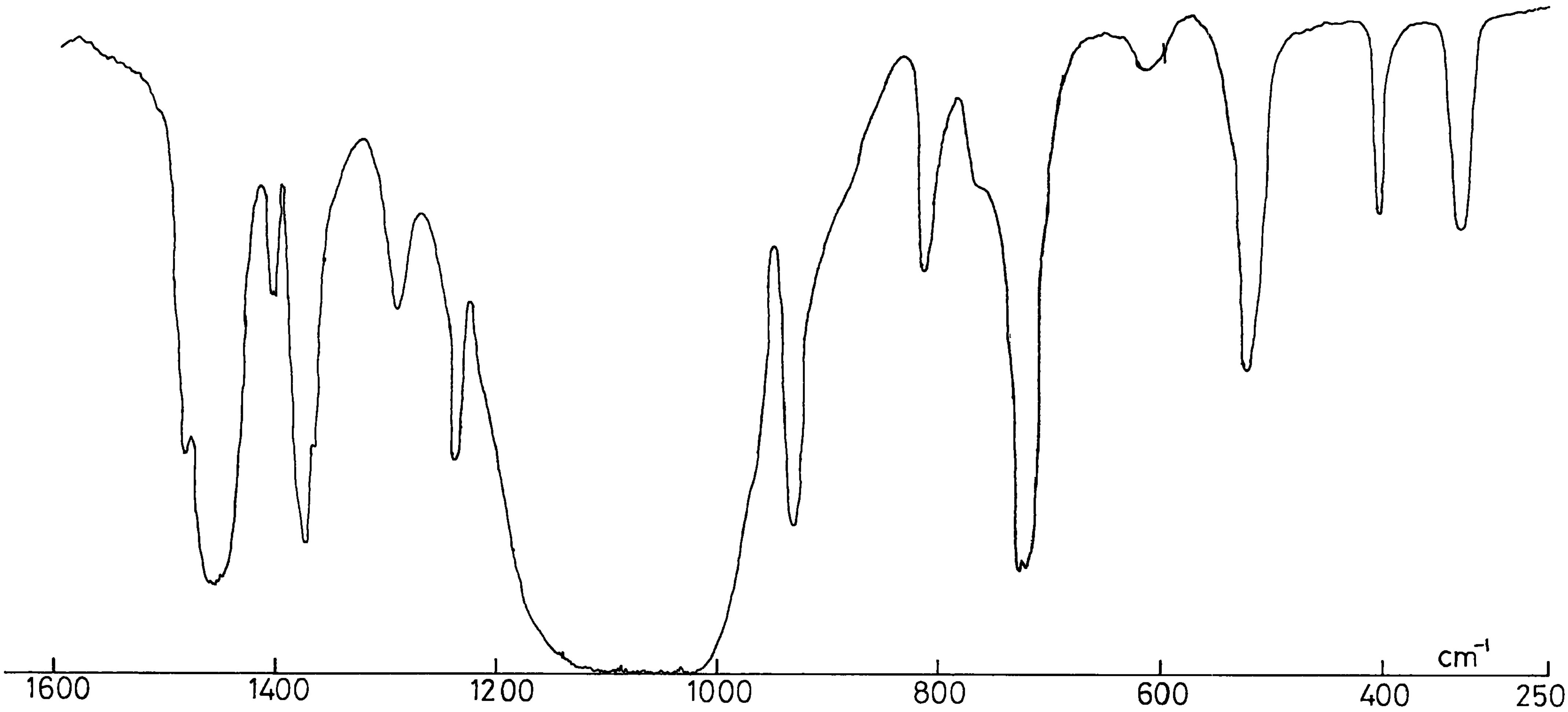
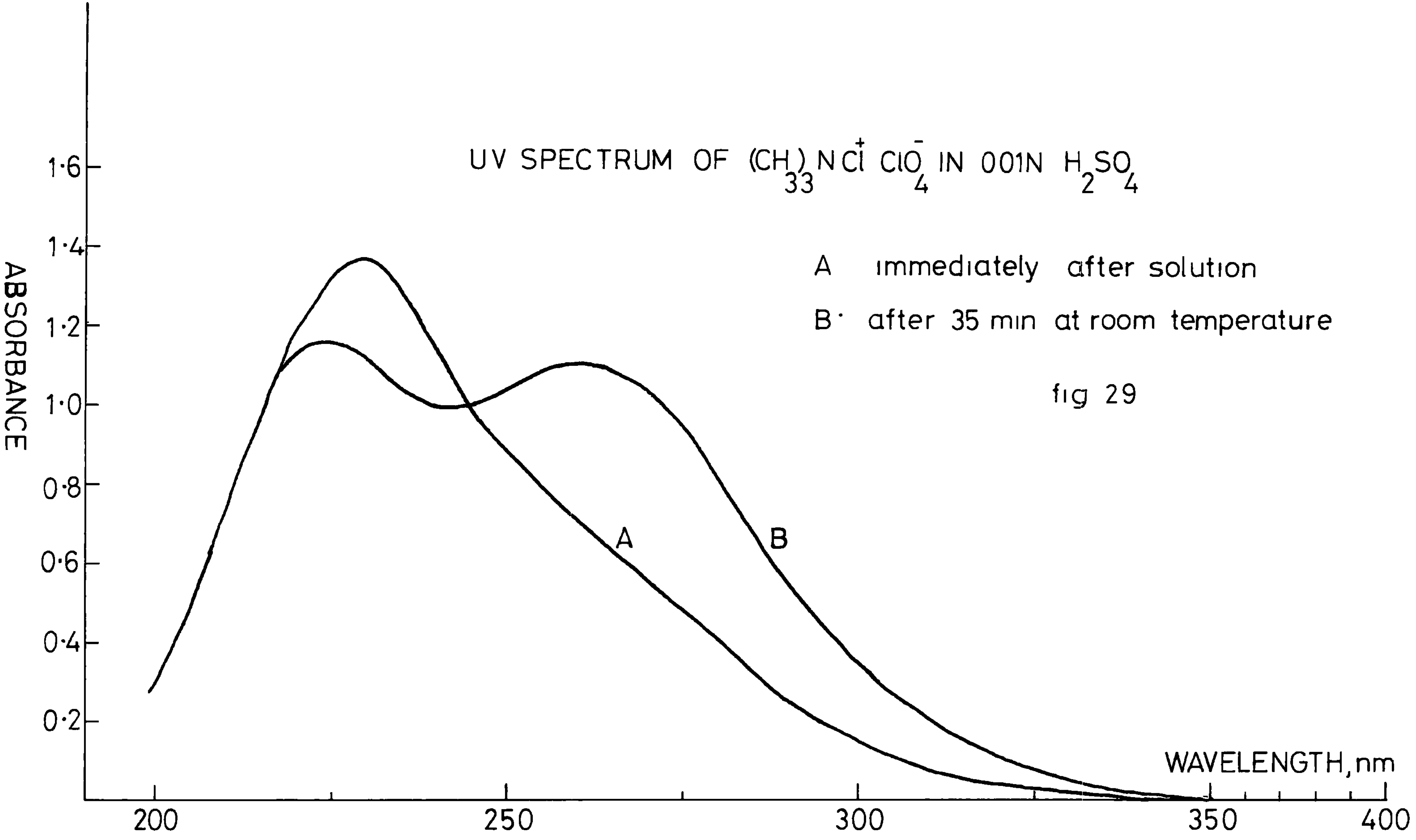


fig 28 INFRA RED SPECTRUM OF
$(CH_3)_3NCl^+ BF_4^-$



UV SPECTRUM OF $(CH_3)_3N\overset{+}{Cl}\ ClO_4^-$ IN 001N $H_2SO_4$

A immediately after solution

B· after 35 min at room temperature

fig 29

The equivalent mass of the salt $(CH_3)_3\overset{+}{N}Cl\ ClO_4^-$, as an oxidising agent, was determined by dissolving an accurately weighed aliquot quickly in water and adding an excess of KI in 0.2M $H_2SO_4$, and titrating the liberated iodine with 0.1149N sodium thiosulphate, previously standardised against potassium iodate. The equivalent mass was found to be 99.71.

The equation:

$$(CH_3)_3\overset{+}{N}Cl + 2e^- + H^+ = (CH_3)_3\overset{+}{N}H + Cl^-$$

requires a theorectical equivalent mass of 97.0 for the perchlorate.

## The Formation Of $(CH_3)_3NCl$ From $(CH_3)_3NCl_2$ And Lewis Acids

Boll (109) reacted solutions of $(CH_3)_3N$, $Cl_2$, $SbCl_5$ in $CCl_4$ and obtained a product which lost chlorine on storing in a vacuum dessicator. The method of Boll suffers from the disadvantage that as the solutions are mixed immediate competition occurs between the two Lewis acids, $Cl_2$ and $SbCl_5$, and the base $(CH_3)_3N$, resulting in a mixture, where $Cl_2$ is trying to substitute into the N-Sb bond in $(CH_3)_3N\text{-}SbCl_5$.

This difficulty was overcome by starting with the $(CH_3)_3N$ complexed to the weaker Lewis acid, $Cl_2$, as in $(CH_3)_3NCl_2$, and adding a stronger volatile, Lewis acid such as $BCl_3$ to it.

Weight analysis experiments with freshly prepared $(CH_3)_3NCl_2$ and $BCl_3$, the course of which was followed by infra red spectroscopy, showed that $BCl_3$ will add to $(CH_3)_3NCl_2$ to give $(CH_3)_3\overset{+}{N}Cl\ BCl_4^-$, to the extent of approximately 90%. In this instance, infra red absorptions due to $BCl_4^-$ were found, as well as those attributable to the cation $(CH_3)_3\overset{+}{N}Cl$. No indication of $(CH_3)_3\overset{+}{N}H$ formation was apparent from the infra red.

With other Lewis acids the picture is not so clear. The use of $BCl_3$ had practical advantages over and above its Lewis acid capabilities, in that it was readily removable during the weight analysis experiments. The Lewis acid $SbCl_5$, is clearly not so volatile, and ideally requires the use of a solvent in which both the Lewis acid and $(CH_3)_3NCl_2$ are soluble, but with which they do not react.
Good high dielectric solvents such as nitrobenzene or nitromethane, do not meet these requirements as the Lewis acid reacts with them, whereas chlorinated hydrocarbon solvents such as $CCl_4$ or $CH_2Cl_2$ were found to be ineffective in dissolving the chlorine, trimethylamine complex.

In a typical weight analysis experiment with $BCl_3$, 0.5322 g (4.09 m mole) of freshly prepared chlorine, trimethylamine complex was placed in a Rotaflow weight analysis cell, as described previously; in the dry box. The Rotaflow had been previously treated with $BCl_3$, so as to coat the inside surfaces and hydrolyse any absorbed, water not removed by gentle heating under vacuum. The Rotaflow being pumped dry after the $BCl_3$ pretreatment and weighed. The Rotaflow was transferred from the dry box to the vacuum line, pumped out, sealed and reweighed.

An excess (7.9191 g, 67.59 m mole) $BCl_3$ was then condensed into the cell, and the whole allowed towarm to room temperature, after which the cell was reweighed. The cell was then placed on a flask shaker and agitated for 16½ hours at room temperature.
The volatile contents of the cell were then removed on the vacuum line by distilling into a cold finger, and the cell reweighed. This procedure was repeated after 24 hours, after which the volatile material was pumped away, the cell transferred to the dry box for infra red investigation.

The spectrum of the product is shown in Figure 30, and since no $(CH_3)_3\overset{+}{N}H$ absorptions could be found, and the spectrum showed $BC\overset{-}{l_4}$ and residual $(CH_3)_3NCl_2$, it was assumed that the mass in the cell could be accounted for by $(CH_3)_3NCl_2$, $(CH_3)_3\overset{+}{N}ClBC\overset{-}{l_4}$ only. The results of the weighings are shown in Table 5 below.

TABLE 5

MASS CHANGES DURING $(CH_3)_3NCl_2$, $BCl_3$ REACTION

| | |
|---|---|
| Starting Mass $(CH_3)_3NCl_2$ | 0.5322 g |
| Residual Mass ($16\frac{1}{2}$ hours) | 0.8806 g |
| Residual Mass after 39 hours | 0.9150 g |
| Residual Mass Required (100% conversion) | 1.0117 g |
| Percentage Conversion | 90.44% |

The required residual mass was calculated assuming 100% conversion according to the equation below:

$$(CH_3)_3NCl_2 + BCl_3 = (CH_3)_3\overset{+}{N}Cl\ BC\overset{-}{l_4}$$

In an experiment with $SbCl_5$, 0.7547 g (5.8 m mole) $(CH_3)_3NCl_2$ which had been freshly prepared, was placed in a 100 ml round bottomed flask followed by 12 ml dry $CH_2Cl_2$ in the dry box. 1 ml (7.79 m mole) $SbCl_5$ was then added, and the flask stoppered and shaken for $1\frac{1}{2}$ hours. The flask contents were then poured into a sintered glass filter in the dry box, and product collected, washed with $CH_2Cl_2$ and found to weigh 1.1214 g. The infra red spectrum of the product was recorded between CsI plates, and is shown in Figure 31, indicating $SbCl_6$ formation from the strong absorption at 345 $cm^{-1}$. Peaks are also attributable to residual $(CH_3)_3NCl_2$, and it is possible to observe a peak attributable to the N-Cl stretch in the cation at 400 $cm^{-1}$.

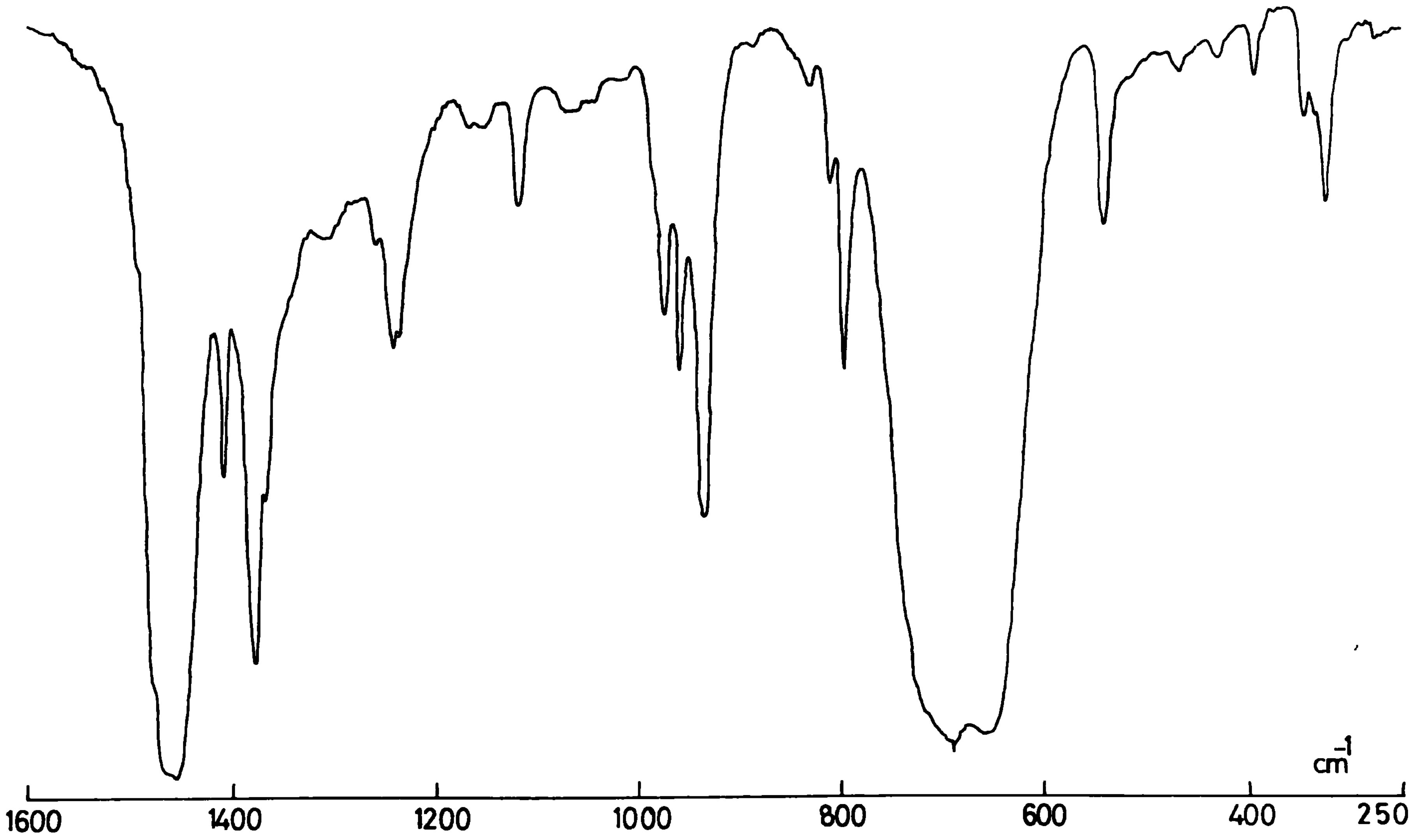
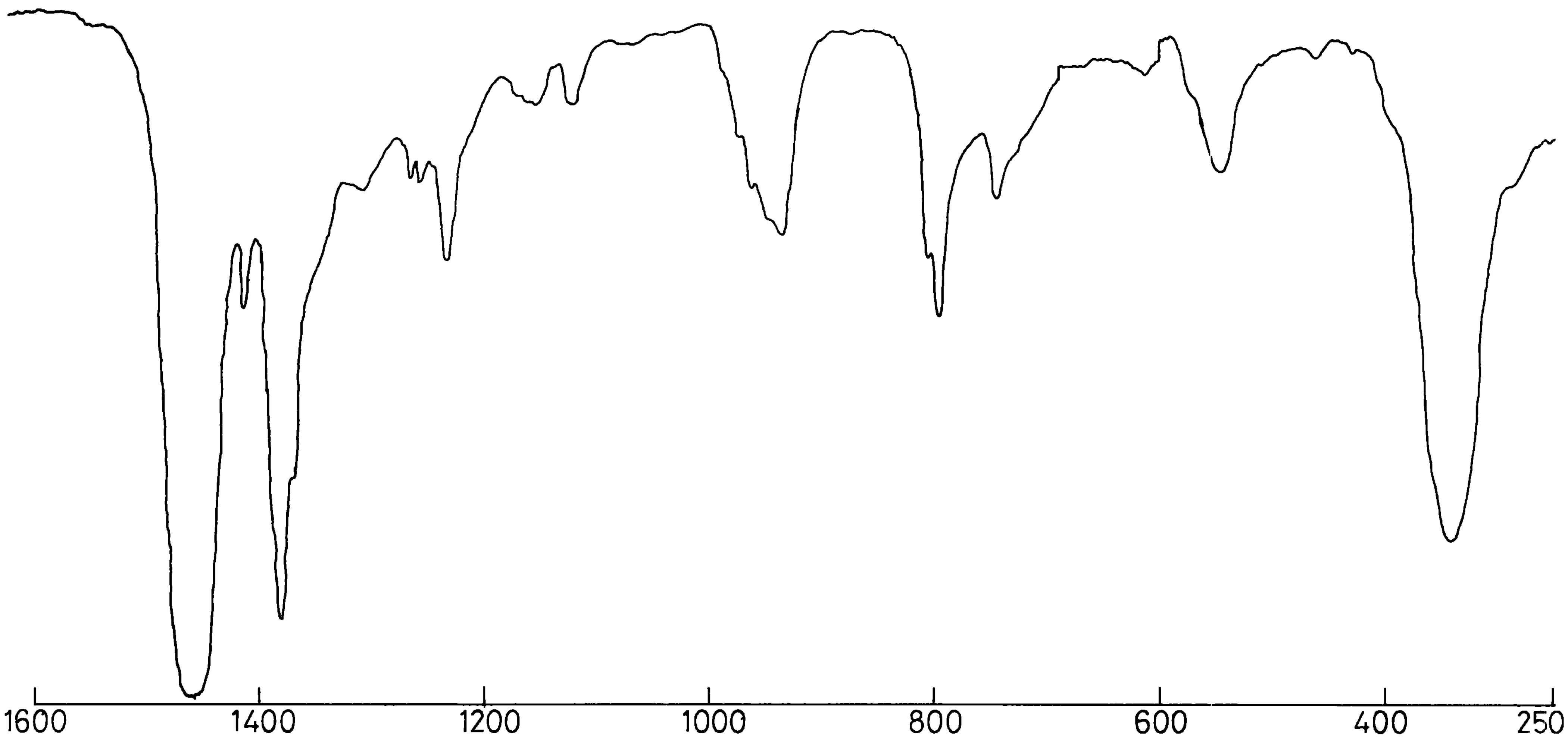


fig 30 INFRA RED SPECTRUM OF THE PRODUCT FROM THE REACTION OF $(CH_3)_3NCl_2$ WITH $BCl_3$



INFRA RED SPECTRUM OF THE PRODUCT OF THE REACTION OF $(CH_3)_3NCl_2$ WITH $SbCl_5$

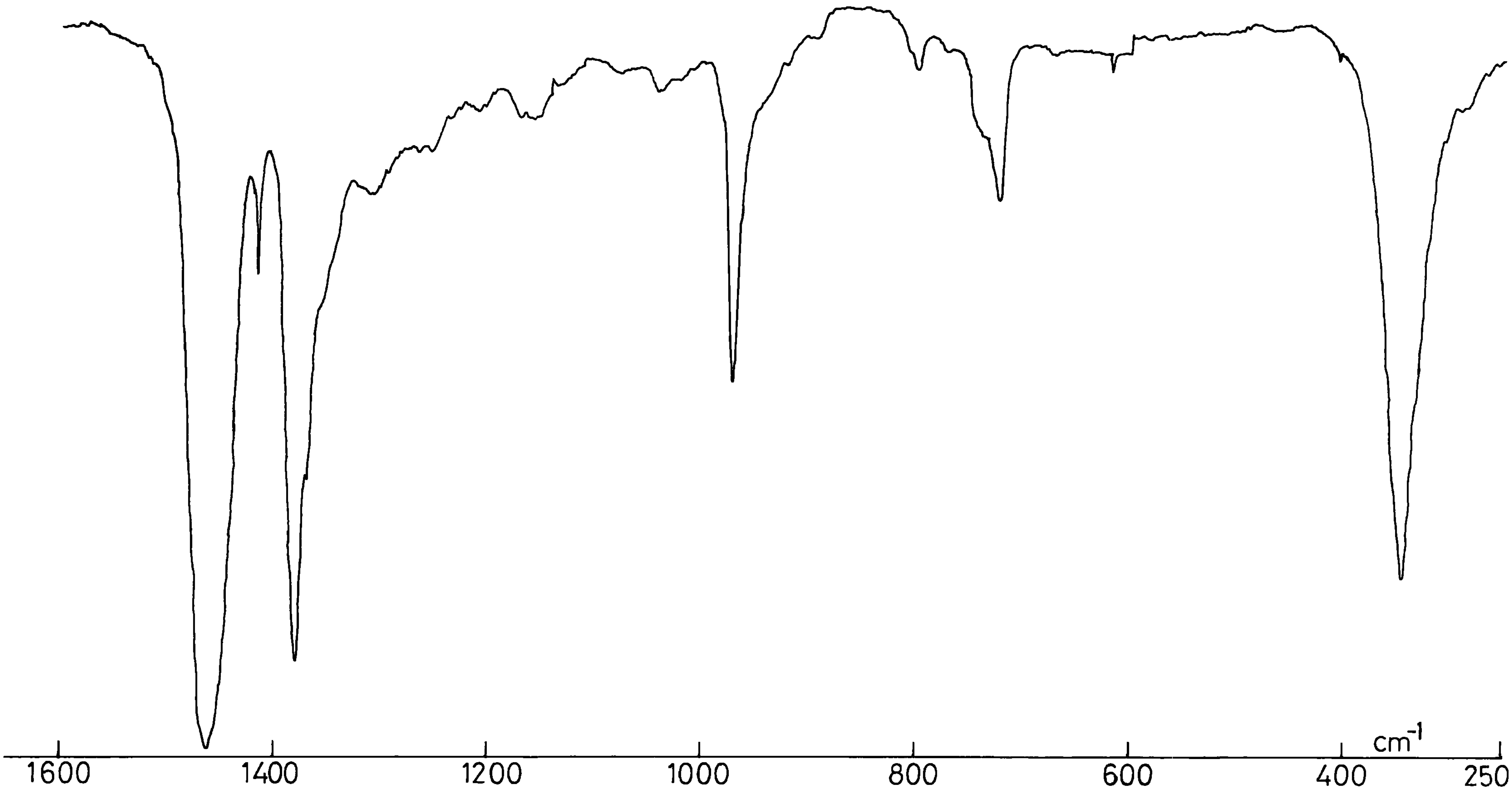
fig 31

The reaction product did not analyse well, (Found, (%), C, 11.6; H, 3.23; N, 4.79; Cl, 57.4; Sb, 25.8). The C:N ratio of 2.8:1 is reasonably close to the 3:1 required by $(CH_3)_3NCl\ SbCl_6$, but the N:Cl ratio is only 4.75:1 instead of 7:1. No determination of the oxidising power of the product was performed.

A second sample of approximately 2 g $(CH_3)_3NCl_2$ was placed in a mortar in the dry box and ground under a solution containing approximately 5 ml $SbCl_5$ in 20 ml dry $CH_2Cl_2$. The resulting slurry was filtered, and the filtrate allowed to stand in the dry box for about 1 hour, after which grey needles deposited. The product was isolated on a sintered glass filter and the infra red spectrum recorded between CsI plates, and is shown in Figure 32. The product was analysed and found to contain (%), C, 9.50; H, 2.73; N, 3.69, Cl, 57.63; Sb, 31.3; which indicates empirically $C_{305}H_{105}NSbCl_{63}$ The infra red spectrum showed a strong absorption at 345 $cm^{-1}$ indicating $SbCl_6^-$, and also an N-H cation vibration at 3200 $cm^{-1}$ .

It was apparent that $(CH_3)_3\overset{+}{N}H\ \overset{-}{SbCl_6}$ had formed and this was confirmed by comparison with an infra red spectrum of $(CH_3)_3\overset{+}{N}H\ \overset{-}{SbCl_6}$ prepared from $(CH_3)_3\overset{+}{N}H\ \bar{Cl}$ and $SbCl_5$ in $CH_2Cl_2$ solution, and is shown in Figure 33.

The formation of $(CH_3)_3\overset{+}{N}H$ is presumably due to attack of $(CH_3)_3\overset{+}{N}Cl$ on the solvent $CH_2Cl_2$ yielding chloroform $CHCl_3$, but since the product was not analytically pure, other side reactions have presumably occurred. This reaction was not investigated further.



INFRA RED SPECTRUM OF THE PRODUCT OF THE REACTION OF $(CH_3)_3NCl_2$ WITH $SbCl_5$

fig 32

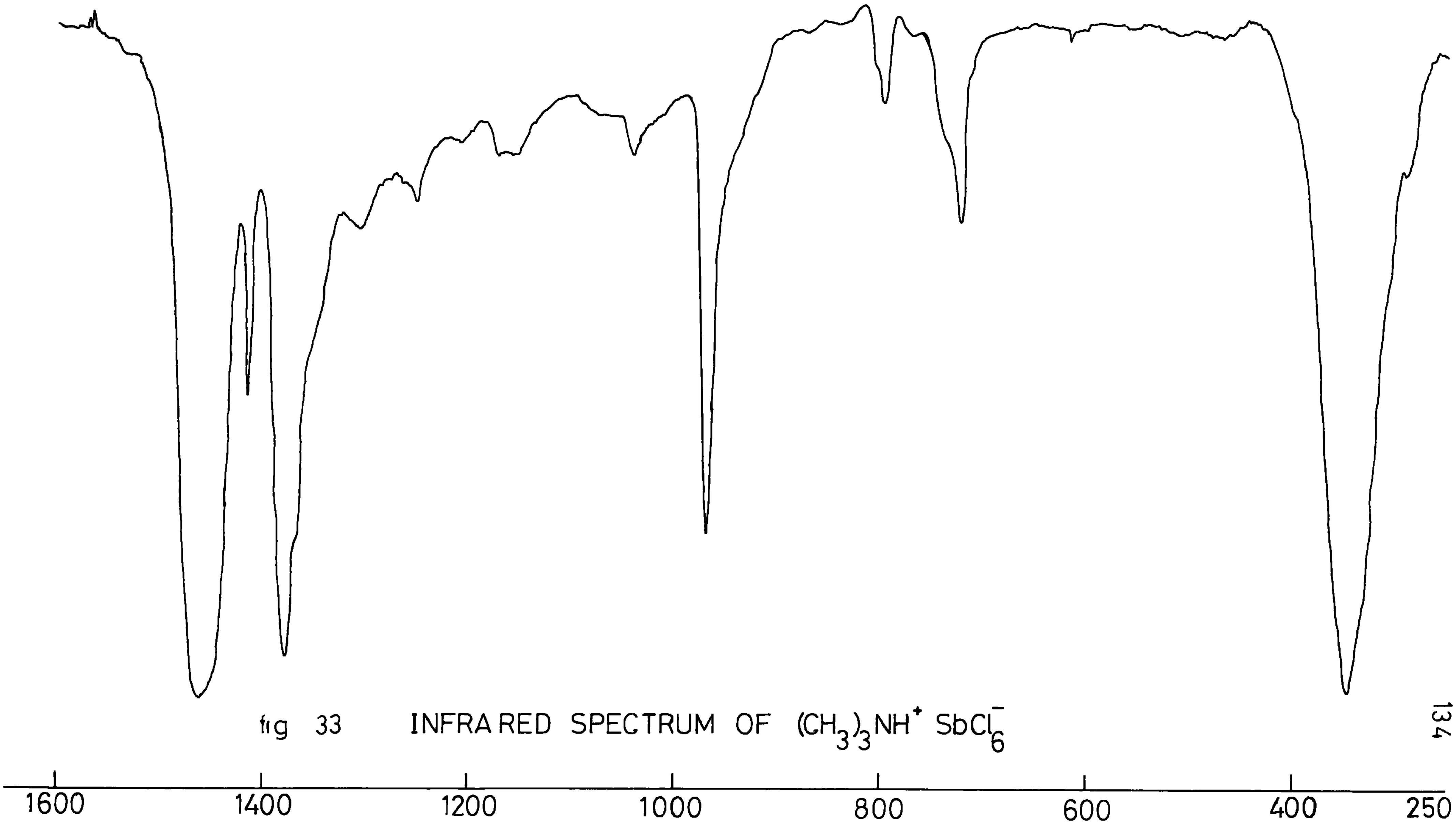
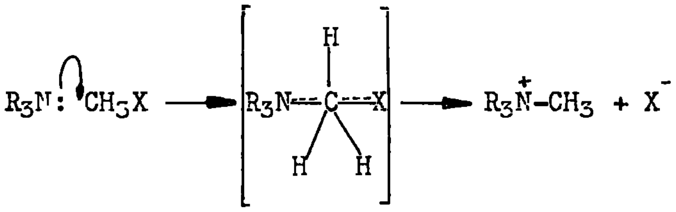


fig 33 INFRARED SPECTRUM OF $(CH_3)_3NH^+ SbCl_6^-$

## The Formation Of $(CH_3)_3\overset{+}{N}Cl$ From $(CH_3)_2NCl$

Reactions involving tertiary amines and alkylating agents are well known, the reaction proceeding via attack of the nitrogen lone pair on suitably positive carbon atom as shown in the scheme below:



The extent to which such alkylations occur depend on two factors, the availability of the nitrogen lone pair, as measured in basicity, and the degree of polarisation of the $CH_3$-X bond such that $C^{\delta+}$ occurs, other things, such as stearic effects being constant.

For weakly basic tertiary amines, such as $(CH_3)_2NCl$ the alkylating agent must compensate in providing a larger effective positive charge on the $CH_3$ group adding onto the base. As a guide to how positive a methyl group is, $^1H$ NMR can be useful. Table 6 lists the $^1H$ absorptions for a selection of methyl esters, indicating those with OXO anions, are much more positive than alkyl halides.

TABLE 6

$^1H$ NMR OF METHYL ESTERS

| Anion | τ | Reference | Remarks |
|---|---|---|---|
| $SbF_6^-$ | 4.4 | 112 | at -78°C; $SbF_5$, $SO_2$, $CH_3F$ |
| $ClO_4^-$ | 5.7 | 111 | $CH_3I$, $AgClO_4$ in $CCl_4$ solution |
| $OSO_2F^-$ | 5.8 | 112 | in $SbF_5$ |
| | 5.79 | 113 | as pure liquid |
| $NO_3^-$ | 5.85 | 111 | |
| $OCl^-$ | 6.01 | 111 | |
| $SO_4^-$ | 6.04 | 111 | |
| $I^-$ | 8.00 | This work | as pure liquid |

Of the anions listed in Table 6, $CH_3OSO_3CH_3$, $CH_3NO_3$, $CH_3OSO_2F$, $CH_3OClO_3$, and $CH_3SbF_6$($CH_3F$,$SbF_5$ in $SO_2$) were reacted with $(CH_3)_2NCl$. $CH_3I$ also reacts, but the product of this reaction, $C_6H_{18}N_2Cl_2I_2$, is considered in Chapter 5.

Only $CH_3NO_3$ failed to provide a product, which in view of its projected power from the table, should be at least as efficient as $CH_3OSO_3CH_3$, dimethyl sulphate. The reason for the lack of reaction may be that at the temperature of the reaction, approximately 16-20°C, a high energy barrier exists to the transition state. Any heating decomposes the dimethylchloramine.
Although $CH_3F$, $SbF_5$ in $SO_2(l)$ reacted with $(CH_3)_2NCl$ the product did not contain the cation $(CH_3)_3\overset{+}{N}Cl$, which in view of the apparent stability of $(CH_3)_3\overset{+}{N}Cl\ ClO_4^-$ or $BF_4^-$, $SbF_6^-$ as an anion ought to stabilise the cation equally well.

The alkylating agent $CH_3OClO_3$, methyl perchlorate, presents a method of obtaining a salt $(CH_3)_3\overset{+}{N}Cl\ ClO_4^-$ preparable also from $(CH_3)_3NCl_2$ and aqueous $ClO_4^-$.
$CH_3OSO_2F$ and $CH_3OSO_3CH_3$ both yielded white solids which contained the cation $(CH_3)_3\overset{+}{N}Cl$ as shown by infra red spectroscopy.

In a typical experiment involving $CH_3OSO_3CH_3$, 1 ml (1.33 g, 10 m mole) $(CH_3)_2SO_4$ was dissolved in 10 ml dry diethyl ether in a 50 ml round bottomed flask equipped with a tap cone connector, and attached to the vacuum line. The solution was degassed and 0.7 g (8.8 m mole) $(CH_3)_2NCl$ was condensed.

The flask was isolated and removed from the vacuum line, and allowed to warm up to -5°C in a refrigerator, where it remained for two hours. The flask was then dried and transferred to the dry box and the solution filtered with suction, yielding 1.32 g of a fine white solid, which represents 73% conversion of chloramine to chlorammonium salt. The solid was analysed and found to contain, (%), C, 23.46; H, 5.95; N, 6.98; Cl, 17.9; S, 15.97. $(CH_3)_3NClOSO_3CH_3$ requires, (%), C, 23.36; H, 5.84; N, 6.81; Cl, 17.27, S, 15.57.

An infra red spectrum was recorded, and is shown in Figure 34, as a nujol mull between CsI plates protected with polyethylene film.

The equivalent weight of the compound as an oxidising agent was determined by adding KI to an acidified solution and titrating the liberated $I_2$ with sodium thiosulphate. The equivalent weight was found to be 104.102, which when compared to the required value, of 102.830, indicates slight decomposition.

A sample of the compound was dissolved in water and its UV spectrum recorded, as shown in Figure 35, which compares with that shown in Figures 26 and 29 for the complex $(CH_3)_3NCl_2$ and the salt $(CH_3)_3\overset{+}{N}Cl\ Cl\overset{-}{O_4}$.

The reaction with $CH_3OSO_2F$, methyl fluorosulphate, was performed in a similar way, typically 1 ml (1.43 g, 12.5 m mole) $CH_3OSO_2$ was condensed into a 50 ml round bottomed flask containing 5 ml dry degassed $CCl_4$. 0.1 g (1.26 m mole) $(CH_3)_2NCl$ was then condensed into the flask and the whole isolated from the vacuum line, placed in a refrigerator for about 10 minutes, and then returned to the vacuum line where all the volatile material was pumped away, leaving a white powder. The flask was transferred

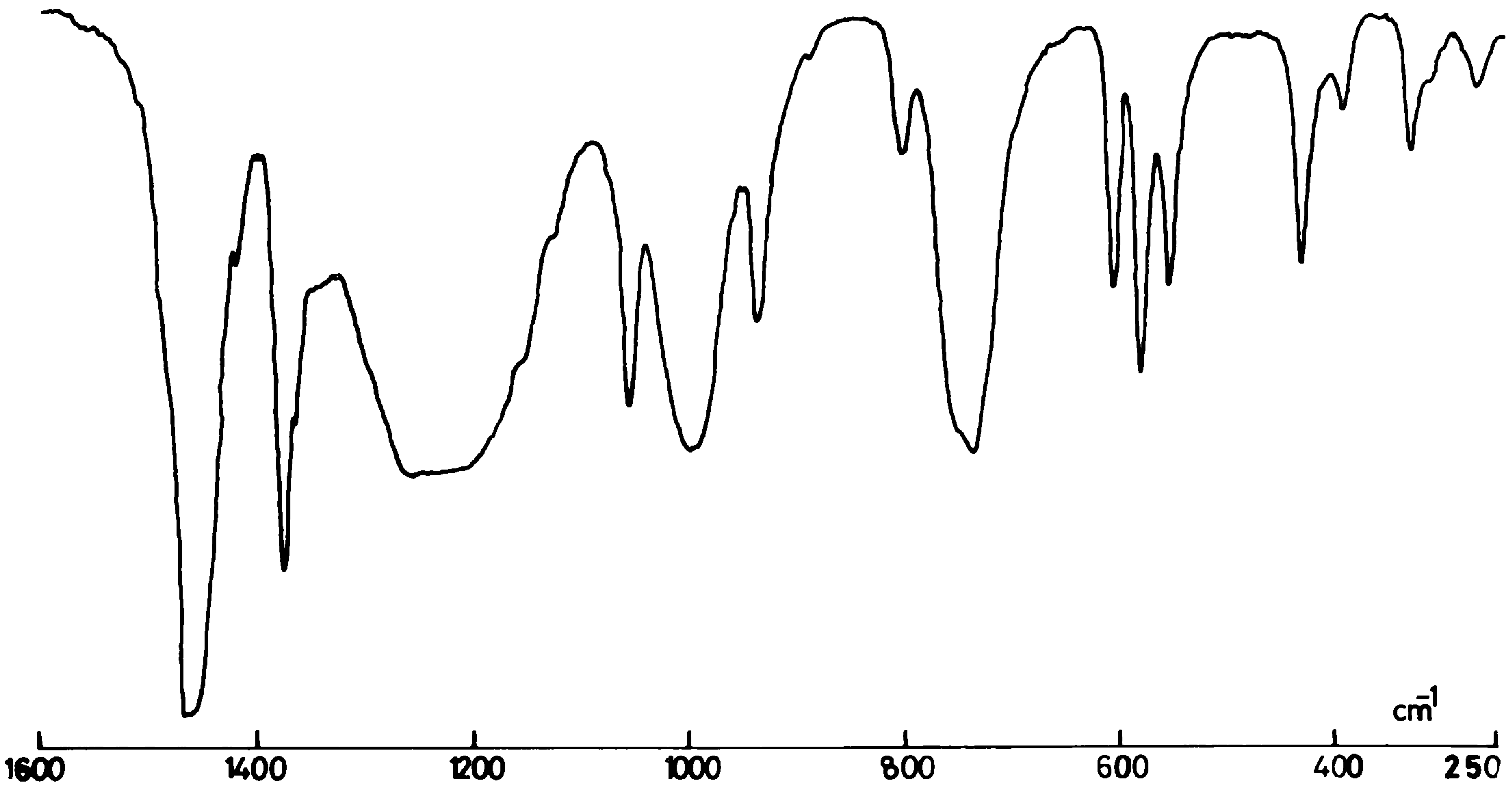
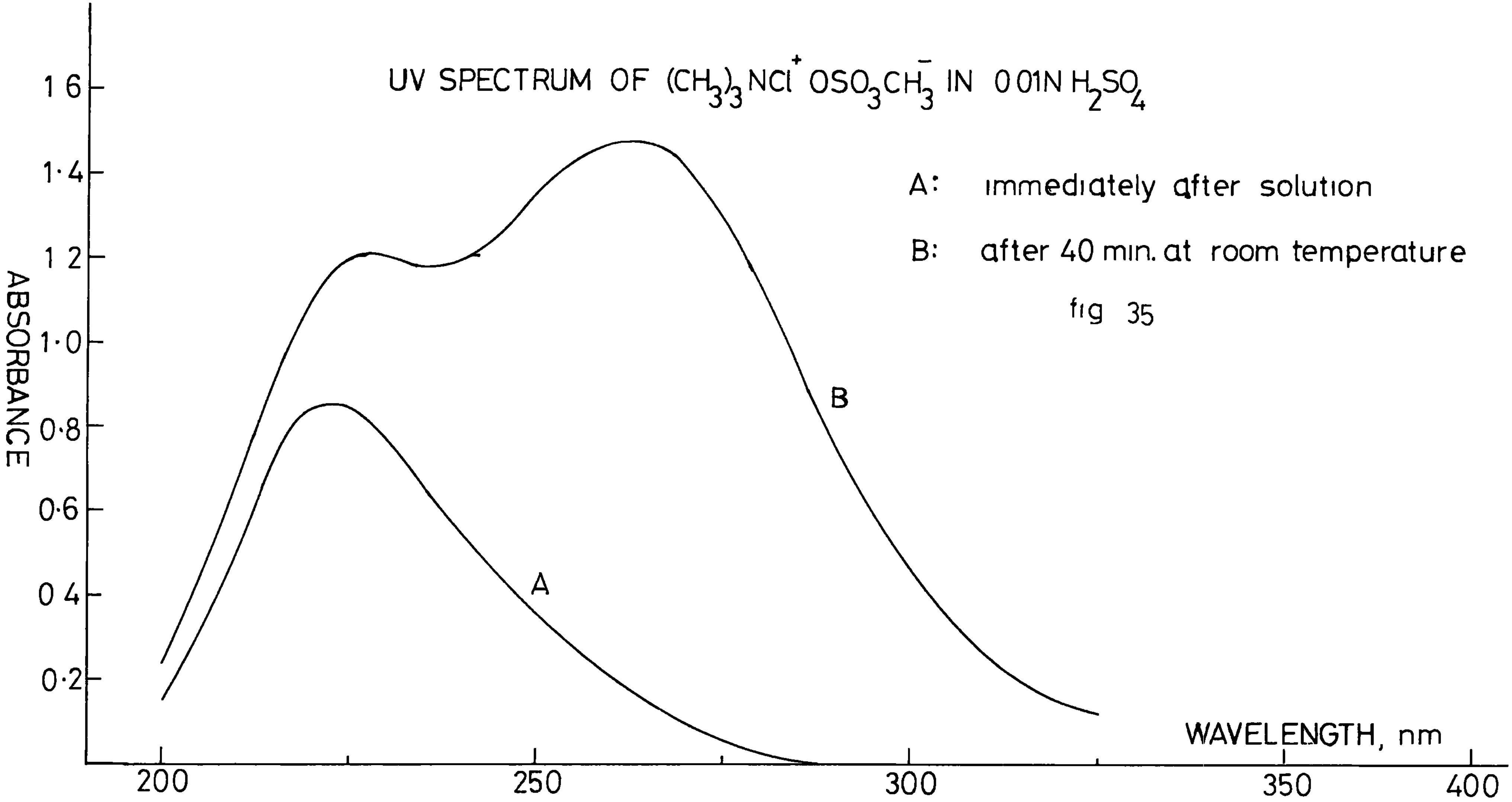


fig 34 INFRA RED SPECTRUM OF
$(CH_3)_3\overset{+}{N}Cl\ \overset{-}{O}SO_3CH_3$



UV SPECTRUM OF $(CH_3)_3NCl^+ OSO_3CH_3^-$ IN 0 01N $H_2SO_4$

A: immediately after solution

B: after 40 min. at room temperature

fig 35

to the dry box and 0.2 g of the fine white powder isolated. This mass represents an 82.5% yield based on the equation below:

$$(CH_3)_2NCl + CH_3OSO_2F = (CH_3)_3NClOSO_2F$$

A sample was analysed and found to contain, (%), C, 18.26; H, 4.59; N, 7.10; Cl, 18.52; S, 16.6; F, 9.99. $(CH_3)_3NClOSO_2F$ requires, (%), C, 18.59; H, 4.65; N, 7.23; Cl, 18.33; S, 16.53; F, 9.80.
The infra red spectrum of a sample of the product is shown, as a nujol mull between polyethylene protected CsI plates, in Figures 36 and 37.

The alkylating agent, $CH_3OClO_3$, was never isolated as the pure compound but used in the solution it was prepared in, as detailed in Chapter 2.
5 ml of the solution, which contained approximately 0.46 g (4 m mole) $CH_3OClO_3$, was placed in a 50 ml round bottomed flask equipped with a tap cone connector. The flask was attached to the vacuum line and the solution degassed, 0.3512 g, 4.42 m mole. $(CH_3)_2NCl$ was then condensed in and the flask isolated from the vacuum line, removed and allowed to warm to room temperature. After approximately 5 minutes a white solid began to form, and after 10 minutes the flask was transferred to the dry box and the contents filtered with suction, the white solid being washed with a small quantity of dry $CCl_4$. The product was analysed and found to contain, (%), C, 18.68; H, 4.73; N, 7.35; Cl, 36.71. $(CH_3)_3NCl\ ClO_4$ requires, (%), C, 18.55; H, 4.64; N, 7.22; Cl. 36.59.

