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(a) AN INVESTIGATION OF CHLOROFLUOROCYCLOHEXANES

(b) THE ACTION OF CHLORINE TRIFLUORIDE ON TRICHLOROACETIC ACID

A thesis submitted by F. Cuthbertson in
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SUMMARY

An investigation of Chlorofluorocyclohexanes

Two new compounds of this class, containing small numbers of halogen atoms, have been isolated. Both the 1,1-difluoro- and the 1-chloro-1-fluorocyclohexane were prepared from hydrogen fluoride and 1-chlorocyclohexene and were isolated by gas chromatography. For this purpose an apparatus was developed to separate liquids boiling up to 180°C. in 10 g. portions. The physical and chemical properties of the new compounds were investigated and the results found to agree with the structures given.

Other syntheses, both by standard and previously unpublished methods have been attempted but no desirable products were isolated.

The reaction between chlorine trifluoride and trichloroacetic acid

The reaction was investigated at 80°C. and 100°C. and the products found to be mostly carbon dioxide and halogenated methanes (containing up to three fluorine atoms). Smaller amounts of carbonyl halides (containing chlorine and fluorine), oxygen, carbon monoxide, hexachloroethane and acid halides were also isolated. Quantitative results were obtained which agreed with the amounts of starting materials used in the reaction.

The reaction between chlorine trifluoride and trichloroacetyl chloride was also investigated at the higher temperature as the acid chloride was thought to be a possible intermediate. Free radical mechanisms have been suggested to account for the products in both cases.

AN INVESTIGATION OF CHLOROFLUOROCYCLOHEXANES

CONTENTS

Attempted syntheses of chlorofluoro-cyclohexanes, -cyclohexenes and -cyclohexadienes

Practical Details

INTRODUCTION

Workers in these laboratories have studied the action of chlorine trifluoride on benzene under varying conditions. Ellis and Musgrave[1] found that when chlorine trifluoride was passed into solutions of benzene in carbon tetrachloride at 0°C. there were formed mainly simple substitution products. When the reaction between benzene and chlorine trifluoride occurred in the vapour phase[2] however a complex mixture resulted. This mixture consisted of chlorofluoro-cyclohexanes, -cyclohexenes and possibly -cyclohexadienes. As little was known about these types of compounds it was considered interesting to attempt their preparation by unambiguous routes and to investigate their properties.

The introduction of fluorine into cyclohexane or its derivatives in such a way that the structure of the product can be easily determined might be accomplished in several ways:-

(Some of the methods referred to have not been applied to cyclic compounds and so examples have to be taken from comparable compounds)

(a) The addition of anhydrous hydrofluoric acid to an olefin, either simple or substituted, can give good yields of fluorinated materials. In this way cyclohexyl fluoride has been made from cyclohexene[3] and 2,2-difluoro-pentane from 2-chloro-pent-1-ene.[4] Whereas the former reaction was accomplished at -78°C. the latter requires the use of elevated temperature and pressure. It is thus seen that reaction conditions have to be matched with the organic starting material.

(b) The action of anhydrous hydrofluoric acid can be accelerated or even modified by the use of suitable inorganic reagents. Boron trifluoride has been used[5] among other substances to facilitate the less ready addition of hydrogen fluoride to a double bond while lead dioxide has been used to cause the effective addition of fluorine to the double bond[6] in the presence of hydrogen fluoride.

(c) Suitable metallic fluorides can replace the halogen (other than fluorine) in alkyl halides and can in some cases replace hydrogen.

Antimony trifluoride with bromine as catalyst and 2,2-dichloro-propane give a good yield of 2,2-difluoro-propane.[7]

Mercuric fluoride can be used as such and in this way 2-fluoro-1,2,3-trichloro-propane was prepared from 1,2,2,3-tetrachloro-propane,[8] or the mercuric fluoride can be generated in situ by the action of hydrogen fluoride on mercuric oxide as in the preparation of 1,1-difluoro-heptane from the dichloride.[9]

Argentic fluoride is rather more vigorous in reaction than mercuric fluoride and tends to replace hydrogen at higher temperatures.

(d) Anhydrous potassium fluoride, when heated in a suitable solvent with alkyl halides can give good yields of the corresponding fluoro compound. This method has been used by Hoffman[10] to prepare ω,ω-difluoro alkanes containing three to six carbon atoms in good yield using ethylene glycol as solvent.

Anhydrous potassium fluoride without solvent has been used under varying conditions to replace by fluorine the chlorine in monochloro-acetic acid[11] and its esters.

(e) A recently discovered method of indirectly replacing a hydroxyl group by fluorine consists of heating the benzene sulphonyl esters of the alcohols with a saturated solution of potassium fluoride. In this way[12] 1-chloro-2-fluoroethane has been prepared from 2-chloroethyl benzene-sulphonate. If the yields obtained with the simpler types of compound can be obtained with alcohols derived from cyclohexane then this will be a useful reaction.

(f) The attractive idea of reducing aromatic fluoro compounds has been investigated by Swarts[13] who found that when noble metal catalysts were used the first step in the reduction was the removal of the fluorine from the ring as hydrofluoric acid. As other methods for the reduction of benzene rings using other catalysts require even more vigorous conditions of temperature and pressure this line of approach was not attempted.

The use of phosphorus pentafluoride to replace the alcoholic hydroxyl group by fluorine has been shown to yield esters of phosphoric acid.[14] The action of phosphorus pentafluoride on ketones has not been reported and will be investigated.

Suitable organic starting materials for the methods (a) - (d) will be halogenated cyclohexanes, cyclohexenes or cyclohexadienes. The most readily available chloro olefin in this case is 1-chlorocyclohexene, which has been prepared by several authors,[15] by the action of phosphorus pentachloride on cyclohexanone under varying conditions. Chlorine can be added onto[16] the double bond and from the resulting 1,1,2-trichlorocyclohexane, hydrochloric acid can be removed to give a mono or diolefin. 1,2-dibromo cyclohexane is readily made by the addition of bromine to cyclohexene.[17]

The esters for the method (e) could be made by standard methods from the alcohols.

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C.A. 48 1406e

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ATTEMPTED SYNTHESIS OF CHLOROFLUORO-CYCLOHEXANES, -CYCLOHEXENES AND -CYCLOHEXADIENES.

It was decided that the following were desirable starting materials.

1-chlorocyclohex-1-ene, 1,1,2-trichloro-cyclohexane, 1,2-dichlorocyclohex-1-ene, 1,2-dibromocyclohexane and the p-toluene-sulphonyl esters of cyclohexanol and 2-chlorocyclohexanol.

PREPARATION OF 1-CHLOROCYCLOHEX-1-ENE.

1-chlorocyclohex-1-ene has been known for more than fifty years but its preparation on a large scale has only recently been described. Although it occurs in the products of the reduction of 1,2-dichlorocyclohex-2-ene with zinc and ethyl alcohol[18] and in the dehydrochlorination of cis-1,2-dichlorocyclohexane with quinoline[15d] the only suitable starting materials for litre scale preparation are phosphorus pentachloride and cyclohexanone. In the present work the different methods were tried, as described later in the experimental section and the results are tabulated below. From this it was decided to employ the method of Braude and Coles. As well as the higher yields, this method has the merit of requiring simple apparatus (A 1 litre flask with air condenser) and hence saves time in both preparing and cleaning apparatus.

Author of Method[15]	Yield of Olefin Quoted	Found
Mousseron et al.	80%	40%
Carroll et al.	46%	31%
Braude and Coles	60%	60%
Stevens et al.	20%	-

ACTION OF HYDROGEN FLUORIDE ON 1-CHLOROCYCLOHEX-1-ENE

(a) WITHOUT CATALYSTS

Estimation of reaction conditions

Although a great many reactions have been carried out with simple and halogenated olefins the reaction conditions required depend very much upon the structure of the olefin. Olefins with chlorine on one doubly bonded carbon atom require more vigorous conditions than unsubstituted olefins but reaction still occurs readily. When both doubly bonded carbon atoms have chlorine attached then addition of hydrogen fluoride requires still more vigorous conditions or does not take place at all. When the double bond is at the end of the carbon chain and chlorine is attached to the terminal carbon atom then reaction is not very easily accomplished, but if the terminal carbon atom has two chlorine atoms attached reaction occurs at reasonable temperatures. In both cases several reaction products are formed. The

Table I

Starting Substance	Max. Reaction Temp. °C.	Product of Reaction	Yield %.	Ref.
C_4H_8	-25	C_4H_9F	-	19
$CH_2{=}CCl{-}C_2H_5$	35	$CH_3CF_2C_2H_5$	67	4
cis $CH_3CCl{=}CHCl$	95	$CH_3CF_2CH_2Cl$	7	
		$CH_3CFCl{-}CH_2Cl$	8	20
		olefin	60	
trans $CH_3CCl{=}CHCl$	95	$CH_3CF_2CH_2Cl$	10	
		$CH_3CFCl{-}CH_2Cl$	5	20
		olefin	62	
$CHCl{=}CHCl$	No reaction			20
$CHCl{=}CH{-}C_2H_5$	65	$CHF_2C_3H_7$	traces	
		$CHFCl{-}C_3H_7$	10	20
		olefin	25	
		$C_4H_8Cl_2$	5	
$CH_3CH_2CH{=}CCl_2$	65	$C_3H_7CF_2Cl$	15	
		$C_3H_7CFCl_2$	28	20
		olefin	23	
$CH_2Cl{-}CCl{=}CH_2$	50 to 60	$CH_2Cl{-}CF_2CH_3$	4	
		$CH_2Cl{-}CFCl{-}CH_3$	74	21
		olefin	10	
$CCl_2{=}CCl{-}CCl_3$ No addition but substitution of the CCl_3 group at higher temperatures.				20
$(CH_3)_2C{=}CHCl$	0 to -23	$(CH_3)_2C{-}CHClF$	65	20
$\overline{CH{=}CH{-}(CH_2)_3}CH_2$	20	$\overline{CHF{-}(CH_2)_4}CH_2$	70	3

presence of chlorine in other parts of the molecule seems to retard the reaction while the presence of a methyl group on a doubly bonded carbon atom accelerates the reaction. In only one case, that of cyclohexene, has the addition of hydrogen fluoride to a cyclic olefin been reported. (For examples see Table I).

In order to obtain an estimate of suitable reaction conditions for a preliminary reaction between 1-chlorocyclohex-1-ene and hydrogen fluoride conditions for reactions between hydrogen fluoride and olefins of comparable structure to 1-monochloro-cyclohex-1-ene are given. (Table II).

Table II

Starting Material	Max. React. Temp. °C.	Products of Reaction	Yield %	Ref.
$CH_2{=}CCl{-}C_2H_5$	35 to 46	$CH_3CF_2C_2H_5$	67	4
$CH_3CH{=}CCl{-}CH_3$	35 to 46	$CH_3CF_2C_2H_5$	67	4
$CH_2{=}CCl{-}CH_2C_2H_5$	35 to 46	$CH_3CF_2CH_2C_2H_5$	64	4
$CH_3CH{=}CCl{-}C_2H_5$	35 to 46	$CH_3CH_2CF_2C_2H_5$	60	4
$CH_2{=}CCl{-}CH_2CH(CH_3)_2$	35 to 46	$CH_3CF_2CH_2CH(CH_3)_2$	70	4
$CH_3CCl{=}CH{-}(CH_2)_4CH_3$	35 to 46	$CH_3CF_2{-}(CH_2)_5CH_3$	59	4
$C_8H_{15}Cl$	35 to 50	$CH_3CF_2{-}C_6H_{13}$	-	22
$\overline{CH_2CH_2CH{=}CH{-}CH_2C}H_2$	20	$\overline{CH_2CH_2CHF{-}CH_2CH_2C}H_2$	70	3

Although in these the maximum temperature was 50° it was thought advisable to allow a generous margin and to increase the final reaction temperature to 100° for the preliminary reaction so that the main product would be the lower boiling difluoride. The separation and purification of this might be relatively easy and when its properties were known the investigation of the lower temperature reactions would perhaps be more easily accomplished.

Products of reactions.

In exploratory experiments the olefin and hydrogen fluoride in a 3:1 ratio at a maximum temperature of 100° yielded mixtures inseparable by simple distillation. The use of a 15 plate distillation column gave two pure compounds analysing to $C_6H_{10}F_2$ and $C_6H_{10}Cl_2$. When the reagents were used in a 1:1 mole ratio at a maximum temperature of 20° and a similar technique applied severe decomposition of less stable products which were now formed in greater quantity resulted during the distillation.

The application of Gas Chromatography to the above reaction mixtures showed the presence of four compounds, 1,1-difluoro-, 1,1-dichloro- and 1-chloro-1-fluoro-cyclohexane and unchanged olefin. At the lower temperature less tar and higher yields of both the chlorofluoro and dichloro compound were produced.

(b) WITH CATALYSTS

Estimation of reaction conditions

The addition of hydrogen fluoride to a double bond has been catalysed by a variety of metal and non-metal halides.[23] For the present work boron trifluoride, stannic chloride and aluminium trichloride were selected since they appeared to be the most suitable and the most readily available.

Anhydrous boron trifluoride has been used to catalyse the less ready addition of hydrogen fluoride to chlorinated olefins. Both addition and substitution of the chlorine occur with polymer formation at higher temperatures. The same reagent also facilitates the addition of hydrogen chloride to simple olefins, sometimes yielding dimers in addition to the expected chlorohydrocarbons.

Stannic chloride and hydrogen fluoride replace chlorine by fluorine in halohydrocarbons while stannic chloride catalyses the addition of hydrogen chloride to simple and halogenated olefins.

Aluminium trichloride has been used to aid fluorinations but few details are given.[23] It catalyses

TABLE III

Starting Material	Catalyst	Other Reagents	Max. Temp.	Products	Yield	Ref.
MeCCl=CHCl	BF_3 4g/M.	HF	160	$MeCF_2CH_2Cl$	4.4	24
				$MeCClFCH_2Cl$	35	
CHCl=CHCl	$BF_3$12g/M.	HF	95	$CH_2ClCHClF$	24	25
				polymer	29	
CHCl=CHCl	BF_3 12g/M.	HF	25	$CH_2ClCHClF$	3	25
				polymer	10	
$CH_2=CHPr$	BF_3/H_3PO_4	HCl	55	MeCClPr		26
MeCH=CHMe	BF_3/H_2O	HCl	55	C_4H_9Cl	25	26
				$C_8H_{17}Cl$	16	
$MeCHCl_2$	$SnCl_4$	HF	100	CH_3CHClF	40	27
				CH_3CHF_2	20	
$\overline{CH=CCl-(CH_2)_3CH_2}$	$SnCl_4$	HCl	10	$C_6H_{10}Cl_2$		15b
C_3H_6	$SnCl_4$	HCl		C_3H_7Cl		28
$C_6H_5CH=CH_2$	$SnCl_4$	HCl	25	$C_6H_5CHClMe$		29
				polymer		
$Me_2CH-CH=CH_2$	$AlCl_3$	HCl	-80	MeCHCHClMe	20	30
				polymer	60	
$C_6H_5CF_3$	$AlCl_3$	MeCOCl	70	$C_6H_5CCl_3$	86	31
$CCl_2=CHCl$	$AlCl_3$	HCl	50	C_6Cl_6, C_4HCl_5, CCl_3CH_2Cl $(CHCl_2)_2$		32
$C_2H_2Cl_2$	$AlCl_3$	HCl	50	$CHCl_2CHCl_2$, $C_4H_3Cl_5$		32

the addition of hydrogen chloride to simple olefins and causes much polymerisation. This reagent can also replace organically held fluorine by its own chlorine and cause the rearrangement of the halogens in organic molecules. (For examples to illustrate the above see Table III)

Products of reaction

Preliminary experiments using excess hydrogen fluoride and boron trifluoride as catalyst indicated that $C_6H_{10}F_2$ was formed as the major product while the use of stochiometric amounts of hydrogen fluoride produced greater amounts of high boiling products. When the former reaction products were separated by gas chromatography the main component was found to be $C_6H_{10}F_2$. This method of analysis was not applied to the second reaction but distillation showed that the products were probably similar to those obtained by using stannic chloride and aluminium chloride.

The initial experiments with both stannic and aluminium chlorides yielded mixtures containing fair amounts of high boiling products that were inseparable by simple distillation and unstable to fractionation at atmospheric pressure. Gas chromatography showed that the major products were $C_6H_{10}ClF$ and $C_6H_{10}Cl_2$ with smaller amounts of $C_6H_{10}F_2$ and unchanged olefin.

STRUCTURES OF THE PRODUCTS

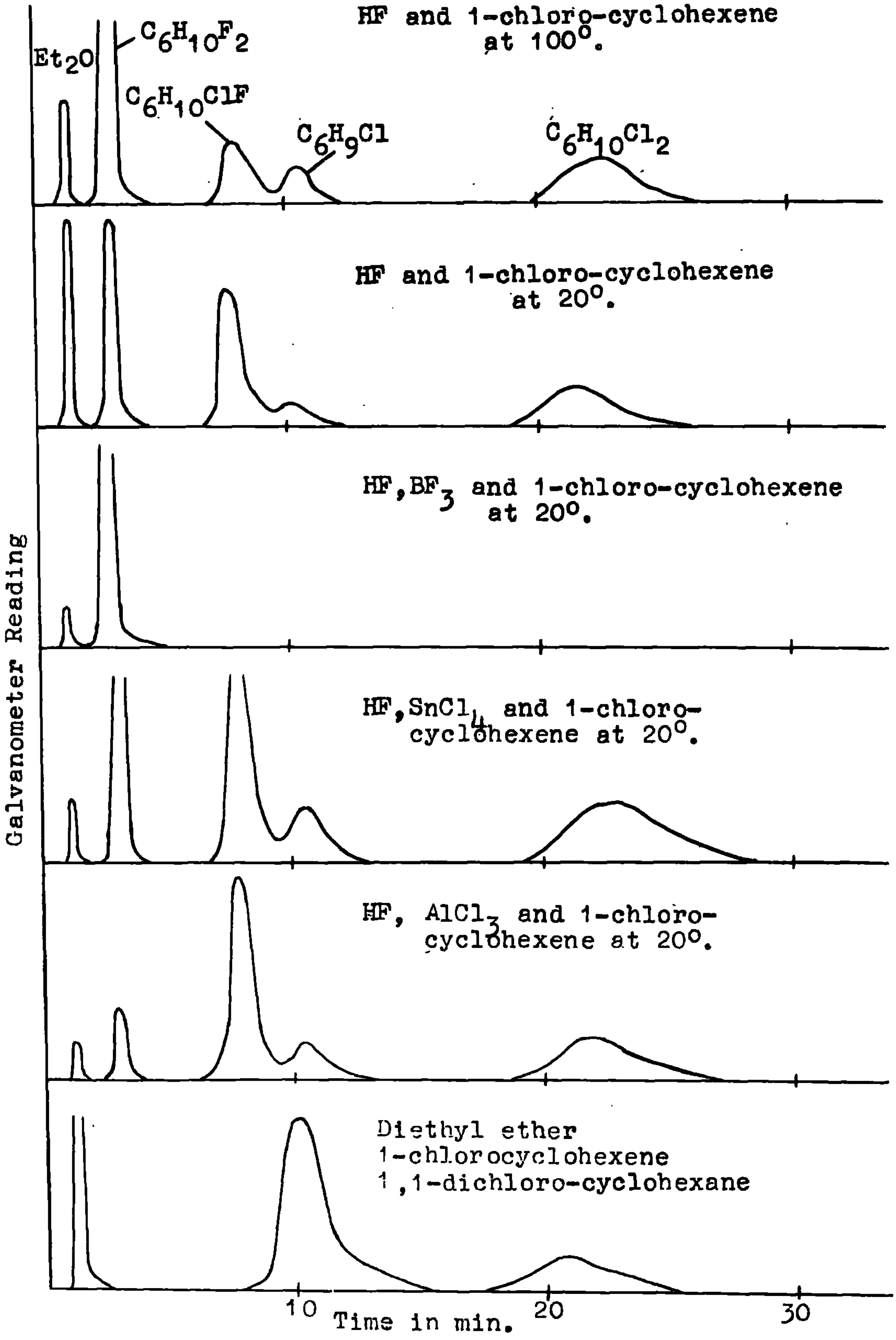
From the reactions between hydrogen fluoride and 1-chloro-cyclohexene, both with and without catalyst, there have been isolated four compounds, two of which have not previously beeen described in the literature. From the positions of the peaks on the chromatograms (Fig. 1) it seems reasonable to assume that the four compounds produced are in each case the same four compounds. This is confirmed by the constancy of the refractive indices of the samples of the compounds isolated and might be expected from the similar nature of the reactions.

The first peak on the chromatograms is due to diethyl ether as was shown by direct comparison of the peak position with that due to authentic diethyl ether and the isolation of a sample

(n_D^{20} = 1.3538 For pure diethyl ether n_D^{20} = 1.3526)

The majority of this was introduced into the sample from that retained by the syringe after washing out the previous sample. This was not objectionable as it was used as a marker in order to eliminate uncertainty in the time of introduction of the sample.

DIAGRAM 1


Et_2O
$C_6H_{10}F_2$
$C_6H_{10}ClF$
C_6H_9Cl
$C_6H_{10}Cl_2$
HF and 1-chloro-cyclohexene at 100°.
HF and 1-chloro-cyclohexene at 20°.
HF, BF_3 and 1-chloro-cyclohexene at 20°.
HF, $SnCl_4$ and 1-chloro-cyclohexene at 20°.
HF, $AlCl_3$ and 1-chloro-cyclohexene at 20°.
Diethyl ether
1-chlorocyclohexene
1,1-dichloro-cyclohexane
Galvanometer Reading
10
20
30
Time in min.

Compound 1

1,1-difluoro-cyclohexane

$n_D^{20} = 1.3906$ b.p. 101.5° at 75.5 cms.

The identity of this substance with the similar compound obtained by distillation was shown by direct comparison of the peak positions. The molecular formula is $C_6H_{10}F_2$. The compound was very resistant to hydrolysis in either acid or alkaline medium. Aqueous solutions of sodium hydroxide up to 10N had no detectable effect while solutions of sodium ethoxide in absolute ethanol and of hydrochloric acid in 80% ethanol produced reaction amounting to a few per cent, it being greater in the case of the acid. Cold aqueous permanganate solutions had no effect but refluxing for long periods produced decomposition with no identifiable organic products. Concentrated nitric acid destroyed the compound to give hydrogen fluoride while palladium carbon in 85% ethanol did not catalyse the reduction with hydrogen.

If we ignore the directing influence of the chlorine atom we might expect three possible products. The two 1,2-difluorocyclohexanes would be expected to have similar properties to cyclohexyl fluoride. The latter hydrolyses more readily in acid solution[33] (5% reaction in 1 hr.) and in alkaline solution[34] (5% reaction in 7 hr.) and dehydrohalogenates and polymerises in the presence of hydrogen fluoride at 100°,[3] the very conditions under which the new compound can be prepared. These differences between the properties of compound 1 and cyclohexyl fluoride show that we have no $>$CHF groupings present and hence it must be 1,1-difluoro-cyclohexane.

Compound 2

1-chloro-1-fluoro-cyclohexane

n_D^{20} 1.4382 b.p. 138.2 at 755 mms.

The molecular formula is $C_6H_{10}ClF$. N.Hydrochloric acid in 80% ethanol and N.sodium ethoxide in absolute ethanol produced 50% reaction. The compound was inert to cold aqueous permanganate solutions and resisted reduction with a palladium carbon catalyst. By analogy to compounds 1 and 4, compound 2 is designated 1-chloro-1-fluorocyclohexane.

Compound 3

1-chloro-cyclohexene

The sample obtained contained a small amount of compound 2. Both analysis by gas chromatography and analysis for halogens indicated the presence of 11.3% $C_6H_{10}ClF$.

The unsaturation detected with acid permanganate solution and a comparison of the chromatograms of this and authentic 1-chloro-cyclohexene showed that compound 3 was unchanged olefin.

Compound 4

1,1-dichloro-cyclohexane

The molecular formula is $C_6H_{10}Cl_2$. N. Sodium ethoxide in absolute ethanol caused 50% reaction and N. hydrochloric acid in 80% ethanol caused 10% reaction. Palladium carbon did not catalyse reduction.

The three possible isomers that could be compound 4 have been prepared[15d] and a comparison of physical constants indicates that we have 1,1-dichloro-cyclohexane

	n_D^{20}	b.p.
Compound 4	1.4801	164-8
1,1dichloro-cyclohexane	1.4803	171
cis 1,2-dichloro-cyclohexane	1.4967	206.9
trans 1,2-dichloro-cyclohexane	1.4902	189

This was confirmed by hydrolysis to cyclohexanone[15d] which was identified as its semicarbazone.

MECHANISM OF REACTION

The products of the reactions were all the 1,1 isomers. It seems that we have normal ionic, as opposed to radical, addition of the acid HX to the double bond, whose ionisation is governed by the mesomeric effect of the vinylic chlorine atom. This is in complete agreement with the results of many other workers, (Table I & ref. 35) but not with those of Mousseron et al[36] who claim to have isolated from the stannic chloride catalysed addition of hydrogen chloride to 1-chlorocyclohexene a product whose identity was found from a density at unspecified temperature to be the trans 1,2 isomer. Mousseron postulates an ionic addition in which the polarisation of the double bond is governed by the inductive effect of the chlorine atom and also states that the 1,1 isomer is unstable at room temperature.

This work of Mousseron et al was repeated and the product found to be 1,1-dichlorocyclohexane. As the addition of HX, must proceed by either an ionic mechanism, to give the 1,1 isomer or by radical mechanism to give the cis 1,2 isomer[35] the isolation of trans 1,2-dichlorocyclohexane is very strange and we must consider Mousseron's identification of the isomer as in error.

The formation of the dichloro and chloro-fluoro compound is explained by the above when HX is either

HCl or HF. The formation of the difluoro compound can be by substitution of the chlorine of the dichloro, or more probably the chloro fluoro compound. An alternative mechanism, similar to that of Henne et al[25], involving the formation of 1-fluorocyclohexene seems improbable as none of the latter was detected.

