The mechanism of the reaction of nitrous acid with olefins

James Roger Park

THE MECHANISM OF THE REACTION OF NITROUS ACID WITH OLEFINS

by

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A thesis submitted for the Degree of Doctor of Philosophy

in the University of Durham

August 1969

Acknowledgements

The author wishes to express his sincere thanks to Dr. D.L.H. Williams for his continual advice and encouragement during his supervision of this work.

Helpful discussions are also acknowledged with Dr. J. Yarwood and Dr. T.D.B. Morgan.

The receipt of a Science Research Council maintenance award is also acknowledged.

- To Alison -

Memorandum

The work described in this thesis was carried out in the University of Durham between October 1966 and June 1969. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

Part of this work has been the subject of a publication: J.R. Park and D.L.H. Williams, Chem. Comm., 332 (1969).

Summary

The reaction of nitrous acid with olefins has been shown to yield nitroso-nitrites. The same products were obtained from the addition of dinitrogen trioxide to the olefins. The orientation of addition of the elements of dinitrogen trioxide was established by a hydrolysis procedure. The product of the reaction of nitrous acid and 3-chloro-2-methylpropene yielded, on hydrolysis, 3-chloro-2-hydroxy-2-methylpropionic acid. The 2-methyl-2-butene addition compound yielded 2-hydroxy-2-methyl-butan-3-one on hydrolysis. The reaction of nitrous acid with 3-chloro-propene gave two products and both were shown to be of the 2-nitroso-1-nitrito form, since they yielded chloroacetic acid on hydrolysis. Other olefins gave two products on reaction with nitrous acid. One of the products was a solid and the other a liquid. The solid products appear to be dimers in the trans form. The infrared spectra and mass spectra were shown to be consistent with those of nitroso-nitrites.

In $1{\cdot}07 \times 10^{-4}$N perchloric acid both 2-methyl-2-butene and 2,3-dimethyl-2-butene underwent reaction by a second order process, which indicated that dinitrogen trioxide was the attacking reagent. In $8{\cdot}56 \times 10^{-4}$ to $2{\cdot}11 \times 10^{-2}$N perchloric acid the reaction of 2,3-dimethyl-2-butene with nitrous acid was first order and the nitrous acidium ion was the nitrosating agent. At acidities greater than 8×10^{-4}N perchloric acid, the nitrosation of 2-methyl-2-butene proceeded by a mixed first and

second order process nitrosation being achieved by dinitrogen trioxide and the nitrous acidium ion. In 0·40 to 1·70N perchloric acid, the kinetics of nitrosation of 3-chloro-2-methylpropene were first order with respect to olefin, nitrous acid and h_o. At constant ionic strength of 2·0M the rate was approximately constant due to a medium effect of the perchlorate anion. The kinetics of the nitrosation of 3-hydroxy-2-methylpropene in 0·20 to 2·70M sulphuric acid were also first order with respect to olefin, nitrous acid and h_o. A solvent isotope effect of 2·19 was observed, which was further strong evidence for nitrosation by the nitrous acidium ion. Halide ions were very effective catalysts of the nitrosation of 3-hydroxy-2-methylpropene and this was shown to be due to the incursion of nitrosation by the nitrosyl halide.

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Section 1.

Chapter 1.

Electrophilic addition to olefins

1.1 Classification of Reactions

A reaction can be classified according to the nature of the interaction and the nature of the reagent. The reactions discussed in this thesis are heterolytic reactions of the type:

$$X: + Y \rightleftharpoons X:Y \qquad 1.01$$

in which both electrons are provided by one reactant to form the bond or accepted by one reactant on the rupture of the bond. These reactions can be classified further into two categories of broadest concern:

i) substitution, in which one atom or group is replaced by another in the substrate, X-Y:

$$X + Y\text{-}Z \longrightarrow X\text{-}Y + Z \qquad 1.02$$

and ii) addition, in which one atom or group becomes attached to the substrate, X-Y:

$$X + Y\text{-}Z \longrightarrow X\text{-}Y\text{-}Z \qquad 1.03$$

Reagents are classified according to their ability to accept or donate electrons, thus an electrophilic reagent will react by acquiring electrons, or a share of electrons, which previously were bound exclusively to another molecule. (It is worth noting that this definition of an electrophilic reagent is the same as the classification by Lewis of reagents as acids[1]). An electrophilic reagent is often attached to a nucleophile. When electrophilic attack occurs,for example in molecular bromination, the

electrophile will become attached to the substrate and the nucleophile will become free and may subsequently complete the reaction. It will be noted that if the reagent is an electrophile, reacting by accepting a share of electrons previously the exclusive property of another molecule, then the substrate must be a nucleophile, since it has the ability to donate electrons to another molecule. Thus it is obvious that the classification of a reaction as electrophilic or nucleophilic depends on the classification of the interacting species as reagent and substrate. Which of the interacting species should be described as reagent and substrate is a pure convention, as shown by the reaction of bromine with naphthalene which is classified as an electrophilic reaction since bromine is the reagent.

Thus the reactions of most interest fall into four classes:

I) Electrophilic substitution SE^2: for example

$$NO_2^+ + Ph\text{-}H \longrightarrow Ph\text{-}NO_2 + H^+ \qquad 1.04$$

II) Nucleophilic substitution SN: for example

$$Et\text{-}O^- + CH_3\text{-}I \longrightarrow CH_3\text{-}OEt + I^- \qquad 1.05$$

III) Nucleophilic addition AdN: for example

$$NH_3 + CH_3CH{=}O \longrightarrow CH_3CH\begin{matrix}OH\\ \diagdown\\ \diagup\\ NH_2\end{matrix} \qquad 1.06$$

IV) Electrophilic addition AdE: for example

$$HCl + CH_3CH{=}CH_2 \longrightarrow CH_3CHClCH_3 \qquad 1.07$$

Class IV is of most concern in this thesis, thus further examples are given in Table 1.1.

Table 1.1.

Electrophilic addition (AdE) to olefins

Reagent	Substrate	Product
H_3O^+	$R_1R_2C{=}CR_3R_4$	$R_1R_2C(H)CR_3R_4(OH)$
X_2 *	$R_1R_2C{=}CR_3R_4$	$R_1R_2C(X)CR_3R_4(X)$
HOX	$R_1R_2C{=}CR_3R_4$	$R_1R_2C(X)CR_3R_4(OH)$
HX	$R_1R_2C{=}CR_3R_4$	$R_1R_2C(H)CR_3R_4(X)$
NOX	$R_1R_2C{=}CR_3R_4$	$R_1R_2C(NO)CR_3R_4(X)$

where * X = halogen.

1.2 Substituent effects in Electrophilic Addition to Olefins

The most characteristic type of reaction of an olefin is that of electrophilic addition, wherein an electrophilic reagent E-Nu attacks the double bond, new bonds are formed and a saturated compound results:

$$\text{E-Nu} + \text{>C=C<} \longrightarrow \text{>C(E)—C(Nu)<} \qquad 1.08$$

The actual mechanism will be discussed later but it involves the initial attack by an electrophile. If the olefin is symmetrical (that is of the form

$R_2C{=}CR_2$), then only one product of addition can result. If, however, the olefin is unsymmetrical (that is of the form $R_1R_2C{=}CR_3R_4$), then there are two possible products of addition, namely:

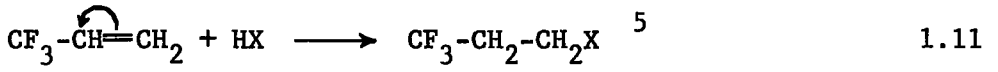
$$R_1R_2C{=}CR_3R_4 \xrightarrow{E\text{-}Nu} \begin{cases} \rightarrow R_1R_2C(E)CR_3R_4(Nu) \\ \rightarrow R_1R_2C(Nu)CR_3R_4(E) \end{cases} \qquad 1.09$$

It is possible to predict the orientation of the addition of halogen acids (HX, where X = halogen) by application of Markownikoff's rule.[3] This rule, stating that the entering halogen atom attached itself to the carbon carrying the smaller number of hydrogen atoms, has been found to predict the correct orientation of addition in all purely electrophilic additions, when proper consideration is taken of the electronic movements in the system. This latter consideration is necessary because the rule was proposed only for the case of hydrocarbon olefins, for which inductive effects are dominant.

The electronic effects of various substituents on the double bond are now well understood[2] in terms of inductive and mesomeric effects, thus it is easy to predict the orientation of addition. Some examples of "normal Markownikoff addition" are:

$$\begin{matrix} Me \\ \diagdown \\ C{=}CH_2 \\ \diagup \\ Me \end{matrix} + HX \longrightarrow \begin{matrix} Me \\ \diagdown \\ C\text{-}CH_3 \\ \diagup \\ Me \quad X \end{matrix} \qquad 1.10$$

[4]

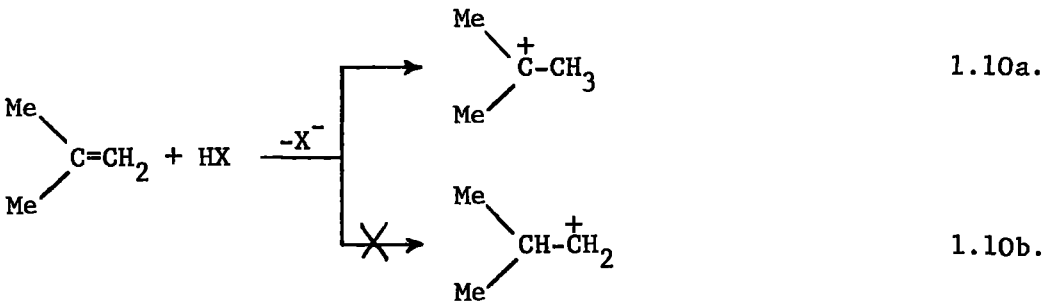


1.11

This rule is readily rationalised when we realise the intermediacy of carbonium ions (discussed in section 1.3) in electrophilic additions. It has been established by study of reactivity in nucleophilic substitution by the carbonium-ion mechanism, that the order of stability of carbonium-ions is:

tertiary > secondary > primary

Application of these relationships to reaction 1.10, yields:

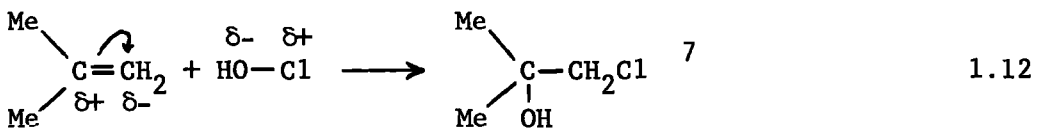


1.10a.

1.10b.

Thus the product will be obtained by reaction 1.10a, which proceeds through the most stable carbonium ion.

Michael[6] sought to generalise on the basis of the "principle of maximum neutralisation", according to which the electronegative group of the attacking reagent will become attached to the more electropositive of the unsaturated carbon atoms. This is illustrated by:



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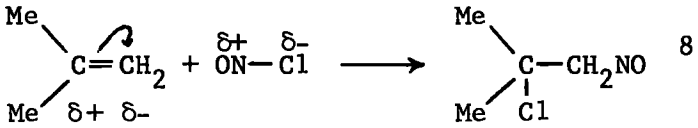
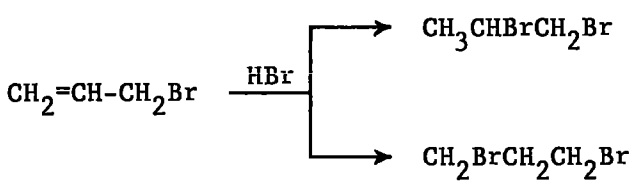


1.13

Thus this extension of the Markownikoff rule can be used to predict the orientation of addition of an electrophilic reagent to any olefin.

It is worthy of note, however, that evidence has been produced, in calculations by Bodot and Jullien[9], that the stability of the resultant carbonium ion is the directing effect in electrophilic addition. They have calculated charge distributions in a series of unsymmetrically substituted olefins from the dipole moments, and show that, although in some cases the attacking electrophile becomes attached to the most electronegative carbon atom, on some occasions the electrophile becomes attached to the most electropositive carbon atom. They have, in addition, calculated the relative energies of the two possible carbonium ions and found that the carbonium ion corresponding to the observed product has the lower energy in every case.

Anti-Markownikoff addition has however been observed, for example in the addition of hydrogen bromide to allyl bromide[8], where the normal addition product would be 1,2-dibromopropane and under certain conditions the observed product was 1,3-dibromopropane:



1.14

However it was realised that the presence of peroxide, accidentally introduced into the reaction mixture, was causing "abnormal addition" of hydrogen bromide. The abnormal addition could be completely eliminated by reaction in the presence of antioxidant or by complete removal of the peroxides. This change of orientation of addition of hydrogen bromide, in the presence of peroxides, is called "the peroxide effect" and is caused by a change of the nature of addition which, under such conditions, proceeds by a free-radical mechanism, with $Br^{\cdot}$ rather than H^{+} attacking the double bond.

In addition to showing a directing effect on the orientation of electrophilic addition, substituent groups attached to the double bond will also depress or increase the rate. Electrophilic addition occurs by attack of a species seeking a source of extra electrons. Thus if the substituents are to increase the availability of electrons on the double bond (that is are electron-donating, for example alkyl substituents), then the rate of electrophilic addition will be enhanced. (This type of observation experimentally is taken as indicating an electrophilic addition reaction). This is illustrated for the relative rates of hydration of olefins, $RC(Me)=CH_2$, in 29·6% $HClO_4$ at 38^{o} [10] in Table 1.2. A similar effect is shown in the electrophilic addition of bromine to olefins, $R_1R_2C=CH_2$.[11] Table 1.3 shows the relative rates of addition reactions in acetic acid containing M/80 bromine at $24^{o}C$.

Table 1.2.

Relative rates of hydration of olefins, $RC(Me)=CH_2$ in 29·6% $HClO_4$ at 38°

Group R	Relative Rates
H	1
CH_2Cl	1
CH_2OMe	30
Ph	5,000
Me	8,000
Et	10,000
t-Bu	8,000

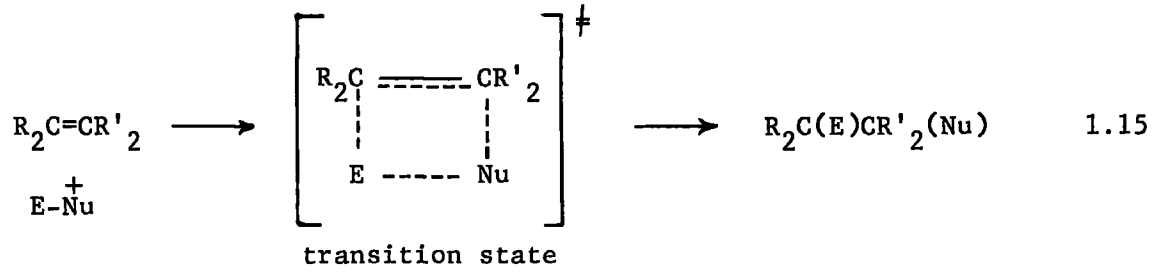
Table 1.3.

Relative rates of bromination of olefins, $R_1R_2C{=}CH_2$ in acetic acid at 24°C

Groups R_1	R_2	Relative rate
Ph	H	~11,000
C_4H_9	H	2,000
H	H	~84
$ClCH_2$	H	1·6
$BrCH_2$	H	1·0
$ClCH_2$	$ClCH_2$	0·019
EtO_2C	H	0·004
Br	H	0·0011

1.3 Carbonium ions as intermediates in electrophilic addition:

Electrophilic addition to olefins can occur by a one-stage process:



for example the addition of nitrosylchloride to norbornene occurs by a four-centre transition state to yield cis-addition,[12] or a two-stage process:

$$E\text{-}Nu + O \xrightarrow{slow} E\text{-}O^{+} + Nu^{-} \xrightarrow{fast} E\text{-}O\text{-}Nu \qquad 1.16$$

where O ≡ olefin.

In a one-stage process there is very little carbonium ion character in the transition state, but there may be varying degrees according to the electrophilicity of the reagent. This mechanism would tend to occur in less polar solvents and would result in stereospecific cis-addition, if there is not free rotation about the C-C bond. Cis-addition has been observed in the addition of deuterium bromide to acenaphthylene, indene and 1-phenylpropene.[13]

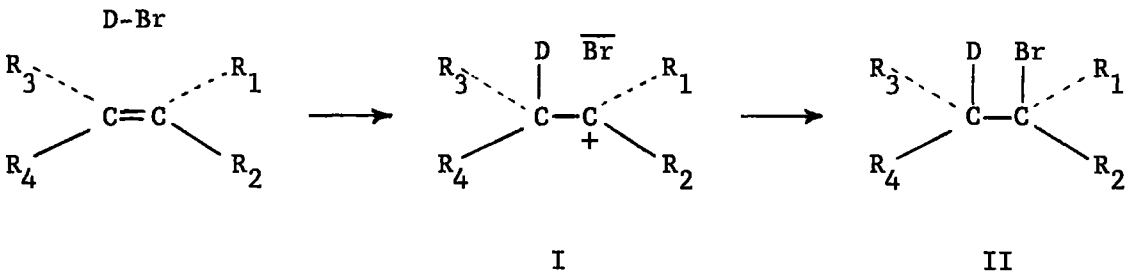
The most important mechanism for electrophilic addition in the liquid phase is stepwise addition through a carbonium ion intermediate. Here, rate-limiting reaction of an olefin with E-Nu gives a cationic intermediate which rapidly collapses to products. Evidence of the importance of cationic intermediates in electrophilic addition of hydrogen chloride was obtained by

Whitmore and Johnston.[14] From the addition of hydrogen chloride to iso-propylethylene in the absence of a solvent they obtained isoamyl chloride accompanied by t-amylchloride. The latter was not produced from the former, since it remains stable under experimental conditions. Thus the rearrangement leading to t-amylchloride must have taken place in some intermediate stage of the reaction, most likely in a carbonium ion produced in a stepwise mechanism of addition:

$$\begin{array}{l} Me_2CHCH{=}CH_2 + HCl \\ \qquad\qquad \downarrow \\ Me_2CH\overset{+}{C}HCH_3 + Cl^- \longrightarrow Me_2CHCHClCH_3 \\ \qquad\qquad \downarrow \\ Me_2\overset{+}{C}CH_2CH_3 + Cl^- \longrightarrow Me_2CClCH_2CH_3 \end{array} \qquad 1.16$$

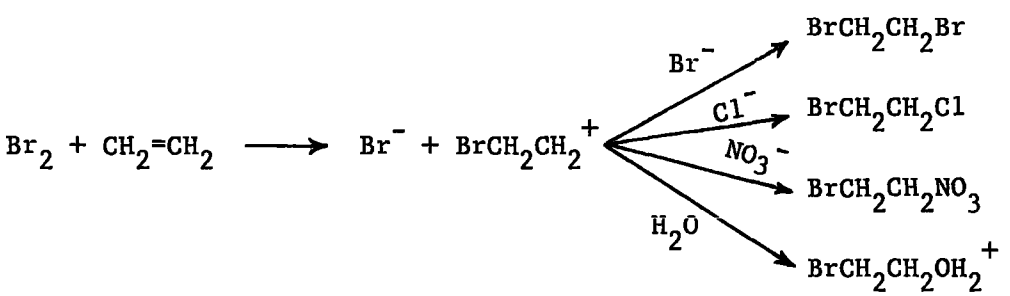
Of course reactions do not always fit automatically into one of these two classes of addition and many electrophilic additions can equally well be explained by either process, for example the addition of deuterium bromide to acenaphthylene, indene and 1-phenylpropene.[13] This can be interpreted as a one-stage process as earlier but is also interpreted as involving a carbonium ion which is not free. The reaction of undissociated deuterium bromide with the olefin gives first an ion-pair (I) in which the bromide ion is retained on the same side of the olefin as the deuterium; collapse of this ion-pair (I) then gives exclusively the cis adduct (II). The trans adduct is only formed if the ion-pair survives long enough for the bromide ion to migrate to the opposite side of the planar carbonium ion. Hence, if

collapse of I is rapid, cis addition will predominate.



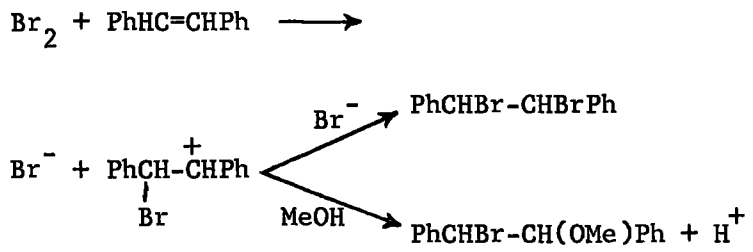
1.17

The additions of halogens, like those of hydrogen halides, are stepwise reactions; that is, they proceed through intermediates in which only one halogen atom has become attached to the olefin. The intervention of such an intermediate in the bromination of ethylene[15] has been clearly demonstrated by carrying out the addition in the presence of sodium chloride or sodium nitrate, for under these conditions a bromochloride or a bromonitrate is formed along with the expected dibromide. These products must then result from nucleophilic attack on an intermediate bromonium cation, since it is known that substitution reactions could not form the observed products



1.18

Moreover, the addition of bromine to stilbene[16] in methanol yields, along with stilbene dibromide, a β-bromoether. This does not result from reaction of methanol with the dibromide, nor does it arise from the addition of methylhypobromite to the double bond:

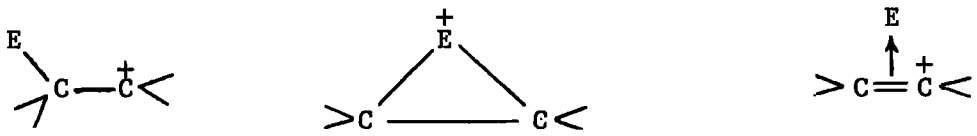


1.19

Thus there must be an intermediate carbonium ion which is then subject to competitive nucleophilic attack by bromide ion and methanol.

1.4 The nature of the carbonium ion in electrophilic addition to olefins

The intermediacy of carbonium ions in the two step process of electrophilic addition is now quite well established and many examples appear in the literature. However much controversy exists as to the detailed nature of the carbonium ion. There are three possibilities:



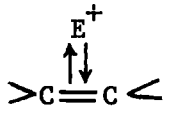
III IV V

Addition via the AdE2 mechanism can lead to either cis or trans adducts depending upon the structure of the intermediate carbonium ion (III, IV or V). If the carbonium ion has the open structure III, a mixture of cis and trans adducts is generally expected.[17] However, ion-pairing phenomena can cause preferential formation of the cis-adduct.[13] Also electronic, steric or conformational effects can cause attack at one or other side of the carbonium ion p-orbital to be favoured.

Alternatively, the intermediate may have a bridged structure IV of the type first postulated by Roberts and Kimball[18] for E = Br and later formulated by Dewar[19,20] as a π-complex V. The intermediates, IV or V, by analogy with nucleophilic displacement, would be opened stereospecifically[18] to a trans product.

Differentiation between the two postulated structures of the non-classical carbonium ion is not possible by kinetic study but depends on the ability of each structure to explain the experimental observations.

If the electrophile, E^+ has unshared p- or d-electrons or π-electrons, these can be used to form a reverse dative bond to the olefin by interaction with the empty anti-bonding π-molecular orbital of the latter.[21] The group E^+ is then attached to the olefin by a double bond composed of two opposed dative bonds involving π-molecular orbitals V.



V

This structure differs from IV only in the state of hybridisation of the olefinic carbon atoms, since the bond between them is only partially double. Thus the two "extreme π-complexes" might be observed in the case of attack by protons and bromine cations:

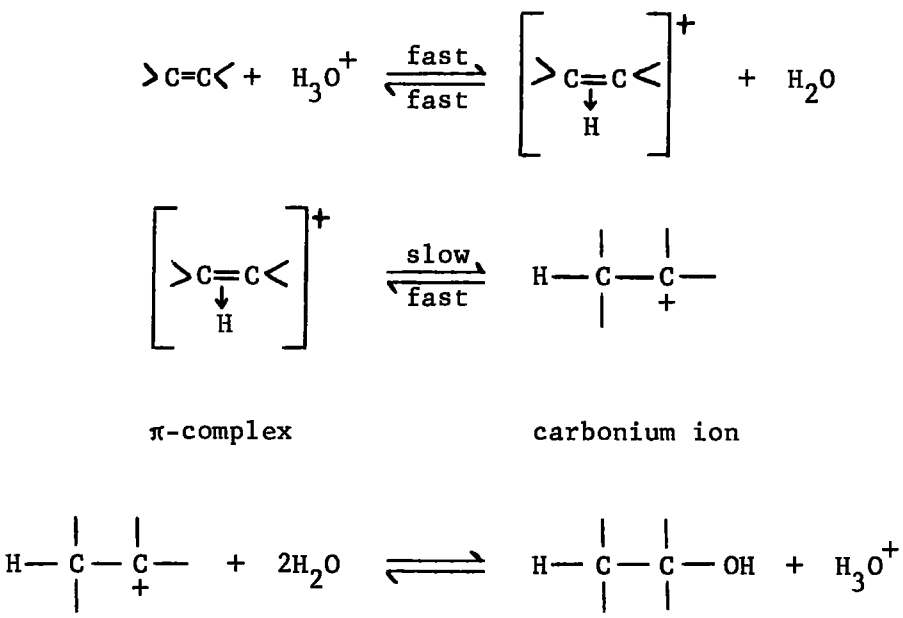
The acid-catalysed addition of water to an olefin has been shown to involve a carbonium ion.[22] Evidence for the intermediacy of a non-classical carbonium ion in the reaction sequence falls into three categories:

(i) 2-butene in the presence of anhydrous perchloric acid does not isomerise, as would occur if a classical carbonium ion were formed in a reversible step.[23]

(ii) Olefin recovered from the reaction of 2-methyl-2-butene with deuterated sulphuric acid does not contain any deuterium.[24]

(iii) The rate of hydration is first order in both olefin and Hammett's h_o function.[25]

To account for these experimental observations, Scheme 1.1 has been proposed[22], where the intermediacy of a π-complex (or bridged carbonium ion) is necessary to account for (i) and (ii) and the slow collapse to a classical carbonium ion explains the observed rate equation and the stereospecificity of the product.



Scheme 1.1.

Chapter 2.

Nitrosation: An electrophilic reaction

2.1 Diazotisation and Nitrosation: Principles of Kinetic Study

Nitrosation and diazotisation of an aromatic amine is considered to occur by the following sequence of reactions:[26]

$$Ar\text{-}NH_2 \xrightarrow[NOX]{slow} Ar\text{-}NH\text{-}NO \xrightarrow{fast} ArN{=}N\text{-}OH \xrightarrow[H^+]{fast} Ar\text{-}N_2^+$$

In diazotisation reactions the formation of the primary nitrosamine has been found to be the slowest of the above steps in acidities up to 3·0M perchloric acid. The kinetic complexity, therefore, arises from the several mechanisms of nitrosation, some of which include two potentially rate-determining steps. The study of the mechanism of diazotisation has thus contributed to the understanding of nitrosation in general and the extensive kinetic investigations of diazotisation by Schmid et al[27] and Ridd et al[26] have given considerable insight into the nature of the various nitrosating entities that may be present in aqueous nitrous acid. Moreover, the conclusions arrived at by these workers can be usefully invoked in any consideration of the nitrosation of other compounds.[28]

N-nitrosation is essentially an electrophilic substitution in which eventually the electrophile NO^+, furnished either in the free form or in a carrier NOX from which NO^+ can be extracted, becomes bound to the nitrogen atom of the amino group. By analogy with other electrophilic substitutions, such as nitration and chlorination, there exists a family of nitrosating agents which can be arranged in order of their decreasing electrophilic

reactivity[29], or in increasing strength of the base, X^-

$$NO^+, \quad H_2O^+-NO, \quad NO\text{-}Hal, \quad NO\text{-}NO_2, \quad NO\text{-}OH$$

However, it is worthy of note that even the most reactive nitrosating species is not nearly so strong an electrophilic reagent as the nitronium ion.[30] The effectiveness of a given nitrosating species depends on two factors:

(i) its specific reactivity as an electrophile,

(ii) its actual concentration.

The generally opposed variation of these two factors from case to case leads to a certain spread of nitrosating ability among the different carriers.

In perchloric acid solutions the possible nitrosating agents are the following:

nitrosonium ion	NO^+
nitrous acidium ion	H_2O^+-NO
dinitrogentrioxide (nitrous anhydride)	$NO\text{-}NO_2$
nitrous acid	NO-OH

The kinetic equations associated with these reagents for nitrosation of aromatic amines in dilute solutions of perchloric acid are listed in Table 2.1.[31]

The rate equations included in Table 2.1 are based on the assumption that all steps following the initial N-nitrosation are very fast and have no effect on the overall rate of the reaction. However, if any of the

Table 2.1

Nitrosating agent		Rate-determining stage	
		Formation of nitrosating agent	Nitrosation of the amine
NO^+	slow supply (via $H_2NO_2^+$)	V $\alpha[HNO_2][H^+]$ (a)	
	slow supply (via N_2O_3)	V $\alpha[HNO_2]^2$ (b)	
	slow attack		V $\alpha[ArNH_2][HNO_2][H^+]$ (c)
$NO\text{-}\overset{+}{O}H_2$	slow attack		V $\alpha[ArNH_2][HNO_2][H^+]$ (d)
$NO\text{-}NO_2$	slow supply	V $\alpha[HNO_2]^2$ (e)	
	slow attack		V $\alpha[ArNH_2][HNO_2]^2$ (f)
NO-OH	slow attack		V $\alpha[ArNH_2][HNO_2]$ (g)

where the brackets indicate the molecular or ionic concentrations of the exact species represented therein.

subsequent steps becomes rate-determining, then additional rate equations must be considered. This is, for instance, what happens in very concentrated acids, when the loss of a proton from the protonated nitrosamine first formed becomes the rate-determining step.

With a general carrier, two limiting kinetic forms can be found, according to whether the attack or formation of the carrier is rate-controlling. In the former case, the carrier remains in equilibrium with other nitrous species, and the overall rate is dependent on the concentrations of both the nitrosating species and the amine. In the latter case, the carrier is consumed by the amine as fast as the carrier is produced, and the overall rate is dependent on the concentration of the nitrosating species only. The rate measured is that of a purely inorganic process and the kinetics considered are those of this process.

With molecular nitrous acid as carrier, one kinetic case disappears, since carrier-supply cannot be rate-controlling and only attack can be rate-determining. For the nitrous acidium ion only attack on the amine can be rate-controlling, since it is formed by a proton-transfer in aqueous solution and such reactions are known to be very fast.

Dinitrogen trioxide is a nitrosating agent for which either the formation or the reaction with the amine can be rate-controlling. In the latter case an equilibrium concentration of carrier is provided by the process:

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O$$

and this concentration will be available for the attack of the amine, hence equation (f). In the former case, the concentration of the amine does not appear in the rate equation, which represents the rate of formation of dinitrogen trioxide in the equilibrium shown above. Equation (e) however, which represents this observation, is the same as that [(b)] observed for the slow formation of nitrosonium ions from dinitrogen trioxide:

$$2HNO_2 \underset{\text{fast}}{\rightleftharpoons} N_2O_3 + H_2O$$

$$N_2O_3 \xrightarrow{\text{slow}} NO^+ + NO_2^-$$

Thus it is not possible to distinguish between the two mechanisms by simple kinetic techniques. Similarly, a slow N-nitrosation of the amine by the nitrous acidium ion or by the nitrosonium ion would show identical kinetics (equations (d) and (c) respectively).

2.2 Physical measurements on solutions of "nitrous acid"

The ultraviolet, visible and Raman spectra of solutions of "nitrous acid" have been studied widely by various workers. Depending on the nature of the medium, that is concentration and type of mineral acid, "nitrous acid" can exist in a variety of forms such as molecular nitrous acid, dinitrogen trioxide, nitrous acidium ion, nitrosonium ion or nitrosyl chloride.

(a) In perchloric and sulphuric acid:

(i) In water and dilute aqueous acid, nitrous acid exists mainly as molecular nitrous acid, with slight dehydration to dinitrogen trioxide. Both of these species have characteristic ultraviolet spectra. The spectrum of nitrous acid shows maxima at[32,33], 347, 356, 370, 384 mμ, and that of dinitrogen trioxide has a single broad maximum at[34], 625 mμ, hence explaining the blue colour of solutions of dinitrogen trioxide.