The infra red spectrum of the compound was recorded as a nujol mull between protected CsI plates and is shown in Figure 38, and if compared with Figure 27, it can be seen that the product from the methylation of

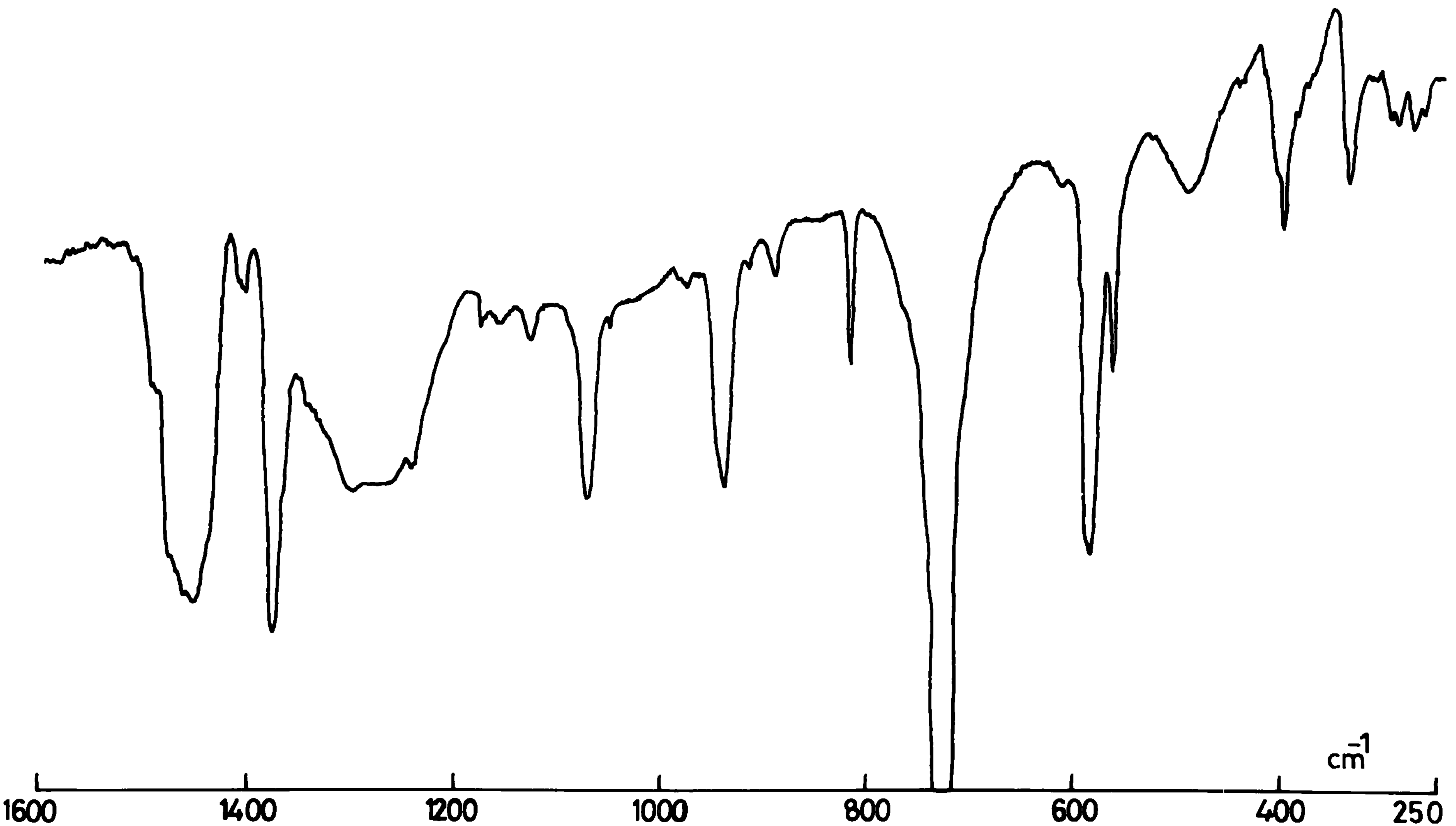


fig 36

INFRA RED SPECTRUM OF
$(CH_3)_3\overset{+}{N}Cl\ \overset{-}{O}SO_2F$

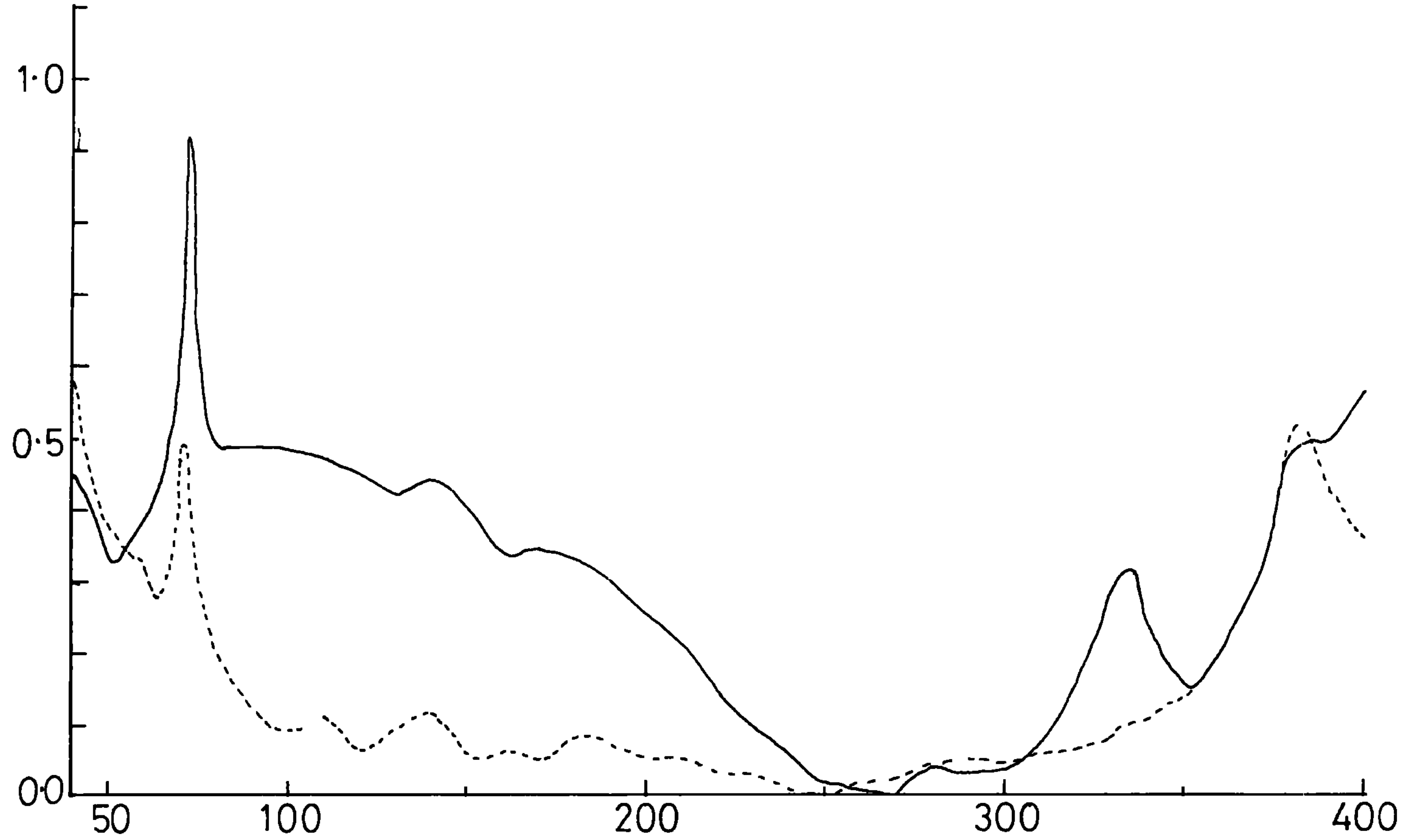


fig 37 PLOT OF THE FAR IR SPECTRUM OF $(CH_3)_3NCl^+ OSO_2F^-$

(------ background)

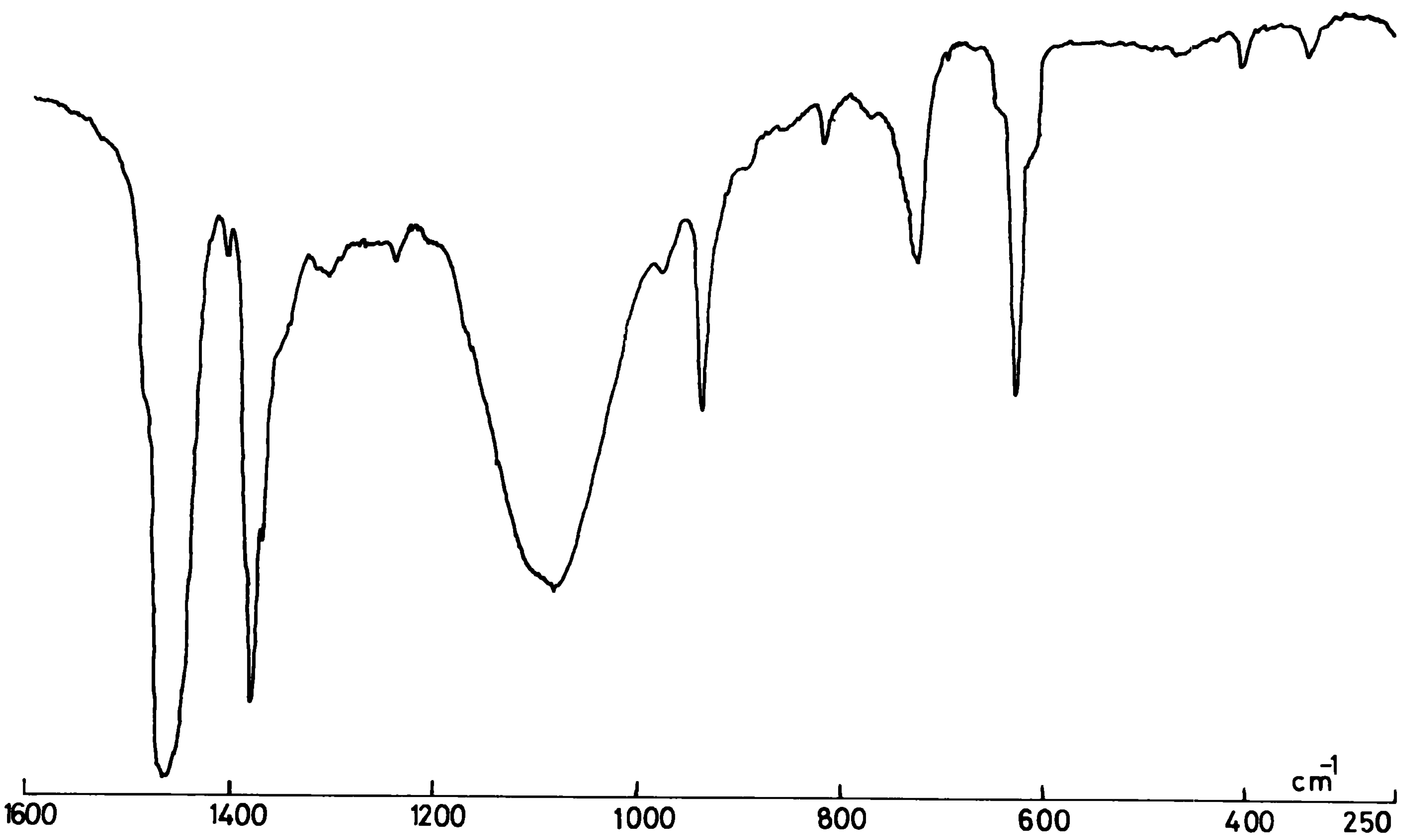


fig 38 INFRA-RED SPECTRUM OF THE PRODUCT FROM THE REACTION OF $(CH_3)_2NCl$ WITH $CH_3ClO_4$

$(CH_3)_2NCl$ contains the same cation as that obtained from aqueous solutions of $(CH_3)_3NCl_2$.

The reaction between $(CH_3)_2NCl$ and $CH_3F/SbF_5$ mixtures in liquid $SO_2$ did not yield a product containing the cation $(CH_3)_3\overset{+}{N}Cl$. In a typical experiment, 2.0722 g (9.56 m mole) $SbF_5$ was then placed in a 50 ml round bottomed flask in the dry box, and the flask sealed with a tap cone connector.
The flask was affixed to the vacuum line and the contents degassed. 4.031 g (62.92 m mole) $SO_2$ was then condensed in and the whole allowed to warm to -23°C (melting $CCl_4$) and the $SbF_5$ allowed to dissolve. When solution was complete, 0.3439 g (10.105 m mole) $CH_3F$ was added, and the flask and contents held at -84°C to allow the solid to dissolve.

0.8232 g (10.35 m mole) $(CH_3)_2NCl$ was then condensed into the refrozen $SbF_5$, $CH_3F$, $SO_2$ solution and the flask warmed to -84°C where the whole dissolved leaving a clear colourless solution. The flask and contents were held at this temperature over night, after which time the contents of the flask appeared solid. The volatile components were distilled into a cold finger at -196°C. The solid residue was transferred to the dry box and a sample removed for oxidation analysis.

An aliquot of the product was dissolved in water acidified with 0.1N $H_2SO_4$ and KI added, to yield a solution which when titrated against sodium thiosulphate resulted in an equivalent weight of 975 indicating little oxidising power. The material elemental analysis showed that the product could be represented by the empirical formula $C_3H_{12}NClSb_{1.5}F_6$.

## 4. Reactions In Which $(CH_3)_3\overset{+}{N}Br$ Is Formed

All the preparative techniques employed in the formation of the $(CH_3)_3\overset{+}{N}Cl$ cation cannot be used in formation of the bromo analogue, since $(CH_3)_3NBr_2$ is not soluble in water. A direct method is found in alkylation of $(CH_3)_2NBr$.

The complex formed in the reaction of $(CH_3)_2NBr$ with the alkylating agent $CH_3OSO_2F$ is extremely unstable, and indeed no satisfactory analytical figures were obtained, however infra red spectroscopy showed that in the compounds prepared, certain parallels could be drawn between the reaction products with the equivalent $(CH_3)_2NCl$ reactions.

In an experiment with $CH_3OSO_2F$, 1 ml of a solution of $(CH_3)_2NBr$ in $CCl_4$, prepared as detailed in Chapter 2, was contained in a test tube in the dry box, and approximately 0.5 ml $CH_3OSO_2F$ added and the tube shaken. After a few seconds, a white precipitate formed. The tube was stoppered removed from the dry box and filtered with suction, washed with a few mls hexane and then transferred to a second test tube.
The solid was taken up in approximately 1 ml distilled water, and to the resulting solution, a few drops of saturated $NaClO_4$ solution were added, resulting in a white precipitate. In a second experiment, 5 ml of the solution of $(CH_3)_2NBr$ was placed in a 50 ml beaker in the dry box. To this 0.4 ml $CH_3OSO_2F$ was added, and the contents swirled. The solid product was filtered off and washed with a few mls of dry $CCl_4$. The product was analysed and found to contain (%) C, 15.91; H, 4.82; N, 5.58; Br, 31.43; S, 12.19; F, 8.32. $(CH_3)_3\overset{+}{N}Br\ OSO_2F^-$ requires, (%), C, 15.13, H, 3.78; N, 5.88; Br, 33.61; S, 13.44; F, 7.98.

The infra red spectrum of the product was recorded as a paraffin mull between protected CsI plates, and is shown in Figure 43 which, when the peaks attributable to $^{-}OSO_2F$, at 1299, 1073, 583 and 565 $cm^{-1}$ are removed, indicated ⊖ in Figure 43, leaves peaks at 295, 325, 805 and 945 $cm^{-1}$. The far infra red spectrum, plotted in Figure 44 shows peaks at 294.2 and 324.5 $cm^{-1}$.

A small quantity of the product was dissolved in water and treated with saturated $NaClO_4$ solution, the resulting white solid being filtered off and dried on the sinter by washing with dry hexane. The infra red spectrum of a sample of this material was recorded and is shown in Figure 45, indicating $ClO_4$ absorptions at 630 $cm^{-1}$ $(\nu_4)$ and a broad absorption centred at 1080 $cm^{-1}$ $(\nu_3)$, and leaving absorptions at 295, 325, 805 and 945 $cm^{-1}$. The far infra red spectrum of this product, plotted in Figure 46 shows absorptions at 294.2 and 323.5 $cm^{-1}$, which agree well with the figures for the $OSO_2F^-$ salt, and are comparable with the figures quoted for the cation $(CH_3)_3\overset{+}{N}Cl$.

A small sample of the product from the $CH_3OSO_2F$ alkylation was dissolved in water and its UV spectrum recorded. The change in the spectrum with time is shown in Figure 47, indicating that the sample was partly decomposed, as seen by the absorption shoulder to the peak at 235 nm. As the course of the decomposition progresses, absorptions attributable to $Br_2$, at 394 and 265 nm, appear, and the peak due to $(CH_3)_2NBr$ (at 286 nm) slowly disappears.

## Discussion And Conclusions

Considering the similarity of the spectra obtained for $(CH_3)_3\overset{+}{N}Cl\ OSO_2\overset{-}{F}$ and $Cl\overset{-}{O_4}$ with those obtained from the product of the reaction of $(CH_3)_2NBr$ and $CH_3OSO_2F$ and the aqueous reaction of this product, it is

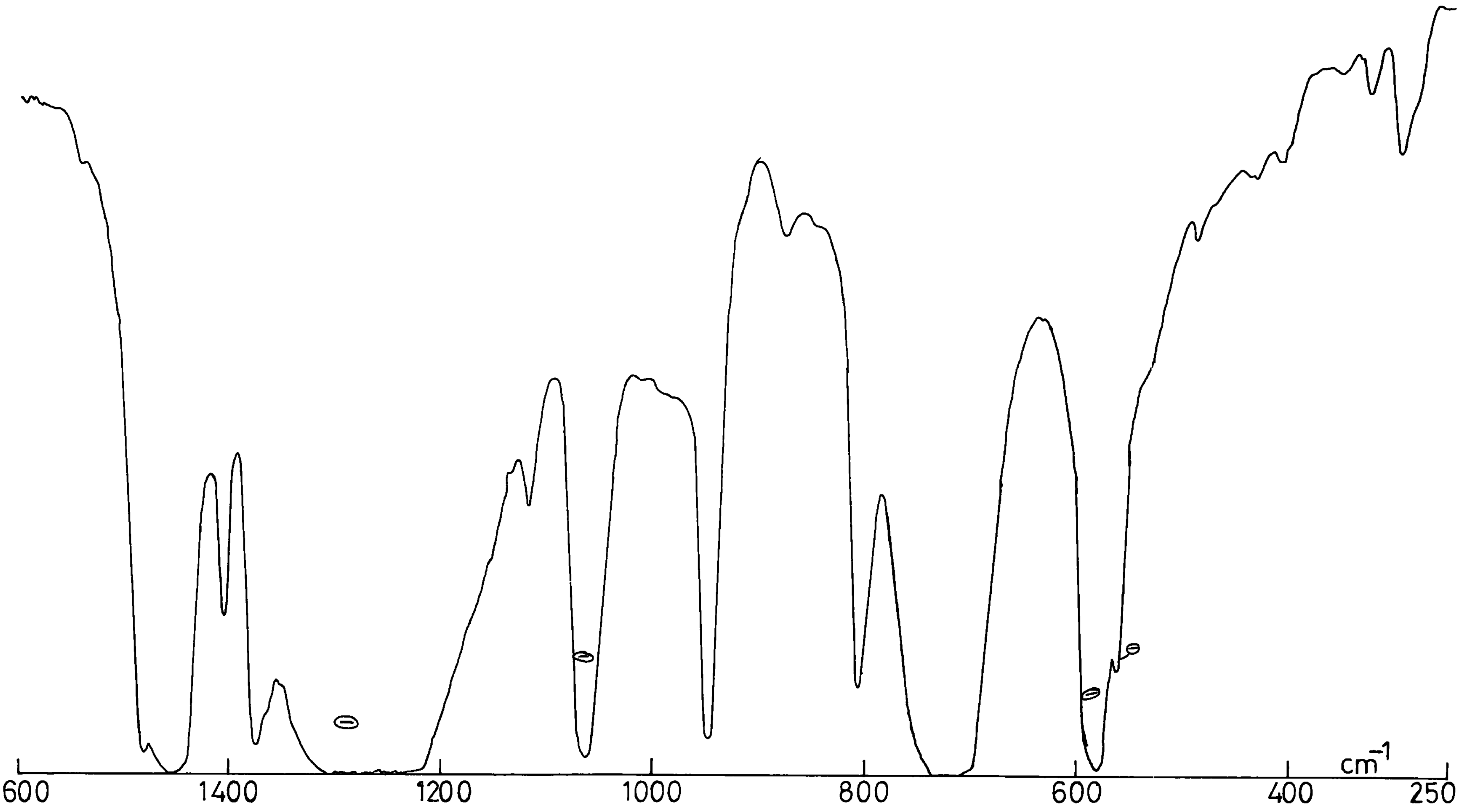


fig 43 INFRA RED SPECTRUM OF THE PRODUCT OF THE REACTION OF $(CH_3)_2NBr$ WITH $CH_3OSO_2F$

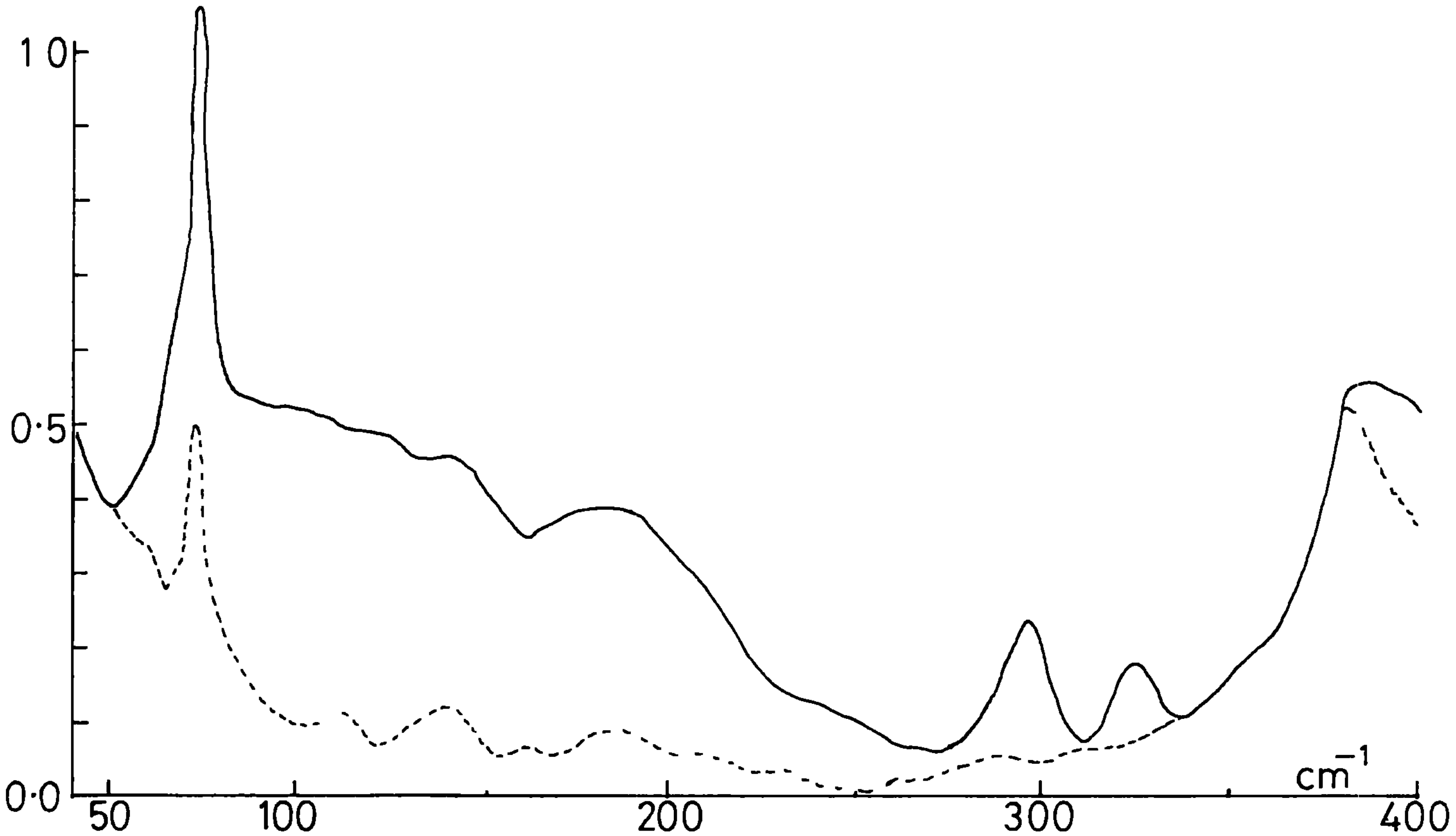


fig 44 PLOT OF THE FAR IR SPECTRUM OF $(CH_3)_3N\overset{+}{Br}OSO_2F^-$
(------background )

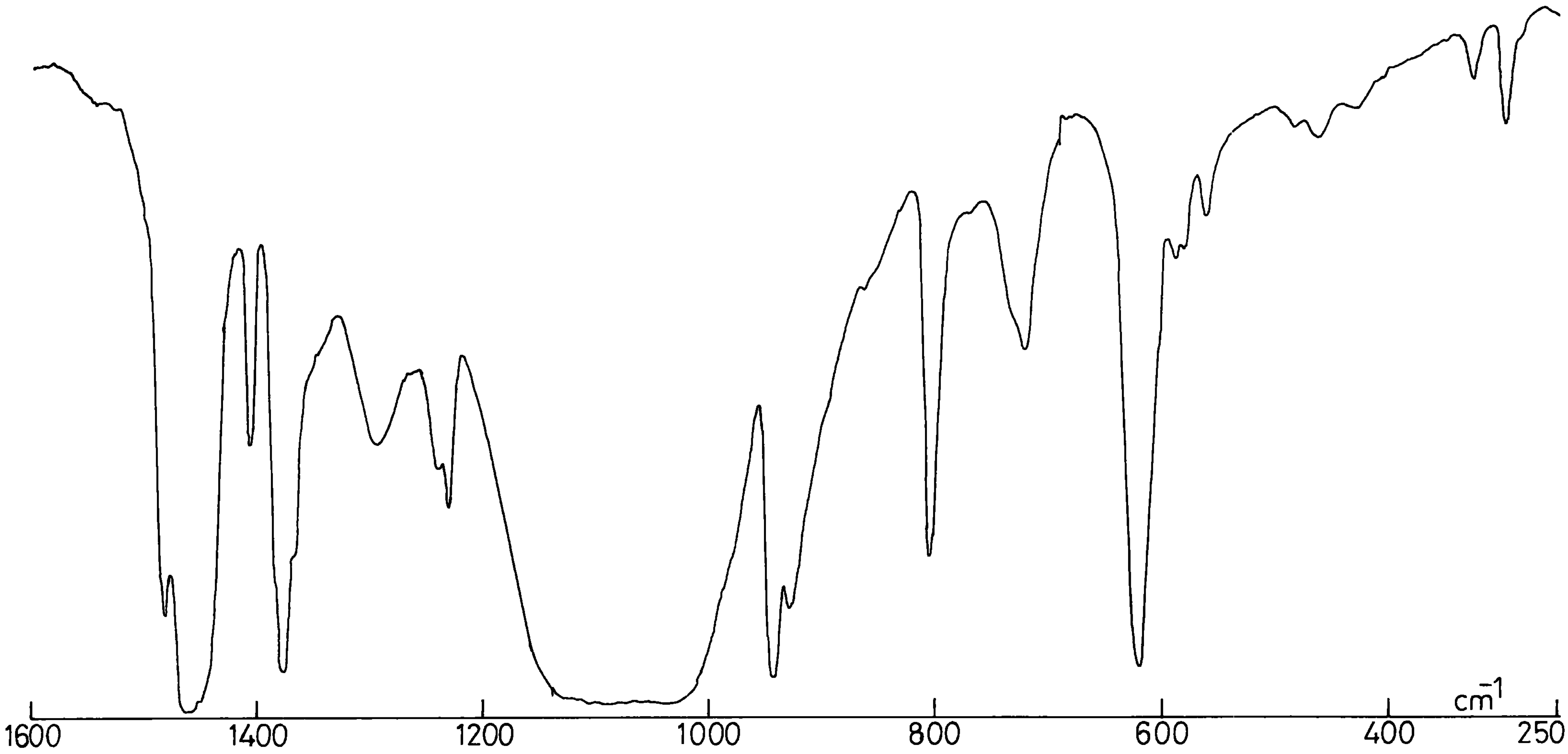


fig 45 INFRA RED SPECTRUM OF $(CH_3)_3NBr^+ ClO_4^-$

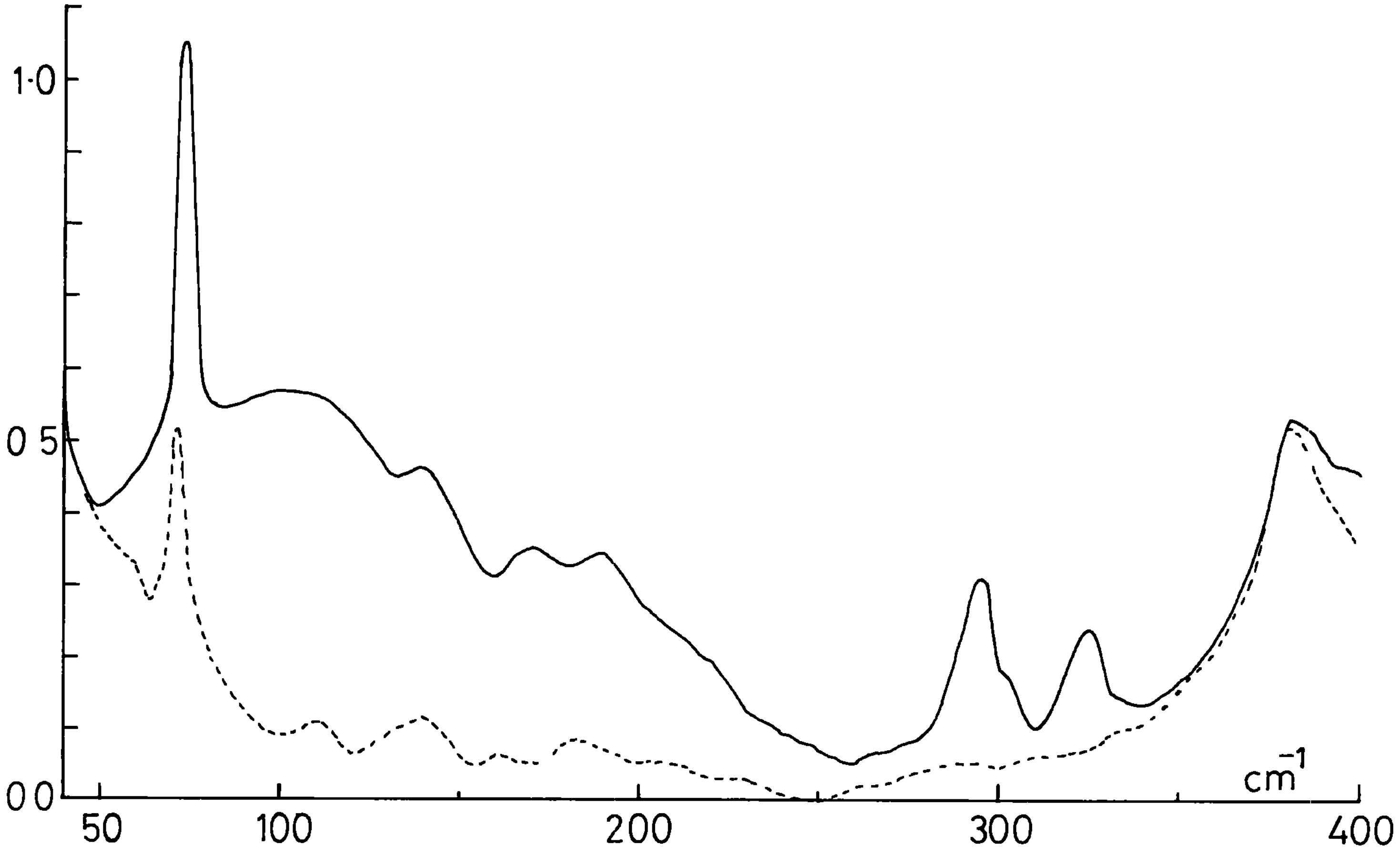
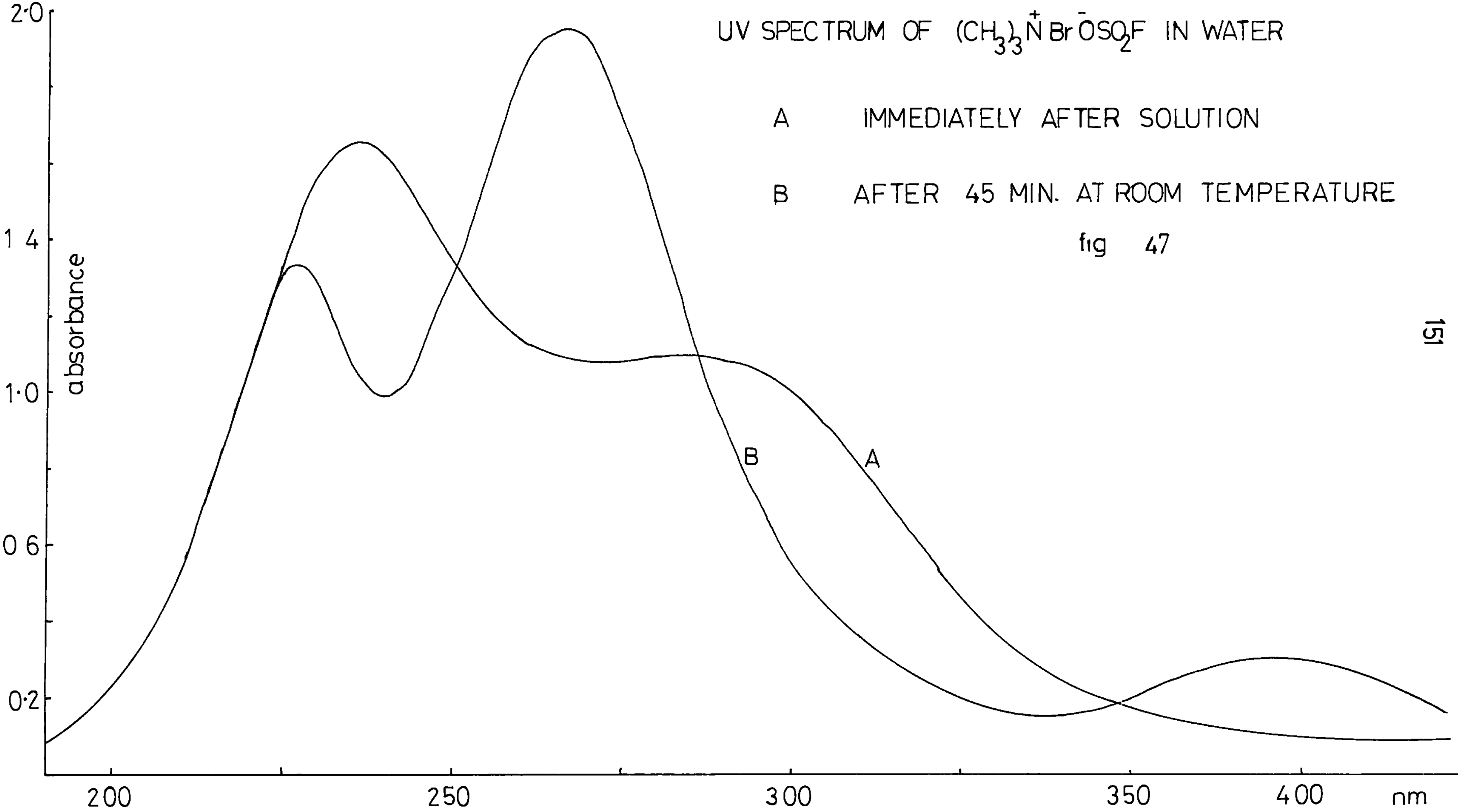


fig 46 PLOT OF FAR IR SPECTRUM OF $(CH_3)_3NBr^+ ClO_4^-$

(----- background)



UV SPECTRUM OF $(CH_3)_3\overset{+}{N}Br\overset{-}{O}SO_2F$ IN WATER

A IMMEDIATELY AFTER SOLUTION

B AFTER 45 MIN. AT ROOM TEMPERATURE

fig 47

reasonable to suppose, despite poor analytical figures, that $(CH_3)_2NBr$ can be alkylated to yield the $(CH_3)_3\overset{+}{N}Br$ cation, this cation can be precipitated from aqueous solutions of the fluorosulphate by $ClO_4^-$. Table 7 lists the infra red absorptions obtained for $ClO_4^-$ and $FSO_3^-$ salts of $(CH_3)_3\overset{+}{N}Cl$ and $(CH_3)_3\overset{+}{N}Br$.

## TABLE 7

## INFRA RED ABSORPTIONS OBSERVED FOR CATIONS $(CH_3)_3NCl$, AND $(CH_3)_3NBr$, $cm^{-1}$

| | | | | | |
|---|---|---|---|---|---|
| $ClO_4^-$ | $(CH_3)_3\overset{+}{N}Cl$ | 336 | 403 | 815 | 935 |
| | $(CH_3)_3\overset{+}{N}Br$ | 295 | 325 | 805 | 945 |
| $FSO_3^-$ | $(CH_3)_3\overset{+}{N}Cl$ | 335 | 400 | 820 | 940 |
| | $(CH_3)_3\overset{+}{N}Br$ | 295 | 325 | 805 | 945 |

The vibrational assignments are discussed in Chapter 6, where the N–Cl stretching frequency was identified at 400 $cm^{-1}$ by isotope splitting. In the case of $(CH_3)_3\overset{+}{N}Br$, neither of the bands at 295 and 325 $cm^{-1}$ were apparently split, however the rough calculation of the expected splitting, as detailed in Chapter 6, indicates that the separation between $^{79}Br$ and $^{81}Br$ isotope absorptions is of the order of 1.8 $cm^{-1}$ at 325 $cm^{-1}$, and since the absorptions are very weak, as seen from the relevant spectra, it is not unduly surprising that no splitting was observed.

The $(CH_3)_3\overset{+}{N}Br$ compounds were considerably less stable than the corresponding chloro compounds, samples rapidly changing from white to dark red at room temperature.

The results obtained from the reaction of $(CH_3)_2NCl$ and $(CH_3)OClO_3$ and the $ClO_4^-$ precipitation of $(CH_3)_3\overset{+}{N}Cl$ show that in solutions of $(CH_3)_3NCl_2$, the cation exists, and from the UV evidence, does not chlorinate $H_2O$ to give HOCl.

In acid solution, $^1$H NMR evidence points to the formation of $(CH_3)_3\overset{+}{N}H$ as a major decomposition product of the cation, $(CH_3)_3\overset{+}{N}Cl$, the spectrum in 0.05M HCl at 0°C being shown diagrammatically in Figure 47a. The spectrum consists of two main features between TMS and down field to $\tau$6.0, a singlet at $\tau$6.25 and a doublet at $\tau$7.23 and 7.18. The doublet splitting of 5 cps and its position, indicates $(CH_3)_3\overset{+}{N}H$.

The spectrum was studied over a period of 1½ hours and the relative peak intensity followed by integration, as detailed in Table 8.

TABLE 8

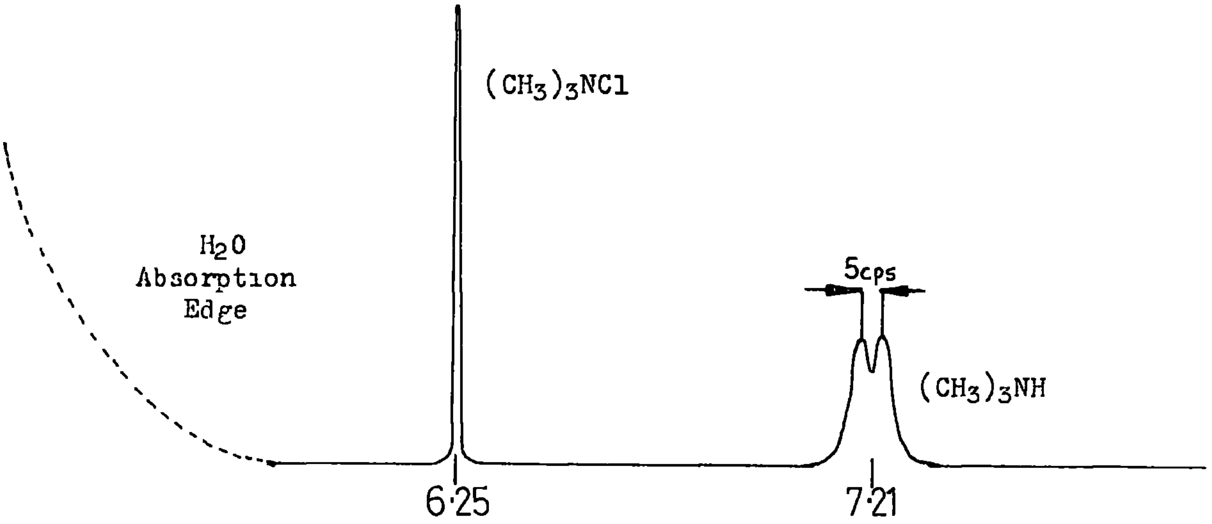
$^1$H NMR DECOMPOSITION STUDY OF $(CH_3)_3\overset{+}{N}Cl\ \overset{-}{Cl}$ IN 0.05M HCl

| Time (hour) | Integrated Peak Area | | | Temperature °C |
|---|---|---|---|---|
| | Singlet | Doublet | Total | |
| Start (10 min old) | 2.9 | 4.1 | 7.0 | 0 |
| 1 | 2.2 | 4.9 | 7.1 | 0 |
| 1.5 | 0.1 | 6.8 | 6.9 | 40 (PROBE) |

The peak at $\tau$6.25 can be assigned to $(CH_3)_3\overset{+}{N}Cl$ methyl protons since it slowly disappears, and from the integrated area results, it is related to the appearance of a $(CH_3)_3\overset{+}{N}H$ doublet at 7.23 and 7.18, the splitting of which is within 0.5 cps of that determined for $(CH_3)_3\overset{+}{N}H$ in 6M HCl. (5.5 cps, centred at $\tau$ 6.84).

## FIGURE 47a

## DIAGRAM OF H NMR SPECTRUM OF $(CH_3)_3NCl\ ClO_4$ IN 0.05M HCl AT 0°C



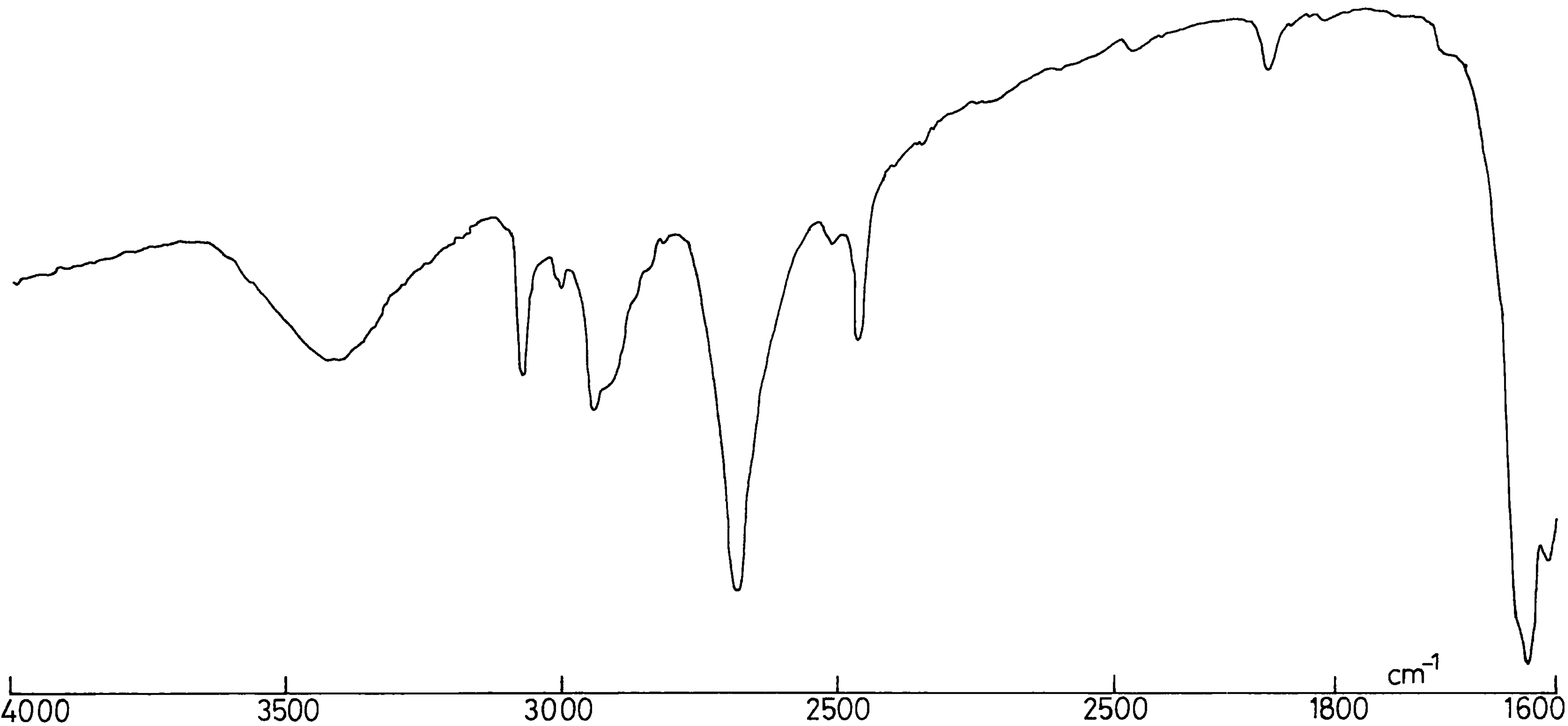
Over the period of the observation, no other absorptions were noted. Other methyl amines such as $(CH_3)_2\overset{+}{N}H_2$ would appear up field from the $(CH_3)_3\overset{+}{N}H$ absorption, and be split as a triplet. $(CH_3)_2NCl$ absorptions would appear between the $(CH_3)_3\overset{+}{N}H$ peaks and the $(CH_3)_3\overset{+}{N}Cl$ singlet, as a singlet, but with increasing intensity with time. Indeed the integrated area totals for the two peak systems observed, remaining essentially constant indicating a straightforward replacement of Cl in $(CH_3)_3\overset{+}{N}Cl$ for H yielding $(CH_3)_3\overset{+}{N}H$. The mode of formation of $(CH_3)_3\overset{+}{N}H$ in this instance is not immediately apparent since its presence implies that the chlorammonium cation has chlorinated either water, forming HOCl and $(CH_3)_3\overset{+}{N}H$ or itself forming chloro species such as $ClCH_2(CH_3)_2NCl$.