PROPERTIES OF THE 1,1-DIHALOCYCLOHEXANES

The properties given for these compounds call for little comment except in the case of reduction and solvolysis or dehydrohalogenation. It appears strange that even the dichloro and chloro fluoro compounds do not lose halogen when attempts are made to reduce them while fluoro benzene[13] is reduced to cyclohexane and hydrofluoric acid under similar conditions. It appears that cyclohexyl halides are resistant to reduction however as the fluoride does not lose hydrofluoric acid on attempted reduction.[13]

The unexpected results in the hydrolysis are associated with the chloro fluoro and dichloro compounds. Here reaction stops when half of the halogen is removed. This is in agreement with work by Goering et al.[37] on the dichloro and chlorobromocyclohexanes. Both the 1,1 and cis 1,2 isomers lose half their halogen

3

to give 1-halocyclohexene which is not further attacked while only the trans 1,2 isomer loses one molecule of halogen hydracid to give the 2-halocyclohexene which rapidly loses its second molecule of acid and thus loses all its halogen.

FLUORINATION OF 1,1,2-TRICHLOROCYCLOHEXANE

a) WITH ANHYDROUS HYDROGEN FLUORIDE

As in the previous work, with hydrogen fluoride and 1-chlorocyclohexene and in the examples in Tables I and II, it seems that hydrogen fluoride, with and without catalyst, substitutes chlorine by fluorine an attempt was made to fluorinate the above trichloro compound with hydrogen fluoride at 100°. All that resulted was a solid polymer. Under less rigorous conditions, for example with stannic chloride as catalyst, no reaction occurred at 20° while boron trifluoride produced much polymerisation and negligible yields of volatile liquids at temperatures as low as -78°. Since it seems that the trichloro compound polymerises almost completely in the presence of free hydrogen fluoride under conditions which might produce substitution it was decided to try other fluorinating agents.

b) WITH ANTIMONY TRIFLUORIDE

Many fluorinations have been carried out with fluorides of antimony in the presence of at least some pentavalent antimony. Much of the work has been carried out with highly halogenated aliphatic[38] and aromatic[39] hydrocarbons but this reagent has been used to fluorinate heterocyclic compounds and lightly halogenated ethanes, propanes and butanes. Table IV gives relevent examples.

TABLE IV.

Starting Material	Max. Temp. oC.	Product	Yield	Ref.
CH_3-CCl_3	70	CH_3CClF_2	85%	41
CH_3 CCl_3	70	CH_3CCl_2F	85%	41
Me_2-CCl_2	70	Me_2CF_2	85%	7
		MeCClF	10%	
$MeCCl_2Et$)	Spontaneous	($MeCF_2Et$		42
$MeCCl_2Pr$)	Reaction	($MeCF_2Pr$		42
$MeCH_2CHCl_2$	much decomposition			42

From this it seems that in some cases even large hydrogen-rich molecules can be fluorinated by antimony trifluoride while other similar compounds decompose. As 1,1,2-trichloro cyclohexane possesses one of the groups that facilitate fluorination, a CCl_2 group remote from the ends of a carbon chain, this method seemed promising.

However there were isolated from the reactions only very small amounts of unsaturated liquids containing little fluorine and probably containing large amounts of a chloro-cyclohexadiene.

c) WITH POTASSIUM FLUORIDE

Early work was carried out with anhydrous potassium fluoride and anhydrous organic compounds at elevated temperatures and pressures. In this way undecyl and hexyl fluorides were made[43] as well as a variety of ethers and esters,[43,44] from the corresponding chloro compound although the yields were generally low. The use of xylene as reaction medium in the fluorination of chloroacetamide[45] was the first attempt to remove the need for pressure resistant apparatus. Most of the work involving solvents has been carried out with aliphatic di and poly-hydroxy compounds and in this way a series of ω,ω-difluoroalkanes have been prepared.[10] In more recent publications the reaction between the organic compound and the potassium fluoride is brought about at ambient temperature and pressure by ultraviolet irradiation[46].

When glycerol was used as solvent for trichloro-cyclohexane and reaction conditions were as for the preparation of 1,5-difluoropentane the product was a liquid composed mostly of a dichloro cyclohexene.

Without solvent even higher temperatures were required to promote reaction and a similar product was obtained.

The lack of fluorine in the products indicates that the high temperature required for the reaction causes elimination of hydrogen chloride to give olefins. Olefins are formed as by products in similar reaction.[10]

d) WITH MERCURIC FLUORIDE

Although it is more convenient to use nascent mercuric fluoride generated from hydrogen fluoride and mercuric oxide,[9] in view of the instability of the trichloro cyclohexane to hydrogen fluoride the dry mercuric fluoride was prepared by the action of chlorine trifluoride on mercuric oxide, or chloride.[47] The reaction of this fluorinating agent was extremely vigorous and difficult to control, yielding products that decomposed when attempts were made to distil them.

FLUORINATION OF TRANS 1,2-DIBROMOCYCLOHEXANE

a) WITH HYDROGEN FLUORIDE

Although it is more common to use hydrogen fluoride to replace chlorine in halohydrocarbons there are isolated examples[48] in which bromine has been replaced. An attempt to use this method with the above dibromo compound produced only a solid polymer.

b) WITH MERCURIC FLUORIDE

Considering the success with which bromo compounds can exchange their bromine for fluorine by means of nascent mercuric fluoride[9] it seemed probable that 1,2-difluorocyclohexane might be formed by the action of this reagent on 1,2-dibromocyclohexane. Attempts to do this merely confirmed the lack of success reported by Henne et al.[47]

A further attempt was made using dry meroric fluoride but the product were unsaturated liquids containing bromine and a little fluorine.

c) WITH ARGENTIC FLUORIDE

Preparation of Argentic Fluoride

As the action of fluorine on silver chloride gives rise to low melting intermediates[49] argentous fluoride was oxidised to argentic fluoride with chlorine trifluoride to give a solid containing 27% of the desired argentic fluoride

Products of reaction

At 0° a small amount of unsaturated liquid was produced which analysis showed contained more fluorine than required for the simple replacement of bromine by fluorine. We must therefore have, in addition, replaced some hydrogen by fluorine.

FLUORINATION OF 1,2 DICHLOROCYCLOHEX-1-ENE

Preparation of starting material

The dehydrochlorination of 1,1,2-trichlorocyclohexane was carried out with quinoline as described by Tischenko.[16]

WITH LEAD TETRAFLUORIDE

This reagent can under suitable conditions add on fluorine to a double bond and replace by fluorine halogens other than fluorine and hydrogen.

Starting Material	Temp.	Product	Yield	Ref.
CHCl=CHCl	100°C	$(CHClF)_2$	17.1%	51
$CHCl=CCl_2$	-	$CHClFCCl_2F$	18%	52

As it was thought advisable to attempt to prepare the more fully fluorinated compound 1,1,2,2-tetrafluoro-cyclohexane, the reaction was conducted at 100°C but only polymers resulted.

ACTION OF POTASSIUM FLUORIDE ON SULPHONIC ACID ESTERS OF CYCLOHEXANOLS

As the action of saturated solutions of potassium fluoride on β-halo ethyl esters of benzene sulphonic acid produced good yields of chloro fluoro ethanes[12] while anhydrous reaction conditions produced poorer yields the action of potassium fluoride solutions on esters of cyclohexanol and 2 chlorocyclohexanol was investigated

$$R'C_6H_4SO_3R + KF \longrightarrow R'C_6H_4SO_3Na + RF$$

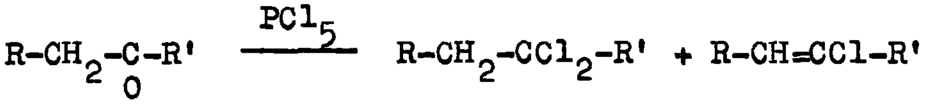
As tosyl esters were easily prepared by standard methods these were used.

From the reaction product of these esters with potassium fluoride solutions no pure products were isolated but the evidence points to the formation of olefins which can then polymerise in the presence of hydrofluoric acid, formed either by elimination from any organic fluoride formed or from hydrochloric acid eliminated and the potassium fluoride present.

Subsequent work has been carried out in which the tosyl esters of highly halogenated alcohols have been converted into chlorides, bromide and iodides[53,54] in hydroxylic solvents without undue loss due to olefin formation or solvolysis of the ester but when this technique was applied to cyclohexyl p-toluene sulphonate and potassium fluoride only cyclohexene was isolated.[54]

Action of phosphorus pentafluoride in ketones

As phosphorus pentachloride reacts with ketones to give two possible products, as shown overleaf



$$R\text{-}CH_2\text{-}\underset{O}{C}\text{-}R' \xrightarrow{PCl_5} R\text{-}CH_2\text{-}CCl_2\text{-}R' + R\text{-}CH{=}CCl\text{-}R'$$

it seems possible that phosphorus pentafluoride might reaction in a similar manner. Lucas et al.[14] state that when phosphorus pentafluoride reacts with amyl alcohol it does not yield amyl fluoride but no reaction between phosphorus pentafluoride and ketones has been reported.

When PF_5 was passed into cyclohexanone, both pure and diluted with ether there were isolated no fluorine containing compounds but only tars and a high boiling unsaturated phosphorus containing compound. When methyl ethyl ketone was similarly treated only tars were isolated. The high boiling compound is probably a phosphoric acid ester of the enol form of cyclohexanone.

18 N.A. Domnin J.Gen.Chem. U.S.S.R. 15 461-8 C.A. 40 4682^{8}

19 C.A. 35 P1413

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23 C.A. 48 P1406e

24 R.C. Arnold C.A. 46 P1022g

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27 W.B. Whalley C.A. 43 2217i

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38 A.L. Henne, Org.React. Vol. II Pages 76-91

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43 E. Gryszkiewicz-Trochimowski Rec.Trav.Chim. 66 412 (1947)

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45 C.W. Bradley C.A. 40 P. 6498^9

46 G. Olah et al. C.A. 48 7533b

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51 T.P. Walkes C.A. 43 P. 5031f

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3

CHROMATOGRAPHIC SEPARATION OF CHLOROFLUORO CYCLOHEXANES

By the action of hydrogen fluoride on 1-chlorocyclohexene a mixture of the above substances and unchanged starting material had been obtained. In view of the thermal instability of some of them it was necessary to develop a means of separation in which the time of heating was of the order of hours and in which the hydrogen fluoride formed by their decomposition was not allowed to collect and autocatalyse further decomposition. Vapour phase chromatography seemed promising and to determine the conditions necessary to produce a good separation in a resonable time investigations were carried out with the homologous series of hydrocarbons from benzene to p-cymene (these substances covering the range of boiling points similar to those of the possible products) on a column packed with 'dinonyl' phthalate on Celite at 113°.

When the gas stream left the column at atmospheric pressure benzene was detected but p-cymene condensed in the tubes immediately after the column. When the exit pressure was reduced to 36 mms. p-cymene gave a reasonable deflection and the separation produced by a new column was acceptable but deteriorated with use.

When this filling was employed in macro scale work it was found that the ester decomposed into nonene, phthalic anhydride and water and so a search was conducted to find a more stable stationary phase. Of the packings tried (see diag. 2.) Edwards 8a high vacuum oil gave the best separation and the addition of stearic acid merely increased the retention volume under the condition of the test (126°C. 65 mms. N_2 flowrate 33 mls./min.).

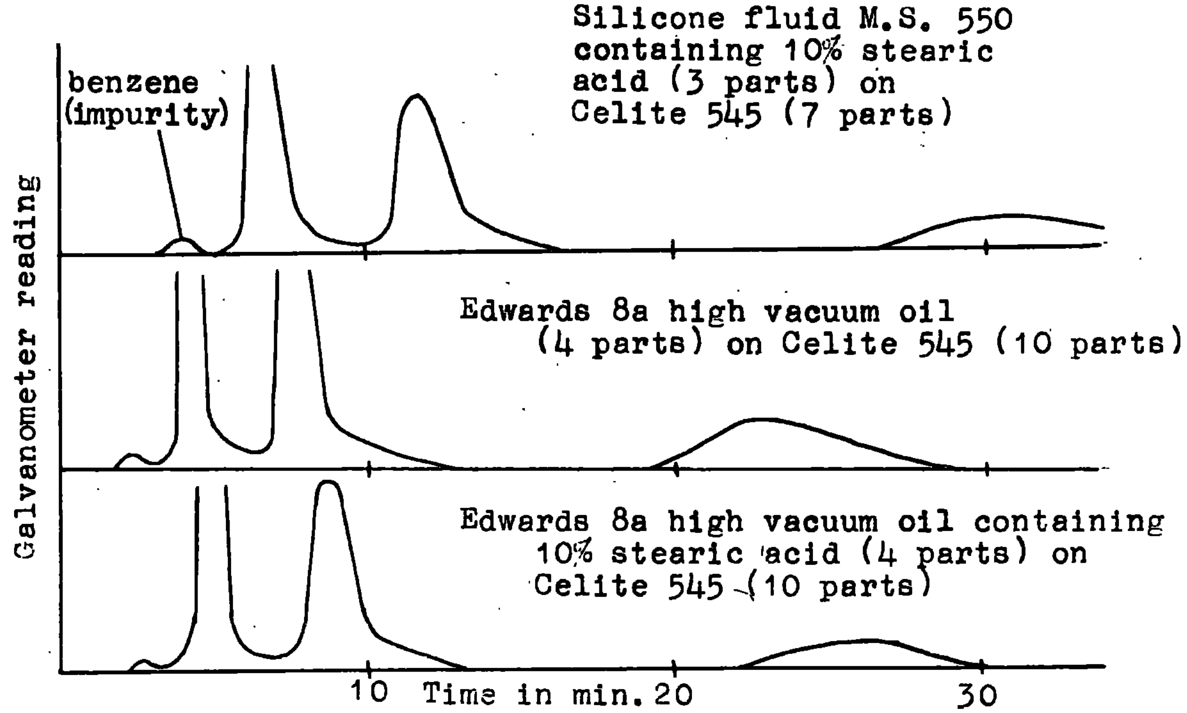
Apparatus and Method of operation

In the apparatus finally adopted for semi-micro work (Fig. 3) the nitrogen was dried (P_2O_5) and passed into the first arm of the detector (Two catharometers and two resistances or four catharometers connected in a Wheatstone bridge network) via a flowmeter, manometer and surge tank. From the detector the nitrogen went to the chromatographic column and the exit gases and vapours were passed through the second arm of the detector and through a cooled trap to a vacuum pump. Valves were inserted between the vacuum pump and the cold trap (V_3), between the manometer and the detector (V_2) and before the drying tube (V_1) to control the rate of flow of nitrogen and the pressure of the gas in the system. The pressure was atmospheric

DIAGRAM 2

Examination of possible substances for stationary phase

a) with mixture of equal parts of toluene, ethyl benzene and p-cymene.



b) Reaction products from HF, $SnCl_4$ and 1-chlorocyclohexene at 20°

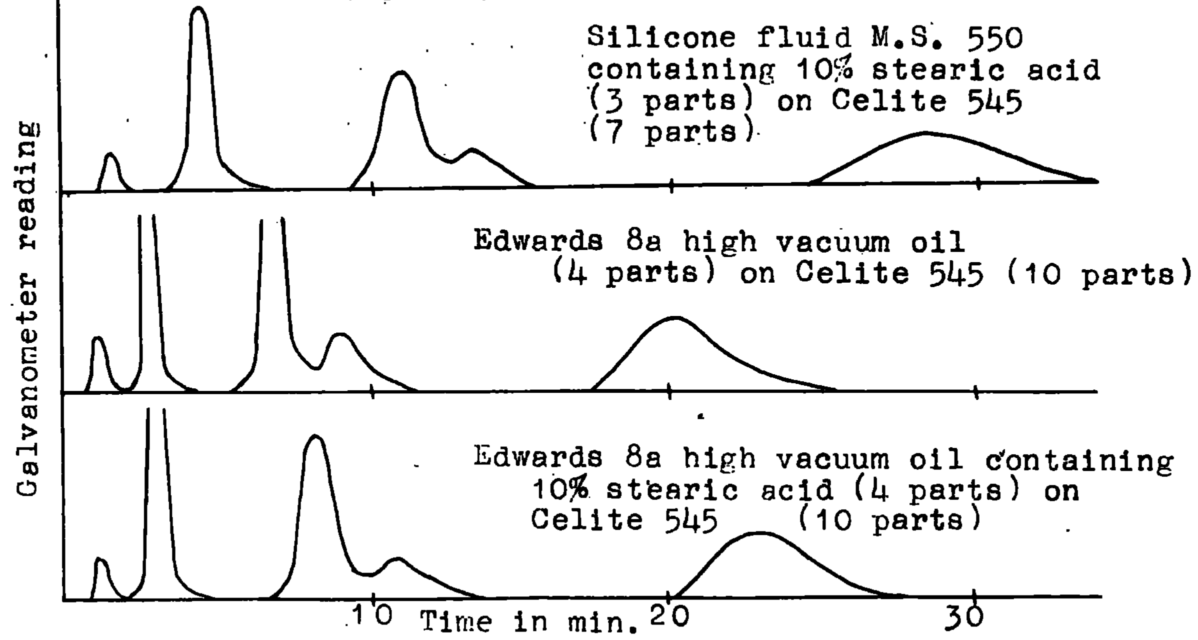
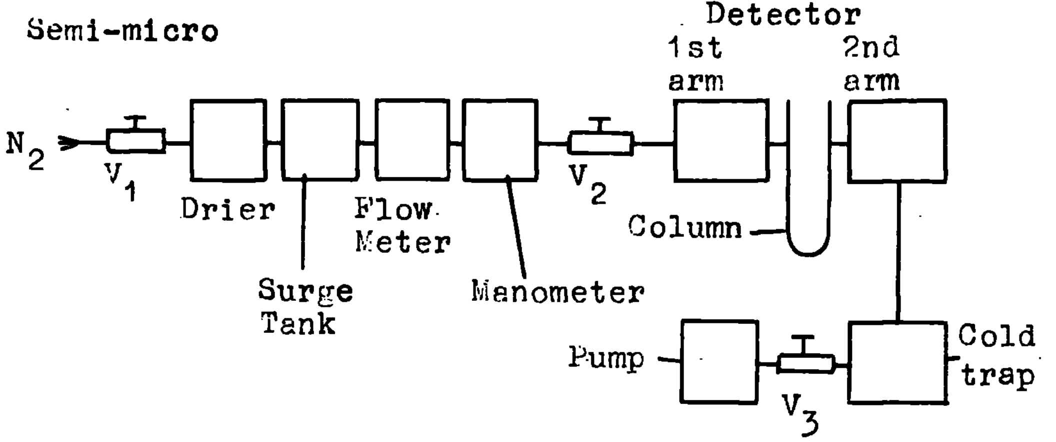


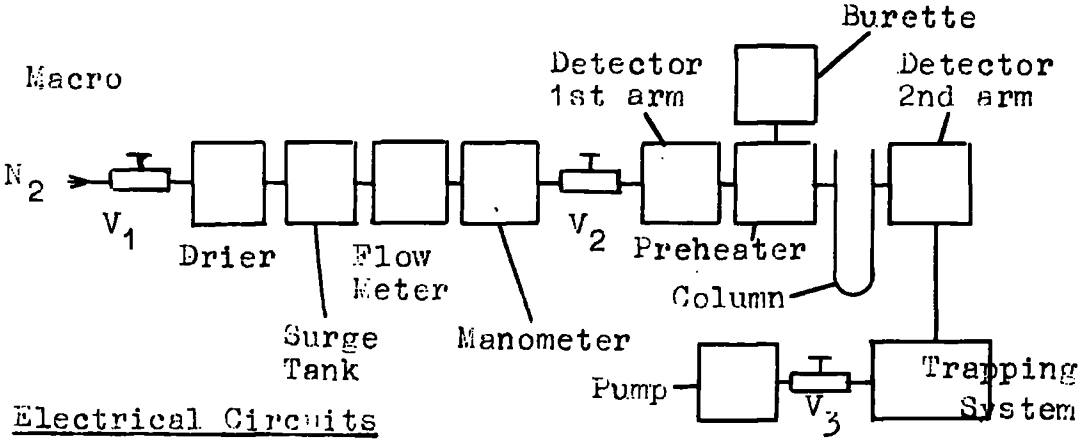
DIAGRAM 3

Block diagram of vapour phase chromatography apparatus

Semi-micro

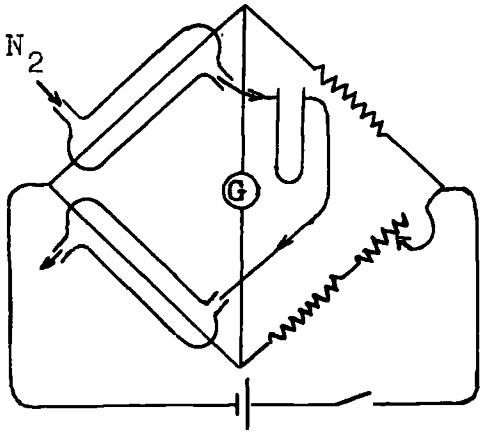


Macro



Electrical Circuits

2 Catharometers and 2 resistances



4 Catharometers

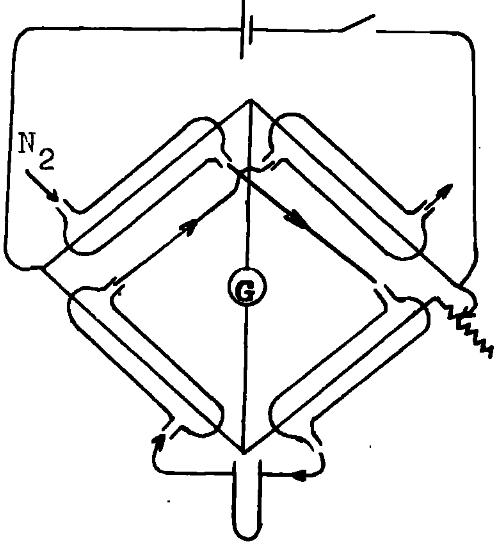
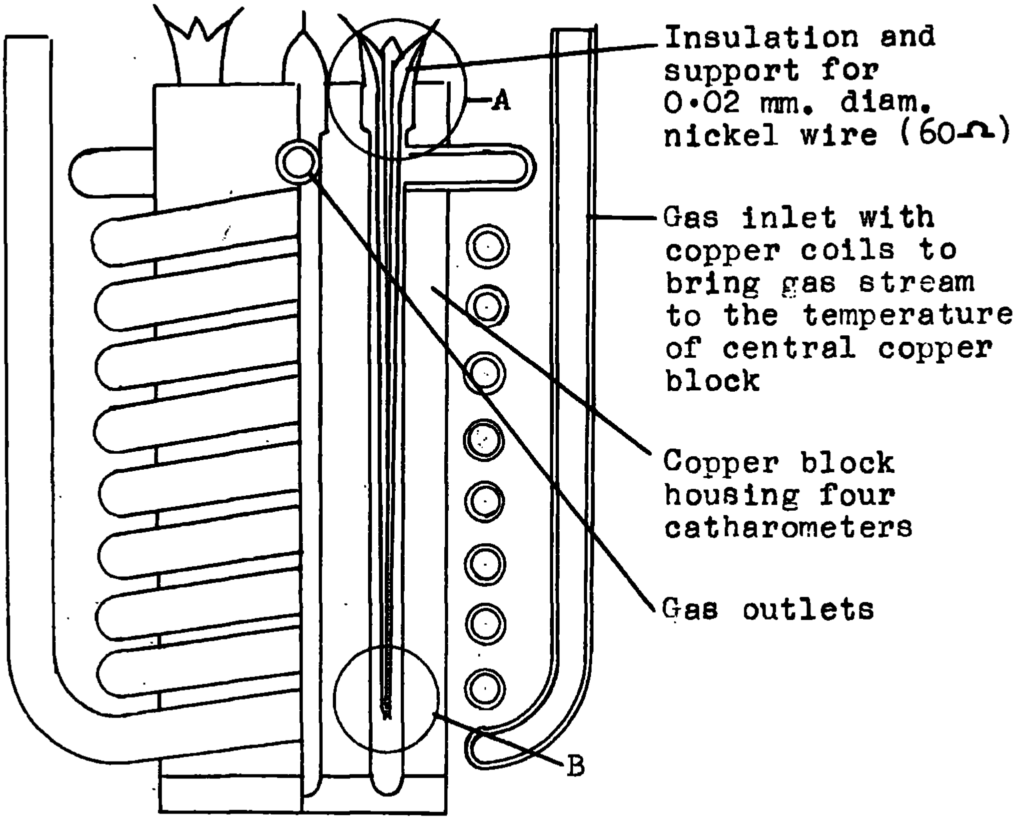


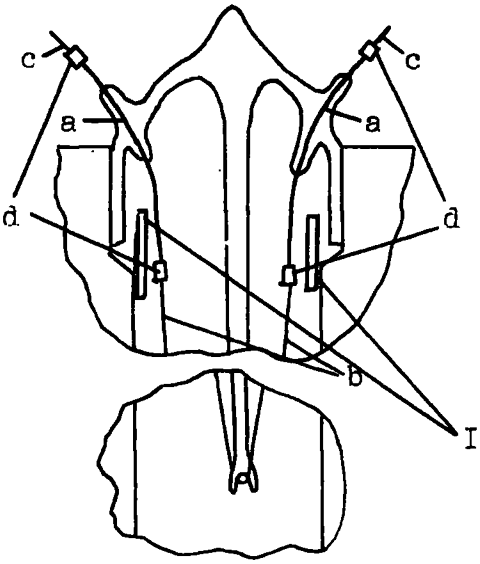
DIAGRAM 4

Copper detector

Elevation and part section (actual size)



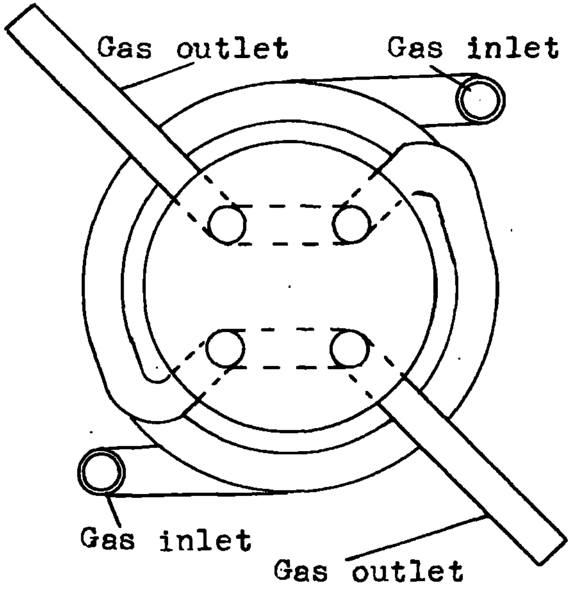
Details of A and B



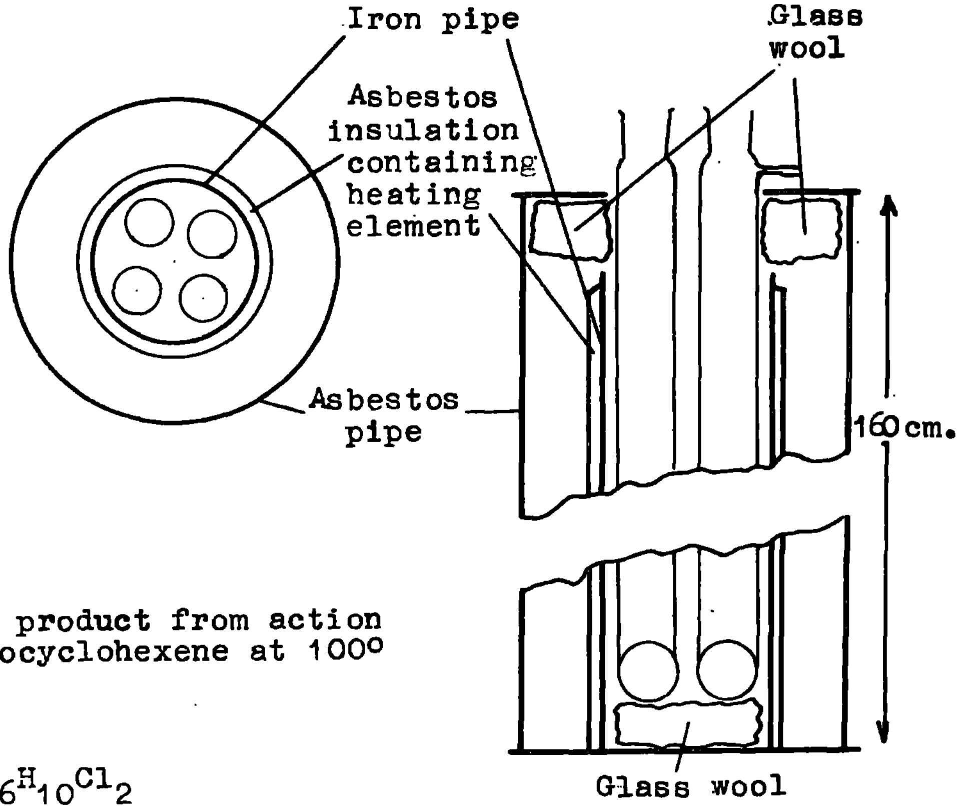
The tungsten wires (a) sealed into the glass and to the ends hard soldered nickel cylinders (d). To these nickel cylinders soft soldered the nickel filament (b) and the connecting wires (c).