(ii) When the concentration of perchloric acid is increased above 45 per cent, the absorption spectrum of nitrous acid changes until, effectively,in 60 per cent perchloric acid there is complete conversion to the nitrosonium ion, absorbing at 260 mμ.[32] In the same region a Raman line appears at 2213-2319 cm^{-1},[35] almost identical with the stretching frequency of the NO^+ ion in crystalline nitrosonium perchlorate (2329 cm^{-1}). For solutions falling in the range 45 per cent to 60 per cent perchloric acid, the observed spectra are consistent with an equilibrium between molecular nitrous acid and the nitrosonium ion.[32]

A similar change in the ultraviolet and Raman spectra occurs in aqueous sulphuric acid in the concentration range 50 per cent to 75 per cent sulphuric acid, although the increase in the concentration of nitrosonium ion, as calculated from the extinction coefficient, does not parallel the calculated decrease in the concentration of nitrous acid.[36] It is suggested the discrepancy could be caused by the intervention of a third, non-absorbing species and this could be the nitrous acidium ion.[36] However

the results still indicate a gradual conversion of nitrous acid to nitrosonium ion, which is complete in 75 per cent sulphuric acid. In a more recent study[37] it has been found, by allowing for nitrous acid decomposition, that the maximum concentration of the nitrous acidium ion is 5 per cent of the total "nitrous acid" present.

For a given "nitrous acid" concentration, the concentration of dinitrogen trioxide reaches a maximum value in about 50 per cent perchloric acid. With further increase in the acidity of the medium, the molecular nitrous acid and dinitrogen trioxide are converted into the nitrosonium ion and possibly the nitrous acidium ion, according to the following sequence of reactions:

$$H^+ + HNO_2 \rightleftharpoons H_2\overset{+}{N}O_2$$

$$H_2\overset{+}{N}O_2 \rightleftharpoons NO^+ + H_2O$$

$$NO_2^- + H_2NO_2^+ \rightleftharpoons N_2O_3 + H_2O$$

$$2H^+ + N_2O_3 \rightleftharpoons 2NO^+ + H_2O$$

The above results suggest, therefore, that various species can co-exist in solution and the processes by which they are formed overlap with one another in a way which depend on the concentration of the acid and the activity of the water.

(b) In HCl:

In solutions of nitrous acid in hydrochloric acid, an additional species,

nitrosyl chloride, has to be considered.[36,38] The spectrum of this compound (with a maximum at 460 mμ) can be detected in about 4M hydrochloric acid and it is supposed to be the only component in about 11M hydrochloric acid. There is no evidence for the nitrous acidium ion in hydrochloric acid.

Thus the physical measurements on the various acidic solutions of "nitrous acid" support the general picture of N-nitrosation of amines, although the identification of the particular nitrosating species concerned must depend essentially on the observed kinetics.

2.3 Investigation of the Mechanism of Diazotisation

The early work on the mechanism of diazotisation is covered in a review[26] and thus it is not proposed to discuss this any further. The results obtained by Ridd and co-workers will be discussed in the light of the information available from the previous two sections and also inasmuch as they are relevant to the present investigations.

In a series of papers, the following kinetic forms have been identified:

(a) Uncatalysed diazotisation:[39]

$$V = k_3''[ArNH_2][HNO_2]^2 \qquad (1)$$

$$V = k_2''[HNO_2]^2 \qquad (2)$$

(b) Hydrogen-ion catalysed reaction:[40]

$$V = k_3^H[ArNH_2][H^+][HNO_2] \qquad (3)$$

(c) Halide-ion catalysed diazotisation:[41]

$$V = k_4^{Hal}[ArNH_2][H^+][HNO_2][Hal^-] \quad (4)$$

$$V = k_3^{Hal}[H^+][HNO_2][Hal^-] \quad (5)$$

Expressions (1) and (2) are two limiting equations, and although each has a wide range of validity, they enclose between them a band of continuously transitional kinetic forms.

(a) Uncatalysed Diazotisation

(i) Experimental Observations:

As the acidity of the medium increased from 0·002M to 0·05M in perchloric acid, the overall reaction order increased from 2 to nearly 3. This established the transition between (1) and (2). In the region where the overall reaction order was 2, Ridd found the kinetic order with respect to the amine was zero and the kinetic order with respect to nitrous acid was 2.

(ii) Mechanistic Implications:

Since it is possible to observe a kinetic expression, and hence a slow step, which does not include the amine concentration, then there cannot be a slow step in the reaction sequence after the initial nitrosation. Also the process leading to nitrosation must involve more than one step, since a different step can be made rate-controlling by increasing the concentration of the amine.

These observations fit the requirements expressed earlier for nitrosation by dinitrogen trioxide. The most plausible scheme for the self-dehydration is

Scheme 2.1, which assumes slow attack by the nitrite ion on the conjugate acid of nitrous acid:

Scheme 2.1

$$H^+ + HNO_2 \underset{\text{fast}}{\rightleftharpoons} H_2\overset{+}{N}O_2$$

$$NO_2^- + ON\text{-}\overset{+}{O}H_2 \underset{\text{slow}}{\rightleftharpoons} N_2O_3 + H_2O$$

When the supply of molecular amine is sufficiently restricted, the last step of Scheme 2.1 becomes fast in comparison to:

$$ArNH_2 + NO.NO_2 \xrightarrow[\text{slow}]{} ArNH_2NO^+ + NO_2^-$$

The intermediacy of dinitrogen trioxide has been confirmed by ^{18}O-exchange studies between nitrous acid and water[42] in the absence of amine. At low acidities and high concentrations of nitrite ion, the rate of this oxygen exchange was second order with respect to nitrous acid and in reasonable agreement with the rate of diazotisation according to the equation, $V = k_2''[HNO_2]^2$.

The results obtained in the reaction of aromatic amines with dinitrogen trioxide according to the equation, $V = k_3''[\text{Amine}][HNO_2]^2$, are summarised in Table 2.2. Larkworthy[43] showed that the diazotisation of aromatic amines by the dinitrogen trioxide mechanism obeys Hammett's linear free-energy relationship, thus establishing the dependence of the reaction rate on the basicity of the amine.

Table 2.2.[26]

Aniline Derivative	Temp.(^{o}C)	10^{-5}k.(mole^{-2}l^{2}sec^{-1})
p-H	25	27
p-H	0	3·11
p-OMe	0	5·56
p-Cl	0	0·92
p-NMe_3^+	0	0·14

(b) Acid-catalysed Diazotisation:

(i) Experimental Observations:

The best experimental conditions for the observation of this mechanism were found to be:

a. an amine of low basicity,

b. the acidity of the medium should not be very low,

c. the concentration of nitrous acid should be about 10^{-4}M.

The kinetic expression of the new mechanism indicates a first order dependence with respect to both the amine and nitrous acid.

(ii) Mechanistic Implications:

Reference to the earlier section shows that two processes could explain the observed kinetics. One, namely a reaction involving the free amine with an equilibrium concentration of the nitrosonium ion, has been

rejected from a consideration of ^{18}O-exchange between nitrous acid and water.[44]

The kinetic expression has been interpreted as the rate-determining attack of the nitrous acidium ion $H_2O.\overset{+}{N}O$ on the free amine as shown in Scheme 2.2.

Scheme 2.2.

$$H^+ + HNO_2 \underset{\text{fast}}{\rightleftharpoons} H_2NO_2^+$$

$$H_2\overset{+}{N}O_2 + ArNH_2 \xrightarrow[\text{slow}]{} ArNH_2\overset{+}{N}O + H_2O$$

$$ArNH_2\overset{+}{N}O \xrightarrow{\text{fast}} ArN_2^+$$

The diazotisation of aromatic amines in dilute perchloric acid can be completely described by the equation:

$$V = k_3''[ArNH_2][HNO_2]^2 + k_3^H[ArNH_2][HNO_2][H^+]$$

The relative importance of the two terms depends on the basicity of the amine and the conditions under which the reaction takes place. For instance, o-chloroaniline diazotises by the nitrous acidium ion mainly, whilst aniline reacts with nitrous anhydride almost exclusively. The second term of the equation becomes more significant at low nitrous acid concentrations and higher acidity.

Study of the diazotisation of a wider variety of amines by the nitrous-

acidium ion showed very little dependence on the basicity of the amine.[43] At higher acidities (up to 3·0M perchloric acid) it was shown that, if allowance was made for the medium effect of perchloric acid, then the reacting species was the nitrous acidium ion[45], although the dependence on $[H^+]$ was replaced by one on h_o.

In very high acidities 10·5-12 M sulphuric acid and 8·5-9·5M perchloric acid, aniline, p-toluidine and p-nitroaniline have been shown to be diazotised according to the rate equation[46,47], $V = k[ArNH_3^+][NO^+]\ h_o^{-2}$ and the following mechanism was proposed:

Scheme 2.3

$$ArNH_3^+ + NO^+ \underset{\text{fast}}{\rightleftharpoons} ArNH_2^+\text{-}NO + H^+$$

$$ArNH_2^+NO \xrightarrow[\text{slow}]{} ArNH\text{-}NO + H^+$$

$$ArNH\text{-}NO \xrightarrow{\text{fast}} ArN_2^+$$

(c) Halide-ion catalysed mechanism

(i) Experimental Observations:

In a study on the effects of the anions of strong acids on the diazotisation of aniline and o-chloroaniline, it was observed that chloride, bromide and iodide ions, with increasing effect in that order, all catalysed the reaction, whilst perchlorate and nitrate ions did not exert a similar effect. Thus the halide ions were not participating in a general acid-base catalysis.

(ii) Mechanistic Implications:

The effect of added halide ions on the rate of diazotisation can be described by an additional catalytic term:

$$\text{Halide ion catalysed rate} = k_4^{Hal}[H^+][ArNH_2][HNO_2][Hal^-] \qquad (4)$$

It was also found that the catalytic dependence on the amine concentration decreases progressively from chloride- to bromide- and to iodide-catalysis. With o-chloroaniline the bromide-catalysis under certain conditions became independent of amine concentration and, in the case of the iodide-catalysis, aniline itself gave similar results. Thus the observed kinetics can be expressed by $V = k_3^{Hal}[H^+][HNO_2][Hal^-]$. This represents a nucleophilic substitution by supplied halide ion in the pre-equilibrium nitrous-acidium ion. This process is completely analogous to the scheme for the formation of dinitrogen trioxide:

Scheme 2.4

$$H^+ + HNO_2 \underset{\text{fast}}{\rightleftharpoons} H_2\overset{+}{N}O_2$$

$$Hal^- + NO\text{-}\overset{+}{O}H_2 \underset{\text{slow}}{\rightleftharpoons} Hal\text{-}NO + H_2O$$

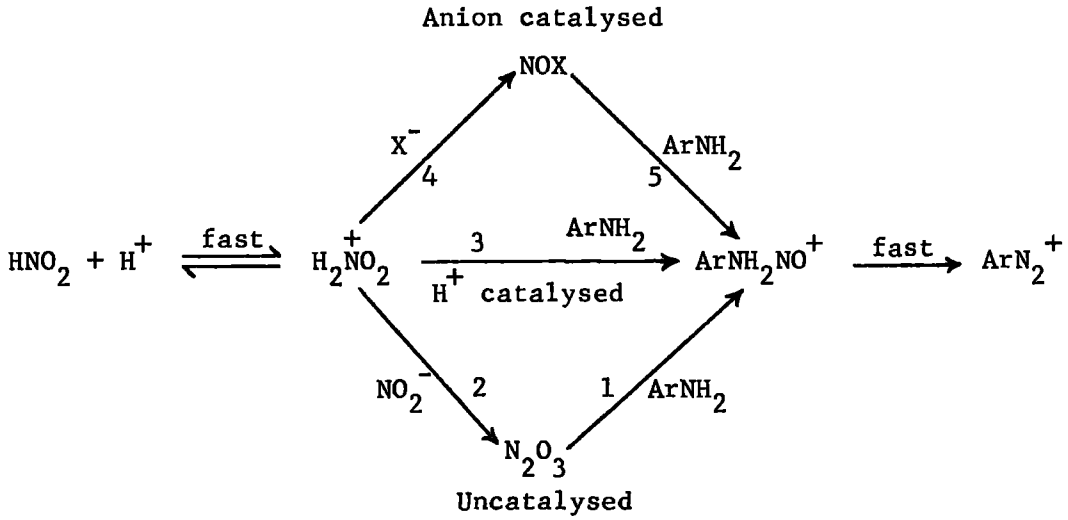
Discussion:

The following carriers have been identified in weakly and moderately acidic ($< \sim 3 \cdot$OM perchloric acid) media

$$H_2\overset{+}{O}NO \qquad NOI \qquad NOBr \qquad NOCl \qquad NO.NO_2$$

The mechanisms by which the effective carriers are formed and act are not independent. The first step in all carriers identified is the formation of the nitrous acidium ion. All possible reaction sequences are shown in Scheme 2.5[44], and only those reactions which are marked fast have not been made rate-controlling.

Scheme 2.5.



The numbers refer to the kinetic equations, as listed earlier.

2.4 Addition of Nitrogen Oxides and NOX compounds to olefins, as electrophilic addition

Many contradictory reports appear in the literature which are easily reconciled in terms of different experimental conditions. This is particularly

the case for the addition of dinitrogen tetroxide to olefins, where it has been recognised recently that using ethers or esters as solvents favours a homolytic addition reaction, whilst using no solvent favours a heterolytic addition reaction.[48] Misconceptions as to the nature of the attacking reagent has also lead to wrong interpretations as shown in the case of addition of dinitrogen trioxide to olefins.[49,50] The addition of nitrogen oxides (N_2O_3, N_2O_4, N_2O_5) under certain conditions is an electrophilic addition, but in ether or ester solution will probably proceed by a free-radical mechanism.

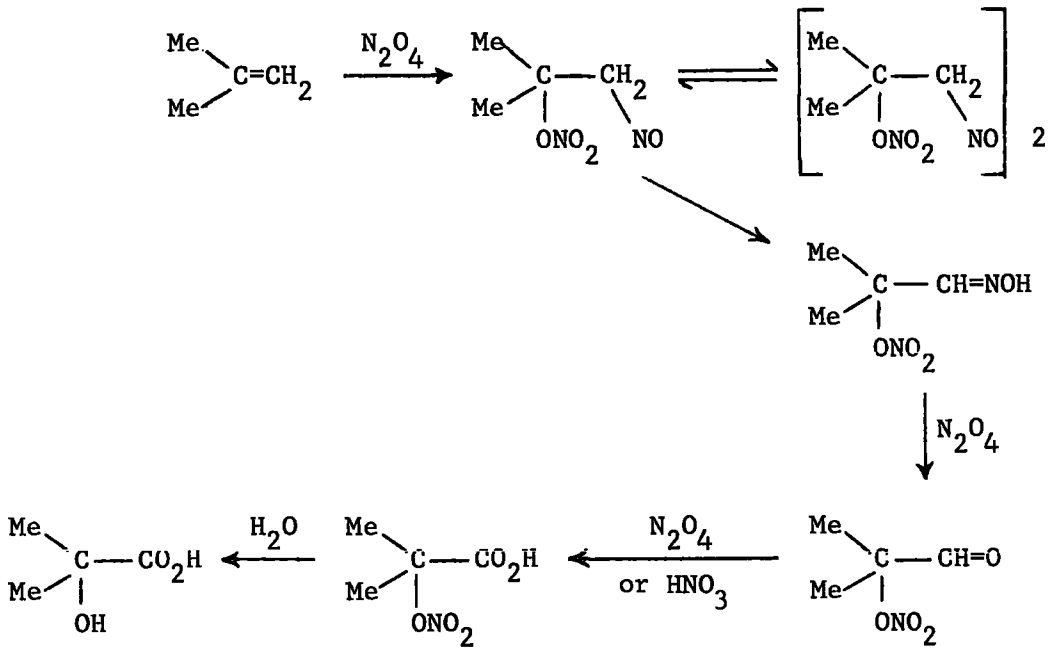
The addition of species NOX (where X^- = Hal^-, HSO_4^- or HCO_2^-) has been shown to obey Markownikoff's rule and to be accelerated by substitution of electron-donating groups on the double bond.[51] These reactions are not subject to the same complications as the addition of nitrogen oxides because of decreased ability to exist as free-radicals.

2.5 Addition of dinitrogen tetroxide to olefins

The products of the reaction of dinitrogen tetroxide with olefins have been shown to be strongly influenced by the manner in which the reaction is carried out. When ethers or esters are used as solvents, Shechter[52,53] has suggested that the reaction proceeds by a free radical mechanism, which leads to primary nitro compounds. Since dinitrogen tetroxide is in equilibrium with the free radical $NO_2^{\cdot}$, this is not surprising. Thus the reaction of both cis- and trans-stilbene with dinitrogen tetroxide yields the same mixture of

products. The lack of dependence of the composition of the products on the isomer attacked led Shechter to postulate a long-lived 2-nitro-1,2-diphenyl ethyl radical. This radical can then react with another $NO_2^{\cdot}$ and produce either a dinitro compound or a nitro-nitrite.

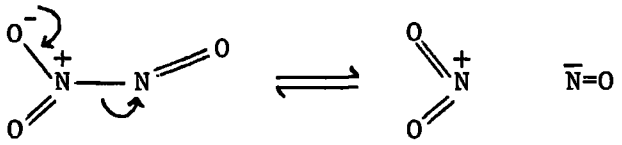
However, in the absence of ether or ester solvents, the products are quite different, and nitro-compounds are not formed. Under these conditions, addition occurs by a heterolytic mechanism with the formation of nitroso nitrates.[54] The orientation of addition has been shown to obey Markownikoff's rule by a hydrolysis procedure in the case of propene[55], and a series of olefins, including 3-chloro-2-methylpropene.[56] The hydrolysis reaction is shown for 2-methylpropene.[48]



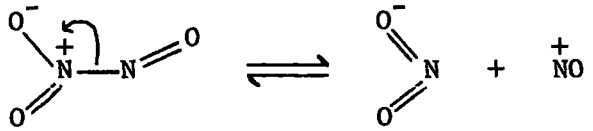
2.6 Addition of dinitrogen trioxide to olefins

The addition reactions of dinitrogen trioxide and nitrous acid have been shown to give the same products.[57,50] The mechanism of addition of dinitrogen trioxide to olefins is subject to the same complexities as the addition of dinitrogen tetroxide. In earlier reports[58] the addition of nitrous fumes to olefins was regarded as addition of dinitrogen trioxide, despite the fact that the composition of the vapour was known to vary considerably as the concentration of the acid was changed.

Another source of error arose in the orientation of heterolysis of dinitrogen trioxide. Ingold[49] inferred that heterolysis would occur as shown:

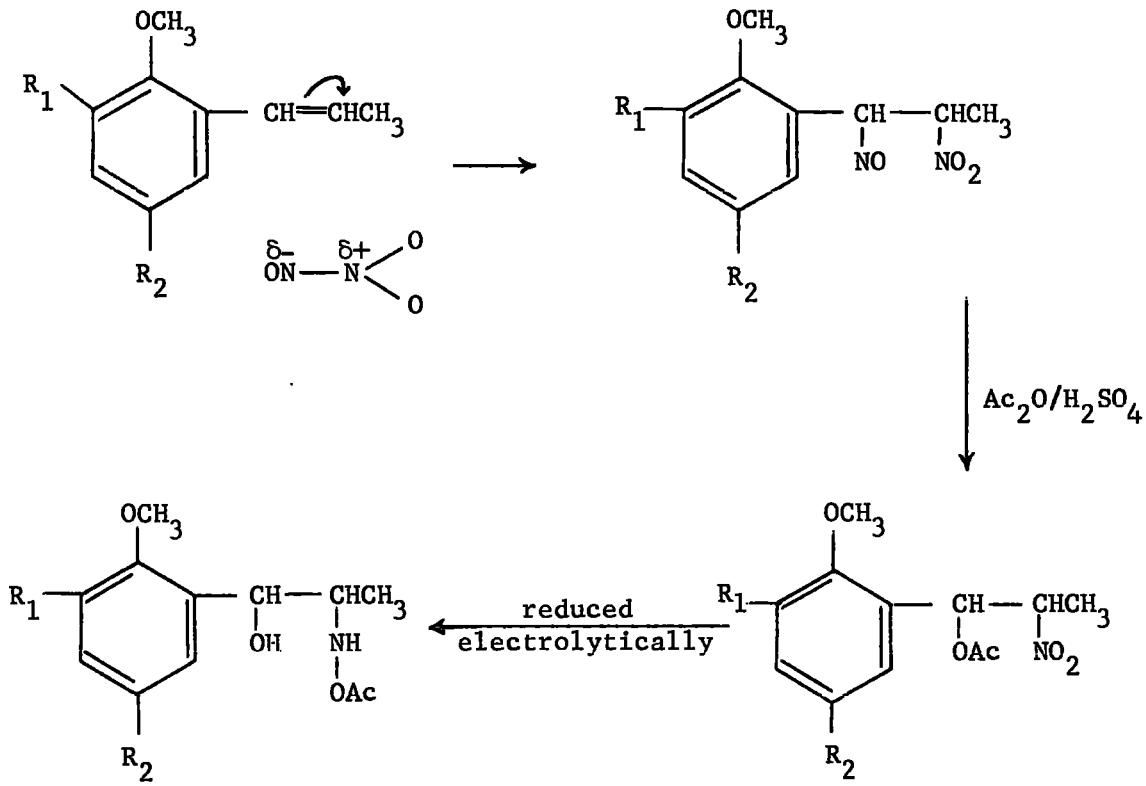


and hence electrophilic attack would occur through the nitronium ion, NO_2^+. The structure has been shown to be of the nitro-nitroso form by ultraviolet, infrared and nuclear magnetic resonance studies[59,60,61], with a weak N-N bond formed by π-π orbital overlap. The charge in the non-bonding molecular orbital of the nitro-nitroso molecule is very largely on the nitro-oxygen atoms[59], whereas in the higher bonding orbital much of the charge is on the nitroso-oxygen, suggesting heterolysis according to:

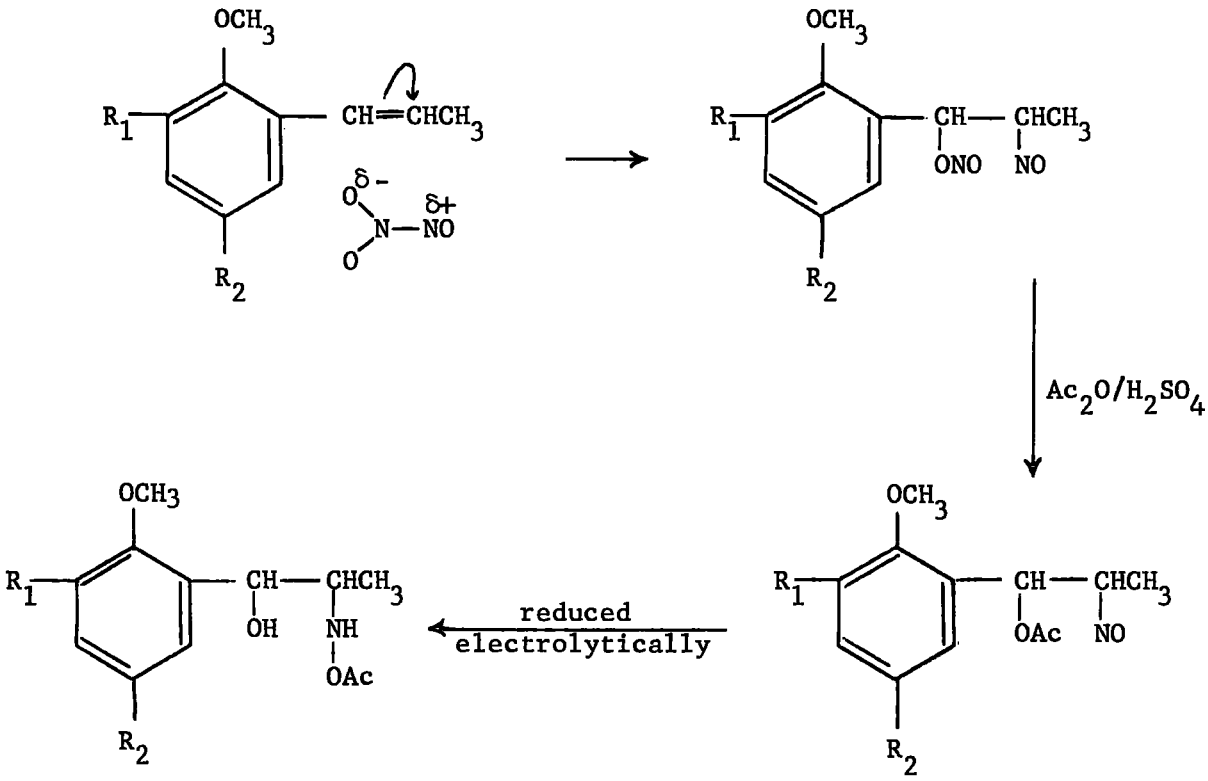


This is in agreement with observations in diazotisation[31] in which the entity NO^+, furnished by a carrier NOX (where X may be NO_2), becomes bound to a nitrogen nucleus in an electrophilic reaction.

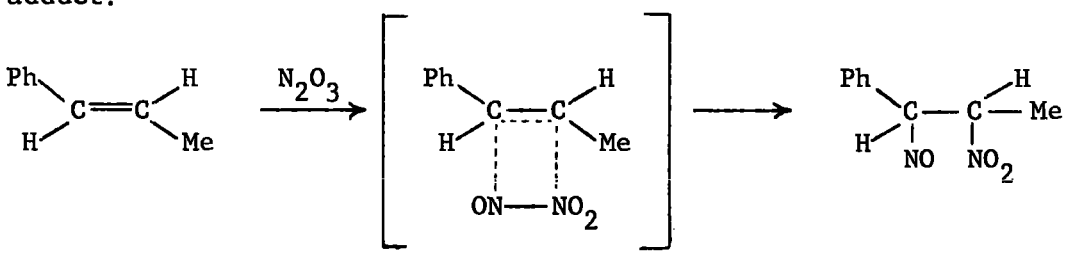
Early work on the addition of dinitrogen trioxide was interpreted in terms of a free radical mechanism or an electrophilic mechanism, in which the erroneous heterolysis was considered.[50] The reaction sequence suggested was:



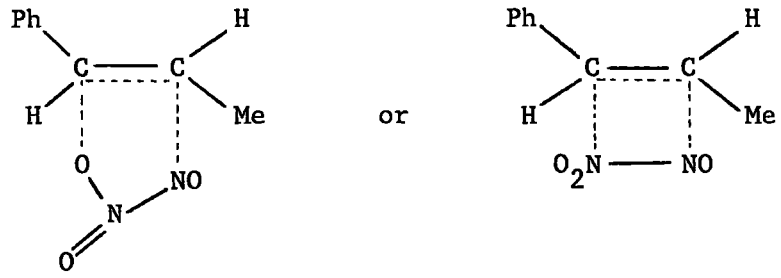
An equally valid representation would be:



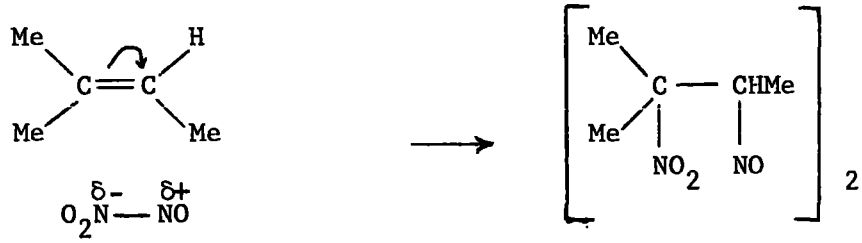
This representation is supported by the report that the addition of dinitrogen trioxide to propenylbenzene involves the formation of a cis-adduct:[62]



Knowing that the heterolysis of dinitrogen trioxide occurs in a different manner, the intermediate could be:



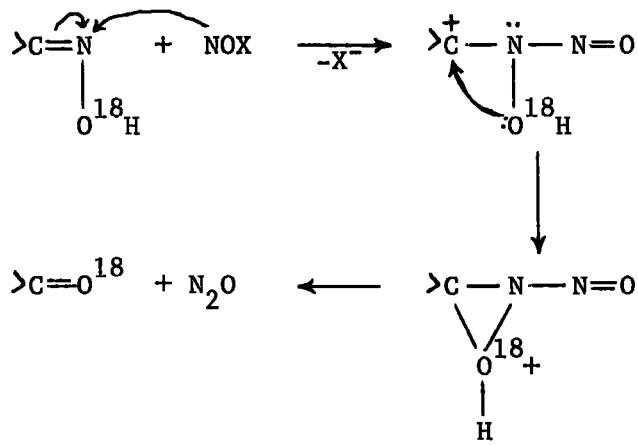
The acetylation reaction as reported must involve replacement of a hyponitrite anion, $N\bar{O}$. This seems unlikely, and in the scheme suggested above, acetylation would involve the replacement of a nitrite ion, NO_2^-, which is known to be easily displaced by water[52] and alcohols.[63] This mode of heterolysis of dinitrogen trioxide also allows explanation of the orientation of addition of dinitrogen trioxide in certain cases which otherwise are difficult to account for, such as:[58]



2.7 Reaction of nitrous acid and oximes

This reaction is analogous to the reactions discussed in the previous section, since it involves attack by an electrophilic nitrogen-containing

species on a π-bond system. Aqueous nitrous acid readily converts oximes into the corresponding carbonyl compounds and nitrous oxide and the mechanism has been elucidated by study using O^{18}-labelling.[64] Reaction of the oxime with O^{18}-labelled nitrous acid yields unlabelled ketone and labelled nitrous oxide, whilst reaction of the labelled oxime with unlabelled nitrous acid gave O^{18}-free nitrous oxide. Thus the oxygen in the oxime becomes the oxygen in the carbonyl compound, and the following mechanism has been proposed to account for the observations:



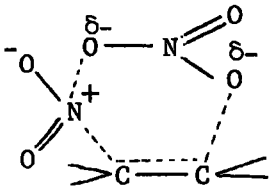
This mechanism is similar to that proposed by Austin[28] except he suggested attack by solvent water on the intermediate.

2.8 Addition of dinitrogen pentoxide to olefins

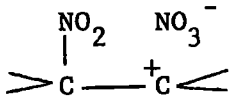
The addition of dinitrogen pentoxide to olefins has been little studied, but it has been shown to obey the Markownikoff rule:[65,66,67]

$$CH_3CH{=}CH_2 \xrightarrow[CH_2Cl_2]{N_2O_5} \begin{matrix} CH_3 \\ \diagdown \\ CH\text{-}CH_2NO_2 \\ \diagup \\ ONO_2 \end{matrix} + \text{substitution products}$$

In the presence of tetraethyl ammonium nitrate the rate of reaction is not altered and there is no change of products. The reaction also yields 1,2-cis-adducts with cis- and trans-2-butene, cyclohexene and cis- and trans-stilbene. Thus the attacking reagent is not the nitronium ion, NO_2^+, but involves a concerted cis-addition of dinitrogen pentoxide:



I



II

Alternatively it has been suggested that the intermediate may be a tight ionic pair (II)[68], which collapses preferentially to the cis-adduct or loses a proton to form substitution products.

2.9 Addition of nitrosyl chloride to olefins

There is an extensive literature on the addition of nitrosyl chloride to olefins[69,70], and an example was reported as early as 1875.[71] The reaction gives 1:1 adducts characterised by their blue colour, but in some cases these form colourless dimers or, if the nitroso group has a labile α-hydrogen,

isomerise to the oxime. Much of the early work is complicated by further reaction of the nitroso chlorides. The possible primary products associated with general additions are summed up in Table 2.3,[72] where each of the products can also possibly exist as a dimer.

Table 2.3.