The formation of HOCl is not apparent in UV spectra of aqueous acid solutions of $(CH_3)_3\overset{+}{N}Cl$ as shown in Figure 26, and by Ellis et. al. (110), but $(CH_3)_3\overset{+}{N}H$ formation can be confirmed by precipitation of the picrate as shown in Figures 48 and 49.
chlorinated cations would be apparent in the NMR spectrum either as such, or as their decomposition products consisting of dealkylated amines. Thus in this instance it would appear that HOCl formation is the most likely explanation for the presence of $(CH_3)_3\overset{+}{N}H$ and absence of other 2 carbon atom amines.

The value of $\tau$ 6.25 for the methyl protons in $(CH_3)_3NCl$, when compared with 6.84 for $(CH_3)_3\overset{+}{N}H$ indicates an increase in positive character of the methyl protons in the chlorotrimethylammonium cation, which is consistent with H in $(CH_3)_3\overset{+}{N}H$ being replaced by the more electronegative Cl in $(CH_3)_3\overset{+}{N}Cl$.

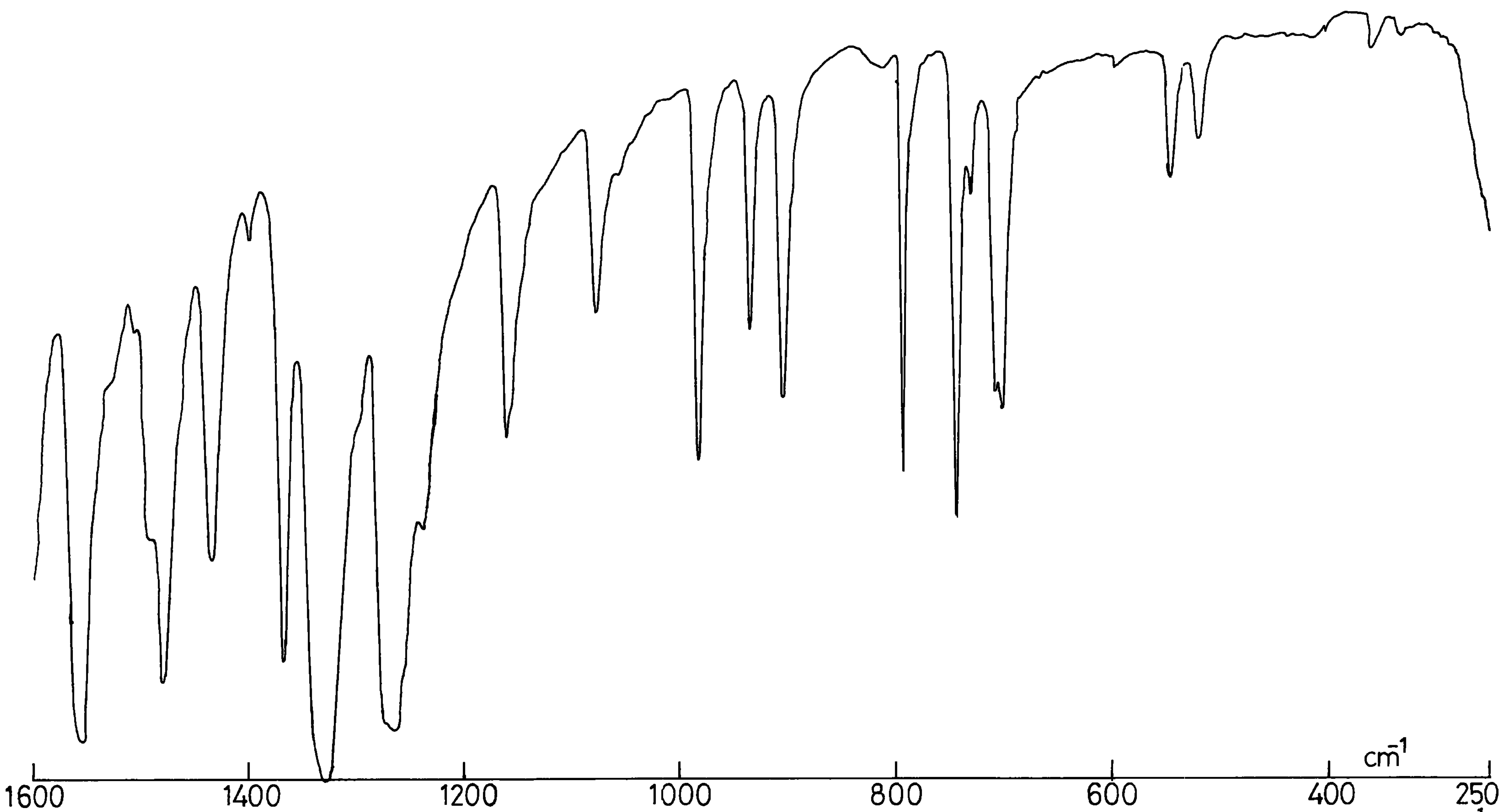
The differences between trimethylamine complexes of other halogens and that of chlorine are quite marked. The chlorine complex is white, and insoluble in solvents such as acetone or chloroform, whereas the complexes $(CH_3)_3NBr_2$ and $(CH_3)_3NI_2$ are fairly deeply yellow coloured, and indeed are soluble in acetone or chloroform but insoluble in water.
The infra red spectra of three halogen complexes are shown in Figure 39, where the three spectra are superimposed. $(CH_3)_3NCl_2$ clearly differs from the other two halogen complexes.

In the solid phase $(CH_3)_3\overset{+}{N}Cl$ can interact with $Cl^-$ to form $(CH_3)_3NCl_2$ as shown in Figure 40, which in this case is a KCl disc of the $ClO_4^-$ salt, the characteristic $(CH_3)_3NCl_2$ bands between 300 and 350 $cm^{-1}$ being clearly



IR SPECTRUM OF TRIMETHYLAMMONIUM PICRATE FROM $(CH_3)_3NCl_2$ DECOMPOSITION (4000–1600 cm$^{-1}$)

fig 48



IR SPECTRUM OF TRIMETHYLAMMONIUM PICRATE FROM $(CH_3)_3NCl_2$ DECOMPOSITION (1600-250cm$^{-1}$)

fig 49

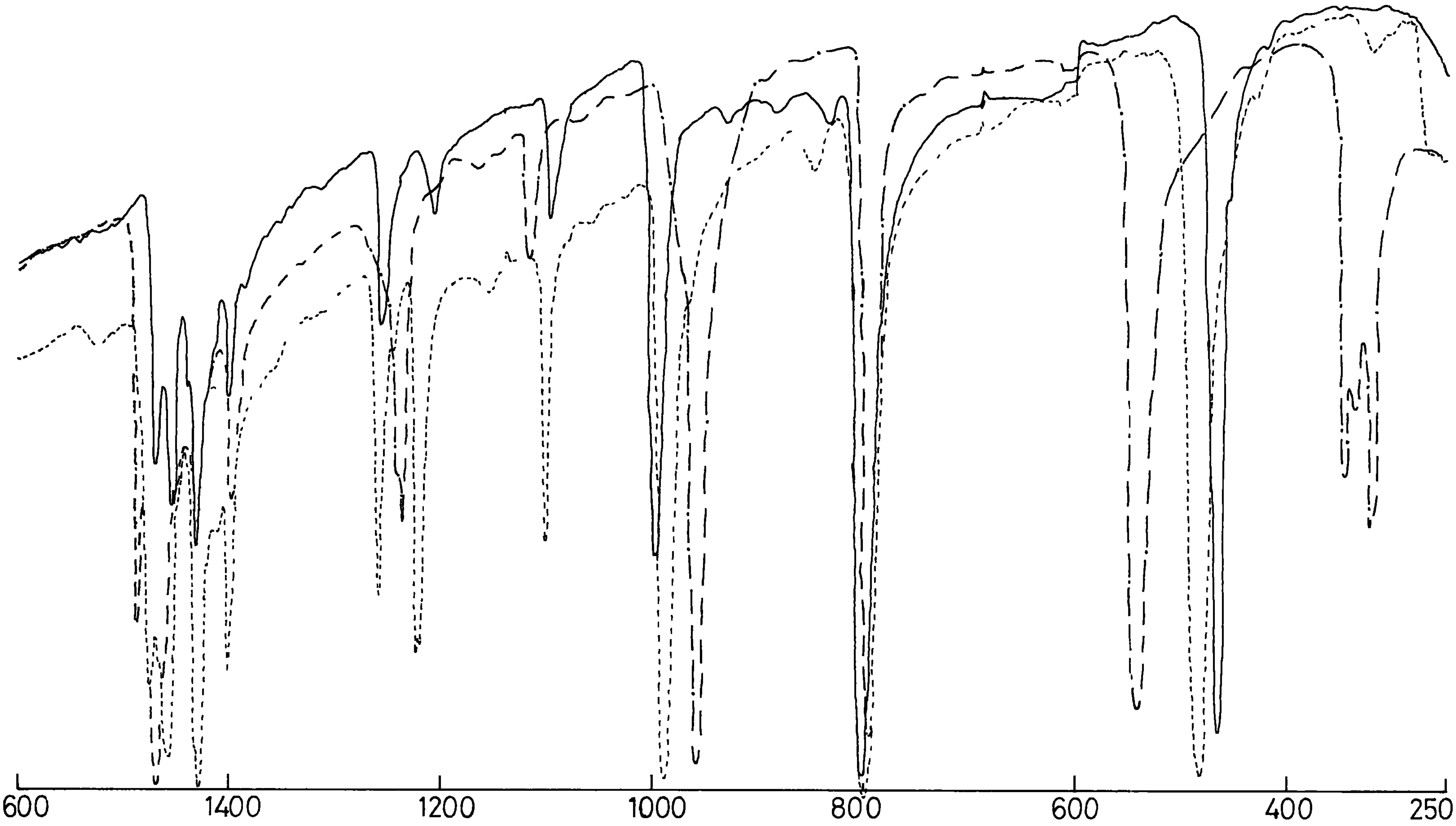


fig 39 INFRA RED SPECTRA OF $(CH_3)_3N\ Cl_2$, — — — , $Br_2$, - - - - - , $I_2$, ———

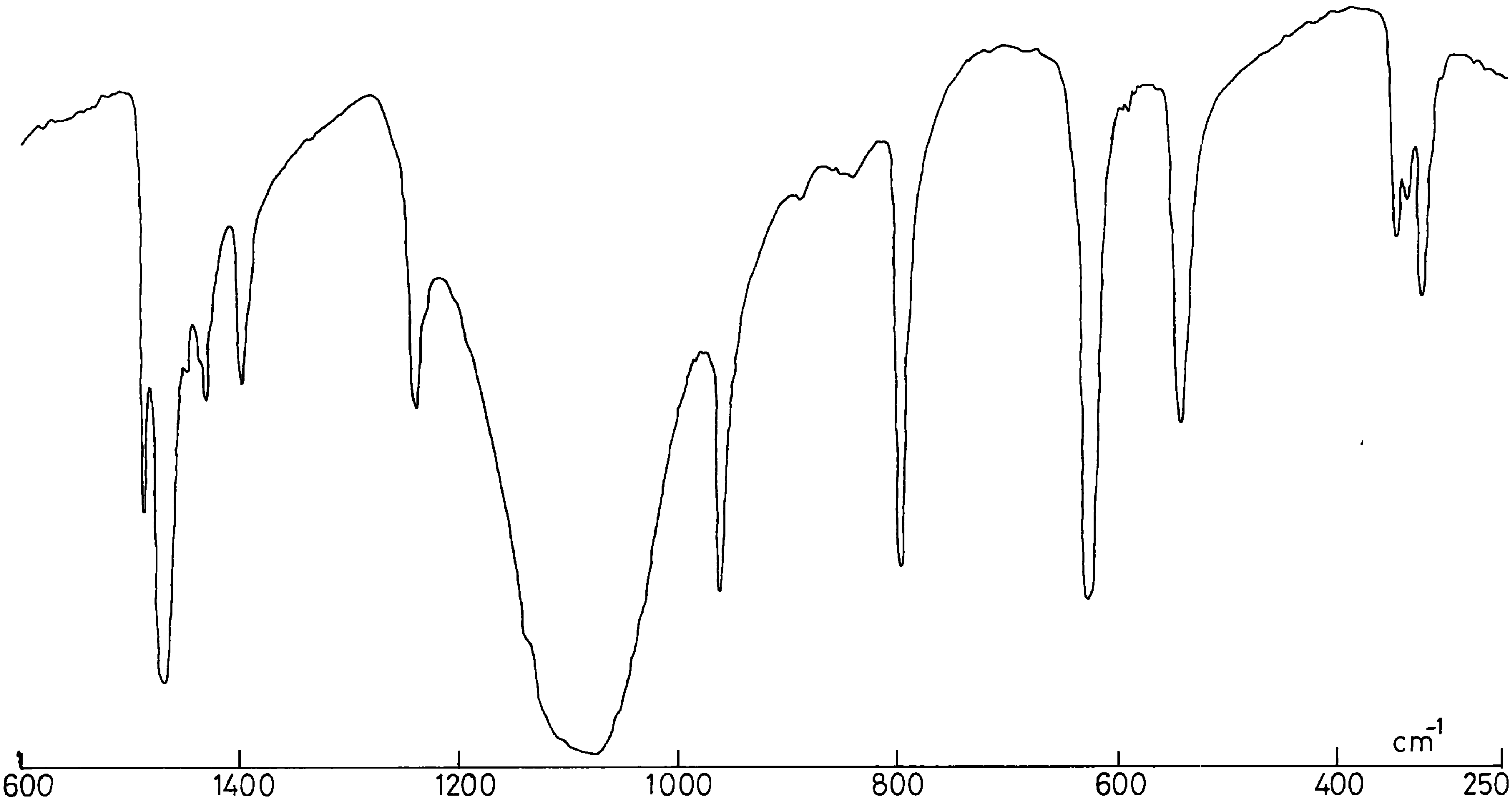
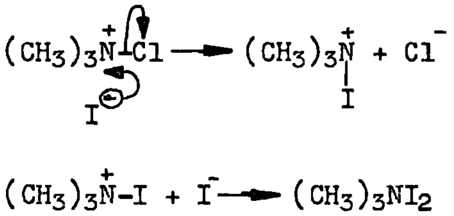


fig 40 INFRA RED SPECTRUM OF $(CH_3)_3NCl^+ ClO_4^-$ IN A KCl PRESSED DISK

visible indicating that fairly extensive $(CH_3)_3N\overset{\delta+}{Cl}\ldots\overset{\delta-}{Cl}$ occurs, since if this interaction did not occur, the spectrum of $(CH_3)_3\overset{+}{N}Cl$ would not be expected to change from that observed in a paraffin mull. It is reasonable to conclude that in the solid phase $(CH_3)_3NCl_2$ does not exist as $(CH_3)_3\overset{+}{N}Cl\ \overset{-}{Cl}$.

The proposition that other halogen complexes exist in this form in the solid phase is equally untenable since evidence from $(CH_3)_2NBr$ alkylations indicate that the $(CH_3)_3\overset{+}{N}Br$ cation has a different infra red absorption spectrum to $(CH_3)_3NBr_2$, in which one would expect, if $(CH_3)_3\overset{+}{N}Br\ \overset{-}{Br}$ wholly existed, no significant spectral differences between the cations in both species.

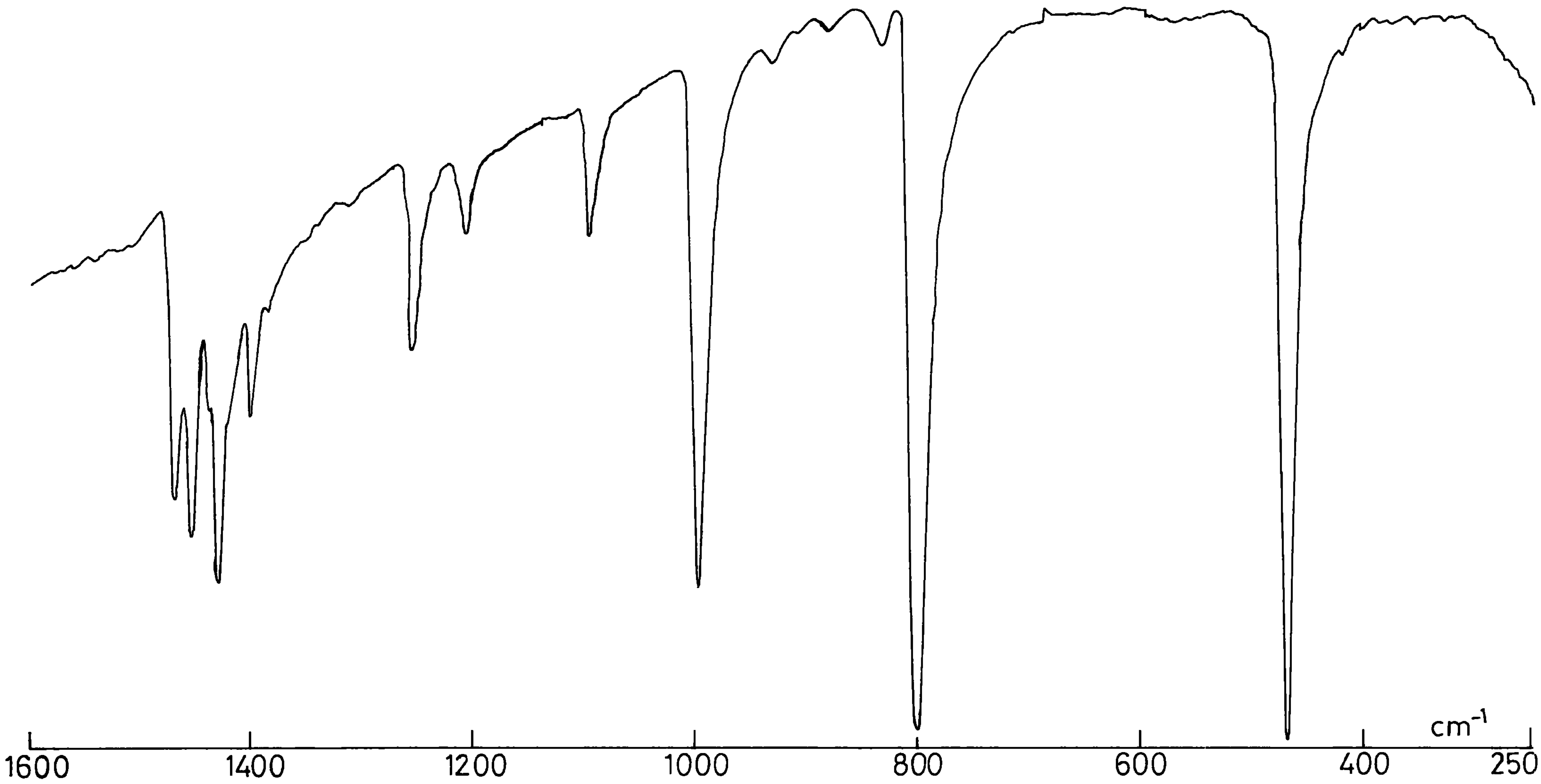
It is interesting to note that reactions between $(CH_3)_3\overset{+}{N}Cl$ and $I^-$ do not yield $(CH_3)_3NCl\text{-}I$, i.e. reverse addition of ICl to trimethylamine, but $(CH_3)_3NI_2$ as shown in Figure 41. This substitution can be considered as attack of $I^-$ on the cationic nitrogen in $(CH_3)_3\overset{+}{N}Cl$ forming $(CH_3)_3\overset{+}{N}I$ which stabilised by the excess $I^-$ forming $(CH_3)_3NI_2$.



$$(CH_3)_3\overset{+}{N}\text{-}Cl + I^{\ominus} \longrightarrow (CH_3)_3\underset{I}{\overset{+}{N}} + Cl^-$$

$$(CH_3)_3\overset{+}{N}\text{-}I + I^- \longrightarrow (CH_3)_3NI_2$$

This exchange process is also true of $(CH_3)_3NBr_2$ and $I^-$, where infra red spectra of $(CH_3)_3NBr_2$ recorded in KI pressed discs show the absorption of $(CH_3)_3NI_2$ and not $(CH_3)_3NBr_2$ nor even $(CH_3)_3NIBr$, as shown in Figure 42, and indeed as Figure 42 shows, $(CH_3)_3NIBr$ in a KI pressed disc also shows the absorptions of $(CH_3)_3NI_2$.



INFRA RED SPECTRUM OF THE PRODUCT OF THE REACTION OF $(CH_3)_3N\overset{+}{Cl}$ WITH $I^-$

fig 41

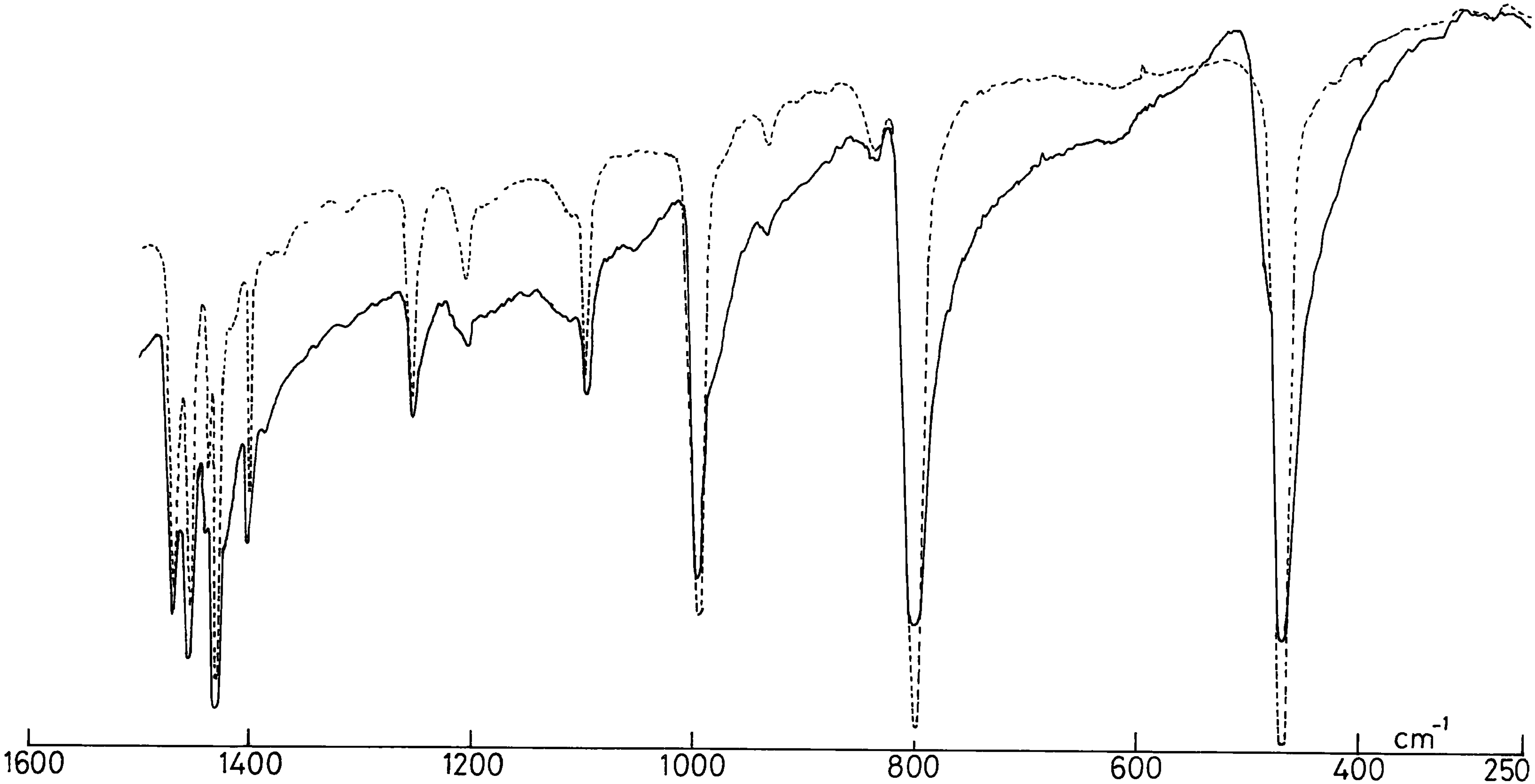


fig 42 INFRA RED SPECTRA, IN KI PRESSED DISKS, OF $(CH_3)_3NIBr$, -------- , $Br_2$, ———

Thus in conclusion, N-halamine cations of the type $(CH_3)_3\overset{+}{N}Hal$ have been shown to exist as such in salts such as $(CH_3)_3\overset{+}{N}Cl\ ClO_4^-$ and $(CH_3)_3\overset{+}{N}Br\ \overset{-}{O}SO_2F$, but the evidence is against the formulation of addition complexes of the halogens and trimethylamine as $(CH_3)_3\overset{+}{N}{-}Hal\ Hal^-$ in the solid phase as suggested by Bohme and Krause (108).

The bromo salts are considerably less stable than the corresponding chloro derivatives, and it would appear that under certain circumstances of pH and concentration $(CH_3)_3\overset{+}{N}Cl$ can produce HOCl in water, although the evidence for this is not conclusive.

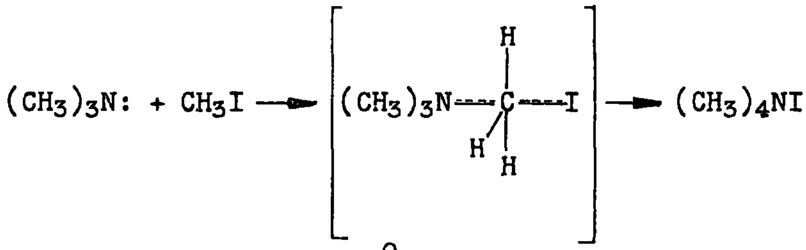
# CHAPTER FIVE

## REACTIONS OF DIMETHYLHALAMINES WITH SIMPLE ALKYL HALIDES

## Introduction

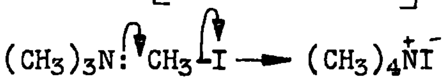
It was seen in Chapter 4, that with methyl esters of certain acids, it was possible to form a chlorotrialkylammonium cation from dimethylchloramine, and that a similar situation probably exists with dimethylbromamine, $(CH_3)_2NBr$.

One class of methyl esters that were not discussed in that chapter were the halides, $CH_3Cl$, $CH_3Br$, and $CH_3I$.
Classically, alkylation of amines to form tetraalkylammonium salts proceeds via nucleophillic attack of the alkyl halide by the basic amine:



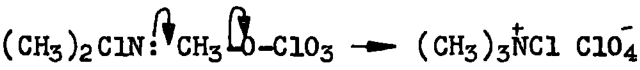
$$(CH_3)_3N: + CH_3I \rightarrow \left[(CH_3)_3N\cdots CH_3\cdots I\right] \rightarrow (CH_3)_4NI$$

or



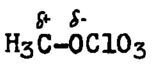
$$(CH_3)_3N{:}\,CH_3{-}I \rightarrow (CH_3)_4\overset{+}{N}\overset{-}{I}$$

and in the case of $(CH_3)_2NCl$, an exactly analogous reaction occurred with, for example methyl perchlorate, $CH_3OClO_3$:



$$(CH_3)_2ClN{:}\,CH_3{-}O{-}ClO_3 \rightarrow (CH_3)_3\overset{+}{N}Cl\ Cl\overset{-}{O_4}$$

It was noted in Chapter 4 that the alkylating agents studied were powerful, as estimated by the $^1H$ NMR absorptions of the methyl groups, indicating considerable polarisation of the C-X bond, in for example $CH_3OClO_3$, the C-O bond would be polarised:



$$H_3\overset{\delta+}{C}{-}\overset{\delta-}{O}ClO_3$$

The extent to which this polarisation occurs compensates for the decrease in basicity of $(CH_3)_2NCl$ over say $(CH_3)_2NH$.

With alkyl halides such as $CH_3I$, the reaction with dimethylchloramine may well be considered to proceed via conventional lines, yielding a product consisting of trimethylchlorammonium cations:

$$CH_3I + (CH_3)_2NCl \longrightarrow (CH_3)_3\overset{+}{N}Cl\ I^-$$

The compound, $(CH_3)_3\overset{+}{N}Cl\ I^-$, is isomeric with the well known addition complex of the Lewis acid ICl and the base, trimethylamine, $(CH_3)_3N$:

$$ICl + (CH_3)_3N \longrightarrow (CH_3)_3NICl$$

The remainder of this chapter will show that the product obtained from the reaction of, for example, $(CH_3)_2NCl$ and $CH_3I$, is not structurally isomeric with the addition complex $(CH_3)_3NICl$, although can be empirically represented as $C_3H_9NICl$.

X ray crystallographic studies, (116) and supporting chemical and spectroscopic evidence will be presented to show that the product from the $CH_3I,(CH_3)_2NCl$ reaction is $C_6H_{18}N_2I_2Cl_2$ and is in fact a tetramethylammonium salt with a novel pseudopolyhalide anion:

$$(CH_3)_4\overset{+}{N}\ (CH_3)_2N(ICl)_2^-$$

## Results And Discussion

It has been found that $CH_3I$ reacts with both dimethylchloramine and dimethylbromamine to yield products which analyse as $C_3H_9NXI$, where $X = Cl, Br$.

The X ray work carried out by N. W. Alcock (116) indicates that the product is $C_6H_{18}N_2X_2I_2$ which is a tetramethylammonium compound containing the anion $(CH_3)_2N(ICl)_2^-$.

## Reaction Between $CH_3Br$ And $(CH_3)_2NCl$

The reaction of $CH_3Br$ with $(CH_3)_2NCl$ yielded a compound which analysed as $C_3H_9NBrCl$ and this compound was identified as the addition complex of trimethylamine and the interhalogen bromine monochloride.

$$(CH_3)_2NCl + CH_3Br \longrightarrow (CH_3)_3N\ BrCl$$

With methyl chloride, dimethylchloramine yielded a mixture of amine salts of empirical formula $C_3H_{11}NCl$, which had no oxidising power, and this together with spectroscopic evidence indicate that $CH_3Cl$ does not alkylate $(CH_3)_2NCl$ to yield the expected $(CH_3)_3NCl_2$.

These results are summarised in Table 9.

TABLE 9

SUMMARY OF $(CH_3)_2NX$, ALKYL HALIDE REACTIONS

| Reactant | Product |
|---|---|
| $(CH_3)_2NCl$, $CH_3I$ | $(CH_3)_4\overset{+}{N}\ (CH_3)_2N(ICl)_2^-$ |
| $(CH_3)_2NBr$, $CH_3I$ | $(CH_3)_4\overset{+}{N}\ (CH_3)_2N(IBr)_2^-$ |
| $(CH_3)_2NCl$, $CH_3Br$ | $(CH_3)_3NBrCl$ |
| $(CH_3)_2NCl$, $CH_3Cl$ | $C_3H_{11}NCl$, $(CH_3)_2NCl$, $CH_3Cl$ |

The infra red absorptions of the products $CH_3I$, $(CH_3)_2NCl$; $CH_3I$, $(CH_3)_2NBr$, and $CH_3Br$, $(CH_3)_2NCl$, are listed in Table 10 and shown respectively in Figures 50, 51 and 52 for the region 1600-250 $cm^{-1}$, and Figures 53 and 54 respectively for the region 300-40 $cm^{-1}$.

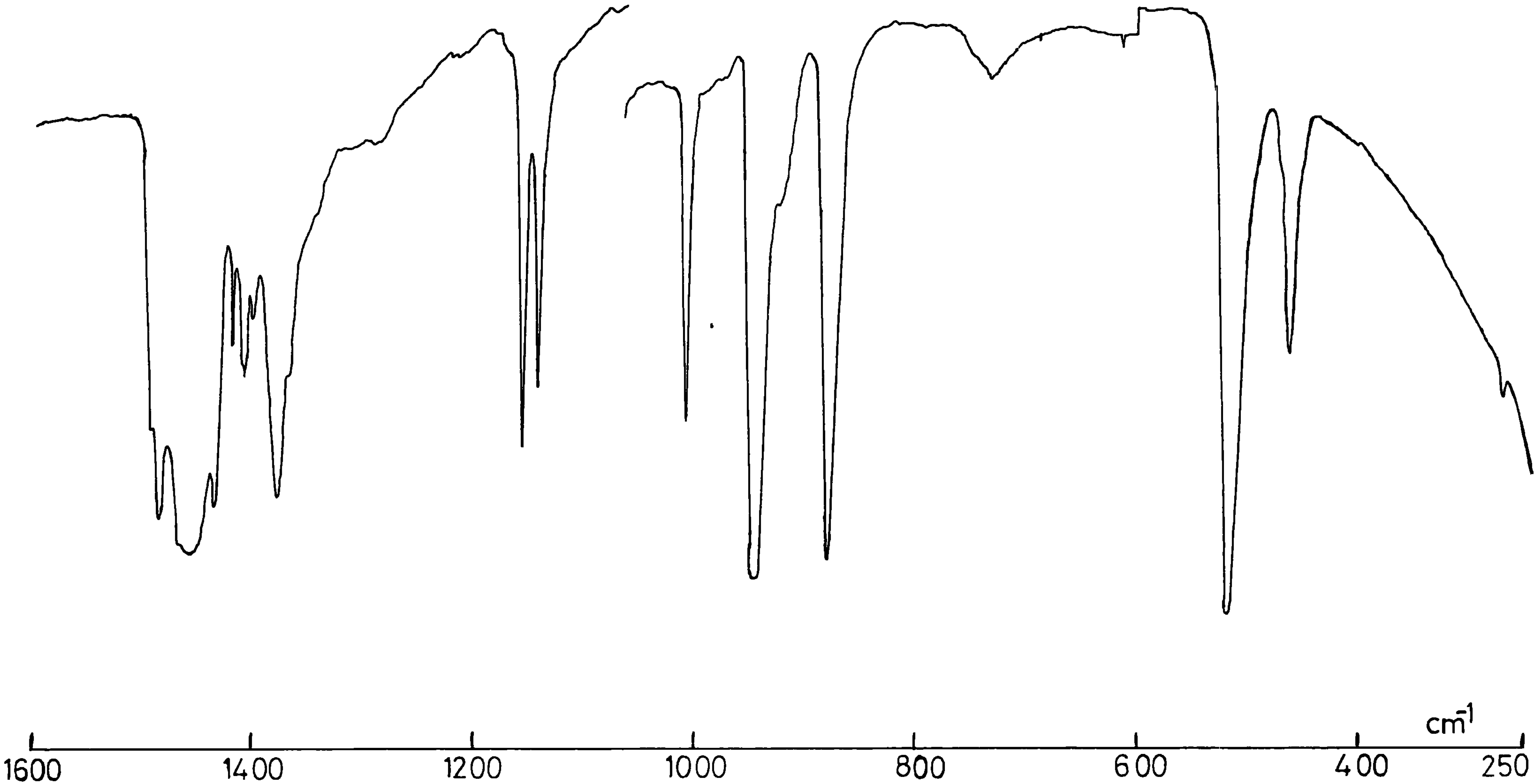
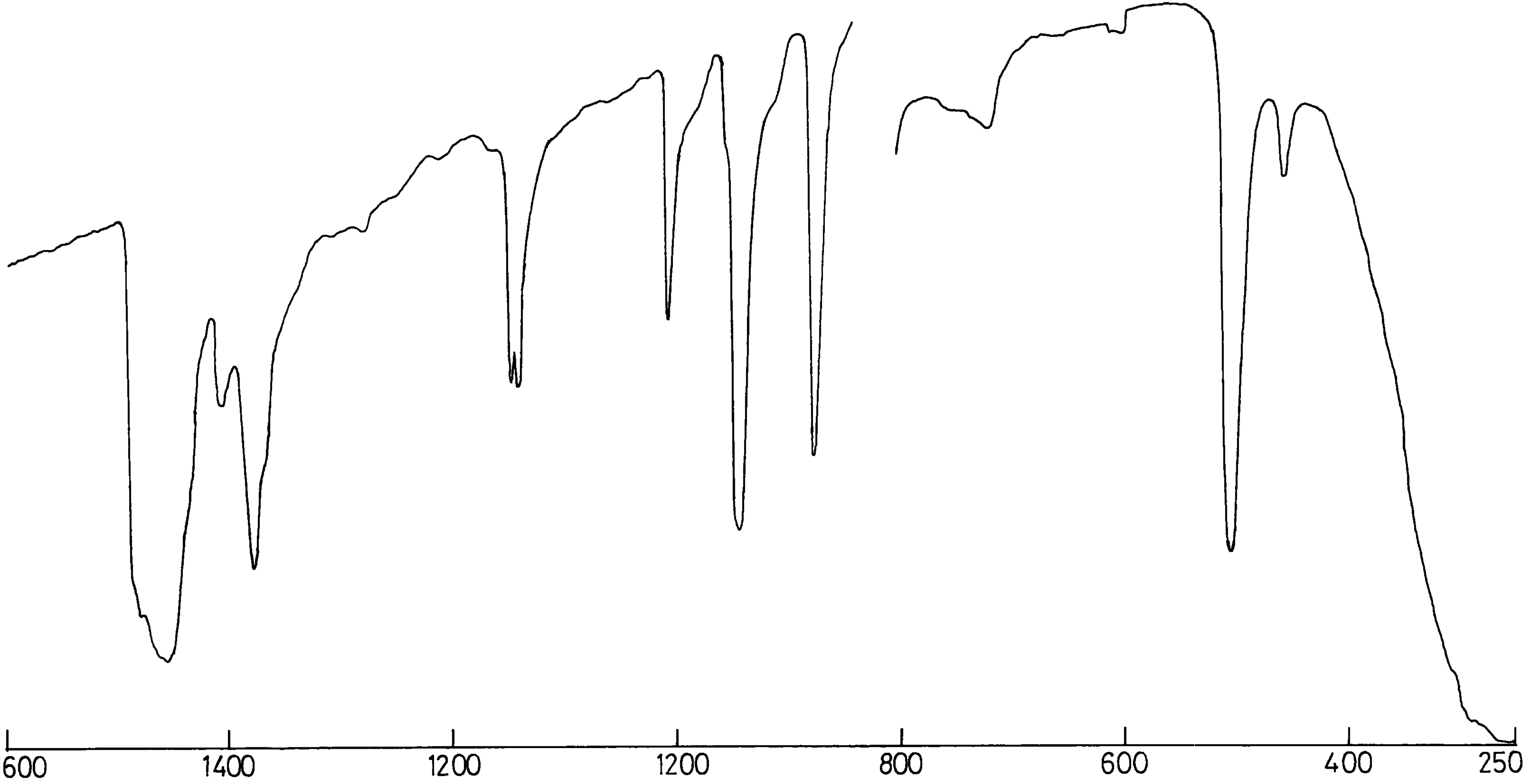


fig 50 INFRA RED SPECTRUM OF THE PRODUCT FROM THE REACTION OF $(CH_3)_2NCl$ WITH $CH_3I$



INFRA RED SPECTRUM OF THE PRODUCT FROM THE REACTION OF $(CH_3)_2NBr$ WITH $CH_3I$

fig 51

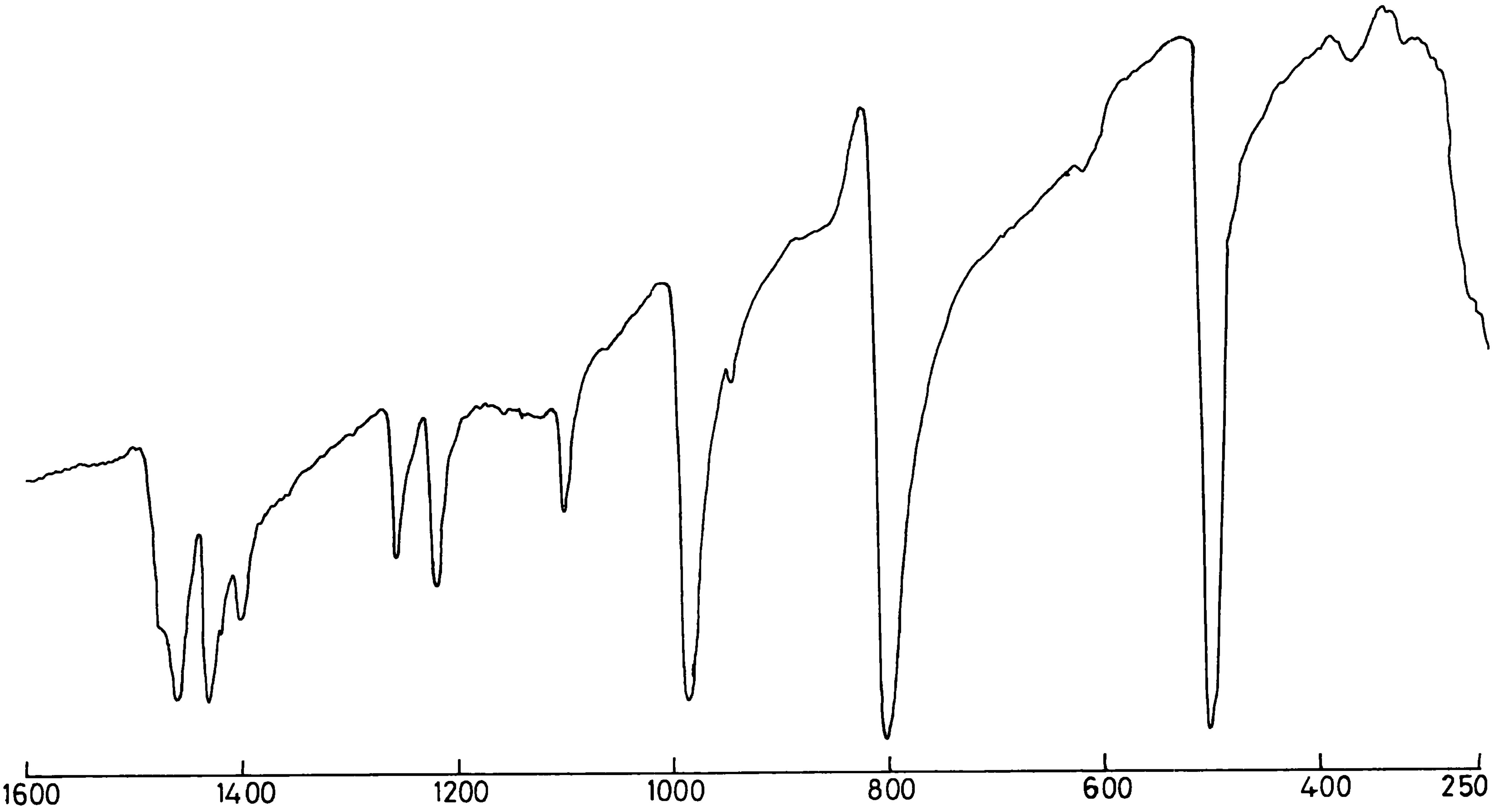
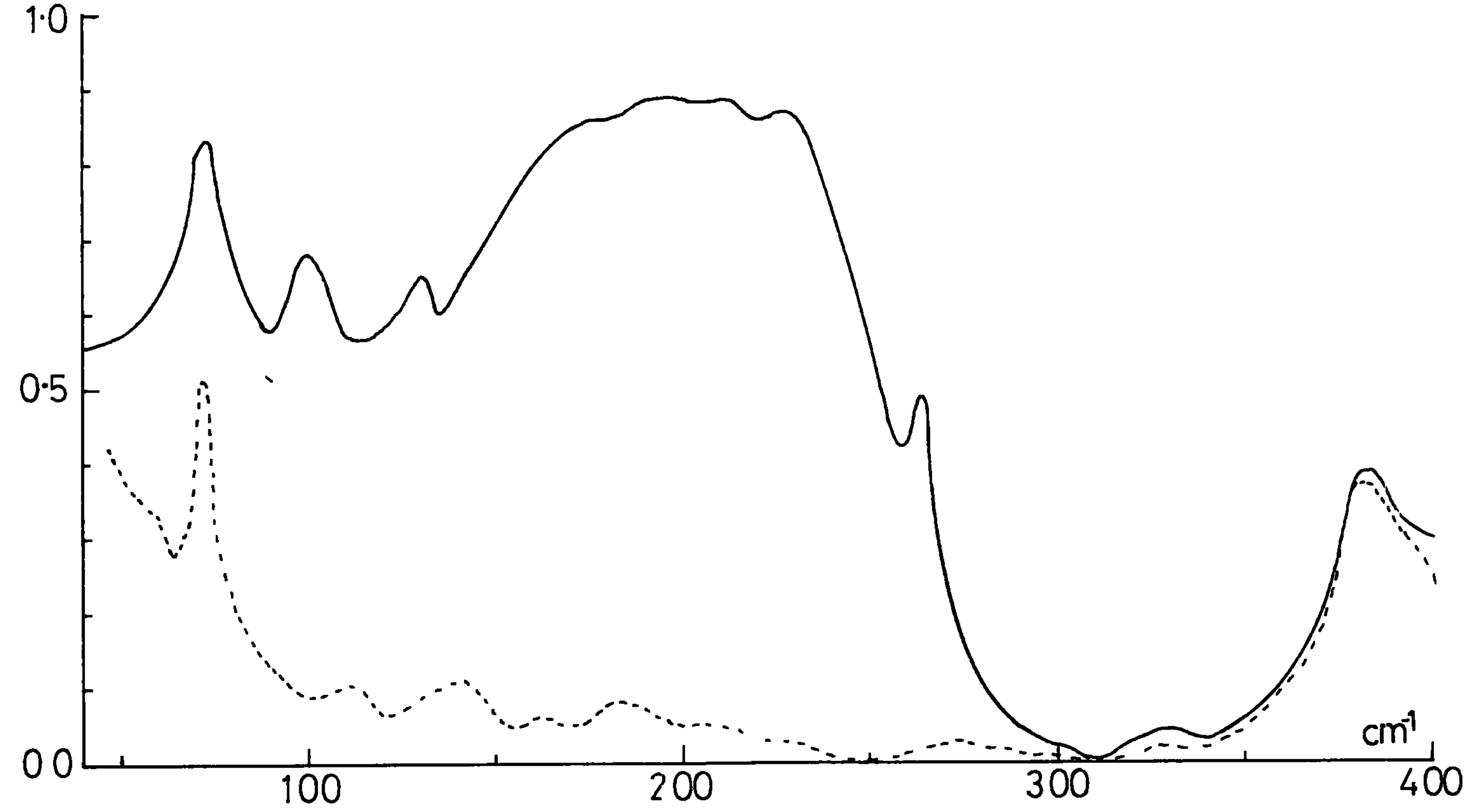