DIAGRAM 5

Plan of copper detector (actual size)



Diametric and vertical sections of heater large V.P.C. column (1/4 actual size)



Chromatogram of macro scale separation

Idealised graph for 10 ml. of reaction product from action of HF on 1-chlorocyclohexene at 100°

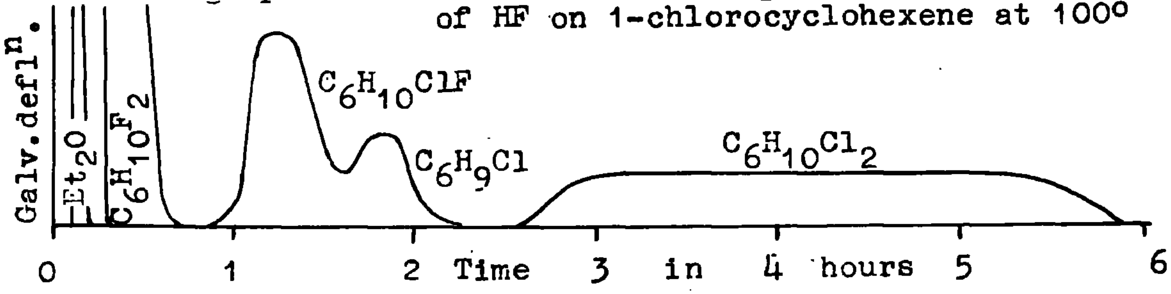
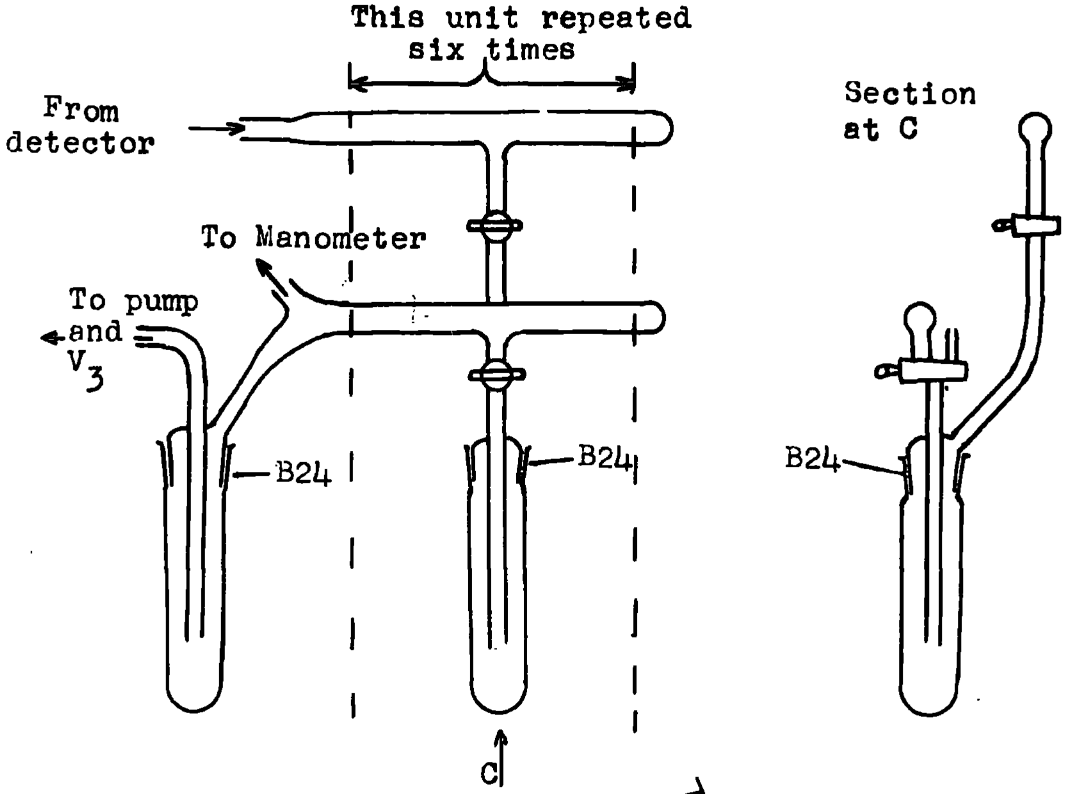


DIAGRAM 6

Trapping system 1/4 full size



One all glass catharometer

The tungsten wires (a) sealed into the glass and to the ends hard soldered the nickel filament (b) [0·02 mm. diam. 60 Ω] and the copper connections(c).

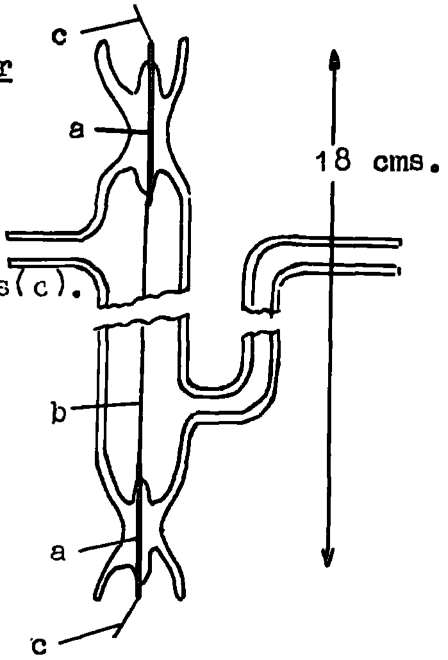
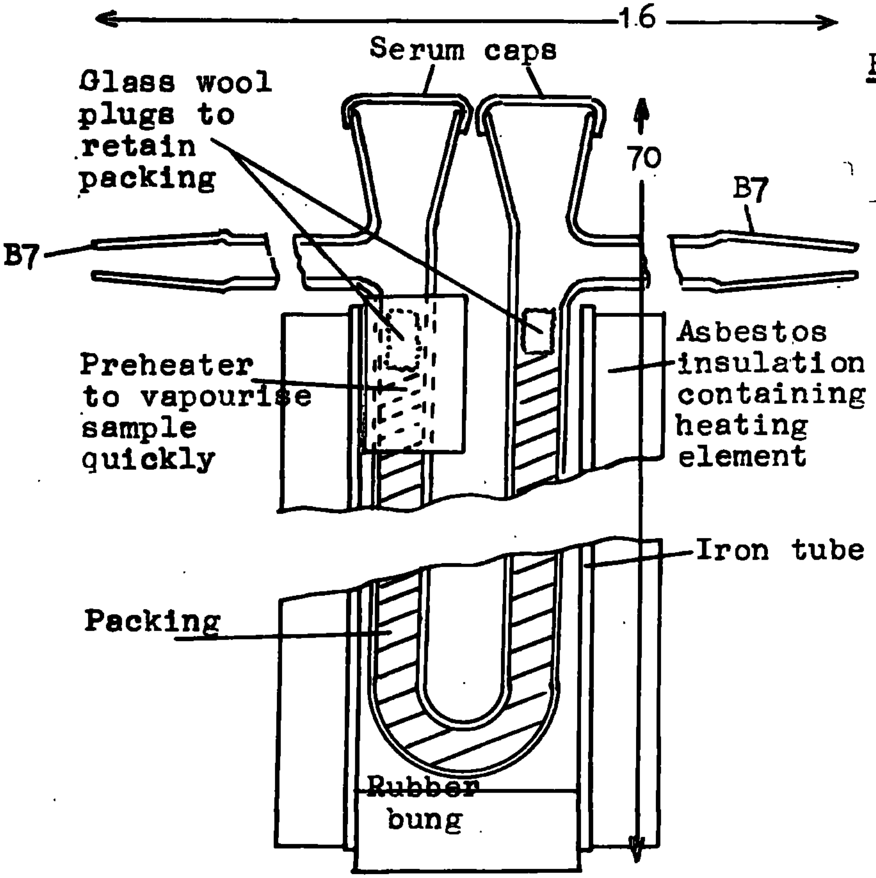


DIAGRAM 7

Small vapour phase chromatography column actual size

Dimensions in cms.

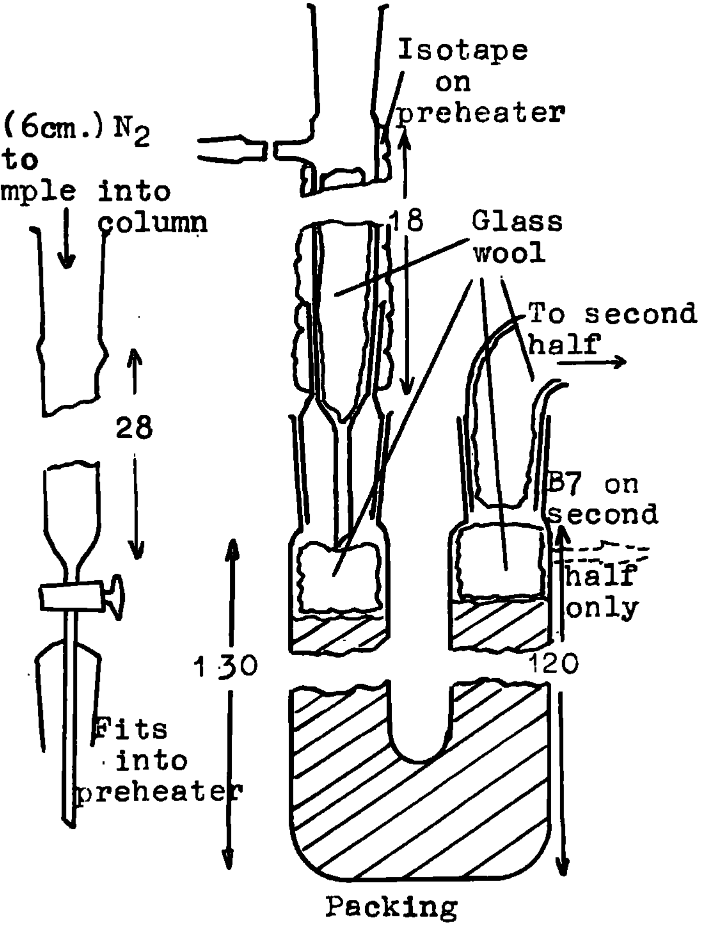


Large vapour phase chromatography column half of column 1/2 size

Dimensions in cms.

Burette

Pressure(6cm.) N_2 applied to force sample into column



up to V_2, falling to the value given in the condition of chromatography upto V_3 (The pressure drop being mostly over the column) while beyond V_3 the pressure was of the order of a few mms. Details of the construction of the detectors (Both types of which were satisfactory), the columns and electrical circuit are given in Diagrams 3-7.

For macro work the apparatus was modified as follows. The larger column was preceeded by a pre-heater (Fig. 3 & 7 to ensure rapid vapourisation of the large sample and a system of traps (Fig. 3&6) was incorporated to collect separately the various samples.

Analytical separations were carried out on small amounts (0.01 ml.) of substance which were introduced with an Agla micrometer syringe and galvanometer readings taken for 30 mins. Larger amounts of liquid (up to 10 ml.) were added with a burette (Fig. 7) and as the pure compounds emerged, as indicated by the galvanometer, they were lead through the appropriate trap cooled in liquid N_2. Complete elution of a sample took 6-8 hours, depending on the age of the packing and although chromatograms of such separations were not constructed an idealised example is given

(Diag. 5).

The Celite 545 was prepared for this work by extracting with concentrated hydrochloric acid, 2N sodium hydroxide solution and grading[55] and the fillings prepared from the stated amounts of material. The semimicro columns contained about 15 g. and the macro columns about 1,000 g. of filling.

PRACTICAL DETAILS

PREPARATION OF 1 CHLORO CYCLOHEXENE

The methods of preparation consist of dropping cyclohexanone onto phosphorus pentachloride. The differences in the methods lie in the use of solvents, the method of working up and the inclusion or ommission of a dehydrochlorination stage.[15] The alternative method of mixing reagents, namely the addition of the solid phosphorus pentachloride to the cyclohexanone, although more easily accomplished, yielded upon hydrolysis of the reaction mixture only tar (see below). In view of the favourable yield and the simplicity of the method that of Braude and Coles was adopted. Gas chromatographic analysis of the olefin so prepared showed the presence of 16% of 1,1-dichlorocyclohexane.

The preparations were carried out as described by the authors but the following observations were made.

a) Carrol et alia[15d]

The steam distillation of the reaction product yielded an initially cold distillate that rapidly warmed. This was thought to be due to hydrolysis of the 1,1-dichlorocyclohexane present. To overcome this loss of product the steam distillate was separated and the organic layer dried as quickly as possible.

b) Mousseron et alia[15b]

The ethereal solution of the reaction products rapidly warmed and eventually boiled in the presence of water and it was found advisable to have ice present until the ethereal solution was dried.

c) Braude et alia[15a]

An additional wash of the crude product with sodium bisulphite solution, to remove any cyclohexanone, did not lower the yield. It was also found that the dry neutral product could be distilled at atmospheric pressure if the distillation was completed in under four hours.

d) Addition of phosphorus pentachloride to cyclohexanone

Cyclohexanone (653 g. 0.68 mole) was stirred in a three necked flask equipped with reflux condenser and phosphorus pentachloride (1,800 g. 0.68 mole) was added from a conical flask via a wide rubber tube with the exclusion of the air while the temperature was kept below 30° by an ice bath. Working up by steam distillation or ice hydrolysis yielded negligible quantities of olefin.

ACTION OF HYDROGEN FLUORIDE ON 1 CHLORO CYCLOHEXENE

WITH OUT CATALYSTS

a) With excess hydrogen fluoride

1-Chloro cyclohexene (50 g. 0.43 mole) was put into a cold autoclave (0°C.) and hydrogen fluoride (26 ml. 1.4 mole) added. The autoclave was rotated, allowed to come to room temperature (30 mins.) and the temperature raised to 100° over one hour when the pressure was 15 atmospheres. After rotating at this temperature for one hour it was allowed to cool overnight and then cooled in ice. The autoclave was vented and the contents sucked out onto crushed ice (200 g.). The resulting heavy dark brown oil was diluted with ether until the relative density of the solytion was less than one, washed with sodium bicarbonate solution and then water until neutral and dried ($MgSO_4$). After distillation to remove most of the ether and leave the tar (10 g.) the remainder, which distilled between 60° and 200° was fractionated through a 15 plate concentric tube column to give intermediate fraction (1 ml.) b.p. 60-100°; 1,1-difluoro cyclohexane

(11.5 ml.) b.p. 100-102°; intermediate fraction (7.3 ml.) b.p. 102°-168°; 1,1 dichlorocyclohexane (1.8 ml.) b.p. 168° and residue (4 ml.)

After a similar experiment the reaction mixture was distilled to remove ether, tar (10.0 g) and high boiling residues (6 g., b.p. $>200^\circ$) and the product (19 g. b.p. 60-200°) analysed chromatographically and found to contain 1,1-difluorocyclohexane (5.9 g.) 1-chloro-1-fluorocyclohexane (2.7 g.), 1 chlorocyclohexene (1.5 g.) and 1,1-dichloro cyclohexane (8.9 g.)

b) <u>With equivalent amount of hydrogen fluoride</u>

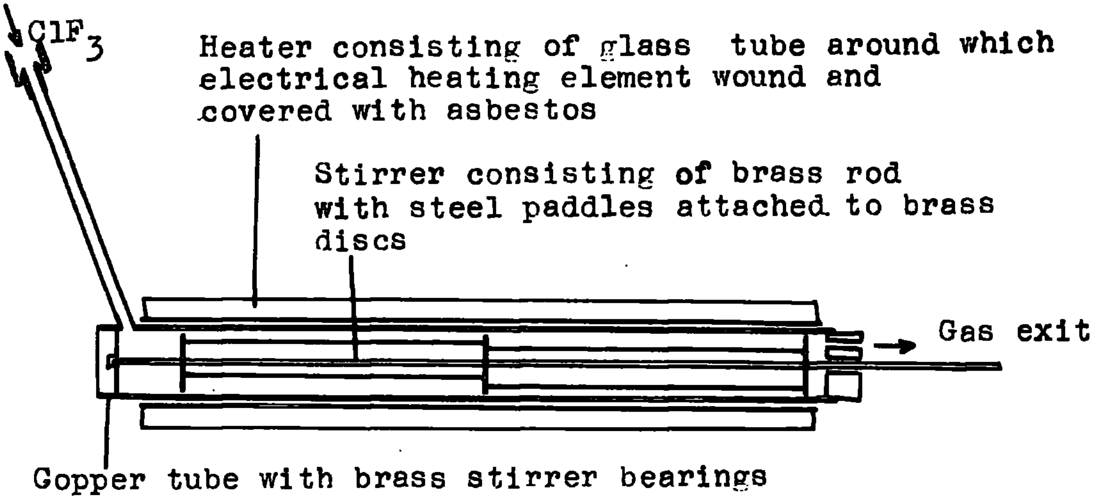
The previous experiment was repeated using 1-chlorocyclohexene (50 g. 0.43 mole) and hydrogen fluoride (8.6 ml. 0.43 mole) but after coming to room temperature the mixture was allowed to stand overnight without heating. No pressure developed and the product was worked up as before. After removal of the ether the crude product (46 g.) was put into the 15 plate concentric-tube still but in bringing it to equilibrium considerable decomposition took place with elimination of halogen acids and formation of tar.

A similar experiment gave on rapid distillation of the ethereal solution of reaction products a

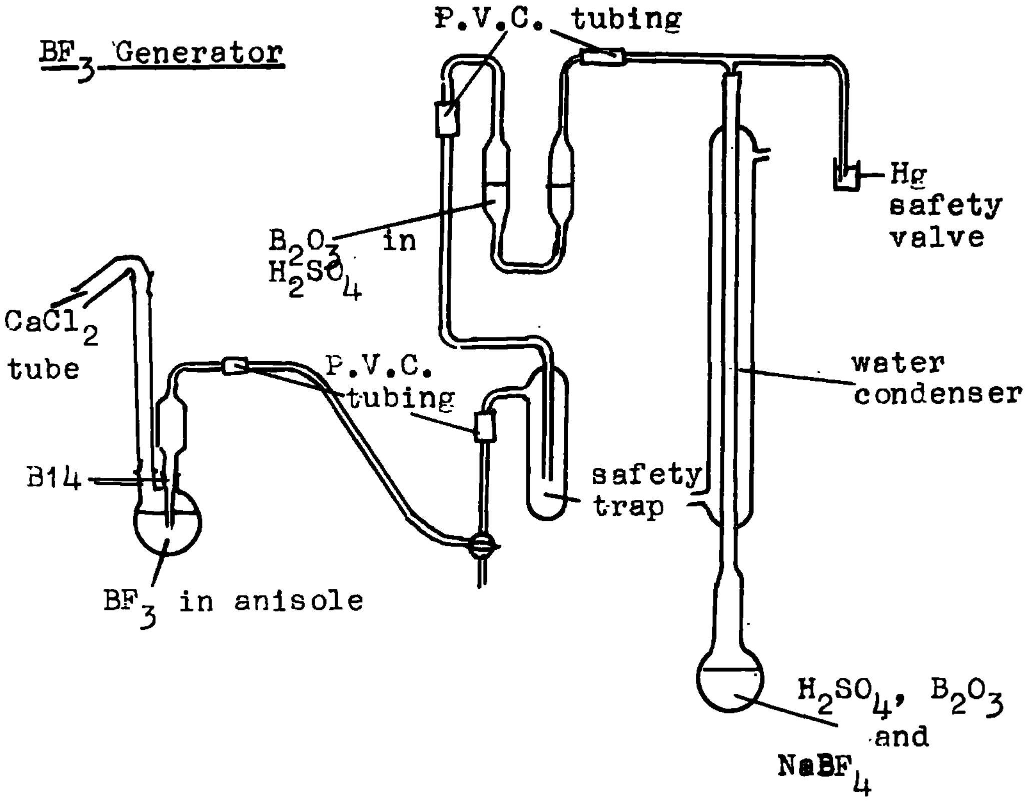
DIAGRAM 8

Reactor used in preparation of AgF_2 and HgF_2

1/3 actual size



BF_3 Generator



crude material (40 g. b.p. 60-180°), still residue (4 g. b.p. > 180°) and tar (2.5 g.). When analysed by gas chromatography the first fraction was shown to contain 1,1-difluorocyclohexane (6.6 g.), 1-chloro-1-fluorocyclohexane (13.3 g.), 1-chlorocyclohexene (2.1 g.) and 1,1-dichlorocyclohexane (18 g.).

WITH CATALYSTS

Boron trifluoride

This gas was prepared by the action of concentrated sulphuric acid on a mixture of sodium borofluoride and boric anhydride as described by H.S. Booth et al.[63] in a glass and polyvinyl chloride apparatus (Diag. 8) and stored in anisole solution, from which it was recovered by heating.

Aluminium trichloride was used without further purification but the stannic chloride was redistilled.

a) With boron trifluoride and excess hydrogen fluoride

1-Chlorocyclohexene (60.5 g. 0.54 mole) and hydrogen fluoride (17.2 g. 0.86 mole) were placed in a brass reaction vessel equipped with a condenser cooled with a solid CO_2/ethanol mixture, and a stream of boron trifluoride passed for two hours. The viscous reaction product was dissolved in ether and

and the ethereal solution washed with sodium bicarbonate solution and water until neutral and dried ($MgSO_4$). Repeated distillations gave intermediate fraction (b.p. < 100°, 2.5 g.), impure 1,1-difluorocyclohexane (b.p. 100-110° n_D^{20} = 1.3981, 9.5 g.) intermediate fraction (b.p. 107°- 158° 4 g.) and a mixture of 1,1-dichlorocyclohexane and 1-chlorocyclohexene formed by decomposition of former during distillation (5 g. b.p. 158-84°/36 mm. 42% Cl 0.35% F)

A similar experiment was conducted using 1-chlorocyclohexene (50 g. 0.43 mole) and hydrogen fluoride (26 ml. 1.3 mole) and the crude product (9 g. b.p. 60-180°) separated from tarry residues (6.5 g.) and liquid residues (3 g. b.p. 80-100/24 mm). When the crude product was analysed by gas chromatography it was found to contain 1,1-difluorocyclohexane (8.9 g.) and negligible amounts of 1-chlorocyclohexene and chlorofluorocyclohexane.