Type of Olefin	Products	Isomerisation
$R_1R_2C{=}CHR_3$	$R_1R_2CClCH(NO)R_3$	$R_1R_2CClC(=NOH)R_3$
$R_1R_2C{=}CR_3R_4$	$R_1R_2CClC(NO)R_3R_4$	-

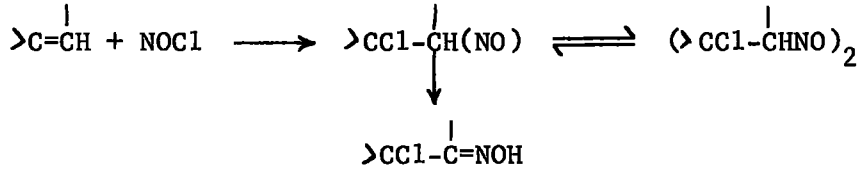
The addition is electrophilic as shown by the increased ease of formation of the nitroso-chlorides on substitution of electron-donating groups on the double bond.[73] It obeys Markownikoff's rule, nitrosyl chloride being known to be polarised in the sense $\overset{\delta+}{O}N\text{—}\overset{\delta-}{Cl}$.[74] This mode of orientation of addition has been observed on many occasions, and a few examples are:

$$Me_2C{=}CH_2 \longrightarrow Me_2CClC{=}NOH \quad [75]$$

$$MeOCH{=}CH_2 \longrightarrow (MeOCHClCH_2NO)_2 \quad [76]$$

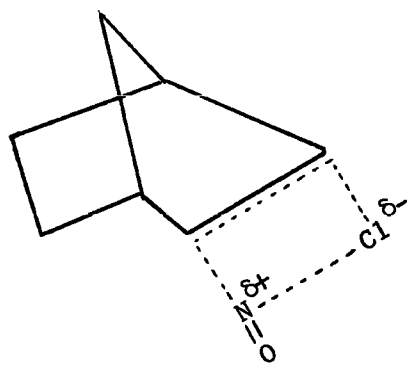
$$Me_2C{=}CHMe \longrightarrow (Me_2CClCH(NO)Me)_2 \quad [77,78]$$

In general terms the reaction can be represented as:



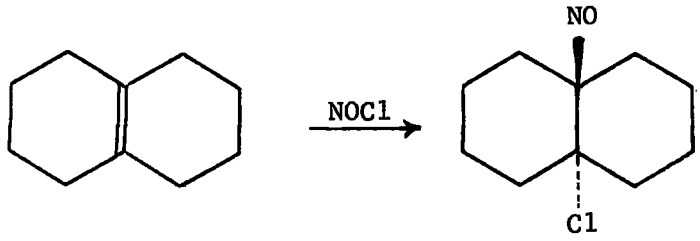
The stereochemistry of nitrosyl chloride addition has not been widely studied and the results obtained present a rather confusing picture. The best understood system is the addition of nitrosyl chloride to bicyclic olefins.[12] It was found that norbornene gave 65% cis-exo adduct (isolated as the dimer) on reaction with nitrosyl chloride, indicating no detectable amounts of rearrangement. Norbornyl carbonium ions tend to rearrange readily[79], and it was concluded that the carbon atoms involved in the addition did not develop much partial positive charge. 2-norbornene-endo-5-carboxylic acid is well known to give lactonic products in electrophilic addition reactions, but less than 10% could have been formed in the addition of nitrosyl chloride.

Thus no appreciable carbonium ion character is developed in the addition of nitrosyl chloride. The prevalence of cis-addition in the addition reactions led Meinwald[12] to postulate a four-centre transition state as has been suggested for the addition of dinitrogen pentoxide and dinitrogen trioxide to olefins:



The preferential addition of nitrosyl chloride to a trans double bond in cis, trans, trans-1,5,9-cyclododecatiene is consistent with a molecular cis-addition, since it is known that trans addition reagents (for example HCl) do not show any selectivity between trans and cis double bonds, whilst cis reagents show preference for a trans double bond (for example OsO_4).[80]

However with Δ^9-octatin[12], nitrosyl chloride forms a trans adduct



Hence the orientation of addition is very dependent on the stereochemistry of the reactant, as has been observed for general electrophilic addition. Also the stereochemistry of addition of nitrosyl chloride is dependent on the solvent used; cyclo-hexene giving cis-addition in liquid sulphur dioxide and trans-addition in chloroform or dichloromethane.[81]

The kinetics of addition of nitrosyl chloride to a range of olefinic compounds have recently been examined by Beier, Hauthal and Pritzkow.[51] They found the rate was first order in both olefin and nitrosyl chloride, that is:

$$\frac{-d[NOCl]}{dt} = k_2[\text{olefin}][NOCl]$$

The relative rates of reaction in chloroform were shown to be consistent with the view that the reaction involves electrophilic attack by $\overset{\delta+}{NO}-\overset{\delta-}{Cl}$, polarised in the sense indicated. Electron-releasing groups (e.g. alkyl groups) accelerated the reaction, whilst electron-withdrawing groups retard the reaction. The effect of structure was similar to that for epoxidation of olefins. Relative rates for the addition of nitrosyl chloride to substituted ethylenes in chloroform increase in the order:

	$RCH=CH_2$	$R_2C=CH_2$	RCH=CHR	$R_2C=CHR$
Relative Rate =	1	20	20-30	> 600

The observed rate constants for the addition in chloroform of nitrosyl chloride to some olefins are shown in Table 2.4.

The effect of solvent on the rate of reaction as measured with cyclohexene is illustrated by the relative rates:

	Et_2O	CCl_4	$n\text{-}C_7H_{16}$	PhCN	$PhNO_2$	$CHCl_3$
Relative Rates =	0·1	0·7	1	7	10	15

The rate tends to increase with polarity of the solvent, but the effect is not as large as for other electrophilic additions. The reaction was very slow in diethyl ether; suggested to be due to interaction of the solvent with NO^+.

2.10 Addition of nitrosyl sulphuric acid to olefins

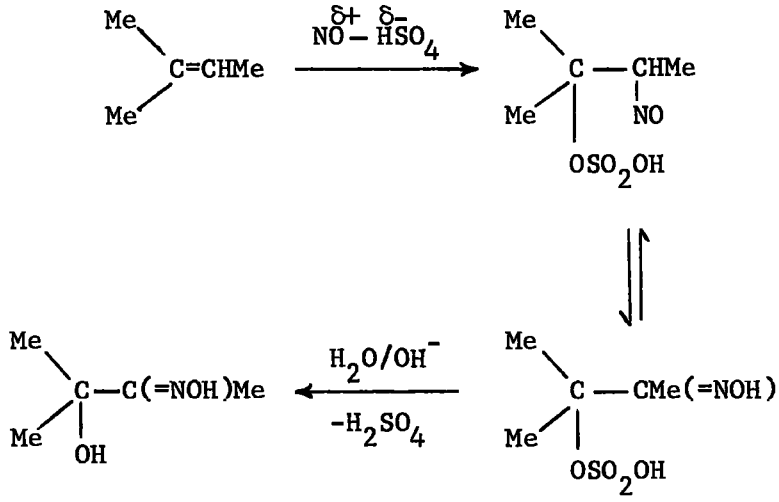
Boller and Whitfield[82] have studied the addition of nitrosyl sulphuric acid across olefinic bonds in liquid sulphur dioxide as solvent. The orientation of addition and acceleration of the reaction by increasing alkyl

Table 2.4

Reaction rates of addition of nitrosyl chloride to olefins in chloroform

Olefin	$k_2 \times 10^4$ (1.mole^{-1}sec^{-1})
3-chloro-2-methylpropene	0·29
1-butene	1·5
1-hexene	1·6
1-octene	1·8
styrene	6·5
1,1-diphenyl ethylene	9·8
2,3-dimethyl-1-butene	20
cyclohexene	29
2-methylpropene	30
2-methyl-1-butene	33
2-methyl-2-butene	>1000
2,3-dimethyl-2-butene	>1000

substitution indicate electrophilic attack by the reagent polarised in the sense $\overset{\delta+}{O}\overset{}{N}-\overset{\delta-}{HSO_4}$. Reaction of 2-methyl-2-butene with nitrosyl sulphuric acid, followed by treatment with aqueous alkali, yielded 3-hydroxy-2-methyl butan-2-one oxime:



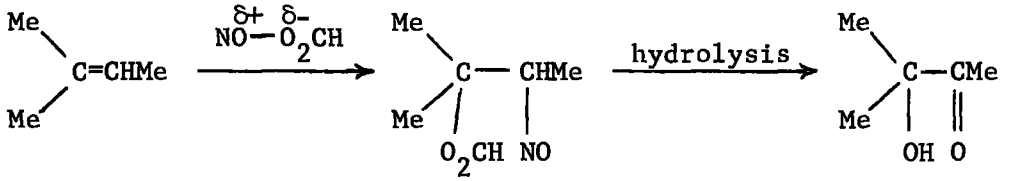
Nitrosyl sulphuric acid does not react with propene but will react with isobutene, hence the authors conclude that two alkyl substituents on the double bond are necessary to make it sufficiently reactive. Thus it seems that nitrosyl sulphuric acid is not as reactive an electrophilic reagent as nitrosyl chloride.

2.11 Addition of nitrosyl formate to olefins

Hamann and Swern[83,84] have reacted nitrosyl formate with many olefins. This reaction is very similar to the addition reaction of nitrosyl chloride with olefins in that the reaction yields monomers and dimers depending upon the structure of the olefin. The addition obeys the Markownikoff rule and is

cis to norbornene and trans to cyclohexene in a polar solvent (formic acid). Also the reaction is accelerated by increased alkyl substitution on the double bond.

The reaction sequence is:



Section 2.

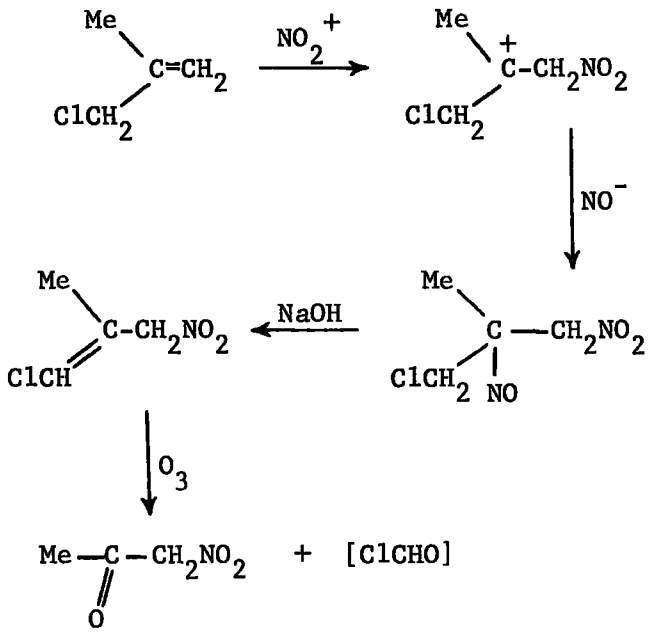
Chapter 3

Products of the addition reaction of nitrous acid and some olefins

3.1 Addition reaction of 3-chloro-2-methylpropene and nitrous acid

3.1.1 Earlier Work

Kooyman, Farenhorst and Werner[85] reacted nitrous acid with 3-chloro-2-methylpropene and obtained a blue oil, which could not be distilled due to decomposition. On reaction with alkali, the blue oil yielded an olefin, which was characterised by ozonolysis and identification of the resultant nitroacetone as its 2,4-dinitrophenylhydrazone. On the basis of this and the then known heterolysis of dinitrogen trioxide, they suggested the following reaction sequence:



Scheme 3.1.

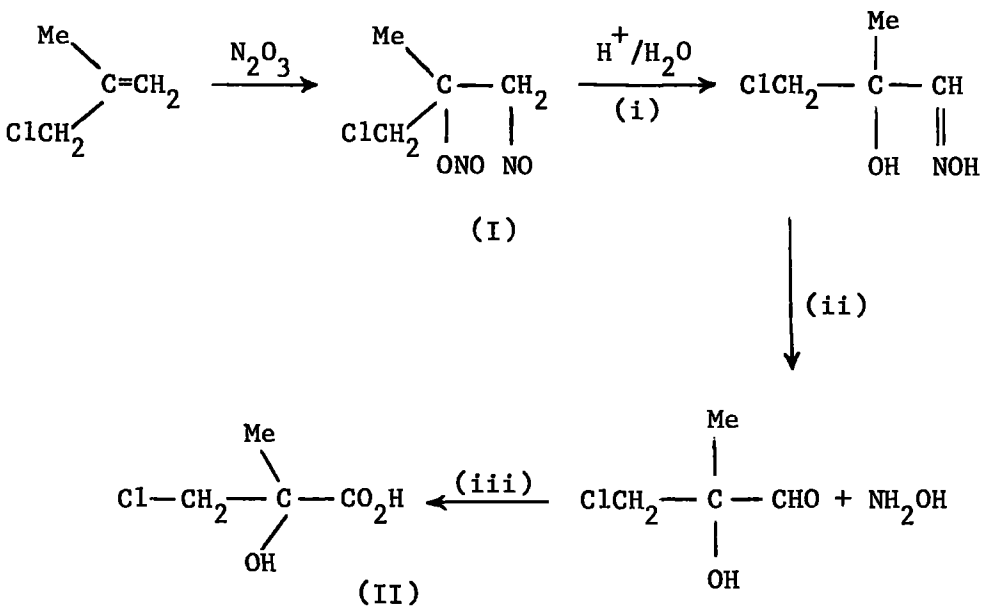
3.1.2 Present Work

The reaction of nitrous acid and 3-chloro-2-methylpropene yielded a blue oil (I), which could be purified by fractional distillation (boiling point 25°C/0·5 mm). The colour of the oil changed to yellow on standing for a prolonged period in the light. The infrared spectrum showed peaks at 2·84, 6·03, 6·09, 6·42, 10·60, 11·16 and 12·00 μ. in addition to those of the olefin. (The infrared spectrum is discussed in more detail in Appendix 1.) There was a weak visible absorption maximum at 665 mμ in carbon tetrachloride solution.

This same blue oil (as shown by identical infrared spectra) was obtained by addition of dinitrogen trioxide to the olefin in the absence of a solvent and also in ether solution, indicating that the elements of dinitrogen trioxide are added to the olefin.

On hydrolysis with 15% sulphuric acid at ca. 65°C for two days, a yellow brown product was obtained, which yielded 3-chloro-2-hydroxy-2-methyl propionic acid (II) on reduced pressure distillation (96°C/1 mm). The identity of II was established by elemental analysis of the acid and its S-benzylthiouronium salt, and was confirmed by preparation of an authentic sample of the acid from methacrylic acid and hypochlorous acid[86], and comparison of physical properties and infrared spectra, and mixed melting points. Also nitrous acid and hydroxylamine were detected in the reaction mixture.

The following Scheme is suggested to account for the experimental observations:



Scheme 3.2.

(i) primary nitroso compounds isomerise easily to oximes.[87]

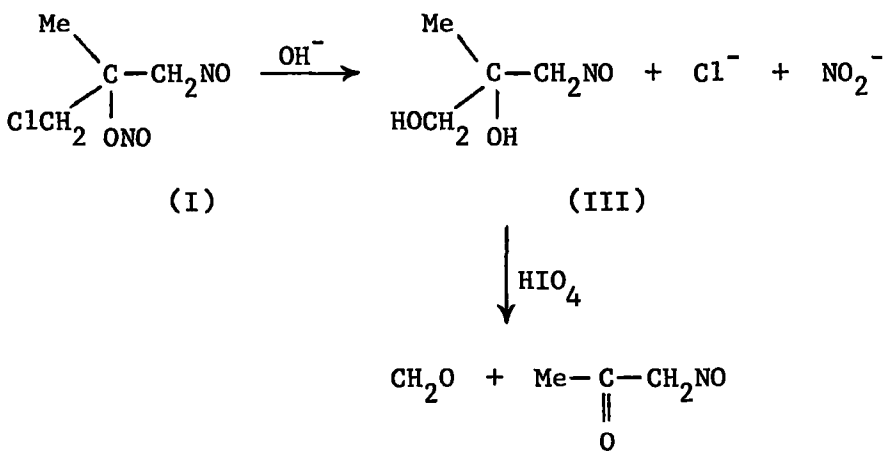
(ii) Oxime hydrolysis produces hydroxylamine.[88]

(iii) α-hydroxyaldehydes are easily oxidised to the corresponding acids.[89]

An analogous hydrolysis procedure has been used to identify the products of addition of dinitrogen tetroxide to a series of olefins.[48] The same product, 3-chloro-2-hydroxy-2-methylpropionic acid (II), was isolated from the reaction of dinitrogen tetroxide and 3-chloro-2-methylpropene.[56] Primary nitro compounds are hydrolysed to carbonyl compounds by acid, but secondary nitro compounds and presumably tertiary nitro compounds do not undergo hydrolysis.[90] Shechter and Ley[57] obtained a nitroso-nitro compound

on addition of nitrous acid to p-nitrostyrene. This compound yielded an α-nitroketone on hydrolysis with concentrated sulphuric acid, which indicates that a nitro group is stable under these conditions.

The blue oil (I) reacted with sodium hydroxide at room temperature to yield III. Quantitative study of the reaction showed that one mole of blue oil (I) reacted with two moles of sodium hydroxide to yield one mole of chloride ion and nitrite ion (not determined quantitatively). One mole of III reacted with one mole of periodic acid. The blue oil (I), however, did not react with periodic acid. Formaldehyde was detected in the reaction of III with periodic acid. Scheme 3.3 represents these observations:



Scheme 3.3.

The reaction of I with sodium hydroxide yielded only III in the cold, but on heating a large quantity of a carbonyl compound was produced, as shown

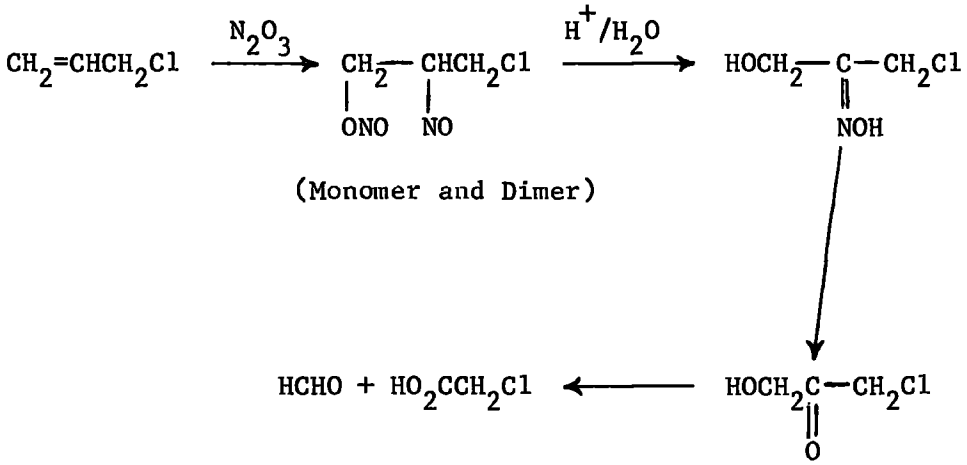
by the appearance of a peak at 5·85 μ in the infrared spectrum.

Refluxing of I in ethanol yielded nitrite ion. The replacement of an organic nitrite group using a general compound ROH (where R is H or alkyl) is well established.[63] Controversy exists in the literature as to whether dinitrogen trioxide (or nitrous acid) produces a nitroso-nitrite or a nitroso-nitro compound.[58] It is sufficient to note here that addition to produce a nitroso-nitrite has been reported[91] and in the analogous addition of dinitrogen tetroxide the formation of a nitroso-nitrate is well established.[48]

3.2 Addition reaction of 3-chloropropene and nitrous acid.

The reaction of 3-chloropropene with nitrous acid or dinitrogen trioxide yielded a white solid (IV) and a green oil (V). The white solid melted to a green oil and had a measured molecular weight of 153·5 (monomer molecular weight is 152·5) in ethyl methyl ketone solution. Similarly,a monomer molecular weight has been observed for the analogous ethylene compound in solution in ethyl methyl ketone.[92] Both IV and V gave chloroacetic acid on hydrolysis in 15% sulphuric acid at ca. 65°C for two days. β-chlorolactic acid, under similar hydrolysis conditions, does not react and can be isolated unchanged from the reaction mixture. Thus both IV and V must be of the 2-nitroso-1-nitrite form, that is with "anti-Markownikoff" orientation of addition, as is mainly the case with the product from the reaction of 3-chloropropene with hypochlorous acid[93] and hypobromous acid.[94] The reaction

sequence is shown in Scheme 3.4.

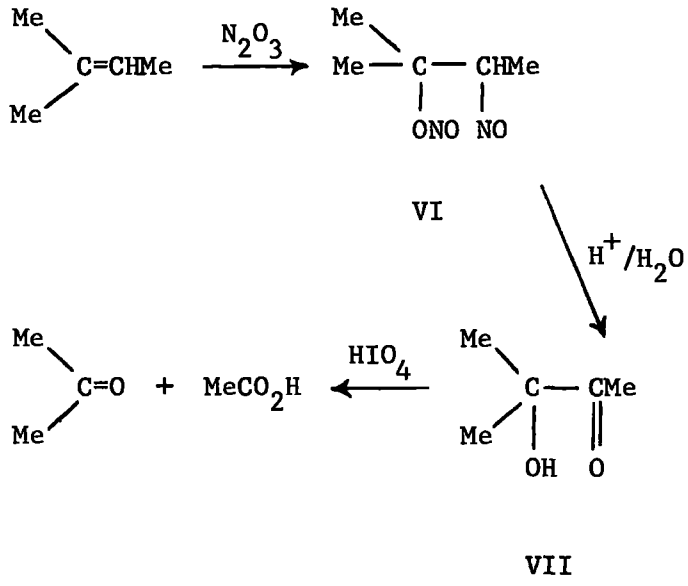


Scheme 3.4.

3.3 Addition reaction of 2-methyl-2-butene and nitrous acid

The reaction of nitrous acid with 2-methyl-2-butene produced a green oil (VI), which was also formed by reaction with dinitrogen trioxide. The products were shown to be identical by comparison of their infrared spectra.

The green oil (VI) did not undergo the isomerisation and hydrolysis reactions that were reported for the corresponding nitroso chloride.[77,78] However, on reaction of the hydrolysis product VII with periodic acid, acetone and acetic acid were detected, as the 2,4-dinitrophenylhydrazone and s-benzylthiouronium salt respectively. This confirmed the constitution of VII as 2-hydroxy-2-methyl-3-butanone. The reaction sequence is presented in Scheme 3.5.



Scheme 3.5.

3.4 Addition reaction of other olefins and liquid dinitrogen trioxide

Liquid dinitrogen trioxide was added to a number of olefins. 3-Hydroxy-2-methylpropene and 2,4,4-trimethyl-2-pentene yielded intensely coloured liquid products, whilst 2,3-dimethyl-2-butene, 2-methylpropene and propene yielded a white solid in addition to an intensely coloured liquid product. Elemental analysis of the solid product from 2-methylpropene and propene were consistent with their classification as nitroso-nitrites. The infrared spectra and mass spectra of all the products were also consistent with those of nitroso-nitrites.

3.5 Nature of the Solid Addition Products

The solid addition products of 3-chloropropene, 2-methylpropene and propene melted to an oil. When dinitrogen trioxide was added to 2-methylpropene, two products were formed. They were separated by filtration and a white solid and a green liquid obtained. On standing, solid settled out of the green oil. This could have been caused by some solid dissolving in the liquid but, even when subject to repeated filtration, solid settled out of the liquid. The same phenomenon was observed for the addition compounds of propene. Thus it appears that the solid was forming continuously from the liquid product.

In general the solid addition products were insoluble in most organic solvents. The solid product from the addition of nitrous acid to 3-chloropropene (IV) was soluble only in ketonic solvents of the common organic solvents. It dissolved in ethyl methyl ketone to give a green solution, and the molecular weight in this solvent, determined with a vapour pressure osmometer, was that of the monomer. Preliminary measurements of the molecular weight of the solid addition compounds of 2-methylpropene and 2,3-dimethyl-2-butene in benzene indicated that the compounds were present as the monomer, which is also suggested by the blue colour of the solution. The monomer molecular weight has been observed for the dimer of the addition product of dinitrogen trioxide and ethylene in solution in ethyl methyl ketone.[92]

The solid products obtained are most likely dimeric nitroso-nitrites and not position isomers, since in the addition of nitrous acid to 3-chloropropene, the ratio of the quantity of green oil (V) to the quantity of white solid (IV) varied from 2·67 to 1·38. If IV and V are position isomers then the ratio of the quantity of the two products would be expected to remain approximately constant.

Production of monomer from dimer on dissolution or heating has been observed many times[95] and forms an essential preliminary to most reactions of dimeric nitroso compounds. Thus, the rate determining step of the isomerisation of secondary dimeric nitroso compounds to oximes in dilute hydrochloric acid is the dissociation to the monomeric nitroso compound.[96]

The observed behaviour of the addition products of the reaction of nitrous acid with some olefins is summarised in Table 3.1.

Nitroso compounds can exist as dimers and the isomeric oximes[95], but isomerisation to the oxime can only occur if the nitroso group is adjacent to an α-hydrogen atom and is accelerated by the presence of hydroxylic solvents.[97] In general[98], solutions of tertiary nitroso compounds are blue, owing to considerable dissociation, whereas solutions of primary and secondary nitroso compounds are colourless because they exist mainly in the dimeric form.

The behaviour observed for the solid addition compounds is typical of dimeric nitroso compounds. Further study of these compounds by ultraviolet absorption techniques is inapplicable since the dimer dissociates on

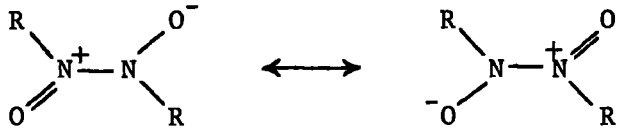
Table 3.1.

Olefin	Product	Result
$ClCH_2C(Me)=CH_2$	$ClCH_2C(Me)(ONO)-CH_2NO$	Monomer only
$HOCH_2C(Me)=CH_2$ *	$HOCH_2C(Me)(ONO)-CH_2NO$	Monomer only
$Me_2C=CHMe$	$Me_2C(ONO)-CHMe-NO$	Monomer only
$ClCH_2CH=CH_2$	$(ClCH_2CH(NO)-CH_2ONO)_n$ n = 1 or 2	Monomer and dimer; dimer gives monomer on dissolution and heating.
$Me_2C=CH_2$ *	$(Me_2C(ONO)-CH_2NO)_n$ n = 1 or 2	Monomer and dimer; dimer gives monomer on dissolution and heating.
$MeCH=CH_2$ *	$(MeCH(ONO)-CH_2NO)_2$ n = 1 or 2	Monomer and dimer; dimer gives monomer on dissolution and heating.

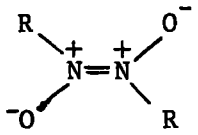
* Structure of products not completely confirmed, but strongly supported by experimental evidence and by analogy with earlier reactions and reactions of these olefins with dinitrogen tetroxide.[48,56]

dissolution in an organic solvent. Also mass spectral studies are not suitable since it is more than likely that the dimer dissociates at the temperature of the ionisation chamber, as observed for dimeric nitroso methane.[99]

An X-ray crystallographic study has been carried out on the trans dimer of 2-nitro-nitrosoethane.[92] This dimer has N-N 1·304 Å, N-O 1·262 Å, C-N 1·47 Å. The short N-N bond length (compare N-N in hydrazine of 1·41 Å) indicates significant double bond character. Thus canonical structures of the type VIIIa and VIIIb do not adequately account for the experimental observations, since the N-N bond length would then be very similar to the typical N-N single bond length in hydrazine. Van Merssche and Leroy[100] have estimated by molecular orbital methods that VIIIa, VIIIb and VIIIc contribute 24, 24 and 53% respectively.



VIIIa VIIIb



VIIIc

Luttke[101,102] found that there were two different patterns exhibited in the infrared spectra of dimeric nitroso compounds, which was in confirmation of ultraviolet absorption observations. He showed that these could only be ascribed to cis-trans isomerisation. The characteristic NO wavelengths in $(RNO)_2$ are presented in Table 3.2.[95] A comparison of the infrared spectra of the solid and corresponding liquid products of the addition reactions allowed the assignment of the typical peaks of the dimeric compounds. These are shown in Table 3.3. Comparison of these typical peaks with those of cis and trans dimers in Table 3.2 indicates that these compounds have infrared spectra which are consistent with those of trans dimers.

Table 3.2.

R	Trans-dimer	Cis-dimer
Aliphatic	Single band between 8·50 and 7·75 μ.	Double band between 7·56 and 7·46 μ, and 7·52 and 7·04 μ.
Aromatic	Single band between 7·98 and 7·70 μ.	Double band between 7·20 and 7·16 μ, and 7·10 μ.
and the aliphatic C-N stretch in the region 9·26 to 9·62 μ.		

Table 3.3.

Addition Compound	Typical Peaks
$\left(\begin{array}{l} ClCH_2CH\text{—}CH_2 \\ \quad\ \ NO \quad\ ONO \end{array}\right)_2$	8·49 and 9·68 μ .
$\left(\begin{array}{l} Me_2C\text{—}CH_2 \\ \ ONO\ NO \end{array}\right)_2$ ✱	8·49 and 9·70 μ .
$\left(\begin{array}{l} MeCH\text{—}CH_2 \\ \ ONO\ \ NO \end{array}\right)_2$ ✱	8·59 and 9·51 μ .

✱ as in Table 3.1.

Chapter 4.

Experimental techniques for the reaction of nitrous acid and some olefins (Chapter 3).

4.1 Reaction of 3-chloro-2-methylpropene with nitrous acid

To sulphuric acid (50 ml., s.g. 1·84) in water (200 ml.) in a three-necked flask was added 3-chloro-2-methylpropene (90 ml.). A solution of sodium nitrite (165 gm. sodium nitrite in 220 ml. water) was introduced slowly from a dropping funnel, whilst the temperature was maintained below 5°C throughout the addition. The blue oil formed almost immediately and, since it was denser than water, could be separated quite easily.

Excess sodium nitrite was always used, but to remove excess olefin the blue oil was pumped on the rotary evaporator for some time. The blue oil was dried overnight ($MgSO_4$) and was stored in the refrigerator, since it changed colour in the light. Vapour phase and column chromatography could not be used as a method of purification.

Ether extraction of the aqueous layer, saturated with sodium sulphate, followed by drying ($MgSO_4$) and removal of the ether by distillation, yielded the blue oil, if the extraction was performed immediately after the reaction was completed. If some time elapsed before extraction, then a yellow-brown oil was obtained.

The blue oil (I) distilled at 25°C/0·5 mm., and the residue, a more viscous green oil, distilled at 40°C/0·5 mm.

The infrared spectrum (contact film) of the blue oil (Spectrum No.1 in Appendix 1) showed the following peaks in addition to those of the olefin; 6·09, 6·42, 7·54, 10·59, 11·18, 12·00 μ. The mass spectrum showed a high

mass peak at M90/92 ($P\text{-}N_2O_3$) and a base peak at M30 (NO^+).

The blue oil had the following elemental analysis: C,34·6%; H,4·5%; Cl,22·0% (expected for nitroso-nitrite; C,28·8%; H,4·2%; Cl,21·3%).

The visible absorption spectrum of the blue oil in carbon tetrachloride solution was recorded on a Unicam SP800. There was a visible absorption maximum at 665 mμ.

4.2 Hydrolysis of addition compound of nitrous acid and 3-chloro-2-methyl-propene (I).

A solution of sulphuric acid (50 ml. concentrated sulphuric acid in 300 ml. water) was added to the blue oil (10 gm.). The reaction mixture was kept at ca.65°C for two days. The solution was ether extracted and the ether removed by distillation. This yielded a yellow-brown oil, the infrared spectrum of which showed peaks appearing at 5·85 and 9·0 μ and disappearing at 6·09 and 6·42 μ. The product was distilled under reduced pressure and yielded a liquid distilling at 56°C/0·1 cm. (which was unreacted starting material) and a white solid distilling as a liquid at 96°C/0·1 cm. This solid was recrystallised from benzene. It was soluble in organic solvents and gave an acidic solution in water. The melting point was 106°C (Literature[103] 106-7°C). The infrared spectrum is Spectrum No.5 in Appendix 1. Elemental analysis: C,34·4%; H,4·7%; Cl,26·2%; (calculated: C,34·7%; H,5·05%; Cl,25·6%).

In order to determine the best experimental conditions for the hydrolysis reaction, three hydrolyses were performed under different experimental

conditions. Identical solutions were prepared in each instance, but experimental conditions were changed as shown:

Reaction	Temperature	Time
(1)	Room Temperature	36 hours
(2)	Room Temperature	48 hours
(3)	ca.65°C	24 hours

The amount of hydrolysis was assessed, after isolation by ether extraction, by comparison of infrared spectra with particular reference to the peak at 5·85 μ. Reactions (1) and (2) produced very little acid whilst (3) produced a large quantity. Thus, to effect hydrolysis in a reasonable time, the reaction must be performed at ca.65°C.