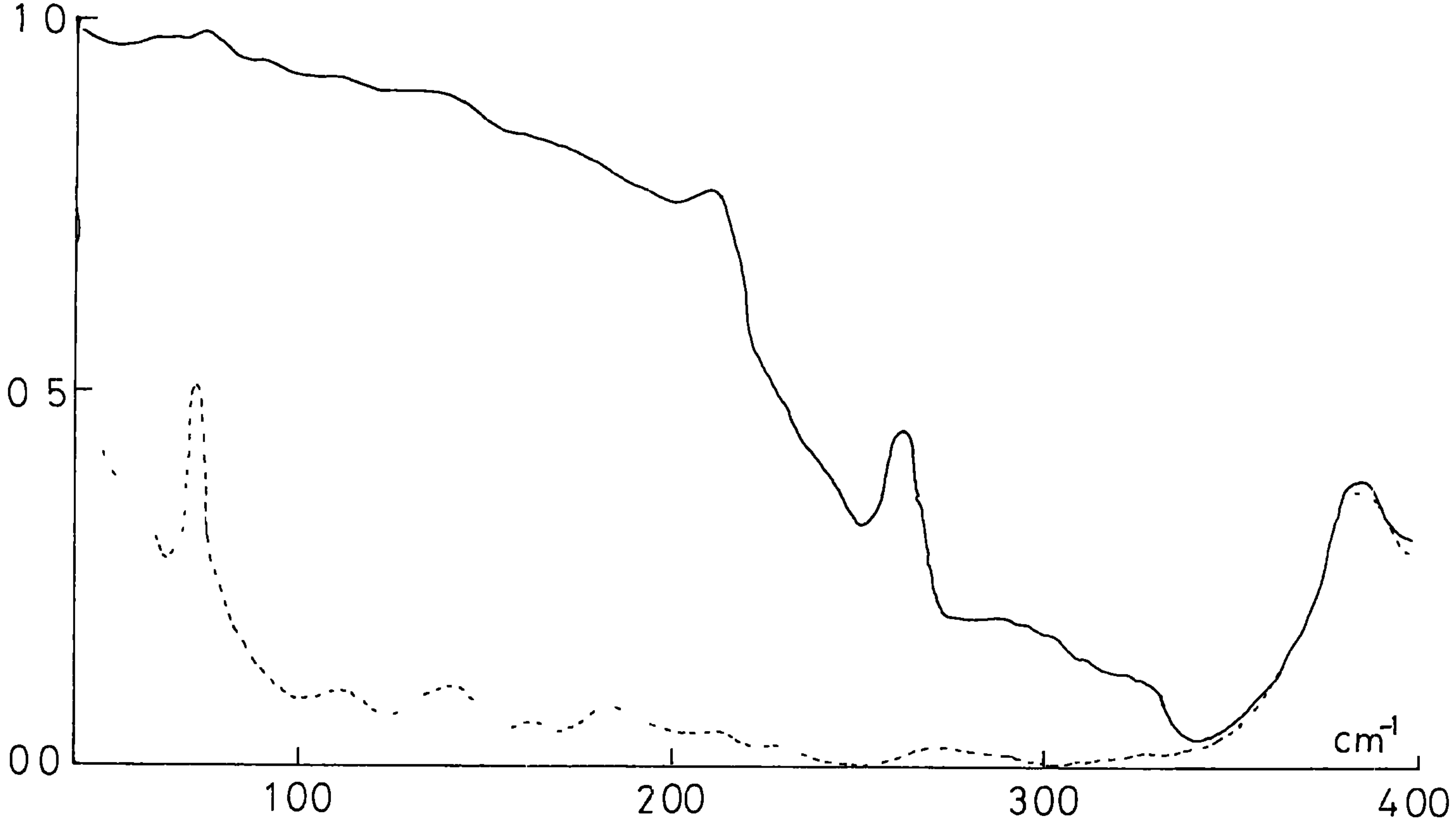
fig 52 INFRA RED SPECTRUM OF THE PRODUCT FROM THE REACTION OF $(CH_3)_2NCl$ WITH $CH_3Br$



FAR INFRA RED SPECTRUM OF THE PRODUCT FROM THE REACTION OF $(CH_3)_2NCl$ WITH $CH_3I$

(------ background)

fig 53



FAR INFRA RED SPECTRUM OF THE PRODUCT FROM THE REACTION OF $(CH_3)_2NBr$ WITH $CH_3I$

( - - - - - - -background)

fig 54

# TABLE 10

## OBSERVED FREQUENCIES, $CM^{-1}$, FOR THE PRODUCTS:

## $CH_3I/(CH_3)_2NCl$, $CH_3I/(CH_3)_2NBr$ AND $CH_3Br/(CH_3)_2NCl$

| $(CH_3)_2NCl/CH_3I$ | $(CH_3)_2NBr/CH_3I$ | $(CH_3)_2NCl/CH_3Br$ |
|---|---|---|
| 3025 | 3020 | 3010 |
| 2955 | 2955 | 2990 |
| 2910 | 2920 | 2920 |
| 2855 | 2860 | 2850 |
| 1495 | 1490 | 1475 |
| 1485 | 1480 | 1460 |
| 1460 | 1455 | 1430 |
| 1440 | 1435 | 1400 |
| 1400 | 1405 | 1260 |
| 1160 | 1400 | 1220 |
| 1145 | 1150 | 1100 |
| 1010 | 1140 | 985 |
| 945 | 1010 | 800 |
| 880 | 945 | 500 |
| 520 | 880 | 370 |
| 465 | 505 | |
| 264.9 | 460 | |
| 126.9 | 261.2 | |
| 100.1 | | |

Initial inspection of the spectra of products of alkylation of $(CH_3)_2NCl$ by $CH_3Br$ and by $CH_3I$ indicate that there are two structurally different compounds present, in particular the region between 1200 $cm^{-1}$ and 700 $cm^{-1}$ show marked differences.

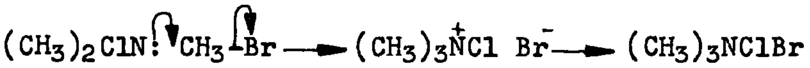
The product of the reaction of $(CH_3)_2NCl$ with $CH_3Br$ resembles, in the infra red, the addition compounds of the halogens and interhalogens with trimethylamine, as indeed the empirical formula suggests.

In order to examine, and perhaps confirm that $CH_3Br$ alkylates $(CH_3)_2NCl$ to yield a $(CH_3)_3N$, interhalogen addition complex, the preparation of the previously unreported $(CH_3)_3NBrCl$ was attempted. Using a mixture of $Cl_2$ and $Br_2$ in $CCl_4$ solution trimethylamine was added to yield a yellow solid whose infra red spectrum indicated that $(CH_3)_3NBr_2$ had formed along with another complex which had a very similar infra red spectrum, differing largely in the 500 $cm^{-1}$ region. The elemental analysis indicated that chlorine was present in this mixture, and it was thought that the additional absorptions indicated in the spectrum were probably due to the presence of $(CH_3)_3NBrCl$.

Further confirmation that $(CH_3)_3NBrCl$ had formed is found in an absorption at 280 $cm^{-1}$ in the infra red, which is absent in $(CH_3)_3NBr_2$, and is attributed to the Br-Cl absorption. This absorption compares well with that observed in the pyridine analogue at 307 $cm^{-1}$ in benzene solution, and 295 $cm^{-1}$ in the solid complex (117).

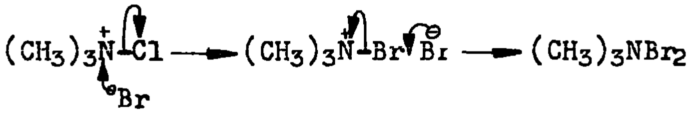
The presence of the 500 $cm^{-1}$ absorption in the spectrum of the $(CH_3)_2NCl$, $CH_3Br$ product, and in view of the great similarity between this spectrum and that of the other $(CH_3)_3N$, halogen complexes, strongly suggests that $(CH_3)_3NBrCl$ is the product of the alkylation reaction. A more comprehensive discussion of the spectrum of $(CH_3)_3NBrCl$ and its relationship with the other trimethylamine, halogen and interhalogen complexes can be found in Chapter 6.

It is thus interesting to note that this is not the expected product from such an alkylation. It would be expected that the reaction should proceed via a chlorotrimethylammonium cation, and thus yield the complex $(CH_3)_3NClBr$:



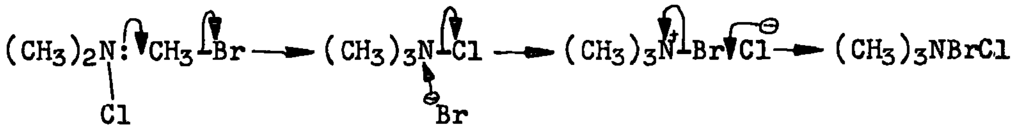
$$(CH_3)_2ClN\!:\ CH_3\!-\!Br \longrightarrow (CH_3)_3\overset{+}{N}Cl\ \ Br^- \longrightarrow (CH_3)_3NClBr$$

but in the reactions observed of the cation $(CH_3)_3\overset{+}{N}Cl$, in Chapter 4, the addition of bromide ions to aqueous $(CH_3)_3\overset{+}{N}Cl$ yielded $(CH_3)_3NBr_2$, where this result was explained by nucleophillic attack of a bromide ion at the positive nitrogen centre:



$$(CH_3)_3\overset{+}{N}\!-\!Cl \longrightarrow (CH_3)_3\overset{+}{N}\!-\!Br\ \ Br^{\ominus} \longrightarrow (CH_3)_3NBr_2$$

In the case of $(CH_3)_2NCl$ and $CH_3Br$, the reaction probably proceeds to the stage where the salt $(CH_3)_3\overset{+}{N}Cl\ Br^-$ forms and then the newly formed bromide ion acts as a nucleophile, and attacks the now positive nitrogen, followed by the establishment of a Br–Cl bond at the same time as the N-Br bond dissociates:

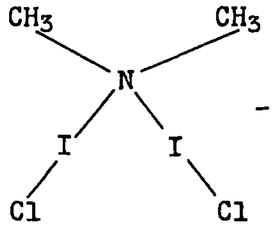


$$(CH_3)_2N(Cl)\!:\ CH_3\!-\!Br \longrightarrow (CH_3)_3\overset{+}{N}\!-\!Cl\ \ Br^{\ominus} \longrightarrow (CH_3)_3\overset{+}{N}\!-\!Br\ \ Cl^{\ominus} \longrightarrow (CH_3)_3NBrCl$$

## Reaction Between $CH_3I$ And $(CH_3)_2NX$, X = Cl, Br

The complexes formed between dimethylchloramine and bromamine and methyl iodide are, certainly spectroscopically different from the trimethylamine halogen addition complexes. The relative stability of the compounds towards heat is noticeable in the infra red beam, $(CH_3)_3NICl$ for example, remaining yellow for considerably longer than the $(CH_3)_2NCl$, $CH_3I$ product.

The structure of the compound $(CH_3)_4\overset{+}{N}\ (CH_3)_2N(ICl)_2^-$ has been shown, by low temperature X ray analysis, to contain the novel anion:



The X ray work was performed at the University of Warwick, and the relevant crystal data are given in Table 11.

TABLE 11

CRYSTALLOGRAPHIC DATA FOR $(CH_3)_4\overset{+}{N}\ (CH_3)_2N(ICl)_2^-$

| | | | | |
|---|---|---|---|---|
| Crystal System: | Monoclinic | | | |
| | a | b | c | β |
| Cell Dimensions (Å): | 11.233(3) | 5.773(1) | 11.078(2) | 98.24(2) |
| Cell Volume ($Å^3$): | 711.6(3) | | | |
| Space Group: | P2/6 | | | |

Data collected using a Syntex $P2_1$ diffractometer at -60°C with an LT-1 low temperature device and Mo Kα radiation, = 0.71069Å

Further evidence confirming the indentity of the $CH_3I$ products as, $(CH_3)_4\overset{+}{N}\ (CH_3)_2N(IX)_2^-$ can be found in comparing the spectra of the alkylation products with those of the parent halamine, where it is found that distinct similarities exist, much in the same way as the $(CH_3)_3NICl$ spectrum resembles that of $(CH_3)_3N$.

Table 12 lists the observed frequencies for $(CH_3)_2NCl$, as a solid film at -196°C, and compares the frequencies with those obtained for the alkylation product. The equivalent $(CH_3)_2NBr$ spectrum, as a solution in $CCl_4$, is also listed, along with the observed spectrum of its $CH_3I$ alkylation product. The respective spectra are presented in Figures 55 and 56 in the region 1400-250 $cm^{-1}$.

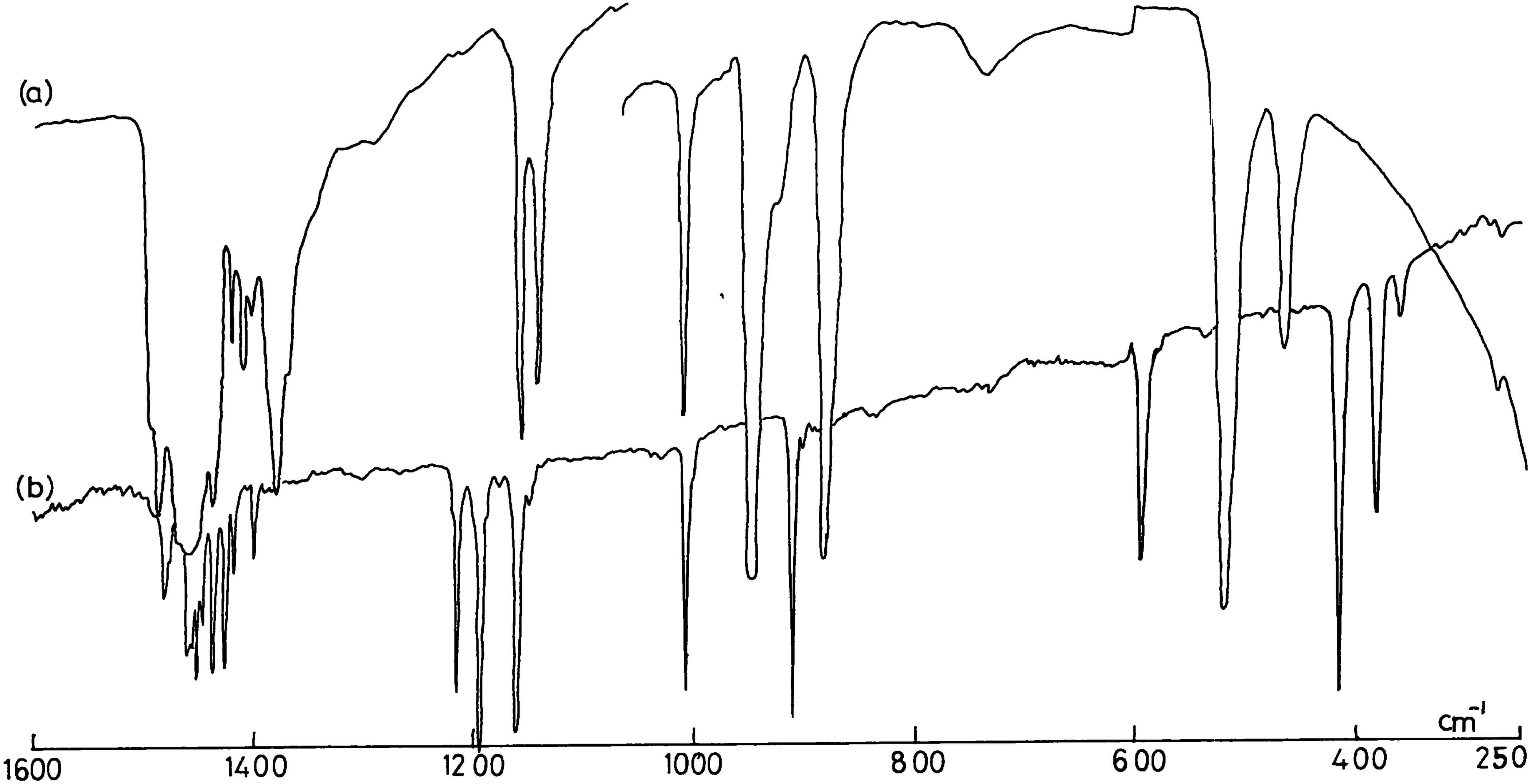
It is interesting to note that the absorptions that do not readily "fit" in Table 12, those at 3020, 1490, 1405, 1400 and 945 $cm^{-1}$, are precisely the absorptions due to the $(CH_3)_4\overset{+}{N}$ cation.

It appears that in the alkylation reaction the dimethylamino moiety has been retained. The infra red spectrum of adducts of $(CH_3)_2NCl$ are interesting and lend further credence to the formulation of the $CH_3I$, $(CH_3)_2NCl$ product as $(CH_3)_4\overset{+}{N}\ (CH_3)_2N(ICl)_2^-$.

With $I_2$, $(CH_3)_2NCl$ forms an addition compound,

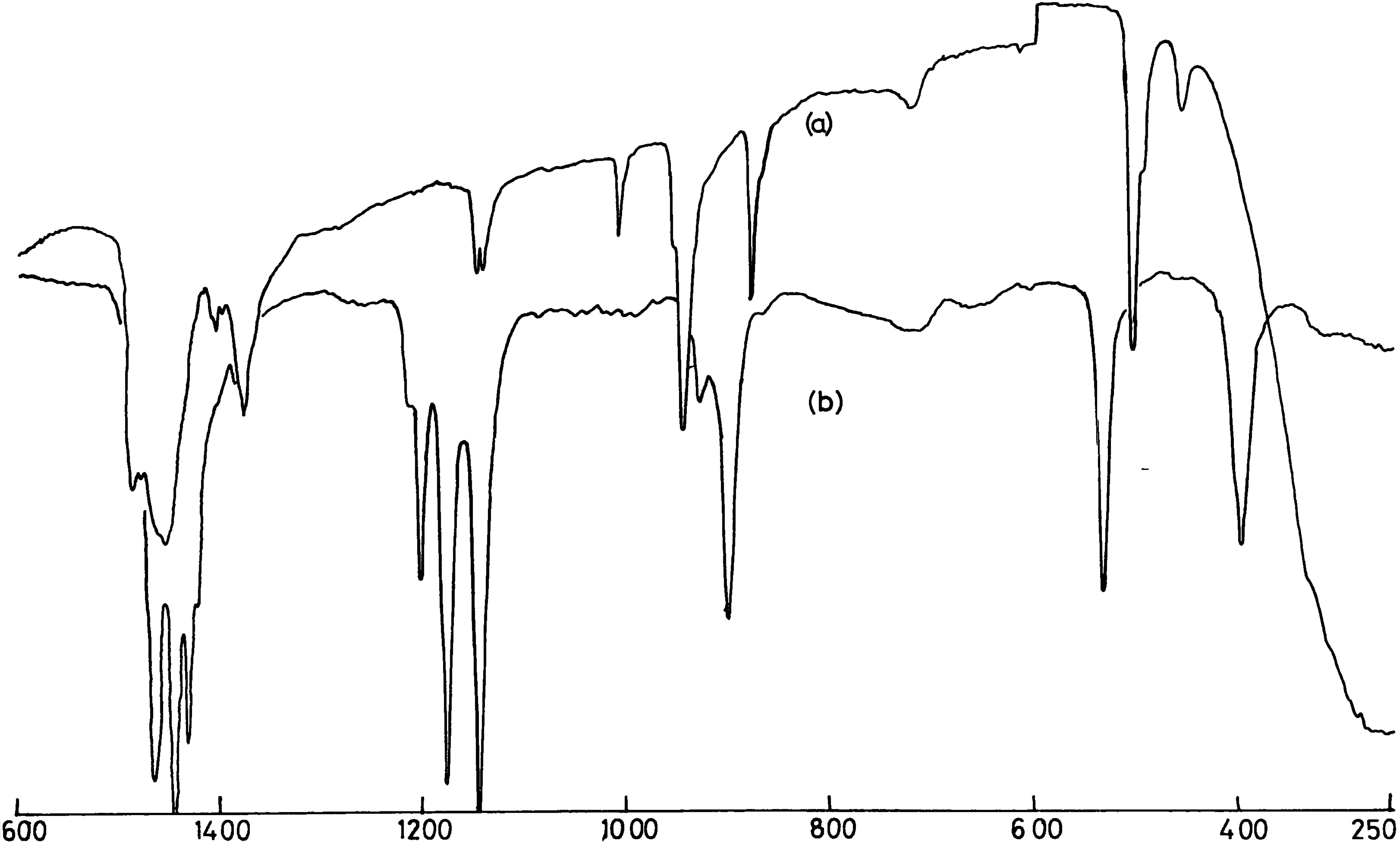
$$(CH_3)_2NCl + I_2 \longrightarrow (CH_3)_2NCl.I_2$$

This compound is yellow, and in the infra red similarities exist to the $CH_3I$, $(CH_3)_2NCl$ product, especially at around 1150 $cm^{-1}$ and at 500 $cm^{-1}$. The infra red spectra are shown in Figure 57, and the frequencies tabulated in Table 13.



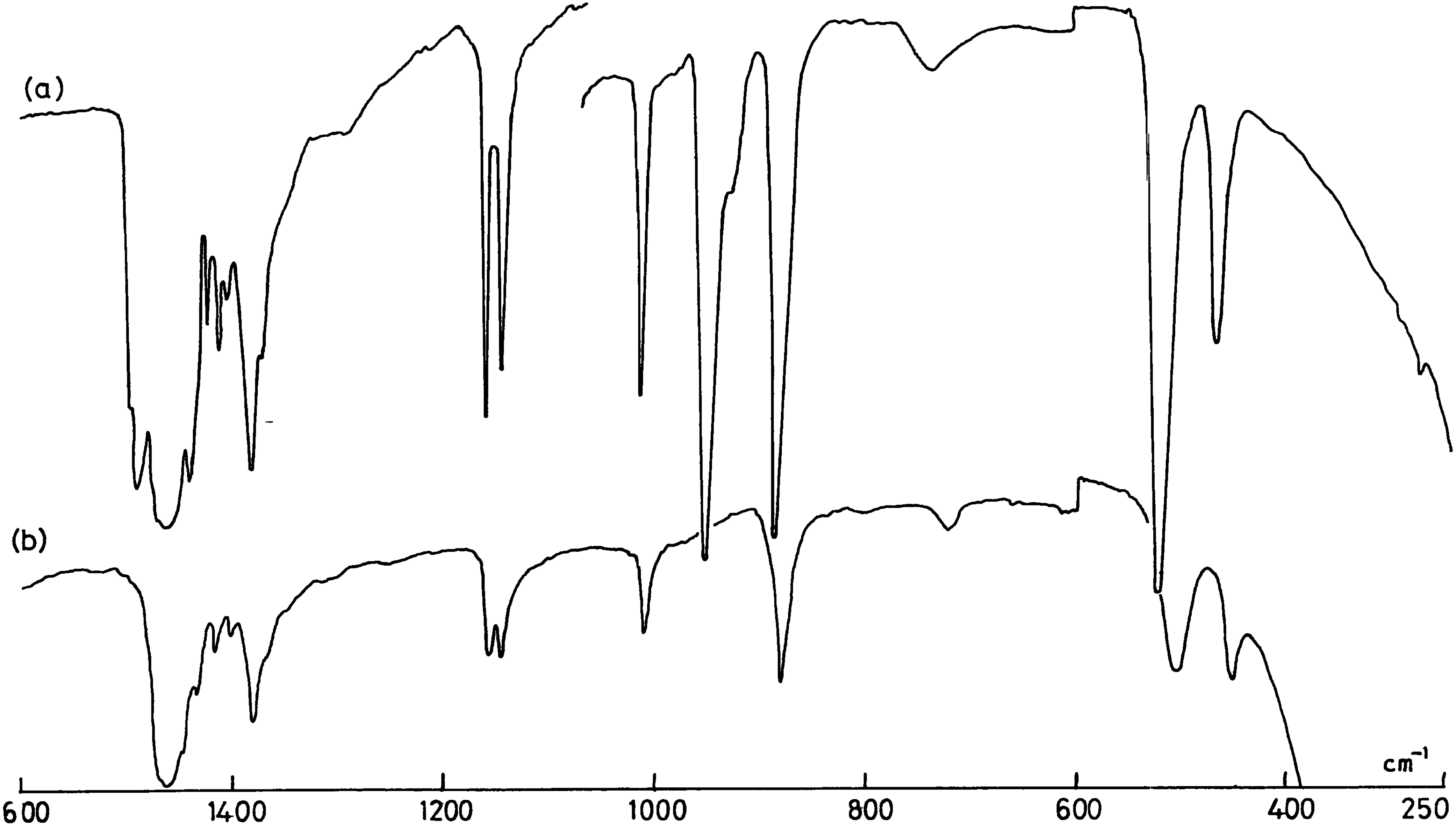
INFRA RED SPECTRA OF (a) $(CH_3)_2NCl$, $CH_3I$ PRODUCT
(b) $(CH_3)_2NCl$ (solid film, 77K)

fig 55



INFRA RED SPECTRA OF (a) $(CH_3)_2NBr$, $CH_3I$ PRODUCT
(b) $(CH_3)_2NBr$ ($CCl_4$ solution)

fig 56



INFRA-RED SPECTRA OF (a) $(CH_3)_2NCl, CH_3I$ PRODUCT

(b) $(CH_3)_2NCl.I_2$

fig 57

## TABLE 12

## COMPARISON OF INFRA RED SPECTRA OF $(CH_3)_2NCl$ AND $(CH_3)_2NBr$ AND THEIR $CH_3I$ ALKYLATION PRODUCTS

| $(CH_3)_2NCl$ | $(CH_3)_4\overset{+}{N}(CH_3)_2N(ICl)_2^{-}$ | $(CH_3)_4\overset{+}{N}(CH_3)_4N(IBr)_2^{-}$ | $(CH_3)_2NBr$ |
|---|---|---|---|
| (-196°C) | (solid) | (solid) | ($CCl_4$ solid) |
| | 3025 | 3020 | |
| 3000 | | | 3000 |
| 2980 | | | |
| 2960 | 2956 | 2955 | 2960 |
| 2925 | | | |
| 2910 | 2910 | 2920 | 2900 |
| 2870 | | | 2885 |
| | 2855 | 2860 | |
| 2825 | | | 2820 |
| 2780 | | | 2780 |
| | 1495 | 1490 | |
| 1480 | 1485 | 1480 | |
| 1455 | 1460 | 1455 | 1465 |
| 1450 | | | |
| 1445 | | | 1445 |
| 1435 | 1440 | 1435 | 1430 |
| 1425 | | | 1420 |
| 1415 | | | |
| 1400 | 1400 | 1405 | 1440 |
| | | 1400 | |
| 1210 | | | 1200 |
| 1190 | | | |
| 1160 | 1160 | 1150 | 1175 |
| | 1145 | 1140 | 1145 |
| | 1010 | 1010 | |
| 1005 | | | 1000 |
| | 945 | 945 | |
| 910 | | | 900 |
| | 880 | 880 | |
| 595 | | | 535 |
| | 520 | 505 | |
| | 465 | 460 | |
| 410 | | | 400 |
| 380 | | | |
| 360 | | | |
| | 265 | 261 | |

## TABLE 13

## COMPARISON OF INFRA RED SPECTRA OF $(CH_3)_2NCl.I_2$, $(CH_3)_2NCl$ (-196°C), $(CH_3)_2NCl/CH_3I$ PRODUCT

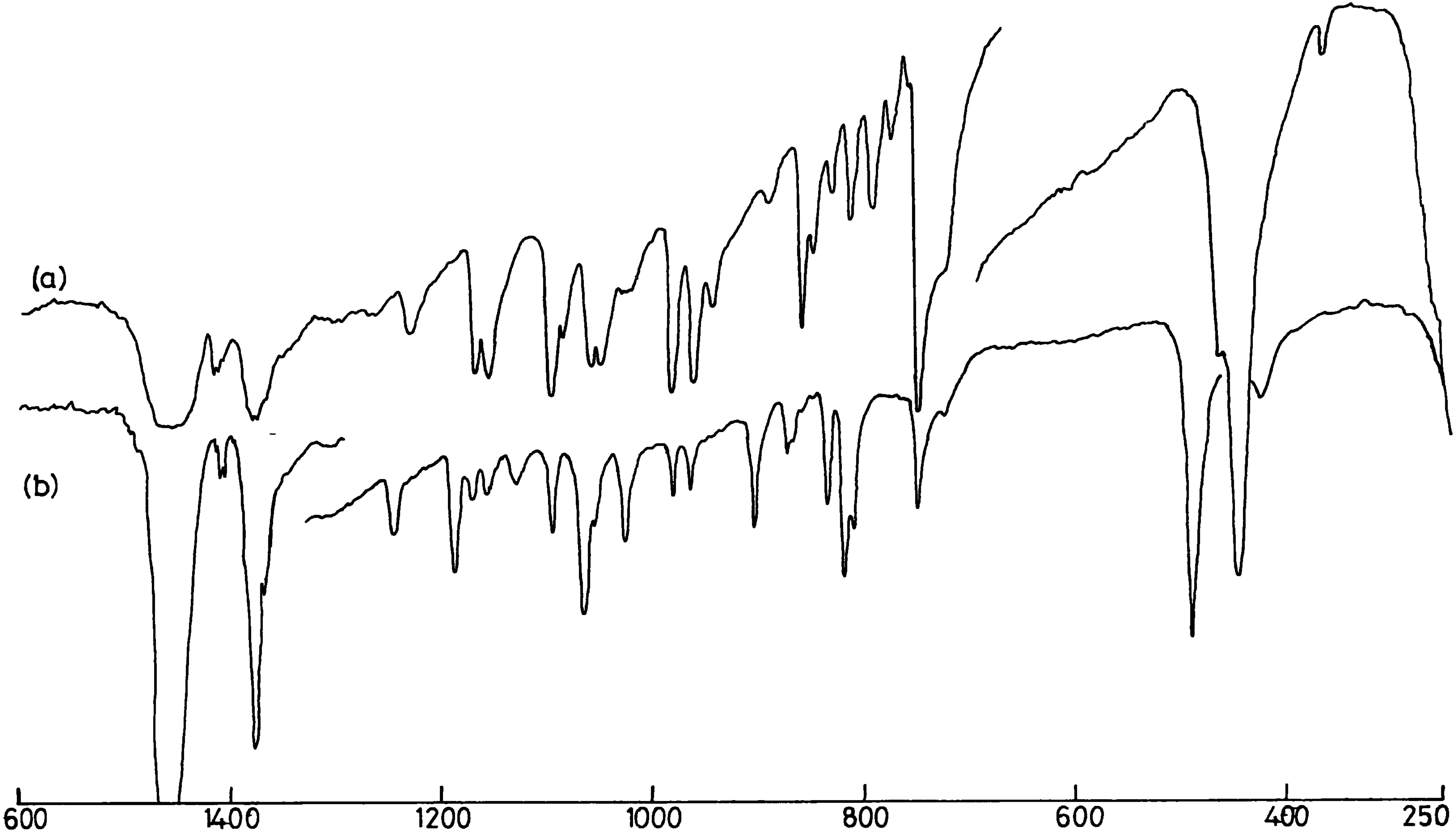
| $(CH_3)_2NCl.I_2$ | $(CH_3)_2NCl/CH_3I$ | $(CH_3)_2NCl$ (-196°C) |
|---|---|---|
|  | 1495 |  |
|  | 1485 | 1480 |
|  | 1460 | 1455 |
|  |  | 1450 |
|  |  | 1445 |
| 1435 | 1440 | 1435 |
|  |  | 1425 |
| 1415 |  | 1415 |
| 1400 | 1400 | 1400 |
|  |  | 1210 |
|  |  | 1190 |
| 1155 | 1160 | 1160 |
| 1145 | 1145 |  |
| 1010 | 1010 | 1005 |
|  | 945 |  |
|  |  | 910 |
| 880 | 880 |  |
|  |  | 595 |
| 505 | 520 |  |
| 455 | 475 |  |
|  |  | 410 |

Where again the retention of the $(CH_3)_2N$ moiety is indicated, and further, that because of the marked similarity, some form of $(CH_3)_2N$-I interaction is also indicated. The comparison between $(CH_3)_2NCl.I_2$ and $(CH_3)_2NCl/CH_3I$ product again points to the presence of $(CH_3)_4\overset{+}{N}$ in the alkylation reaction product. This is emphasised by the absence of the strong 945 $cm^{-1}$ band in $(CH_3)_2NClI_2$.

The use of deuterated halamine and alkyl halide species can again support the crystallographic structure. The products of the reaction of $CH_3I$ and $CD_3I$ with $(CH_3)_2NCl$, $CH_3CD_3NCl$ and $(CD_3)_2NCl$ were all prepared and are all yellow solids. The infra red spectra of these products are shown in Figures 58 to 63. The position of the absorption bands are listed for each complex in Table 14.

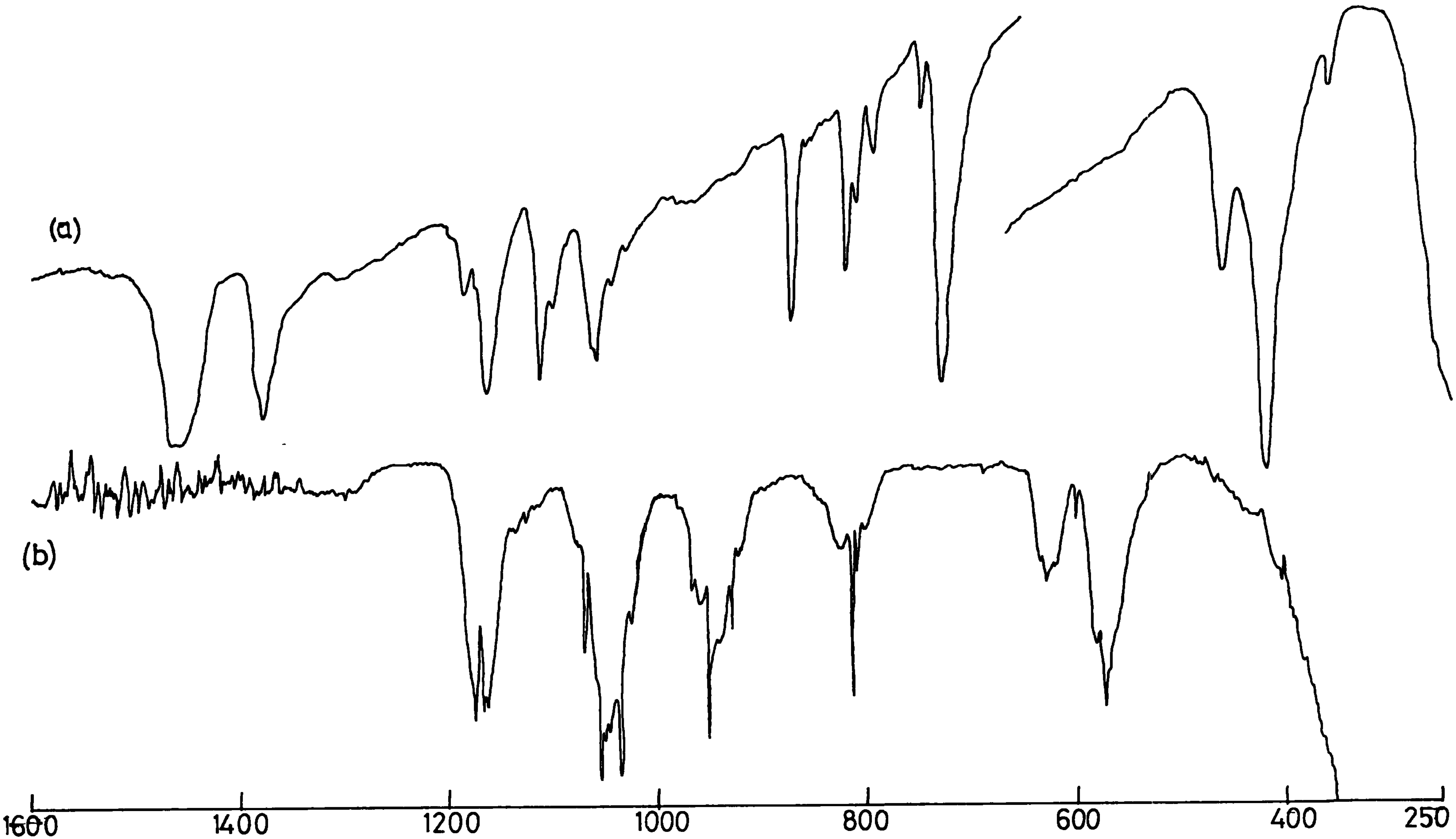
It can be seen immediately from Figures 62 and 63, showing the infra red spectra of the products $CH_3I$, $CH_3CD_3NCl$ and $CD_3I$, $(CH_3)_2NCl$, that the two complexes are different indicating that the product of the alkylation reaction contains at least two different carbon atoms.

The noted resemblance between $(CH_3)_2NCl$ and $(CH_3)_2NCl/CH_3I$ spectra are again shown where the $(CD_3)_2NCl/CD_3I$ product resembles $(CD_3)_2NCl$. This is shown in Figures 60, 61. Another interesting feature of the spectra is the great similarity the $(CH_3)_2NCl/CD_3I$ product has with the $(CH_3)_2NCl/CH_3I$ product. This indicates that the bulk of the spectrum in the region 1400-250 $cm^{-1}$ is determined more by the dimethylamino structure than the alkyl iodide, again consistent with structures where the $(CH_3)_2N$ moiety is retained, and indeed influenced only slightly by the



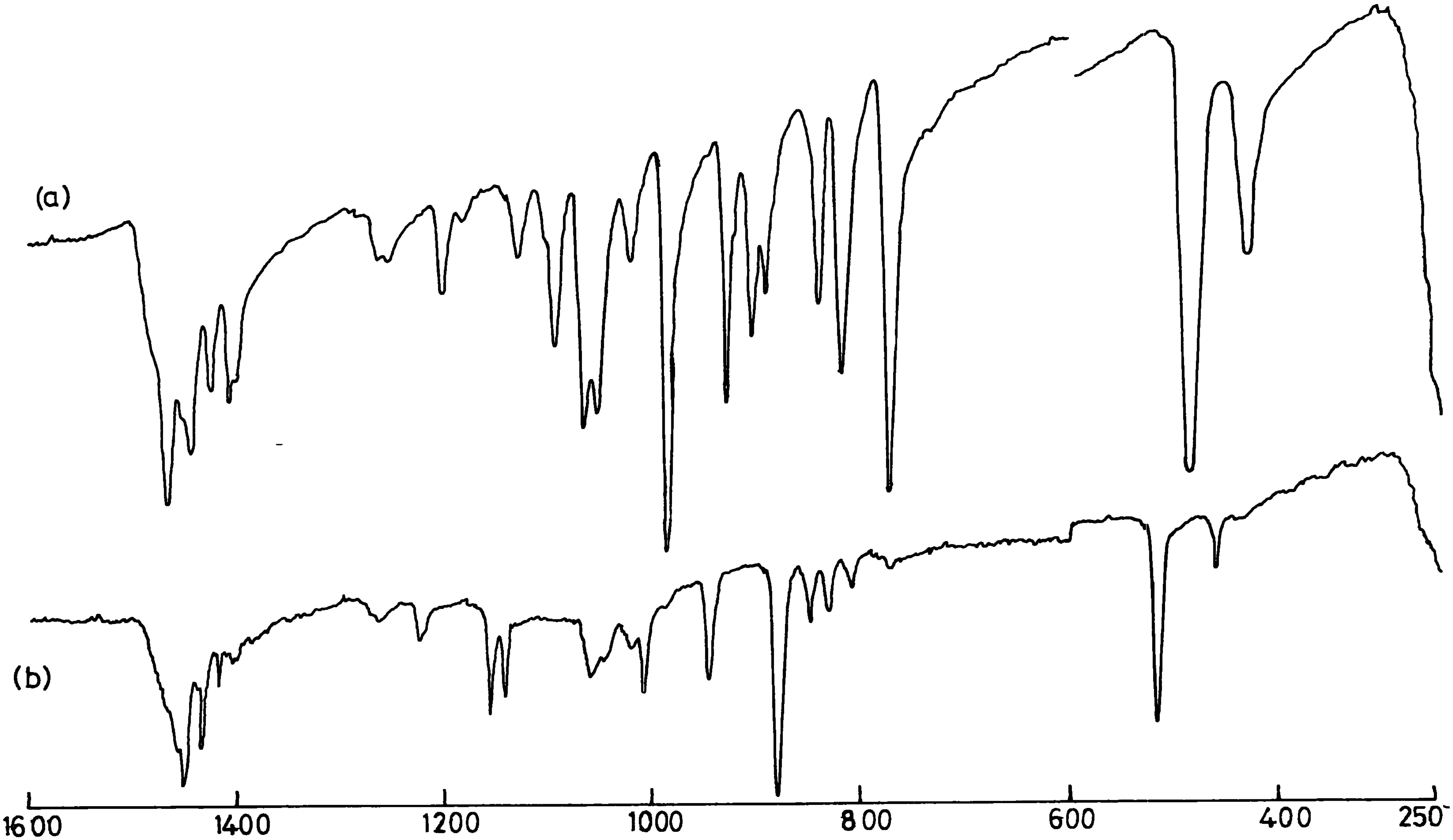
INFRA RED SPECTRA OF THE PRODUCTS (a) $(CD_3)_2NCl, CH_3I$ fig 58

(b) $CH_3CD_3NCl, CD_3I$ fig 59



INFRA RED SPECTRA OF THE PRODUCTS (a) $(CD_3)_2NCl$, $CD_3I$ fig 60

(b) $(CD_3)_2NCl$ (at 15 mm Hg) fig 61



INFRA RED SPECTRA OF THE PRODUCTS (a) $CH_3CD_3NCl$ , $CH_3I$ fig 62

(b) $(CH_3)_2NCl$ , $CD_3I$ fig 63

## TABLE 14

## INFRA RED ABSORPTION FREQUENCIES, $CM^{-1}$, FOR PRODUCTS OF REACTIONS OF $CH_3I$ AND $CD_3I$ WITH $(CH_3)_2NCl$, $CH_3CD_3NCl$, AND $(CD_3)_2NCl$

| $CH_3I$ | | | $CD_3I$ | | |
|---|---|---|---|---|---|
| $(CH_3)_2NCl$ | $CH_3CD_3NCl$ | $(CD_3)_2NCl$ | $(CH_3)_2NCl$ | $(CH_3)CD_3NCl$ | $(CD_3)_2NCl$ |
| 1494 | 1420 | 1415 | 1430 | 1415 | 1185 |
| 1483 | 1410 | 1410 | 1415 | 1405 | 1160 |
| 1461 | 1395 | 1230 | 1400 | 1240 | 1115 |
| 1433 | 1200 | 1170 | 1220 | 1185 | 1100 |
| 1402 | 1080 | 1155 | 1165 | 1170 | 1055 |
| 1159 | 1065 | 1100 | 1140 | 1155 | 870 |
| 1145 | 1050 | 1085 | 1060 | 1130 | 820 |
| 1010 | 1020 | 1060 | 1045 | 1095 | 815 |
| 945 | 985 | 1050 | 1010 | 1060 | 795 |
| 830 | 900 | 980 | 945 | 1025 | 725 |
| 520 | 890 | 960 | 870 | 980 | 465 |
| 465 | 840 | 945 | 845 | 960 | 425 |
| 265 | 820 | 860 | 830 | 900 | |
| | 770 | 850 | 810 | 870 | |
| | 470 | 830 | 770 | 830 | |
| | 430 | 815 | 515 | 810 | |
| | | 795 | 460 | 745 | |
| | | 775 | 265 | 490 | |
| | | 750 | | 425 | |
| | | 450 | | | |
| | | 400 | | | |

presence of the rest of the molecule.