With boron trifluoride and equivalent amount of hydrogen fluoride

The experiment was repeated using 1-chlorocyclohexene (50 g. 0.43 mole) and hydrogen fluoride (8.6 ml. 0.43 mole). Less tar and undistillable residues (4 g.) were obtained and larger amounts of a mixture (35 g. b.p. 80° at At.press. to 96° at 14 cms.)

whose composition was probably similar to that produced when aluminium trichloride and stannic chloride were used. The mixture was not analysed by gas chromatography.

b) <u>With stannic chloride</u>

1-chlorocyclohexene (50 g. 0.43 mole) was cooled to -78° in a brass reaction vessel of about 150 ml. capacity, anhydrous stannic chloride (1 g.) and hydrogen fluoride (8.6 ml. 0.43 mole) were added and the vessel fitted with a screw on lid carrying a delivery tube attached to a calcium chloride tube. The mixture was allowed to warm up to room temperature overnight as the solid CO_2 evaporated, poured onto ether and washed with water, sodium bicarbonate solution, water until neutral and dried ($MgSO_4$). Distillation of this solution yielded a mixture (40.3 g. b.p. 60°-190°) liquid residues (3 g., b.p. 190°-200°) and tar (1.5 g.). The mixture was analysed by gas chromatography and shown to contain 1,1-difluorocyclohexane (5.5 g.) 1-chloro-1-fluorocyclohexane (11.3 g.), 1-chlorocyclohexene (4.0 g.) and 1,1-dichlorocyclohexane (19.4 g.).

c) <u>With aluminium trichloride</u>

The previous experiment was repeated using aluminium trichloride (1 g.) as catalyst instead of stannic chloride. The ethereal solution of reaction products yielded a mixture (42 g. b.p. 60°-180°), liquid residues (3 g. b.p. 180°) and tar (1.5 g.). Gas chromatographic analysis of the mixture showed that it contained 1,1-difluorocyclohexane (1.9 g.), 1-chloro-1-fluorocyclohexane (18.7 g.), 1-chlorocyclohexene (3.7 g.) and 1,1-dichlorocyclohexane (17.8 g.).

The addition of aluminium trichloride to 1-chlorocyclohexene at room temperature produced a vigorous reaction in the absence of hydrogen fluoride and most of the reaction mixture was lost.

COMPARATIVE HYDROLYSES OF THE DIHALO-CYCLOHEXANES

As the difluoro compound was expected to be the least reactive of these three compounds experiments were carried out to find conditions that would just produce hydrolysis of this compound and apply these conditions to the chloro-fluoro and dichlorocyclohexanes.

Hydrolyses with aqueous solutions

1,1-difluorocyclohexane (0.8925 g.) was refluxed on a water bath with 25 ml. N. sodium hydroxide solution samples (0.5 ml.) were removed after 5 hours and 8½ hours and the alkali present titrated with N. acid. Comparison with a blank experiment run in parallel showed that no hydrolysis had occurred.

The sodium hydroxide was brought up to 4N. After a further 5 hours heating qualitative tests (zirconium nitrate and sodium alizarin sulphonate in acid solution) showed the absence of fluoride ion.

After adding more sodium hydroxide to bring the solution to 10 N. the mixture was heated for a further 9 hours. A sample (0.1 ml.) when passed through a cation exchange column (Amberlite IR 120 H)[56] showed, when compared with the blank experiment, that no hydrolysis had occurred.

Hydrolyses in ethanolic solutions

Dry reduced[57,58] ethanol was used throughout and simply by dissolving metallic sodium in this solvent the sodium ethylate solutions were prepared. The hydrochloric acid solutions were made up from ethanol, water and A.R. hydrochloric acid. The hydrolysis mixtures were sealed into hard glass tubes and heated in an oil bath at 130°. At the end of the required time the tubes were cooled to -78°, opened and the contents made up to 100 ml. after

TABLE V

Cpd (g)	Reagent 10 ml. of:	Reaction time (hours)	Alk. required for 10ml. aliquot - Blank (ml.)	Strength of Alkali	% Hydrol
$C_6H_{10}F_2$ (0.7008)	1.042 N.HCl in 80% EtOH and 20% H_2O	16	0.42	0.1016 N NaOH	3.6
$C_6H_{10}ClF$ (0.2520)			1.64		45.1
$C_6H_{10}Cl_2$ (0.6067)			0.76		9.7
$C_6H_{10}F_2$ (0.4848)	1.482 N.NaOEt in EtOH	16	0.87	0.02238 NaOH	2.4
$C_6H_{10}ClF$ (0.3412)			10.82		48.5
$C_6H_{10}Cl_2$ (0.6116)			17.21		48.2

TABLE VI

Cpd (g)	Reagent 10 ml. of:	Reaction time (hours)	Alk. required for 10ml. aliquot - Blank (ml.)	Strength of Alkali	% Hydrol
$C_6H_{10}F_2$ (0.6374)	0.375 N NaOEt in abs. EtOH	$17^3/4$	0.53	0.02224	1.1
$C_6H_{10}F_2$ (0.5466)	1.483 N NaOEt in abs. EtOH	$17^1/2$	1.06	0.02224	2.6
$C_6H_{10}F_2$ (0.4886)	1.042 N.HCl in 80% EtOH	$17^1/2$	0.42	0.1016	5.2

removal of the organic layer in the case of acid hydrolysis.

The amount of reaction in alkaline hydrolyses was determined by passing an aliquot (10 ml.) through a cation exchange column (Amberlite I.R. 120 H)[56] and estimating the halide ion as the halogen hydracid. Blank reaction were run in parallel to allow for the attack of glass.

In acid hydrolyses there was much loss of hydrochloric acid as ethyl chloride. The amount of reaction was estimated from the difference in the acid present in the sample and in a blank experiment. It was found necessary to heat the aliquot to boiling to sharpen the end point. (Tables give details of the reagents etc.)

Attempted reduction of 1,1-dihalocyclohexanes

Samples of the organic halide (0.2-0.5 g.) were shaken with 85% ethanol in the reaction flask of a Towers Atmospheric Pressure Hydrogenation apparatus in the presence of palladised carbon (0.2 g.) at a pressure 1 cm. greater than atmospheric pressure for 1-2 hours. In no case was any hydrogen absorbed or any free halogen acid detected in excess of that liberated in a blank experiment carried out with catalyst and solvent only.

Preparation of cyclohexanone from 1,1-dichlorocyclohexane

A mixture of 1,1-dichlorocyclohexane (11.0 g.) and concentrated sulphuric acid (110 ml.) was stirred and warmed on a water bath at 45°.^{15d} There was a vigorous evolution of hydrogen chloride and after 1 hour the mixture was poured onto ice. After neutralising with sodium carbonate and allowing the crystalsof sodium sulphate to settle the mixture was ether extracted (4 x 25 ml.), the extract dried ($MgSO_4$) and the ether distilled to leave cyclohexanone (4 g. 57%, b.p. 157° n_D^{20} 1.4512 semicarbazone m.p. 165.5° mixed m.p. with authentic specimen 166°).

THE ADDITION OF HYDROGEN CHLORIDE TO 1-CHLOROCYCLOHEXENE

1-Chlorocyclohexene (50 g.) and stannic chloride (2.5 ml.) were cooled to 0° in a flask fitted with a stirrer and calcium chloride tube while anhydrous hydrogen chloride was passed in at the rate of three bubbles per second. After two hours the weight had increased by 6 g. and did not increase on further passage of hydrogen chloride. After dissolving in ether the reaction mixture was washed with dilute hydrochloric acid, water, sodium bicarbonate solution and then water until neutral and dried ($MgSO_4$).

Distillation failed to give pure samples of either starting material or dichlorocyclohexane and so the product, after removal of the ether, was separated roughly into a mixture of monochlorocyclohexene and dichlorocyclohexane (44.5 g. b.p. 100-180°), liquid residues (3 g. b.p. >180°) and tar (1 g.). The mixture was analysed chromatographically and shown to contain 1-chlorocyclohexene (16.4 g.) and 1,1-dichlorocyclohexane (28.0 g.). Allowing for the dichlorocyclohexane already present and for the recovered olefin this represents a yield of 55%.

PREPARATION OF 1,1,2-TRICHLOROCYCLOHEXANE

As 1,1,2-trichlorocyclohexane produced by the action of phosphorus pentachloride on 2-chlorocyclohexanone[15b] contains in addition chloro olefins, the trichloro compound was prepared by the direct addition of chlorine to 1-chlorocyclohexene as described by Tischenko[16].

1-chlorocyclohexene (160 g. 1.4 mole) had chlorine bubbled through until the theoretical increase in weight occurred. (11 hours). The mixture was diluted with ether, washed with water and dried. After several distillations 1,1,2-trichlorocyclohexane

(28 g., 0.15 mole, 10.8% yield) was obtained.

(b.p. 104/19.5 mms - 107/15 mms: Cl found 56.7% required for $C_6H_9Cl_3$ 54.5% n_D^{20} 1.5360 - 1.5300).

By anology to the additive chlorination of cyclohexene[21] an attempt was made to increase the yield and decrease the reaction time by addition of $\frac{1}{4}$ of the theoretical amount of chlorine.

1-Chlorocyclohexene (1,074 g. 9.06 mole), sodium carbonate (10 g.) and anhydrous magnesium sulphate (10 g.) were kept below 20° in a cylindrical reaction vessel while chlorine (170 g. 2.4 mole) was absorbed. In spite of the sodium carbonate, some of which remained, there was a copious evolution of hydrogen chloride. The reaction mixture was poured onto dilute sodium carbonate solution, the organic material ether extracted, washed, dried ($MgSO_4$) and distilled. After several distillations 1,1,2-trichlorocyclohexene (379 g., 2 mole, 83% yield with respect to chlorine absorbed) was obtained and 1-chlorocyclohexene (304 g. 2.6 mole 29%) recovered. In view of the labour involved in recovering unchanged olefin and the losses this involves this method was not adopted.

In the third attempt chlorine was passed down the stirrer into the olefin (170 g. 1.4 mole) in a cylindrical ice cooled reaction vessel in the dark until the solution was green (dissolved chlorine). After stirring for 5 mins. to allow hydrogen chloride to escape the mixture was poured onto ice, and the organic layer washed dried and distilled. Over a series of reactions the product (n_D^{20} 1.4499 - 1.5290) was isolated in yields of 36-49%.

FLUORINATION OF 1,1,2-TRICHLOROCYCLOHEXANE

WITH HYDROGEN FLUORIDE

1,1,2-Trichlorocyclohexane (37 g. 0.20 mole) and hydrogen fluoride (60 mls. 3.0 mole) were placed in an autoclave and heated to 100° and 18 atmospheres and then allowed to cool overnight. The contents of the autoclave,a viscous oil, contained much hydrogen fluoride and when poured onto ice yielded only a solid, soluble in benzene.

WITH BORON TRIFLUORIDE AND HYDROGEN FLUORIDE

The trichloride (50 g. 0.27 mole) and hydrogen fluoride (10.6 ml. 0.53 mole) mixed in a brass reaction vessel and boron trifluoride (11 g.) passed for 45 mins. The thick tarry product in ether solution was washed with sodium bicarbonate solution, water until neutral and dried ($MgSO_4$). Distillation of this solution yielded a negligible amount of unsaturated liquid (b.p. 58-99/29 mms., n_D^{20} 1.4924), acid fumes and solid polymer.

WITH BORON TRIFLUORIDE AND HYDROGEN FLUORIDE AT -78°

1,1,2-Trichlorocyclohexane (50 g. 0.27 mole) and hydrogen fluoride (10.6 ml., 0.53 mole) were mixed in a brass reaction vessel at -78° and boron trifluoride passed for 1 hour. When allowed to warm up the contents were found to be only tars. As the tarring might occur during the warming up the above experiment was repeated but immediately the reaction was completed the contents were poured onto ether and the ethereal solution washed with sodium bicarbonate solution, with water until neutral and dried ($MgSO_4$). Distillation of this solution yielded an unsaturated liquid (3.5 g. b.p. 78-88/17 mm. n_D^{20} 1.4938) and much polymer.

WITH STANNIC CHLORIDE AND HYDROGEN FLUORIDE

The trichloride (50 g. 0.27 mole) and hydrogen fluoride (10.6 ml. 0.53 mole) and stannic chloride (1 g.) were mixed in a brass reaction vessel at -78° and allowed to come to room temperature. The contents were poured onto ether and the ethereal solution washed, dried and distilled to give mainly starting material (8.5 g. b.p. 38^{0}/75 cms. 88^{0}/23 mms. n_D^{20} 1.4946) containing a little low boiling substance and unreacted starting material (19.5 g. b.p. 88/23 mm. - 96^{0}/20 mms. n_D^{20} 1.5056).

WITH ANTIMONY TRIFLUORIDE

The antimony trifluoride was purified by recrystallisation from dry methanol[59] and the antimony pentachloride was redistilled.

a. 1,1,2-trichlorocyclohexane (20 g. 0.11 mole) and antimony trifluoride (20 g. 0.11 mole) and antimony fluoride chloride (3 g. prepared by passing chlorine into molten antimony trifluoride) were mixed in a distillation flask and heated until reaction took place (280^{0}). The distillate was dissolved in ether, washed with sodium bicarbonate solution and water until neutral and dried ($CaCl_2$). Distillation of the ether solution gave an unsaturated liquid (1 g. b.p. 140-150^{0} n_D^{15} = 1.4786).

Slight alterations of the experimental technique were tried

b. Antimony trifluoride (18 g. 0.10 mole) and antimony pentachloride (1 g.) were mixed and heated to 180^{0} in a flask equipped with dropping funnel and condenser in distillation position. The trichloride

(18 g. 0.10 mole) was added slowly and the distillate worked up as before to give an unsatured liquid (1 g. b.p. 146-156 n_D^{20} 1.4734 34.7% Cl 8.3% F)

c. 1,1,2-Trichlorocyclohexane (20 g. 0.11 mole) and antimony pentachloride (1 g.) were heated together to 180° in a flask equipped for distillation and antimony trifluoride (20 g. 0.11 mole) added with the exclusion of air. The distillate was worked up as before and yielded an unsaturated liquid (3 g. b.p. 146-170 n_D^{19} = 1.4790).

WITH POTASSIUM FLUORIDE

The potassium fluoride was dried under reduced pressure (about 2.0 cms.) at 170°. The glycerol was distilled under reduced pressure rejecting the initial distillate. The samples used had the following properties b.p. 173°/16 mms. n_D^{20} 1.4741.

a) With solvent

Potassium fluoride (12 g. 0.21 mole) and glycerol (30 g.) were stirred at 180° in a creased flask[60] equipped with dropping funnel and delivery tube to cooled receiver. 1,1,2-Trichlorocyclohexane (20 g. 0.18 mole) was added slowly over 3 minutes. A vigorous reaction then took place and after 10 minutes 8 mls. of liquid had distilled over. The apparatus was flushed with CO_2 (30 mins.) and the distillate (10 g.) washed with water, sodium bicarbonate solution, water until neutral and dried ($MgSO_4$). Distillation gave an unsaturated liquid (b.p. 79°/24 mm. n_D^{19} 1.4994 43.4% Cl, negligible F) which appeared to be mostly dichlorocyclohexenes.

b. Without solvent

Potassium fluoride (20 g. 0.35 mole) was heated to 150° and the trichloro compound (20 g., 0.18 mole) added slowly as above. No reaction occurred until the temperature was raised to 210° when a rapid distillation took place which subsided after 10 minutes. The distillate was worked up as before to give an unsaturated liquid (8.5 g. b.p. 80-92/18 mm. n_D^{19} 1.5083 44.2% Cl negligible F) as well as small amounts of a more volatile unsaturated fraction (3.5 g. 54°/26 mm-80/19 mms. n_D^{19} 1.4940.) It thus seems we again have the formation of dichlorocyclohexenes with the possibility of some chlorocyclohexadienes.

WITH MERCURIC FLUORIDE

Preparation of mercuric fluoride

The reactor (Diag. 8) was charged with mercuric chloride (100 g. 0.36 mole) and the temperature raised to 150° while chlorine trifluoride initially diluted with nitrogen was passed for 5 hours (27 g. 0.29 mole). The pale yellow product contained negligible chlorine.

The use of mercuric oxide (100 g. 0.47 mole) and chlorine trifluoride (36 g. 0.39 mole) in a similar but unstirred reactor at 150° produced a solid containing 75% of mercuric fluoride.

Attempted fluorination

1,1,2-trichlorocyclohexane (34.5 g. 0.18 mole) was placed in a brass reaction vessel and mercuric fluoride (71 g. of 75% pure, 0.22 mole) was added portionwise. As a vigorous reaction took place immediately the reaction vessel was cooled and a condenser attached. After standing 30 minutes at room temperature the products were dissolved in ether and the organic layer washed with water only and dried. When distillation of this solution was attempted decomposition occurred at 40°.

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ATTEMPTED FLUORINATION OF 1,2-DIBROMOCYCLOHEXANE

a. WITH HYDROGEN FLUORIDE

1,2-Dibromocyclohexane (64 g. 0.25 mole) and hydrogen fluoride (21 mls. 1 mole) were sealed in an ice cold autoclave and heated to 100° and then allowed to cool. The product (solid and a little liquid) was poured onto ice and ether and the ethereal solution washed with sodium bicarbonate solution and water until neutral and dried ($MgSO_4$). When distilled this yielded only ether while there was recovered from the washings a solid polymer (10 g.).

b. WITH MERCURIC FLUORIDE

i) Nascent mercuric fluoride. 1,2-Dibromocyclohexane (121 g. 0.5 mole) and mercuric oxide (100 g. 0.5 mole) were stirred together in a brass reaction pot and hydrogen fluoride added until the red colour of the mercuric oxide disappeared (8 hours). Ether (300 ml.) was added, the solid mercuric bromide washed with ether and the ethereal solutions washed with water only and dried ($MgSO_4$). Distillation produced complete decomposition of the distilland at 160°C, up to which point only ether had distilled. This reaction was repeated and the distillation carried out under reduced pressure to give a liquid (20.5 g. b.p. $22^{o}/29$ mms. - $55^{o}/18$ mms) that decomposed completely when attempts were made to redistil at atmospheric pressure.

b.ii) Solid mercuric fluoride. 1,2-Dibromocyclohexane (36 g. 0.15 mole) was placed in a cooled brass vessel and mercuric fluoride (24 g. of 75% 0.07 mole) added portionwise. After standing 30 minutes the products were dissolved in ether and ice added. The ethereal solution was washed with water only and dried ($MgSO_4$). Distillation yielded a liquid containing negligible fluorine (5 g. b.p. 40^{o}/At. Press. -45/25 mm. $n_D^{19.5}$ 1.3690, 5.2% Br 2% F) and starting material (14 g. b.p. $45^{o}/25$ mms - $96^{o}/11$ mms) and 7 g. residue. More vigorous conditions were tried.

Mercuric fluoride (36 g. 0.15 mole) was placed in a flask equipped with dropping funnel, stirrer and lead to condenser in distillation position and receivers at -78^{o}C. 1,2-Dibromocyclohexane (36 g. 0.15 mole) was added, the temperature being raised after the first few drops were added until reaction occurred and then the addition being completed slowly. There were recovered from the cold traps two very small samples of liquid. The first was unsaturated (9.1% F. 18.7% Br) while the second was saturated and probably contained starting material (0.6% F and 40.1% Br).

c. WITH ARGENTIC FLUORIDE

Preparation of argentic fluoride Argentous fluoride[60] (102 g. 0.8 mole) was placed in a reactor and heated while nitrogen was passed to dry the substance. Chlorine trifluoride was then passed for 9 hours (21 g. 0.23 mole) and the dark powder so produced analysed by titrating the iodine it liberates from aqueous potassium iodide solution, showed it to be 27% AgF_2.

Attempted fluorination Argentic fluoride (73 g. of 27% 0.14 mole) was placed in an ice cooled flask equipped with stirrer, dropping funnel and lead to traps at -78°. 1,2-Dibromocyclohexane (15.5 g. 0.06 mole) was added when a vigorous reaction took place. When this subsided the pressure was reduced to ensure removal of volatile products to the cooled traps. The reaction products when distilled from solid potassium fluoride yielded two unsaturated liquids ($\frac{1}{2}$ ml. b.p. $< 20^\circ/10$ mms. 27.8% F) and ($\frac{1}{2}$ ml. b.p. $> 20^\circ/10$ mm. 30.3% F, 10.4% Br) in both of which hydrogen as well as bromine had been replaced by fluorine.

FLUORINATION OF 1,2-DICHLOROCYCLOHEX-1-ENE

Preparation of 1,2-dichlorocyclohex-1-ene 1,1,2-trichlorocyclohexane (50 g. 0.27 mole) and quinoline (34.5 g. 0.27 mole) were mixed and heated under reflux to 210° during 25 minutes and kept there for 20 minutes by which time the vigorous reaction had subsided. The reaction product was poured onto water, ether extracted, washed with water only and dried. Distillation gave a mixture of the desired olefin with the lower boiling chlorocyclohexadiene as a liquid with a wide boiling range (24 g. 60% b.p. 76°/200 mms - 84/12 mms.).

As the diolefin was formed by the elimination of two molecules of hydrogen chloride from one molecule of starting material the trichlorocyclohexane (234 g. 1.19 mole) was heated to 210° and quinoline (153 g. 1.19 mole) was added slowly and the temperature raised when a violent reaction set in at 235°. The reaction mixture was cooled, poured onto water, and ether extracted. The ethereal solution was washed with 2N hydrochloric acid, 2N sodium bicarbonate solution, with water until neutral and dried ($MgSO_4$). Distillation gave 1,2-dichlorocyclohex-1-ene containing less of the chlorocyclohexadiene (130 g. 0.86 mole 72% b.p. 62/35 mms - 96°/10 mms).

As potassium fluoride at 190° caused the dehydrochlorination of 1,1,2-trichlorocyclohexane an attempt was made to use this on a preparative scale with potassium fluoride that had only been oven dried at 100°. The product was mainly starting material. The second method of preparation was adopted.

Attempted fluorinations. Dry lead dioxide, (79 g. 0.33 mole) hydrogen fluoride (68 ml. 3.4 mole) precooled to -78° and 1,2-dichlrocyclohex-1-ene (50 g. 0.33 mole) also precooled to -78° were sealed in an autoclave at 0° and heated to 100°. After cooling overnight the contents in ether were washed with hydrochloric acid and water until neutral and dried ($MgSO_4$). Distillation of this solution gave only tar and an unsaturated liquid (a few drops, b.p. 54°/25 mms) probably the decomposition product of the tar. There remained in the autoclave a resin like solid.

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ACTION OF POTASSIUM FLUORIDE SOLUTIONS ON SULPHONIC ACID ESTERS OF CYCLOHEXANOLS

Preparation of esters A modification of one of the methods given by Wild[61] for the esterification of phenols was used. Tosyl chloride (20 g. 0.1 mole) & cyclohexanol (10 g. 0.1 mole) were dissolved in pyridine (15 ml. 019 mole) and left overnight.

The excess pyridine was then removed with 2N hydrochloric acid to give the crude ester (24.0 g. 0.094 mole, 94%).

Recrystallisation from petroleum ether gave the pure ester, m.p. 44-44.5° (reported 43.3-43.8[54], 44-44.5[62]). The tosyl ester of trans 2-chlorocyclohexanol was prepared in a similar way from the alcohol in 83% yield and after recrystallisation from methylated spirit the pure ester (m.p. 52-52.5°) was obtained.

Attempted fluorination Cyclohexyl tosylate (15 g. 0.06 mole) and aqueous potassium fluoride solution (7.8 ml. of 50% solution, 0.13 mole) were sealed in a glass tube and heated to 150° for 8¾ hours. The tube was then cooled, opened and the contents washed out onto more water. The oily product was ether extracted and the ether solution washed, dried

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($MgSO_4$) and distilled to give 1 ml. of an ether solution of product (1.4% F, smells of cyclohexene) and tar while the reaction tube was etched.

The second ester (0.03 mole) and aqueous potassium fluoride solution (4 mls. of 50% solution, 0.03 mole) were similarly treated to yield an unknown solid and an etched reaction tube.

ACTION OF PHOSPHORUS PENTAFLUORIDE ON KETONES

Preparation of phosphorus pentafluoride Calcium fluoride (500 g. 6.4 mole) was ignited in an iron vessel for 1 hour and then sealed and allowed to cool. Phosphorus pentoxide (220 g. 1.6 mole) was stirred in and the iron vessel resealed and heated, the phosphorus pentafluoride being allowed to escape for 5 mins. to flush the apparatus out and then lead through the ketone in a brass reaction pot equipped with water condenser and calcium chloride tube.

Attempted fluorinations When cyclohexanone (25 ml. 0.24 mole) was used the reaction products were dissolved in ether, washed with water only and dried ($MgSO_4$). Distillation gave only ether and a tar that decomposed at 190°. When the cyclohexanone (47 ml. 0.46 mole) was diluted with ether (200 ml.) and the reaction mixture similarly worked up there was produced an ethereal solution from which the ether was removed at 20° under reduced pressure to leave a tar which distilled up to 260°/15 mms. The distillate was redistilled to give a liquid (b.p. 107/25.5 cms. to 120°/4.2 cms.) containing cyclohexanone. The latter was removed as the bisulphite compound and the insoluble liquid ether extracted, washed with water and dried ($MgSO_4$). On distillation this yielded a liquid (b.p. 140-44/21 mms. 5 g.) containing phosphorus but no fluorine, possibly a phosphoric acid ester of the enol form of the ketone.

Similar experiments with methyl ethyl ketone yielded only unchanged starting material and tar.

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THE REACTION BETWEEN CHLORINE TRIFLUORIDE AND TRICHLOROACETIC ACID

CONTENTS

Experimental details

Action of chlorine trifluoride on trichloroacetic acid and trichloroacetyl chloride

Results

INTRODUCTION

In the pursuit of an ionising solvent for liquid phase reactions with chlorine trifluoride Tanner[1] found that chlorine trifluoride decomposed trifluoro- and trichloro-acetic acids and trichloroacetyl chloride and fluoride. Although few quantitative results were obtained the presence of inert halocarbons (carbon tetrachloride and hexachloro-ethane), carbonyl chloride, carbon monoxide, carbon dioxide, oxygen and chlorine was shown while, in the case of trichloroacetic acid, trichloroacetyl chloride was also detected.