4.3 Preparation of the S-benzylthiouronium salt of a carboxylic acid[104a]

The acid (0·25 gm.) was dissolved in warm water (5 ml.) a drop or two of phenolphthalein added, and the solution neutralised with sodium hydroxide solution. 2-3 drops of 0·1N hydrochloric acid were added to ensure that the solution was very slightly acidic. A solution containing S-benzyl-iso-thiouronium chloride (1 gm.) in water (5 ml.) was introduced, and the solution cooled in ice until precipitation was complete. The crystalline product was recrystallised from aqueous alcohol. The derivative melted at 146°C. Elemental Analysis: C,46·4%; H,5·2%; Cl,19·2%. (Calculated: C,47·3%; H,5·6%; Cl,11·7%).

4.4 Preparation of 3-chloro-2-hydroxy-2-methylpropionic acid by addition of hypochlorous acid to methacrylic acid

4.4.(a) Preparation of methacrylic acid from methylmethacrylate

Alkaline or acidic hydrolysis under reflux was ineffective since it yielded polymeric material. Hydrolysis was carried out by stirring with sodium hydroxide (20%) at room temperature for 24 hours.[105] Methacrylic acid was isolated by ether extraction from acidic solution.

4.4.(b) Addition of hypochlorous acid to methacrylic acid[86]

Chlorine was bubbled through water and the solution was shaken with freshly precipitated yellow mercuric oxide[106] (dissolved in concentrated nitric acid and re-precipitated by adding sodium hydroxide) for an hour. The solution was then rapidly distilled under reduced pressure at 30-35°C.

Methacrylic acid (7 gm.) was dissolved in water. 60% perchloric acid (10 ml.) and hypochlorous acid (300 ml., ca.0·35N) were added and the bulk diluted to ca.900 ml. with water. The mixture was shaken and left to react overnight. The aqueous solution was extracted with ether, the extracts dried ($MgSO_4$) and the ether removed by distillation, yielding a viscous white liquid. This product was recrystallised from petroleum ether (40/60) and then from benzene, giving white needle-shaped crystals (melting point, 106°C). Elemental analysis: C,34·6%; H,4·83%; Cl,26·1%. The mixed melting point with the acid produced in the hydrolysis of the blue oil was 105-6°C.

The S-benzylthiouronium salt was prepared as described in the previous

section (melting point, 146°C). A mixed melting point with the sample prepared before showed no depression. Elemental analysis: C,44·7%; H,5·04%; Cl,18·0%.

The infrared spectrum of the acid was recorded and was identical with that of the acid isolated before (Spectrum No.5 in Appendix 1). No molecular ion peak was present in the mass spectrum at 70eV. The highest mass peak was at M93/95 ($P-CHO_2$) and the base peak was M43 (C_2H_3O). Other peaks were M89 ($P-CH_2Cl$), M77/79 ($P-CHO_3$), M57($P-CH_2O_2Cl$), M41 ($P-CH_2O_3Cl$) and M28 ($P-C_2H_3O_3Cl$). At 16eV the highest mass peak also became the base peak.

4.5 Detection and Determination of Hydroxylamine and detection of nitrous acid

In the hydrolysis of the addition compound of 3-chloro-2-methylpropene (I) with sulphuric acid, a scheme has been proposed which explains the formation of 3-chloro-2-hydroxy-2-methylpropionic acid, which has been isolated from the reaction mixture. In further support of this scheme it was necessary to show the presence of hydroxylamine and nitrous acid.

4.5.(a) Detection of hydroxylamine

The aqueous layer from a hydrolysis reaction of the addition compound of 3-chloro-2-methylpropene(I) was tested in the following ways.

(1) To a small sample of neutralised aqueous layer was added a few drops of neutral ferric chloride solution. The reddish-brown colour formed indicates the presence of an oxime or hydroxylamine.[107]

(2) A sample of the aqueous layer was neutralised with sodium hydroxide. To this solution was added aqueous picric acid (a saturated solution) and 1% sodium hydroxide solution. An orange-red colour was produced which indicates the presence of hydroxylamine.[108]

4.5.(b) Quantitative Determination of Hydroxylamine

For the quantitative determination the following hydrolysis procedure was carried out.

The addition compound (I) (0·5315 gm.) in dioxan/water (35 ml.) and concentrated sulphuric acid (5 ml.) was stirred for six days. When reaction was complete the solution was made up to 50 ml.

(1) To 5 ml. of the hydrolysis solution was added an aqueous picric acid solution and 1% sodium hydroxide solution. The whole was made up to 10 ml. The optical density was measured in the region 570-590 mμ. The concentration of hydroxylamine present was $2{\cdot}02 \times 10^{-2}$M. Thus there were 0·034 gm. hydroxylamine in the original solution. This has to be compared with the theoretical quantity of 0·1054 gm. hydroxylamine.

(2) The hydroxylamine was also determined by back-titration of excess standard potassium bromate solution.[109] Thus to 5 ml. of hydrolysis solution was added 5 ml. of potassium bromate solution (0·5039N) and dilute sulphuric acid. The solution was allowed to stand for 15 minutes and then titrated with standardised sodium thiosulphate solution (0·0984N), after adding excess potassium iodide. The titre was 21·75 ml., which indicates that the solution was 0·0126M in hydroxylamine and the hydrolysis solution

contained 0·0208 gm. hydroxylamine (theoretical quantity was 0·1054 gm.).

The accuracy of the method was tested by using a standard hydroxylamine solution. To the hydroxylamine solution (5 ml., ca.0·07M) was added potassium bromate solution (10 ml., ca.0·5N) and dilute sulphuric acid. The solution was allowed to stand for 15 minutes and then excess potassium iodide added. This was titrated with sodium thiosulphate solution (ca. 0·1N). The calculated weight of hydroxylamine from titration agreed within 1% with the weighed amount.

The agreement of the two methods of estimation of hydroxylamine is not very good, but they indicate that the hydrolysis reaction does not proceed to completion in this case. However, no heating was used, and it has subsequently been observed that heating is required for the hydrolysis reaction to proceed to completion.

4.5.(c) Detection of Nitrous Acid

Nitrous acid was shown to be present in the reaction solution using the Greiss method (described more fully in a later chapter).

4.6 Reaction of blue oil (I) with Sodium Hydroxide

4.6.(a) Detection of Chloride and Nitrite Ions

The blue oil (13·8 gm.) was added to sodium hydroxide (ca.200 ml., 0·01N) and the mixture stirred. No product was obtained on ether extraction from alkaline solution but a brown viscous liquid (III) was obtained on ether extraction from acidic solution.

To the aqueous layer was added a few drops of silver nitrate solution, and a white precipitate was formed immediately, indicating the presence of chloride ion in the solution.

The aqueous layer was also tested with the Greiss reagent and nitrite ion was shown to be present in the solution.

4.6(b) Quantitative Reaction of the blue oil (I) with Sodium Hydroxide

The blue oil (1·142 gm.) in dioxan/water as solvent was added to sodium hydroxide (30 ml., 0·50N) and the solution made up to 100 ml. with dioxan/water. The reaction was followed by acid-base titration with hydrochloric acid (0·108N). After 24 hours the titre remained unchanged and was 5 ml. hydroxide solution ≡ 0·48 ml. of 0·108N hydrochloric acid. Thus 0·0140 moles hydroxide have reacted with 0·0069 moles of blue oil, (that is 2 $\pm$ 0·05 moles hydroxide ion reacted with 1 mole of blue oil). The amount of chloride ion produced in the reaction was estimated gravimetrically. To the solution (10 ml.) was added silver nitrate solution (ca.10 ml., ca.0·1N). The solution was filtered through a previously washed, dried and weighed sintered filter funnel. The precipitate and funnel were dried to constant weight. $8{\cdot}2 \times 10^{-4}$ moles chloride ion were produced by $6{\cdot}9 \times 10^{-4}$ moles blue oil (that is 1 mole blue oil produces 1 $\pm$ 0·2 moles chloride ion). The large error is explained by the occlusion of organic material on the surface of the precipitated silver chloride, which was shown by the precipitate turning black immediately.

Thus, within experimental error; 1 mole I reacts with 2 moles hydroxide ion to produce 1 mole chloride ion and nitrite ion (not determined quantitatively).

4.6.(c) Conditions for the reaction of I with Sodium Hydroxide

I was reacted with sodium hydroxide solution and the mixture stirred at room temperature. The solution was ether extracted and the infrared spectrum was recorded. This indicated that no carboxylic acid had been formed.

The reaction was repeated but with heating. The product, obtained on ether extraction, displayed a large peak at 5·85 μ in its infrared spectrum. Thus reaction of I with sodium hydroxide produced a carboxylic acid only when heated.

4.7 Reaction of III with Periodic Acid

4.7.(a) Qualitative Reaction of III with Periodic Acid

III was reacted with periodic acid in dioxan/water and one drop of concentrated nitric acid was introduced. Silver nitrate solution was added and a white precipitate formed. This precipitate was silver iodate and indicates that the periodate anion has been reduced to iodate.[104b] This is indicative of the presence of an α-glycol or an α-hydroxy carbonyl compound.

4.7.(b) Quantitative Reaction of III with Periodic Acid

III (0·9809 gm.) was reacted with periodic acid (120 ml., 0·1N). The

reaction was followed by titration of 10 ml. aliquots with standardised sodium thiosulphate (0·1N) in the presence of excess potassium iodide. The final titre was 6·2 ml. of 0·1N sodium thiosulphate. Thus the amount of periodic acid present in the total volume of 120 ml. was $37{\cdot}2 \times 10^{-4}$ moles.

Both periodate and iodate react, in the presence of excess potassium iodide, to produce iodine.[110] With a moles of periodic acid:

$$aIO_4^- + 7aI^- + 8aH^+ \longrightarrow 4aI_2$$

however, after reaction with III, x moles of periodate has been reduced to iodate, and hence:

$$(a - x)IO_4^- + 7(a - x)I^- + 8(a - x)H^+ \longrightarrow 4(a - x)I_2$$

$$xIO_3^- + 5xI^- + 6xH^+ \longrightarrow 3xI_2$$

Thus the difference in the amount of iodine produced (given by titration with sodium thiosulphate) before and after reaction with III is:

$$4a-[4(a - x) + 3x] = x \text{ moles}$$

120×10^{-4} moles periodic acid were present initially and $37{\cdot}2 \times 10^{-4}$ moles were present after reaction, hence $82{\cdot}8 \times 10^{-4}$ moles periodic acid have reacted with $82{\cdot}4 \times 10^{-4}$ moles of III. Thus 1 mole III reacted with 1 mole of periodic acid, which indicates the presence of an α-glycol or an α-hydroxy acid.

I (1 gm.) was added to periodic acid (20 ml., 0·1N). After reaction the titre was 20 ml. of sodium thiosulphate. Thus I does not react with periodic acid.

4.8 Detection and Determination of Formaldehyde

4.8.(a) Detection of Formaldehyde

III was reacted with periodic acid. To the solution was added concentrated sulphuric acid (ca. 2 ml.) and a solution of the disodium salt of 4,5-dihydroxynaphthalene-2,7-disulphonic acid (chromotropic acid) (ca. 0·05%) in concentrated sulphuric acid. The purple colour formed indicates the presence of formaldehyde.[111,112]

4.8.(b) Quantitative Determination of Formaldehyde

To III (0·00962 gm.) was added sodium paraperiodate solution (2 ml., ca.0·3M) in dilute sulphuric acid. The mixture was diluted with water and left overnight in a stoppered flask in the dark. Sodium bisulphite solution (4 ml., s.g. 1·3) was added with shaking to destroy excess periodate.[113] A solution of chromotropic acid (10 ml., ca.0·1N) was added, followed by concentrated sulphuric acid (225 ml.) and the whole bulk diluted to 500 ml. The optical density was measured at 570 mμ The method was calibrated by reacting glucose with periodic acid under identical conditions and treating the resultant solution in an analogous way. The extinction coefficient was $2{\cdot}14 \times 10^{5}$ moles^{-1} litre cm^{-1}. The concentration of formaldehyde was determined as $2{\cdot}10 \times 10^{-5}$ moles. $8{\cdot}10 \times 10^{-5}$ moles of III were used. Hence formaldehyde was not produced quantitatively. This phenomenon has been observed quite widely in the analogous reaction of periodic acid with sugars.[113]

4.9 Mass Spectrum of III

The base peak occurred at M44 (CH_2NO). A molecular ion peak appeared at M119 (30%). Intense peaks occurred at M89 (P-NO; 66%) and M30 (NO^+; 66%). Other peaks appeared at M101 ($P-H_2O$), M84 ($P-H_3O_2$), M74 ($P-CH_3NO$), M59 ($P-C_2H_6NO$), M53 ($P-H_4NO_3$), M40 ($P-CH_5NO_3$) and M27 ($P-C_2H_6NO_3$).

4.10 Reaction of Nitrous Acid with 3-chloropropene

The reaction was carried out as for 3-chloro-2-methylpropene. The reaction produced a white solid IV, insoluble in water, and a green oil V, which was miscible with water in the large volumes used. The solid was separated by filtration and then washed with ether. The oil was extracted with ether, the extracts dried ($MgSO_4$) and then the ether removed by distillation.

The white solid (IV) melted to a green oil at 96°C. The molecular weight, determined with a vapour pressure osmometer in ethyl methyl ketone, was found to be 153·5 (the monomer molecular weight is 152·5). Elemental analysis: solid; C,23·7%; H,3·3%; Cl,23·3%; N,20·6%: liquid; C,27·4%; H,3·8%; Cl,21·4%. (Calculated: C,23·6%; H,3·3%; Cl,23·3%; N,18·4%).

The mass spectrum showed no molecular-ion peak. The base peak was M30 (NO^+) and the most intense peak was M75/77 ($P-N_2O_3$).

The infrared spectrum of V showed typical peaks at 6·09 and 6·42 μ (Spectrum No.3 in Appendix 1). The infrared spectrum of IV had a typical peak at 6·44 μ (Spectrum No.2 in Appendix 1).

In a series of identical reactions of nitrous acid and 3-chloropropene, the ratio of the weights of green oil and white solid were determined as 2·67, 2·21 and 1·38.

One addition reaction was carried out in an aqueous solution saturated with sodium chloride and using hydrochloric acid in the place of sulphuric acid. The reaction yielded the same white solid and green oil.

4.11 Hydrolysis of addition compounds IV and V

The hydrolyses were carried out as described earlier. The acid was separated by recrystallisation from 40/60 petroleum ether. It was confirmed to be chloroacetic acid in both cases by comparison of infrared spectra [Spectrum No.6] and melting point with those of an authentic sample. The melting point was 64°C (Literature value 63°C). Mixed melting point with an authentic sample showed no depression.

In the hydrolysis reaction of both IV and V, formaldehyde could not be detected either in the reaction solution or by attempting to carry the formaldehyde away in a stream of nitrogen gas and then forming a 2,4-dinitrophenylhydrazone or dimedone derivative.

4.12 Preparation of β-chlorolactic Acid.[114]

To cold nitric acid (70% W/W; 88 ml.) in a one litre round-bottomed three-necked flask, surrounded by an ice bath, was added glycerol-α-monochlorohydrin (16·7 ml., 22·1 gm.) from a dropping funnel over a period of ten minutes. The flask was placed in a boiling water-bath until the liquid

and air-space above it assumed a reddish-brown colour. This marked the beginning of a very vigorous reaction and the water bath was removed to allow the reaction to proceed spontaneously. After about ten minutes the reaction subsided and the flask was returned to the boiling water bath for thirty minutes. The reaction mixture was cooled rapidly and transferred to a flask on the rotary evaporator which was left in a bath at lower than 55°C for three hours. The residue was dissolved in water (74 ml.) and the solution brought to pH 6·0-6·5 by the addition of anhydrous sodium carbonate (15 gm.). Some sodium oxalate precipitated and was separated by filtration on a Buchner funnel and washed with water. The filtrate and washings were freed from oxalic acid by dropwise addition of a concentrated solution of calcium chloride. The calcium chloride was added until the supernatant liquid of a centrifuged sample was found to be free from oxalic acid. The calcium oxalate was removed by filtration. To the ice-cold filtrate was added concentrated sulphuric acid (8·2 ml.) with stirring, to lower the pH to 2. The solution was saturated with sodium sulphate and then extracted with ether. The ether extracts were dried ($MgSO_4$), the ether removed and the residue left on the rotary evaporator for two hours in a water bath at 60°C. The crude sample of β-chlorolactic acid was recrystallised from boiling di-isopropyl ether. The melting point was 77/8°C. (Literature value[115] 78°C). Elemental analysis: C,28·6%; H,3·9%; Cl,25·2%. (Calculated: C,28·9%; H,4·0%; Cl,28·5%).

4.13 Reaction of β-chlorolactic Acid with Sulphuric Acid

β-chlorolactic acid (5 gm.) was heated under reflux with sulphuric acid (10 ml. concentrated acid in 60 ml. water) for two days. The product was isolated by continuous ether extraction and yielded a solid which was recrystallised from di-isopropyl ether, and was shown by its infrared spectrum and melting point ($78^{o}C$) to be unchanged β-chlorolactic acid.

4.14 Reactions of IV and V

Boiling IV with absolute ethanol under reflux for three hours, followed by removal of the ethanol, yielded a product which contained no oxime, in contrast to the observation of Thorne.[77]

IV dissolved in acetone to produce a green solution. Removal of the acetone yielded a product with many of the properties of V, including a similar infrared spectrum.

IV was dissolved in ether and hydrogen chloride gas bubbled through for three hours. On removal of the ether IV was obtained unchanged, as shown by the infrared spectrum. The same reaction was repeated using V and V remained unchanged on isolation. This is in contrast to the behaviour of secondary nitroso compounds observed by Danilov and Oglobin.[78]

4.15 Reaction of Nitrous Acid with 2-methyl-2-butene

The procedure was the same as that described for the reaction with 3-chloro-2-methylpropene, except that smaller quantities were used. The product was a green oil VI.

Some of the green oil VI was dissolved in absolute ethanol and heated

to boiling point. The ethanol was removed and the infrared spectrum showed that the product was identical with VI. Thus, in contrast to the observation with the nitrosyl chloride addition product of 2-methyl-2-butene[77], VI does not isomerise to the oxime on refluxing in ethanol.

VI was dissolved in ether and hydrogen chloride gas was bubbled through for three hours. The product obtained, when the ether was removed, was unchanged VI as shown by the infrared spectrum. This is again in contrast to the behaviour of the nitrosyl chloride addition compound with 2-methyl-2-butene.[78]

4.16 Hydrolysis of the Addition Compound of 2-methyl-2-butene(VI)

VI (4 gm.) was added to sulphuric acid (10 ml. concentrated sulphuric acid in 60 ml. water) and the solution heated under reflux for two days. The solution was saturated with sodium sulphate, ether extracted and the extracts dried ($MgSO_4$). On removal of the ether a brown oil was obtained, the infrared spectrum of which indicated that some nitroso group was still present but had been partially replaced by a carbonyl group. This brown oil failed to form a 2,4-dinitrophenylhydrazone, so was subjected to distillation. The distillate was of the same constitution as the brown oil, as shown by the infrared spectrum, and also failed to form a 2,4-dinitrophenylhydrazone. The distillate also failed to form a p-nitrobenzoate.

4.17 Reaction of Hydrolysis Product of VI with Periodic Acid

The hydrolysis product (brown oil, 2·5 gm.) was added to sodium para-

periodate (10 gm.) in sulphuric acid (6 ml. concentrated sulphuric acid in 20 ml. water). The mixture was shaken at intervals and kept in a stoppered flask overnight. This solution was ether extracted and the ether removed by careful distillation. The product was divided into two halves and they were treated in the following ways.

(1) A solution was prepared containing 2,4-dinitrophenylhydrazine (0·9 gm.) in concentrated sulphuric acid (4·5 ml.). Absolute ethanol (21·5 ml.) and water (57 ml.) were added. The solution was filtered and was added to half of the above product. This yielded a 2,4-dinitrophenylhydrazone which melted at 119°C. (The melting point of an authentic sample of acetone 2,4-dinitrophenylhydrazone was 123°C.)

(2) An S-benzyl thiouronium salt was prepared from the other half as described for 3-chloro-2-hydroxy-2-methylpropionic acid. The product, recrystallised from aqueous alcohol, had a melting point of 142°C. That of an authentic sample of S-benzyl thiouronium acetate was 140°C. A mixed melting point showed no depression.

4.18 Preparation of Dinitrogen Trioxide[116]

Dried sodium nitrite was introduced into a three-necked flask fitted with a gas inlet, a dropping funnel and a phosphorus pentoxide/glass wool drying tower. Intermixed with the sodium nitrite were some glass beads to prevent 'caking' of the resultant sodium sulphate. Before commencement of production of dinitrogen trioxide the apparatus was flushed out with dry nitrogen gas. When concentrated sulphuric acid was added dropwise from the

dropping funnel, evolution of an equimolar mixture of gaseous nitric oxide and nitrogen dioxide commenced without application of heat. The brown gases were passed through the tower packed with phosphorus pentoxide and glass wool and were passed over a cold finger containing a cooling mixture of acetone and solid carbon dioxide. Blue dinitrogen trioxide condensed on the cold finger and was collected in a vessel immersed in an ice-salt cooling mixture. The gases were carried through the apparatus by a stream of dry nitrogen gas and the rate of production of dinitrogen trioxide was controlled by the rate of addition of concentrated sulphuric acid.

4.19 Addition of Dinitrogen Trioxide to 3-chloro-2-methylpropene

4.19.(a) In the absence of a solvent:

3-chloro-2-methylpropene was added dropwise to the dinitrogen trioxide at $0^{o}C$. The reaction proceeded rapidly with much evolution of heat. Excess dinitrogen trioxide was used. When all the olefin had been introduced, the reaction mixture was allowed to warm to room temperature and hence any excess dinitrogen trioxide could escape as nitrous fumes (boiling point $2.3^{o}C$). The product was purified further by pumping on a rotary evaporator for some time.

4.19.(b) In ether as solvent:

An ether solution of 3-chloro-2-methylpropene was prepared. This solution was introduced into the receiving vessel in the apparatus for the preparation of dinitrogen trioxide, prior to commencement of the preparation.

The dinitrogen trioxide condensed on the cold finger and then dripped into the ether solution of the olefin, which was cooled in an ice-salt mixture. Thus the addition reaction proceeded as the dinitrogen trioxide dripped into the ether solution. Again excess dinitrogen trioxide was used. The ether was removed on the rotary evaporator and the product obtained was identical with that from the direct preparation.

4.19.(c) Continuous process in absence of a solvent:

(b) was repeated in the absence of ether and the product was purified as described earlier. (c) was used in preference to (a) because of the large amount of heat produced by a rapid direct addition of dinitrogen trioxide to the olefin.

4.20 Addition of Dinitrogen Trioxide to Olefins

The reaction was carried out as described in 4.19.(b).

(i) 3-chloropropene:

Direct addition of dinitrogen trioxide and addition in ether yielded a white solid and a green oil, which were separated in the usual way. The melting point of the solid was 96/7°C and a mixed melting point with IV showed no depression. The infrared spectra of the solid, prepared by three different methods and recorded as potassium bromide discs and as Nujol mulls, were all identical. The solid was also shown to be identical with IV by the elemental analysis: C,24·7%; H,3·2%; Cl,23·3%.

The green oil was also identical with that prepared earlier (V), as shown by the infrared spectrum.

Elemental analysis: C,27·4%; H,3·8%; Cl,21·4%.

(ii) 2-methyl-2-butene:

The product was a green oil and was identical to VI. The infrared spectrum had peaks appearing at 6·13 and 6·47 μ. Elemental analysis: C,45·6%; H,7·05%. (Calculated: C,41·1%; H,6·85%).

(iii) 3-hydroxy-2-methylpropene:

The product was a green oil and the infrared spectrum showed peaks appearing at 6·11 and 6·40 μ.

(iv) 2,4,4-trimethyl-2-pentene:

The product was a blue oil and showed peaks at 6·11 and 6·44 μ in the infrared spectrum.

(v) 2,3-dimethyl-2-butene:

A white solid and a blue liquid were obtained. The infrared spectrum of the liquid had peaks appearing at 6·11 and 6·45μ and that of the solid had a peak appearing at 6·50 μ. The melting point of the solid was 208-9^{o}C. The solid dissolved in benzene to give a blue solution and the nuclear magnetic resonance spectrum of this solution had one absorption at 8·7 p.p.m.

(vi) 2-methylpropene:

Isobutene gas was bubbled through ether as liquid dinitrogen trioxide was added. Two products were obtained, a green liquid and a white solid. They were separated by filtration and the solid was washed with ether. More solid, however, settled from the green liquid, even after repeated filtration. The solid melted at 82^{o}C to a blue liquid. Both products were analysed:

Solid: C,36·6%; H,6·3%; N,21·3%: liquid; C,36·4%; H,5·9%; N,15·6%; (calculated: C,36·4%; H,6·1%; N,21·2%).

The infrared spectrum of the liquid had peaks appearing at 6·08 and 6·41μ and that of the solid had a peak appearing at 6·41 μ.

The nuclear magnetic resonance spectrum of the solid in benzene showed two single absorptions at 5·5 p.p.m. and 9·1 p.p.m. The spectrum of the liquid product in carbon tetrachloride showed absorptions at 5·2 p.p.m. and 8·3 p.p.m. These absorptions, however, are not singlets and they show a complex splitting pattern.

(vii) Propene

Propene gas was bubbled through ether as dinitrogen trioxide was added. A white solid and a yellow oil were obtained and separated by filtration, the white solid being washed with ether. Further white solid was precipitated from the yellow oil on standing. Elemental analysis: liquid; C,34·7%; H,5·12%: solid; C,30·3%; H,5·1%; N,23·6%. (Calculated; C,30·5%; H,5·1%; N,23·7%). The white solid melted to a yellow oil at 108^{o}C. The infrared spectrum of the liquid had peaks appearing at 6·10 and 6·43 μ, whilst that of the solid had a peak appearing at 6·39 μ.

Section 3.

Chapter 5.

Kinetic study of the nitrosation of some olefins at low acidity (< 0·1M)

5.1 Kinetic Study of the reaction of Nitrous Acid with 2-methyl-2-butene

The kinetics were studied in 10^{-4} - 0·1N perchloric acid. The reaction was followed initially to determine any dependence on the concentration of the olefin at two different acidities. In both cases the dependence was obtained by maintaining a constant acidity and a constant concentration of sodium nitrite. The results are collected in Table 5.1 and Table 5.2.

Table 5.1.

Nitrosation of 2-methyl-2-butene at constant concentration of perchloric acid and sodium nitrite

Run	3 + log (rate)	3 + log [olefin]
60	0·204	0·011
56	0·455	0·224
61	0·532	0·279
57	0·771	0·519

Temperature = 0°C; $[H^+]$ = 0·0024N; $[NaNO_2]$ = 2 x 10^{-4}N. The rate is the initial rate, determined by using a tangentimeter. The slope obtained by least squares analysis was 1·1.

Table 5.2.

Nitrosation of 2-methyl-2-butene at constant concentration of perchloric acid and sodium nitrite

Run	2 + log (rate)	4 + log [olefin]
37	0·462	0·875
41	0·567	1·079
39	0·678	1·250
45	0·892	1·328

Temperature = $0^{o}C$; $[H^{+}]$ = 0·0303N; $[NaNO_2]$ = 2 x 10^{-4}N.

The slope obtained by least squares analysis was 1·1.

To determine the effect of changing acidity on the rate of nitrosation of 2-methyl-2-butene a series of runs were set up at different acidities. The results are collected in Table 5.3 and show a dependence on the acidity of 1·1.

Within the range of acidity that it was possible to study using 2-methyl-2-butene the order of the reaction with respect to nitrous acid decreased from 2 at very low acid to significantly less than 2 but greater than 1 in 0·1M perchloric acid.

Table 5.3.

Nitrosation of 2-methyl-2-butene at changing acidity and constant concentration of sodium nitrite

Run	$\log \frac{(\text{rate})}{[\text{olefin}]}$	$4 + \log [H^+]$
37	3·462	2·479
56	2·242	1·391
23	1·954	1·041
19	1·663	0·799

Temperature = $0^{\circ}C$; $[NaNO_2] = 2 \times 10^{-4}N$. The olefin concentration could not be maintained constant throughout the series of runs, thus the initial rate had to be divided by the olefin concentration to yield an olefin concentration independent quantity.

At low acidity, however, sodium nitrite is not completely converted to nitrous acid, as shown in Table 5.4.

Since nitrous acid is a Bronsted acid then it will be present in both its acid and base forms unless there is a large excess of mineral acid present, as shown in Table 5.4. It is therefore possible to calculate two

Table 5.4.

Concentration of nitrous acid in a solution containing 1×10^{-4} N sodium nitrite at different acidities

$[H^+] \times 10^4$ N	$[HNO_2] \times 10^4$ N
1	0·16
2	0·28
5	0·50
10	0·68
20	0·81
50	0·92
100	0·96
200	0·98
500	0·99

The calculations use Ka = $4{\cdot}5 \times 10^{-4}$ mole 1^{-1} 40 but this value is subject to significant experimental uncertainties.

distinct types of rate constant.[31] One, the stoichiometric rate constant, is the proportionality constant of a rate equation containing only the stoichiometric concentration of nitrous acid, that is the sum of the concentration of the acidic and basic forms of nitrous acid as measured experimentally. The other, the molecular rate constant, is the proportionality constant of a rate equation involving the concentration in which nitrous acid is actually present in its uncharged molecular form. In general, in a solution of constant hydrogen ion concentration the ratio of the molecular to the stoichiometric concentration of nitrous acid will remain constant throughout a run. Thus the kinetic form of the run will be the same irrespective of which type of rate constant is calculated, but the value will change. The stoichiometric rate constants are easily calculated because they depend only on the concentration of nitrous acid measured, whereas the molecular rate constant calculations require the use of the equilibrium constant of dissociation of nitrous acid which introduces further uncertainties.

At acidities lower than $7{\cdot}21 \times 10^{-4}$ N perchloric acid with excess olefin present the reaction was second order with respect to nitrous acid. This is shown for the run at $3{\cdot}79 \times 10^{-4}$ N perchloric acid in Fig.5.01, which includes both first and seond order plots. The second order nature of the reaction at very low acid is further illustrated by the first and second order rate constants shown in Table 5.5.

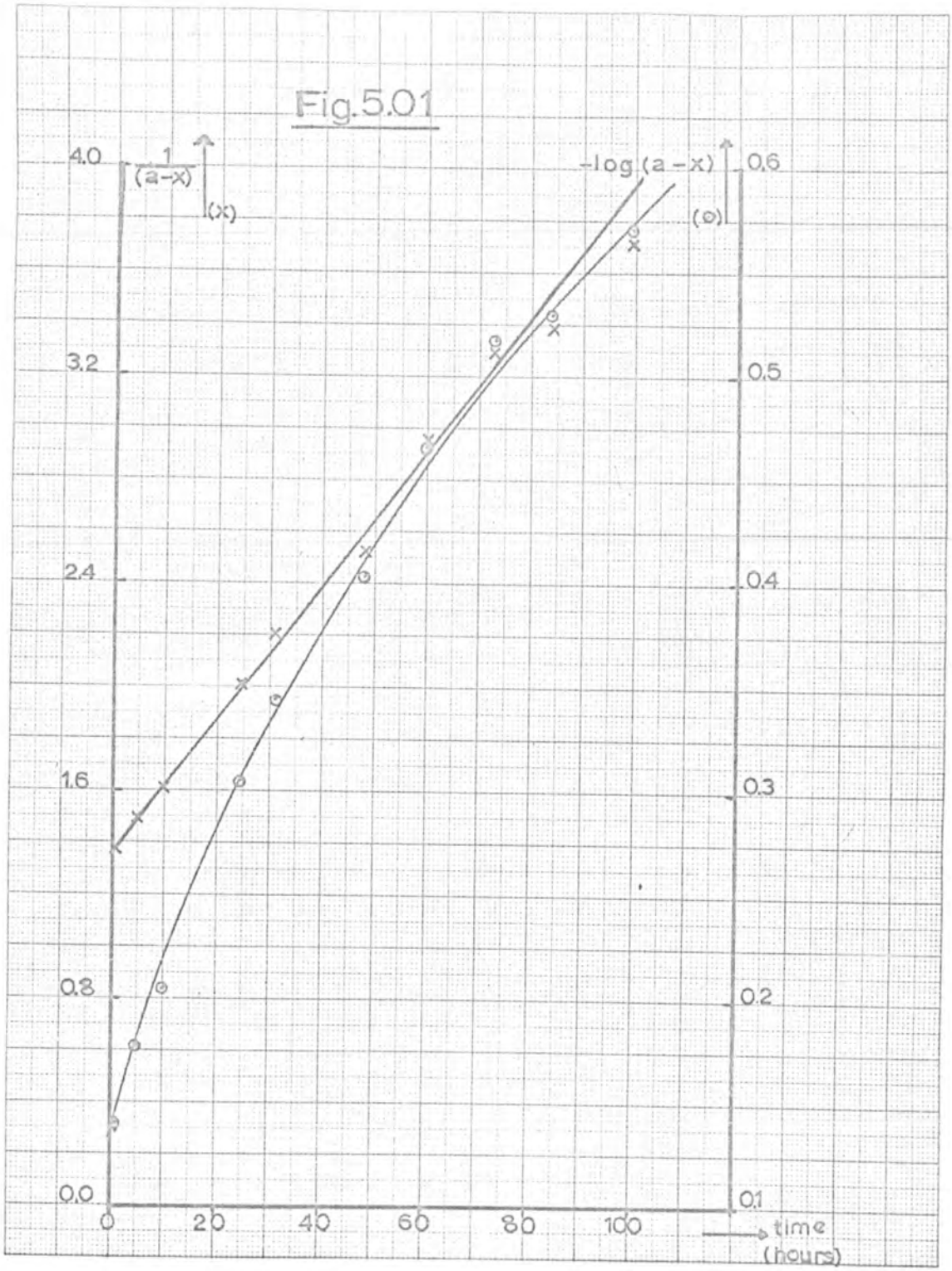


Fig.5.01
4.0
3.2
2.4
1.6
0.8
0.0
1/(a-x)
(x)
-log (a-x)
(⊙)
0.6
0.5
0.4
0.3
0.2
0.1
0
20
40
60
80
100
time
(hours)

Table 5.5.