The vibration at 520 cm$^{-1}$ in $(CH_3)_2NCl/CH_3I$ is little affected by the use of $CD_3I$ indicating an independence of this vibration on C-D bonds. Had this vibration been a C-I mode then it would be expected to shift significantly with the use of $CD_3I$ instead of $CH_3I$. However, in the case of the reaction of $CH_3I$ with $(CD_3)_2NCl$ the band at 520 cm$^{-1}$ has moved to 450 cm$^{-1}$ indicating clearly that this vibration is associated with the $(CH_3)_2N$ part of the $CH_3I$, $(CH_3)_2NCl$ product. Table 15 lists the position of the absorption at 520 cm$^{-1}$ in the $CH_3I/(CH_3)_2NCl$ product, as a function of increasing $CD_3$ substitution on the chloramine.

### TABLE 15

### VARIATION OF 520 CM$^{-1}$ VIBRATION WITH INCREASING $CD_3$ SUBSTITUTION OF $(CH_3)_2NCl$

| | $(CH_3)_2NCl$ | $CH_3CD_3NCl$ | $(CD_3)_2NCl$ |
|---|---|---|---|
| $CH_3I$ | 520 | 470 | 450 |
| $CD_3I$ | 515 | 490 | 425 |

An interesting feature of Table 15, is the way the frequencies fall into three distinct groups, one at around 520 cm$^{-1}$, one at around 480 cm$^{-1}$, and a third at around 440 cm$^{-1}$. Since the band at 520 cm$^{-1}$ in the $(CH_3)_2NCl/CH_3I$ product is also present, at 505 cm$^{-1}$, in the $(CH_3)_2NClI_2$ complex, it is reasonable to assume that it is a function of the $(CH_3)_2N$ structure. The grouping observed in Table 15 can thus be explained in terms of increasing mass in the $(CH_3)_2N$ moiety. The group that absorb at 520, 515 cm$^{-1}$ clearly contain $(CH_3)_2N(ICl)_2$ ions whilst those at 425, 450 cm$^{-1}$ contain $(CD_3)_2N(ICl)_2$ ions. Thus the group at 470, 490 must contain $CH_3CD_3N(ICl)_2$ ions.

This absorption is useful in postulating a possible mechanism for the reaction. The formation of tetramethylammonium ions can be explained if dimethylchloramine is alkylated by methyl iodide in the normal way, as indeed occurred with methyl bromide or with methyl perchlorate:

$$(CH_3)_2NCl + CH_3I \longrightarrow (CH_3)_3\overset{+}{N}ClI^-$$

As has been seen with methyl bromide, and the reactions of the $(CH_3)_3NCl$ cation, noted in Chapter 4, the following can occur:

$$(CH_3)_3\overset{+}{N}Cl + I^- \longrightarrow (CH_3)_3\overset{+}{N}I + Cl^-$$

The production of trimethylamine, necessary for $(CH_3)_4\overset{+}{N}$ production, and ICl for $(CH_3)_2N(ICl)_2^-$ production follows:

$$(CH_3)_3\overset{+}{N}I + Cl^- \longrightarrow (CH_3)_3NICl \rightleftharpoons (CH_3)_3N + ICl$$

The trimethylamine is then alkylated, it now being the strongest base present, by a further mole of $CH_3I$:

$$CH_3I + (CH_3)_3N \longrightarrow (CH_3)_4N + I$$

ICl, I, and $(CH_3)_2NCl$, then react to form the anion:

$$ICl + I^- + (CH_3)_2NCl \longrightarrow (CH_3)_2N(ICl)_2^-$$

Following this scheme through with the various deuterated compounds, leads to the following equations:

$$2(CH_3)_2NCl + 2CH_3I \longrightarrow (CH_3)_4\overset{+}{N}\ (CH_3)_2N(ICl)_2^-$$

$$2(CH_3)_2NCl + 2CD_3I \longrightarrow (CH_3)_2\overset{+}{N}(CD_3)_2\ (CH_3)_2N(ICl)_2^-$$

$$2CH_3CD_3NCl + 2CH_3I \longrightarrow (CH_3)_3\overset{+}{N}(CD_3)\ CD_3CH_3N(ICl)_2^-$$

$$2CH_3CD_3NCl + 2CD_3I \longrightarrow CH_3\overset{+}{N}(CD_3)_3\ CD_3CH_3N(ICl)_2^-$$

$$2(CD_3)_2NCl + 2CH_3I \longrightarrow (CH_3)_2\overset{+}{N}(CD_3)_2\ (CD_3)_2N(ICl)_2^-$$

$$2(CD_3)_2NCl + 2CD_3I \longrightarrow (CD_3)_4\overset{+}{N}\ (CD_3)_2N(ICl)_2^-$$

Resulting in the formation of six distinct compounds which was observed in the six different infra red spectra, and also that these six compounds fall into three groups of two, each group having a common anion.

In the non deuterated instance, the vibrations at 3020, 1490, 1405, 1400, 945 and 460 cm$^{-1}$ are accountable for by the cation $(CH_3)_4\overset{+}{N}$, a comparison of these frequencies with those found in the literature for other $(CH_3)_4\overset{+}{N}$ compounds is given in Table 16.

TABLE 16

COMPARISON OF INFRA RED ABSORPTION FREQUENCIES OF THE $(CH_3)_4N$ CATION WITH VARIOUS ANIONS (DATA ON Cl, $IBr_2$, AND $I_3$ FROM REF. (118))

| $(CH_3)_4N$ $(CH_3)_2N(ICl)_2$ | $(CH_3)_4NCl$ | $(CH_3)_4NIBr_2$ | $(CH_3)_4NI_3$ |
|---|---|---|---|
| 3020 | 3019 | 3020 | 3018 |
| 1490 | 1490 | 1487 | 1478 |
| 1405 | 1405 | 1416 | 1417 |
| 1400 | 1398 | 1405 | 1409 |
| 945 | 958 | 957 | 945 |
| 460 | 456 | 458 | 456 |

The remaining bands are therefore due to the anion. The vibrations at 1150, 1145, 880 and 520 cm$^{-1}$ are presumably skeletal modes of the dimethylamino moiety. The split vibrations at 1150 cm$^{-1}$ and 1145 cm$^{-1}$, along with the vibration at 1010 cm$^{-1}$ are presumably C-N stretching modes, whilst the absorption at 880 cm$^{-1}$ may be a CNC deformation mode. The 520 cm$^{-1}$ mode may be a rocking or twisting mode of the $N(CH_3)_2$ system it dropping from 520 to 470 cm$^{-1}$ and finally 450 cm$^{-1}$ on successive $CD_3$ substitutions. Its intensity is fairly large. The absorptions at 265 cm$^{-1}$

in $(CH_3)_4\overset{+}{N}\ (CH_3)_2N(ICl)_2^-$ could be associated with the I-Cl function, since in $(CH_3)_3NICl$, ICl was reported (120) at 249 cm$^{-1}$. In various $ICl_2^-$ salts of Rb and Cs the $\nu_1$ mode of the anion is at 282 (Rb) and 268 (Cs), whilst the strong $\nu_3$ is at 218 cm$^{-1}$ in both (119).

The vibration was also found in the corresponding $(CH_3)_2N(IBr)_2^-$ analogue which perhaps suggests that this band is also a skeletal mode of the CN framework, perhaps a $N(CH_3)_2$ wagging mode, it certainly appears a little high for a N-I vibration, since in $(CH_3)_3NICl$ the N-I mode is reported at 196 cm$^{-1}$, dropping to 172 cm$^{-1}$ in $(CH_3)_3NIBr$ (120). However, in view of the shortening of the N-I distance, from 2.30Å in $(CH_3)_3NICl$ (122) to 2.218Å in the anion, (116), it is expected that the N-I frequency would increase in the anion, which would be accompanied by a corresponding reduction in the I-Cl frequency, since the ICl bond length is longer in the anion (2.671, (116)) than in $(CH_3)_3NICl$ (2.52, (122)).

The band at 127 cm$^{-1}$ appears a more likely contender for the I-Cl assignment with the 100 cm$^{-1}$ band being an N-I-Cl deformation mode, it being found at 147 cm$^{-1}$ in $(CH_3)_3NICl$ (120).

The infra red spectrum of the methylation product of dimethylchloramine with methyl iodide thus supports the crystallographic evidence for the product formulation as $(CH_3)_4\overset{+}{N}\ (CH_3)_2N(ICl)_2^-$, and strongly suggests that the less stable bromo analogue is of similar structure, $(CH_3)_4\overset{+}{N}(CH_3)_2N(IBr)_2^-$.

$^1$H NMR spectra, run in acetone, a solvent in which although dissolving the material does not allow successful crystallisation, yield further supporting evidence for this structure. Two singlets were observed, at -30°C, at $\tau$6.97 and 6.85, from external TMS. The integrated ratio was found to be respectively 2:1.

The reaction of trimethylamine with the compound $(CH_3)_4\overset{+}{N}(CH_3)_2N(ICl)_2^-$ and product from the $CD_3I$ alkylation of $(CH_3)_2NCl$ is interesting, since the reaction products contained tetramethylammonium cations, confirming the presence of the cation in the starting material, and the base $((CH_3)_2N)_2CH_2$, tetramethylmethylenediamine, a product found in the reaction of $(CH_3)_2NCl$ with $(CH_3)_3N$. The overall stoichiometry indicated, can be expressed by the equation:

$$(CH_3)_4\overset{+}{N}\ (CH_3)_2N(ICl)_2^- + 2(CH_3)_3N \longrightarrow (CH_3)_4\overset{+}{N} + (CH_3)_3\overset{+}{N}H + \overset{-}{I} + ICl_2^- + ((CH_3)_2N)_2CH_2$$

When the products of this reaction, after removal of the base $((CH_3)_2N)_2CH_2$, were treated with NaOH, only $(CH_3)_3N$ was found.

A similar reaction, when carried out on the product of the reaction between $CD_3I$ and $(CH_3)_2NCl$, yielded $(CH_3)_3N$ on NaOH treatment of solid residues, and only C-D bonds were found in the solid phase. The reaction is thus indicated:

$$(CD_3)_2\overset{+}{N}(CH_3)_2\ (CH_3)_2N(ICl)_2^- + (CH_3)_3N \longrightarrow (CD_3)_2\overset{+}{N}(CH_3)_2 + \overset{-}{I} + ICl_2^- + (CH_3)_3\overset{+}{N}H + ((CH_3)_2N)_2CH_2$$

It is thus clear that the reaction between trimethylamine and $(CH_3)_4\overset{+}{N}(CH_3)_2N(ICl)_2^-$ involves only the anion, and that the dimethylamino portions remains intact. A possible reaction scheme would be:

$$(CH_3)_4\overset{+}{N}(CH_3)_2N(ICl)_2^- + (CH_3)_3N \longrightarrow (CH_3)_3NICl + (CH_3)_4\overset{+}{N} + (CH_3)_2NICl^-$$

$$(CH_3)_2NICl^- \longrightarrow (CH_3)_2NCl + I^-$$

$$(CH_3)_2NCl + (CH_3)_3N \longrightarrow (CH_3)_2NCH_2N(CH_3)_2 + HCl$$

$$HCl + (CH_3)_3NICl \longrightarrow (CH_3)_3\overset{+}{N}H\ ICl_2^-$$

resulting in an overall reaction:

$$(CH_3)_4\overset{+}{N}(CH_3)_2N(ICl)_2^- + 2(CH_3)_3N \longrightarrow (CH_3)_4\overset{+}{N} + (CH_3)_3\overset{+}{N}H + ICl_2^- + \overset{-}{I} + ((CH_3)_2N)_2CH_2$$

From the X ray work, the N-I and I-Cl distances are 2.218(6)Å and 2.671(3)Å respectively, and the N-I-Cl system is almost linear, N-I-Cl = 176.9(1)°, witn the other angles about the nitrogen close to the tetrahedral values.
One particular analogue of this anion is the $I_5^-$ ion, which is found to be V shaped (121), as $(CH_3)_2N(ICl)_2^-$ essentially is, so it is possible to consider $(CH_3)_2N^-$ as a pseudohalide.

The N-I bond length of 2.218Å, is shorter than the N-I length in $(CH_3)_3NICl$, which is 2.30Å (122), and a corresponding lengthening of the I-Cl distance of 2.671 in the anion, compared to 2.52 in $(CH_3)_2NICl$.

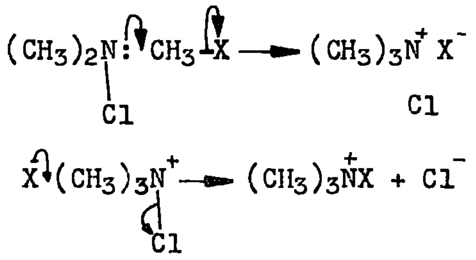
Such a shortening of the N-I bond length is consistent with a stronger N-I interaction than is present in for example $(CH_3)_3NICl$, perhaps as a consequence of the negative charge being delocalised over the I-N-I system. Such delocalisation has been proposed to account for the appreciable ionic character found in the $ICl_2^-$ anion (121), from NQR measurements, where it is suggested that the ionic character of the I-Cl bond corresponded to about a half an electron on each chlorine atom.

In summary, methyl iodide reacts with dimethylchloramine in a conventional manner yielding, a cationic species which rearranges and further reacts to yield a novel anion in which it can be thought that the dimethylamino group acts as a pseudohalide.

With methyl bromide, dimethylchloramine did not react in exactly the same way, but evidence points to conventional alkylation followed by nucleophillic attack of bromide ion to yield the charge transfer complex $(CH_3)_3NBrCl$.

With methyl chloride, in view of the recovery of some of the starting materials, indicates no reaction but decomposition of the chloramine.

The reaction of dimethylchloramine with methyl iodide and bromide can be rationalised as follows:



$$(CH_3)_2\underset{Cl}{N}{:}\,CH_3{-}X \longrightarrow (CH_3)_3\underset{Cl}{\overset{+}{N}}\,X^-$$

$$X^-\,(CH_3)_3\underset{Cl}{\overset{+}{N}} \longrightarrow (CH_3)_3\overset{+}{N}X + Cl^-$$

$$(CH_3)_3\overset{+}{N}{-}X + Cl^- \longrightarrow (CH_3)_3N \longrightarrow X{-}Cl$$

on the basis that the N-I bond is less stable than the N-Br bond, when X = Br the reaction proceeds no further, but when X = I then the reaction proceeds thus: ?

$$(CH_3)_3N{-}I{-}Cl \xrightarrow{CH_3I} (CH_3)_4\overset{+}{N} + ICl + I^-$$

$$(CH_3)_2NCl + I^- + ICl \longrightarrow (CH_3)_2N(ICl)_2^-$$

## Experimental

### 1. The Reaction Of Dimethylchloramine With Methyl Iodide

The reaction between pure anhydrous dimethylchloramine, $(CH_3)_2NCl$, and pure anhydrous methyl iodide, $CH_3I$, was studied in a weight analysis cell on the vacuum line.

Dimethylchloramine, 1.6472 g, (20.72 m mole), was condensed into a Rotaflow weight analysis cell, followed by an excess, 5.4312 g, (38.25 m mole) methyl iodide.

The weight analysis cell was allowed to warm slowly to room temperature where, after a period of approximately thirty minutes a quantity of yellow solid had precipitated. The reaction was stopped at this point by cooling the Rotaflow to -196°C, and then distilling out all the volatile products, by allowing it to warm up slowly to room temperature. The residual mass of the Rotaflow was determined and returned to the vacuum line, frozen at -196°C, and the reactants returned. After a period of 10-15 minutes, the process was repeated and it was found that the residual mass of the Rotaflow did not vary significantly from the previous determination, and it was concluded that the reaction had reached completion.

From the mass of product formed, and on the basis of the equation

$$(CH_3)_2NCl + CH_3I \longrightarrow C_3H_9NClI$$

the reaction had gone to almost 100% completion.

The elemental analysis confirmed the empirical formula $C_3H_9NClI$, which requires, (%); C, 16.26; H, 4.07; N, 6.32; Cl, 16.03; I, 57.32. Found, (%); C, 16.40; H, 4.07; N, 6.03; Cl, 16.16; I, 55.40.

The infra red spectrum of the product was recorded as a nujol mull between CsI plates protected with polyethylene film, and is shown in Figure 50. The far infra red was recorded as a thick mull in nujol, in an airtight cell between polyethylene discs, and a plot of the spectrum is shown in Figure 53.

Perdeuteromethyl iodide, $CD_3I$, was used in conjunction with variously deuterated dimethylchloramines, to prepare deuterated examples of the product $C_3H_9NClI$. The method employed was exactly analogous to that described above, namely the direct interaction of the alkyl iodide with dimethylchloramine without solvent. By this method the products listed in Table 17 were prepared.

## TABLE 17

| Reactants | Product | Infra Red Spectrum |
|---|---|---|
| $CH_3I$, $CD_3CH_3NCl$ | $C_3H_6D_3NClI$ | 62 |
| $CH_3I$, $(CD_3)_2NCl$ | $C_3H_3D_6NClI$ | 58 |
| $CD_3I$, $(CH_3)_2NCl$ | $C_3H_6D_3NClI$ | 63 |
| $CD_3I$, $CD_3CH_3NCl$ | $C_3H_3D_6NClI$ | 59 |
| $CD_3I$, $(CD_3)_2NCl$ | $C_3D_9NClI$ | 60 |

The preparation of the deuterated chloramines was performed by the method detailed in Chapter 2, where the deuterated amine was treated with an excess of N-chlorosuccinimide:

$$CD_3CH_3NH + (CH_2CO)_2NCl \longrightarrow CD_3CH_3NCl + (CH_2CO)_2NH$$

Attempts were made to produce crystals of the compound $C_3H_9NClI$ suitable for X ray work. A variety of solvents were used to crystallise the material, but none met with reproducible success. In most cases rapid darkening of the solvent occurred, indicating decomposition. The most promising, liquid $SO_2$, yielded a strong solution at -84°C, but on warming above this temperature the solution rapidly darkened, turning black at room temperature. Table 18 summarises the solvents used and the results obtained.

Attempts to precipitate a crystalline product from solutions of $C_3H_9NClI$ by adding solvents in which the complex was insoluble, for example $CCl_4$ or the aromatic hydrocarbons benzene or toluene, yielded only powders. The method that met with most success was by preparing the compound in excess dimethylchloramine. Approximately 1 mm cubes were obtained in this way but unfortunately were twinned, however preparation of the compound at -30°C in tetrahydrofuran, over several months, was found successful (116).

## TABLE 18

## CRYSTALLISATION OF $C_3H_9NClI$ IN VARIOUS SOLVENTS

| Solvent | Solution Stability | Comments |
|---|---|---|
| $CH_3CN$ | Fair<br>(room temperature) | Starting material recoverable, usually as a fine powder and often brown. Crystals obtained only once. |
| $(CH_3)_2CO$ | Poor<br>(room temperature) | Fine powder recoverable, frequently darkened in colour. |
| $(CH_3)_2NCHO$ | Fair<br>(room temperature) | Pumping solvent off yielded tiny cubes. Crystallising by evaporation yielded fine powder, very dark. ) |
| $(C_6H_5)CH_3$ | Fair<br>(room temperature) | Only very slightly soluble. Fine yellow powder recovered. |
| $(CH_3)_2SO_2$ | | Insoluble. ? |
| $HCONH_2$ | Poor<br>(room temperature) | Involatile solvent, very dark tar recovered on pumping. |
| $C_6H_5NO_2$ | Poor<br>(room temperature) | Very slightly soluble. |
| $C_6H_6$ | Poor<br>(room temperature) | Very slightly soluble. |
| $SO_2(1)$ | Apparently good<br>(-84°C) | Immediate decomposition at temperatures in excess of -84°C. |
| $(CH_3)_2NCl$ | Apparently good ?<br>(0°C) | Preparation in excess $(CH_3)_2NCl$ yielded crystals of suitable size, but twinned. |
| $C_2H_5OH$ | Fair | Fine powder recovered. |

## 2. The Reaction Of $(CH_3)_2NCl$ With Methyl Bromide

The reaction of dimethylchloramine and methyl bromide was studied in a sealed, 16 mm OD pyrex reaction ampoule, over a period of several months, at -23°C.

A 16 mm OD heavy walled pyrex reaction ampoule, was evacuated on the vacuum line and 0.7843 g (9.86 m mole) dimethylchloramine introduced by condensation at -196°C. After the introduction of 2.6132 g (27.53 m mole) methyl bromide at -196°C, the ampoule was sealed, and allowed to warm to room temperature with occasional shaking.

The ampoule was placed in a freezer at -23°C for approximately 12 weeks. The progress of the reaction being observed from time to time, by noting the amount of solid material separating at the base of the ampoule. After 12 weeks no further increase in the amount of solid material was apparent, and the ampoule was then allowed to warm to room temperature, and fitted to an ampoule breaker.

The ampoule was frozen at -196°C and opened to the fractionation section of the vacuum line, and no significant manometer depression was observed, indicating the absence of any non condensible material. The ampoule was allowed to warm to room temperature whilst the volatile contents distilled through a trap at -84°C and into a trap at -196°C.

The solid residue was transferred to the dry box, and the identity of the components of the volatile fraction determined by infra red spectroscopy. Only methyl bromide and dimethylchloramine was observed in the volatile fraction.

1.3768 g of a pale yellow solid was isolated from the ampoule in the dry box, and elemental analysis indicated the empirical formula

$C_3H_9NClBr$: found (%), C, 20.55; H, 5.03; N, 8,02; Cl, 20.30; Br, 44.93: $C_3H_9NClBr$ requires, (%), C, 20.64; H, 5.16; N, 8.03; Cl, 20.35; Br, 45.80. The infra red spectrum was recorded as a nujol mull between CsI plates and is shown in Figure 52.

## The Preparation Of $(CH_3)_3NBrCl$

The interhalogen BrCl was prepared by mixing solutions of $Cl_2$ and $Br_2$ in carbon tetrachloride.

A solution of bromine in carbon tetrachloride was made up by adding approximately 0.7 g $Br_2$ to 10 $cm^3$ dry $CCl_4$ by condensation of the carbon tetrachloride onto the frozen $Br_2$ at -196°C on the vacuum line.

A solution of chlorine in carbon tetrachloride was made up by bubbling $Cl_2$ gas into 100 ml $CCl_4$ at room temperature until saturated. The strengths of the solutions were estimated by adding a known volume of aqueous KI solution, of known concentration, to an aliquot of the halogen solution, and titrating the liberate iodine with $KIO_3$.
By this method the bromine solution was found to be 0.0715 g $Br_2/cm^3$, and the chlorine solution, 0.0855 g $Cl_2/cm^3$.

The solutions were mixed in the ratio according to the reaction:

$$Br_2 + Cl_2 \rightleftharpoons 2BrCl$$

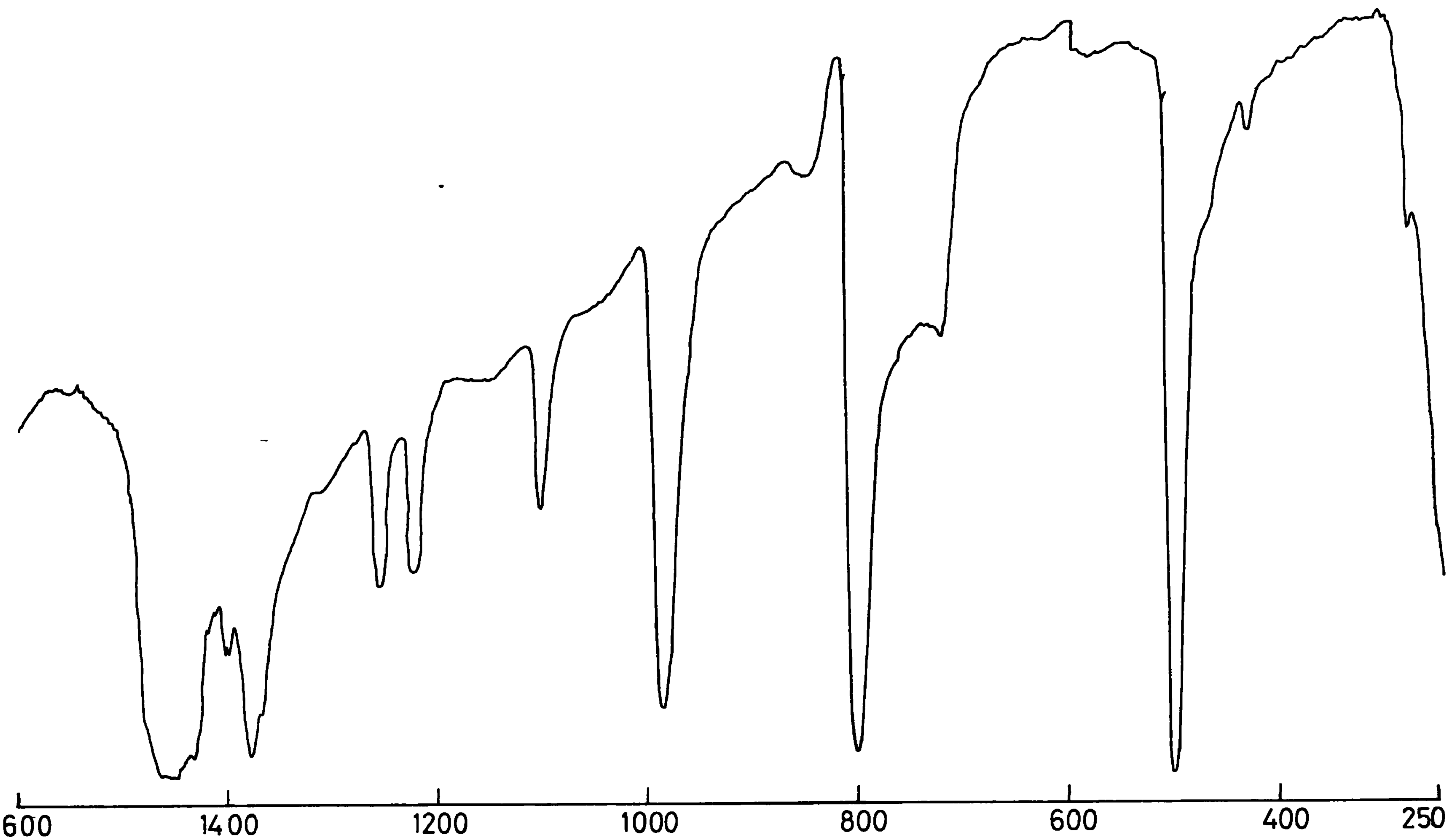
such that 10 $cm^3$ of the bromine solution was mixed with 3.7 $cm^3$ of the chlorine solution, so that the mixture was almost equimolar.

To the pale red solution of the mixed halogens, a solution of trimethylamine in sodium dried hexane was added. The trimethylamine solution was made up by dissolving 5.2797 g $(CH_3)_3N$ in 100 $cm^3$ sodium dried hexane, on the vacuum line. The solution thus contained 0.0528 g per $cm^3$, and 10 $cm^3$ was used in the reaction. As the amine solution was added to the mixed halogen solution, an immediate precipitate occurred which was very pale yellow in colour.

The precipitate was separated on a sintered glass filter and washed once with dry hexane and allowed to dry to a free flowing pale yellow powder on the sinter.

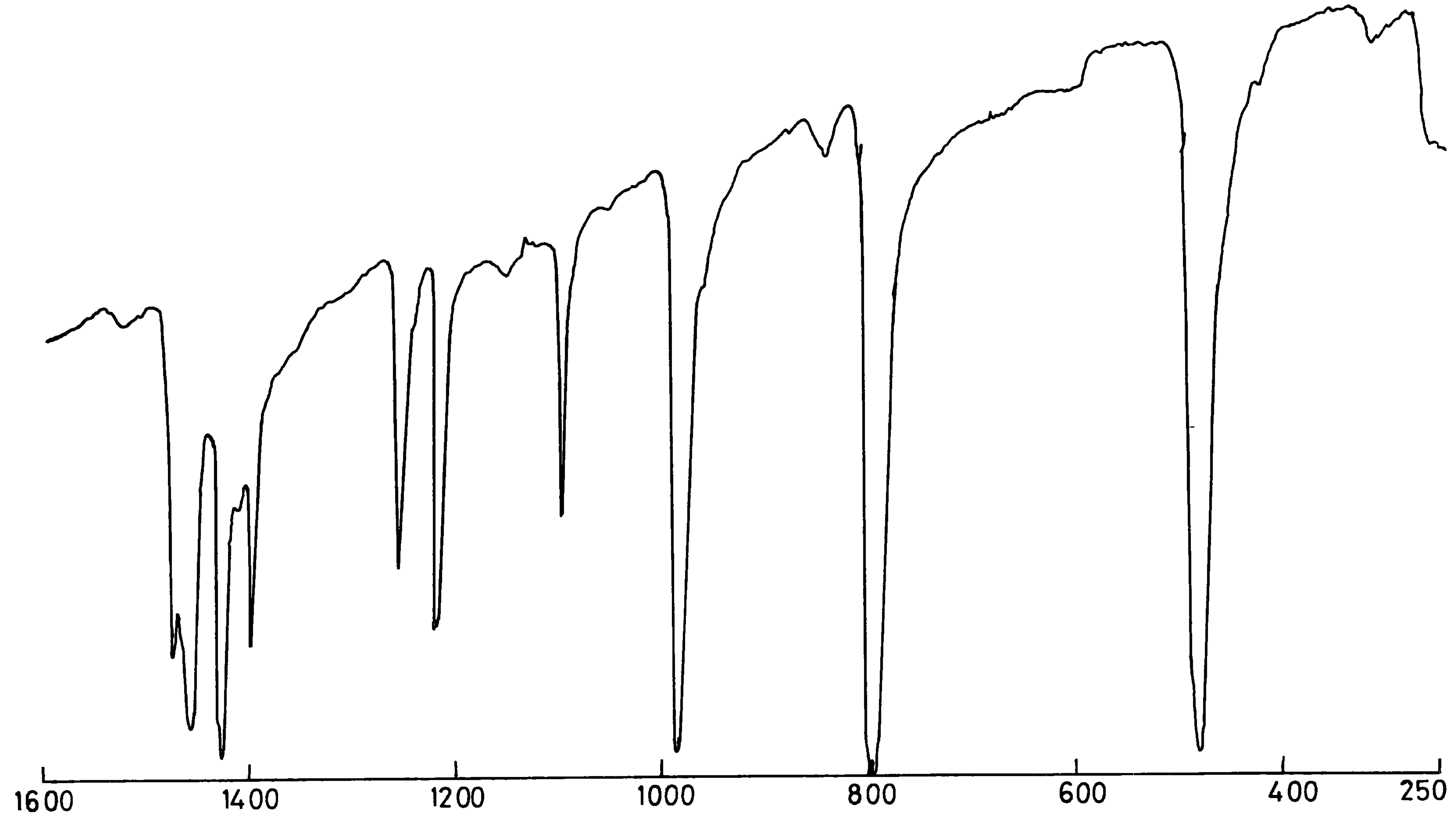
The infra red spectrum of the material, shown in Figure 64, consists of a mixture of two $(CH_3)_3N$ adducts. There was no evidence of $(CH_3)_3NCl_2$ formation. The analytical figures show that the compound is not pure; (%), C, 19.61; H, 5.19; N, 7.25; Cl, 17.69; Br, 50.03. $C_3H_9NBrCl$ requires, (%), C, 20.64; H, 5.16; N, 8.03; Cl, 20.35; Br, 45.80.

Figure 64 supports the mixture proposition, since the absorptions appear broad, and the vibration at around 500 $cm^{-1}$ is split, indicating more than one $(CH_3)_3N$-XY adduct.
Comparing Figure 64 with Figure 65, which is a genuine spectrum of $(CH_3)_3NBr_2$, indicates that the result of the reaction between $(CH_3)_3N$ and the mixture $Cl_2$, $Br_2$ contains $(CH_3)_3NBr_2$ and presumably $(CH_3)_3NBrCl$, since the spectrum of the reaction product and that of $(CH_3)_3NBr_2$ are very similar, indicating that the total product contains only $(CH_3)_3N$- adducts, and since the $(CH_3)_3NBr_2$ spectrum can be found in the product spectrum, the remaining band at 500 $cm^{-1}$, along with the presence of Cl in the analysis, indicates that $(CH_3)_3NBrCl$ has formed. The Br-Cl vibration can be found at 278 $cm^{-1}$ in the far infra red, (Figure 66).



INFRA RED SPECTRUM OF THE PRODUCT FROM THE REACTION OF $(CH_3)_3N$ WITH A MIXTURE OF $Cl_2$ AND $Br_2$,($CCl_4$ sol$^{\underline{n}}$)

fig 64



INFRA RED SPECTRUM OF $(CH_3)_3N{\cdot}Br_2$ fig 65

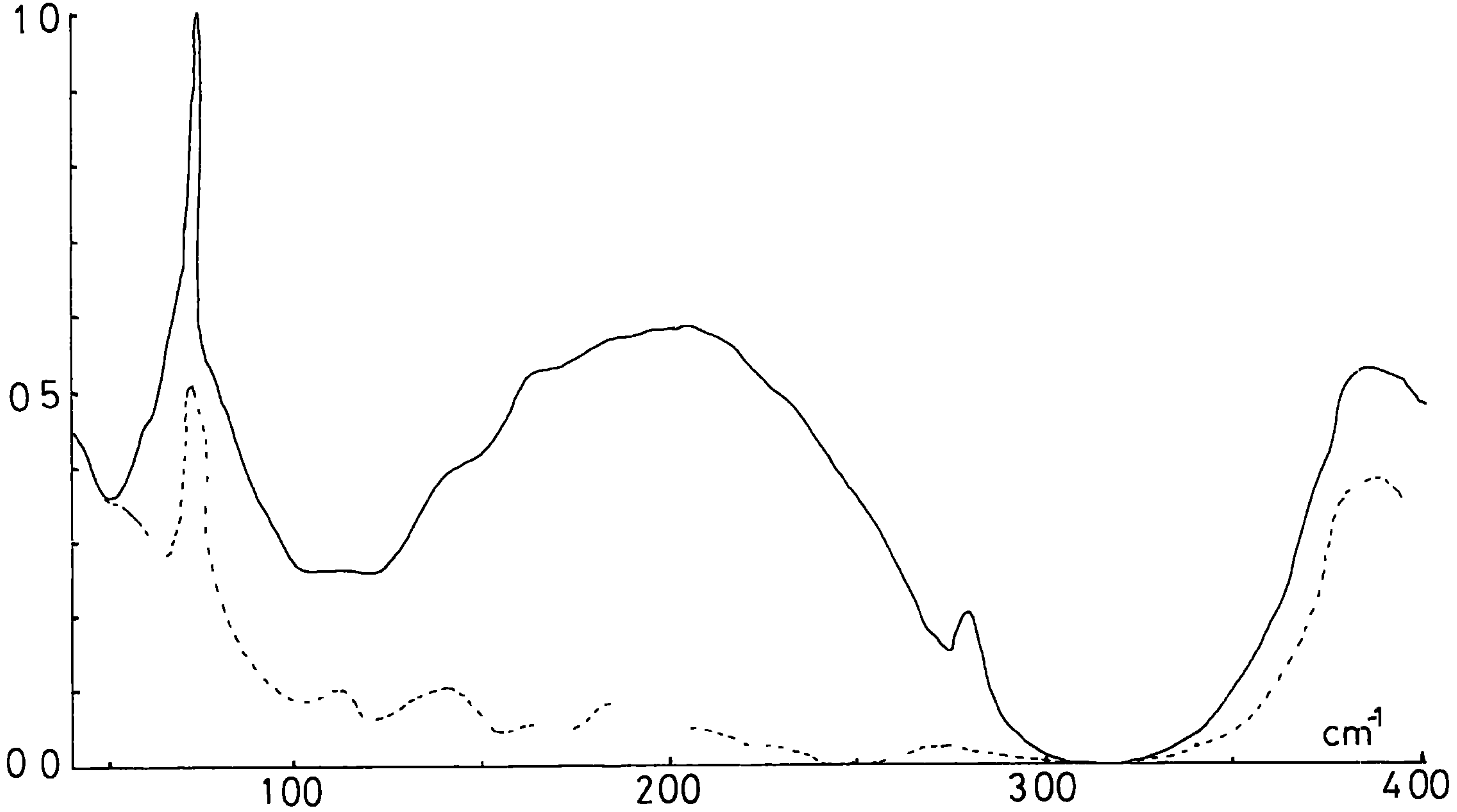


fig 66 FAR INFRA RED SPECTRUM OF $(CH_3)_3NBrCl$

(------- background )

## 3. The Reaction Of Dimethylchloramine With Methyl Chloride

The reaction between dimethylchloramine $(CH_3)_2NCl$, and methyl chloride, $CH_3Cl$, was studied in a sealed tube at 0°C for several months.

A 16 mm heavy walled pyrex ampoule was evacuated and frozen at -196°C on the vacuum line. Dimethylchloramine, 0.4875 g (6.13 m mole) was introduced by condensation.

A standard volume of 2.3343 litre was attached to the fractionation section of the vacuum line and evacuated. Methyl chloride, $CH_3Cl$, was admitted to the fractionation section and standard volume, until a depression of approximately 10 cm was recorded. The system was allowed to stabilise and the actual depression recorded using a cathetometer, and was found to be 8,696 cm Hg. The standard volume was isolated, and the excess methyl chloride pumped away, the contents of the standard volume were then condensed into the reaction ampoule containing dimethylchloramine. By noting the temperature and atmospheric pressure during the transference of methyl chloride it was found that 0.5564 g (11.02 m moles) had been added. The ampoule was then sealed and allowed to attain room temperature with occasional shaking and then stored at around 0°C in a refrigerator.

The reaction was allowed to continue and the amount of solid material forming was noted periodically until after approximately six months no further precipitation appeared to be occurring.

The ampoule was attached to an ampoule breaker and fitted to the fractionation section of the vacuum line, frozen at -196°C, and opened to the manometers, where no significant depression was noted. The ampoule was allowed to slowly warm to room temperature, whilst the volatile fraction distilled through a trap at -84°C and was collected at -196°C.

Infra red spectroscopy revealed that $(CH_3)_2NCl$ was collected at -84°C whilst at -196°C a mixture of predominantly methyl chloride and some dimethylchloramine was present. The fraction collected at -84°C was distilled into the trap at -196°C, the course of the distillation being monitored by infra red spectroscopy and no further components were detected.

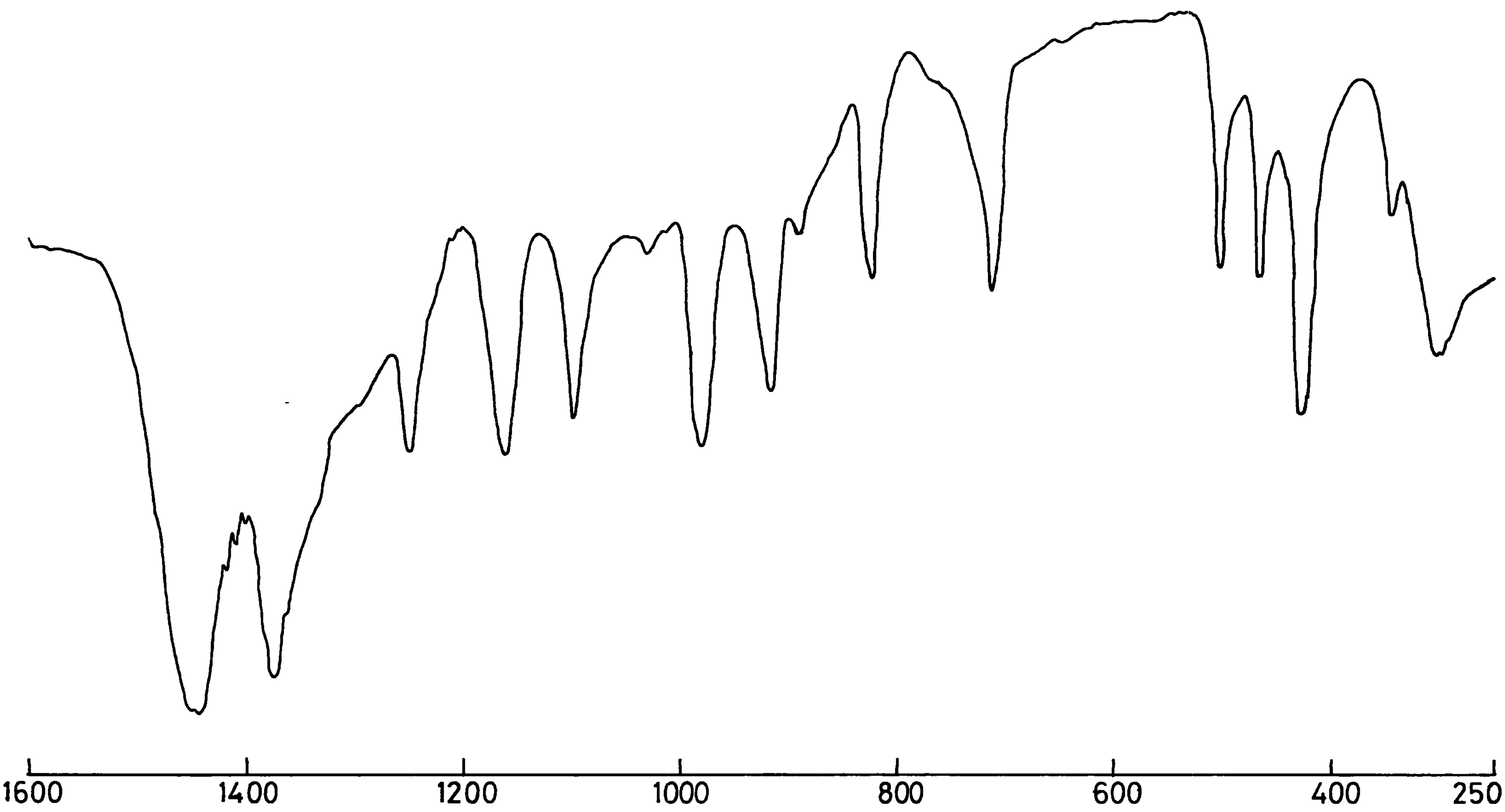
The solid residue in the ampoule was transferred to the dry box and the white free flowing powder analysed as, (approximately), $C_3H_{11}NCl$. Found (%), C, 36.68; H, 10.75; N, 15.83; Cl, 35.63. The infra red spectrum of the solid material was recorded as a nujol mull between CsI plates and is shown in Figure 67.

The oxidising power of the product was tested by dissolving an aliquot of the white solid in distilled water, and adding acidified potassium iodide solution. No iodine formed as indicated by no colour change on the addition of a few drops of starch solution.

### 4. The Reaction Of Dimethylbromamine, $(CH_3)_2NBr$, With Methyl Iodide

The reaction between methyl iodide and dimethylbromamine was carried out in carbon tetrachloride solution because of the great instability of pure $(CH_3)_2NBr$ at room temperature.

Dimethylbromamine, was prepared immediately prior to the addition of methyl iodide, by the method described in Chapter 2, in this instance, the halamine was prepared in carbon tetrachloride solution. 5.0124 g



INFRA RED SPECTRUM OF THE PRODUCT FROM THE REACTION OF $(CH_3)_2NCl$ WITH $CH_3Cl$

fig 67

(28.17 m mole) N-bromosuccinimide was slurried in approximately 10 cm$^3$ dry carbon tetrachloride in a 100 cm$^3$ beaker. To this slurry, 5 cm$^3$ of a solution of dimethylamine in $CCl_4$, made up by condensing 10.4315 g $(CH_3)_2NH$ into 100 cm$^3$ $CCl_4$ on the vacuum line, was run in from a burette. The slurry was stirred for approximately 20 minutes and the now white residue filtered from the greenish yellow solution of $(CH_3)_2NBr$ in $CCl_4$. The residue on the filter was washed with $CCl_4$ and the total volume of solution made up to 20 cm$^3$. The concentration of $(CH_3)_2NBr$ was estimated to be 0.0178 g/cm$^3$ by assuming 100% yield from the reaction:

$$(CH_2CO)_2NBr + (CH_3)_2NH = (CH_3)_2NBr + (CH_2CO)_2NH$$

To 5 cm$^3$ of the solution of $(CH_3)_2NBr$ in $CCl_4$ (0.3590 g, 2.9 m mole) in a beaker, 2 cm$^3$ methyl iodide was added, and the beaker covered with a polyethylene film, and placed in a refrigerator. After two hours a yellow solid had formed. This was filtered off at room temperature. The residue washed with $CCl_4$ and then dry diethyl ether, and dried on the sinter by allowing air to flow through for about 30 seconds. By this method 0.5123 g of the yellow solid was obtained, representing 66.5% yield on the basis of the equation:

$$(CH_3)_2NBr + CH_3I = C_3H_9NBrI$$

Elemental analysis indicated the empirical formula $C_3H_9NBrI$: found for product: (%), C, 13.69; H, 3.35; N, 5.31; Br, 30.32; I, 47.82. $C_3H_9NBrI$ requires, (%), C, 13.54; H, 3.38; N, 5.27; Br, 30.05; I, 47.76.

The infra red spectrum of the compound was recorded as a nujol mull between CsI plates and is shown in Figure 51. The spectral region from 400 cm$^{-1}$ down to 40 cm$^{-1}$ was also recorded, using a thick mull in nujol on a piece of high density polyethylene. This spectrum is plotted in Figure 54.

### 5. The Interaction Of The Product, $C_3H_9NClI$, With Trimethylamine, $C_3H_9N$

The reaction between the alkylation product of dimethylchloramine and methyl iodide, and excess anhydrous trimethylamine was studied in a weight analysis cell at room temperature.

0.1637 g of the yellow product from the reaction of $CH_3I$ with $(CH_3)_2NCl$ was placed in a preweighed Rotaflow weight analysis cell. After the introduction of 7.6148 g (129.06 m mole) anhydrous trimethylamine by condensation on the vacuum line, the Rotaflow was allowed to attain room temperature, where the supernatent liquor was observed to be slightly yellow in colour.