Little work has been published on the decomposition of pure trichloroacetic acid. Various catalysts and reagents have been used to promote the thermal decomposition of this acid into products similar to those above. (Table I). The decomposition of solutions of acetic acid and its salts has been more extensively studied and the products are again similar to those above. (Table II).

The decomposition of the acid chloride can only be compared to the pyrolysis of trifluoroacetyl bromide to yield trifluoromethyl bromide[2] and of trichloroacetyl chloride and bromide to give carbon tetrachloride and

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bromotrichloromethane respectively.[3]

There are several reactions that although not directly connected with the reaction being studied have from the similarity of the products some possible connection with the reaction and for this reason are included in the example given (Table III).

Table I

Thermal decomposition of CCl_3COOH

catalyst or reagent	Temp. °C.	Product	Ref.
C	250-300	$CHCl_3$, CO_2 (little CO, C_2Cl_4, C_2Cl_6, HCl)	4
ThO_2	260-320	CO_2, CO, $CHCl_3$, C_2Cl_4 (little C_2Cl_6, $COCl_2$)	4
Kaolin	230		4
C	135	$CHCl_3$, CO_2	5
ThO_2	165	CO, HCl, $COCl_2$ (also CO_2 from $COCl_2 + H_2O$ in apparatus)	5
Pummice stone	180		5
Aniline	100	$CHCl_3 + CO_2$	6

Table II

Decomposition of CCl_3COOH in solution

Solvent	Temp.	Products	Ref.
H_2O	70-90	$CHCl_3$ & CO_2	7
$PhNMe_2$ $PhNEt_2$ Ph_2NMe	70	$CHCl_3$ & CO_2	8
$PhNH_2$	45	$CHCl_3$ and CO_2	9

Decomposition of salts of CCl_3COOH in solution

Solvent	Salt	Activation	Products	Ref.
H_2O	Trace of Fe^{3+} in acid	hv	CO_2 & C_2Cl_6	10
H_2O	all Fe^{3+}	hv	CO_2 & $CHCl_3$	10
H_2O	K^+	hv	CCl_3CHO, HCl CO_2, CO	10
H_2O	Na^+	temp. 40 - 100	$CHCl_3$ CO_2	11

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Table III

Related Reaction.

Starting Material	Temp.	Activation	Products	Ref.
$CCl_3CHO + O_2$	90	$hv+Cl_2$	$COCl_2$, HCl, CO	12
$CCl_3CHO + O_2$	90	$hv+Br_2$	$COCl_2$, CO, HCl BrCl, H_2O	13
$CCl_3CHO + Br_2$	90	hv	CO, HBr, CCl_3Br $COBr_2$ & $CHCl_3$	14
$CCl_3CHO + Cl_2$	90	hv	CCl_4, CO, HCl	15
CF_3COONa	170	-	CF_3H & CO_2	
$CF_3COOH + Br_2$	540	active C	CF_3Br	3
CCl_3COOH and KF in $PhNO_2$ soln.	130	-	$CHCl_3$, CO_2	17
$CHCl_3$ and O_2		rays	$COCl_2$, HCl, & Cl_2	18

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DEVELOPMENT OF METHOD

The experiments carried out were required to furnish quantitative information about the reaction products. These products can be classified as active or inert according to their behaviour towards alkaline sodium sulphite solutions. Into the former class fall halogens, acid halides (including carbonyl halides), halogen hydracids and carbon dioxide while the inert materials appear from Tanner's work to be mostly fully halogenated methanes and ethanes with small amounts of oxygen and carbon monoxide.

From Tanner's thesis it appeared difficult to design an apparatus such that all the desired information could be derived from one experiment. Accordingly it was decided to derive the information by comparison of the results of several experiments.

As gas chromatography was considered to be the most promising means of identifying and estimating the halogenated methanes the first necessity was to obtain them as gases or liquids in the absence of halogens and acids, or substances capable of generating acids. As chlorine trifluoride is probably present among the products of the reaction an alkaline solution of sulphite seemed a reasonable scrubbing liquid. Preliminary experiments in which the reaction products were scrubbed with such a solution and then passed through a series of cooled traps showed that the halogenated methanes were satisfactorily retained by the use of ethanol/Drikold and liquid oxygen cooled traps while the halogenated ethanes were retained by the water cooled condenser in the metal apparatus. Gas chromatographic analysis could be satisfactorily carried out on the samples of halogenated methanes so obtained.

The estimation of the active constituents required rather more development. The first necessity was a means of removing the excess chlorine trifluoride from the reaction products and leaving other halogens. It was found that when chlorine trifluoride was passed over both liquid and solid hydrocarbons the chlorine trifluoride was either inefficiently absorbed or chlorine was generated. When pure chlorine was passed into or over the hydrocarbons it was found to dissolve or react, in some cases quite appreciably.

These facts were utilised to develop a method of phosgene analysis. The chlorine trifluoride was removed with benzene and the chlorine was removed by antimony metal leaving only the phosgene together with carbon dioxide and inert materials which did not interfere with the iodometric determination of the phosgenes.[23]

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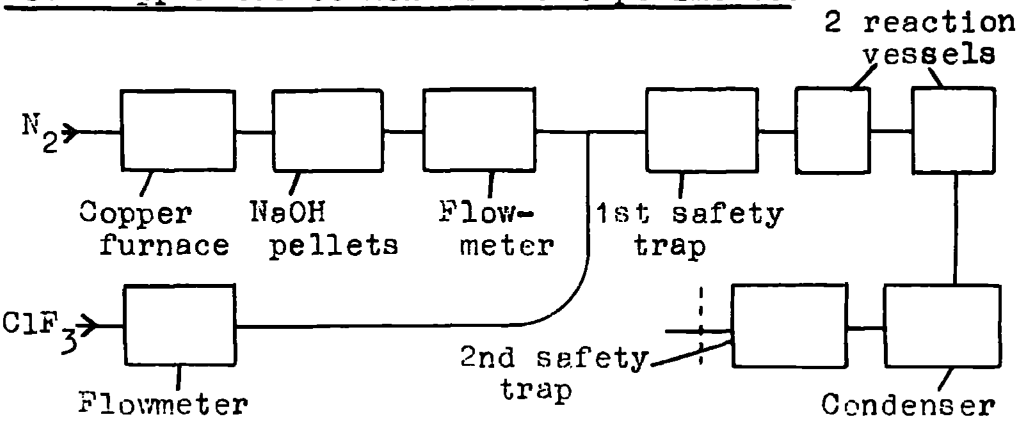
DIAGRAM 1

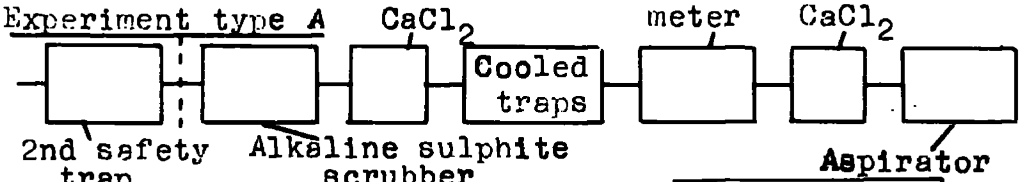
Block diagram of apparatus used to investigate the action of ClF_3 on CCl_3COOH & CCl_3COCl

Metal apparatus common to all experiments.

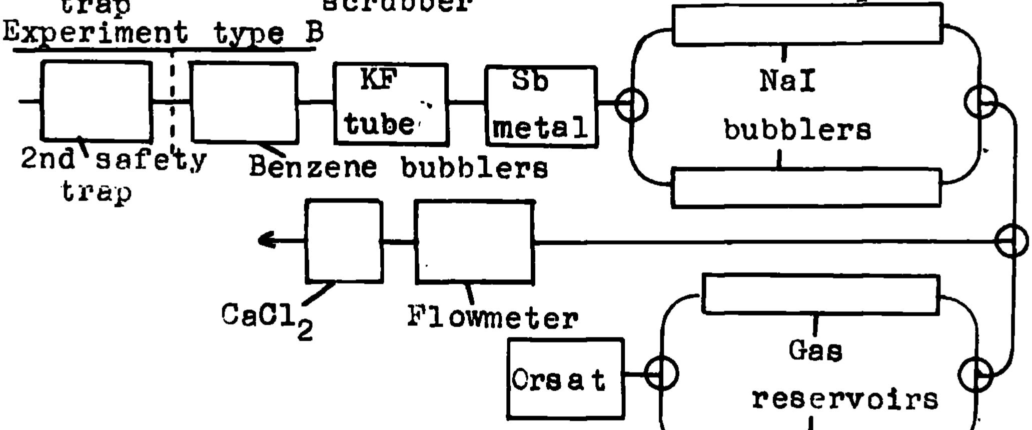


Glass apparatus

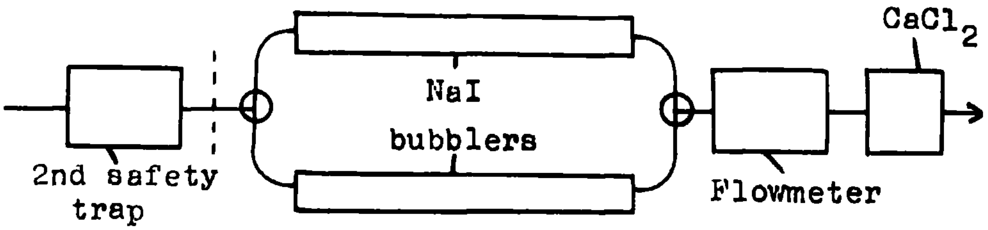
Experiment type A



Experiment type B



Experiment type C



It was also found that the whole of the reaction products could be safely passed into a solution of sodium iodide in dry acetone, thus giving the total amount of halogens and phosgenes including the excess chlorine trifluoride.

Estimates of the carbon dioxide, oxygen and carbon monoxide were easily obtainable by use of a standard Orsat apparatus to analyse the gas stream emerging from the solution of sodium iodide in acetone used to estimate the phosgene. Attempts to remove the entrained acetone failed but it was found not to interfere with the gas analysis. No direct figures were obtained for the halogen hydracids and trichloroacetyl halides but estimates were made by comparison of the results of all three experiments.

In order that the reliability and mode of expression of the results given may be more easily understood a short description of the three types of experiment finally adopted will be given.

In all experiments the reaction occurred in metal apparatus from which the products passed through a water cooled condenser. (See diag. 1).

Type A. The active components were removed by an alkaline sulphite scrubber from which the resultant gas stream was dried and passed through traps cooled in ethanol/Drikold and liquid oxygen.

Type B. The reaction products were passed through benzene, over potassium fluoride, antimony metal and then into sodium iodide dissolved in dry acetone. The iodine liberated according to the equation

$$COX_2 + 2NaI \longrightarrow CO + I_2 + 2NaX$$

being estimated by titration with sodium thiosulphate solution. The gas stream was analysed by means of an Orsat apparatus for carbon dioxide, oxygen and carbon monoxide.

Type C. The reaction products were passed into a solution of sodium iodide in dry acetone and the iodine estimated as before. In experiments of types B and C some of the iodine containing solutions had their fluoride content estimated.

The previous results have been calculated on the assumption that

a. No substitution of the CCl_3- group occurs in the CCl_3COOH prior to its decomposition.

b. There was a negligible amount of carbonyl halides in the acid residues in the reaction vessels.

c. The halogenated ethanes were confined to the metal apparator before the reflux condenser and that none of the more fluorinated ethanes were present in the liquid in the cooled traps.

d. No carbon containing compounds were carried out on the N_2 stream.

Attempts were made to justify these conclusions by performing the following experiments.

_a_ and _b_ An experiment of type A was carried out for three hours at 100°. A sample of the residual acid was converted to the methyl ester by a method designed not to lose low boiling compounds. Chromatographic analysis of these esters showed only the presence of dimethyl carbonate and methyl trichloroacetate. This experiment also yielded information about the rate of formation of the halogenated methanes.

_c_ Samples of halogenated methanes from the cooled traps were chromatographed for periods much in excess of those required to elute carbon tetrachloride but no further peaks occurred in the chromatogram showing the absence of other compounds. This was also apparent from the fact that during analysis the weights of detected components gave a reasonable value for the density of the sample, which would not be the case if a component was omitted.

_d_ Samples of the exit gases were analysed by gas chromatography and found not to give peaks. Hence low boiling halogenated methanes, in particular carbon tetrafluoride, were not being lost.

The results given in table I are the results of types B and C give the variation of the rate of production of some of the products with time (diags. 2, 3 and 4). The rate of production of carbon dioxide was found to pass through two maxima. When the reaction was carried out in a larger single reaction vessel the rate of production of carbon dioxide rose initially and then slowly decreased.

DIAGRAM 2

Variation of rate of production of CO_2 with time

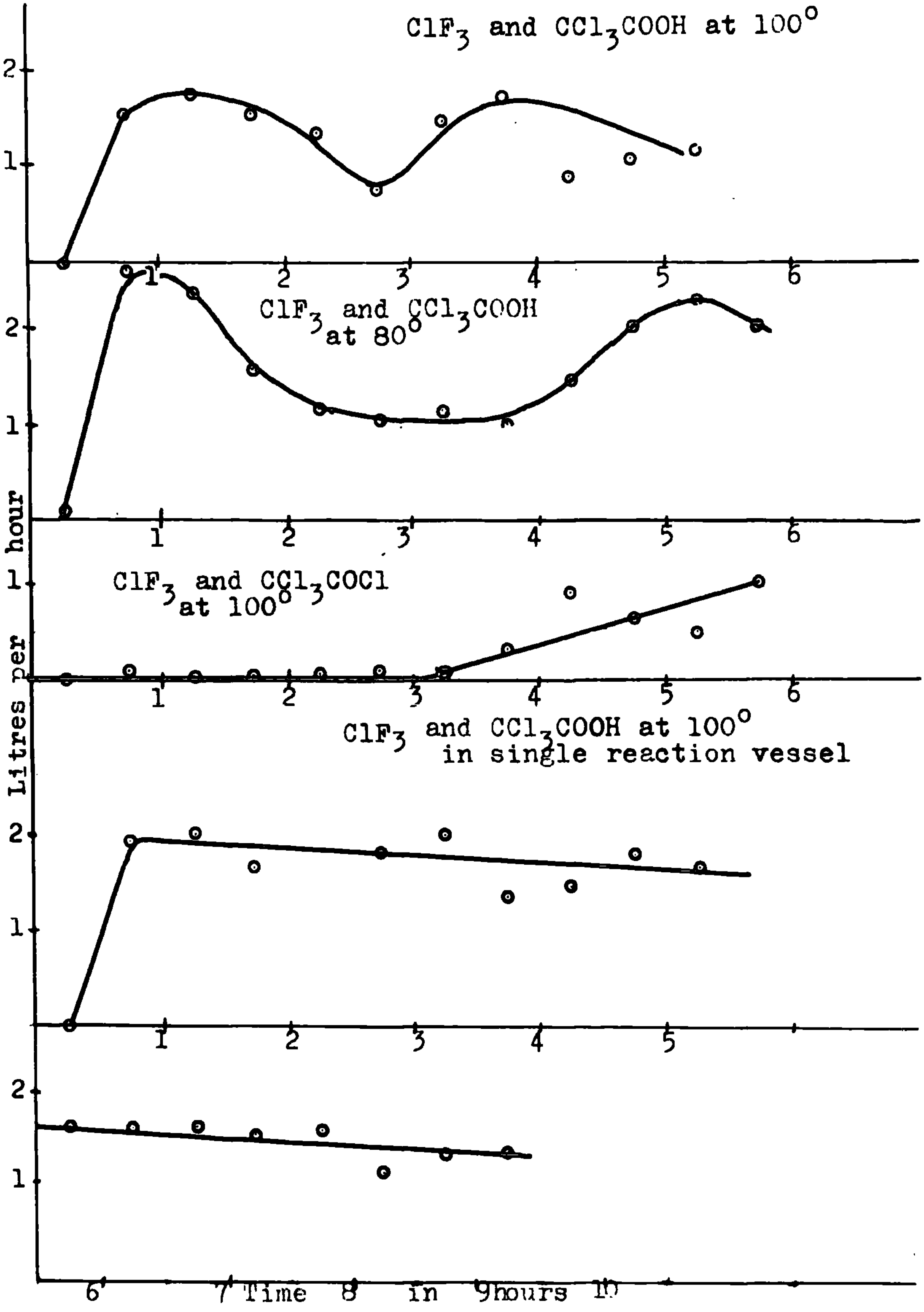


DIAGRAM 3

Variation of rate of production of phosgenes with time

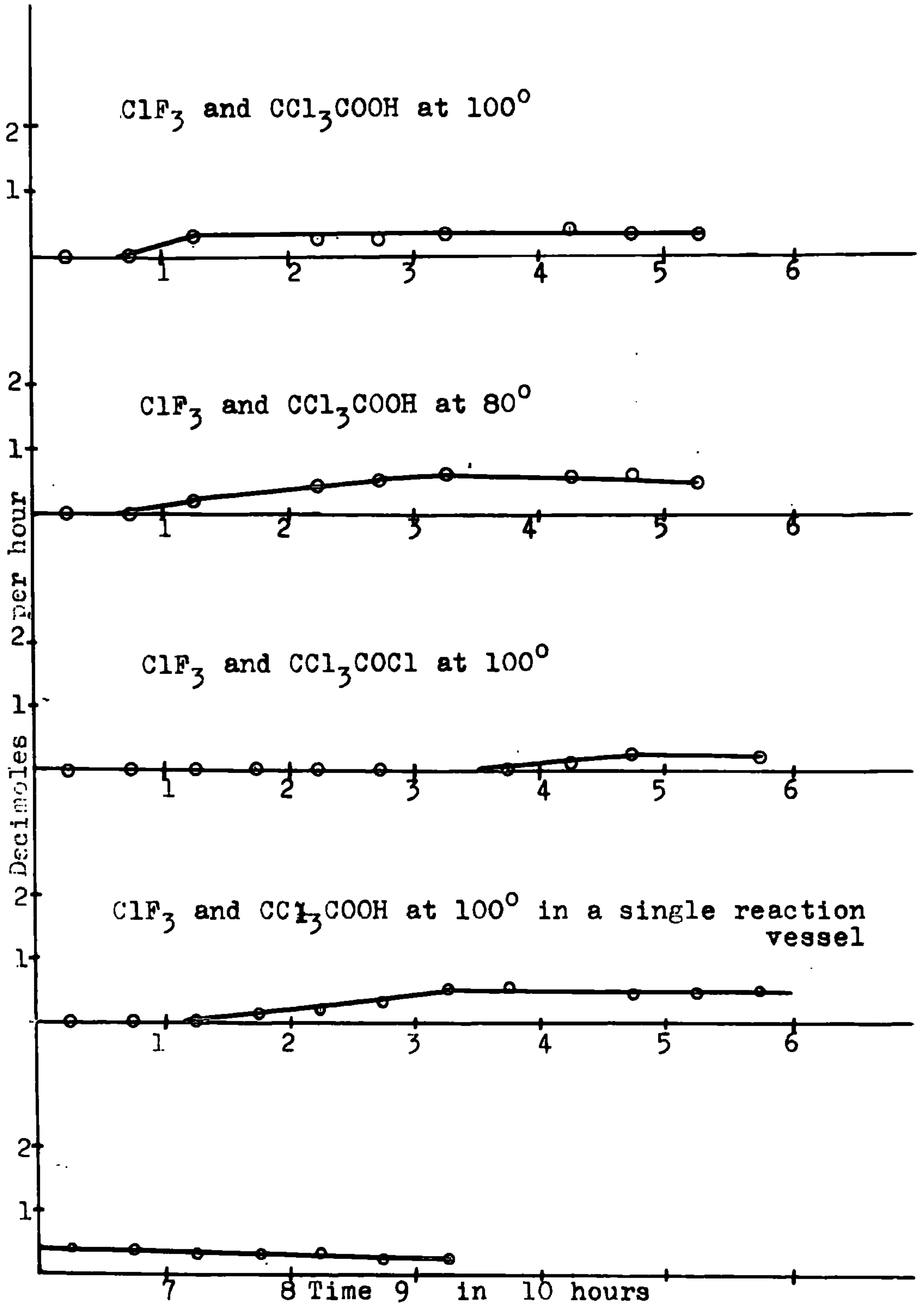
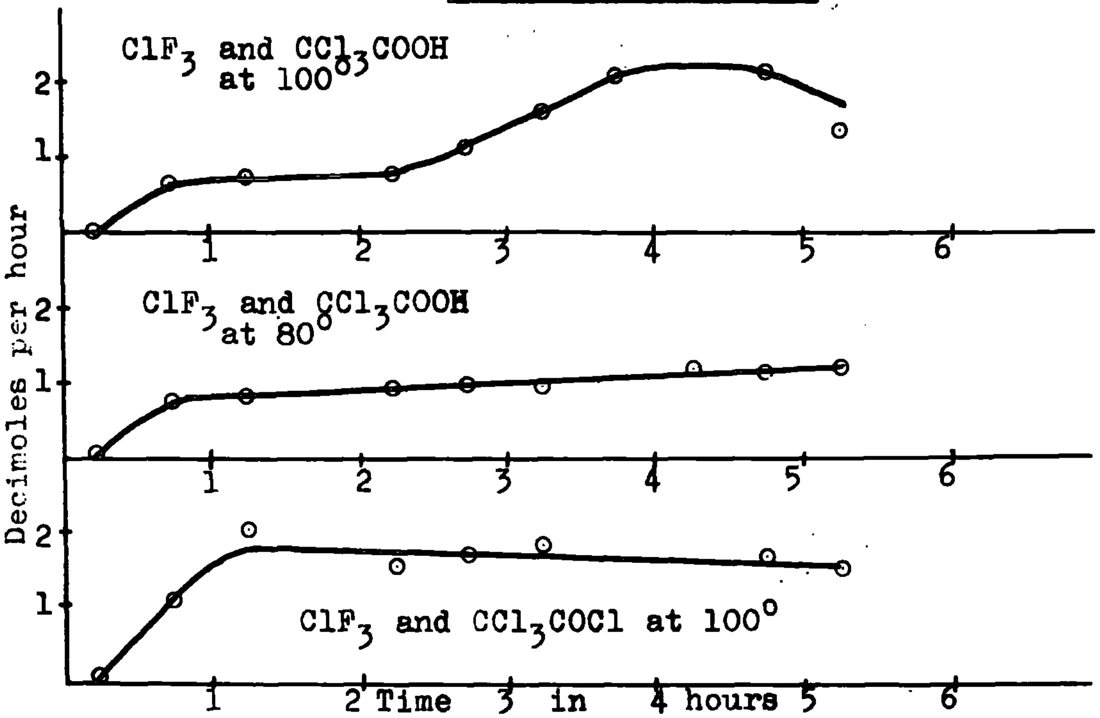
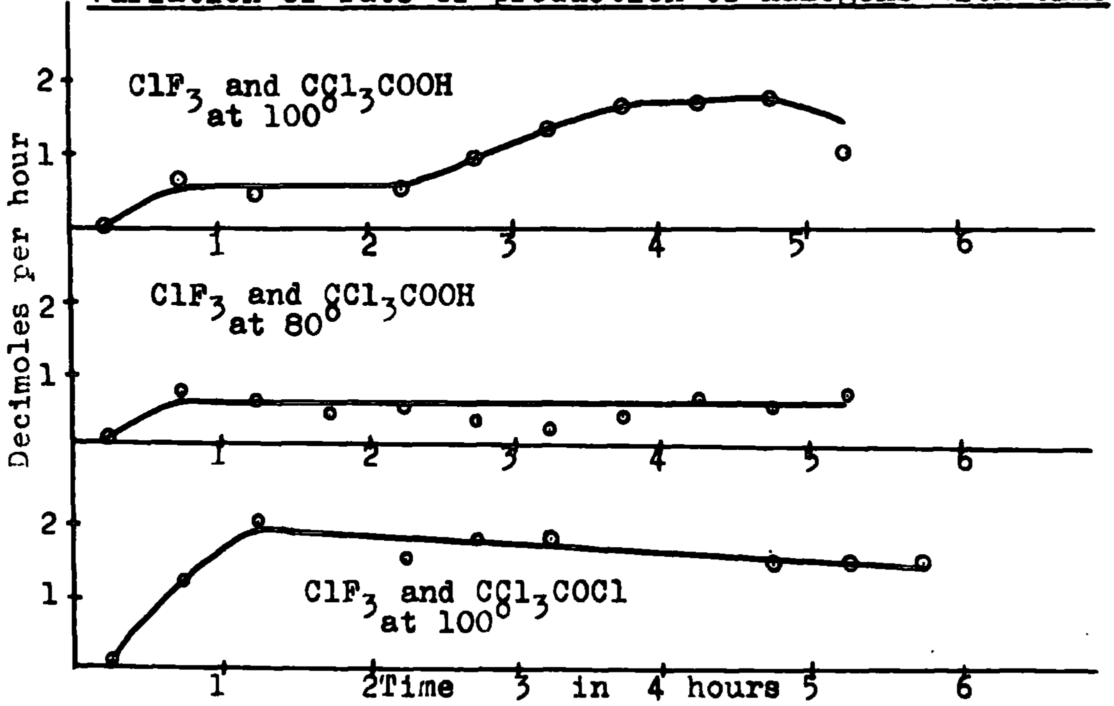


DIAGRAM 4

Variation of rate of production of halogens and phosgenes with time



Variation of rate of production of halogens with time



Products of reaction from 0.62 mole acid (or acid chloride) and 0.31 mole of ClF_3.