First and second order rate constants of the nitrosation of 2-methyl-2-butene at $[HClO_4] = 1{\cdot}07 \times 10^{-4}N$

Time (hours)	Optical Density	$\bar{k}_1$ (hr^{-1})	$\bar{k}_2$ ($mole^{-1}$ litre hr^{-1}) $\times 10^{-2}$
0·00	0·389		
3·017	0·359	0·027	2·77
5·850	0·338	0·024	2·58
8·767	0·315	0·024	2·68
13·567	0·281	0·024	2·83
24·567	0·234	0·021	2·76
33·750	0·210	0·018	2·52
54·333	0·159	0·017	2·66
71·600	0·134	0·015	2·66
95·450	0·105	0·014	2·83
143·650	0·074	0·012	2·96

The third order stoichiometric rate constants are calculated from the rate equation:

$$V = {}^{2}\bar{k}_3[\text{olefin}][\text{nit}]^2$$

where [nit] is the stoichiometric concentration of nitrite ion and nitrous acid. The observed values of these rate constants are shown in Table 5.6.

Table 5.6.

Third order stoichiometric rate constants for the nitrosation of 2-methyl-2-butene at low acidity at $0^{\circ}C$

Run	$[H^+] \times 10^4 N$	$[NaNO_2] \times 10^4 N$	${}^{2}\bar{k}_3 \times 10^{-2}$ (mole^{-2} litre^2 min^{-1})
267	1·07	1·0	7·17
15	3·79	2·0	16·00
16	7·21	2·0	33·40

Third order molecular rate constants were derived from the rate equation:

$$V = {}^{2}k_3[\text{olefin}][HNO_2]^2$$

and are shown in Table 5.7.

Table 5.7.

Third order molecular rate constants for the nitrosation of 2-methyl-2-butene at low acidity at $0^{o}C$

Run	$[H^+] \times 10^4$	$[HNO_2] \times 10^4$	$^2k_3 \times 10^{-4}$ ($mole^{-2} litre^2 min^{-1}$)
267	1·07	0·16	2·87
15	3·79	0·80	1·00
16	7·21	1·15	1·01

At acidities greater than 7×10^{-4} N perchloric acid, the kinetics took the form of a mixed first and second order reaction with respect to nitrous acid. The method of analysis is discussed in Appendix 3 and is intrinsically an inaccurate process. The molecular third order rate constants derived from the equation:

$$V = {}^2k_3[\text{olefin}][HNO_2]^2 + {}^1k_3[\text{olefin}][H^+][HNO_2]$$

are shown in Table 5.8. At acidities higher than 0·0033 N perchloric acid the reaction remained mixed order with respect to nitrous acid but did not yield satisfactory rate constants. The highest acidity studied was 0·1 N perchloric acid, when the kinetics still indicated a mixed order reaction with respect to nitrous acid.

Table 5.8.

Third order molecular rate constants for the nitrosation of 2-methyl-2-butene at low acidity at 0°C

Run	$[H^+] \times 10^4 N$	$[HNO_2] \times 10^4 N$	$k_3 \times 10^{-2}$ (mole^{-2} litre^2 min^{-1})
11	33·3	1·75	$^1k_3 = 3{\cdot}48$
			$^2k_3 = 0{\cdot}627 \times 10^2$
23	12·4	1·40	$^1k_3 = 4{\cdot}87$
			$^2k_3 = 1{\cdot}06 \times 10^2$

Mean $^1k_3 = 4{\cdot}18 \times 10^2$ mole^{-2} litre^2 min^{-1}

Mean $^2k_3 = 8{\cdot}50 \times 10^3$ mole^{-2} litre^2 min^{-1}

5.2 Kinetic study of the reaction of nitrous acid with 2,3-dimethyl-2-butene

The kinetics were studied in the range 10^{-4} - 0·02 N perchloric acid. At 1·07 x 10^{-4} N perchloric acid the kinetics indicated a second order process with respect to nitrous acid. The first and second order rate plots are included in Fig.5.02. The calculated first and second order rate constants are shown in Table 5.9.

The third order molecular rate constants for the reaction of nitrous acid with 2,3-dimethyl-2-butene calculated from the rate equation: $V = {}^{2}k_3[\text{olefin}][HNO_2]^2$ are recorded in Table 5.10.

As the acidity was increased from 1·07 x 10^{-4}N to 4·28 x 10^{-4}N perchloric acid, the order of the reaction became non-integral, between 2 and 1. The kinetics were analysed as a mixture of a first and a second order process at two different acidities and the observed rate constants are shown in Table 5.11, the molecular rate constants being the proportionality constants in the rate equation:

$$V = {}^{2}k_3[\text{olefin}][HNO_2]^2 + {}^{1}k_3[\text{olefin}][H^+][HNO_2]$$

In the acidity range 8·56 x 10^{-4}N to 211·1 x 10^{-4}N perchloric acid, the kinetics indicated a first order process with respect to nitrous acid. Fig. 5.03shows the first and second order plots at 8·56 x 10^{-4}N perchloric acids and examples of the first order plots are illustrated in Fig.5.04and Fig. 5.05. The third order rate constants are collected in Table 5.12. At higher acidities the reaction was too rapid to follow by the techniques used.

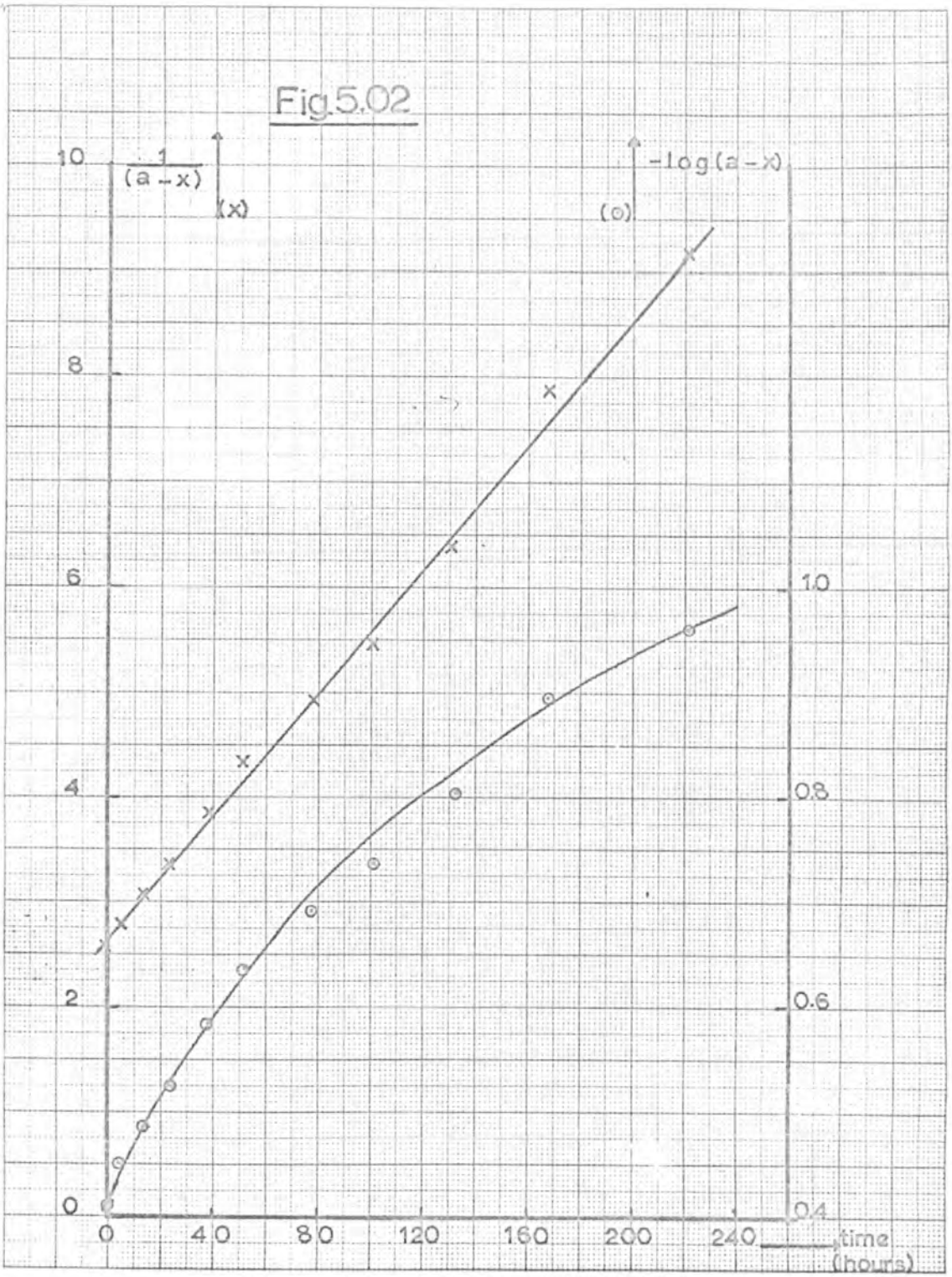


Fig.5.02
10
8
6
4
2
0
1/(a-x)
(x)
-log(a-x)
(o)
1.0
0.8
0.6
0.4
0
40
80
120
160
200
240
time
(hours)

Table 5.9.

First and second order stoichiometric rate constants for the nitrosation of 2,3-dimethyl-2-butene at 0°C in $[HClO_4]$ = 1·07 x 10^{-4}M

time (hours)	Optical Density	$\bar{k}_1 \times 10^3$ (hr^{-1})	$\bar{k}_2 \times 10^{-2}$ ($mole^{-1}$ litre hr^{-1})
0·00	0·389	-	-
8·68	0·346	13·4	1·43
13·57	0·325	13·2	1·45
23·43	0·298	11·3	1·30
37·52	0·260	10·7	1·32
51·57	0·230	10·1	1·34
78·30	0·203	8·3	1·17
102·47	0·184	7·3	1·09
132·90	0·156	6·8	1·12
167·62	0·127	6·6	1·23
222·23	0·109	5·7	1·16

Table 5.10

Third order molecular rate constants for the nitrosation of 2,3-dimethyl-2-butene

Run	$[HNO_2] \times 10^4 N$	$^2k_3 \times 10^{-4}$ ($mole^{-2} litre^2 min^{-1}$)
260	0·16	7·15
264	0·16	6·84

Mean $^2k_3 = 7{\cdot}00 \times 10^4$ $mole^{-2}$ $litre^2$ min^{-1}

Temperature = 0^oC; $[NaNO_2] = 1 \times 10^{-4} N$, $[HClO_4] = 1{\cdot}07 \times 10^{-4}$ N

Table 5.11.

Third order molecular rate constants observed at low acidity for the nitrosation of 2,3-dimethyl-2-butene

Run	$[HClO_4] \times 10^4 N$	$[HNO_2] \times 10^4 N$	$k_3 \times 10^{-2}$ (mole^{-2} litre^2 min^{-1})
261	2·14	0·30	$^1k_3 = 18·95$
			$^2k_3 = 4·47 \times 10^2$
265	2·14	0·30	$^1k_3 = 15·45$
			$^2k_3 = 4·59 \times 10^2$
262	4·28	0·47	$^1k_3 = 5·42$
			$^2k_3 = 4·22 \times 10^2$

Mean $^1k_3 = 13·3 \times 10^2$ mole^{-2} litre^2 min^{-1}

Mean $^2k_3 = 4·43 \times 10^4$ mole^{-2} litre^2 min^{-1}

$[NaNO_2] = 1 \times 10^{-4}$N; Temperature = 0°C

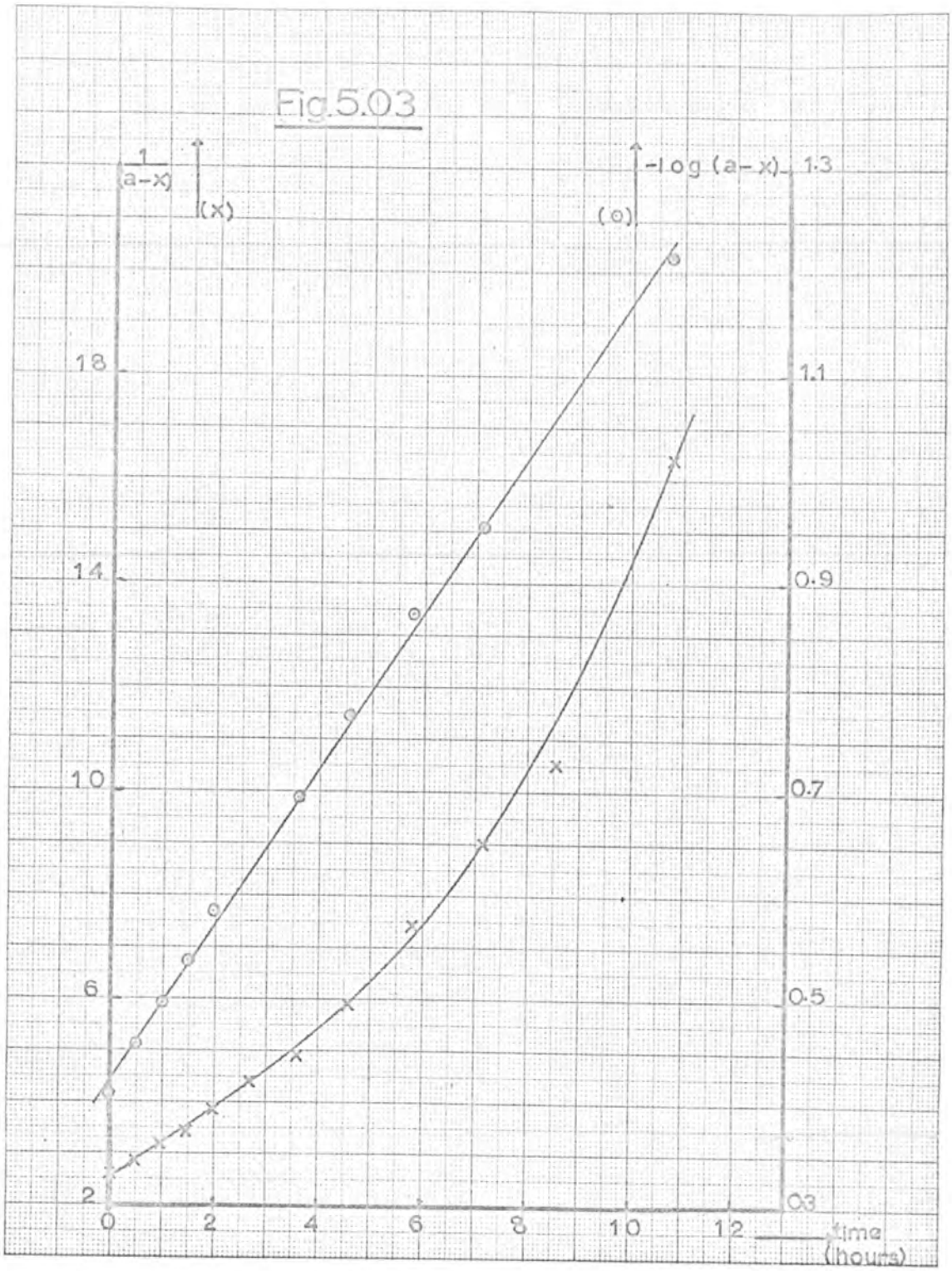


Fig.5.03
1/(a-x)
(x)
-log (a-x)
(o)
18
14
10
6
2
1.3
1.1
0.9
0.7
0.5
0.3
0
2
4
6
8
10
12
time
(hours)

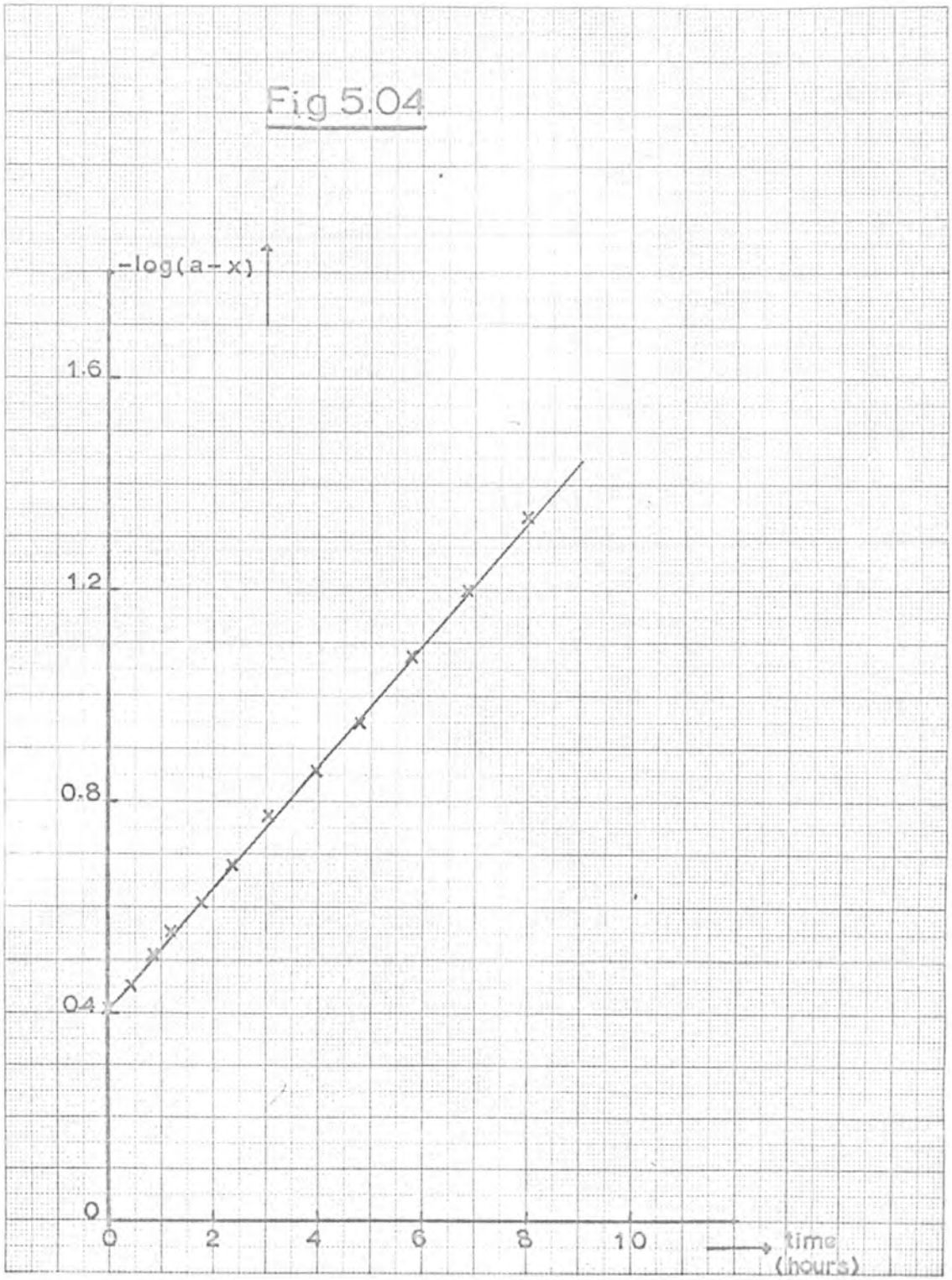


Fig 5.04
-log(a-x)
1.6
1.2
0.8
0.4
0
0
2
4
6
8
10
Time
(hours)

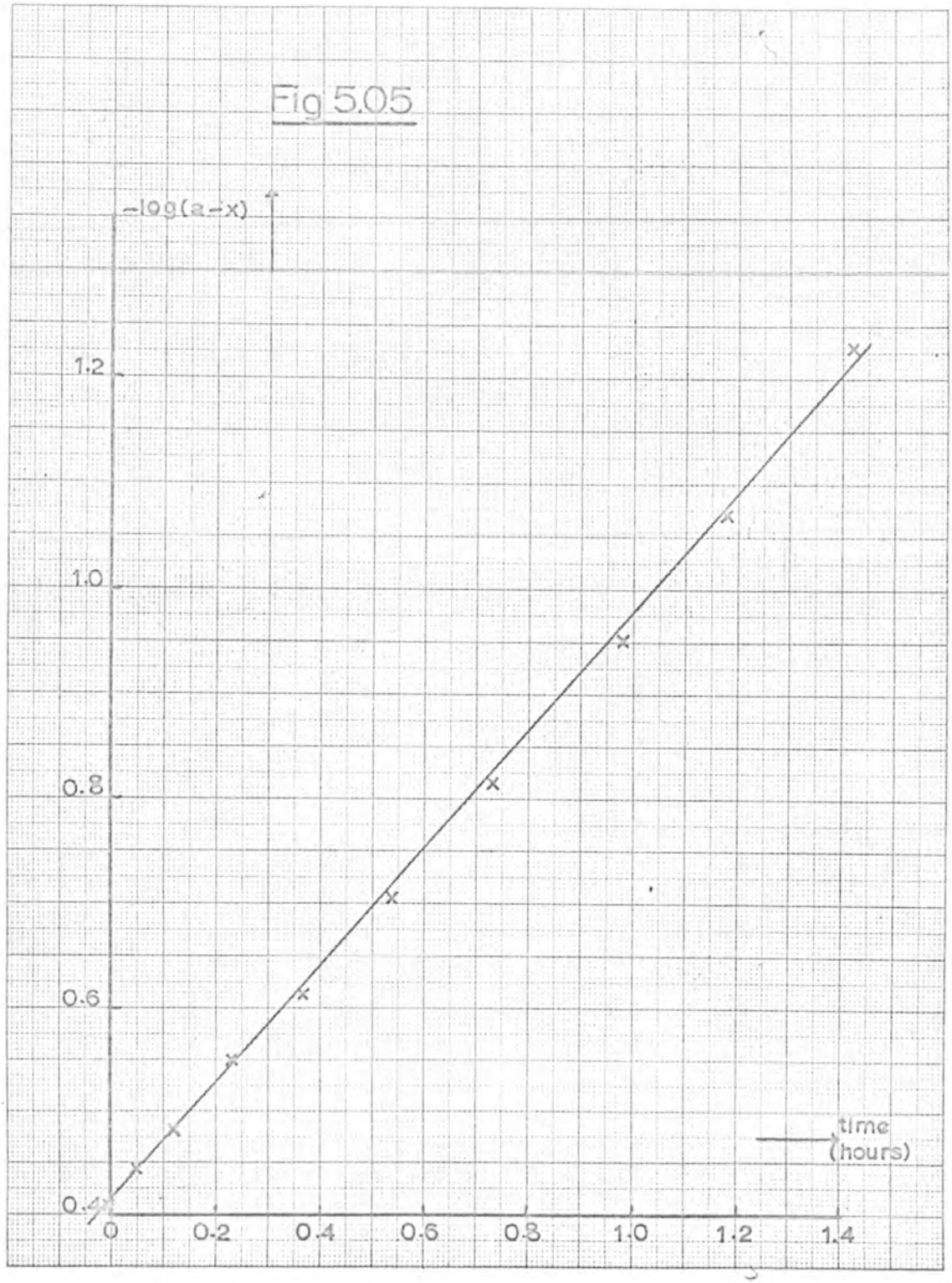


Fig 5.05
-log(a-x)
1.2
1.0
0.8
0.6
0.4
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
time
(hours)

Table 5.12.

Third order rate constants (molecular and stoichiometric) for the nitrosation of 2,3-dimethyl-2-butene at low acidity

Run	$[HClO_4] \times 10^4$ N	$[HNO_2] \times 10^4$ N	$^1\bar{k}_3 \times 10^{-3}$ ($mole^{-2}\,litre^2\,min^{-1}$)	$^1k_3 \times 10^{-3}$ ($mole^{-2}\,litre^2\,min^{-1}$)
266	8·56	0·64	3·07	4·58
268	12·85	0·73	3·73	5·00
269	17·13	0·78	3·52	4·45
274	42·6	0·90	4·28	4·74
275	85·2	0·95	4·56	4·80
279	211·1	0·98	4·75	4·82

Mean $^1k_3 = 4{\cdot}73 \times 10^3$ $mole^{-2}$ $litre^2$ min^{-1}

$[NaNO_2] = 1 \times 10^{-4}$; Temperature = 0^oC

5.3 Discussion of mechanistic significance of results

Quantitative comparison of the reactivity of 2-methyl-2-butene and 2,3-dimethyl-2-butene is not straightforward since their behaviour is not parallel over the region studied. However, the increased reactivity of 2,3-dimethyl-2-butene relative to 2-methyl-2-butene does serve to indicate the electrophilic nature of the nitrosation reaction. The acidity region which will yield the most reliable comparison of reactivity is the very low acidity region. Here the reaction is second order with respect to nitrous acid and thus reaction must be occurring by attack of dinitrogen trioxide and is shown in Scheme 5.1.

$$HNO_2 + H^+ \underset{\text{fast}}{\rightleftharpoons} H_2NO_2^+$$

$$H_2NO_2^+ + NO_2^- \underset{\text{fast}}{\rightleftharpoons} N_2O_3$$

$$>C=C< + N_2O_3 \xrightarrow{\text{slow}} \text{products}$$

Scheme 5.1.

The rate constants of the reaction of 2,3-dimethyl-2-butene and 2-methyl-2-butene with dinitrogen trioxide can be obtained by using the equilibrium constant for formation of dinitrogen trioxide measured at 20°C,[117] which is 0·2 mole litre^{-1}, and are shown in Table 5.13.

The relative reactivity of 2,3-dimethyl-2-butene and 2-methyl-2-butene towards dinitrogen trioxide is 2·4 in 1·07 x 10^{-4}N perchloric acid. The

relative reactivities towards nitrosyl chloride in chloroform are not recorded but it was shown by Beier, Hauthal and Pritzkow[51] that 2,3-dimethyl-2-butene was more reactive than 2-methyl-2-butene. However, in the bromination reaction, 2,3-dimethyl-2-butene was found to be ten times as reactive as 2-methyl-2-butene.[118]

Table 5.13.

Second order molecular rate constants for the reaction of olefins with dinitrogen trioxide at 0°C

Olefin	$[HClO_4] \times 10^4 N$	$[HNO_2] \times 10^4 N$	$^1k_2 \times 10^{-4}$ (mole^{-1} litre min^{-1})
2,3-dimethyl-2-butene	1·07 [a]	0·16	35
2-methyl-2-butene	1·07 [a]	0·16	14·35

[a] $[NaNO_2] = 1 \times 10^{-4} N$

The first order process identified for 2,3-dimethyl-2-butene and indicated for 2-methyl-2-butene must be rate-determining nitrosation of the olefin by the nitrous acidium ion as identified in the diazotisation of aromatic amines and as shown in Scheme 5.2.

The concurrent processes identified in the mixed first and second order reaction must consist of the two processes already described. The formation

$$H^+ + HNO_2 \overset{\text{fast}}{\rightleftharpoons} H_2\overset{+}{N}O_2$$

$$>C=C< + H_2NO_2 \xrightarrow{\text{slow}} \text{products}$$

Scheme 5.2.

of all nitrosating agents involves the initial protonation of nitrous acid to give the nitrous acidium ion[44], which can then either react with an anion, for example nitrite ion or halide ion, to yield another nitrosating agent or can react with the substrate. Thus, in the nitrosation of 2,3-dimethyl-2-butene at very low acidity, there is competition between the nitrite ion and the olefin to react with the nitrous acidium ion, and an equilibrium concentration of dinitrogen trioxide is formed, second order kinetics being observed. The nitrous acidium ion is a more reactive nitrosating agent than dinitrogen trioxide but at this acidity the comparative reactivity of the two species is governed by their relative concentrations. As the acidity is increased the bulk reactivity[¤] of the nitrous acidium ion increases. Nitrosation by the nitrous acidium ion now becomes a viable reaction sequence and so first order kinetics are observed. There is a gradual change from pure second order to pure first order kinetics. This is expected because there is a certain range of acidity when the bulk reactivity of dinitrogen trioxide and the nitrous acidium ion are comparable, or

---

¤ Bulk-reactivity = concentration x specific reactivity

alternatively when the reaction of both the olefin and the nitrite ion with the nitrous acidium ion contribute significantly to the total nitrosation reaction. With 2-methyl-2-butene in the acidity range studied the nitrosation reaction is still compounded from the first and the second order processes and it has not been possible to isolate a pure first order process.

5.4 Summary

Nitrosation of 2-methyl-2-butene at low acidity occurs by a second order process and at higher acidities by a mixed first and second order reaction. 2,3-dimethyl-2-butene behaves similarly in low acid but at higher acidity nitrosation occurs by a pure first order process.

At low acidity nitrosation is suggested to occur by dinitrogen trioxide whilst that at higher acidity occurs by attack of the nitrous acidium ion. In the region of acidity in which mixed order behaviour was observed, nitrosation occurs by both of these processes.

The ratio of the reactivity of 2,3-dimethyl-2-butene and 2-methyl-2-butene towards dinitrogen trioxide is much lower than in the bromination reaction.

Chapter 6.

Kinetic study of nitrosation of some olefins at high acidity (> 0·25M)

6.1 Decomposition of nitrous acid at high acidity

Solutions of nitrous acid are known to be unstable. Several kinetic studies of the decomposition of solutions of nitrous acid have been made. Dinitrogen tetroxide has been postulated as a likely intermediate, but the rate determining stage was shown to depend on the experimental conditions.[119] Ridd and co-workers[31] found that the rate of decomposition was independent of the acidity in the region of 0·002M perchloric acid. They found the rate of decomposition was also negligible in comparison with the rate of their diazotisation reactions.

In the present studies the rates of nitrosation were very low and runs took up to ten days to reach completion. In these runs, therefore, the quoted rate of nitrous acid decomposition of 1-2% per hour is very significant compared with the rate of nitrosation. To allow for the decomposition of nitrous acid a blank run, containing the same concentrations of acid and sodium nitrite, was followed concurrently with a nitrosation run. In an attempt to discover any acid-catalysis in this range of acidity, 0·40 to 1·70N perchloric acid and 0·20 to 1·35M sulphuric acid, a blank run was followed for every individual run.

No acid-catalysis was observed in the nitrous acid decomposition in perchloric or sulphuric acid in the range of acidity studied (0·20 to 1·80N acid). In addition no acceleration was detected in the presence of sodium perchlorate or sodium bromide. The observed decomposition was first order with respect to nitrous acid, the first order rate constant being larger in

perchloric acid than sulphuric acid. The mean first order rate constants for the decomposition of nitrous acid are shown in Table 6.1.

Table 6.1.