The Rotaflow was placed on a flask shaker and agitated for 24 hours at room temperature, after which time it was returned to the vacuum line, and all the volatiles removed to a cold finger. After the mass of the residue had been determined, the volatile contents were redistilled into the Rotaflow, and returned to the flask shaker. The process was repeated at 36 and 48 hours from the start of the reaction, and no significant increase in the residue mass was noted at 48 hours over that recorded at 36 hours.

The volatile fraction was distilled into the fractionation train and found to contain only trimethylamine and the amine, $(CH_3)_2NCH_2N(CH_3)_2$, tetramethylmethylenediamine, the identity of which was found by infra red spectroscopy.
The trimethylamine and tetramethylmethylenediamine were separated at -84°C, and 0.0384 g (0.376 m mole) of $(CH_3)_2NCH_2N(CH_3)_2$ was found. From the mass of trimethylamine at the start of the reaction and that recovered, 0.0410 g (0.69 m mole) had been used up.

The solid residue, which was an off white colour, and amounted to 0.1683 g, was investigated in the dry box.
Approximately half of the product was transferred to a two-necked round bottomed flask, equipped with a small bulb as shown in Figure 20 Chapter 3, and removed from the dry box. The solid was taken into solution in the minimum quantity of distilled water, and potassium hydroxide pellets packed into the small bulb. The apparatus, completed with a tap cone connector was fitted to the fractionation section of the vacuum line, and the solution frozen and degassed three times. By carefully twisting the flask the KOH pellets were allowed to slide into the pale yellow aqueous solution, and the volatile material so produced distilled through a trap at -84°C and into a trap at -196°C.

The distillation was allowed to continue for approximately 10 minutes, then the flask isolated from the vacuum line. The volatile materials so collected were investigated by infra red spectroscopy, and found to contain only trimethylamine.

The caustic residue in the flask was exposed to the air and water was added to dissolve the excess KOH, and on cooling, under the tap a fine white solid appeared to form, which was filtered off using a porosity 4 sintered glass filter, dried by washing twice with dry hexane, and its identity found by infra red spectroscopy as a nujol mull, to be a tetramethylammonium salt.

The residue from the filtration was treated with a few drops of saturated sodium perchlorate solution and again a quantity of white solid precipitated. The infra red spectrum of this material showed $(CH_3)_4\overset{+}{N}$ absorptions as well as those attributable to $ClO_4^-$.

Part of the solid residue from the trimethylamine reaction was analysed and found to contain, (%), C, 18.17; H, 4.93; N, 5.91; Cl, 15.35; I, 55.52.

Thus, assuming the alkylation product of $(CH_3)_2NCl$ and $CH_3I$ to be of formula $C_6H_{18}N_2I_2Cl_2$, 0.1637 g (0.37 m mole) reacted with 0.69 m mole trimethylamine to yield 0.1683 g of solid, and 0.38 m mole tetramethylmethylenediamine, which indicates:

$$(CH_3)_4\overset{+}{N}\ (CH_3)_2N(ICl)_2^{-} + 1.9(CH_3)_3N = (CH_3)_2NCH_2N(CH_3)_2 + \text{SOLID}$$

The analytical figures for the solid indicate an empirical formula of $C_7H_{22}N_2I_2Cl_2$, 0.1683 g of which would correspond to 0.37 m mole. $C_7H_{22}N_2I_2Cl_2$ can be interpreted as $(CH_3)_4\overset{+}{N} + (CH_3)_3\overset{+}{N}H + \overset{-}{I} + ICl_2^{-}$, in which case the reaction with trimethylamine would be:

$$(CH_3)_4\overset{+}{N}(CH_3)_2N(\overset{-}{ICl})_2+2(CH_3)_3N \longrightarrow (CH_3)_4\overset{+}{N}+(CH_3)_3\overset{+}{N}H+\overset{-}{I}+ICl_2^{-}+(CH_3)_2NCH_2N(CH_3)_2$$

### 6. The Reaction Of $(CH_3)_3N$ With The Product Of The Alkylation Of $(CH_3)_2NCl$ By $CD_3I$

The reaction between $(CD_3)_2N(CH_3)_2$ $(CH_3)_2N(ICl)_2$ and $(CH_3)_3N$ was performed in an exactly analogous manner to that with the non deuterated product described in 5 above.

0.2729 g of the product from the alkylation of $(CH_3)_2NCl$ by $CD_3I$ was placed in a preweighed Rotaflow weight analysis cell, and evacuated on the vacuum line. 3.8515 g (65.28 m mole) anhydrous trimethylamine was then condensed into the cell, and the whole allowed to attain room temperature, and then placed on a flask shaker and agitated for 48 hours. On return to the vacuum line the cell was treated in the same way as described in 5 above, where 0.0639 g (6.26 m mole) $(CH_3)_2NCH_2N(CH_3)_2$ and

3.7826 g (64.41 m mole) $(CH_3)_3N$ were recovered, leaving 0.2801 g of a white solid in the weight analysis cell.

The white solid was treated with excess KOH as described above, and the products collected on the vacuum line. Infra red spectroscopy indicated that only trimethylamine had been formed and that it contained no C-D bonds.

In this reaction 0.61 m mole $(CH_3)_2N(CD)_3$ $(CH_3)_4N(ICl)_2$ reacted with 0.0689 g (1.17 m mole) $(CH_3)_3N$ to yield 6.26 m mole $((CH_3)_2N)_2CH_2$ and a solid residue. These figures indicate the stoichiometry:

$$(CH_3)_2\overset{+}{N}(CD_3)_2\ (CH_3)_2N(ICl)_2^- + 2(CH_3)_3N \rightarrow (CH_3)_2\overset{+}{N}(CD_3)_2 + (CH_3)_3\overset{+}{N}H + I^- + ICl_2^- + ((CH_3)_2N)_2CH_2$$

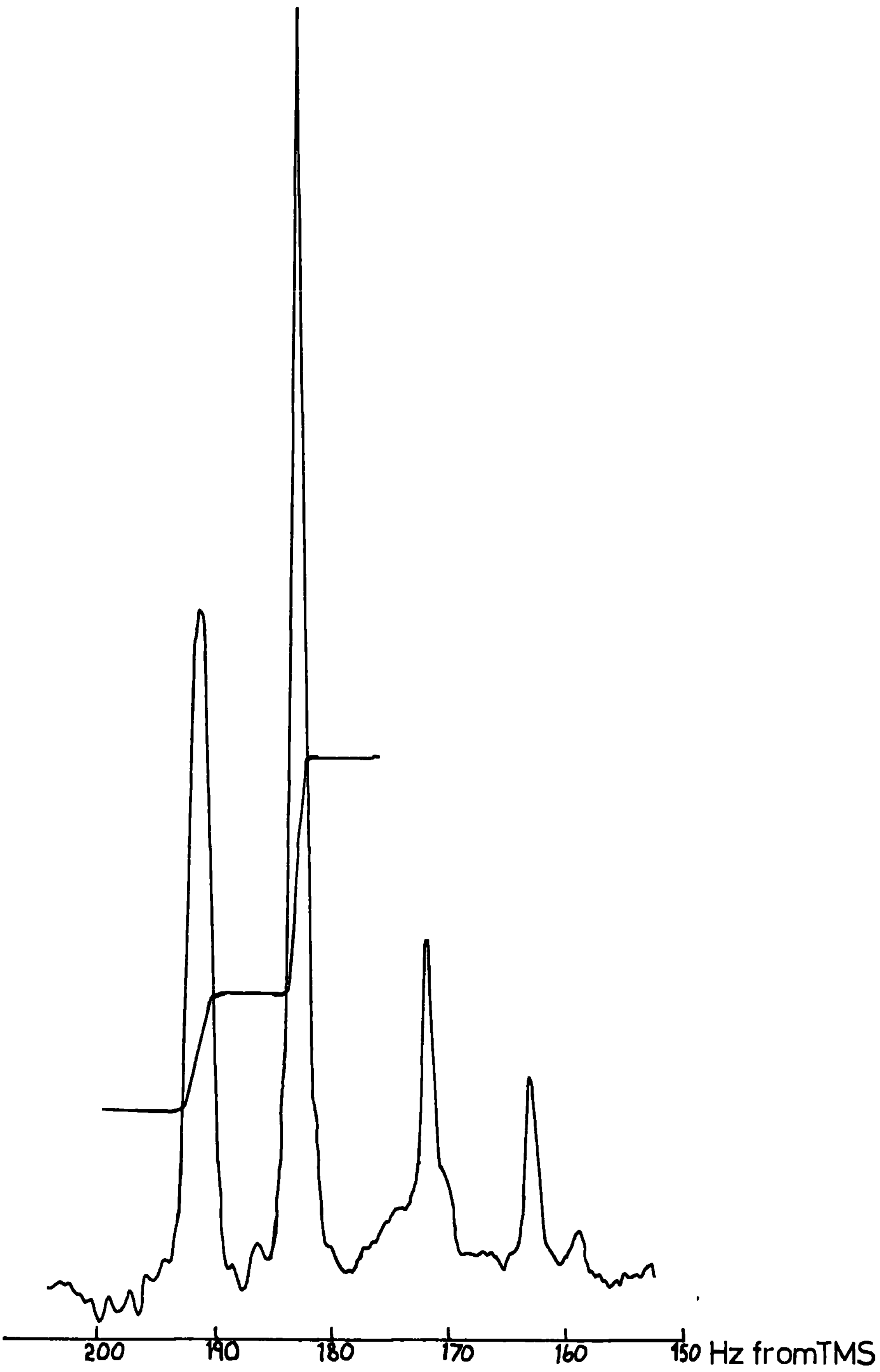
## 7. $^1H$ NMR Spectrum Of The Complex $(CH_3)_4\overset{+}{N}\ (CH_3)_2N(ICl)_2^-$

$^1H$ NMR spectroscopy in acetone, in which the complex dissolves, revealed two singlet absorptions, attributable to the complex. The sample was run at low temperature, (-30°C) and allowed to warm to room temperature where the decomposition was followed.

The initial spectrum recorded as quickly as possible, at -30°C is shown in Figure 68. The integration indicates a 2:1 ratio (1.82:1) for the peaks at (τ6.97) and (6.85) from external TMS. Figure 69a shows the spectrum as it warms to the probe temperature, (40°C), and Figure 69b shows the same spectrum after approximately 1 minute.

Thus the NMR data obtained indicates, that there are two types of protons in the molecule, and that they are sufficiently far apart not to influence one another. The integrated ratio's indicate that there are twice as many of one type as the other.

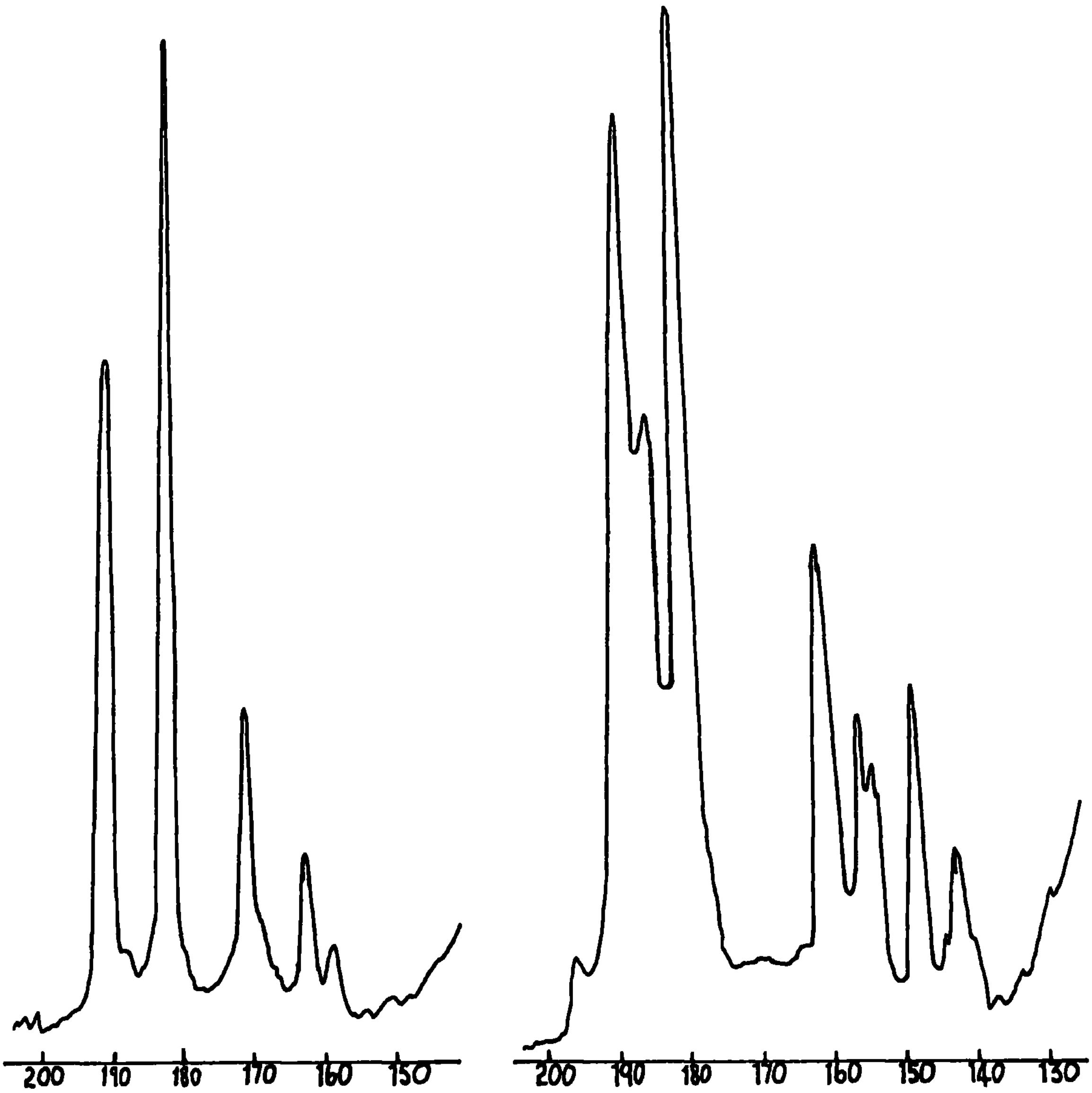
? er /



60MHz 'H NMR SPECTRUM OF $C_3H_9NClI$
IN ACETONE (at 0°C)

fig 68

fig69



(a) at 40° C

(b) after 1min at 40°C

60MHz $^1$H NMR SPECTRA OF $C_3H_9NClI$ IN ACETONE

# CHAPTER SIX

## NUCLEAR QUADRUPOLE RESONANCE AND INFRA RED SPECTROSCOPY

## Introduction

This Chapter deals with the application of Nuclear Quadrupole Resonance, and infra red spectroscopy, to the compounds prepared containing the species $(CH_3)_3\overset{+}{N}Cl$, and $(CH_3)_3\overset{+}{N}Br$.

The first technique gives information about the chlorine ionicity, and some insight into the electron density distribution in the N-Cl bond.

Infra red spectroscopy relates the compounds in which the ion $(CH_3)_3NCl$ appear with the compound $(CH_3)_3NCl_2$ in which polarisation of the Cl-Cl bond has been suggested in the extreme $((CH_3)_3\overset{+}{N}Cl,Cl^-)$ by Hantzch for all trimethylamine halogen complexes.

Infra red spectra were recorded using a Perkin Elmer model 457 spectrometer in the range 4,000-250 $cm^{-1}$, whilst for the range 400-40 $cm^{-1}$, a Beckman-RIIC FS720 Fourier spectrometer was used.

### 1. Nuclear Quadrupole Resonance Spectroscopy

Nuclear Quadrupole Resonance (NQR) is an important method of radio frequency spectroscopy. NQR is observed in nuclii of elements with an electric quadrupole moment, for example the halogens. The nuclii of over sixty isotopes of various elements have nuclear quadrupole moments.

Nuclear Quadrupole Resonance arises out of the interaction of an atomic nucleus, of non spherical symmetry, with a non uniform field of electrons surrounding it. The nuclear electric quadruple moment is the deviation of the nuclear charge distribution from spherical symmetry. The magnitude of the non uniformity of the electric field is given by the electric field gradient.

In general the charge distribution in nuclear spheroids can be either oblate or prolate in the direction of the nuclear spin, I. Such a charge distribution is termed an axial quadrupole. The non spherical distribution of charge about the nucleus can be represented as a sum of the charge, (a monopole), and a quadrupole. Only nuclii with $I > 1$ may have a nuclear electric quadrupole moment, Q. Such moments range in magnitude from -2 barn to 10 barn for all known values.

When two atoms A and B combine to form a molecule A-B, the formation of the bond A-B is accompanied by a strong, non uniform electric field along the bond direction (conventionally the z direction), and its magnitude is the component of the total field gradient tensor in this direction.

The field gradient, q, is a 3 x 3 tensor, such that

$$q_{xx} + q_{yy} + q_{zz} = 0 \qquad \text{(i)}$$

and in the z direction is given by

$$q_{zz} = \frac{\partial^2 V}{\partial z^2} \qquad \text{(ii)}$$

For axial symmetry, $q_{xx} = q_{yy}$, but where no such symmetry exists, i.e. when $q_{xx} \neq q_{yy}$, an additional term is defined, to describe the deviation of the field gradient from axial symmetry. This term is known as the asymmetry parameter, $\eta$, and is defined as

$$\eta = \frac{|q_{xx} - q_{yy}|}{q_{zz}} \qquad \text{(iii)}$$

There are several factors which result in the atomic nucleus experiencing a non uniform electric field. The field gradient is mainly determined by the valence electrons, and the largest contribution is that of electrons in uncompletely filled p orbitals. Charges lying close to the atom under consideration, for example neighbouring ions, atoms or molecules, are also significant contributors to the value of the electric field gradient.

The interaction of the quadrupole moment, Q, and the electric field can be expressed by the Hamiltonian:

$$H = Q\nabla E \qquad \text{(iv)}$$

or

$$H = \frac{e^2Qq}{4I(2I-1)}\left[3I_z^{\,2} - I(I+1) + \frac{\eta}{2}(I+^2 + I-^2)\right] \qquad \text{(v)}$$

where I+ and I- are raising and lowering operators, or sometimes termed shift operators.

Hamiltonian (v) has Eigenvalues:

$$E = \frac{e^2Qq}{4I(2I-1)}\left[3m^2 - I(I+1)\right]\left(1 + \frac{\eta^2}{3}\right)^{1/2} \qquad \text{(vi)}$$

where $m_I$ = I, I-1, -I, the magnetic quantum number.

Equation (vi) shows that for states where $m_I$ differ only by sign thus preclude the separate determination of asymmetry parameter and coupling constant.

Transitions between quadrupole levels are brought about by coupling the nuclear magnetic dipole moment with an oscillating magnetic field of appropriate frequency. For nuclii of spin $^3/_2$, there are two doubly degenerate energy levels and thus only one transition between them. The frequency of the transition, $\nu$, can be deduced from (vi) above and is given by (vii), for $\eta = 0$,

$$\nu = \frac{e^2Qq}{2h} \qquad \text{(vii)}$$

where the term $e^2Qq/h$ is known as the nuclear quadrupole coupling constant, and for instances where the gradient is not axially symmetric, $\nu$ is given by:

$$\nu = \frac{e^2Qq}{2h}\left(1 + \frac{\eta^2}{3}\right)^{1/2} \qquad \text{(viii)}$$

For nuclii where $I > 3/2$, the number of transitions possible increases, as does the complexity of the expressions relating the frequency of the transition to the coupling constant. Many can only be solved numerically, and the transition frequency equations tabulated for reference (153), for example $^{127}I$ has a spin of $5/2$, and the equations for the two observable transitions are:

$$\nu_2(\pm 5/2 \quad \pm 3/2) = \frac{6}{20}\,\frac{e^2Qq}{h}(1 - 0.2037\eta^2 + 0.162\eta^4 \ldots\ldots) \qquad \text{(ix)}$$

$$\nu_1(\pm 3/2 \quad \pm 1/2) = \frac{3}{20}\,\frac{e^2Qq}{h}(1 + 0.0926\eta^2 - 0.634\eta^4 \ldots\ldots) \qquad \text{(x)}$$

for small asymmetry parameter, ($< 0.3$).

For nuclii of spin $3/2$, such as chlorine, determination of both asymmetry parameter and coupling constant can be carried out if the degenerancy of the $m_I$ levels are lifted. This in practice utilises the Zeeman effect, where a weak external magnetic field of the order of 10-50 gauss is applied to the sample.

In the case of certain classes of compounds, however, ignorance of the asymmetry parameter need not significantly affect the accuracy of the coupling constant determination, since for $\eta$ of 10%, the value of $(e^2Qq/h)$ from the measured frequency is $1.9967\nu$ as opposed to $2\nu$ for

$\eta = 0$, imposing an error of $1.6 \times 10^{-5}\%$ for frequencies around 45 MHz.

The measurement of nuclear quadrupole coupling constants can provide a great insight into concepts useful to the chemist, yet difficult to quantify. Terms such as ionic character, and partial double bond character, can be given new meaning by applying approximate methods to the results obtained from NQR experiments.

The interpretation of NQR data, in terms of concepts which are useful to the chemist, such as ionic character, has been considered by several workers.

Townes and Dailey (123) deduced expression (xi) below, relating the quadrupole coupling constants to the amount of s character in a covalent bond, between two atoms:

$$e^2Qq_{cov} = -(1 - s)e^2Qq_{at} \qquad \text{(xi)}$$

This equation can be modified by introducing factors to take account of the ionic character, d-character, and $\pi$-character of the bond, and the resulting equation is shown below

$$e^2Qq_{cov} = -(1 - s + d)(1 - \cancel{I}) - \pi)\ e^2Qq_{at} \qquad \text{(xii)}$$

Equation (xii) above is normally applied to compounds in which the atom exhibiting NQR, is at the negative end of a bond dipole, or, where the electronegativity of the resonating atom is less than, or equal to, the electronegativity of its partner in the bond.

If the resonating atom is at the positive end of a bond dipole, such that the bond is polarised thus $\overset{\delta-}{A}\text{—}\overset{\delta+}{B}$ , then account should be taken of the effect that this positive charge has on the orbitals of the atom, which contribute to the electric field gradient at the nucleus.

Townes and Dailey (123) suggest that a unipositive formed charge on an atom requires the number of unbalanced p electrons to be multiplied by a factor of 1.25, estimated from atomic fine structure. Further, a multiplicand of 1/1.25 should be applied in cases where a negative formal charge is apparent in the atom. Clearly a factor is required to account for instances in which the atom is neither charged -1, 0 or +1, but some intermediate value determined by the ionic character.

Equation (xiii) below relates the coupling constants to the ionic character and s character in cases where the atom is the more electropositive.

$$e^2Qq_{mol} = -(1 - s)\ 1 + i(1 + 2\varepsilon)\ e^2Qq_{at} \qquad \text{(xiii)}$$

where $\varepsilon$ has been estimated for chlorine as 0.14 (124).

Chandra (125), obtained a similar type of expression relating the ionic character and s hybrid character of a bond to the nuclear quadrupole coupling constant.

If $N_x$, $N_y$ and $N_z$ represent the electron population in the $p_x$, $p_y$ and $p_z$ orbitals respectively, then if an amount of double bond character, $\pi$ ; s character s, d character d, and ionic character i, are present then, $N_x = 2$, $N_y = (2 - \pi)$ and $N_z = (1 + s - d + i)$, where the z axis is along the bond.

Now the number of unbalanced p electrons on the atom is related to the coupling constant in the free atom, by equation (xiv)

$$e^2Qq = \left[\frac{N_x + N_y}{2} - N_z\right] e^2Qq_{at} \qquad \text{(xiv)}$$

and hence

$$e^2Qq_{mol} = (1 - s + d - i) - \pi/2)e^2Qq_{at} \qquad \text{(xv)}$$

Wilmshurst (126), derived a simple relation between coupling constant, ionic character and percentage s hybridisation of the resonating nucleus. Using orbital functions of Gordy (127) expression (xvi) was deduced.

$$e^2Qq_{mol} = 3\alpha(1 - i)e^2Qq_{at} \qquad \text{(xvi)}$$

where $\alpha$ is the percentage s hybridisation of the p orbitals such that the normalised bonding orbital is given by equation (xvii)

$$\psi = \sqrt{(1 - 3\alpha)}\, s + \sqrt{3\alpha}\, p_z \qquad \text{(xvii)}$$

and in order to account for orbital contraction when the atom in question is the more electropositive partner in the bond, equation xvi is adjusted by a factor 1 + c as shown below

$$e^2Qq_{mol} = 3\alpha(1 + c)(1 - i)e^2Qq_{at} \qquad \text{(xviii)}$$

The value of c given by Wilmshurt (126) was that due to Townes and Dailey (123), i.e. 0.25.

Gordy (128) does not consider changes in both ionic character and hybridisation when accounting for changes in coupling constant. He maintains that the hybridisation, and hence s character, of halogen bonding orbitals are fixed, and changes in coupling constant from one compound to another is due entirely to changes in ionic character, and only in exceptional circumstances, such as when the halogen is the more electropositive partner in a bond, such that a large positive charge exists, then hybridisation can be considered.

Gordy obtained the expression

$$1 - \frac{e^2Qq}{e^2Qq_{at}} = i(1 + 0.13\frac{e^2Qq}{e^2Qq_{at}} - a_s^2 - a_d^2) + a_s^2 - a_d^2 \qquad \text{(xix)}$$

in which $a_s^2$ and $a_d^2$ are respectively the amounts of s and d character of the bond orbital, which re-arranges to (xx), neglecting nuclear screening.

$$\frac{e^2Qq}{e^2Qq_{at}} = (1 - s + d) - i(1 - s - d) \qquad \text{(xx)}$$

where s and d are now the amounts of s and d character, and i is the ionic character.

Simplification of expression (xix), above was accomplished by Gordy, by considering two extreme cases of halogen bonding namely, purely ionic, as in KCl or KBr, and purely covalent as in $Cl_2$ or $Br_2$.

Gordy argued that, since from $Cl_2$ coupling constant data the ratio $e^2Qq_{mol}/e^2Qq_{at}$ was unity, and the ionic character zero, hence application of (xix) led to $a_s^2 = a_d^2$ or no hybridisation.

Considering KCl, where the coupling constant ratio is observed to be zero, and the ionic character equal to unity, equation (xix) shows that $a_d^2 = 0$, i.e. no d hybridisation, and terms in $a_s^2$ cancel out. This led Gordy to the conclusion that hybridisation does not exist either in pure covalent $Cl_2$ or in pure ionic KCl, unless it exists in such a form as to have no effect on the coupling constant, and further that based on the preceding observation, little if any detectable hybridisation exists in mixtures of the two bonding forms.

Utilising this deduction, that s = d = 0, equation (xx) becomes:

$$\frac{e^2Qq}{e^2Qq_{at}} = (1 - i) \qquad \text{(xxi)}$$

There thus appears to be some conflict in the interpretation of changes in coupling constant in terms of ionic character, and hybridisation. Gordy on the one hand considering no hybridisation of the chlorine bonding orbitals in the greater majority of carbon halogen compounds, whereas Townes and Dailey, at the other pole, consider both hybridisation and ionicity changes. Townes and Dailey however, do go part way to the Gordy concept, in later appraisals of their treatment, where a rule, somewhat arbitrarily, states that in compounds such as X-Cl, the halogen bonds are hybridised with 15% s character whenever the halogen is more electronegative by 0.25 unit than the atom to which it is bonded (129).

In all these treatments, whichever is nearest the true situation, no unique value for ionic character or hybrid character can be obtained, and since it is not possible to obtain independant values of ionic and hybrid character, then assumptions must be made either of hybridisation or ionic character.

It is common to assume the hybridisation and determine ionic character from coupling data, or to utilise other methods of determining ionic character and obtain hybridisation.
Most methods of determining ionic character depend on its relationship

with electronegativity, and indeed there are many varied expressions.

Pauling (130), obtained an exponential relationship shown in (xxii)

$$\text{ionic character} = 1 - \exp(-0.25(Xa - Xb)^2) \qquad \text{(xxii)}$$

where Xa, Xb are the atomic electronegativities. This does not fit particularly well with values obtained from dipole moment determinations.

Gordy (128) utilised equation (xxi), above and plotted ionic character of diatomic molecules obtained from quadrupole coupling data, against the electronegativity difference of the two atoms, and found a linear relationship up to around 90% ionic character, or electronegativity difference of around 2 units, after which the curve levelled off toward 100% ionicity, with increasing electronegativity difference. This led Gordy to the approximate rule:

$$\text{ionic character} = \tfrac{1}{2}|( Xa - Xb )| \quad \text{for} \quad |Xa - Xb| < 2 \qquad \text{(xxiii)}$$

Hannay and Smyth (131) from bond dissociation energy considerations obtained:

$$\text{ionic character} = 0.16(|Xa - Xb|) + 0.035(|Xa - Xb|)^2 \qquad \text{(xxiv)}$$

which fits the experimentally determined ionicity from dipole moments, better than that of Pauling.

Other methods of ionic character estimation are due to Wilmshurst (126), and (132), where consideration is given to electron distribution in a bond A-B. For a two electron bond the pair of electrons will divide themselves between the two atoms in the ratio of their relative electronegativities, such that $\tfrac{1}{2}Xa/[Xa + Xb]$ electrons are on atom A and $\frac{1}{2}Xb/[Xa + Xb]$ electrons are on atom B. Definition of the ionic character as one half the excess number of electrons on one atom relative to the other results in equation (xxv)

$$\text{ionic character} = \frac{|Xa - Xb|}{|Xa + Xb|} \qquad \text{(xxv)}$$

In order to utilise any one of these expressions in the correlation of nuclear quadrupole coupling constants, requires a knowledge of the electronegativity of the atoms involved in the bonding. It is clearly unsatisfactory to consider the electronegative of nitrogen, in for example $(CH_3)_3N$, as being equal to that in for example $(CH_3)_3NCl$, or in $N_2$, and this situation has led to the development of group electronegativity and effective electronegativities.

The Mulliken definition of electronegativity (133) as:

$$Xa = \frac{1}{2}(I^a + E^a) \qquad \text{(xxvi)}$$

where $I^a$ and $E^a$ are the ionisation potential and electron affinity of atom A, is satisfactory, but not parameterised for A in structures such as $R_4A$, but the definition due to Gordy (134), that the electronegativity of an atom is "the potential resulting from the unscreened nuclear charge of the bonded atom effective on a bonding electron when the electron is at a distance from the nucleus equal to the covalent radius r",

$$Xa = \frac{(Zeff)e}{r}$$

led to the empirical expression (xxvii), for the electronegativity of an isolated atom:

$$Xa = 0.31\,\frac{n + 1}{r} + 0.5 \qquad \text{(xxvii)}$$

where n is the number of valence electrons.

Allred and Rochow (135), derived a similar expression considering the force of attraction between an electron and its nucleus, when the electron is at the covalent boundary, r, of the atom. By simple electrostatics, this force is given by:

$$\text{Force} = \frac{e^2 Zeff}{r^2} \qquad \text{(xxviii)}$$

where eZeff is the charge which is effective at the electron due to the nucleus and its surrounding electrons, and the force obtained is thus a measure of the "absolute electronegativity" of the atom.

In order to bring values obtained by (xxviii) in to line with scales such as that due to Pauling (130), obtained from bond energy considerations, the equation (xxix) was derived.

$$Xa = 0.359 \frac{Zeff}{r^2} + 0.744 \qquad \text{(xxix)}$$

by plotting $Zeff/r^2$ against Pauling electronegativities.

The values obtained for the elements, by both Gordy and Allred and Rochow, are in reasonable agreement, but there are exceptions. A good example is the Si and Ge figures, where Allred and Rochow give 1.74 for Si and 2.02 for Ge, whilst Gordy gives 1.82 for Si and 1.77 for Ge. Not only are the values numerically different, but in one case Ge is more electronegative than Si, and in the other case Ge is less electronegative than Si. Evidence (136), suggests that Ge is more electronegative than Si.

The differences in the two scales are probably accountable for by Gordy's consideration of the potential at the covalent boundary whilst Allred and Rochow consider the force.

Wilmshurst (137), and Chandra (132) used expression (xxvii) to calculate the electronegativity of species such as $-CH_3$. The method of Wilmshurst differs slightly to that of Chandra and consequently differing values of electronegativity result, for example, Wilmshurst calculates a value of 2.63 for $-CH_3$ whereas Chandra calculates 2.42, and for $-CCl_3$ Wilmshurst finds 3.03 whereas Chandra 2.07.

It should be pointed out, however, that a group electronegativity must depend on the rest of the molecule, because it is a property of the group obtained by adiabatic breaking of the bond between the group and the rest of the molecule . This is a limitation to the concept of group electronegativities not considered by Chandra or Wilmshurst, and of course the values must therefore depend on the compound from which they were obtained. Expression (xxvii) can be used, however, as long as the value of r, the covalent radius, is known, or can be estimated for the particular compound in which the group appears.

The inadequacy of atomic electronegativities in dealing with atoms in real situations such as nitrogen in $(CH_3)_4N^+$, indicates that a radically new approach be considered. Work by Hinze (137) defined a a quantity termed orbital electronegativity, much in the same way as Pauling defined atomic electronegativity (139) as a measure of the power of an atom, to attract an electron to itself, and thus the orbital electronegativity defined, as the derivative of the energy of the atom with respect to the charge in the orbital, so that the orbital electronegativity is a measure of the power of an atom, as it may exist in a molecule, to attract an electron in a given orbital, to itself.

The definition implies that the occupation number of the orbital considered can take both integral and non integral values and, that, if this is true then the energy of the atom is a continuous and differentiable function of the occupation number.

That the occupation number can be non integral is not entirely satisfactory from a strict quantum mechanical point of view, but nevertheless, partial atomic charges are freely used and thus by implication acknowledge non integral values of the occupation number. ? [illegible]

Utilising this concept of electronegativity, ionic character can be defined in terms of charge transfer necessary to make the bond electronegativities of the bonded atoms equal. Thus if the occupancy of the j th bonding orbital of atom A in A-B is n; then the ionic character of the bond is:

$$\text{ionic character} = |n_j - 1| \qquad (xxx)$$

and in terms of electronegativity:

$$\text{ionic character} = 1/2 \left| \frac{X^{\circ}a - X^{\circ}b}{c_a + c_b} \right| \qquad (xxxi)$$

where $X^{\circ}$ refers to orbital electronegativity and the constants $c_a$, $c_b$ are formulated from ionisation potentials and electron affinities of the orbitals concerned.

This relationship for ionic character reduces to that of Gordy when $c_a + c_b = 1$, but in real terms $|c_a + c_b|$ is found to be generally greater than 1 (140), for compounds such as H-X (X = F, Cl, Br, I, Li, Na).

It is interesting to note that values of ionic character calculated in this way, agree, in general, better with those calculated by Hannay and Smyth,(equation (xxiv)),using their own electronegativities, since for small differences in Xa and Xb equation (xxiv) reduces to:

$$\text{ionic character} = 0.16|Xa - Xb| \qquad \text{(xxxii)}$$

This is because the Hannay and Smyth electronegativities were calculated from bond dissociation energies and thus include effects due to hybridisation.

In order to use equation (xxxi), values for $c_a$ and $c_b$ must be known, not only for the orbitals in the particular hybridisation they are in, but for the orbitals in the particular compound being considered, and since the values of c are determined by the ionisation potential and electron affinity of the orbitals considered, the limitations are clear.

It is further clear that according to equation (xxxi), no unique relation exists between electronegativity and ionic character.

Thus in the interpretation of NQR data there are three areas in which there is uncertainty.

Firstly, the hybridisation of the absorbing atom, secondly, the assessment of ionic character, and thirdly, the values of electronegativity necessary to estimate ionic character, or, in the case of Townes and Dailey, s character. The latter of the three is highlighted by considering nitrogen and chlorine. According to Townes and Dailey's rule relating s character to electronegativity difference, then if Mullikens electronegativities are used, nitrogen is less electronegative than chlorine by 0.67 (N, 2.33; Cl, 3.00) and would thus indicate 15% s character, whereas if Pauling's values are used then nitrogen is less electronegative than chlorine by only 0.12 (N, 3.04; Cl, 3.16) indicating 0% s character, since the difference is less than 0.25. (Electronegativity values from ref. 141).

The question of hybridisation is related to bond strengths which is in turn related to the extent to which two orbitals overlap when a bond is formed.

Both molecular orbital and valence bond theory require that in order to form a strong bond, the atomic orbitals forming the bond must overlap to as great an extent as possible, and that the energies of the overlapping orbitals should be of comparable magnitude (142). It is known that sp hybrid orbitals can overlap more strongly than pure s or pure p orbitals, and thus it seems likely that in order to meet the energy matching requirement for strong bonds then hybridisation would occur to an extent required by the energy mis-match of the combining orbitals.

Gordy's original suggestion that hybridisation does not occur, except on, for example, halogens with positive charges in compounds such as A-Cl, appears untenable, indeed hybridisation is certainly likely on halogens polarised $Cl^{\delta+}$, but it seems reasonable that hybridisation can occur on halogens polarised $Cl^{\delta-}$.

Gordy's explanation of no hybridisation, outlined earlier, can be examined more closely. Coupling constant data for the halogens was used by Whitehead (143) to show that for the gaseous molecule $Cl_2$, some s hybridisation does occur, since the ratio of the observed frequencies for atomic chlorine (54.87 MHz) and for molecular chlorine (54.2475 MHz) indicate 2% s character. Bromine and iodine do not show this, but no d hybridisation was accounted for.

It would thus appear that hybridisation should be considered when interpreting NQR data, and that the hybridisation of the atom under observation is unique, and not equatable to that of the same atom in a variety of different compounds.

This was summed up by Whitehead (144) who studied a large number of halides of C, Si, N, B, P, S and found that although a general relationship exists between the s character of chlorine and its solid state NQR frequency, a unique value of hybridisation of the chlorine covering all types of compounds is meaningless. Each molecule must be considered on its own, and assessment of s character made from what element the chlorine is bonded to.

Thus since hybridisation cannot be assumed in equations relating coupling constants to hybridisation and ionic character, an independant assessment of ionic character is necessary, with the possible exception of the method of Whitehead involving orbital electronegativities, since expressions for hybrid orbital electronegativities, in terms of pure s or p orbital electronegativities involve the amount of s character in the bonding orbitals (145). Indeed this method appears to be the most satisfactory since no assumptions, apart from those implicit in the concept of orbital electronegativity outlined earlier, are made. However, as pointed out, the method requires a knowledge of ionisation potentials and electron affinities of orbitals involved in the actual compound under investigation.

Independant assessment of ionic character is most easily carried out from electronegativity values, and although many scales exist, in general as long as one scale is used throughout a correlation, trends may be observed even though absolute values are not determined.

In order to utilise methods of obtaining ionic character from electronegativities, it is necessary to estimate the effective electronegativity of atoms in a group, and to this end the method of Chandra (132) appears to give values most consistent with the literature.

## Results and Discussion

Nuclear quadrupole resonance spectroscopy has been carried out on the compounds $(CH_3)_3\overset{+}{N}\text{-}Cl\ ClO_4^-$ , $(CH_3)_3\overset{+}{N}\text{-}Cl\ BF_4^-$ and $CH_3NCl_2$, using a Decca NQR spectrometer. The frequencies observed at -196°C are shown in Table 19 along with the coupling constants calculated assuming no asymmetry parameter, the spectra are shown in Figures 70, 71 and 72.

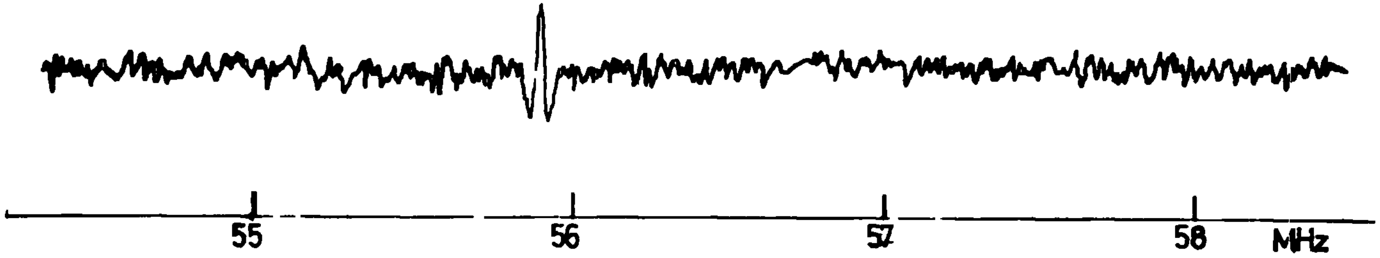
### TABLE 19

### $^{35}$Cl NQR FREQUENCIES AND COUPLING CONSTANTS FOR $CH_3NCl_2$, $(CH_3)_3N^+Cl\ ClO_4^-$ AND $(CH_3)_3N^+Cl\ BF_4^-$

| Compound | MHz | $e^2Qq/h$ ( $^{35}$Cl) |
|---|---|---|
| $CH_3NCl_2$ | 47.95 | |
| | 48.01 | 96.70 ?<br>average |
| | 48.32 | |
| | 49.07 | |
| $(CH_3)_3N^+Cl\ ClO_4^-$ | 56.09 | 112.18 |
| $(CH_3)_3N^+Cl\ BF_4^-$ | 55.89 | 111.78 |

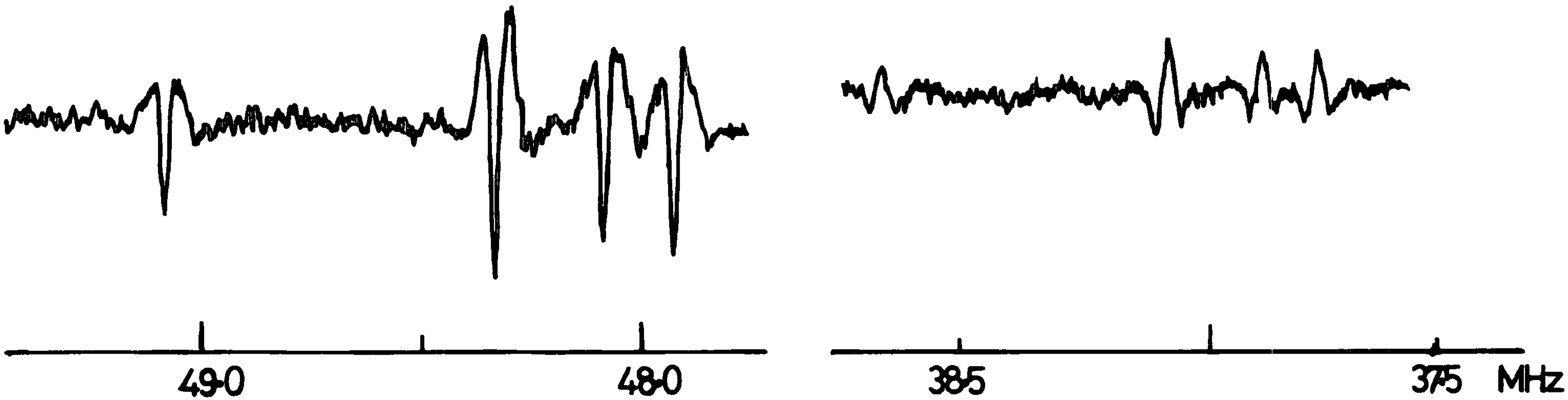
Cl$^{35}$ NQR SPECTRUM OF $(CH_3)_3\overset{+}{N}Cl\ Cl\overset{-}{O}_4$
AT 77K

fig 70



Cl$^{35}$ NQR SPECTRUM OF $(CH_3)_3\overset{+}{N}Cl\overset{-}{B}F_4$
AT 77K

fig 71



(a) $Cl^{35}$ (b) $Cl^{37}$

fig 73 NQR SPECTRUM OF $CH_3NCl_2$ AT 77 K

Absorptions due to other compounds containing this cation, $(CH_3)_3N^+Cl\ OSO_3CH_3^-$; $(CH_3)_3N^+Cl\ OSO_2F^-$, were not observed.

The position of the absorptions in the $^{35}$Cl NQR spectral range indicate that the chlorine is at the positive end of the N-Cl bond dipole in the cations, since both the frequencies are in excess of that of molecular chlorine (54.873 MHz, (146)). The values found are compared with those found for other nitrogen chlorine compounds in Table 20.

### TABLE 20

### $^{35}$Cl NQR FREQUENCIES FOR SOME NITROGEN CHLORINE COMPOUNDS

| Compound | MHz (-196°C( $^{35}$Cl)) | Ref. |
|---|---|---|
| N-chlorobenzotriazole | 56.743 | 147 |
| Chlorotrimethylammonium perchlorate | 56.09 | This work |
| Chlorotrimethylammonium fluoroborate | 55.89 | This work |
| N-chlorosuccinimide | 54.10 | 147 |
| Dichloramine T | 51.60 | 148 |
| Methyldichloramine | 48.35 | This work |
| 2,6 dibromo,N-chloro,p-benzoquinninimide | 46.306 | 147 |
| Dimethylchloramine | 43.67 | 151 |

## Interpretation Of The NQR Data In Terms Of The Approximate Methods

The methods of Townes and Dailey, and, Wilmshurst and Chandra, can be used to interpret the data given in Table 19, to determine how ionic, and how the chlorine is hybridised in the ion $(CH_3)_3N^+Cl$. For comparative purposes values for the isostructural phosphorous analogue, $(CH_3)_3P^+Cl$ can be obtained.

## Electronegativities

The values of electronegativity given by Pauling (130) for the relevant atoms are shown in Table 21.