Product	Acid at 100°		Acid at 80°		Acid halide at 100°		Acid at 100° (50% reaction)	
	g.	mole	g.	mole	g.	mole	g.	mole
C_2Cl_6	6.5	0.028	16.8	0.070	2.5	0.011	14.8	0.062
CCl_4	19.2	0.13	11.2	0.075	1.5	0.0098	4.9	0.032
CCl_3F	6.1	0.045	7.7	0.056	6.9	0.050	1.6	0.011
CCl_2F_2	1.8	0.015	0.2	0.0015	0.1	0.00083	0.3	0.0025
$CClF_3$	4.9	0.046	0.1	0.00096	0.1	0.00096	0.2	0.0019
CO_2	14.5	0.33	22.3	0.51	5.1	0.12	6.7	0.15
O_2	0.2	0.0047	0.1	0.0032	0.1	0.0031	0.1	0.0031
CO	0.3	0.0011	2.3	0.0083	-	-	0.2	0.0071
CCl_3COCl	-	-	0.5	0.0027	76.5	-	0.4	0.0022
CCl_3COF	-	-	2.0	0.012		-	1.5	0.0091
CCl_3COOH	11.0	0.067	1.0	0.0062	-	-	40.3	0.25
COX_2 containing								
CO	2.3	0.084	3.7	0.13	0.5	0.019	0.7	0.026
Cl	2.6	0.073	6.5	0.18	0.8	0.023	0.8	0.023
F	1.8	0.095	1.6	0.84	0.3	0.015	0.6	0.029
Halogen containing								
Cl	14.7	0.41	5.9	0.17	26.0	0.73	3.7	0.105
F	3.3	0.17	3.0	0.16	2.9	0.15	0.7	0.037
CCl_3COX & HX containing								
Cl	8.2	0.23	9.1	0.25	6.2	0.18	4.5	0.13
F	7.2	0.39	9.8	0.52	4.6	0.24	6.4	0.34

MECHANISM OF REACTION

Trichloracetic acid

The action of chlorine trifluoride on trichloroacetic acid has been shown to produce a variety of products. Carbon dioxide occurred in the greatest amount with smaller quantities of halogenated methanes (mostly carbon tetrachloride) and carbonyl halides while traces of hexachloroethane, carbon monoxide, oxygen and acid halides were detected. The hydrogen of the carboxyl group was assumed to be evolved as halogen hydracid.

Taking into account the similarity between the products obtained in this reaction and those products obtained in other reactions proceeding by free radical mechanisms (Table III), a free radical mechanism is proposed for this reaction. This is supported by the isolation of hexachloroethane, whose presence can be most readily accounted for by such a mechanism.

Although only traces of acid halides were detected at the end of the reaction it is possible that quite large amounts were present during the process but that during the period in which all traces of chlorine trifluoride were blown out with N_2 gas they, especially the more volatile fluoride, were carried out of the reaction vessels. The more reactive acid fluoride[1] would also be speedily removed by reaction. It is thus possible that the acid halide might be an intermediate in the reaction. Cady and Kellog[19], by the action of fluorine on trifluoroacetic acid,have prepared trifluoroacetyl hypofluorite. It is possible that analagous hypohalites might take part in the present reaction. Bearing in mind the unstable nature of trifluoroacetyl hypofluorite it is not expected that, at the temperature of the experiment, the suggested trichloracetyl hypohalite would exist for long periods or would be isolated.

The free radicals necessary to initiate the process probably came from the chlorine trifluoride. Tanner[1] suggests that chlorine trifluoride splits as below

$$ClF_3 \longrightarrow 2F^{\bullet} + ClF.$$

but since the present work throws no further light on the subject we will merely assume that chlorine trifluoride furnishes fluorine and chlorine atoms. An alternative source of free radicals is from the suggested trichloroacetyl hypohalite

1. $CCl_3COOH + X_2 \longrightarrow CCl_3COOX + HX$

2. $CCl_3COOX \longrightarrow CCl_3COO\cdot + X\cdot$

However the attack of halogen atoms on the acid would probably be as follows

3. $CCl_3COOH + X\cdot \longrightarrow CCl_3COO\cdot + HX$

so if either, or a combination, of the above mechanisms operates the result is the formation of $CCl_3COO\cdot$ and $X\cdot$ radicals and HX.

The rapid production of large amounts of carbon dioxide is almost certainly due to reaction or decomposition of the $CCl_3COO\cdot$ radical. Several possible mechanisms are given below.

4. $CCl_3COO\cdot \longrightarrow CCl_3\cdot + CO_2$

5. $CCl_3COO\cdot + X_2 \longrightarrow CCl_3X + CO_2 + X\cdot$

6. $CCl_3COO\cdot + X\cdot \longrightarrow CCl_3X + CO_2$

The decomposition of $CH_3COO\cdot$ in analagous manner to reaction 4 is not observed in the gas phase[20] but methyl radicals have been detected in the liquid phase decomposition of acetic acid. In the liquid phase the reunion of two radicals has a low probability[21] so that reaction 6 should occur only to a limited extent. Thus the initial formation of carbon dioxide is probably due to reactions 4 and/or 5. The action of chlorine trifluoride on trichloroacetyl chloride also produces carbon dioxide and therefore this source must be considered. The mechanism of the production of carbon dioxide from the acid chloride will be dealt with later.

The carbonyl halides can be formed by one of two sets of reactions

a) From carbon monoxide and halogen atoms and molecules according to the Bodenstein mechanism.[22]

7. $CO + X\cdot \longrightarrow \cdot COX$

8a. $\cdot COX + X_2 \longrightarrow COX_2 + X\cdot$

8b. $COX\cdot + X\cdot \longrightarrow CO + X_2$

but the reaction 9 is doubtful in the liquid phase reaction.

b) By oxidation of the $CCl_3\cdot$ radical by the oxygen known to be present in very small amounts.

9. $CCl_3\cdot + O_2 \longrightarrow COCl_2 + \cdot OCl$

To furnish the required carbon monoxide and trichlormethyl radicals a trichloracetyl radical is the most probable precursor. This radical can originate in several ways

10. a) From the acid halide

10. b) $CCl_3COO\cdot \longrightarrow CCl_3CO\cdot + O\cdot$

The dichlorodifluoromethane and chlorotrifluoromethane are easily explained as being derived from the other halogenated methanes.

21. a) $CCl_4 + F^{\cdot} \longrightarrow CCl_3F + Cl\cdot$

b) $CCl_3F + F\cdot \longrightarrow CCl_2F_2 + Cl\cdot$

c) $CCl_2F_2 + F\cdot \longrightarrow CClF_3 + Cl\cdot$

or even from the hexachloroethane.

22a. $CCl_3CCl_3 + F\cdot \longrightarrow CCl_3F + CCl_3^{\cdot}$

The required CCl_4 and CCl_3F can be formed as below

22 b. $CCl_3^{\cdot} + X_2 \longrightarrow CCl_3X + X\cdot$

Thus, by a series of reactions, many of which have been accepted as parts of the mechanism of other reactions most of the reaction products have been accounted for.

Trichloroacetyl chloride

The same reaction products were obtained but in slightly different proportions and because of this and the different oxygen content of the trichloracetyl chloride alternative reaction mechanisms must be postulated. The initial evolution of large quantities of chlorine and little else indicate we have the formation of the acid fluoride

$$2CCl_3COCl + ClF_3 \longrightarrow 2CCl_3COF + 2Cl_2$$

The radical mechanism

$$CCl_3COCl + F\cdot \longrightarrow CCl_3CO\cdot + FCl$$

is ruled as it would yield the active trichloroacetyl radical and there would be much more fluorine in the exit gases in the early stages. When the concentration of the acid fluoride is sufficiently large in the acid chloride (which acts as diluent, to moderate the vigorous reaction between chlorine trifluoride and the acid fluoride[1]) reaction sets in. The initial reaction below is postulated

12. $CCl_3COF + X\cdot \longrightarrow CCl_3CO\cdot + FX$

The trichloroacetyl radical can then react as below

13. $CCl_3CO\cdot + X_2 \longrightarrow CCl_3X + CO + X\cdot$

14. $2CCl_3CO\cdot \longrightarrow C_2Cl_6 + 2CO$

(Reaction 14 only to a very small extent since little hexachloroethane was isolated in the reaction between chlorine trifluoride and trichloroacetyl chloride). The lack of even traces of carbon monoxide in the exit gases must be attributed to the presence there of much halogen and the formation of one halogen atom per molecule of carbon monoxide formed.

Tanner[1] suggested a different mechanism

15. $CCl_3COF + X\cdot \longrightarrow CCl_3\cdot + COFX$

This followed by

$$2CCl_3\cdot + M \longrightarrow C_2Cl_6 + M$$

(to a very small extent)

$$CCl_3\cdot + X_2 \longrightarrow CCl_3X + X\cdot$$

would equally well explain the observed facts.

There remain to be explained, in the case of the acid chloride, the presence of oxygen and carbon dioxide and in the case of the acid, the presence of the acid halides and of oxygen. The more obvious route for the formation of the acid halide from the acid

1. & 2. or 3. $CCl_3COOH \longrightarrow CCl_3COO\cdot$

10b. $CCl_3COO\cdot \longrightarrow CCl_3CO\cdot + O\cdot$

16a. $CCl_3CO\cdot + X_2 \longrightarrow CCl_3COX + X\cdot$

b. $CCl_3CO\cdot + X\cdot \longrightarrow CCl_3COX$

is not possible as the alternative reaction

$$CCl_3CO\cdot + X_2 \longrightarrow CCl_3X + CO + X\cdot$$

occurs[24] while 16b is very unlikely to take place to any appreciable extent in view of the improbability of two radicals meeting.[21] Hence the acid halide must come directly from the acid

e.g. 17. $CCl_3COOH + X\cdot \longrightarrow CCl_3COX + \cdot OH$

or as suggested by Tanner[1]

18. $CCl_3COOH + X_2 \longrightarrow CCl_3COCl + HX + O\cdot$

The hydroxyl and oxygen radical can then produce molecular oxygen as below

19. $O\cdot + O\cdot + M \longrightarrow O_2 + M$

20. $\cdot OH + X_2 \longrightarrow O\cdot + HX + X\cdot$

The oxygen atoms can also be removed by the reaction[25]

25. $CX_4 + O\cdot \longrightarrow COX_2 + X_2$

This is also an alternative route to the phosgene.

The production of carbon dioxide from the acid chloride (via the acid fluoride) is very difficult to account for and the following reactions are highly speculative. They are not considered to be the only reaction mechanisms if they are even possible.

26. $CCl_3CO\cdot + CCl_3COCl \longrightarrow CCl_3CO{-}CO{-}CCl_3 + Cl\cdot$

The $(CCl_3CO)_2$ being immediately attacked by halogen atoms or radicals.

27a. $CCl_3CO{-}CO{-}CCl_3 + X_2 \longrightarrow CCl_3X + C_2Cl_3X + CO_2$

b. $CCl_3CO{-}CO{-}CCl_3 + X\cdot \longrightarrow CCl_3\cdot + C_2Cl_3X + CO_2$

and the C_2Cl_3X then being completely halogenated

28. $C_2Cl_3X + X_2 \longrightarrow C_2Cl_3X_3$

An alternative route can involve the oxygen atom or hypofluorite radical.

29. $CCl_3COF + X\cdot \longrightarrow C_2Cl_3X + \cdot OF$

30. $\cdot OF + CCl_3COF \longrightarrow CCl_3F + CO_2 + F\cdot$

or the hypofluorite radical can give atomic oxygen

31. $\cdot OF + X_2 \longrightarrow XF + X\cdot + O\cdot$

19

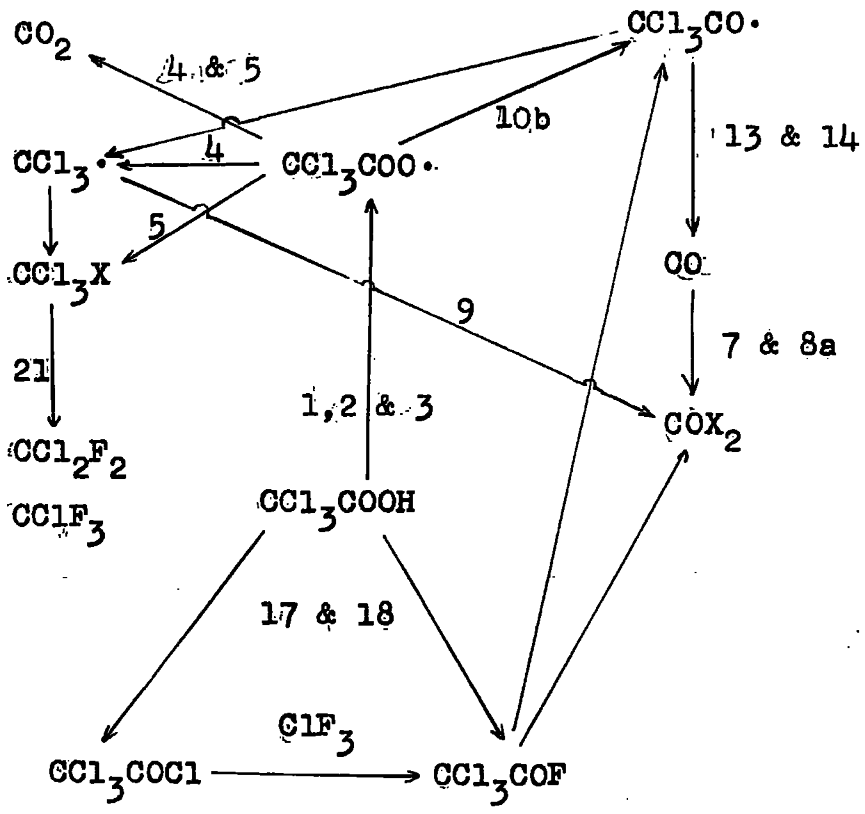
which could easily react as below

32. $CCl_3COF + O\cdot \longrightarrow CCl_3F + CO_2$

Thus the above mechanisms can explain all the products obtained. The two maxima in the rate of production of carbon dioxide when the experiment was carried out in the two reaction vessels can be explained as follows. The initial reaction occurs in the first vessel where acid halides are formed which distil over into the second vessel, carrying some acid with them, where they are retained by the reflux condenser. As the reaction proceeds the amount of organic material in the first vessel decreases, both by reaction and distillation and the radicals have a smaller chance of meeting molecules with which they can react but there is a larger chance now of recombination and a less efficient use of radicals formed, leading to a drop in the rate of production of carbon dioxide. When the centre of reaction is transferred to the second reaction vessel the same cycle of events takes place.

There was always found (in the reaction involving the acid) a quantity of hexachloroethane in the first reaction vessel. This would react with chlorine trifluoride to give some chlorofluorinated ethanes and, by fission of the carbon bond halogenated methanes. The accounts for the isolation of less halogenated ethanes after 6 hours reaction than after 3 hours reaction.

POSSIBLE REACTION ROUTES



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GAS CHROMATOGRAPHY

The application of this technique to the present problem can be divided into two parts.

(a) The estimation of carbon tetrachloride in the mixtures of halogenated methanes and the separation of methyl esters of trihaloacetic acids were carried out using the semi-micro apparatus as described in the first part of this thesis. (pages 33-42). The conditions and packing were suitably modified to obtain a reasonable separation.

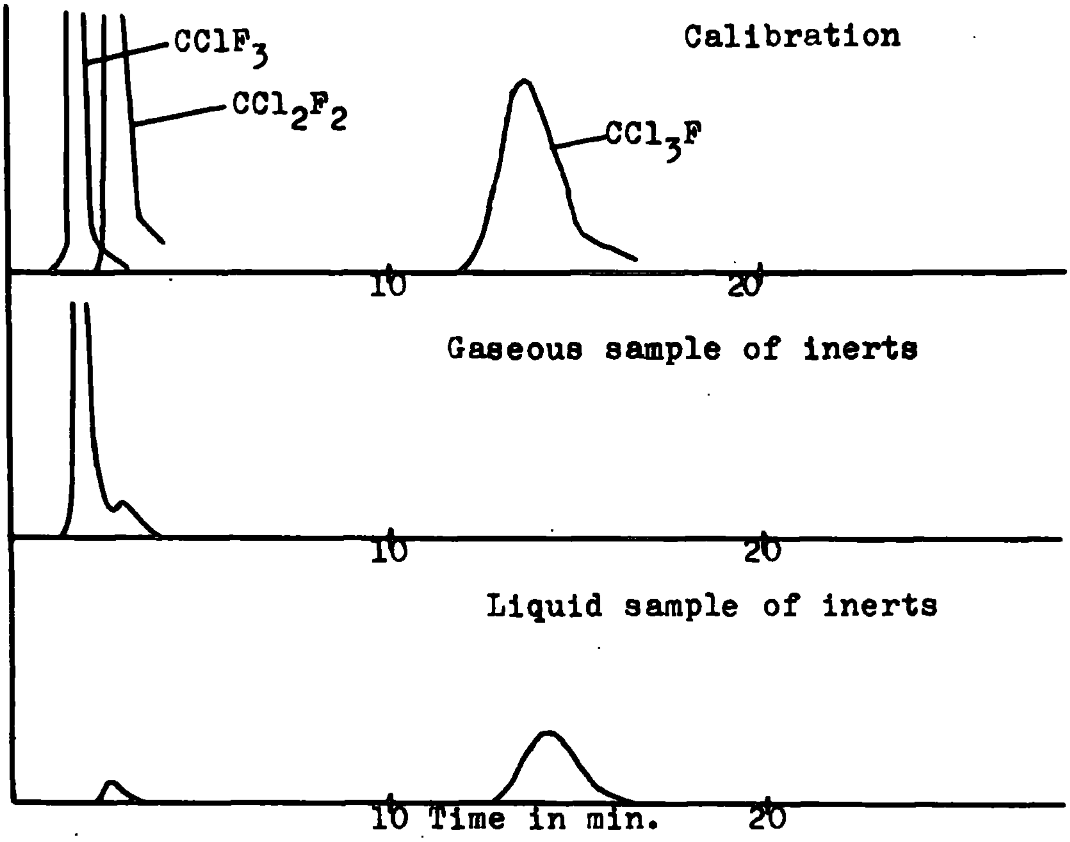
(Esters - 'dinonyl' phthalate (4 parts) on Celite 545 (10 parts) 126°, pressure 18 cms., N_2 flowrate 34 ml./min.

CCl_4 'dinonyl' phthalate (as above) 60°, pressure 37 cm., N_2 flowrate 30 ml./min.)

(b) The chromatography of the gaseous halogenated methanes required a modified apparatus (Diag. 7). The nitrogen was passed through a drier, surge tank and manometer as before and then through the first arm of the detector. From here the nitrogen passed through the gas pipette and into the column, packed with di-n-butyl phthalate (4 parts) on Celite 545 (10 parts).[226] The emergent mixture of nitrogen and vapours passed through the second arm of the detector and out to the atmosphere via a cold trap, flowmeter and drying tube.

DIAGRAM 5

Chromatograms for the separation of halogenated methanes at 20°



Chromatograms for the separation of halogenated methanes at 60°

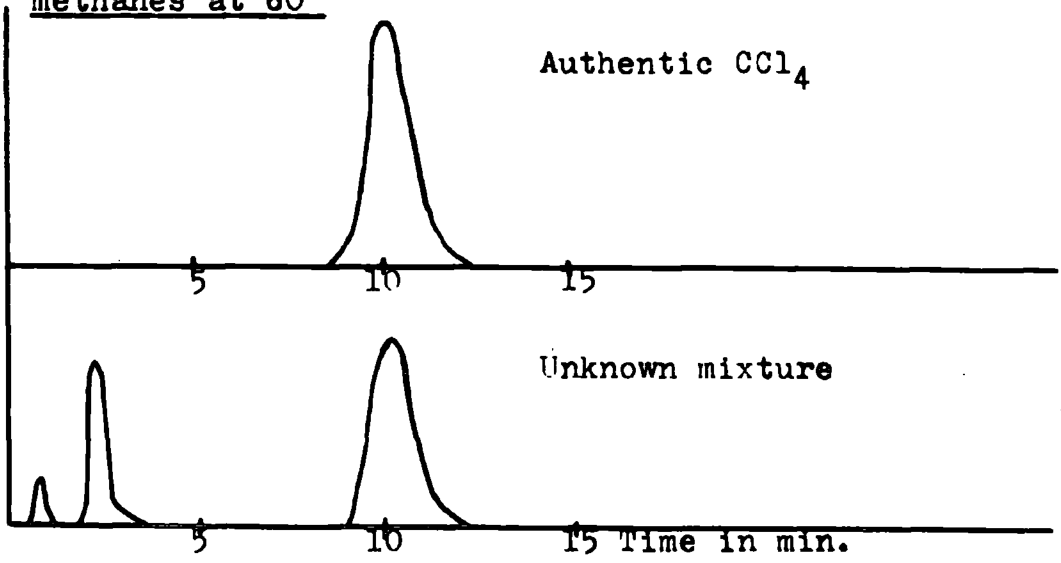


DIAGRAM 6

Chromatograms for the separation of the methyl esters of trihaloacetic acids and connected compounds

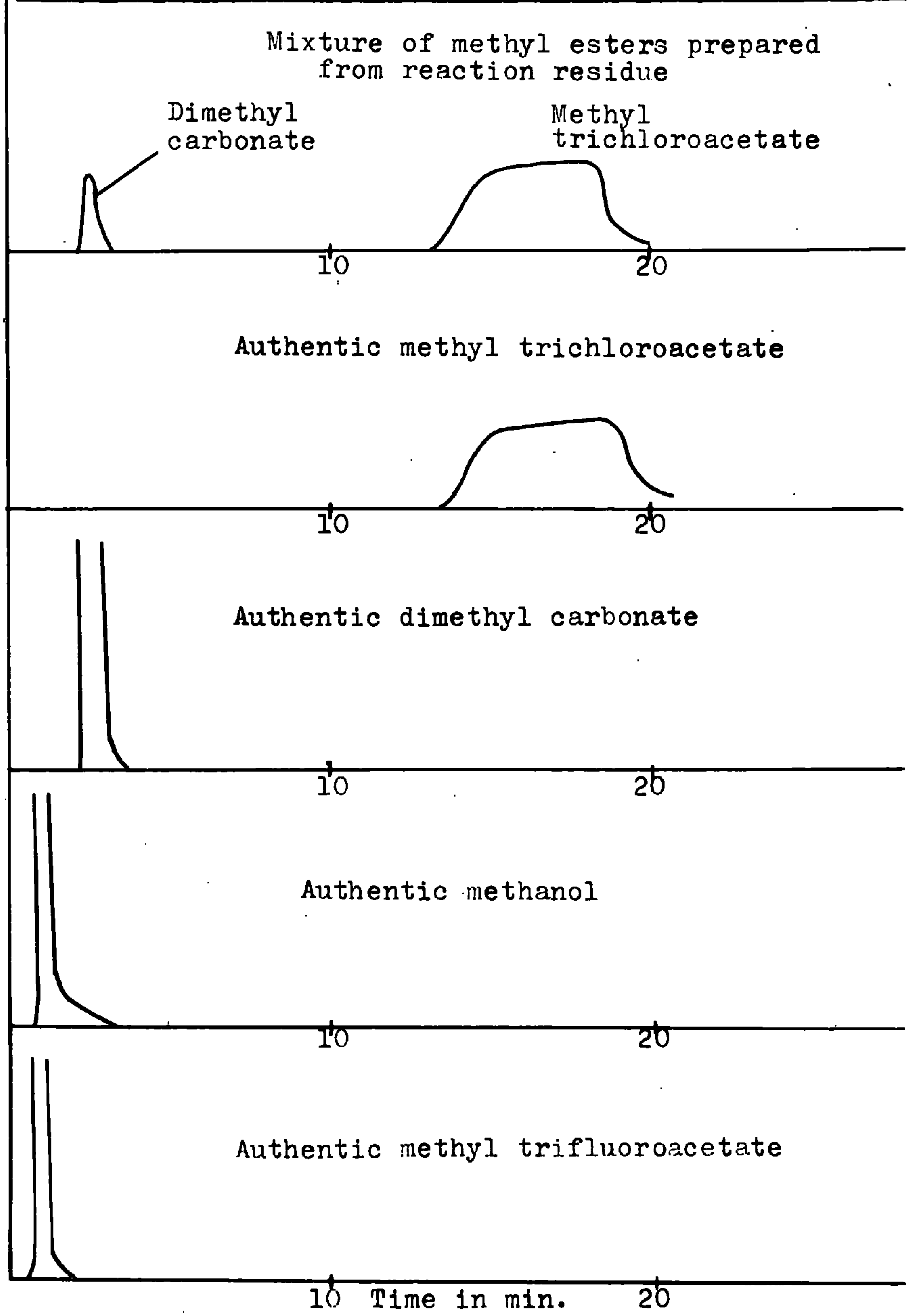


DIAGRAM 7

Block diagram of apparatus for gas chromatography of gaseous halogenated methanes