First order rate constants for the decomposition of nitrous acid in perchloric and sulphuric acid

Acid	$k_1 \times 10^3$ (hr^{-1})
Sulphuric[(a)]	3·0 ± 0·1
Perchloric[(b)]	4·6 ± 0·4

(a) Acidity range 0·20 to 1·35M

(b) Acidity range 0·40 to 1·70N

These observations are in agreement with those of Bayliss and Watts[120], who were studying decomposition at higher acidity. In addition these workers were using much higher concentrations of sodium nitrite and hence it was necessary to remove the products of decomposition. The mechanism suggested by Bayliss and Watts is shown in Scheme 6.1 and requires that the rate of decomposition be dependent upon the acidity of the medium. In the narrow range of acidity studied in the present investigation no acid-catalysis was detected. This is difficult to rationalise with the proposed mechanism. Bayliss and Watts, however, were studying a region of acidity in

$$HNO_2 + H^+ \underset{}{\overset{\text{fast}}{\rightleftharpoons}} H_2\overset{+}{N}O_2$$

$$H_2\overset{+}{N}O_2 \underset{}{\overset{\text{slow}}{\rightleftharpoons}} NO^+ + H_2O$$

$$NO^+ + HNO_2 \rightleftharpoons N_2O_3 + H^+$$

$$N_2O_3 \longrightarrow \text{products}$$

Scheme 6.1.

which the nitrosonium ion has been positively identified. A first order decomposition with respect to nitrous acid would be expected to show an acidity dependence. The range of acidity studied is probably not broad enough to indicate any dependence on the acidity and further study would be required to give more concrete evidence.

6.2 Nitrosation of 3-chloro-2-methylpropene in perchloric acid

The nitrosation of 3-chloro-2-methylpropene was initially studied in the range 0·40 to 1·70N perchloric acid. The kinetics were first order with respect to nitrous acid and a typical first order plot is shown in Fig.6.01 at 0·84N perchloric acid. The second order rate constants at different acidities are shown in Table 6.2. Fig.6.02 shows the plot of log $^1k_2$ against $-H_o$ and the slope of the line, calculated by least squares analysis, is 0·8.

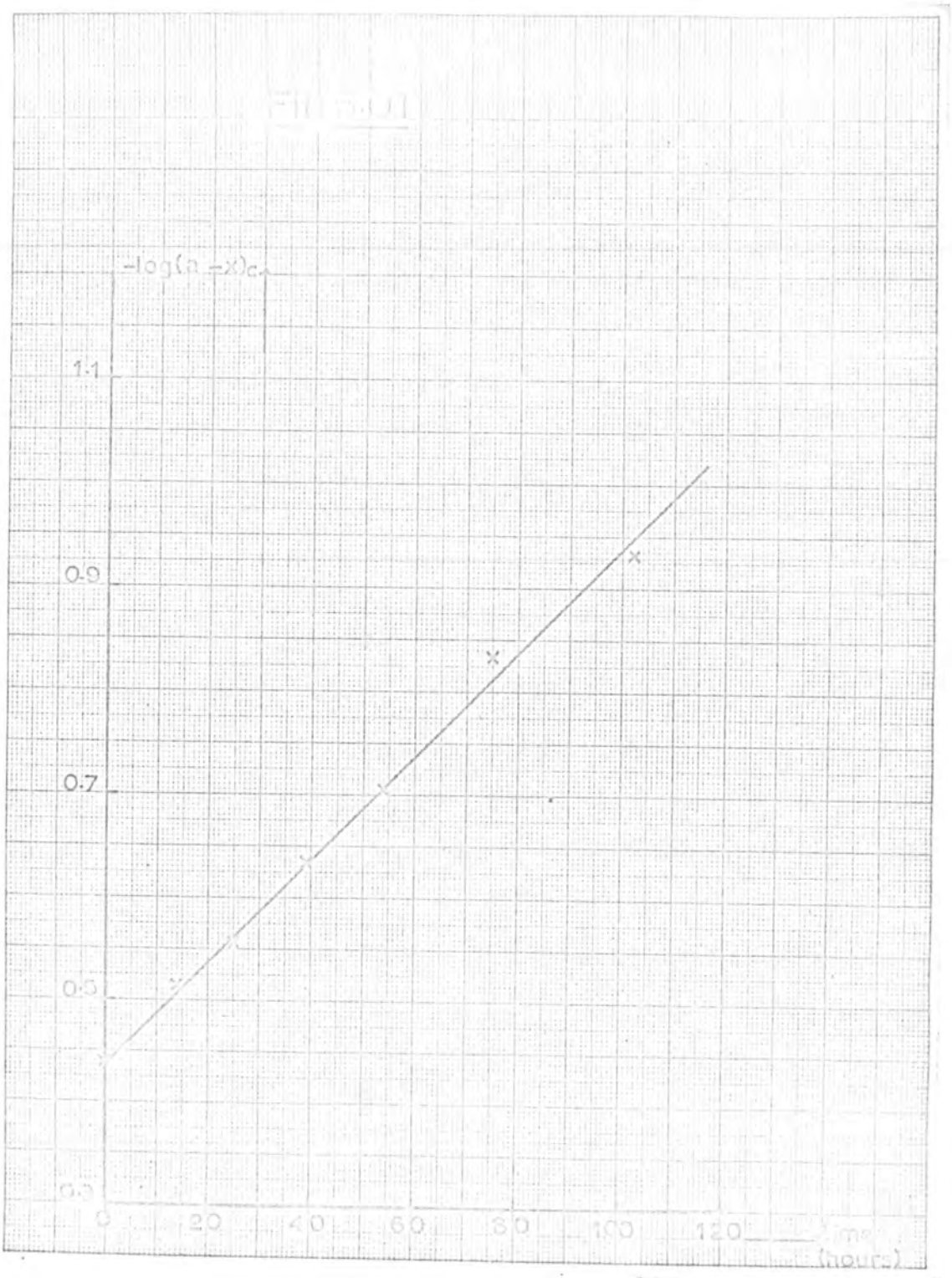

-log(a-x)c
1·1
0·9
0·7
0·5
0·3
0
20
40
60
80
100
120
time
(hours)

Table 6.2.

Second order rate constants for the nitrosation of 3-chloro-2-methylpropene in perchloric acid at 0°C

Run	$[HClO_4]M$	$-H_o$ (a)	$^1k_2 \times 10^2$ (moles^{-1}litre min^{-1})
191	1·68	0·62	4·88
192	1·26	0·40	3·11
193	0·84	0·14	2·21
194	0·42	-0·17	1·23

(a) H_o values from reference 121

A series of runs were now set up at constant ionic strength of 2·0M using analar sodium perchlorate. The results are shown in Table 6.3. It is evident that the rate constants at different acidities are effectively unchanged at constant ionic strength, in contrast to diazotisation of aromatic amines in a constant ionic strength of 3·0M[45], where k_2 increases with h_o.

In the diazotisation of aromatic amines the salt effect was expressed by equation[122] 6.01 where $[ClO_4^-]$ is the concentration of sodium perchlorate

$$\log k_2 = \log k_2^{o} + m[ClO_4^-] \qquad 6.01.$$

Fig 6.02

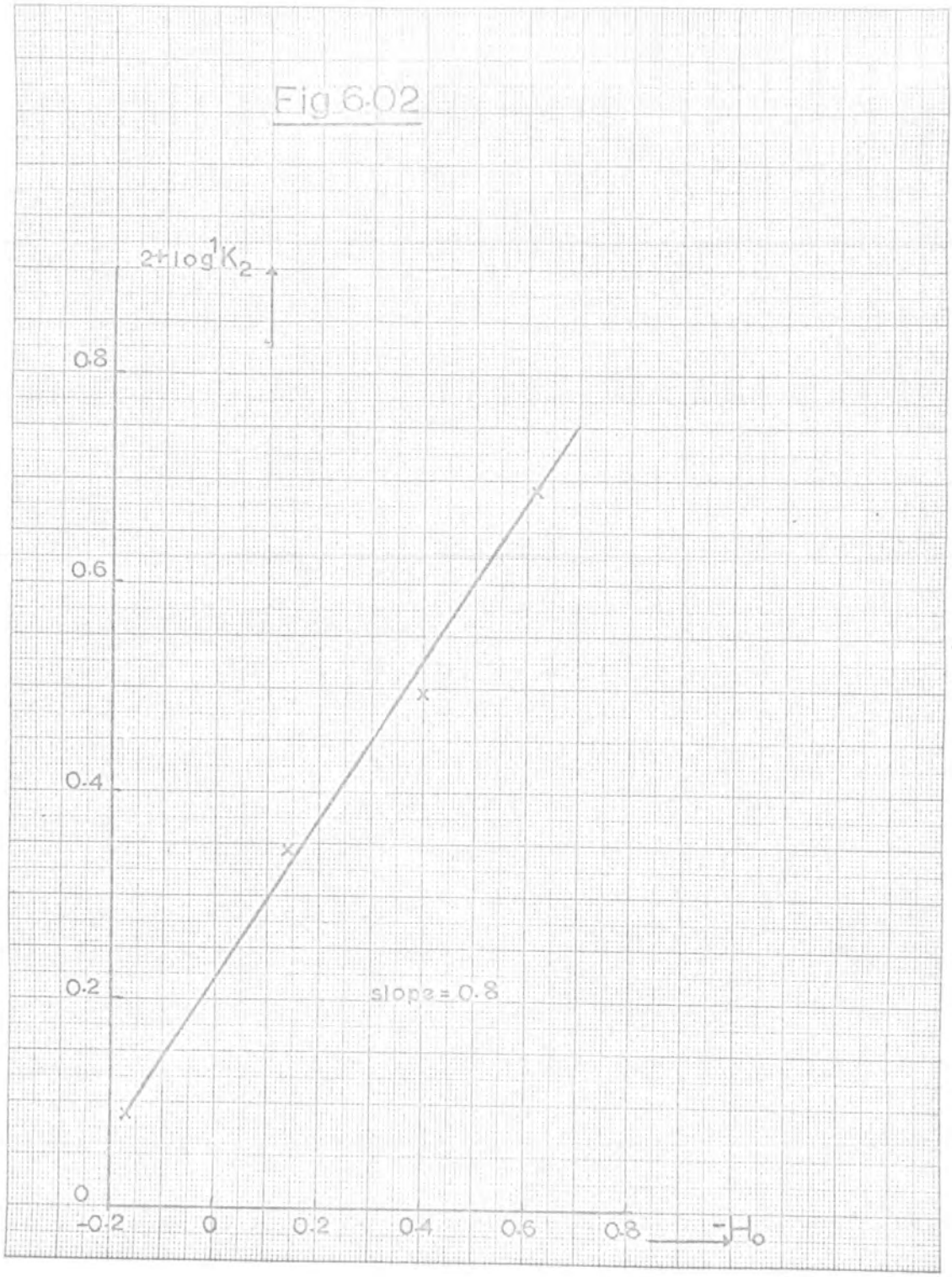


Table 6.3.

Second order rate constants for the nitrosation of 3-chloro-2-methylpropene at constant ionic strength at 0°C

Run	$[HClO_4]M$	$[NaClO_4]M$	$-H_o$ (a)	$^1k_2 \times 10^2$ ($mole^{-1}$ litre min^{-1})
201	1·68	0·32	0·70	6·36
202	1·26	0·74	0·58	6·55
203	0·84	1·16	0·42	5·63
204	0·42	1·58	0·13	5·58

(a) Values of H_o taken from reference 45.

Mean $^1k_2$ = 6·0 ± 0·2 x 10^{-2} $mole^{-1}$ litre min^{-1}.

added and m depends upon the cation present. Using rate constants from Runs 194 and 204 it is possible to calculate a value of m, since these rate constants are equivalent to k_2 and k_2^o respectively. The calculated value of m is 0·41. However, addition of sodium perchlorate increases the value of $-H_o$,[45] and so k_2 has to be corrected[123] to the same H_o value as k_2^o. The value of m obtained after this correction is 0·22. This is to be compared with the value of 0·27 in the diazotisation of o-chloroaniline[122] and 0·219 in the diazotisation of 4-aminopyridine.[123]

Thus the perchlorate anion exerts a medium effect as observed in the diazotisation of aromatic amines. In contrast to the diazotisation of aromatic amines, nitrosation of 3-chloro-2-methylpropene in perchloric acid follows h_o.

The rate-expression for the nitrosation of 3-chloro-2-methylpropene in perchloric acid is:

$$\text{Rate} = {}^1k_3[\text{Olefin}][HNO_2]h_o \qquad 6.02.$$

This expression can be interpreted as the direct reaction of 3-chloro-2-methylpropene with the nitrous acidium ion. The possibility of attack of the nitrosonium ion on the olefin is eliminated[123] because this would require a rate-expression of the type; Rate = ${}^1k_3[\text{Olefin}][HNO_2]h_o^2$, since the concentration of the nitrosonium ion is proportional to $[HNO_2]h_o^2$.

In the diazotisation of p-nitroaniline[47], the plot of log k_2 against $-H_o$ was a curve and the slope exceeded unity. To allow for the medium effect of perchloric acid values of k_2^o were calculated from equation 6.03;

$$\log k_2 = \log k_2^{o} + m[HClO_4] \qquad 6.03.$$

In the plot of log k_2^{o} against $-H_o$ the values were on a straight line of approximately unit slope. Thus k_2^{o} was proportional to h_o. The equivalent treatment of Runs 191 to 194 yielded a straight line plot of log k_2^{o} versus $-H_o$, but the slope was approximately 0·4.

Thus the nitrosation of 3-chloro-2-methylpropene in perchloric acid can be accounted for completely by attack of the nitrous acidium ion without the incursion of a medium effect. However, at constant concentration of perchlorate anion, the rate constant is effectively unchanged, although the acidity of the medium was varied. Under these conditions, a medium effect, of the type identified by Ridd and co-workers, appears to become the dominant factor.

2,3-dimethyl-2-butene was observed to be nitrosated by the nitrous acidium ion in very low acid. Obviously 2,3-dimethyl-2-butene is much more reactive than 3-chloro-2-methylpropene. The ratio of the third order rate constants for the nitrosation by the nitrous acidium ion of 2,3-dimethyl-2-butene and 3-chloro-2-methylpropene in perchloric acid is

$$\frac{4{\cdot}73 \times 10^{3}}{1{\cdot}45 \times 10^{-2}} \simeq 3 \times 10^{5}$$

6.3 Nitrosation of 3-chloro-2-methylpropene and 3-hydroxy-2-methylpropene in sulphuric acid

The kinetics of nitrosation of 3-chloro-2-methylpropene were studied in

0·20 to 1·40M sulphuric acid. Table 6.4 shows a run at 0·225M sulphuric acid, including the correction for nitrous acid decomposition. The first order plots before and after correction are shown in Fig.6.03. The second order rate constants before and after correction for nitrous acid decomposition are shown in Table 6.5. Plots of log $^1k_2$ against log[H^+] and H_o do not yield straight lines.

To determine whether nitrosation in sulphuric acid followed the Hammett acidity function, a series of runs were set up in a broader range of acidity (0·20 to 2·70M) to study the nitrosation of 3-hydroxy-2-methylpropene. In an investigation of the suitability of organic solvents as the reaction medium for nitrosation of olefins, it was discovered that alcohols reacted with nitrous acid. Thus, prior to the kinetic investigation of the nitrosation of the above olefin, the reaction of nitrous acid with purified isobutanol was shown to be insignificant in comparison to the rate of nitrosation of the olefin under the same experimental conditions.

To confirm that the rate is still dependent on the concentration of the olefin, a series of runs were followed in 1·35M sulphuric acid with varying olefin concentrations. The runs were first order with respect to nitrous acid and the variation of the first order rate constants with olefin concentration is shown in Table 6.6. The dependence on the olefin, determined by least squares analysis, is 0·95.

The second order rate constants for the nitrosation of 3-hydroxy-2-methylpropene in sulphuric acid are collected in Table 6.7.

Table 6.4.

Run 190

Nitrosation of 3-chloro-2-methylpropene in 0·225M sulphuric acid at 0°C

Time (hours)	Optical Density	Corrected Optical Density
0·00	0·363	0·363
3·12	0·349	0·353
14·45	0·311	0·328
24·28	0·298	0·325
37·20	0·259	0·296
56·03	0·214	0·261
85·53	0·180	0·241
125·77	0·131	0·198
174·27	0·097	0·168
205·53	0·067	0·127

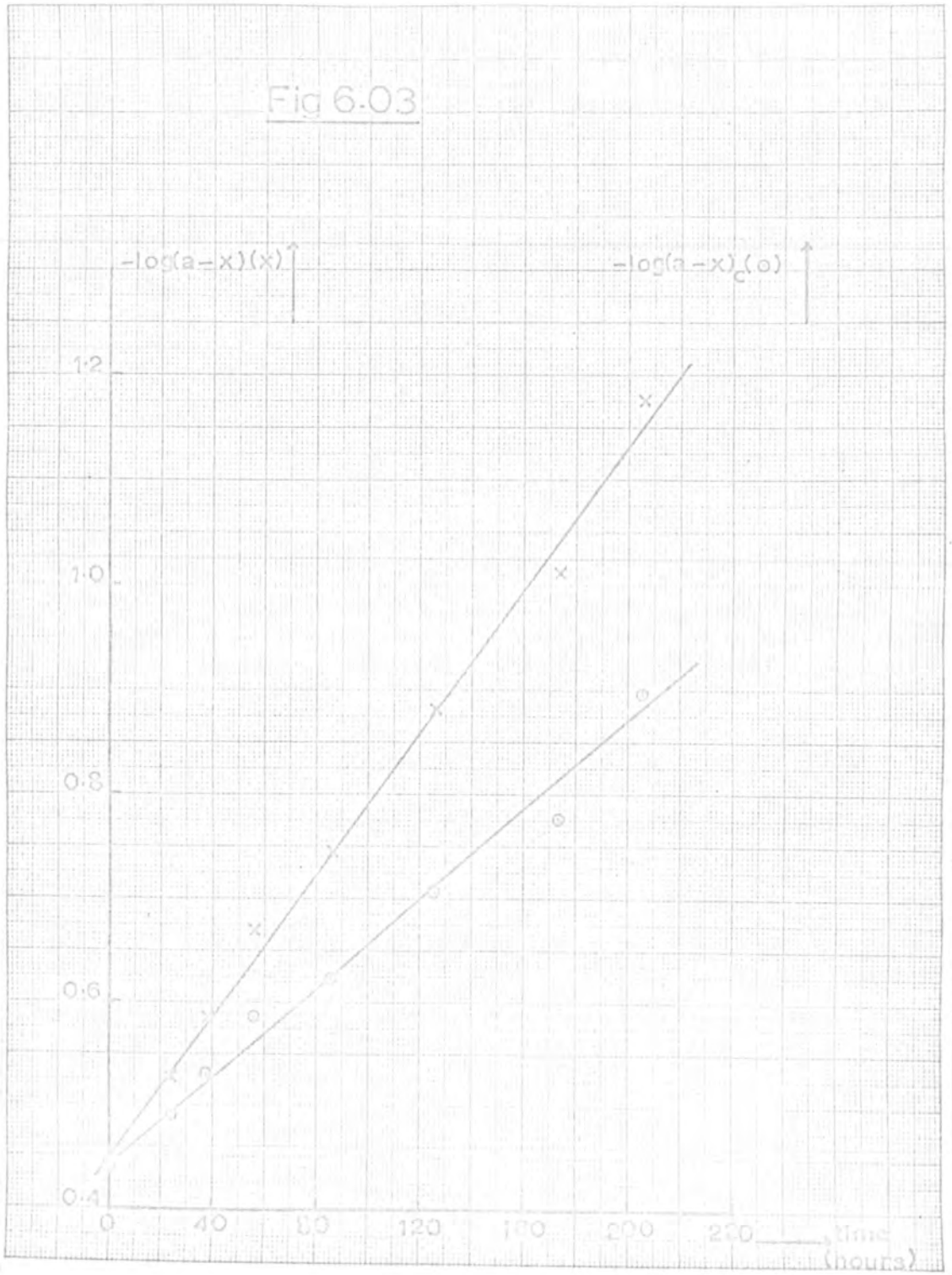


Fig 6.03
-log(a-x)(x)
-log(a-x)(o)
1·2
1·0
0·8
0·6
0·4
0
40
80
120
160
200
240
Time (hours)

Table 6.5.

Second order rate constants for the nitrosation of 3-chloro-2-methylpropene in sulphuric acid at 0°C

Run	$[H_2SO_4]M$	$[H^+]N$(a)	h_o(a)	$^1k_2 \times 10^2$ (moles^{-1}litre min^{-1})	$^1k_2 \times 10^2$ (corrected) (moles^{-1}litre min^{-1})
198	1·35	1·74	3·10	3·62	2·70
199	0·90	1·16	1·58	2·75	2·08
189	0·675	0·858	1·03	2·53	1·63
200	0·45	0·581	0·66	2·04	1·33
190	0·225	0·297	0·30	2·09	1·26

(a) Taken from reference 124.

Table 6.6.

Variation of first order rate constants for the nitrosation of 3-hydroxy-2-methylpropene in 1·35M sulphuric acid at 0°C

Run	3 + log[olefin]	$1 + \log {}^{1}k_{1}$
217	0·722	0·428
210	0·883	0·572
216	0·961	0·676
223	0·999	0·683

Table 6.7.

Second order rate constants for the nitrosation of 3-hydroxy-2-methylpropene in sulphuric acid

Run	$[H_2SO_4]$M	$[H^+]_N$(a)	h_o(a)	$^1k_2 \times 10^2$ (mole^{-1}litre min^{-1})	Mean $^1k_2 \times 10^2$ (mole^{-1}litre min^{-1})
257	2·70	3·58	17·5	847	847
256	2·25	2·98	10·6	293·3	285 ± 6
250	2·25	2·98	10·6	276·7	
255	1·80	2·38	5·89	121·7	111 ± 8
251	1·80	2·38	5·89	100	
210	1·35	1·74	3·10	81·4	83·3 ± 1·2
216	1·35	1·74	3·10	86·4	
217	1·35	1·74	3·10	84·7	
223	1·35	1·74	3·10	80·6	
213	0·90	1·16	1·58	28·4	28·3 ± 0·1
220	0·90	1·16	1·58	28·1	
214	0·45	0·581	0·66	8·05	7·9 ± 0·1
221	0·45	0·581	0·66	7·73	
215	0·225	0·297	0·30	3·45	3·7 ± 0·2
222	0·225	0·297	0·30	4·02	

(a) Values taken from reference 124

The plot of log $^{1}k_2$ against $-H_o$ is shown in Fig.6.04. This plot is a straight line and has a slope of 1·3, which is quite near to unity.

The solvent isotope effect was determined by setting up two runs in 1·50M sulphuric acid at 4°C, one in D_2O. The runs yielded good first order plots. The results are shown in Table 6.8.

Table 6.8.

Run	Solvent	$^{1}k_2$ (mole^{-1}litre hr^{-1})
280	H_2O	36·6
281	D_2O	76·6

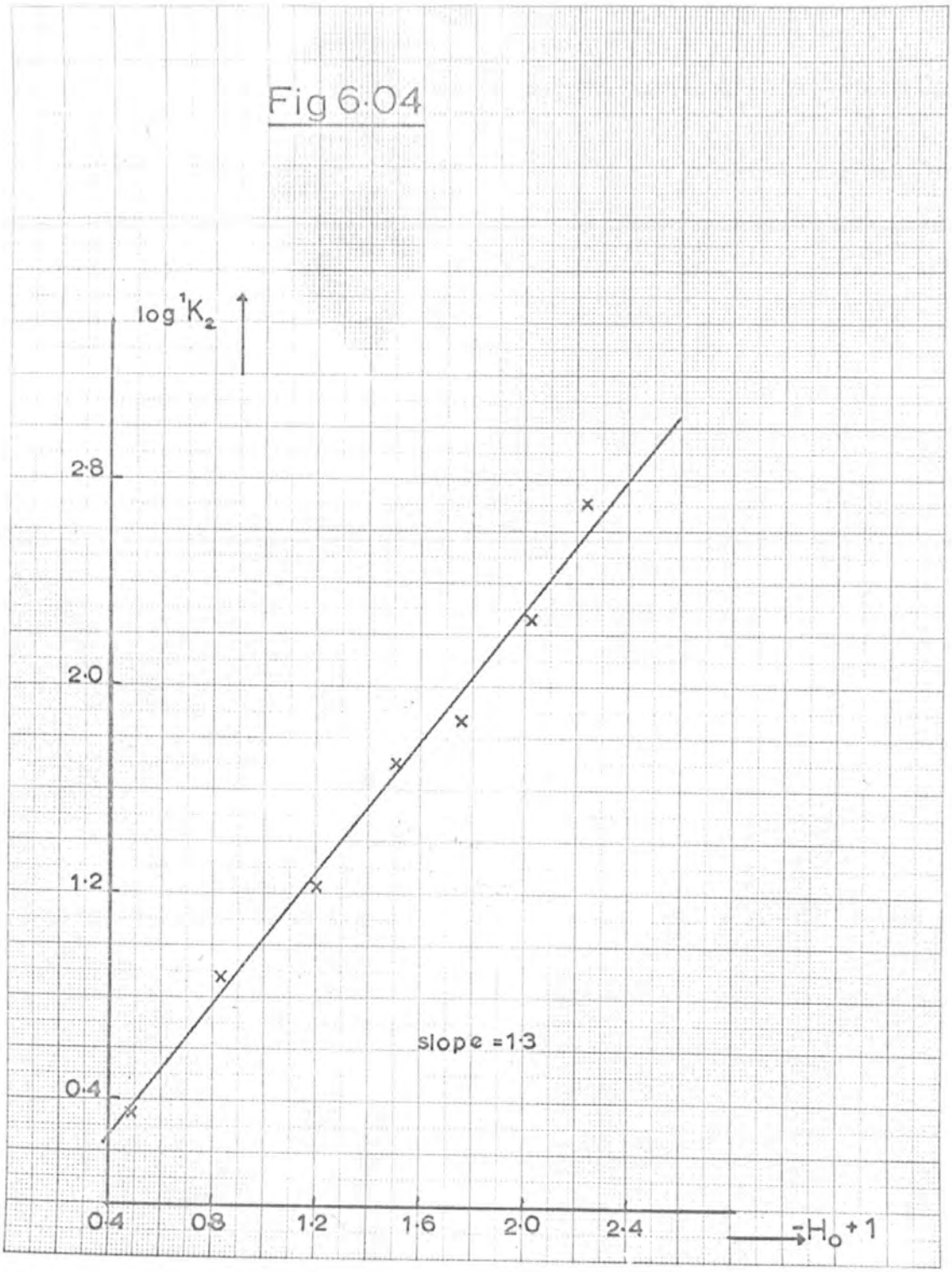
$$\therefore \frac{^{1}k_2^{D_2O}}{^{1}k_2^{H_2O}} = 2{\cdot}10$$

However, the deuterium oxide was only 99% D_2O

Hence, the isotope effect was $\dfrac{k_2^{D_2O}}{k_2^{H_2O}} = 2{\cdot}19$

The observed solvent isotope effect of 2·19 is comparable with that observed in the diazotisation of p-nitroaniline[47], which was the same in

Fig 6·04



both sulphuric and perchloric acids. A similar isotope effect (a factor of 2·2) has been observed in the formation of nitrosyl iodide from iodide ions and the nitrous acidium ion at low acidities.[125] This has been interpreted as suggesting that proton transfer to the nitrous acid molecule is essentially complete before the nucleophilic attacks the nitrous acidium ion. If the medium effect and reactivity of the nitrous acidium ion remain the same when the solvent is changed from water to D_2O, then the isotope effect can be ascribed to a two-fold increase in nitrous acidium ion concentration in the deuterated medium. The concentration of the nitrous acidium ion would be expected to increase on changing solvent to a deuterated medium since D_3O^+ in D_2O is a stronger acid than H_3O^+ in H_2O.

The solvent isotope effect in the nitrosation of 3-hydroxy-2-methyl-propene confirms the nitrous acidium ion as the nitrosating agent. This supports the results obtained in perchloric acid where the nitrous acidium ion was suggested as the nitrosating intermediate. In addition these results indicate that the nitrous acidium ion is formed in an equilibrium reaction before attacking the olefin, that is the possibility of synchronous protonation of nitrous acid and nitrosation of the olefin is eliminated.

The kinetic form of this reaction can be further rationalised in terms of the "Hammett-Zucker" treatment of acid-catalysed reactions.[126] Consider the following reaction scheme:

$$S + H^+ \overset{\text{fast}}{\rightleftharpoons} SH^+$$

$$SH^+ + Y \rightleftharpoons \neq \xrightarrow{\text{slow}} \text{products}$$

transition state

where $K_1 = \dfrac{[SH^+]}{[S][H^+]} \dfrac{f_{SH^+}}{f_S f_{H^+}}$

and $K_2 = \dfrac{[\neq]}{[SH^+][Y]} \dfrac{f_{\neq}}{f_{SH^+} f_Y}$

$\therefore V = k^{\neq}[\neq] = k^{\neq} K_2 [SH^+][Y] \dfrac{f_{SH^+} f_Y}{f_{\neq}}$

$= k^{\neq} K_1 K_2 [S][H^+][Y] \dfrac{f_S f_{H^+} f_Y}{f_{\neq}}$

$\therefore k_1 = \dfrac{V}{[S]} = k^{\neq} K_1 K_2 [H^+][Y] \dfrac{f_S f_{H^+} f_Y}{f_{\neq}}$

$= k^{\neq} K_1 K_2 [Y] a_{H^+} \dfrac{f_S f_Y}{f_{\neq}}$

$k_2 = \dfrac{V}{[S][Y]} = k^{\neq} K_1 K_2 h_o \dfrac{f_{BH^+}}{f_B} \dfrac{f_S f_Y}{f_{\neq}}$

Now, if $f_{\neq} = f_{SH^+} f_Y$

$$\text{then } k_2 = k^{\neq} K_1 K_2 h_o \frac{f_{BH^+}}{f_B} \frac{f_S}{f_{SH^+}}$$

It is quite reasonable to say that $\frac{f_{BH^+}}{f_B} = \frac{f_S}{f_{SH^+}}$ since it has been found that, although bearing no structural resemblance to anilines, the protonation of nitrous acid follows the Hammett acidity function.[127]

$$\text{Thus } k_2 = k^{obs} . h_o$$

The second order rate constants in the nitrosation of 3-hydroxy-2-methylpropene in sulphuric acid have been shown to follow h_o and so, as discussed earlier, this reaction can be interpreted as a rate determining attack of the nitrous acidium ion on the olefin.

Comparison of the second order rate constants for the nitrosation of 3-chloro-2-methylpropene in perchloric acid and sulphuric acid at the same h_o shows that the rate constant in perchloric acid is in general greater than that in sulphuric acid. This is in support of the identified perchlorate ion catalysis and at least shows that a catalytic effect of this nature is greater in perchloric acid than sulphuric acid.

Nitrosation of 2,3-dimethyl-2-butene by the nitrous acidium ion was studied in perchloric acid. However, an approximate ratio of the reactivities of 2,3-dimethyl-2-butene and 3-hydroxy-2-methylpropene towards the nitrous acidium ion can be obtained from the ratio of the rate constants;

$$\frac{4{\cdot}73 \times 10^{3}}{17{\cdot}5 \times 10^{-2}} \simeq 3 \times 10^{4}$$

Thus the following relative reactivities towards the nitrous acidium ion can be obtained, bearing in mind that they are very approximate:

Olefin	Relative rate of nitrosation by the nitrous acidium ion
3-chloro-2-methylpropene	1
3-hydroxy-2-methylpropene	~10
2,3-dimethyl-2-butene	$\sim 3 \times 10^{5}$

Thus, the rate of nitrosation of an olefin by the nitrous acidium ion is dependent on the reactivity of the olefin. In 1·35M sulphuric acid the rate constant for nitrosation of 3-hydroxy-2-methylpropene is greater by a factor of 30 than that for the nitrosation of 3-chloro-2-methylpropene. Although this factor is not the same in all the acidities studied, the rate constant for nitrosation of 3-hydroxy-2-methylpropene is always significantly greater than that for the nitrosation of 3-chloro-2-methylpropene. In addition the rate constant for nitrosation of 2,3-dimethyl-2-butene is much larger than that for either of the other two olefins. Thus the nitrous acidium ion is a very selective nitrosating agent in the nitrosation of olefins. This is in contrast to the observed lack of discrimination of the nitrous acidium ion in the nitrosation of aromatic amines as shown in Table 6.13[26]; which was suggested to be due to an encounter-controlled reaction.

Table 6.13.

Amine	k_3 (litre^2 mole^{-2} sec^{-1})	pKa
o-chloroaniline	175	2·77
p-nitroaniline	161	0·99
o-nitroaniline	145	-0·29

6.4 Nitrosation of 3-hydroxy-2-methylpropene and 3-chloro-2-methylpropene in the presence of halide ions in sulphuric acid

The kinetics of the halide-ion catalysed nitrosation of 3-hydroxy-2-methylpropene and 3-chloro-2-methylpropene were studied under conditions of acidity in which nitrosation by the nitrous acidium ion would be expected in the absence of catalysis.