TABLE 21

| Atom: | H | C | N | O | P | Cl |
|---|---|---|---|---|---|---|
| Electronegativity: | 2.1 | 2.5 | 3.0 | 3.4 | 2.1 | 3.0 |

In order to utilise any of the relationships between coupling constant and ionic and hybrid character, the electronegativities of entities such as $(CH_3)_3\overset{+}{N}-$ or $(CH_3)_3\overset{+}{P}-$ must be computed. The method used to obtain these values is that of Chandra (132) based on Gordy's definition of electronegativity from nuclear screening considerations.

Gordy's expression for the electronegativity of an isolated atom (128, 134) is given by

$$X = 0.31\,\frac{n+1}{r} + 0.50 \qquad \text{(xxvii)}$$

where n is the number of valence electrons and r is the covalent radius.

In order to use equation (xxvii) in the estimation of group electronegativities, n must be replaced by n*, where n* is now the effective number of valence electrons the central atom A, of a group $AB_y$, has, due to the effects of the combined electronegativity differences between A and $B_y$.

Chandra (132) formulated n* as

$$n^* = n + m - 2m\left[\frac{Xa}{Xa + Xb}\right] - p\left[\frac{Xa}{Xa + Xb}\right] \qquad \text{(xxxiii)}$$

since in the group AB, derived from X-AB, the number of electrons on atom A due to m bonds with atom B will be

$$2m \frac{Xa}{Xa + Xb}$$

and if B has any non bonded valence electrons, the effect of p resonance contributors of the type $^{-}AB^{+}$ is given by

$$\frac{p\,Xa}{Xa + Xb}$$

n is the number of valence electrons atom A has conventionally.

Using this method, values for the effective electronegativities of various central atoms in both N and P -Cl compounds are shown in Table 22.

TABLE 22

CALCULATED GROUP ELECTRONEGATIVITIES

| Group | Effective Electronegativity |
|---|---|
| $(CH_3)_3\overset{+}{N}$ - | 3 |
| $(CH_3)_2N$- | 2.9 |
| $(CH_3)NCl$- | 2.9 |
| $(CH_3)_3\overset{+}{P}$ - | 2.2 |
| $(CH_3)_2P$- | 2.2 |
| $(CH_3)ClP$- | 2.1 |

The electronegativity of A , where A is N or P was calculated by adding half the electronegativity difference between the atom and the next in the periodic table, to the value of the atom. Calculations involving groups with lone pairs included values for the electronegativity of the filled orbital, assumed to be $sp^3$, from Whitehead (149). The values used were $N(sp^3)$, 1.32; $P(sp^3)$, 1.59.

The values for the covalent radii are shown below.

| Element or ion: | N | $N^+$ | P | $P^+$ | C |
|---|---|---|---|---|---|
| Covalent radius: | 0.70 | 0.69 | 1.10 | 1.09 | 0.77 |

## Ionic Character

Using the values for the electronegativities calculated above, the ionic characters of various N-Cl and P-Cl compounds are shown in Table 23, determined by various methods.

### TABLE 23

### CALCULATED IONIC CHARACTERS OF X-Cl BOND

| Compound/ion | Ionic Character of X-Cl Bond | | | |
|---|---|---|---|---|
| | 1* | 2* | 3* | 4* |
| $(CH_3)_3\overset{+}{N}-Cl$ | 0 | 0 | 0 | 0 |
| $(CH_3)_2NCl$ | 0.017 | 0.05 | 0.016 | 0.0025 |
| $(CH_3)NCl_2$ | 0.017 | 0.05 | 0.016 | 0.0025 |
| $(CH_3)_3\overset{+}{P}-Cl$ | 0.15 | 0.4 | 0.15 | 0.15 |
| $(CH_3)_2PCl$ | 0.15 | 0.4 | 0.15 | 0.15 |
| $(CH_3)PCl_2$ | 0.18 | 0.45 | 0.17 | 0.18 |

* Method 1 $i = \frac{Xa - Xb}{Xa + Xb}$, Wilmshurst, Chandra

Method 2 $i = \frac{Xa - Xb}{2}$, Gordy

Method 3 $i = 0.16\,|Xa - Xb| + 0.035\,|Xa - Xb|^2$, Hannay & Smyth

Method 4 $i = 1 - \exp(-0.25(Xa - Xb)^2)$, Pauling

## Hybrid Character

Using the values of ionic character determined in Table 23, the s character of the halogen bonding orbital can be estimated. Tables 24 and 25 show s character obtained using methods of Townes and Dailey (Table 24),

$$\frac{e^2Qq}{e^2Qq_{at}} = [(1 - s + d)(1 - i) - \pi]$$

and by Wilmshurst, (Table 25),

$$\frac{e^2Qq}{e^2Qq_{at}} = 3\alpha(1 - i), \ s = 1 - 3\alpha$$

### TABLE 24

### s CHARACTER OF X-Cl BOND CALCULATED USING THE TOWNES AND DAILEY EXPRESSION

| Compound | $\nu^{35}Cl$ MHz (-196°C) | $\frac{e^2Qq}{e^2Qq_{at}}$ | s Character (Townes and Dailey) 1* | 2* | 3* | 4* |
|---|---|---|---|---|---|---|
| $(CH_3)_3\overset{+}{N}-Cl$ | 56.09 | 1.022 | -0.022 | -0.022 | -0.022 | -0.022 |
| $(CH_3)_2NCl$ | 43.67 | 0.7959 | 0.19 | 0.16 | 0.19 | 0.20 |
| $CH_3NCl_2$ | 48.35 | 0.8221 | 0.16 | 0.13 | 0.16 | 0.17 |
| $(CH_3)_3\overset{+}{P}Cl$ | 29.09 | 0.5302 | 0.38 | 0.11 | 0.38 | 0.38 |
| $CH_3PCl_2$ | 26.08 | 0.4753 | 0.44 | 0.14 | 0.43 | 0.42 |

## TABLE 25

## s CHARACTER OF X-Cl BOND CALCULATED USING THE WILMSHURST EXPRESSION

| Compound | $\nu\,^{35}$Cl MHz (-196°C) | $\frac{e^2Qq}{e^2Qq_{at}}$ | s Character (Wilmshurst) | | | |
|---|---|---|---|---|---|---|
| | | | 1* | 2* | 3* | 4* |
| $(CH_3)_3\overset{+}{N}Cl$ | 56.09 | 1.022 | -0.02 | -0.02 | -0.02 | -0.02 |
| $(CH_3)_2NCl$ | 43.67 | 0.7959 | 0.19 | 0.16 | 0.19 | 0.22 |
| $(CH_3)NCl_2$ | 48.35 | 0.8221 | 0.16 | 0.13 | 0.16 | 0.19 |
| $(CH_3)_3\overset{+}{P}Cl$ | 29.09 | 0.5302 | 0.37 | 0.13 | 0.37 | 0.37 |
| $(CH_3)PCl_2$ | 26.08 | 0.4753 | 0.43 | 0.13 | 0.43 | 0.43 |

* see footnote to Table 23.

Values for $(CH_3)_3\overset{+}{P}$-Cl from ref. 151, and for $CH_3PCl_2$ from ref. 124.

From Tables 23, 24 and 25 it can be seen that the s character is fairly insensitive to large changes in ionic character when the ionic character is small and non zero, indeed if Gordy's estimate of ionic character is used, then the s character does not change appreciably over several orders of magnitude change in ionic character.

The small negative s character for $(CH_3)_3\overset{+}{N}$-Cl indicates that the estimate of the group electronegativity of $(CH_3)_3\overset{+}{N}$- is too small, since from the resonance frequency, the s character would be expected to be small, and if the same order as in $Cl_2$ (around 2%). A value of zero for the ionic character in this ion again seems unreasonable since some polarity does exist.

For analogous compounds ($CH_3NCl_2$, $CH_3PCl_2$) a tenfold increase in ionic character is indicated by all methods except Paulings. On this basis the ionic character of the N-Cl bond in $(CH_3)_3\overset{+}{N}-Cl$ would be expected to be around 0.015, which would indicate an almost pure p chlorine orbital.

A value of 0.015 for the ionic character would indicate an effective electronegativity for $(CH_3)_3\overset{+}{N}-$ of 3.09, using the expression

$$i = \frac{Xa - Xb}{Xa + Xb}$$

which if substituted into equation (xxvii), gives a value of 0.67 for the covalent radius of nitrogen in $(CH_3)_3\overset{+}{N}-Cl$. This represents a fairly large shortening of the C-N bond, it being 1.44 A°, as opposed to 1.47 A° in $(CH_3)_4\overset{+}{N}$ $ClO_4^-$ and $ICl_2^-$ (152).

The ratio of the coupling constants of chlorine in $(CH_3)_3\overset{+}{N}-Cl$ to $(CH_3)_3\overset{+}{P}-Cl$ is 1.93, assuming of course, zero asymmetry parameter. This and the change in ionic character is a consequence of the greater electronegativity of nitrogen. The possibility of d orbital participation in partial P-Cl $\pi$-bonding cannot be ruled out, however it is unlikely in the N-Cl case. The trend in coupling constant from $(CH_3)_2N-Cl$ to $CH_3NCl_2$ is reasonable because both increased chlorine substitution and loss of a methyl group would tend to cause positive shifts in the NQR frequency. The negative effect of adding a methyl group to $(CH_3)_2NCl$ is completely swamped by the formation of a cationic species, $(CH_3)_3\overset{+}{N}-Cl$, so that the frequency and coupling constant increase, from 43.67 to 56.09 MHz.

## 2. Infra Red Spectroscopy

The infra red spectra of a variety of new nitrogen halogen compounds have been recorded using a PE 457 grating spectrometer in the range 4000-250 cm$^{-1}$. The region 400 cm$^{-1}$-40 cm$^{-1}$ was investigated using a Beckman RIIC FS720 interferometer. Spectra in this region were obtained from the recorded interferrogram using a fourier transform based on that by Cooley and Tukey (154).

The infra red absorption frequencies observed for the cations $(CH_3)_3\overset{+}{N}$—Cl and $(CH_3)_3\overset{+}{N}$—Br are shown in Table 26.

### TABLE 26

### OBSERVED INFRA RED ABSORPTION FREQUENCIES FOR CATIONS $(CH_3)_3\overset{+}{N}Cl$ AND $(CH_3)_3\overset{+}{N}Br$ WITH DIFFERENT ANIONS

| | | $(CH_3)_3\overset{+}{N}Cl$ | | | | $(CH_3)_3\overset{+}{N}Br$ | |
|---|---|---|---|---|---|---|---|
| $ClO_4^-$ (a) | $ClO_4^-$ (b) | $BF_4^-$ | $OSO_3CH_3^-$ | $OSO_2F^-$ | $BCl_4^-$ | $OSO_2F^-$ | $ClO_4^-$ |
| 336 | 336 | 336 | 335 | 335 | 330 | 295 | 295 |
| 403 | 403 | 403 | 400 | 400 | 400 | 325 | 325 |
| 815 | 815 | 815 | 810 | 820 | 815 | 805 | 805 |
| 935 | 935 | 935 | 940 | 940 | 940 | 945 | 945 |

(a) cation prepared from $(CH_3)_2NCl$ and $CH_3ClO_4$

(b) cation prepared from $(CH_3)_3NCl_2$ and aq $ClO_4^-$

The spectra were obtained as mulls in nujol using CsI plates protected by a thin film of polyethylene. Spectra were run against a polyethylene blank.

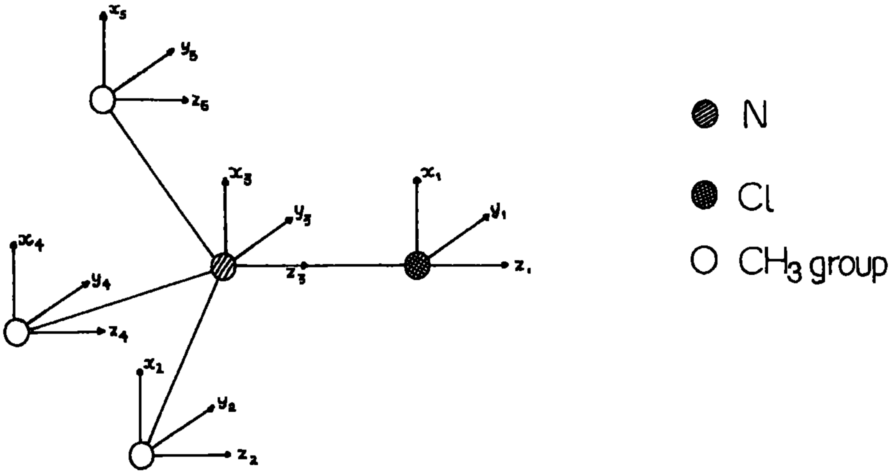
Vibrational assignments can be made by considering that the cation $(CH_3)_3\overset{+}{N}$-X is a 5 atom $C_3v$ structure, all methyl groups being equivalent and of mass 15. This method has been used by Gayles (155) and by Yokobayashi and co-workers (120) in consideration of the infra red spectra of complexes of the type $(CH_3)_3NXY$, and by Zeil (156) in the compound $(CH_3)_3CCl$, which is isoelectronic with $(CH_3)_3\overset{+}{N}$-Cl.

The restriction imposed by this assumption is that only absorptions below 1000 $cm^{-1}$ can be considered, since those above, in these compounds are predominantly C-H modes.

For the 5 atom $C_3v$ structure, shown in Figure 73, the number and activity of the normal modes can be deduced from the character table for the $C_3v$ point group (157). Such a table, including the number of reducible representations, found by applying the indicated symmetry operand to the co-ordinate system, and summing the diagonal elements of the generated matrix, is shown in Table 27.

FIGURE 73

5 ATOM $C_3v$ STRUCTURE WITH CO-ORDINATES FOR $(CH_3)_3\overset{+}{N}$-Cl



## TABLE 27

### CHARACTER TABLE FOR POINT GROUP $C_{3}v$

| $C_{3}v$ | E | $2C_{3}$ | $3\sigma_{v}$ | | |
|---|---|---|---|---|---|
| $A_1$ | 1 | 1 | 1 | $T_z$ $[\mu_z]$ | $\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$ |
| $A_2$ | 1 | 1 | -1 | $R_z$ | |
| E | 2 | -1 | 0 | $(T_x,T_y)(R_x,R_y)$ $[(\mu_x,\mu_y)]$ | $(\alpha_{xx}-\alpha_{yy},\alpha_{xy}),(\alpha_{yz},\alpha_{xz})$ |
| $\Gamma_t$ | 15 | 0 | 3 | | |

The irreducible representations can be found from the reducible representations as follows:

$A_1$: $1/6[(15 \times 1) + (0 \times 1 \times 2) + (3 \times 1 \times 3)] = 4$

$A_2$: $1/6[(15 \times 1) + (0 \times 1 \times 2) + (3 \times -1 \times 3)] = 1$

E: $1/6[(15 \times 2) + (0 \times -1 \times 2) + (3 \times 0 \times 3)] = 5$

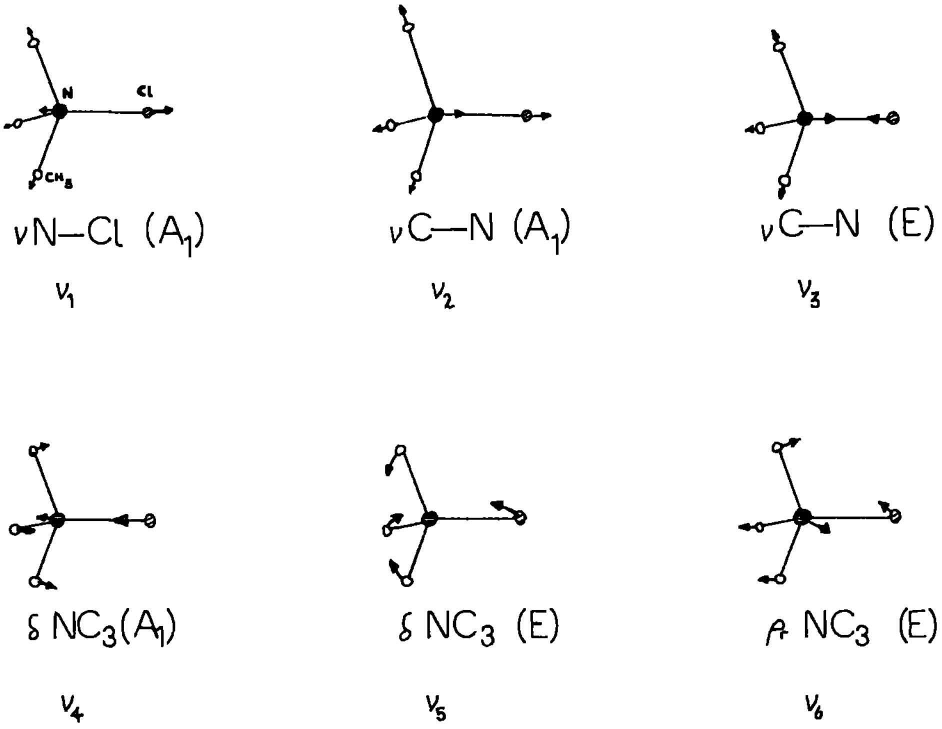
resulting in $4A_1 + A_2 + 5E$ modes. From the character table however, these are $1A_1 + 1E$ for translation. T, and $1A_2 + 1E$ for rotation, R, to be subtracted, leaving for the ion $(CH_3)_3\overset{+}{N}$-Cl, $3A_1 + 3E$ modes..

The character table shows that both $A_1$ and E vibrations are both infra red and Raman active since the components of the polarisability, $\alpha$, and dipole moment, $\mu$, belong to these species in this point group.

The six vibrations for $(CH_3)_3\overset{+}{N}$-Cl are shown in Figure 74, and described in Table 28.

## FIGURE 74

## NORMAL MODES OF VIBRATION FOR $(CH_3)_3\overset{+}{N}$-Cl ION



$\nu$N–Cl ($A_1$) $V_1$

$\nu$C—N ($A_1$) $V_2$

$\nu$C—N (E) $V_3$

$\delta$ $NC_3$($A_1$) $V_4$

$\delta$ $NC_3$ (E) $V_5$

$\rho$ $NC_3$ (E) $V_6$

## TABLE 28

## VIBRATIONAL DESCRIPTION FOR $(CH_3)_3\overset{+}{N}$-Cl STRUCTURE

| Vibration | Description |
|---|---|
| $V_1$ | N-Cl stretch |
| $V_2$ | Symmetric C-N stretch |
| $V_3$ | Asymmetric C-N stretch |
| $V_4$ | Symmetric C-N-C deformation or N-C-N bend |
| $V_5$ | Asymmetric, C-N-C deformation or C-N bend |
| $V_6$ | $NC_3$ rocking mode |

The absorptions observed for the cations $(CH_3)_3\overset{+}{N}\text{-}Cl$ and $(CH_3)_3\overset{+}{N}\text{-}Br$ may now be assigned vibrational modes. From Table 27, the absorptions at 815 and 935 $cm^{-1}$ are assigned to the $A_1$ and E carbon nitrogen stretching modes, in accordance with the C-N modes in a variety of $(CH_3)_3N\rightarrow$(acceptor) complexes as well as $(CH_3)_3N$ itself, as shown in Table 30.

The N-Cl stretching vibration was identified in the spectrum by utilising the two chlorine isotopes. Provided sufficient resolution is available, the absorption recorded by the instrument will appear as a doublet, the ratio of intensities reflecting the ratio of $^{35}Cl$ and $^{37}Cl$ isotopic abundances.

An expanded scale record of the absorption observed at 403 $cm^{-1}$ is shown in Figure 75, where it can be seen that the intensity ratio is approximately 3:1, and the separation is 5 $cm^{-1}$ .

The magnitude of the splitting can be calculated by making two assumptions. Firstly the ion $(CH_3)_3\overset{+}{N}\text{-}Cl$ is considered a mixture of diatomic molecules, comprising of an atom of mass 59, $((CH_3)_3N\text{—})$ bonded to either of the chlorine isotopes of mass 35 and 37. Secondly, the force constants for the $^{59}M\text{—}^{35}Cl$ and $^{59}M\text{—}^{37}Cl$ bonds are considered equal and that it is possible to express the vibration in terms of a harmonic oscillator whose frequency of vibration is given by the equation

$$\nu = \frac{1}{2\pi}\sqrt{\frac{f}{\mu}}$$

where f is the force constant and $\mu$ is the reduced mass given by the

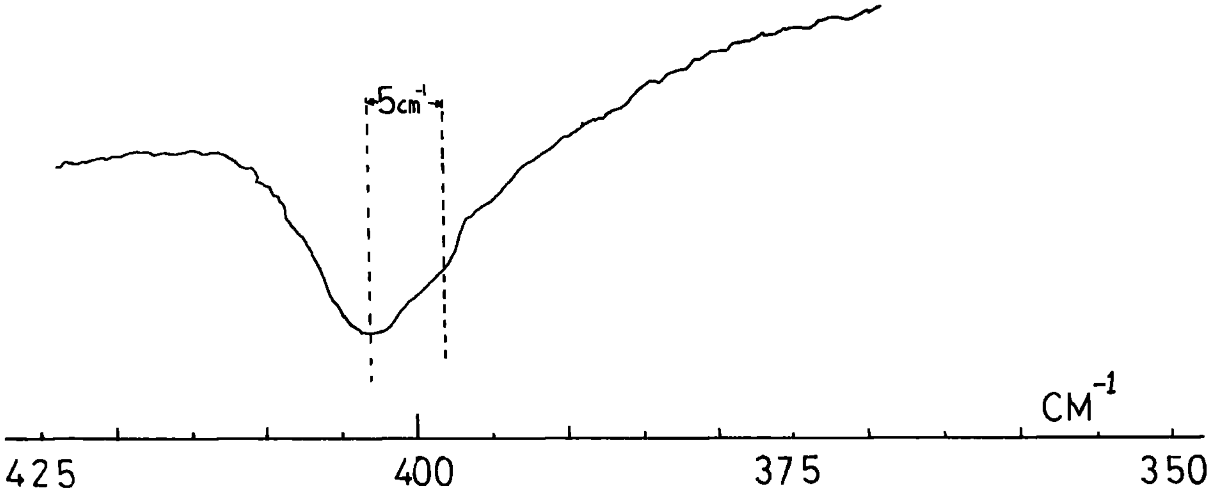


fig 75 EXPANDED SCALE SPECTRUM OF THE ABSORPTION AT 403cm IN $(CH_3)_3\overset{+}{N}Cl$ $ClO_4^-$

equation

$$\frac{1}{\mu} = \frac{1}{Mi} + \frac{1}{Mr}$$

where Mi refers to the mass of the chlorine isotope (35, 37) and Mr refers to the mass of the residue (59).

It is thus possible to write two similar equations relating the frequency of each isotopic vibration:

$$\nu_{35} = \frac{1}{2\pi}\sqrt{\frac{f_{35}}{\mu_{35}}}, \qquad \nu_{37} = \frac{1}{2\pi}\sqrt{\frac{f_{37}}{\mu_{37}}}$$

and the ratio of the frequencies is given by:

$$\frac{\nu_{35}}{\nu_{37}} = \sqrt{\frac{\mu_{37}}{\mu_{35}}} \qquad \text{since } f_{35} = f_{37}$$

where $\mu_{37} = \frac{37 \times 59}{37 + 59}$ and $\mu_{35} = \frac{35 \times 59}{59 + 35}$

hence $\nu_{35} = 1.017\nu_{37}$

or the separation between the two vibrations, $\Delta\nu$, is

$$\Delta\nu = 1.017\nu_{37} - \nu_{37}$$

$$\Delta\nu = 0.017\nu_{37}$$

and at 403 $cm^{-1}$, the separation is found to be 6.9 $cm^{-1}$.

This value, approximately 7 $cm^{-1}$, compares favourably with the observed value of 5 $cm^{-1}$, considering the assumptions made. The intensity ratio of 3:1 is in agreement with the abundance ratio for the two chlorine isotopes of 3.09:1 (158).

and the [illegible] 77K Smith

The vibration observed at 335 $cm^{-1}$ is either a $NC_3$ deformation or $NC_3$ rocking mode. It seems likely that in view of the low intensity of the $NC_3$ rocking modes observed in the trimethylamine halogen addition compounds (120, 155), the vibration at 335 $cm^{-1}$ is assigned to either of the $NC_3$ deformation modes, and most probably the symmetric mode since this appears the strongest in the isoelectronic $(CH_3)_3CCl$ spectrum shown in Figure 76. The missing $NC_3$ deformation and rocking modes were not detectable even in very strong mulls in the far infra red (350-10 $cm^{-1}$). The vibrational assignments are summarised in Table 29.

Assignments can be made on a similar basis for the bromo cation, $(CH_3)_3\overset{+}{N}Br$, where the absorptions at 805 and 945 $cm^{-1}$ are the $A_1$ and E carbon nitrogen stretches. the N-Br vibration should, like the N-Cl, appear as a doublet of, in this case, equal intensity because, of the approximately equal abundance of $^{79}Br$ and $^{81}Br$ (1.02:1, $^{79}Br$: $^{81}Br$, (158)), and by carrying out a similar calculation as above, the expected splitting, at say 300 $cm^{-1}$, is only 1.5 $cm^{-1}$. No splitting was detected on either of the 325 $cm^{-1}$ or 295 $cm^{-1}$ vibration in $(CH_3)_3\overset{+}{N}BrClO_4^-$ or $(CH_3)_3\overset{+}{N}Br\ OSO_2F^-$, ?
which is not (strictly) surprising.

Comparing C-Cl and C-Br frequencies for $(CH_3)_3CCl$ and $(CH_3)_3CBr$, from Table 29, a 60 $cm^{-1}$ reduction is experienced, which is the same as that experienced in going from $(CH_3)_2NCl$ ( N-Cl, 595 $cm^{-1}$ ) to $(CH_3)_2NBr$ ( N-Br, 535 $cm^{-1}$ ). It thus seems likely that the absorption at 325 $cm^{-1}$ in both the $FSO_3^-$ and $ClO_4^-$ anion of $(CH_3)_3\overset{+}{N}Br$ is attributable to this absorption, representing a 78 $cm^{-1}$ reduction in frequency.

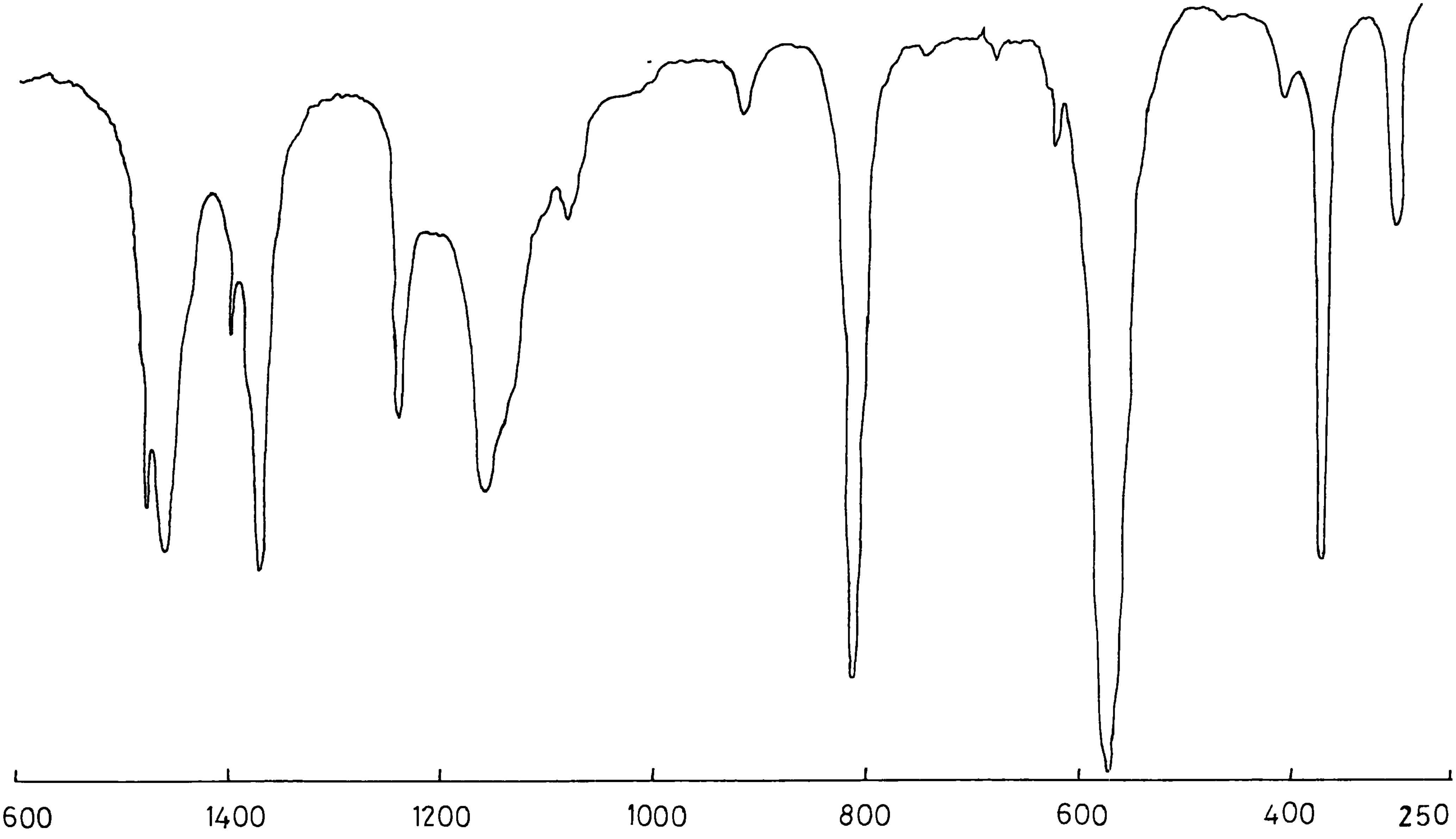


fig 76 INFRA RED SPECTRUM OF $(CH_3)_3CCl$

## TABLE 29

## VIBRATIONAL ASSIGNMENTS FOR HALOTRIMETHYLAMMONIUM PERCHLORATES COMPARED WITH THE ISOELECTRONIC t-BUTYL HALIDES

| Vibration | $(CH_3)_3N$ Cl | $(CH_3)_3N$ Br | $(CH_3)_3CCl$ | $(CH_3)_3CBr$ |
|---|---|---|---|---|
| $\nu_1$ (N-X) $A_1$ | 403 | 325 | 580 | 520 |
| $\nu_2$ (C-N) $A_1$ | 865 | 805 | 815 | 806 |
| $\nu_3$ (C-N) E | 935 | 945 | 1396 | 1413 |
| $\nu_4$ $\delta NC_3$ $A_1$ | 335 | 295 | 370 | 303 |
| $\nu_5$ $\delta NC_3$ E | - | - | 404 | 398 |
| $\nu_6$ $\rho_r NC_3$ E | - | - | 300 | 268 |
| Reference | This work | This work | 155 | 155 |

The absorption at 295 $cm^{-1}$ in $(CH_3)_3\overset{+}{N}$-Br appears to correlate with the 335 $cm^{-1}$ absorption in $(CH_3)_3\overset{+}{N}$-Cl, tentatively assigned to the $A_1$ $\delta NC_3$ skeletal mode. Comparison again with the chloro and bromo t butyl analogues indicate a 67 $cm^{-1}$ reduction from $(CH_3)_3CCl$ to $(CH_3)_3CBr$, which is compared with 40 $cm^{-1}$ in the halotrimethylammonium species if the 295 $cm^{-1}$ absorption is, as it seems likely, the $A_1$ $\delta NC_3$ skeletal mode.

As with the $(CH_3)_3\overset{+}{N}Cl$ case, very strong mulls of $(CH_3)_3\overset{+}{N}Br\ ClO_4^-$ or $FSO_3^-$ failed to yield any further absorptions which could be attributed to the E $\delta NC_3$ and E $\rho_r NC_3$ modes of the bromotrimethylammonium cation. The vibrational assignments for $(CH_3)_3\overset{+}{N}$-Br in $(CH_3)_3\overset{+}{N}BrClO_4^-$ are shown in Table 29.

When the 5 atom $C_{3}v$ structure assumed for the analysis of the halotrimethylammonium cation is extended to a 6 atom $C_{3}v$ structure as in for example $(CH_3)_3NI_2$, then the number of reducible representations from the $C_{3}v$ character table yield $5A_1 + A_2 + 6E$ modes, which when $1A_1 + 1A_2$ and 2E modes are subtracted for rotation and translation, there are $4A_1$ and 4E modes remaining, which are, of course all infra red active. The extra two modes are a N-X-Y, (E) bend and X-Y ($A_1$) stretch.

Table 30 lists the assignments and frequencies for all known trimethylamine halogen and interhalogen complexes along with the frequencies for trimethylamine itself.

The complex $(CH_3)_3NCl_2$, presents a situation intermediate between structures such as $(CH_3)_3N \rightarrow XY$ where X and Y are halogens, e.g. $(CH_3)_3NICl$, and structures involving the cation $(CH_3)_3\overset{+}{N}\text{-}Cl$, $Z^-$ where $Z^- = ClO_4^-$ for example.

TABLE 30

COMPARISON OF FREQUENCIES OF $(CH_3)_3N$ HALOGEN AND INTERHALOGEN COMPLEXES

| Vibration | $(CH_3)_3N$ | Trimethylamine Complex | | | | | |
|---|---|---|---|---|---|---|---|
| | | $I_2$ | $Br_2$ | $Cl_2$ | ICl | IBr | BrCl |
| $\nu_1$ N-X | - | 148 | 166 | 336 | 196 | 172 | 302 ? |
| $\nu_2$ C-N | 827 | 801 | 800 | 800 | 809 | 807 | 800 |
| $\nu_3$ C-N | 1063 | 999 | 989 | 962 | 993 | 996 | 985 |
| $\nu_4$ $\delta NC_3$ $A_1$ | 358 | 365 | 320 | 324 | 434 | 434 | 435 |
| $\nu_5$ $\delta NC_3$ E | 434 | 468 | 494 | 544 | 490, 471 | 482 | 500 |
| $\nu_6$ $\rho r NC_3$ | 269 | - | 267 | - | - | 269 | - |
| $\nu_7$ X-Y | - | 188 | 224 | 348 | 249 | 206 | 278 |
| $\nu_8$ $\delta$ NXY | - | 50 | 70 | 88 | 147 | 90 | - |
| Reference | 154 | 154 | 154 | This work | 120 | 120 | This work |

This situation is clear from a chemical point of view as for example $(CH_3)_3NCl_2$ is very soluble in water yielding $(CH_3)_3\overset{+}{N}\text{-}Cl^-$ cations whilst $(CH_3)_3NICl$ for example is not, indicating a strengthening of the N-halogen bond and a corresponding weakening of the halogen-halogen bond.

In the solid phase however, the ionic formulation $(CH_3)_3\overset{+}{N}\text{-}Cl\ Cl^-$ cannot be entirely correct since if it were the infra red spectrum of $(CH_3)_3NCl_2$ would resemble closely that of $(CH_3)_3\overset{+}{N}Cl$ , which of course it does not. A complete spectrum of $(CH_3)_3NCl_2$ is shown in Figure 77, and the assigned frequencies listed in Table 30.

The assignment of the vibrations at 962 and 800 $cm^{-1}$ to the E and $A_1$ C-N stretching modes is in accord with the other trimethylamine halogen data. The $NC_3$ deformation modes at 544 (E) and 324 ($A_1$) were assigned on the basis of intensity and trend. The asymmetric mode at 544 fits with the trend in increased frequency with reducing total mass, as shown in Figure 78 where the frequency of the $\delta NC_3$ vibration is plotted against the reciprocal of the square root of the total halogen mass for the complexes $(CH_3)_3NI_2$, $Br_2$ and $Cl_2$. The intensity of this vibration is high, and this is true of all the $(CH_3)_3N$ $(halogen)_2$ species.

The symmetric $\delta NC_3$ mode at 324 in $(CH_3)_3NCl_2$ compares with 365 $cm^{-1}$ in $(CH_3)_3NI_2$ and 320 $cm^{-1}$ in $(CH_3)_3NBr_2$, all of which are little moved from the pure trimethylamine absorption at 358 $cm^{-1}$ .

The N-Cl stretching frequency would be expected to be a weak absorption, lowered in position and intensity relative to that found in the cation $(CH_3)_3\overset{+}{N}\text{-}Cl$, at 403 $cm^{-1}$ , because of the influence of the second chlorine atom. Looking at the trend in N-hal frequency indicated

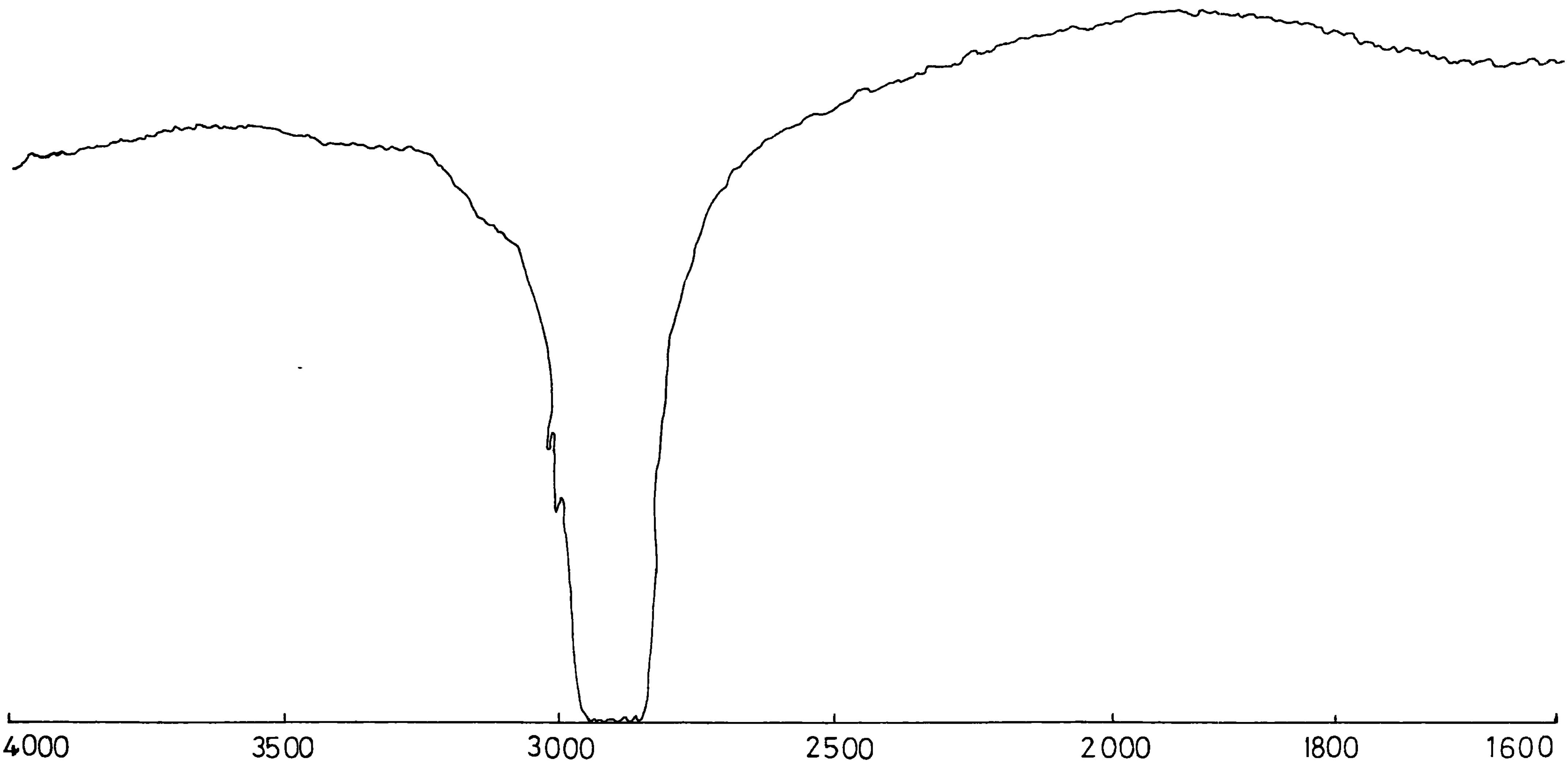


fig 77a INFRA RED SPECTRUM OF $(CH_3)_3NCl_2$ [4000-1600cm$^{-1}$]

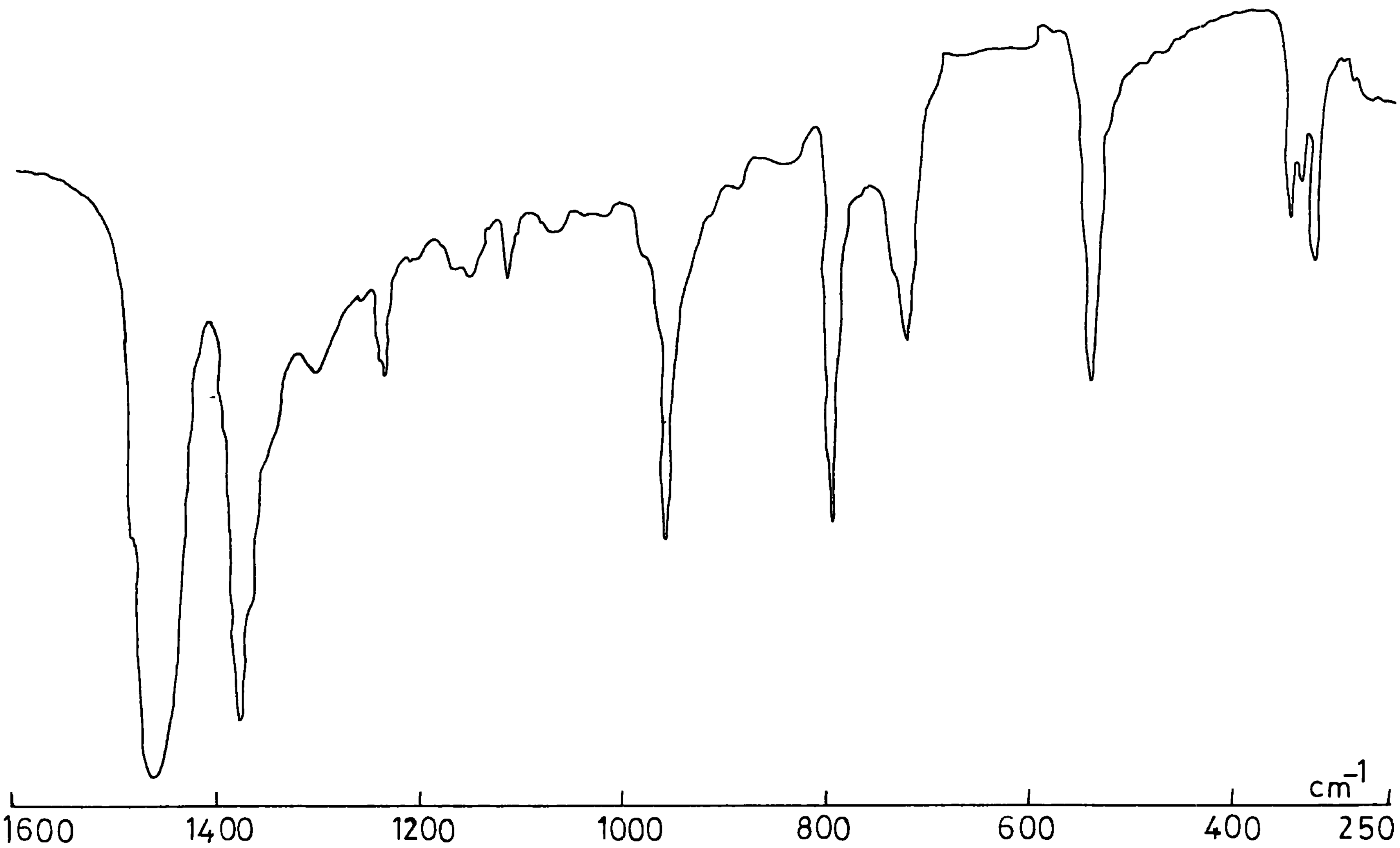


fig 77b INFRA RED SPECTRUM OF $(CH_3)_3NCl_2$ [1600-250cm$^{-1}$]

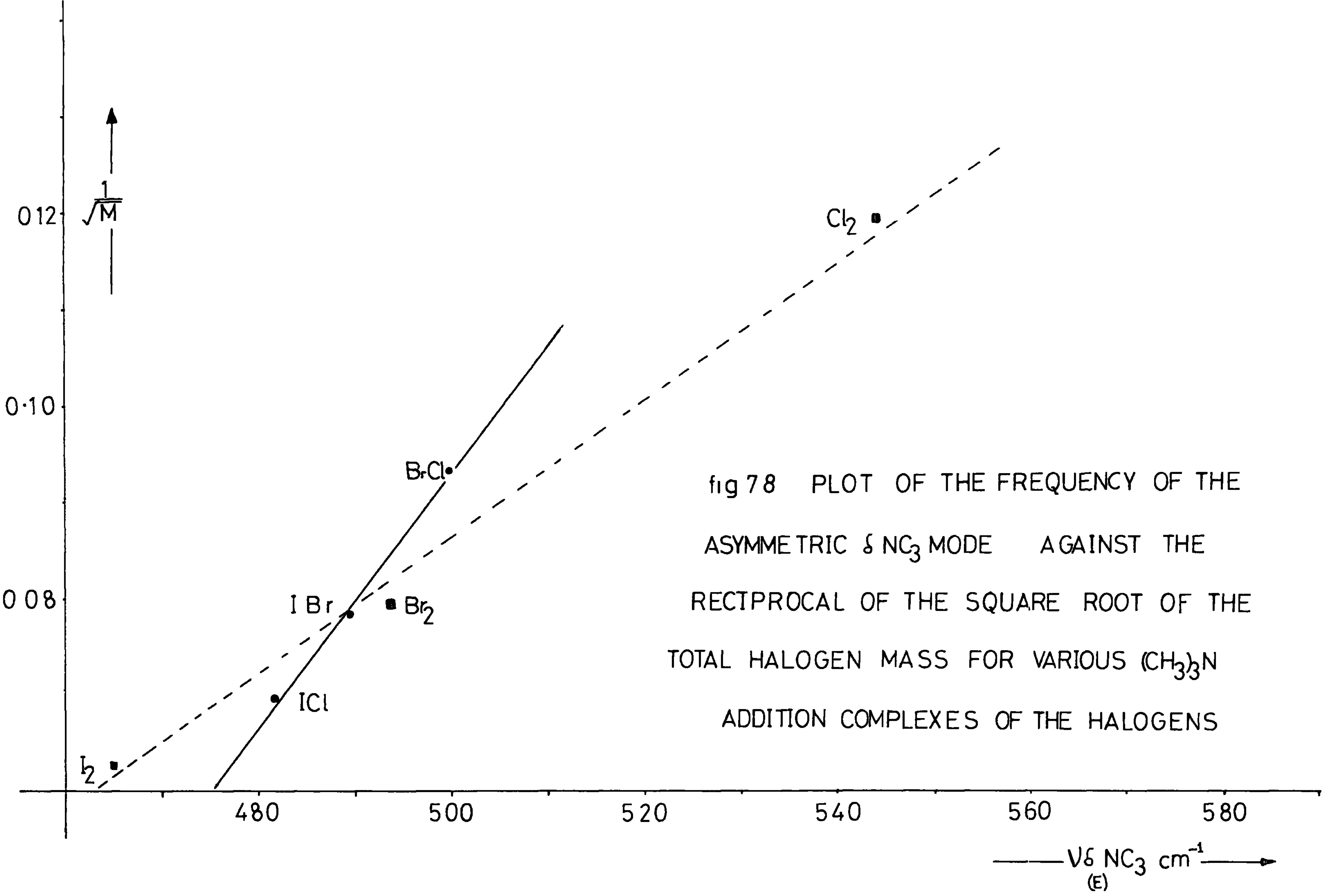


fig 78 PLOT OF THE FREQUENCY OF THE ASYMMETRIC $\delta$ $NC_3$ MODE AGAINST THE RECTIPROCAL OF THE SQUARE ROOT OF THE TOTAL HALOGEN MASS FOR VARIOUS $(CH_3)_3N$ ADDITION COMPLEXES OF THE HALOGENS

in Table 30, the move from N-I to N-Br is accompanied by only an 18 $cm^{-1}$ change in frequency, from 148 $cm^{-1}$ to 166 $cm^{-1}$, and taking into account the mass differences, on a simple basis, the N-Cl frequency ought to be in the 200-300 $cm^{-1}$ region. There are no absorptions in this particular band of the spectrum, the nearest weak absorption being at 336 $cm^{-1}$, to which the N-Cl frequency is assigned. This represents an increase in frequency over what would be expected and should be accompanied by a Cl-Cl frequency which exhibits a proportionally larger diminuition from free $Cl_2$ than the I-I or Br-Br frequencies in the complexes do from the free halogen. This is understandable if a weaker Cl-Cl interaction exists in $(CH_3)_3NCl_2$ than Br-Br or I-I interaction in $(CH_3)_3NBr_2$ or $(CH_3)_3NI_2$. Certainly this situation would be expected since $(CH_3)_3\overset{+}{N}$-Cl forms readily from $(CH_3)_3NCl_2$ whilst there is no evidence of a similar situation in $(CH_3)_3NBr_2$ or $(CH_3)_3NI_2$.