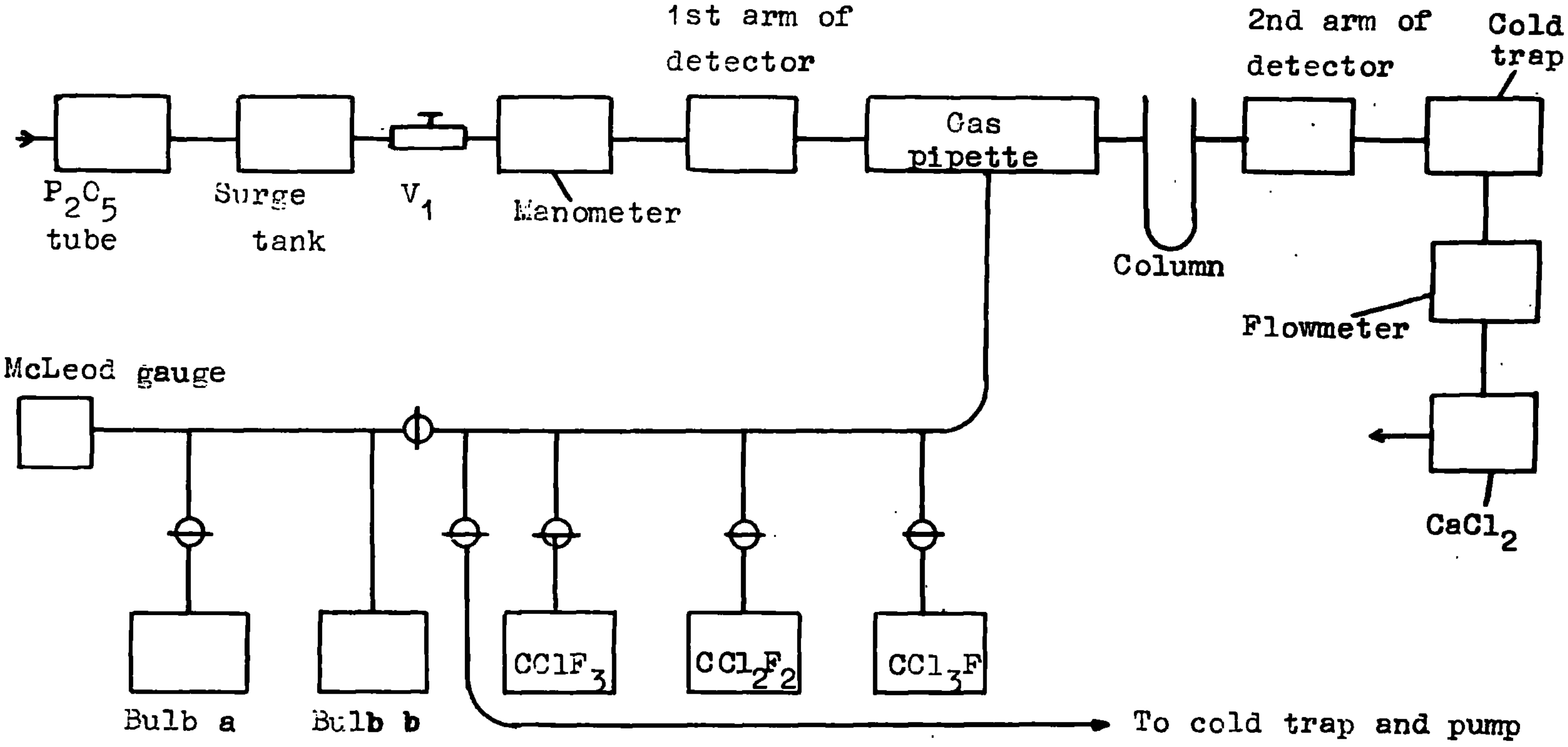
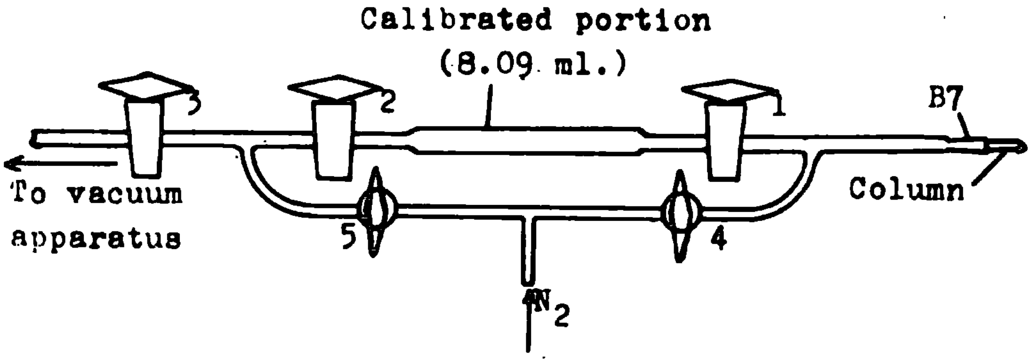
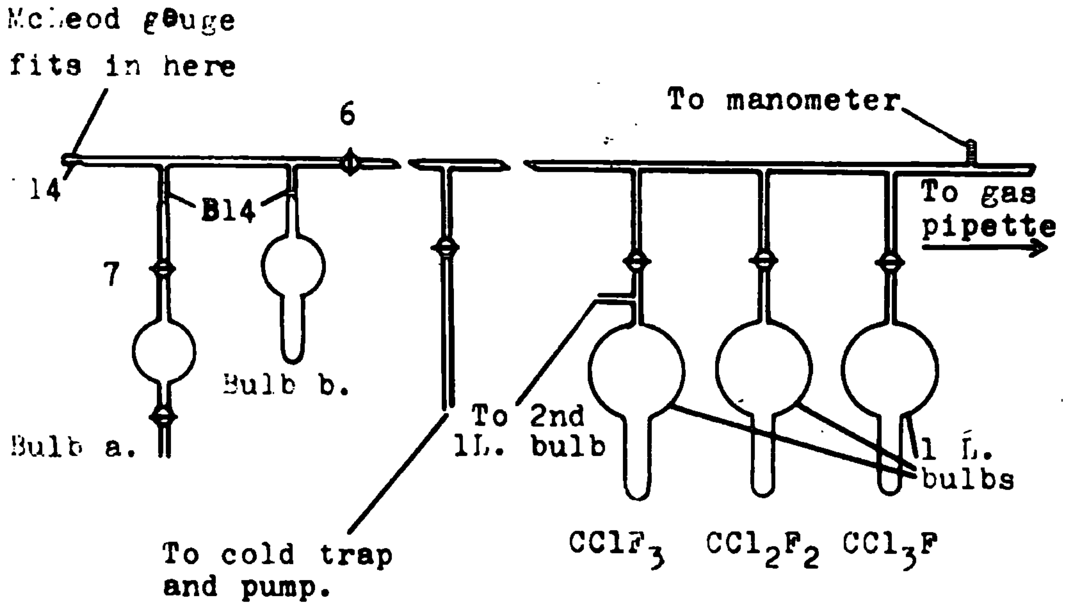


DIAGRAM 8

Gas pipette (1/4 full size)



Vacuum apparatus (1/10 full size)



The gas pipette was connected to a vacuum system in which pure samples of halogenated methanes and the unknown mixtures could be handled.

Method of operation

The condensed sample of halogenated methanes produced in the reaction was allowed to warm up to room temperature and pressure and the gas produced allowed to leave the trapping system (Diag 10) by tap 8 and was collected in a reservoir of similar construction to those in Diag, 11, rejecting the initial portion used to remove air from the connecting tubes. The removable bulb of the vacuum apparatus (bulb a, Diag 8) was filled with the gas and then attached to the vacuum apparatus. The apparatus (including the calibrated portion of the gas pipette, which had taps 2, 3 & 4 open and taps 1 & 5 closed) was evacuated and then the pump and its protecting cold trap sealed off from the vacuum system. Tap 6 was closed and tap 7 opened and the sample condensed onto Anhydrone in bulb b to remove any water present. The sample was then allowed to warm up and expand into the gas pipette to a known pressure through tap 6 which was now opened. Tap 2 was closed, the gas pumped out of the space between taps 2, 3 & 5 and then tap 3 closed.

The chromatography apparatus having previously been allowed to come into equilibrium (Column temperature 20°, N_2 flowrate 33 ml/min. entry press. atmospheric + 10 cm.)

with the nitrogen flowing through tap 4 all that remained was to introduce the sample without disturbing the equilibrium. To accomplish this the tap 5 was opened (causing a deflection of the galvanometer) and after a few minutes tap 2 was opened momentarily to bring the pressure of the calibrated portion of the pipette to that of the N_2 stream. When all was again in equilibrium the sample was blown into the column by opening tap 2 and then in one movement opening tap 1 and shutting tap 4. The gas stream now passed through taps 5, 2 & 1.

The calibration of the apparatus was carried out in a similar fashion, using pure samples of CCl_3F, CCl_2F_2 and $CClF_3$. The estimation of these gases when dissolved in the CCl_4 produced in the reaction was carried out by injecting a known volume of solution containing them through the serum cap onto the column in the normal way.

ANALYSIS

Estimation of chloride

During these experiments it frequently became necessary to determine the amount of chloride ion present in solutions of varying origin (from the alkaline sulphite scrubber, solutions of the trichloroacetic acid in the reaction vessels, solutions of sodium halides precipitated in the determination of COX_2 and X_2), usually containing a large excess of other solutes. On this account adsorption indicators did not seem an attractive proposition and in view of the errors possible in other measurements (e.g. the ClF_3 could only be measured to ± 1 g., i.e. ± 3%) it was not considered necessary or desirable to produce an elaborate method of analysis. The estimation of chloride by titration with silver nitrate solution in neutral solution with potassium chromate as indicator proved entirely satisfactory.

Reagents	$AgNO_3$	0.01 N
	K_2CrO_4	2 g./100 ml. aq. solution
	NaOH and HNO_3	2N, 0.1N and 0.02N "
	$CaCO_3$	Analar.

Solutions containing sulphite were heated to boiling with excess concentrated nitric acid to remove the sulphite as SO_2 or by oxidation to sulphate. The solution was cooled and then treated in the same manner as those of other origin. The solution was neutralised, using phenol phthalein as indicator with progressively more dilute acids and alkalis. (An alternative procedure is to add acid, if necessary, and excess calcium carbonate). The estimation was then carried out by titrating the chloride with silver nitrate using potassium chromate solution as indicator. (1 ml.) The size of the aliquot was so chosen that a titre of 5 to 50 ml. in a final volume of 50-150 ml. was obtained.

Estimation of fluoride

As in the estimation of chloride various solutions had to be analysed for fluoride. The titration with thorium nitrate in a buffered solution, using sodium alizarin sulphonate as indicator was suitable for the simpler solutions but the solution from the alkaline sulphite scrubber produced poor end points. The spread of the end point was caused by the presence of sulphate as was demonstrated by performing the titrations in the presence of sulphate. As sulphate is formed in the process of absorbing halogen

$$X_2 + Na_2SO_3 + 2NaOH \longrightarrow Na_2SO_4 + 2NaX + H_2O$$

little could be done to better this defect and it was considered sufficient to acknowledge that an error of ± 10% might be present in the figures for fluoride determinations.

Reagents	$Th(NO_3)_4$	0.05N
	Buffer solution	2 g. NaOH 9.448 g. $CH_2ClCOOH$ in 100 ml. of solution
	Sodium alizarin sulphonate	0.05 % aq. solution
	$NaOH_4HNO_3$	2N, 0.1N & 0.02N solutions

The sample (if containing sulphite) was heated to boiling with excess conc. nitric acid. After cooling sodium alizarin sulphonate was added and the solution made neutral. The buffer solution (2 ml./100 ml. of solution) was added and the titration carried out with thorium nitrate solution. Further neutral samples were prepared and buffer added. Enough thorium nitrate solution was added to precipitate most of the fluoride, the precipitate was filtered off and the titration completed on the filtrate.

Estimation of carbon dioxide

In order to check the amounts of carbon dioxide calculated from the gas analyses conducted in the Orsat apparatus the sodium carbonate present in the solution from the alkaline sulphite scrubber was decomposed by acid to give carbon dioxide which was measured as a gas.

A sample of the solution containing the sodium carbonate (5 ml.) was placed in a flask with sodium chloride (to reduce the solubility of the carbon dioxide), sodium hydroxide (½ g.) and iodine (2 g.), to oxidise the sulphite according to the equation

$$SO_3^{=} + 2OH^- + I_2 \longrightarrow SO_4^{=} + H_2O + 2I^-$$

Concentrated hydrochloric acid was added in a separate container and the flask attached to a gas burette. When steady conditions were obtained the concentrated acid was tipped into the alkaline solution and the liberated carbon dioxide measured after conditions were again steady. A blank experiment was carried out to allow for the carbon dioxide in the original alkaline sulphite solution.

Estimation of trichloroacetic acid

The alkaline sulphite solutions could easily contain sodium trichloroacetate carried over as the acid halide and several attempts were made to obtain the free acid. Samples of the scrubbing solution were made acid with hydrochloric acid (nitric and sulphuric acids would be extracted at a later stage and are difficult to remove) the SO_2 boiled off and the solution, saturated with sodium chloride, continuously ether extracted. Negligible amounts of acid were obtained from the ether extract.

Attempts to isolate the S-benzyl thiuronium[27] salt were more successful and the presence of trichloroacetic acid was clearly demonstrated (m.p. of S-benzyl thiuronium salt 149°C. mixed melting point with authentic specimen 149°C.) but attempts to make the method quantitative were not successful. In spite of attempts to reduce the solubility of the partly saturated with sodium chloride the results were not reproducible. Consequently attempts to estimate trichloroacetic acid were abandoned.

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EXPERIMENT DETAILS

Y

ACTION OF CHLORINE ON SOME HYDROCARBONS

Chlorine, diluted with nitrogen was passed through bubblers of the liquid (2 x 12.5 ml.) or over the solid hydrocarbon packed in a glass tube (50 cm. x 1.5 cm. I.D.). The emergent chlorine was passed into N. aqueous potassium iodide solution and the liberated iodine titrated with sodium thiosulphates solution. Paraffin wax (cubes of ½ cm. edge) absorbed the least (25%) followed by isopropyle benzene (41%), naphthalene (cubes of ½ cm. edge 84%) and benzene (86%). The amount absorbed was calculated after steady values were obtained and takes no account of the amounts used to produce saturation of the solution which took longer in the case of benzene and isopropyl benzene (6 mins.) than for naphthalene and paraffin wax (1 min.). The amount of chlorine in solution was also estimated iodometrically and found to be very small in comparison with that retained by any of the absorbents.

ACTION OF CHLORINE TRIFLUORIDE ON SOME HYDROCARBONS

The chlorine trifluoride was diluted with nitrogen and passed through bubblers of the liquid (2 x 12.5 ml.) or through tubes (50 cm. x 1.5 cm. I.D.) packed with the solid. Paraffin wax (cubes of ¼ cm. edge) would not remove chlorine trifluoride at a rate of ½ g./hour when diluted with nitrogen (75 ml./min.). Cyclohexane would not remove chlorine trifluoride at a rate of 1 g./hour when diluted with nitrogen (60 ml./min.). Doubling the amount of cyclohexane did not improve the results. Benzene did not remove chlorine trifluoride passed under the same conditions as for cyclohexane. As the liquid hydrocarbon became green during these experiments and in view of the reactive nature of chlorine trifluoride it was thought that the emergent halogen (detected by starch/potassium iodide paper) was in fact chlorine but no attempts were made at accurate analysis.

ACTION OF CHLORINE TRIFLUORIDE ON TRICHLOROACETIC ACID AND TRICHLOROACETYL CHLORIDE

APPARATUS

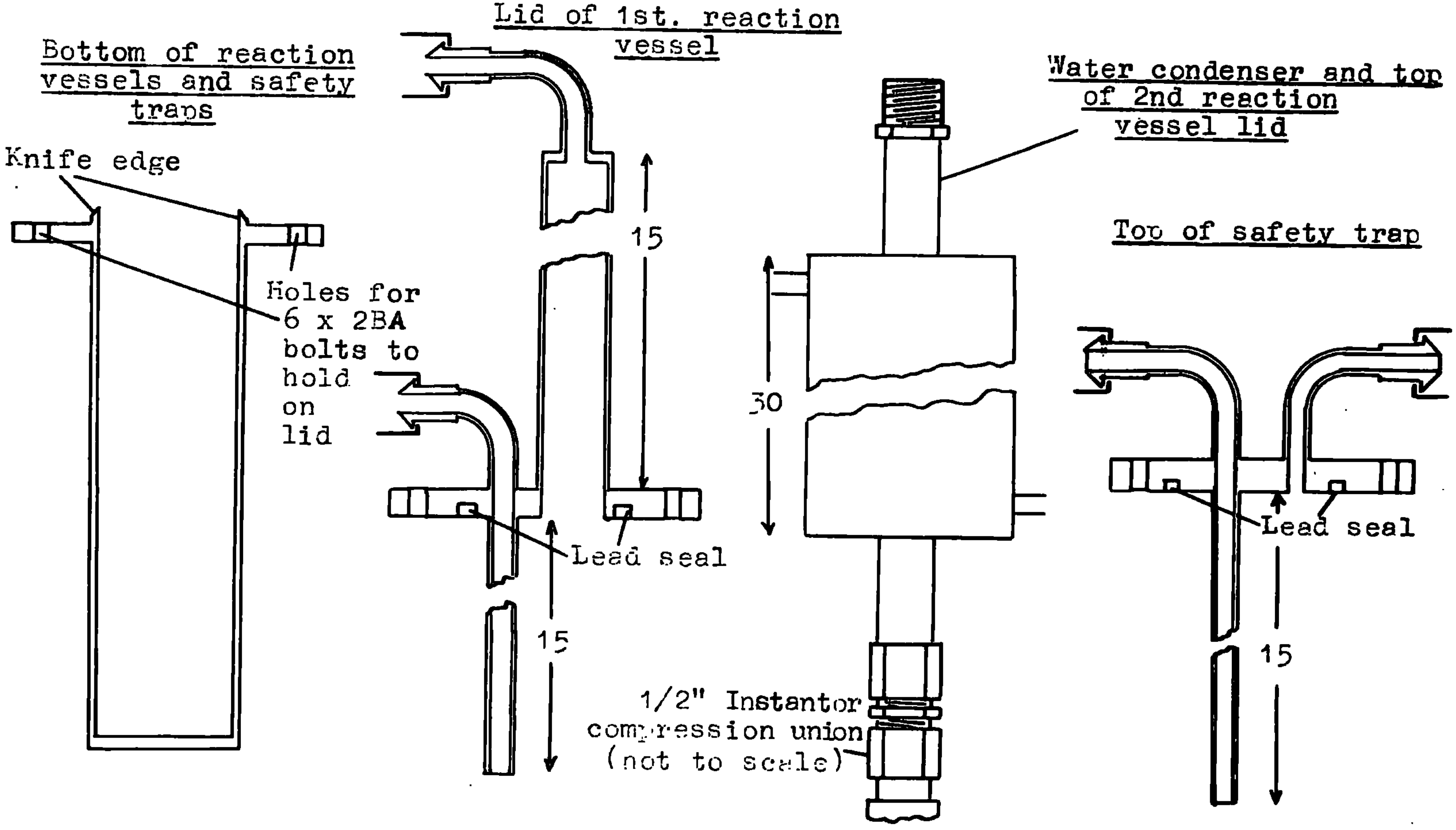
The apparatus can most easily be described if it is divided up into sections, some of which are common to several types of experiment.

All metal section in which reaction occurs

The chlorine trifluoride was passed through a flowmeter and mixed with nitrogen that had been passed

DIAGRAM 9

All metal apparatus (brass and copper where in contact with reaction mixture)
[Half size] (dimensions in cm.)



through a copper furnace and over sodium hydroxide pellets to remove oxygen, carbon dioxide and water. The mixed gases then passed through a safety trap into the two reaction vessels in series, the second of which was surmounted by a watercooled condenser. The reaction products then passed into the second safety trap and leave this section of the apparatus.

Experiment type A

The reaction products left the second safety trap and passed through a stainless steel tube into a solution of sodium hydroxide (140 g. 3.5 mole) and sodium sulphite (442 g. of the heptahydrate 1.73 mole) in water (to make 1,750 ml. of solution) contained in a 2L. three necked flask equipped with a mercury seal stirrer and lead for the unreacted gases. These were then lead over anhydrous calcium chloride (tube 50 cm. x 1.5 cm. I.D.) and into the trapping system (diag. 10). The incondensable gases were passed through a flowmeter and collected in an aspirator.

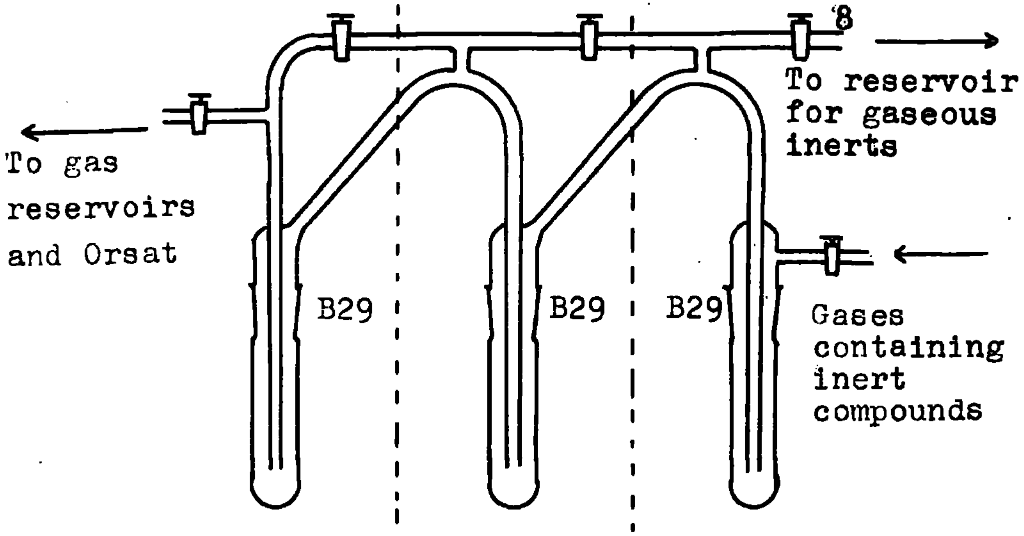
Experiment type B

In this case the second safety trap was filled with soft glass tubes to prevent attack of the glass immediately after the glass-to-metal connection by prior removal of all substances liable to attack glass. The reaction

DIAGRAM 10

Trapping system for halogenated methanes

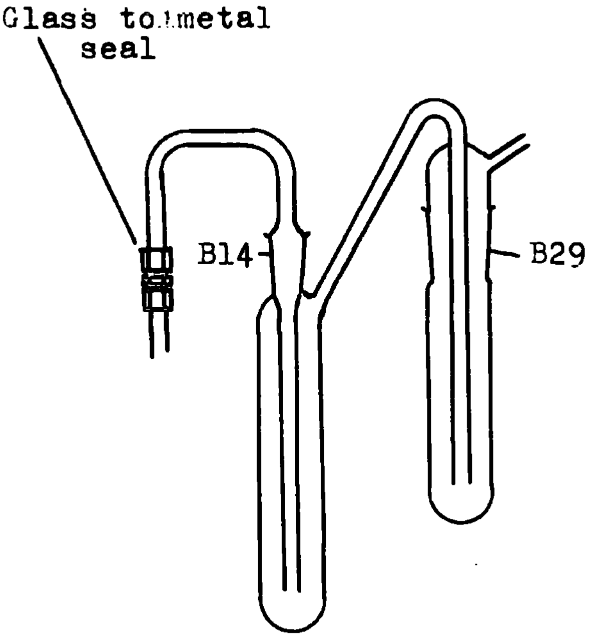
(1/5 full size)



This unit repeated three times

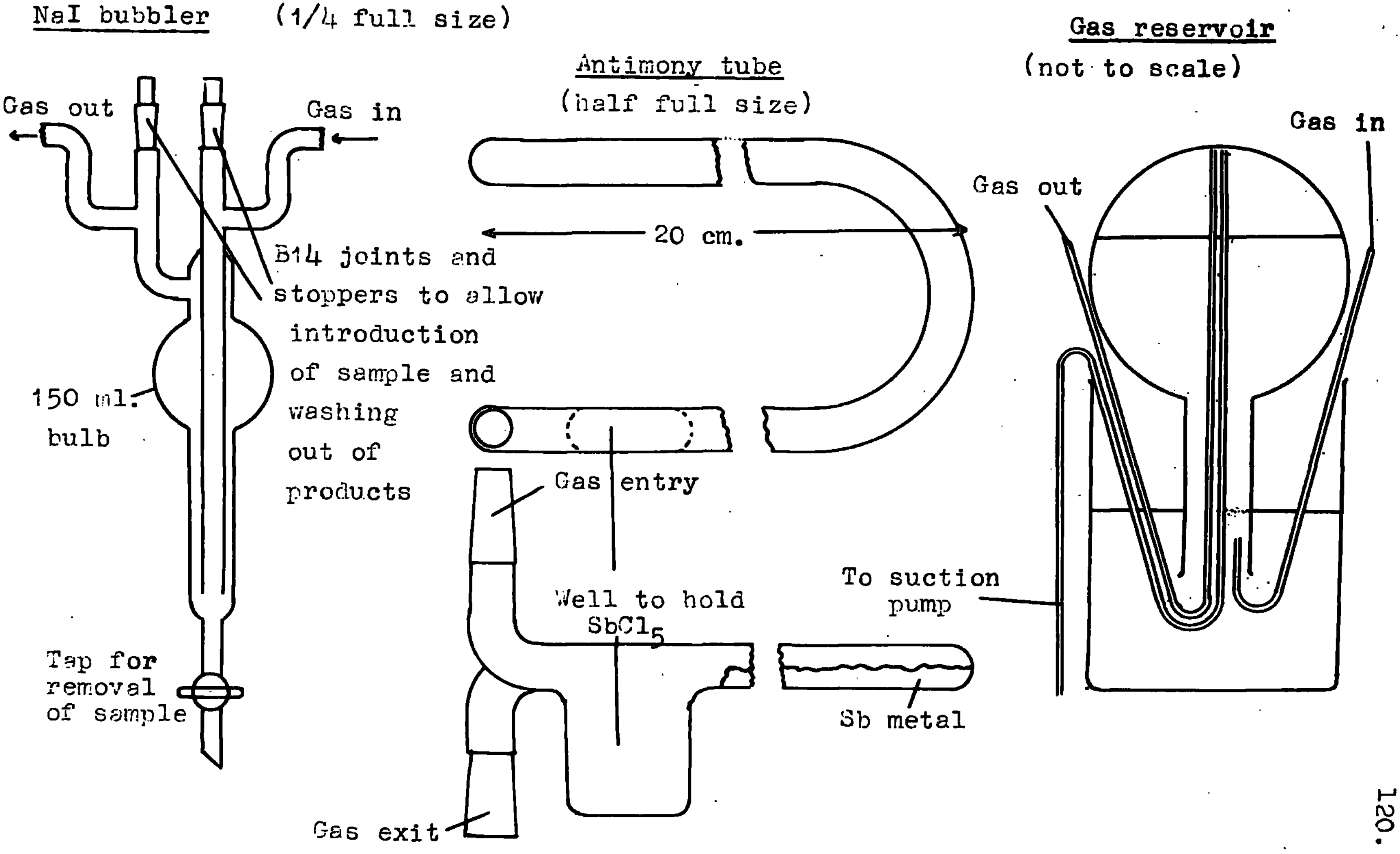
Benzene bubblers

(1/4 full size)



The glass to metal seal consisted of a Neoprene washer around a glass tube so that it came between the nipple and seating of a petrol union.