Catalysis of the nitrosation of 3-hydroxy-2-methylpropene by added sodium bromide was studied initially and good first order plots were obtained. The first order rate constants were observed to show the same dependence on the olefin concentration and h_o as the rate constants for the uncatalysed process.

The results have been interpreted in terms of the following scheme of reactions:

$$H_2NO_2^+ + \rangle C{=}C \langle \xrightarrow{{}^1k_3}$$

$$NOBr + \rangle C{=}C \langle \xrightarrow{{}^1k_3^{Br}}$$

$\therefore$ Total rate $= {}^1k_3^{obs}$ [Olefin][Total nitrite] h_o

$= {}^1k_3^{obs}$ [Olefin][HNO_2] $h_o + {}^1k_3^{Br}$ [Olefin][NOBr]

$= {}^1k_3$[Olefin][HNO_2] $h_o + {}^1k_3^{Br} K^{Br}$[Olefin][$HNO_2$][$Br^-$] h_o

$\therefore {}^1k_3^{obs}$ [Total Nitrite] $= {}^1k_3$[HNO_2] $+ {}^1k_3^{Br} K^{Br}$[HNO_2][Br^-]

$\therefore {}^1k_3^{obs}\left([HNO_2] + [NOBr]\right) = {}^1k_3^{obs}\left([HNO_2] + K^{Br}[HNO_2][Br^-]\ h_o\right)$

$= {}^1k_3$[HNO_2] $+ {}^1k_3^{Br} K^{Br}$[Br^-][HNO_2]

$\therefore {}^1k_3^{obs}(1 + K^{Br}[Br^-]h_o) = {}^1k_3 + {}^1k_3^{Br} K^{Br}[Br^-]$

$$\therefore {}^1k_3^{obs} = \frac{{}^1k_3 + {}^1k_3^{Br} K^{Br}[Br^-]}{1 + K^{Br}[Br^-]h_o}$$

But $K^{Br}[Br^-]h_o \ll 1$, since $K^{Br} = 2{\cdot}2 \times 10^{-2}$

$\therefore {}^1k_3^{obs} = {}^1k_3 + {}^1k_3^{Br} K^{Br}[Br^-]$

$^1k_3$ is known from the previous section and $K = 2{\cdot}2 \times 10^{-2}$ at 0^oC for nitrosyl bromide.[128]

$$\therefore\ ^1k_3^{Br} = \frac{^1k_3^{obs} - {}^1k_3}{K[Br^-]}$$

The calculation of $^1k_3^{Br}$ for the nitrosation of 3-hydroxy-2-methylpropene in 0·45M sulphuric acid in the presence of varying concentrations of sodium bromide is shown in Table 6.9. The calculated third order rate constants for nitrosation by nitrosyl bromide are inaccurate. The calculation includes significant assumptions and also any ionic strength effect of the added sodium bromide has been ignored. This has, however been kept to a minimum by working at low concentrations of sodium bromide.

A series of runs were set up in which the catalysis due to the chloride ion could be studied. The results obtained are shown in Table 6.10 and are subject to similar inaccuracies to the nitrosyl bromide studies. The ionic strength effect would be expected to be greater in the case of nitrosyl chloride than nitrosyl bromide since the overall catalytic effect is less for nitrosyl chloride.

The relative reactivity of nitrosyl chloride and nitrosyl bromide towards 3-hydroxy-2-methylpropene is;

$$\frac{^1k_3^{Cl}}{^1k_3^{Br}} = \frac{1{\cdot}6 \times 10^2}{24} = 6{\cdot}7$$

Table 6.9.

Third order rate constants for the nitrosation of 3-hydroxy-2-methyl propene in the presence of sodium bromide at 0°C

$[H_2SO_4]$ = 0·45M; h_o = 0·66

Run	$[Br^-]$	$^1k_3^{obs} \times 10^2$ (mole^{-2}litre^{2}min^{-1})	Mean $^1k_3^{obs} \times 10^2$ (mole^{-2}litre^{2}min^{-1})	$^1k_3^{Br}$ (mole^{-2}litre^{2}min^{-1})
214	0	12·2	12·0 ± 0·2	-
221	0	11·7		
235	0·1	17·0	16·9 ± 0·1	22
236	0·1	16·7		
239	0·2	19·1	19·3 ± 0·1	17
240	0·2	19·5		
233	0·5	44·5	44·5	30
234	0·5	44·5		

Mean $^1k_3^{Br}$ = 24 ± 5 mole^{-2}litre^{2}min^{-1}

Table 6.10

Third order rate constants for the nitrosation of 3-hydroxy-2-methylpropene in the presence of sodium chloride at 0°C (Using K = 5·4 x 10^{-4} at 0°C.[129])

Run	$[Cl^-]$	$^1k_3^{obs}$ x 10^2 ($mole^{-2}litre^2min^{-1}$)	$^1k_3^{Cl}$ x 10^{-2} ($mole^{-2}litre^2min^{-1}$)
214/221	0	12·0	-
248	0·3	13·8	1·1
245	0·5	17·8	2·1

Mean $^1k_3^{Cl}$ = 1·6 ± 0·4 x 10^2 $mole^{-2}litre^2min^{-1}$

$[H_2SO_4]$ = 0·45M; h_o = 0·66

If nitrosyl bromide attacks 3-hydroxy-2-methylpropene, then the product should be that obtained by the attachment of the elements of nitrosyl bromide to the olefin. The product from a reaction simulating run conditions contains bromine and has properties which indicate that the elements of nitrosyl bromide were added to the olefin in the reaction. The mass spectrum had no parent peak, the highest mass peak was M151/3 (P-NO). The base peak was M30 (NO^+). The following peaks were present M137/139 (P-CH_2NO), M120/122 (P-CH_3NO_2), M72 (P-NOBr), M58 (P-CH_2NOBr), M41(P-CH_3NO_2Br) and M27 (P-$C_2H_5NO_2Br$). This is consistent with the mass spectrum of 3-hydroxy-2-bromo-2-methylnitrosopropane.

A series of runs were now set up to study the catalytic effect of sodium bromide on the nitrosation of 3-chloro-2-methylpropene. Once more they yielded good first order plots and the third order rate constants are included in Table 6.11.

Table 6.11

Third order rate constants for the nitrosation of 3-chloro-2-methylpropene in the presence of sodium bromide at $0^{o}C$

$[H_2SO_4] = 1{\cdot}35M; \quad h_o = 3{\cdot}1$

Run	$[Br^-]$	$^1k_3^{obs} \times 10^3$ (moles^{-2}litre^{2}min^{-1})	$^1k_3^{Br}$ (moles^{-2}litre^{2}min^{-1})
198	0	8·7	-
197	0·1	51·9	19·6
207	0·3	107·2	14·9
196	0·5	151·2	13·0

Mean $^1k_3^{Br} = 15{\cdot}8 \pm 1{\cdot}6$ moles^{-2}litre^{2}min^{-1}

If a comparison of the reactivity of nitrosyl bromide to 3-chloro-2-methylpropene and 3-hydroxy-2-methylpropene is valid, then it is

$$\frac{\left({}^{1}k_{3}^{Br}\right)OH}{\left({}^{1}k_{3}^{Br}\right)Cl} = \frac{24}{15{\cdot}8} = 1{\cdot}5$$

Thus the hydroxy group increases the reactivity of the olefin towards electrophilic nitrosation.

It should be possible to obtain further quantitative comparison of the reactivity of 3-hydroxy-2-methylpropene and 3-chloro-2-methylpropene from the study of the acid-catalysed mechanism of nitrosation. However, this is not possible since, in the region studied, the nitrosation of 3-chloro-2-methylpropene is not accurately described by a dependence on h_o or $[H^+]$. The dependence on h_o is inferred from the study of the nitrosation of 3-hydroxy-2-methylpropene.

The reactivity of 3-hydroxy-2-methylpropene to nitrosyl bromide as compared with 3-chloro-2-methylpropene is only increased by a factor of 1·5. In a study of the comparative reactivity of 3-hydroxypropene and 3-chloropropene in the bromination reaction in methanol, the hydroxy compound was more reactive by a factor of 130.[130] It will be remembered that a similar difference was noted in the comparative reactivities of 2,3-dimethylbutene and 2-methylbutene, but the difference was not so significant. It appears that, although the reactivity of the olefin has been increased very significantly (a factor of 130), the rate constant changes only very little.

The very small change of the rate constant for nitrosation by nitrosyl bromide on changing to a more reactive olefin shows that nitrosyl bromide is not a very selective nitrosating agent. Similarly, the rate of nitrosation of aromatic amines by nitrosyl chloride has been shown to be almost independent of the basicity of the amine. The rate constants are collected in Table 6.12.[26] For comparison, p-toluidine is more basic than o-chloroaniline by a factor of 250 whilst the rate constant is only increased by a factor of 2·5.

Table 6.12.

Nitrosation of aromatic amines by nitrosyl chloride at 25°C

Amine	$10^{-9}k$ ($mole^{-1}$ litre sec^{-1})
o-chloroaniline	1·16
m-chloroaniline	1·63
p-chloroaniline	1·89
aniline	2·60
o-toluidine	2·44
m-toluidine	2·70
p-toluidine	3·00

6.5 Summary

The decomposition of nitrous acid in the range of acidity studied was first order with respect to nitrous acid and independent of the acidity. An acid-catalysed nitrosation has been identified in the reaction with 3-chloro-2-methylpropene, which is subject to a medium effect of the perchlorate anion similar to that observed in diazotisation. The nitrous acidium ion has been shown to be the nitrosating agent in 0·40 to 1·70N perchloric acid and in 0·20 to 1·40M sulphuric acid. This was positively confirmed by the solvent isotope effect of 2·2. The nitrosation has been shown to be subject to specific halide ion catalysis by bromide and chloride ions. This was consistent with rate determining attack by nitrosyl bromide or nitrosyl chloride on the olefin. The reaction of nitrosyl bromide with an olefin has been shown to have only a small dependence on the reactivity of the olefin whereas the nitrous acidium ion has been shown to be a very selective nitrosating agent.

Chapter 7.

Experimental techniques for the kinetic study.

(Chapter 5 and 6)

7.1 Materials

"AnalaR" grade chemicals have been used, when available, without further purification, except for drying where necessary.

(a) 2-methyl-2-butene: A commercial sample was shown to be pure by vapour phase chromatography and was used without further purification.

(b) 3-chloro-2-methylpropene and 3-hydroxy-2-methylpropene: Commercial samples were purified by preparative scale vapour phase chromatography.

(c) 2,3-dimethyl-2-butene: This was prepared[131] in the laboratory because the commercial sample contained large amounts of impurities. A mixture of pinacolyl alcohol (100 gm.) and 85% phosphoric acid (75 ml.) was slowly heated to 135°C while volatile material formed was allowed to distill. The distillate was washed with water, dried, and distilled from Drierite through a column. This distillate was very impure as shown by vapour phase chromatography and thus was purified by preparative scale vapour phase chromatography.

(d) Sodium nitrite: "AnalaR" sodium nitrite was recrystallised from distilled water and dried over phosphorous pentoxide.

7.2 Kinetic Method

Runs were carried out at 0°C, temperature control being obtained in a thermostat. The thermostat was maintained at 0°C with a cold finger unit and accurate temperature control was provided by a contact thermometer.

The thermostat bath contained dilute antifreeze to prevent ice formation on the cold finger unit.

Kinetic runs were performed in a total volume of 100 ml. 90 ml. of reaction solution containing the olefin and acid were allowed to reach the thermostat temperature over a period of time. To commence the run 10 ml. of a stock sodium nitrite solution, already at $0^{o}C$, was added and the solution shaken vigorously. Samples were withdrawn by either a 2 ml. or a 5 ml. pipette at suitable time intervals, and run into the analytical solution "A", the time being noted when the pipette was half discharged. The reaction of nitrous acid with sulphanilic acid in solution "A" is virtually instantaneous and so the reaction is quenched immediately. The diazonium salt formed in solution"A"was coupled with solution "B" to form the azo-dye and the whole made up to a total volume of 50 ml. Runs were done in duplicate so that reproducibility of runs should be easier.

The kinetic run on the deuterium solvent isotope effect of the nitrosation of 3-hydroxy-2-methylpropene was carried out at $4^{o}C$, by simply raising the temperature of the thermostat.

7.3 Analytical Techniques

7.3.(a) Nitrous acid

Analysis for nitrous acid was done colorimetrically and was based on the Ridd-Halevi variation of the Greiss-Ilosvay colorimetric method.[132] α-Naphthylamine was not used as the coupling agent in these studies since it is

carcinogenic. It was replaced by 2-naphthol-3,6-disulphonic acid.

Two stock solutions were required for this method:

(1) Solution "A": 10 gm. of sodium bromide
0·5 gm. sulphanilic acid
13 ml. of 60% perchloric acid
} in 500 ml.

(2) Solution "B": 0·25 gm. 2-naphthol-3,6-disulphonic acid
30 gm. borax
} in 1000 ml.

Preparation for a kinetic run involved adding 5 ml. of solution "A" to a series of 50 ml. volumetric flasks. Reaction samples were run into this solution "A" and allowed to stand for 5 minutes. 10 ml. of solution "B" were added and the solution allowed to stand for 10 minutes to allow time for colour development. Immediately prior to recording the optical density on a Unicam S.P.500, the total volume was increased to 50 ml. with distilled water. Since the concentration of nitrous acid in the runs only varied by a factor of 2, the optical density always fell into a convenient range. When long runs were followed (longer than two days), it was necessary to take more reaction samples and thus a 2 ml. pipette was used. The optical density was obtained in a convenient range by changing the 1 or 2 cm. cells for 4 cm. cells. Sulphanilic acid and 2-naphthol-3,6-disulphonic acid were always maintained in excess concentration so that the diazotisation and coupling reactions were rapid.

At higher acidities the borax added in 10 ml. of solution "B" was insufficient to buffer the coupling solution to the correct pH. Thus, an

appropriate volume of sodium hydroxide was introduced prior to the addition of solution "B" to neutralise some of the acid and allow the borax to buffer the coupling solution to the correct pH.

7.3(b) Olefin

It was found to be inaccurate to make up aqueous solutions of olefin by introducing a weighed quantity of olefin. The solubility of the olefins, excepting 3-hydroxy-2-methylpropene, was very low and to obtain homogeneous solutions they had to be shaken for some hours. When it is realised that the boiling point of 2-methyl-2-butene is $38{\cdot}4^{o}C$, it is not surprising that significant quantities were lost by evaporation on shaking.

10 ml. of the aqueous olefin solution was added to 2 ml. of standard N/5 bromide-bromate solution, followed by excess dilute acid. This solution was allowed to stand for 10 minutes. The excess bromide-bromate was determined by adding excess potassium iodide solution and titrating the liberated iodine with standardised sodium thiosulphate. No indicator was required since the end-point was quite distinct.

The bromide-bromate used was M/30 with respect to bromate and hence M/10 or N/5 with respect to bromine. The reaction taking place is:

$$BrO_3^- + 5Br^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

$$Br_2 + \rangle C{=}C \langle \longrightarrow$$

2 ml. of N/5 bromine is equivalent to 4 ml. of M/20 bromine, therefore to remove all the bromine, the olefin must be xM, where x is given by:

$$4 \times 0{\cdot}05 = 10 \times xM$$

$$\therefore \quad \underline{x = 0{\cdot}02M}$$

Therefore, this technique is capable of measuring the concentration of 10 ml. of an olefin solution up to 0·02M. Higher olefin concentrations can be measured by using a smaller volume of the olefin solution.

7.3(c) Perchloric acid and sulphuric acid

Stock solutions were standardised by titration with sodium hydroxide solution, which itself was standardised by titration with B.D.H. standard acid. The acidity of reaction solutions was determined either by titration or by dilution of a standardised stock solution.

The normality of dilute sulphuric acid solutions was easily determined by titration. In more concentrated solutions, however, it was only possible to determine the molarity of the sulphuric acid solutions. The normalities and h_o values of sulphuric acid solutions were taken from Table 7.1.

7.3.(d) Spectrophotometric Measurements

The optical density of the solutions of the azo-dye was measured in 1, 2 or 4 cm. glass cells on a Unicam SP.500 at 492 mμ. The azo-dye was shown to obey the Beer-Lambert law over the range of optical density studied. The optical density corresponding to various concentrations of nitrous acid is shown in Table 7.2. The plot showing the obedience of the Beer-Lambert law is shown in Fig.7.01.

Table 7.1.[a]

$[H_2SO_4]$M	$[H^+]$M	h_o
0·0994	0·132	0·136
0·1981	0·260	0·275
0·2961	0·383	0·418
0·3933	0·508	0·572
0·4899	0·631	0·735
0·5858	0·754	0·907
0·6809	0·874	1·09
0·7754	0·992	1·28
0·8691	1·11	1·51
0·9623	1·24	1·77
1·417	1·82	3·43
1·855	2·46	6·28
2·277	3·01	10·6
2·683	3·58	17·5
3·073	4·08	27·1
3·448	4·59	40·6

(a) Taken from reference 124.

Table 7.2.

Optical density of azo-dye produced by sodium nitrite in the presence of excess perchloric acid

$[NaNO_2] \times 10^4$ N	Optical Density (in 1 cm. cells)
2·00	0·510
1·75	0·443
1·50	0·372
1·25	0·314
1·00	0·249
0·75	0·182
0·50	0·120
0·25	0·055

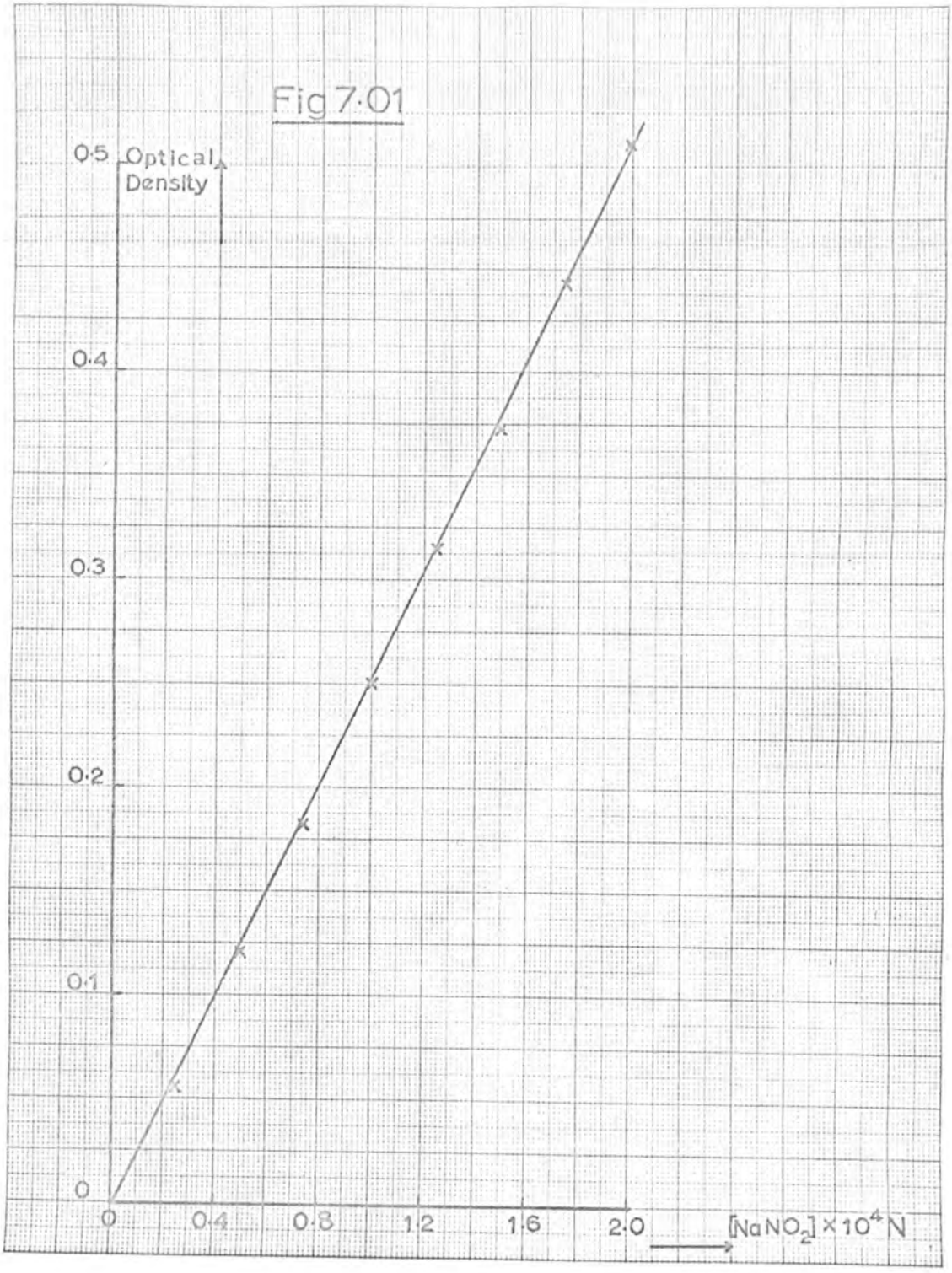


Fig 7·01
0·5
Optical Density
0·4
0·3
0·2
0·1
0
0
0·4
0·8
1·2
1·6
2·0
[NaNO2] × 10⁴ N

7.4 Typical Kinetic Runs

7.4.(a) At low acidity (<0·1M)

Kinetic runs representative of the conditions under which runs have been carried out are shown in Tables 7.3, 7.4 and 7.5.

7.4.(b) At high acidity (>0·2M)

First order rate constants were obtained from the slope of the plot of -log(a - x) v time. The slope is

$$\frac{-\log(a - x)}{t} = \frac{k}{2{\cdot}303}$$

therefore k = 2·303 x (slope). The first order plots shown in this section are listed in Table 7.6.

7.4.(c) Solvent-isotope effect

Details of the runs in water and D_2O to determine the solvent-isotope effect in 1·50M sulphuric acid are shown in Table 7.7. The first order plots for the runs are shown in Fig.707. and Fig.7.08.

Table 7.3.

Nitrosation of 2-methyl-2-butene

Run 15

$[HClO_4] = 4{\cdot}21 \times 10^{-4}$ M [Olefin] = 0·001 M

$[NaNO_2] = 2 \times 10^{-4}$ N Temperature = 0°C

Sample 5 ml. Cells 2 cm.

Time (hours)	Optical Density	$\bar{2}k_2 \times 10^2$ ($O.D.^{-1}\ hr^{-1}$)
0·00	0·730	-
5·02	0·665	2·66
7·03	0·643	2·63
9·95	0·623	2·36
24·65	0·495	2·63
31·35	0·453	2·67
48·37	0·395	2·40
60·28	0·338	2·63
70·97	0·304	2·63
84·43	0·295	2·39
99·58	0·269	2·35

Mean $\bar{2}k_2 = 2{\cdot}54 \times 10^{-2}\ O.D.^{-1}\ hr^{-1}$

$\therefore\ \bar{2}k_3 = 1{\cdot}60 \times 10^{3}\ mole^{-2}\ litre^{2}\ min^{-1}$

Table 7.4.

Nitrosation of 2,3-dimethyl-2-butene

Run 261

$[HClO_4]$ = 2·14 x 10^{-4} M [Olefin] = 0·00165 M

$[NaNO_2]$ = 1 x 10^{-4} N Temperature = 0°C

Sample 2 ml. Cells 4 cm.

Time (hours)	Optical Density	$\overline{k}_1$ (hour^{-1})	$\overline{k}_2$ (O.D.$^{-1}$ hr.$^{-1}$)
0·00	0·389	-	-
0·73	0·356	0·125	0·34
1·18	0·350	0·089	0·24
2·35	0·328	0·073	0·20
3·50	0·307	0·068	0·20
4·87	0·288	0·062	0·19
6·27	0·280	0·052	0·16
8·13	0·279	0·041	0·13
10·80	0·258	0·038	0·12
13·23	0·230	0·040	0·13
23·73	0·163	0·037	0·15
29·72	0·137	0·035	0·16
38·00	0·109	0·033	0·17
47·65	0·089	0·031	0·18
61·77	0·070	0·028	0·19
78·10	0·056	0·025	0·20
99·80	0·035	0·024	0·26

contd./

Table 7.4. (contd.)

Mixed first and second order treatment

dx/dt	$dx/dt/(a-x)$	$(a-x)$
0·0154	0·047	0·325
0·0117	0·039	0·300
0·0062	0·031	0·200
0·0056	0·032	0·175
0·0045	0·030	0·150
0·0031	0·025	0·125
0·0020	0·020	0·100
0·0012	0·016	0·075

Hence $\overline{1_{k_3}} = 9{\cdot}17 \times 10^2$ mole^{-2} litre^2 min^{-1}

$\overline{2_{k_3}} = 4{\cdot}35 \times 10^3$ mole^{-2} litre^2 min^{-1}

Table 7.5.

Nitrosation of 2,3-dimethyl-2-butene

Run 274

$[HClO_4]$ = 42·6 x 10^{-4} M [Olefin] = 0·00119 M

$[NaNO_2]$ = 1 x 10^{-4} N Temperature = 0°C

Sample 2 ml. Cells 4 cm.

Time (minutes)	Optical Density	$\bar{1}_{k_1}$ x 10^2 (min^{-1})
0·00	0·389	-
7·00	0·329	2·39
14·00	0·282	2·30
22·00	0·244	2·12
32·50	0·197	2·09
44·00	0·153	2·12
58·50	0·112	2·13
71·00	0·085	2·11
85·00	0·059	2·22
101·00	0·048	2·07

Mean $\bar{1}_{k_1}$ = 2·17 x 10^{-2} min^{-1}

Mean $\bar{1}_{k_3}$ = 4·28 x 10^3 $mole^{-2}$ $litre^2$ min^{-1}.

Table 7.6.

First order plots shown in this section

(i) For 3-hydroxy-2-methylpropene

Figure Number	$[Br^-]$ or $[Cl^-]$	Acid	Concentration
7·02	0	Sulphuric	0·45M
7·03	0	Sulphuric	1·80M
7·04	0·5N $[Br^-]$	Sulphuric	0·45M
7·05	0·3N $[Cl^-]$	Sulphuric	0·45M

(ii) For 3-chloro-2-methylpropene

7.06	0·5N $[Br^-]$	Sulphuric	1·35M

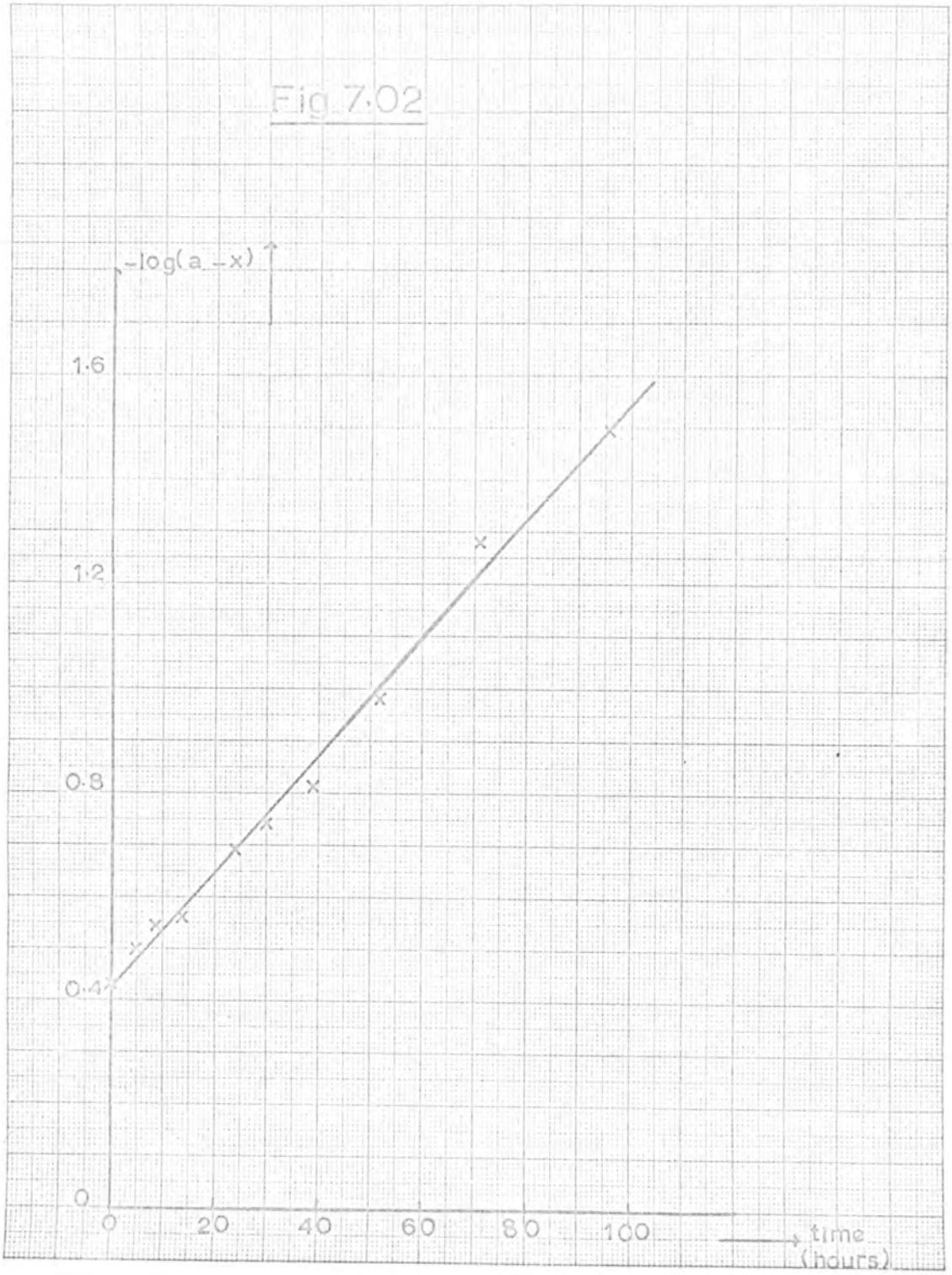


Fig. 7·02
-log(a-x)
1·6
1·2
0·8
0·4
0
0
20
40
60
80
100
time
(hours)