An assignment of 348 $cm^{-1}$ for the Cl-Cl frequency would be consistent with the above argument, representing a 209 $cm^{-1}$ reduction in frequency from the free $Cl_2$ Raman absorption at 557 $cm^{-1}$ (157), the equivalent $Br_2$ and $I_2$ figures being 93 $cm^{-1}$ from 317 $cm^{-1}$ and 41 $cm^{-1}$ from 213 $cm^{-1}$ (157).

At low wavenumbers, an absorption at 88 $cm^{-1}$ is assigned to the N-Cl-Cl deformation mode ($\nu_8$ Table 30) which is in agreement with the trends observed for the other two halogen trimethylamine complexes.

The remaining $NC_3$ rocking mode would be expected at a similar position to that found in trimethylamine itself or its halogen adducts. It is at 269 $cm^{-1}$ in free $(CH_3)_3N$, 267 $cm^{-1}$ in $(CH_3)_3NBr_2$ and 269 $cm^{-1}$

in $(CH_3)_3NIBr$, thus appearing fairly insensitive to the group associated with the nitrogen lone pair. It is a very weak absorption, and indeed even in very thick mulls of $(CH_3)_3NCl_2$, no absorptions could be found in this region.

The $(CH_3)_3NBrCl$ addition complex completes the set of $(CH_3)_3N$, halogen and interhalogen complexes. The frequencies of the absorption found for this complex are also listed in Table 30. Again, assignment of the C-N modes at 800 $cm^{-1}$ and 985 $cm^{-1}$ is consistent within this group of trimethylamine addition complexes, both from intensity and position points of view. The asymmetric $NC_3$ deformation mode at 500 $cm^{-1}$ is in good agreement with the trend observed for $(CH_3)_3NICl$ and $(CH_3)_3NIBr$, indeed a plot of this frequency against the reciprocal of the square root of the total halogen mass is a good straight line, as shown in Figure 78. It is interesting to note that the interhalogen class show slightly better agreement than the dihalogen class, and also the slope of the line is slightly different for these two groups of complexes, as is reflected in the symmetric mode for this vibration, where the $(CH_3)_3NI_2$, $Br_2$ and $Cl_2$ complexes absorb in the region 320-365 $cm^{-1}$, the $(CH_3)_3NICl$, IBr and BrCl absorb at 435 $cm^{-1}$.

The position of the N-Br absorption at 278 $cm^{-1}$ is in agreement with the expected trend in going from the free ion, $(CH_3)_3\overset{+}{N}-Br$, at 325 $cm^{-1}$, to the bromine complex at 166 $cm^{-1}$. A value of 302 $cm^{-1}$ is consistent with increasing mass on the bromine in $(CH_3)_3\overset{+}{N}-Br$ and a weakening of the N-Br bond in going from $(CH_3)_3\overset{+}{N}-Br\ \overset{-}{Cl}$ to $(CH_3)_3NBr-Cl$.

The absorption at 278 $cm^{-1}$ is assigned to the Br-Cl stretching frequency, it showing a similar trend in its frequency reduction from the free compound. The values for the free and complexed interhalogen and halogen frequencies are shown in Table 31.

TABLE 31

REDUCTION IN HALOGEN-HALOGEN STRETCHING FREQUENCY IN COMPLEXES WITH $(CH_3)_3N$

| | $I_2$ | $Br_2$ | $Cl_2$ | ICl | IBr | BrCl |
|---|---|---|---|---|---|---|
| $\nu$(X-X) free | 213 | 317 | 557 | 381.5 | 266.8 | 439.5 |
| $\nu$(X-X) complex | 172 | 224 | 348 | 249 | 206 | 278 |
| $\Delta\nu$ | 41 | 93 | 209 | 132.5 | 60.8 | 161.5 |

(Data for free halogens from reference (156), complexed $I_2$, $Br_2$ from reference (154), ICl, IBr from reference (120); $Cl_2$, BrCl, this work).

The data in Table 31 can be considered in several different ways. The trend observed for $(CH_3)_3NICl$, BrCl and $Cl_2$, shows an increase in the reduction from the free interhalogen or halogen frequency which is consistent with a change in strength of the X-Y bond, the greater the diminuition from the free halogen frequency indicating a greater weakening of the X-Y bond, or strengthening of the N-hal bond, which would be expected in going from $(CH_3)_3NCl_2$ where $(CH_3)_3\overset{+}{N}Cl\ \ Cl^-$ occurs readily, to $(CH_3)_3NICl$.

Conversely, the trend observed in $(CH_3)_3NICl$, IBr, $I_2$ indicates a weakening of the N-I bond, which is consistent with the decrease in electronegativity encountered in going from Cl to I, which in turn would influence the ionic character of the I-X bond, ICl being more ionic than $I_2$, which in turn would tend to increase the N-I bond strength in $(CH_3)_3NICl$ over that in $(CH_3)_3NI_2$.

## 3. Conclusions

In conclusion, chlorine NQR spectroscopy has shown that in the compounds of $(CH_3)_3\overset{+}{N}Cl$ with anions such as $ClO_4^-$ and $BF_4^-$, the chlorine atom possesses a slight positive charge. The bonding between nitrogen and chlorine atoms is expected to be between a $sp^3$ hybrid nitrogen orbital and an almost pure p chlorine orbital. It is expected that the C-N and N-Cl bond lengths are shorter than those expected from the sum of the covalent radii.

The small bond dipole is reflected in the low intensity of the N-Cl stretching frequency in the infra red. In the complex $(CH_3)_3NCl_2$, the $C_3v$ symmetry noted for $(CH_3)_3\overset{+}{N}$–Cl is maintained, and infra red data correlate well with that for other $(CH_3)_3N$ halogen complexes.

The trends in N-X and X-X frequencies for $(CH_3)_3NX_2$ species is consistent with the expected changes in bonding in going from a N-Cl-Cl structure to a N-I-I, a greater N-Cl interaction being indicated in $(CH_3)_3NCl_2$ than N-I interaction in $(CH_3)_3NI_2$.

The interhalogen addition compounds of trimethylamine show similar trends, data for the BrCl complex fitting well with the existing data for $(CH_3)_3NIBr$ and $(CH_3)_3NICl$.

The expected gradation in N-Br stretching frequency in going from $(CH_3)_3\overset{+}{N}Br$, $(CH_3)_3NBrCl$, $(CH_3)_3NBr_2$ is apparent, again consistent with electronegativity considerations influencing the N-Br bond.

# CHAPTER SEVEN

## DISCUSSION AND CONCLUSIONS

# GENERAL DISCUSSION AND CONCLUSIONS

The reactions of dimethylchloramine and related compounds are shown schematically in Figure 78, where differences in behaviour of the N-Cl bond can be seen. In most cases, the N-Cl bond is broken, chlorine usually present at the end of the reaction as Cl. Only in the case of reactions with powerful alkylating agents, for example $CH_3OSO_2F$ or $CH_3OClO_3$, is the N-Cl bond preserved, contrasting with the behaviour towards $CH_3I$, where the anion $(CH_3)_2N(ICl)_2^-$ forms.

Dimethylchloramine acts exclusively, as an oxidising agent towards the methyl hydrazines and hydrazine itself, yielding products resulting from either the complete breakdown of the N-N bond as in $CH_3NHNH_2$ or $N_2H_4$, or products resulting from oxidative coupling as in $(CH_3)_2NNH_2$, or partial oxidation leading to immine formation as in $(CH_3)_2NNHCH_3$, yielding $(CH_3)_2NN{=}CH_2$.

With the methyl amines and ammonia, differing behaviour was noted depending on the extent of alkyl substitution. With ammonia, $(CH_3)_2NNH_2$ formed whilst with trimethylamine, C-N bond formation occurred yielding the diamine $(CH_3)_2NCH_2N(CH_3)_2$, which is in contrast with the corresponding reaction of $NH_2Cl$ where a N-N bond was established yielding the cationic species $(CH_3)_3NNH_2$ .

In the case of methylamine and dimethylamine, the situation is far less clear. In both cases appreciable quantities of methane were observed, along with $NH_3$ and the immine $(CH_3)_2NN{=}CH_2$ with $CH_3NH_2$, and the diamine $(CH_3)_2NCH_2N(CH_3)_2$, tetramethylmethylenediamine, TMMD, in the case of $(CH_3)_2NH$.

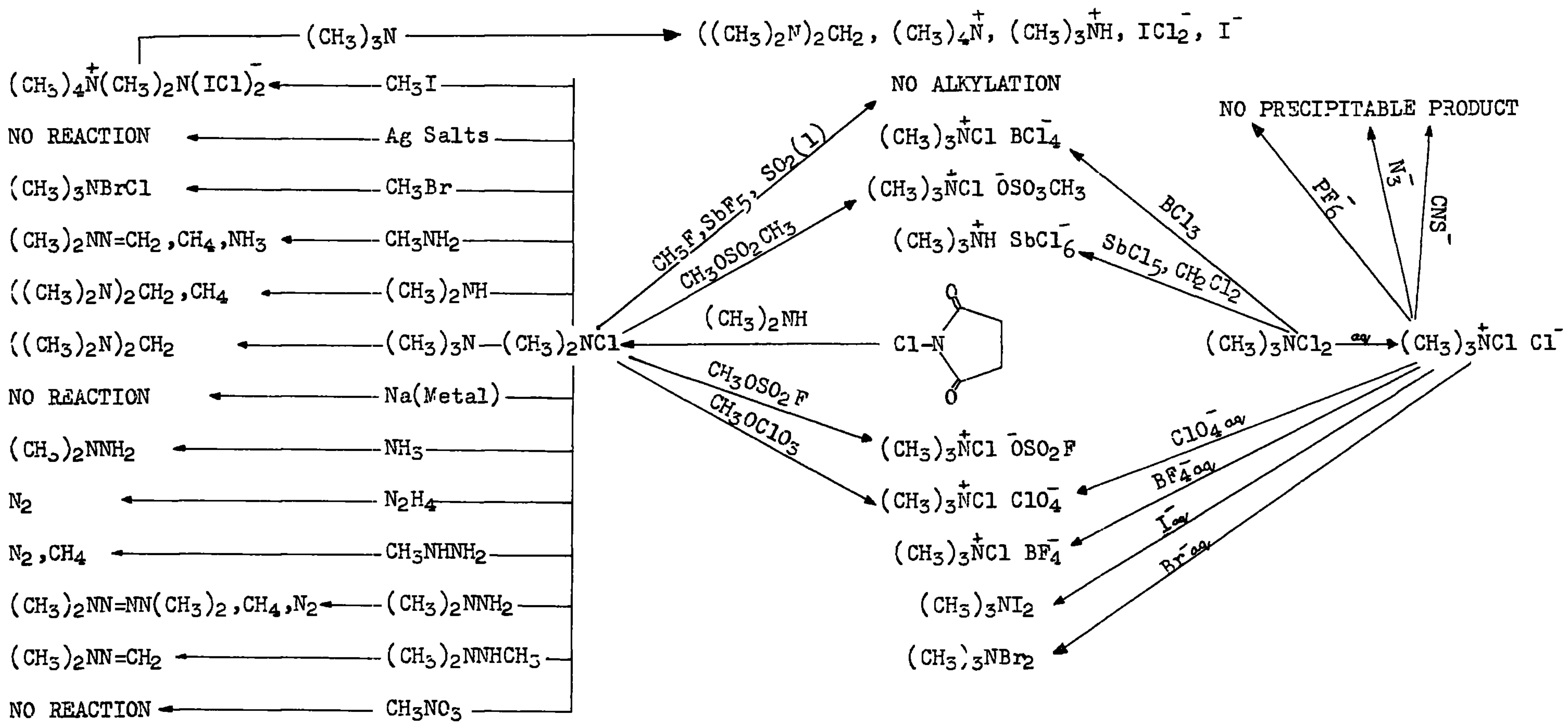

$(CH_3)_3N$
$((CH_3)_2N)_2CH_2$, $(CH_3)_4\overset{+}{N}$, $(CH_3)_3\overset{+}{N}H$, $ICl_2^-$, $I^-$
$(CH_3)_4\overset{+}{N}(CH_3)_2N(ICl)_2^-$
$CH_3I$
NO REACTION
Ag Salts
$(CH_3)_3NBrCl$
$CH_3Br$
$(CH_3)_2NN=CH_2$, $CH_4$, $NH_3$
$CH_3NH_2$
$((CH_3)_2N)_2CH_2$, $CH_4$
$(CH_3)_2NH$
$((CH_3)_2N)_2CH_2$
$(CH_3)_3N$—$(CH_3)_2NCl$
NO REACTION
Na(Metal)
$(CH_3)_2NNH_2$
$NH_3$
$N_2$
$N_2H_4$
$N_2$, $CH_4$
$CH_3NHNH_2$
$(CH_3)_2NN=NN(CH_3)_2$, $CH_4$, $N_2$
$(CH_3)_2NNH_2$
$(CH_3)_2NN=CH_2$
$(CH_3)_2NNHCH_3$
NO REACTION
$CH_3NO_3$
$CH_3F$, $SbF_5$, $SO_2(l)$
NO ALKYLATION
$CH_3OSO_2CH_3$
$(CH_3)_3\overset{+}{N}Cl\ \bar{O}SO_3CH_3$
$(CH_3)_2NH$
Cl-N
O
O
$CH_3OSO_2F$
$(CH_3)_3\overset{+}{N}Cl\ \bar{O}SO_2F$
$CH_3OClO_3$
$(CH_3)_3\overset{+}{N}Cl\ ClO_4^-$
$(CH_3)_3\overset{+}{N}Cl\ BCl_4^-$
$BCl_3$
$(CH_3)_3\overset{+}{N}H\ SbCl_6^-$
$SbCl_5$, $CH_2Cl_2$
$(CH_3)_3NCl_2$
aq
$(CH_3)_3\overset{+}{N}Cl\ Cl^-$
NO PRECIPITABLE PRODUCT
$PF_6^-$
$N_3^-$
$CNS^-$
$ClO_4^-{}_{aq}$
$BF_4^-{}_{aq}$
$I^-_{aq}$
$Br^-_{aq}$
$(CH_3)_3\overset{+}{N}Cl\ BF_4^-$
$(CH_3)_3NI_2$
$(CH_3)_3NBr_2$

FIGURE 78

The products noted for $NH_3$, $CH_3NH_2$ and $(CH_3)_3N$ can be rationalised in terms of not nucleophillic attack of the amine on the chloramine nitrogen as is the case with $NH_2Cl$, but by a simple dehydrohalegonation reaction involving a C-H bond in the case of $(CH_3)_3N$ and N-H bonds in the case of $NH_3$ and $CH_3NH_2$, however with $CH_3NH_2$ the reaction must have an alternative pathway since $CH_4$ and $NH_3$ were observed.

TMMD formation from the dimethylamine reaction is perhaps explicable in terms of the chloramine decomposition where this amine was observed. $(CH_3)_2NBr$ decomposes, at -84°C, to yield, amongst other products, $(CH_3)_3N$, which has been shown to react with $(CH_3)_2NCl$ to yield TMMD. It is unclear why $(CH_3)_2NH$ should behave in a different manner to the other simple amines.

The behaviour of both $(CH_3)_2NCl$ and $(CH_3)_2NBr$ towards alkylating agents is extremely interesting in that two different pathways are found, depending on the alkylating agent employed.

With methyl esters of certain oxo acids, such as $HOSO_2F$, $HOSO_3CH_3$ and $HClO_4$, reaction proceeds in the conventional manner, as would be expected of a tertiary amine and an alkylating agent, yielding the halotrimethylammonium cation. However with the methyl halides, completely different products are formed. Methyl iodide, the usual methylating agent, forms, with $(CH_3)_2NCl$, a pseudo polyhalide, $(CH_3)_2N(ICl)_2^-$, and with $(CH_3)_2NBr$, the analogous $(CH_3)_2N(IBr)_2^-$, in which the $(CH_3)_2N$ moiety can be considered as a pseudo halide.

Methyl bromide, on the other hand, yields the addition complex of trimethylamine and the interhalogen BrCl, $(CH_3)_3NBrCl$.

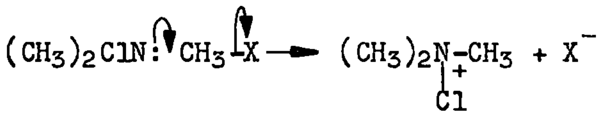
The cation, $(CH_3)_3\overset{+}{N}Cl$, from NQR evidence, contains a chlorine atom which is very slightly positive, i.e. the N-Cl bond is polarised such that the positive end of the dipole resides on the chlorine atom. The bond is considered as being formed from a nitrogen $sp^3$ orbital and an almost pure chlorine 3p orbital, since the s character is around 2%. As a consequence of this, and an ionic character of around 1.5%, calculations involving electronegativities indicate that the C-N and N-Cl bonds are shorter than that indicated by a straightforward sum of covalent radii by around 2%.

In aqueous solution, the cation $(CH_3)_3\overset{+}{N}Cl$, shows the same UV spectrum as the trimethylamine chlorine addition complex, $(CH_3)_3NCl_2$, and indeed the salts $(CH_3)_3\overset{+}{N}Cl\ Cl\overset{-}{O_4}$ and $(CH_3)_3\overset{+}{N}Cl\ B\overset{-}{F_4}$ can be precipitated from aqueous solutions of $(CH_3)_3NCl_2$ by addition of $Cl\overset{-}{O_4}$ or $B\overset{-}{F_4}$ ions. The hexafluorophosphate, azide and thiocyanate of the cation are freely soluble in water. Confirmation that $(CH_3)_3NCl_2$ yields $(CH_3)_3\overset{+}{N}Cl$ ions in aqueous solution can be found in the reaction of $(CH_3)_2NCl$ with $CH_3OClO_3$, where $(CH_3)_3\overset{+}{N}Cl\ Cl\overset{-}{O_4}$ is formed, and the infra red spectrum of this is identical with that of the product precipitated when $(CH_3)_3NCl_2$ is treated with an excess of $Cl\overset{-}{O_4}$ ions in aqueous solution.

A parallel situation exists with $(CH_3)_2NBr$, where $CH_3OSO_2F$ forms the unstable $(CH_3)_3\overset{+}{N}Br\ OSO_2\overset{-}{F}$, which is soluble in water, and yields, when treated with an excess of $Cl\overset{-}{O_4}$ ions, $(CH_3)_3\overset{+}{N}Br\ Cl\overset{-}{O_4}$, as a precipitate.

Considering the reaction of the dimethyl halamines with alkylating agents as a whole, it seems unreasonable to suppose that the basic mechanism of the reaction is different for, for example $CH_3OSO_2F$ and $CH_3I$.

It seems likely that the initial step of the alkylation reaction, which it is in both product types, as the C:N ratio has been increased, is nucleophillic attack of the halamine on the positive alkyl group in the ester.



$$(CH_3)_2ClN{:}\;CH_3{-}X \longrightarrow (CH_3)_2\underset{Cl}{\overset{+}{N}}{-}CH_3 + X^-$$

In the case of $X = {}^-OSO_2F$, ${}^-OSO_3CH_3$ or ${}^-OClO_3$, the reaction stops here, since further attack of the oxo-anion on the positive nitrogen would not occur, however when X is a halogen, for example $I^-$, there appears to be no reason why an N-I bond cannot be established:

$$(CH_3)_3\overset{+}{N}Cl + I^- \longrightarrow (CH_3)_3\overset{+}{N}I + Cl^-$$

and indeed, the addition of $I^-$ to aqueous solutions of $(CH_3)_3\overset{+}{N}Cl$ precipitates $(CH_3)_3NI_2$, the known addition complex of $I_2$ and $(CH_3)_3N$.

The chloride ion formed in the $I^-$ reaction can now yield $(CH_3)_3NTCl$ with the iodotrimethylammonium cation, and in the reaction medium, the equilibrium

$$(CH_3)_3NICl \rightleftharpoons (CH_3)_3N + ICl$$

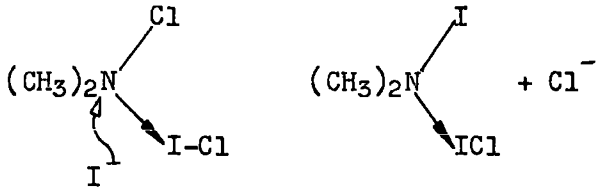
occurs.

It is now possible for a further mole of $CH_3I$ to reaction with the much stronger base, $(CH_3)_3N$, to yield $(CH_3)_4N$ and further $I^-$ ions.

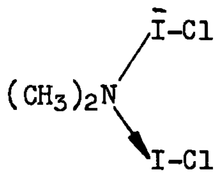
The ICl formed above can associate itself with a chloramine molecule to yield the addition complex $(CH_3)_2NClICl$:

$$(CH_3)_2NCl + ICl \rightleftharpoons (CH_3)_2ClN{\rightarrow}ICl$$

and an $I^-$ ion can act as a nucleophile towards the slightly positive co-ordinated nitrogen:



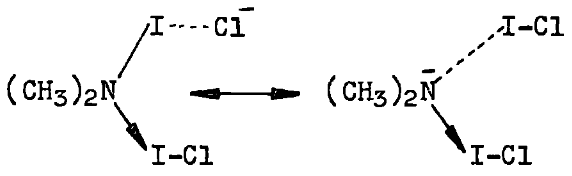
The chloride ion now associates itself with the N-I iodine to yield the anion



It is possible to envisage the chloride ion association in the last step of the reaction as part of a resonance structure for the anion, much in the same way as that considered (159) in $ICl_2$ where structures such as

$$Cl{-}I\cdots\cdots Cl^- \longleftrightarrow Cl^- \quad I{-}Cl$$

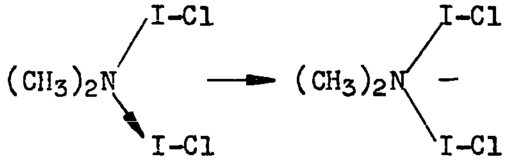
account for longer I-Cl bond lengths, a lowering of the I-Cl stretching frequency, and appreciable ionic character of the I-Cl bond. In the case of the $(CH_3)_2N(ICl)_2$ anion structures such as



would occur.

Such a system, however, would imply a certain amount of asymmetry about the nitrogen atom, one N-I bond being of differing length to the other. Such asymmetry from crystallographic work, was not observed, and it seems more likely that the negative charge is distributed over the I-N-I system resulting in a shortening of the N-I bond length, which is observed, and a consequent lengthening of the I-Cl distance.

The final step in the reaction would thus be:



The reaction between $CH_3Br$ and $(CH_3)_2NCl$ can be considered to follow a similar pathway to that described above, but the reaction stops after the attack of Br on the $(CH_3)_3NCl$ cation:

$$(CH_3)_2NCl + CH_3Br \longrightarrow (CH_3)_3\overset{+}{N}Cl + Br^-$$

$$Br^- + (CH_3)_3\overset{+}{N}Cl \longrightarrow (CH_3)_3\overset{+}{N}Br + Cl^-$$

$$(CH_3)_3\overset{+}{N}Br + Cl^- \longrightarrow (CH_3)_3NBrCl$$

since presumably either $(CH_3)_3NBrCl$ is not soluble in the reaction medium, ($(CH_3)_2NCl$ and $CH_3I$) or that the equilibrium postulated for the $CH_3I$ reaction does not occur:

$$(CH_3)_3NBrCl \rightleftharpoons (CH_3)_3N + BrCl$$

A possible reason why this does not occur is that the equilibrium demands that the N-Br bond be broken, which would be less likely in this case than in the equivalent $CH_3I$ reaction.

If the above speculations into the mechanism for the formation of the various alkylated species found in the reaction of $(CH_3)_2NCl$ or $(CH_3)_2NBr$ are true, then the initial step in these reactions are effectively equivalent, product differences being controlled by the reaction of the anion of the methyl ester with the initially formed halotrimethylammonium cation.

## Suggestions For Further Work

The reaction of $(CH_3)_2NCl$ with the methyl amines has indicated that with $CH_3NH_2$ and $(CH_3)_2NH$ a different mechanism appears to occur when compared with the reaction with $NH_3$ and $(CH_3)_3N$. It would be interesting to investigate this mechanism further, and explain why methyl and dimethylamine behave in a differing manner.

The anion $(CH_3)_2N(ICl)_2^-$ is very interesting from a bonding point of view, and $^{14}N$ NQR could provide an insight into the charge distribution around the nitrogen atom.

The formation of the cation $(CH_3)_3\overset{+}{N}Cl$ from $(CH_3)_3NCl_2$ in aqueous solution, or in the solid phase with, for example $BCl_3$, could yield a means of preparing other chlorammonium cations, as reacting variously substituted chloramines with chlorine would yield, for methyl derivatives:

$$(CH_3)_2NCl + Cl_2 \longrightarrow (CH_3)_2NCl\ Cl_2 \xrightarrow{BCl_3} (CH_3)_2\overset{+}{N}Cl_2\ BCl_4^-$$

$$CH_3NCl_2 + Cl_2 \longrightarrow CH_3NCl_2\ Cl_2 \xrightarrow{BCl_3} CH_3\overset{+}{N}Cl_3\ BCl_4^-$$

$$NCl_3 + Cl_2 \longrightarrow NCl_3\ Cl_2 \xrightarrow{BCl_3} \overset{+}{N}Cl_4\ BCl_4^-$$

however due account must be taken of the decreased nitrogen basicity with increased chlorine substitution.

Since the cation, $(CH_3)_3\overset{+}{N}Cl$, possesses a chlorine atom which is slightly positive, compounds containing this cation ought to be a better chlorinating agent than chlorine itself, and from a water treatment point of view it may be that an equimolar mixture of chlorine and trimethylamine would be more effective than chlorine on its own.

## REFERENCES

1 MELLOR, J. W., "A Comprehensive Treatise On Inorganic And Theoretical Chemistry", Vol VIII, p 598ff, 1928 Vol VIII, Suppl. II, Part II, p 409ff, 1967, Longmans New York.

2 "Gmelin's Handbuch Der Anorganischen Chemie", 8th ed, No. 6, 1927 Ed. MEYER, R. J., 1927.

3 SNELDERS, H. A. M., Chem. Absr., 68, 9212, 1968.

4 DRAGO, R. S., J. Chem. Ed., 34, 541, 1957.

5 COLTON, E., And JONES, M. M., Ibid 32, 485, 1955.

6 BERLINER, J. F. T., J. Am. Water Works Assoc., 23, 1320, 1931.

7 KOVACIC, P., LOWERY, M. K., And FIELD, K. W., Chem. Rev., 70, 639, 1970.

8 POLLOCK, G. H., J. Appl. Physiol., 1, 802, 1949.

9 NEALE, R. S., And WALSH, M. R., J. Am. Chem. Soc., 87, 1255, 1965.

10 RUSCHIG, H., Med. Chem., 4, 327, 1942.

11 SHARTS, C. M., J. Org. Chem., 33, 1008, 1968.

12 MINISCI, F., GALLI, R., GALLI, A., And BERNARDI, R., Tetrahedron Lett., 2207, 1967.

13 MINISCI, F., GALLI, R., BERNARDI, R., And PERCHINUNNO, M., Chem. Ind. (Milan), 51, 280, 1969.

14 MINISCI, F., GARDINI, G. P., And BERTINI, F., Can. J. Chem., 48, 544, 1970.

15 MINISCI, F., BERNARDI, R., And GALLI, R., J. Chem. Soc. B, 324, 1968.

16 MINISCI, F., GALLI, R., And BERNARDI, R., Chem. Ind. (Milan), 49, 594, 1967.

17 MINISCI, F., GALLI, R., PERCHINUNNO, M., And BERNARDI, R., Chem. Ind. (Milan), 50, 453, 1968.

18 TANNER, D. D., And MOSHER, M. W., Can. J. Chem., 47, 715, 1969.

19 INGOLD, K. U., And SPANSWICK, J., Ibid., 48, 546, 1970.

20 OGATA, Y., IZAWA, Y., And TOMOIKA, H., Tetrahedron, 23, 1509, 1967.

21 KOVACIC, P., And FIELD, K. W., Synthesis, 135, 1969.

22 DANILOV, S. N., And KOZMINA, O. P., J. Gen. Chem. USSR., 19, 269, 1949.

23 ELLIS, A. J., And SOPER, F. G., J. Chem. Soc., 1750, 1954.

24 KOVACIC, P., HOPPER, R. J., CHAUDHARY, S. S., LEVISKY, J. A., And LIEPKALNS, V. A., Chem. Comm., 232, 1966.

25 KOVACIC, P., And CHAUDHARY, S. S., Tetrahedron, 23, 3563, 1967.

26 KOVACIC, P., FIELD, K. W., And HERSKOVITZ, T., J. Org. Chem., 35, 2140, 1970.

27 KOVACIC, P., And LOWERY, M. K., Chem. Comm., 651, 1966.

28 COLEMAN, G. H., And HOWELLS, H. P., J. Am. Chem. Soc., 45, 3084, 1923.

29 COLEMAN, G. H., And CAMPBELL, Ibid., 50, 2754, 1928.

30 NEALE, R. S., And MARCUS, N. L., J. Org. Chem., 32, 3273, 1967.

31 MINISCI, F., And GALLI, R., Tetrahedron Lett., 167, 1964.

32 MINISCI, F., And GALLI, R., Chem. Ind. (Milan), 45, 1400, 1963.

33 MINISCI, F., And GALLI, R., Ibid., 46, 546, 1964.

34 MINISCI, F., Ibid., 49, 705, 1967.

35 MINISCI, F., GALLI, R., And CERERE, M., Tetrahedron Lett., 3163, 1966.

36 COLEMAN, G. H., And Hauser, C. R., J. Am. Chem. Soc., 50, 1193, 1928.

37 COLEMAN, G. H., YAGER, C. B., And SORDOS, H., Ibid., 56, 965, 1934.

38 COLEMAN, G. H., BUCHANAN, M. A., And PAXSON, W. L., Ibid, 55, 3669, 1933.

39 COLEMAN, G. H., Ibid., 55, 3001, 1933.

39a COLEMAN, G. H., HERMANSON, J. L., And JOHNSON, H. L., Ibid., 59, 1896, 1937.

40 KUFFNER, F., And SIEFRIED, W., Montash. Chem., 83, 784, 1952.

41 BOCK, H., And KOMPA, K., Chem. Ber., 99, 1347, 1966.

42 BOCK, H., And KOMPA, K., Ibid., 99, 1356, 1966.

43 BOCK, H., And KOMPA, K., Ibid., 99, 1361, 1966.

44 MINISCI, F., GALLI, R., And CECERE, M., Tetrahedron Lett., 4663, 1965.

45 KOVACIC, P., LANGE, M. R., FOOTE, J. L., GORALSKI, C. T., HILLER, J. J., And LEVISKY, J. A., J. Am. Chem. Soc., 86, 1650, 1964.

46 KOVACIC, P., LEVISKY, J. A., And GORALSKI, C. T., Ibid., 88, 100, 1966.

47 HEASLEY, V. L., KOVACIC, P., And LANGE, R. M., J. Org. Chem., 31, 3050, 1966.

48 HAUSER, C. R., And HAUSER, M. L., J. Am. Chem. Soc., 52, 2050, 1930.

49 HAUSER, C. R., HAUSER, M. L., And GILLASPIE, A. G., Ibid., 52, 4158, 1930.

50 PETROV, K. A., And SOKOL'SKII, G. A., J. Gen. Chem. USSR., 26, 3378, 1956.

51 SISLER, H. H., SARKIS, A., AHUSA, H. S., DRAGO, R. J., And SMITH, N. L., J. Am. Chem. Soc., 81, 2982, 1959.

52 SISLER, H. H., And HIGHSMITH, R. E., Inorg. Chem., 7, 1740, 1968.

53 SISLER, H. H., And HART, W. A., Ibid., 3, 617, 1964.

54 SISLER, H. H., And CLEMENS, D. F., Ibid., 4, 1222, 1965.

55 SISLER, H. H., NEILSEN, R. P., And VINCENT, J. F., Ibid., 2, 760, 1963.

56 SISLER, H. H., And JAIN, S. R., Ibid., 7, 104, 1968.

57 SISLER, H. H., And KRANNICH, L. K., Ibid., 8, 1032, 1969.

58 SISLER, H. H., And McKENNEY, R. L., Ibid., 6, 1178, 1967.

59 SISLER, H. H., And HIGHSMITH, R. E., Ibid., 8, 1029, 1969.

60 APPEL, R., And BUCHNER, W., Chem. Ber., 95, 849, 1962.

61 APPEL, R., And HANSSGEN, D., Angew. Chem., Int. Ed. Engl., 6, 91, 1967.

62 WAWZONEK, S., And CULBERTSON, T. P., J. Am. Chem. Soc., 81, 3367, 1959.

63 NEALE, R. S., WALSH, M. R., And MARCUS, N. L., J. Org. Chem., 27, 3726, 1962.

64 BAUMGARTEN, H. E., And BOWER, F. A., J. Am. Chem. Soc., 76, 4561, 1954.

65 BAUMGARTEN, H. E., And PETERSON, J. H., Ibid, 82, 459, 1960.

66 HATCH, M. J., And CRAM, D. J., Ibid., 75, 38, 1953.

67 ALT, G. H., And KNOWLES, W. S., J. Org. Chem. 25, 2047, 1960.

68 OAE, S., And FURUKAWA, N., Bull. Chem. Soc. Japan, 38, 62, 1965.

69 GASSMAN, P. G., And FOX, B. L., Chem. Comm., 153, 1966.

70 GASSMAN, P. G., And FOX, B. L., J. Am. Chem. Soc., 89, 338, 1967.

71 GASSMAN, P. G., And CRYBERG, R. L., Ibid., 91, 2047, 1969.

72 GASSMAN, P. G., Accounts Chem. Res., 3, 26, 1970.

73 YATES, K. P., Phys. Rev., 71, 349, 1947.

74 HAMMOND, P. R., J. Chem. Soc., 2565, 1963.

75 CLASS, J. B., J. Am. Chem. Soc., 75, 2937, 1953.

76 OLSEN, A. L., J. Chem. Phys., 24, 1106, 1956.

77 SEPPELT, K., And SUNDERMEYER, W., Z. Naturforsch, B, 24, 774, 1969.

78 RUSCHIG, H., FRITSCH, W., SCHMIDT-THOMÉ, J., And HAEDE, W., Chem. Ber., 88, 883, 1955.

79 DRAGO, R. S., J. Chem. Educ., 34, 541, 1957.

80 JANDER, J., And KURZBACH, E., Angew. Chem., 72, 919, 1960.

81 SISLER, H. H., COLLIER, F. N., CALVERT, J. G., And HURLEY, F. R., J. Am. Chem. Soc., 81, 6177, 1959.

82 YAGIL, G., And ANBAR, M., Ibid., 84, 1797, 1962.

83 KOVACIC, P., Chem. Rev. 70, 639, 1970.

84 OHME, R., SCHMITZ, E., And DOLGE, P., Chem. Ber., 99, 2104, 1966.

85 SISLER, H. H., And UTVARY, K., Inorg. Chem., 5, 1835, 1966.

86 SISLER, H. H., KREN, R. M., And UTVARY, K., Ibid., 8, 2007, 1969.

87 HOEGERLE, K., And ERLENMEYER, H., Helv. Chim. Acta., 39, 1203, 1956.

88 GASSMAN, P. G., MIENWALD, J., And MILLER, E. G., J. Am. Chem. Soc., 81, 995, 1959.

89 RUNDEL, W., Angew. Chem., Int. Ed. Eng., 1, 403, 1962.

90 FUCHS, J. J., US Patent 3346554, 1967, Chem. Abs., 68, 2593, 1968.

91 BOCK, H., And KOMPA, K. L., Z. Anorg. Aug. Chem., 332, 238, 1964.

92 YAGIL, G., And ANBAR, M., J. Am. Chem. Soc., 84, 1790, 1962.

93 SOPER, F. G., J. Chem. Soc., 1927, 1953.

94 SHORT, W. F., Chem. News., 126, 100, 1923

95 MARKWALD, W., And WILLE, M., Chem. Ber., 56, 1325, 1923.

96 RASCHIG, F., Ch. Ztg., 31, 926, 1907.

97 TRUITT, P., J. Am. Chem. Soc., 70, 2829, 1948.

98 THEILACKER, W., And EBKE, K., Angew. Chem., 68, 303, 1956.

99 KLAGES, F., Ann., 1, 547, 1941.

100 Comprehensive Chemical Kinetics, Vol 7, Ed. TIPPER, C. F.,H., And BAMFORD, C. H., Elsevier, 275, 417, 1972.

101 VERNOT, E. H., J. Am. Hyg. Assoc., 28, 343, 1967.

102 OSLEN, A. L., J. Chem. Phys., 24, 1956.

103 LUDMAN, C. J., Priv. Comm.

104 NORTHERN GAS BOARD, Priv. Comm.

105 AUDRETTH, L. F., J. Am. Chem. Soc., 80, 2516, 1958.

106 CLASS, J. B., And OAKWOOD, T. S., J. Am. Chem. Soc., 75, 2937, 1953.

107 HANTZCH, A., And GRAFFE, W., Chem. Ber., 38, 2154, 1905.

108 BOHME, H., And KRAUSE, W., Ibid., 84, 170, 1951.

109 BOHME, H., And BOLLE, E., Z. Anorg. Aug. Chem., 292, 61, 1957.

110 SOPER, F. G., And ELLIS, A. J., J. Chem. Soc., 3, 576, 1953.

111 HAMMOND, P. R., J. Chem. Soc., 1370, 1962.

112 OLAH, G. A., DeMEMBER, R. J., SHLOSBERG, R. H., J. Am. Chem. Soc., 1, 156, 1972.

113 LUDMAN, C. J., Priv. Comm.

114 WATERS, W. A., STEPHENSON, O., FORREST, J., CRANE, W. C., J. Chem. Soc., 827, 1946.

115 WEIL, I., And MORRIS, J. C., J. Am. Chem. Soc., 71, 3123, 1949.

116 ALCOCK, N. W., Priv. Comm.

117 GINN, S. G. W., HAQUE, I., And WOOD, J. L., Spec. Acta., 24A, 1531, 1968.

118 HAYWARD, G. C., And HENDRA, P. T., Ibid., 23A, 2309, 1967.

119 MAKI, A., And FORENS, R., Ibid., 23A, 867, 1967.

120 YOKOBAYASHI, K., WATARI, F., And AIDA, K., Ibid., 24A, 1651, 1968.

123 TOWNES, C. H., And DAILEY, B. P., J. Chem, Phys., 17, 782, 1949.

124 LUKEN, E. A. C., Nuclear Quadrupole Coupling Constants, Acad. Bress. Lond., 1969.

125 CHANDRA, S., Trans, Farad. Soc., 1570, 1967.

126 WILMSHURST, J. K., J. Chem. Phys., 30, 561, 1959.

127 GORDY, W., SMITH, W. V., And TRAMBARULO, R. F., Microwave Spectroscopy, McGraw-Hill, N.Y., 1955.

128 GORDY, W., Disc. Farad. Soc., 17, 19, 1955.

129 TOWNES, C. H., And DAILEY, B. P., J. Chem. Phys., 23,,118, 1955.

130 PAULING, L., The Nature Of The Chemical Bond, 3rd ed., Cornell, N.Y., 1960.

131 HANNAY, N. B., And SMYTH, C. P., J. Am. Chem. Soc., 68, 171, 1948.

132 CHANDRA, S. And CHANDRA, S., Tetrahedron, 22, 3403, 1966.

133 MULLIKEN, R. S., J. Chem. Phys., 46, 497, 1949.

134 GORDY, W., Phys. Rev., 69, 604, 1946.

135 ALLRED, A. L., J. Inorg. And Nucl. Chem. 17, 215, 1961.

136 ALLRED, A. L., And ROCHOW, E. G., J. Inorg. And Nucl. Chem. 5, 269, 1958.

137 WILMSHURST, J. K., J. Chem. Phys., 27, 1129, 1957.

138 HINZE, J., And JAFFE, H. H., J. Am. Chem. Soc., 84, 540, 1962.

139 PAULING, L., Ibid., 54, 3570, 1932.

140 BAIRD, N. C., And WHITEHEAD, M. A., Th. Chim. Acta. (Ber), Z, 559, 1964.

141 COTTON, F. W., And WILKINSON, G., "Advanced Inorganic Chemistry", Ind. Ed., Interscience, 1966.

142 COULSON, C. A., "Valence", 2nd ed., Oxford Univ. Press., 1961.

143 WHITEHEAD, M. A., And JAFFE, H. H., Trans. Farad. Soc., 57, 1854, 1961.

144 WHITEHEAD, M. A., And KAPLANSKY, M., Mol. Phys., 16, 481, 1969.

145 WHITEHEAD, M. A., And JAFFE, H. H., Th. Chim. Acta. (Ber)., 1, 209, 1963.

146 LIVINGSTON, R., J. Chem. Phys., 19, 1434, 803, 1951.

147 WHITEHEAD, M. A., And HART, R. M., Trans. Farad. Soc., 67, 1569, 1971.

148 HOOPER, H. O., And BRAY, P. J., J. Chem. Phys., 33, 334, 1960.

149 WHITEHEAD, M. A., HINZE, J., And JAFFE, H. H., J. Am. Chem. Soc., 85, 148, 1963.

150 STEPHENSON, D. P., And SHOMAKER, V., Ibid., 62, 1913, 1940.

151 WADDINGTON, T. C., And LYNCH, R. J., Advances In NQR., 37, 1974.

152 WYCKOFF, R. W. G., Crystal Structures, 2nd ed., Vol 5, Ch. XIL. 149, Wiley Lond.

153 SEGEL, S. L., And BARNES, R. G., Catalog Of Nuclear Quad. Inter. And Resonance Frequencies In Solids, USA EC Report IS-520 Parts 1-2, 1962, And, Physical Chemistry, Vol IV, Ed. EYRING, H., HENDERSON, D., And JOST, W., Acad. Lond., 1970.

154 COOLEY, J. W., And TUKEY, J. W., Math. Comp., 19, 195, 1965.

155 GAYLES, J. N., J. Chem. Phys., 49, 1841, 1968.

156 ZEIL, W.. And HUTTNER, W.. Spec. Acta., 22. 1007. 1966.

157 NAKAMOTO, K., Infra Red Spectra Of Inorganic And Co-Ordination Compounds, 1st ed., Wiley, N.Y., 1963.

158 Documenta Geigy Scientific Tables, Ed. DIEM, K., And LENTNER, C., 7th ed., Geigy Pharmaceuticals, 325, 1950.

159 WIEBENGA, E. H., BROEKEMA, J., And HAVINGA, E. E., Adv. Inorg. Chem. And Radiochem., 3, 133, 1961.