DIAGRAM 11



NaI bubbler (1/4 full size)

Antimony tube (half full size)

Gas reservoir (not to scale)

products were passed through benzene (2 x 12.5 ml.) in bubblers (diag.10), designed to facilitate speedy replacement of the glass-to-metal joint and then over dry potassium fluoride (in tube 50 cm. x 1.5 cm. I.D.). After passing over antimony metal (2-6 mm. diam.) in a tube designed to prevent blockage (diag. 11) and over antimony metal powder on glass wool (to ensure complete removal of halogen) the gas stream was lead into one of the bubblers containing the solution of sodium iodide in acetone (diag.11) and from there to one of the two gas storage bulbs (diag. 11).

Experiment type C

The safety trap was prepared as for B. The reaction products were led into the solution of sodium iodide in acetone in the bubbler and the exit gases passed out of the apparatus via a flowmeter and calcium chloride tube..

PREPARATION OF REAGENTS

Trichloroacetic acid

This was distilled under reduced pressure, rejecting the initial water containing distillate.

Trichloroacetyl chloride

This was prepared according to the method of Rabcewicz et al.[28] Trichloroacetic acid (420 g. 2.6 mole) and anhydrous zinc chloride (25 g.) as catalyst were heated to 150° in a 1L. flask equipped with dropping funnel and reflux condenser. Redistilled benzotrichloride (580 g. 2.96 mole) was added dropwise (40 min.) and heating continued for a further 60 min. when little hydrogen chloride was being given off. The crude product was then distilled off up to 155° (480 g.). This was redistilled to give pure trichloroacetyl chloride (b.p. 117-120° 326 g. 1.8 mole 70% yield. eq. wt. by hydrolysis 90 .2 theory requires 90.9).

Sodium iodide

Heating at 184° for 6 hours at 2.0 cm. pressure produced a sufficiently dry sample.

Potassium fluoride

As for sodium iodide.

Acetone

This was distilled after standing over potassium permanganate and anhydrous magnesium sulphate.

Benzene

Redistilled from sodium wire.

Antimony metal

Oven dried at 110°.

The displacing liquid in the gas storage bulbs and in the Orsat apparatus was a mixture of glycerol (500 ml.), water (430 ml.) and conc. sulphuric acid (70 ml.).

METHOD OF OPERATION

Experiment type A

The clean dry apparatus was purged with N_2. The trichloroacetic acid (or acid chloride) was weighed into the reaction vessels (80% in the first reaction vessel), the alkaline sulphite solution was placed in the flask and the apparatus again purged with N_2. The cold traps were immersed in refrigerant and when equilibrium was established chlorine trifluoride was admitted, diluted with N_2. The initial chlorine trifluoride rate of 1 g./hour was increased after 5 min. to 5 g./hour at which rate it was maintained for 6 hours. The rate of flow of N_2 was kept as low as was necessary to prevent blocking of the stainless steel tube (8 m I.D.) leading into the alkaline sulphite scrubber (30 ml./min.). At the end of the 6 hours the chlorine trifluoride cylinder was shut and N_2 passed for ½-1hour to ensure complete removal of the volatile products from the reaction vessels. The apparatus was then sealed off into various sections. The trapping system containing the halogenated methanes was dealt with as described in the chromatography section. The alkaline sulphite scrubbing solution was made up to 2L. and aliquots used to determine the chloride, fluoride, carbon dioxide and trichloroacetic acid as described in the analytical section.

The contents of the reaction vessels were usually solid. This solid was melted out and dissolved in water. The halogenated ethanes were filtered off and the aqueous filtrate made up to a known volume in order that the chloride and fluoride present might be determined.

In experiments using the acid chloride an aliquot of the liquid remaining in the reaction vessel was placed in a flask equipped with dropping funnel and ethanol/Drikold reflux condenser. Excess conc. sodium hydroxide solution was added and the halogenated ethanes filtered off as before and the filtrate made up to a known volume.

The connecting tubes, lids of reaction vessels and condenser were washed with methanol and the halogenated ethanes so removed precipitated by adding excess water to the methanol solution. The gas in the aspirators was analysed for oxygen and carbon monoxide.

Experiment type B

The clean dry apparatus was purged with N_2.

The trichloroacetic acid (or acid chloride) was weighed into the reaction vessels and the apparatus again purged with N_2. The solution of sodium iodide in dry acetone (saturated - about N.) was placed in the bubblers and when equilibrium was established chlorine trifluoride was passed as in the previous type of experiment.

The gas stream, after removal of halogens and hydrogen fluoride, was passed for 30 min. through the iodide solution. Forthe first 10 min. period of this time the gases leaving the iodide solution were allowed to leave the apparatus via a flowmeter. At the end of this 10 min. period it was assumed that the acetone was saturated with carbon dioxide etc. and for the next 20 mins. the gases passing from the solution of sodium iodide in acetone were collected to be analysed later for carbon dioxide, oxygen and carbon monoxide in an Orsat apparatus, using as adsorbents 30% KOH solution, alkaline pyrogallol and ammoniacal cuprous chloride. At the end of the 30 minutes the phosgene containing gas stream was diverted into the second sodium iodide in acetone bubbler and the collection of the gas sample stopped. The previous cycle of operations was then repeated during the next and subsequent 30 min. intervals and in this way 12 gas samples and 12 solutions containing iodine (equivalent to the phosgene absorbed) were obtained. The solution of sodium iodide in acetone containing iodine was washed into a beaker with dry acetone and the iodine titrated in acid solution with 2N sodium thiosulphate solution. The bubbler was immediately refilled with a fresh solution of sodium iodide in acetone. The reaction vessels were treated as for experiment type A.

Experiment type C

The apparatus was prepared and charged with trichloroacetic acid (or acid chloride) and solutions of sodium iodide in acetone as for experiment type B. The iodide solution was changed and the iodine titrated every 30 minutes as above but no gas samples were collected. The reaction vessels were treated as for experiment type A. The samples of iodide solution retained for fluoride determination were filtered and the sodium chloride and fluoride (insoluble in dry acetone) washed free of iodine and most of the sodium iodide with dry acetone. The sodium halides were then dissolved in water and fluoride determined as described in the analytical section.

Action of ClF_3 on CCl_3COOH at 100°

Experiment type A

Starting Materials

CCl_3COOH	105.5 g.	(0.64 mole.)
ClF_3	35.0 g.	(0.38 mole.)

Products

The alkaline sulphite scrubbing solution contained

Cl^-	25.5 g.	(0.72 mole.)
F^-	11.9 g.	(0.63 mole.)
CO_2	18.2 g.	(0.41 mole.)

Halogenated methanes

CCl_4	19.2 g.	(0.13 mole.)
CCl_3F	6.1 g.	(0.045 mole.)
CCl_2F_2	1.8 g.	(0.015 mole.)
$CClF_3$	4.9 g.	(0.046 mole.)

Halogenated ethanes

6.5 g. (C_2Cl_6 containing a little fluorinated material - 0.028 mole.)

Recovered CCl_3COOH 11 g. (0.067 mole.)

Experiment type B

Starting Materials

CCl_3COOH	106.5 g.	(0.65 mole.)
ClF_3	26.5 g.	(0.29 mole.)

Products

COX_2 0.167 eq. as estimated according to the equation.

$$COX_2 + 2NaI \text{ —— } CO + NaX + I_2$$

The approximate composition is

CO	2.3 g.
Cl	2.6 g.
F	1.8 g.

There were recovered 1 g. of C_2Cl_6, 34 g. of unreacted CCl_3CCOH, containing 0.3 g. Cl and 0.2 g. F.

Analysis of the exit gases showed that they contained

CO_2	12.8 g.
O_2	0.15 g.
CO	2.9 g. (including that from COX_2)

There were formed 0.167 eq. COX_2 which is equivalent to 2.4 g. CO i.e. actual CO produced is 0.3 g.

Experiment type C.

Starting Material

CCl_3COOH	101 g.	(0.38 mole.)
ClF_3	35 g.	(0.62 mole.)

Products of reaction

$COX_2 + X_2$ 0.736 equivalents containing approximately

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Cl	17.3 g.	(0.49 mole.)
F	4.7 g.	(0.25 mole.)

There were also recovered

C_2Cl_6	3.5 g.	(0.015 mole.)

and unreacted CCl_3COOH 16.5 g. (0.103 mole.)

Combining these results it is seen we have from 105.5 g. of CCl_3COOH and 35.0 g. of ClF_3 the following:

Products

	C_2Cl_6	6.5 g.	(0.028 mole.)
	CCl_4	19.2 g.	(0.13 mole.)
	CCl_3F	6.1 g.	(0.045 mole.)
	CCl_2F_2	1.8 g.	(0.015 mole.)
	$CClF_3$	4.9 g.	(0.046 mole.)
Carbonyl halides containing	CO	2.3 g.	(0.084 mole.)
	Cl	2.6 g.	(0.073 mole.)
	F	1.8 g.	(0.095 mole.)
Halogens containing	Cl	14.7 g.	(0.41 mole.)
	F	3.3 g.	(0.17 mole.)
Halogens as CCl_3COX and HX	Cl	8.2 g.	(0.23 mole.)
	F	7.2 g.	(0.39 mole.)

CO_2 (from alkaline sulphite scrubber after correction for that from COX_2)

14.5 g. (0.33 mole.)

CO_2 (By gas analysis	17.2 g.	(0.39 mole.))
O_2	0.2 g.	(0.0047 mole.)
CO	0.3 g.	(0.0011 mole.)

Action of ClF_3 or CCl_3COOH at 70-80°

Experiment type A.

Starting Material.

CCl_3COOH	100 g.	(0.61 mole.)
ClF_3	29 g.	(0.31 mole.)

Products

The alkaline sulphite scrubbing solution contained

Cl^-	21.5 g.	(0.61 mole.)
F^-	14.4 g.	(0.76 mole.)
CO_2	28.0 g.	(0.64 mole.)

Halogenated methanes

CCl_4	9.1 g.	(0.059 mole.)
CCl_3F	7.7 g.	(0.056 mole.)
CCl_2F_2	0.2 g.	(0.0015 mole.)
$CClF_3$	0.1 g.	(0.0009 mole.)

Halogenated ethanes

13.5 g. (C_2Cl_6 containing a little fluorinated material) (0.057 mole.)

The 1st. reaction vessel contained the C_2Cl_6 above but the second reaction vessel and 2nd safety trap contained a liquid (about 18 g.) consisting of CCl_3COOH, CCl_3COX and halogenated methanes and ethanes. This was analysed as follows. A known weight (3.3556 g.) was shaken with water and the acid titrated with alkali using phenol phthalein as indicator (31.76 ml. of 0.2110 N. NaOH 0.0670 eq.). The neutral organic layer was washed and the aqueous solution and washing made up to 100 ml. and halogens estimated (Cl^- 00053 eq. F^- 0.00226 eq.).

The organic layer was dried ($MgSO_4$) and distilled under a static vacuum to give a liquid (1.2940 g.). By sublimation and by ethanol extraction of the $MgSO_4$, a solid (C_2Cl_6 0.3836 g.) was obtained.

These facts are interpreted as follows.

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The 3.3556 g. of mixture contain

CCl_3COF	0.376 g.	(0.00452 eq.)
CCl_3COCl	0.096 g.	(0.00106 eq.)
CCl_3COOH	0.184 g.	(0.00112 eq.)
(Total acid		0.6670 eq.)
CX_4	1.294 g.	
C_2X_6	0.384 g.	
Total	2.334 g.	

The deficit of 1.022 is attributed to loss of CX_4 and C_2X_6 in the washing procedure. Accordingly this amount is added in proportion to each of the values obtained for the amounts of CX_4 and C_2X_6 present. i.e.

CCl_3COF	0.376 g.
CCl_3COCl	0.096 g.
CCl_3COOH	0.184 g.
CX_4	1.294 + 0.788 = 2.082 g.
C_2X_6	0.384 + 0.234 = 2.618 g.

A sample of the CX_4 when analysed by gas chromatography was shown to be mostly CCl_4 with negligible amounts of CCl_3F and CCl_2F_2. The presence of carbonyl halides has been ignored but other experiments (see later) showed that the amount of halogen present as carbonyl halides was negligible.

Thus in the 18 g. of liquid we have

CCl_4	11.2 g.
CCl_3COF	2.0 g.
CCl_3COCl	0.52 g.
CCl_3COOH	0.99 g.
C_2Cl_6	3.3 g.

Exit gases Oxygen 2 g.

Hence in this reaction we have accounted for

CCl_4	20.3 g.
CCl_3F	7.7 g.
CCl_2F_2	0.2 g.
$CClF_3$	0.1 g.
CO_2	30.0 g.
Cl^-	21.5 g.
F^-	14.4 g.
CCl_3COF	2.0 g.
CCl_3COCl	0.5 g.
CCl_3COOH	1.0 g.
C_2Cl_6	16.8 g.

Experiment type B.

Starting Materials

CCl_3COOH	99.5 g.	0 .61 mole.
ClF_3	30.5 g.	0.33 mole.

Products

COX_2 0.266 eq. of approximate composition

CO	3.7 g.	0.13 mole.
Cl	6.5 g.	0.18 mole.
F	1.6 g.	0.084 mole.

Analysis of the exit gases showed that they contained

CO_2	17.2 g.
O_2	0.1 g.
CO	6.0 g.

The 0.266 eq. of COX_2 generated

3.7 g. CO

Therefore the actual CO produced is 2.3 g.

The 1st. reaction vessel contained a solid (C_2Cl_6) while the second contained a liquid (15 g.) containing CCl_3COX (.011 eq. Cl^-, 0.013 eq. F^-) similar to that of the previous experiment.

From this liquid and other parts of the apparatus 9.5 g. C_2Cl_6 were recovered. A more complete analysis was not attempted.

Experiment type C.

Starting Materials

CCl_3COOH	102 g.	(0.62 mole.)

ClF_3	34.5 g.	(0.37 mole.)

Products

0.592 eq. of halogen as COX_2 and X_2 was detected. The approximate composition was

Cl	12.4 g.	(0.35 mole.)
F	4.6 g.	(0.24 mole.)

From the 1st reaction vessel only C_2Cl_6 was recovered while the second yielded a liquid (11 g.) as before. No attempts were made at a complete analysis. In all 13.5 g. (0.057 mole.) of C_2Cl_6 were recovered. Combining these results it is seen that we have from 100 g. of CCl_3COOH and 29 g. of ClF_3 the following products:

	C_2Cl_6	16.8 g.	(0.070 mole.)
	CCl_4	11.2 g.	(0.075 mole.)
	CCl_3F	7.7 g.	(0.056 mole.)
	CCl_2F_2	0.2 g.	(0.0015 mole.)
	$CClF_3$	0.1 g.	(0.0009 mole.)
Carbonyl halides containing	CO	3.7 g.	(0.13 mole.)
	Cl	6.5 g.	(0.18 mole.)
	F	1.6 g.	(0.084 mole.)
Halogens containing	Cl	5.9 g.	(0.017 mole.)
	F	3.0 g.	(0.016 mole.)

CO_2 (from alkaline sulphite scrubber after correction for that generated from COX_2

22.3 g. (0.51 mole.)

	CO_2 (by gas analysis	17.2 g.	(0.39 mole.))
	CO	2.3 g.	(0.083 mole.)
Actually isolated	CCl_3COF	2.0 g.	(0.012 mole.)
	CCl_3COCl	0.5 g.	(0.0027 mole.)
	CCl_3COOH	1.0 g.	(0.0062 mole.)
halogens as HX and CCl_3COX	Cl	9.1 g.	(0.25 mole.)
	F	9.8 g.	(0.52 mole.)
	O_2	0.1 g.	(0.0032 mole.)

Action of ClF_3 on CCl_3COCl at 100°

Experiment type A.

Starting Materials

CCl_3COCl	111.5 g.	(0.61 mole.)
ClF_3	3.2 g.	(0.35 mole.)

Products The alkaline sulphite solution contained

Cl^-	33.0 g.	(0.93 mole.)
F^-	7.8 g.	(0.41 mole.)
CO_2	5.9 g.	(0.13 mole.)

The halogenated methanes were composed of

CCl_4	1.5 g.	(0.0098 mole.)
CCl_3F	6.9 g.	(0.050 mole.)
CCl_2F_2	0.1 g.	(0.00083 mole.)
$CClF_3$	0.1 g.	(0.00096 mole.)

The first reaction vessel was empty and the liquid remaining in the second reaction vessel (79.0 g.) was analysed as follows:

A sample (9.5 g.) was dissolved in excess NaOH solution and the C_2Cl_6 filtered off (0.2 g.). The filtrate was made up to 250 ml. and the halide estimated (0.0013 eq. Cl^- and 0.037 eq. F^-). This indicates the presence of

CCl_3COCl	0.2 g.
CCl_3COF	6.1 g.
C_2Cl_6	0.2 g.

This rather large deficit is accounted for in the loss of the volatile liquid during the vigorous neutralisation in spite of the CO_2/Ethanol condenser. The relative proportions of these products was therefore used and the liquid from the reaction vessels is considered to be

CCl_3COCl	2.5 g.	(0.014 mole.)
CCl_3COF	74.0 g.	(0.50 mole.)
C_2Cl_6	2.5 g.	(0.011 mole.)

Exit gases contained O_2 0.1 g. (00031 mole.)

Hence in the experiment we have accounted for 134.4 g. of products.

Experiment type B.

Starting Materials

CCl_3COCl	115.0 g.	(0.63 mole.)
ClF_3	35.0 g.	(0.38 mole.)

Products

0.0384 eq. of phosgenes were detected, of approximate composition

CO	0.53 g.	
Cl	0.83 g.	(0.023 mole.)
F	0.29 g.	(0.015 mole.)

Analysis of the exit gases showed that they contained

CO_2	3.4 g.	(0.077 mole.)
O_2	0.2 g.	(0.0062 mole.)

and no CO in excess of that generated from the COX_2. The liquid remaining in the second reaction vessel (55.5 g.) was analysed in a similar fashion to that in the previous experiment. The sample (16.6 g.) contained 1 g. C_2Cl_6 3.3 g. CCl_3COF and 9.086 g. CCl_3COCl and again there was an apparent loss of volatile halides.

Experiment type C.

Starting Materials

CCl_3COCl	112.5 g.	(0.62 mole.)
ClF_3	30g.	(0.32 mole.)

Products

0.924 eq. of X_2 + COX_2 were detected containing approximately

Cl	26.8 g.	(0.76 mole.)
F	3.2 g.	(0.16 mole.)

60 g. of material remained in the second reaction vessel.

From these experiments we can state that the reaction between ClF_3 (32 g.) and CCl_3COOH (111.5 g.) produced.

C_2Cl_6	2.5 g.	(0.011 mole.)
CCl_4	1.5 g.	(0.0098 mole.)
CCl_3F	6.9 g.	(0.050 mole.)
CCl_2F_2	0.1 g.	(0.00083 mole.)
$CClF_3$	0.1 g.	(0.00096 mole.)
CO_2 (from alkaline scrubber after correction for that from COX_2)	5.1 g.	(0.19 mole.)
By gas analysis	3.4 g.	(0.077 mole.)
COX_2 containing		
(CO	0.5 g.	(0.019 mole.)
(Cl	0.8 g.	(0.023 mole.)
(F	0.3 g.	(0.015 mole.)
halogen containing		
(Cl	26.0 g.	(0.73 mole.)
(F	2.9 g.	(0.15 mole.)
halogen as CCl_3COX carried over into alkaline sulphite scrubber		
(Cl	6.2 g.	(0.18 mole.)
(F	4.6 g.	(0.24 mole.)

A mixture of CCl_3COF and CCl_3COCl containing appreciable amounts of the acid fluoride

76.5 g.

Oxygen	0.1 g.	(0.0031 mole.)

Experiment to determine degree of substitution of CCl_3 group in CCl_3COOH

Starting Materials

ClF_3	15 g.	(0.16 mole.)
CCl_3COOH	104.5 g.	(0.64 mole.)

A reaction of type A was carried out at 100° for 3 hours.

Products

The alkaline sulphite scrubber contained

Cl^-	9.0 g.	(0.25 mole.)
F^-	7.6 g.	(0.40 mole.)
CO_2	21.0 g.	(0.48 mole.)

Halogenated methanes

CCl_4	4.9 g.	(0.032 mole.)
CCl_3F	1.6 g.	(0.011 mole.)
CCl_2F_2	0.3 g.	(0.0025 mole.)
$CClF_3$	0.2 g.	(0.0019 mole.)

Halogenated ethanes

C_2Cl_6	14.8 g.	(0.062 mole.)

The residue in the reaction vessels (55.5 g. of solid) was analysed as follows. A sample of the crude acid (16.5 g.) and 0.5 g. of anhydrous $ZnCl_2$ were heated to 150° in a 100 ml. flask equipped with dropping funnel, reflux CO_2/EtOH condenser and $CaCl_2$ tube. Redistilled benzotrichloride (20 g. 0.14 mole.) was added and the mixture kept at this temperature for a further 30 minutes. The solid CO_2 was removed from the cold finger and replaced by oil. Using the cold finger as a thermometer well the acid chlorides were distilled until the distillation temperature rose to 126°C. (CCl_3COCl b.p. 118°) when 3.5 g. had distilled. The trap containing the acid chlorides was fitted with a dropping funnel, reflux CO_2/EtOH condenser and $CaCl_2$ tube and anhydrous MeOH (1 ml.) added. After the initial vigorous reaction occurred the mixture was heated to 160°C. and then left overnight. The crude esters were poured onto water, separated and washed with water (4 x 20 ml.) and dried ($MgSO_4$). The crude product was distilled under a static vacuum to give 2 g. of mixed esters for chromatographic analysis (see that section for details) which showed the presence of only CCl_3COOMe and Me_2CO_3. Authentic CF_3COOMe and CCl_3COOMe were prepared by the same process.

A second sample (6.4632 g.) was dissolved in water and the precipitate of C_2Cl_6 filtered off (1.5509 g.) and the filtrate made up to 100 ml. for Cl^- and F^- estimations.

There were found for the whole 55.5 g.

$$\left.\begin{array}{ll} Cl^- & 0.0085 \text{ eq.} \\ F^- & 0.0023 \text{ eq.} \end{array}\right) \quad 0.0108 \text{ eq.}$$

4R

By gas chromatography there were detected 0.000058 eq. of Me_2CO_3. Thus it is seen that most of the halogen must be present as CCl_3COX. Using this information we have present in the 55.5 g. of reaction residues

C_2Cl_6	13.3 g.
CCl_3COCl	1.5 g.
CCl_3COF	0.4 g.
CCl_3COOH	40.3 g.

The connecting tubes etc. yielded 1.5 g. C_2Cl_6. The exit gases contained 0.2 g. of O_2. From previous experiments of types B and C we can say that after 3 hours reaction the following had been formed

COX_2 containing	CO	0.7 g.	(0.026 mole.)
	Cl	0.8 g.	(0.023 mole.)
	F	0.6 g.	(0.029 mole.)
halogen containing	Cl	3.7 g.	(0.105 mole.)
	F	0.7 g.	(0.037 mole.)

Gas analysis indicated the presence of

CO_2	6.7 g.	(0.15 mole.)
O_2	0.1 g.	(0.0031 mole.)
CO	0.2 g.	(0.0071 mole.)

Hence the products from the action of ClF_3 (15 g. 0.16 mole) on CCl_3COOH (104.5 g. 0.64 mole.) for 3 hours are

C_2Cl_6	14.8 g.	(0.062 mole.)
CCl_4	4.9 g.	(0.032 mole.)

CCl_3F	1.6 g.	(0.011 mole.)
CCl_2F_2	0.3 g.	(0.0025 mole.)
$CClF_3$	0.2 g.	(0.0019 mole.)

CO_2 (from alkaline scrubber after correction for that from COX_2) 19.8 g. (0.45 mole.) (By gas analysis. 6.7 g. (0.15 mole.))

COX_2 containing

CO	0.7 g.	(0.026 mole.)
Cl	0.8 g.	(0.023 mole.)
F	0.6 g.	(0.029 mole.)

halogen containing

Cl	3.7 g.	(0.105 mole.)
F	0.7 g.	(0.037 mole.)

halogen as CCl_3COX or HX	Cl	4.5 g.	(0.13 mole.)
	F	6.4 g.	(0.34 mole.)

CCl_3COF	1.5 g.	(0.0091 mole.)
CCl_3COCl	0.4 g.	(0.0022 mole.)
CCl_3COOH	40.3 g.	(0.25 mole.)
Oxygen	0.1 g.	(0.0031 mole.)
CO	0.2 g.	(0.0071 mole.)

Experiment to determine effect of number of reaction vessels

The experiments types B and C gave results that had a rather strange variation with time. In order to investigate this phenomenon an experiment of type B was carried out using a single reaction vessel of larger

capacity (300 ml.) instead of the two in series.
The reaction (type B) was carried out in 10 hours and products resulting from the reaction between the ClF_3 (57 g. 0.61 mole.) and the CCl_3COOH (200 g. 1.22 mole.) were C_2Cl_6 (8.5 g. 0.037 mole.), recovered acid (91 g. 0.56 mole.) and COX_2, CO_2, O_2 and CO as represented graphically (Diagram 2 & 3).

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