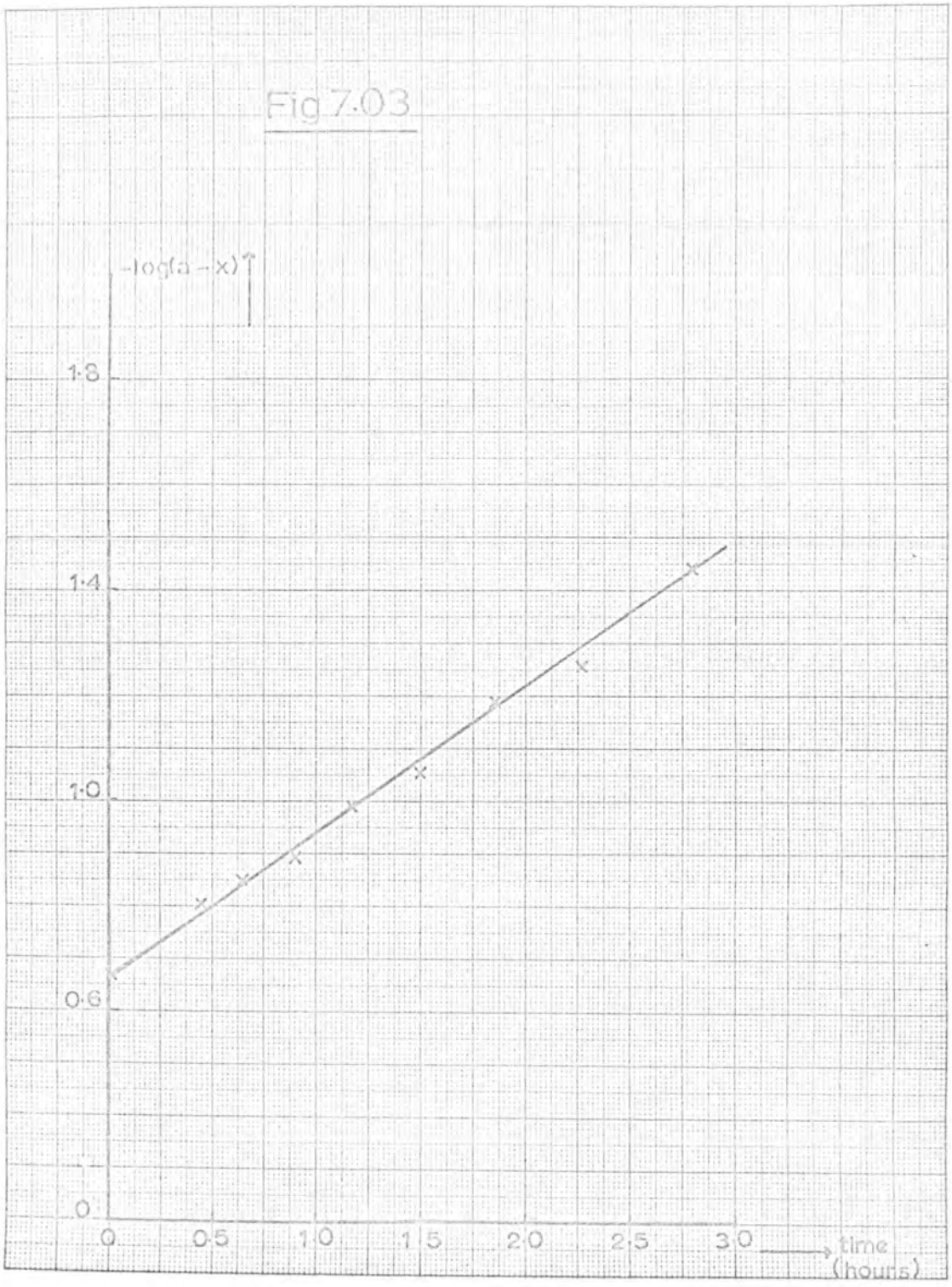
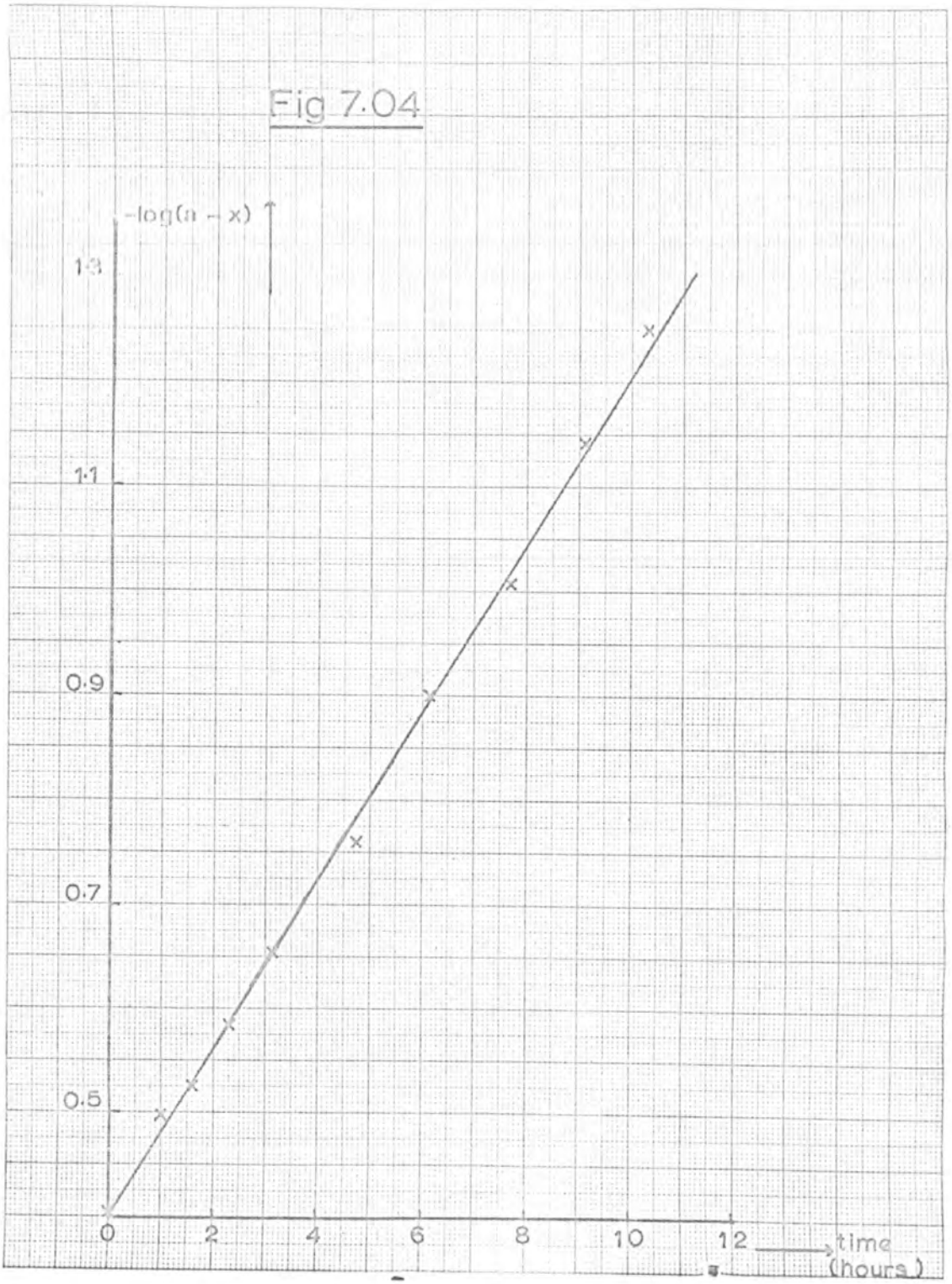


Fig 7.03
-log(a-x)
1·8
1·4
1·0
0·6
0
0
0·5
1·0
1·5
2·0
2·5
3·0
time
(hours)

Fig 7.04



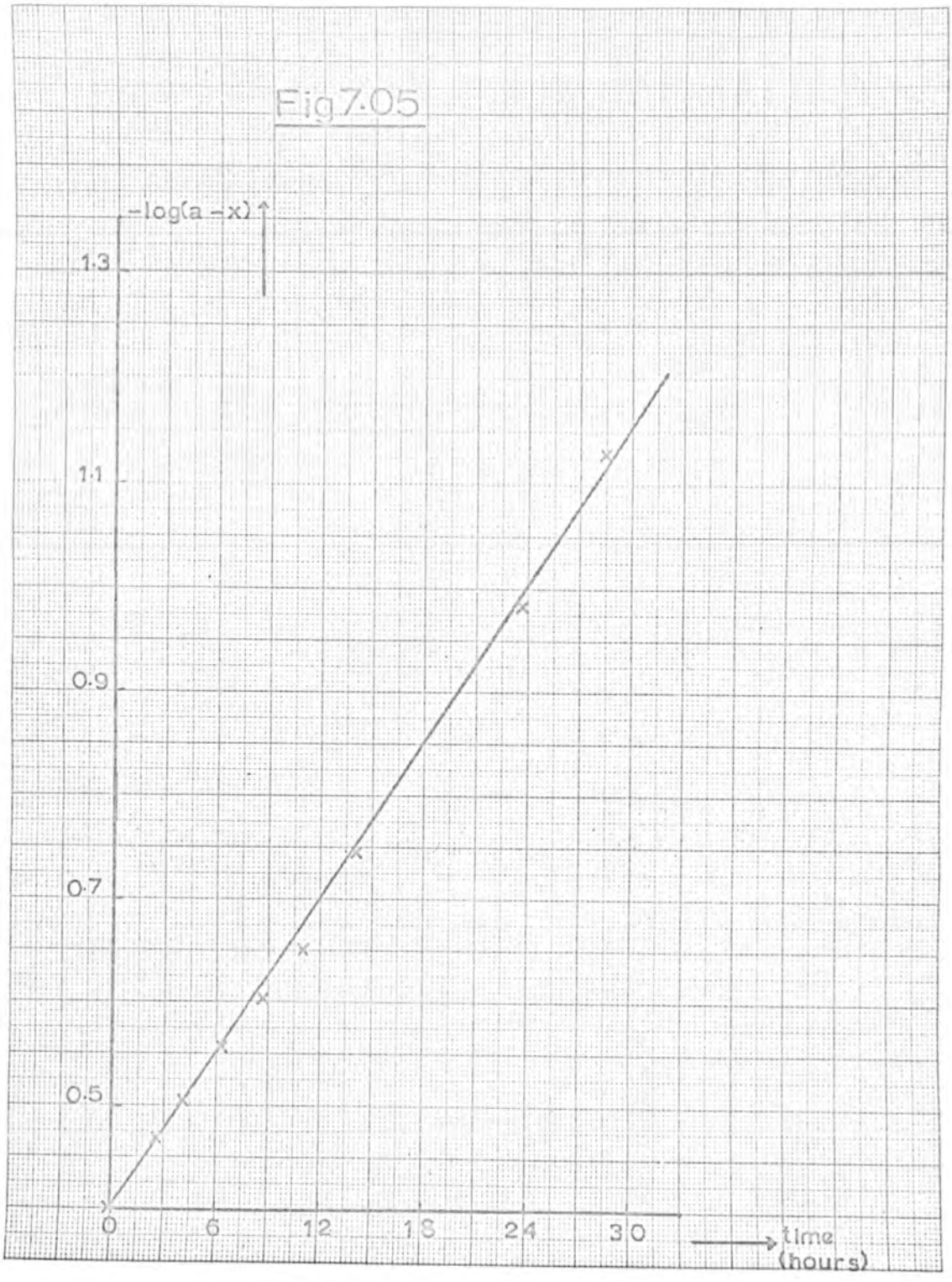


Fig 7.05
-log(a-x)
1.3
1.1
0.9
0.7
0.5
0
6
12
18
24
30
time
(hours)

Fig 7.06

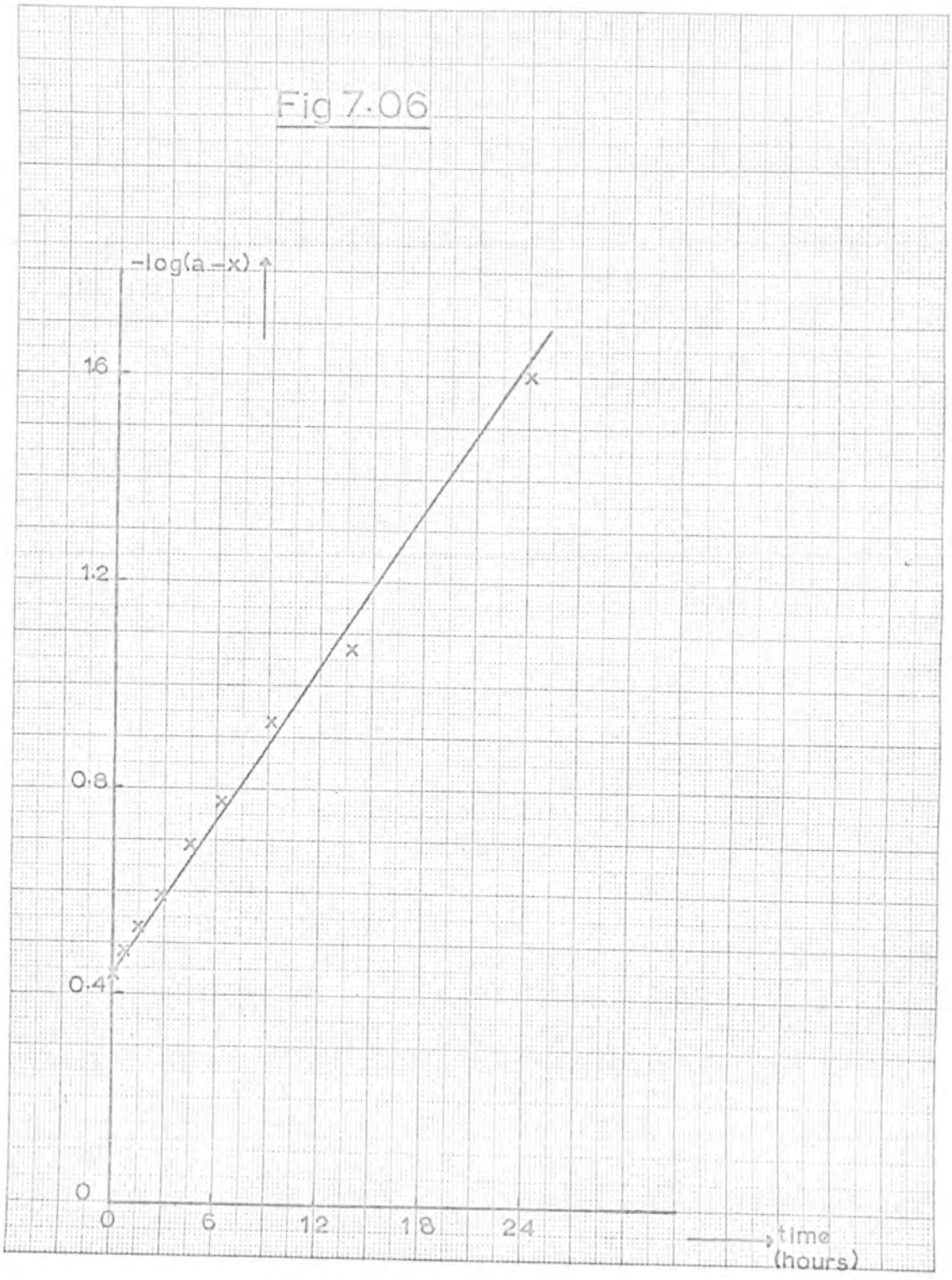


Table 7.7.

Nitrosation of 3-hydroxy-2-methylpropene in 1·50M sulphuric acid at 4°C

H_2O		D_2O	
[Olefin] = 0·0126M		[Olefin] = 0·0134M	
Time (hours)	Optical Density	Time (hours)	Optical Density
0·00	-	0·00	-
0·02	0·320	0·02	0·283
0·05	0·310	0·07	0·273
0·18	0·293	0·14	0·244
0·42	0·267	0·32	0·214
0·59	0·250	0·42	0·198
0·88	0·218	0·55	0·173
1·16	0·195	0·71	0·149
1·64	0·160	0·93	0·114
2·21	0·121	1·17	0·095
2·78	0·094	1·43	0·072
3·52	0·065	1·68	0·054
4·22	0·044	2·00	0·037
5·16	0·030	2·42	0·023

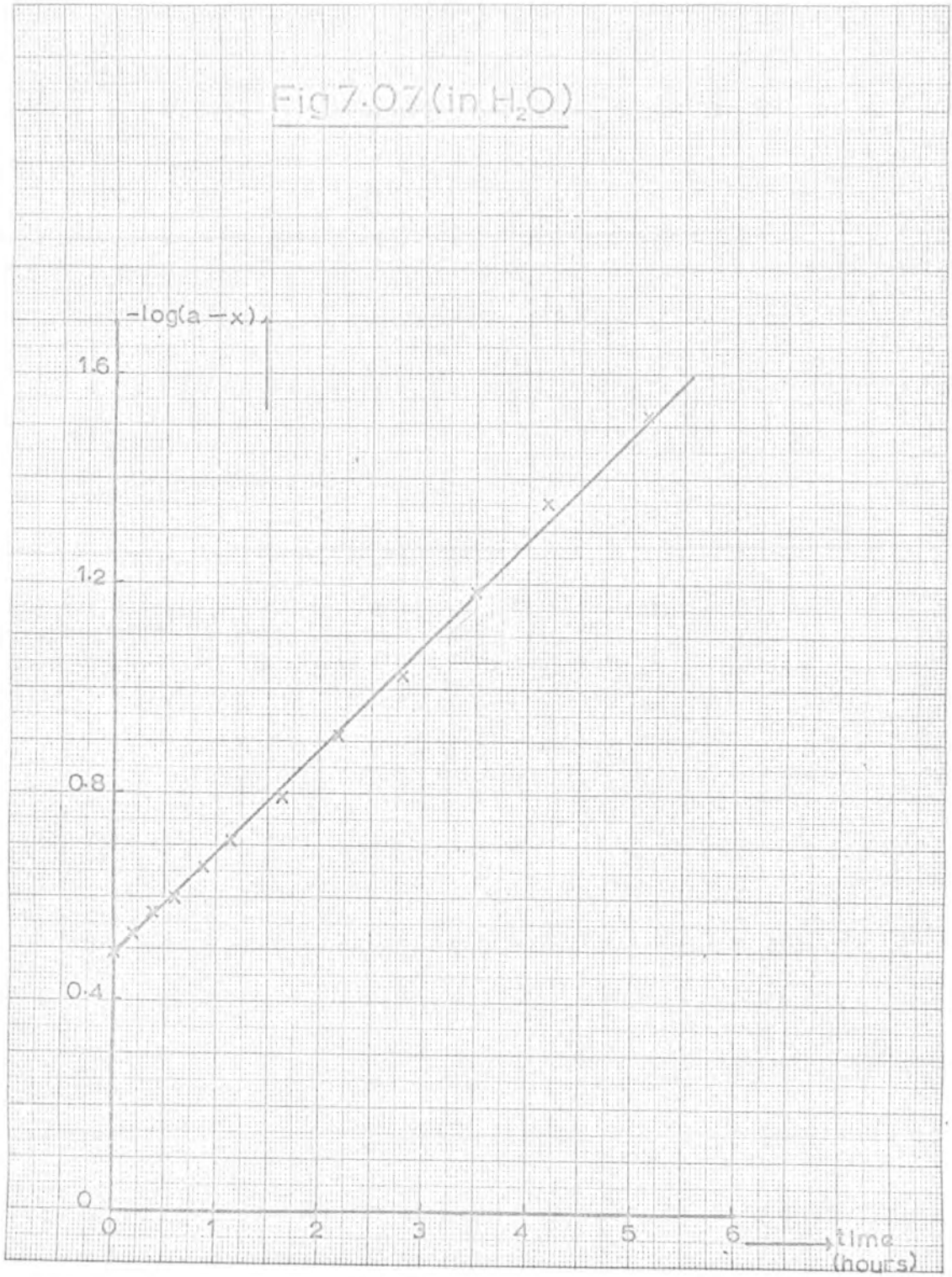


Fig 7.07 (in H_2O)
$-\log(a-x)$
1.6
1.2
0.8
0.4
0
0
1
2
3
4
5
6
time (hours)

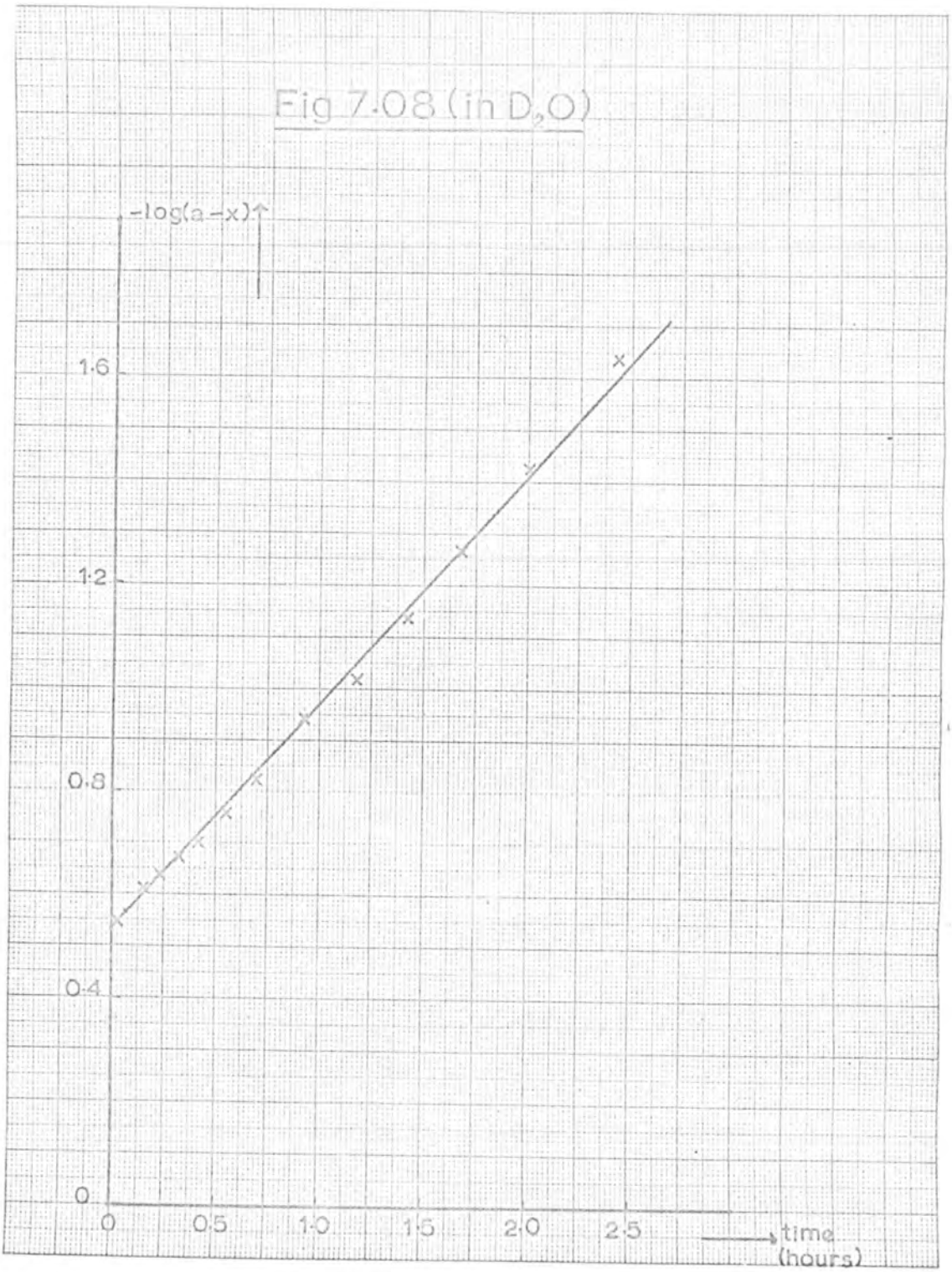


Fig 7·08 (in D_2O)
$-\log(a-x)$
1·6
1·2
0·8
0·4
0
0
0·5
1·0
1·5
2·0
2·5
time (hours)

7.5 Correction of runs at high acidity for the decomposition of nitrous acid

This correction was only necessary for the runs on the nitrosation of 3-chloro-2-methylpropene, since in other studies the decomposition was insignificant. A blank run, containing the same concentrations of acid and sodium nitrite, was followed concurrently with the nitrosation run. Thus at a particular time the concentration of nitrous acid in the blank run was either measured or could be read off a concentration-time curve

Each individual point was corrected in the following manner:

At time t, the concentration of nitrous acid in the blank was C_B moles and in the nitrosation run was C_R moles. The concentration of nitrous acid in the blank at time zero was C_O moles.

(C_O-C_B) moles of nitrous acid had decomposed at time t.

$$\frac{\text{Nitrous acid decomposed}}{\text{Nitrous acid remaining}} = \frac{C_O-C_B}{C_B}$$

Thus amount of nitrous acid in the nitrosation run which has disappeared by decomposition $= \left(\frac{C_O-C_B}{C_B}\right)C_R$

Hence the total concentration of nitrous acid that should be present in the nitrosation run is given by:

$$C_R + \left(\frac{C_O-C_B}{C_B}\right)C_R = C_R \cdot \frac{C_O}{C_B}$$

Run 193 was treated in this way and the results are included in Table 7.8.

7.6 Reaction simulating the conditions for the kinetic addition of nitrosyl bromide to 3-hydroxy-2-methylpropene

AnalaR concentrated sulphuric acid (25 gm.), sodium bromide (52 gm.) and 3-hydroxy-2-methylpropene (20 ml.) were added to 400 ml. water. This reaction solution was maintained at $0^{o}C$ and over the period of a week a sodium nitrite solution (17·5 gm. sodium nitrite in 50 ml.) was added. The aqueous layer was saturated with sodium sulphate and then ether extracted. On removal of the ether a brown oil was obtained.

The brown oil showed the typical peaks of a nitroso compound in its infrared spectrum. The mass spectrum (discussed in previous chapter) is consistent with a nitroso-bromide.

The elemental analysis observed was: C,29·9%; H,4·8%; N,4·4%; Br,39·6% whilst that expected for a nitroso bromide is C,26·3%; H,4·3%; N,7·6%; Br,43·9%.

Table 7.8.

Run 193

Nitrosation of 3-chloro-2-methylpropene in 0·84N perchloric acid at 0°C

Time (hours)	Optical Density	Corrected Optical Density
0·00	0·363	0·363
0·02	0·352	0·352
3·47	0·314	0·323
8·40	0·291	0·307
13·82	0·282	0·305
24·83	0·242	0·277
38·78	0·190	0·232
53·90	0·152	0·197
74·62	0·105	0·147
102·42	0·076	0·117
133·85	0·053	0·091

Section 4.

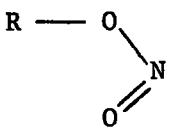
Appendix 1.

Infrared spectra of addition compounds of nitrous acid with some olefins

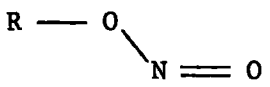
A1.1. Infrared spectra of organic nitrites, nitro and nitroso compounds

A1.1.(a) Organic nitrites

Alkyl nitrites exist as a mixture of cis and trans geometrical isomers;



cis



trans

They show different stretching wavelengths in the infrared region for the N=O bond, due to the proximity of the oxygen atom to the alkyl group.[133] The observed N=O stretching wavelengths of the cis and trans isomers of some alkyl nitrites are shown in Table A1.1.[134] This wavelength for the N=O stretching vibration in alkyl nitrites is to be compared with the value obtained for C-nitroso compounds in the region 6·4-6·8 μ. The N-O vibration of alkyl nitrites is observed in the region of 12·5 μ.[135]

The ratios of cis and trans isomers present for a given alkyl nitrite have been calculated from dipole moment measurements and are shown in Table A1.2.[136] Thus trans > cis, and the ratio increases markedly from primary through secondary to tertiary.

The infrared spectra of alkyl nitrates have also been widely studied and show significant similarities to those of the nitrites. The main features are summed up in Table A1.3.[137]

Table A1.1.

Observed N=O stretching wavelengths in alkyl nitrites

Compound	Solution	Trans-isomer (μ)	Cis-isomer (μ)
EtONO	Carbon Tetrachloride	6·05	6·20
Bu^nONO	Liquid (neat)	6·07	6·22
	Carbon Tetrachloride	6·06	6·22
$nC_5H_{11}ONO$	Liquid (neat)	6·06	6·21
	Carbon Tetrachloride	6·05	6·21
$isoC_5H_{11}ONO$	Liquid (neat)	6·05	6·21
	Carbon Tetrachloride	6·05	6·22

Table A1.2.

trans/cis for organic nitrites at 25°C

Nitrite	State	trans/cis
Methyl	g	1·77
Ethyl	g	1·94
n-Propyl	1	1·70
n-Amyl	1	1·33
Allyl	1	1·17
Isopropyl	1	4·26
t-Butyl	1	∞
t-Amyl	1	∞

Table A1.3.

Band	Mode
6·10 - 6·15 μ	$\nu a(NO_2)$ asymmetric stretching mode
7·80 - 7·86 μ	$\nu s(NO_2)$ Symmetric stretching mode
11·49 - 11·70 μ	ν(O-N) O-N stretching mode

A1.1.(b) Organic nitro compounds

In nitromethane the position of the CNO_2 group fundamental vibrations have been shown, by a theoretical study, to be:[138]

NO_2 asymmetric stretch	6·37 μ
NO_2 symmetric stretch	7·25 μ
C-N stretch	10·90 μ

Similar bands were seen in other nitroalkanes and thus empirical assignments of the CNO_2 group fundamentals were made as follows:[138]

NO_2 asymmetric stretch	near 6·4 μ
NO_2 symmetric stretch	near 7·3 μ
C-N stretch	near 11·6 μ

However it has been found that empirical assignments of the C-N stretching vibration are not justified, owing to the large observed differences.[139] The correlation of the type of compound with observed frequency of the NO_2 group fundamental vibrations are shown in Table A1.4.[139]

Table A1.4.

Nitro group fundamental vibrations in a selection of compounds

Compound Type	NO_2 asymmetric stretch (μ)	NO_2 symmetric stretch (μ)
$RONO_2$	6·10 ± 0·05	7·82 ± 0·04
CH_3NO_2	6·38	7·26
R_2CClNO_2	6·39	7·45
RCH_2NO_2	6·42 ± 0·03	7·27 ± 0·04
R_2CHNO_2	6·45 ± 0·02	7·30 ± 0·06
R_3CNO_2	6·49 ± 0·02	7·41 ± 0·04
$ArNO_2$	6·55 ± 0·08	7·42 ± 0·06

Normally the symmetrical C-H bending vibration of C-methyl groups and the symmetrical NO_2 stretching vibrations of the simple nitroalkanes would both give bands at 7·25 μ. However, when methyl and nitro groups are bonded to the same carbon atom, splitting rather than coincidence of the bands is observed. In compounds containing the CH_3-C-NO_2 structure, the observed bands lie near 7·17 and 7·3 μ.

A1.1.(c) Organic Nitroso compounds

The infrared spectra of nitroso compounds are made complex by isomerisation and dimerisation. There is quite a significant difference between the N=O stretching wavelength region for aromatic nitroso compounds (6·61 to 6·72 μ) and aliphatic nitroso compounds (6·17 to 6·50 μ)[140,141] The characteristic wavelengths were assigned on the detailed comparison of wavelengths of the nitroso compound and a product in which the N=O group had been removed.

The infrared spectra of oximes are easy to differentiate from those of nitroso compounds due to the appearance of the typical absorptions:[139]

Strong O-H stretching band	near 3·0 μ
Weak/medium C=N stretch	6·0 - 6·1 μ
Strong N-O stretch	10·3 - 10·8 μ

A1.2. Infrared spectra of the addition compounds

The infrared spectra were recorded on a Spectromaster instrument using a contact film for liquids and a Nujol mull or potassium bromide disc for solids. The outstanding feature of the spectrum of the product of the addition to 3-chloro-2-methylpropene was the appearance of two prominent peaks at 6·09 and 6·42 μ. These peaks are characteristic of nitroso-nitrites and equivalent peaks were observed in all the addition products of olefins. The position of the characteristic peaks are shown in Table A1.5.

Table A1.5.

Position of characteristic peaks in infrared spectra of addition compounds

Olefin	Peaks (μ)	
3-chloro-2-methylpropene	6·09	6·42
3-chloropropene	6·09	6·42
propene	6·10	6·43
2-methylpropene	6·08	6·41
2-methyl-2-butene	6·13	6·47
2,3-dimethyl-2-butene	6·11	6·45
2,4,4-trimethyl-2-pentene	6·11	6·45

This lack of variation of absorption wavelength on changing the structure of the olefin is consistent with a similar observation with regard to the stretching vibration in organic nitrites.[134] The absorptions can be assigned as follows:

$6{\cdot}10 \pm 0{\cdot}03\mu$ - N=O stretching vibration in a trans nitrite[134], consistent with the observation that tertiary nitrites are trans.

$6{\cdot}44 \pm 0{\cdot}03\mu$ - N=O stretching vibration in a nitroso group[140,141], which is the same as that observed in the products of the addition of dinitrogen tetroxide to olefins.[48]

The infrared spectrum of the addition compound (I) of nitrous acid and 3-chloro-2-methylpropene is consistent with its assignment as a nitroso nitrite, with the hint of some isomerisation to the oxime. The spectrum, however, did not change significantly with the change of colour from blue to yellow on standing. The bands which are present in I and not in 3-chloro-2-methylpropene can be assigned as shown in Table A1.6.

Table A1.6.

Assignment of bands in infrared spectrum of I

Band (μ)	Assignment
2·84 (weak)	ν(O-H) in oxime
6·03 (weak)	ν(C=N) in oxime
6·09	ν(N=O) in trans nitrite
6·42	ν(N=O) in nitroso group
10·6 (weak)	ν(N-O) in oxime
11·16	ν(C-N) in nitroso group
12·00	ν(N-O) in nitrite
14·60	ν(O-N-O) bend in nitrite

Some of the addition reactions produced a solid and a liquid. The solid compounds were typified by a peak near 6·4 μ in the infrared spectrum and no peak near 6·10 μ. The position of the peak near 6·4 μ in the solid compound was not significantly changed from the position in the equivalent liquid product.

A1.3. Infrared Spectra

Spectrum No.1. Blue oil I from 3-chloro-2-methylpropene and nitrous acid (contact film).

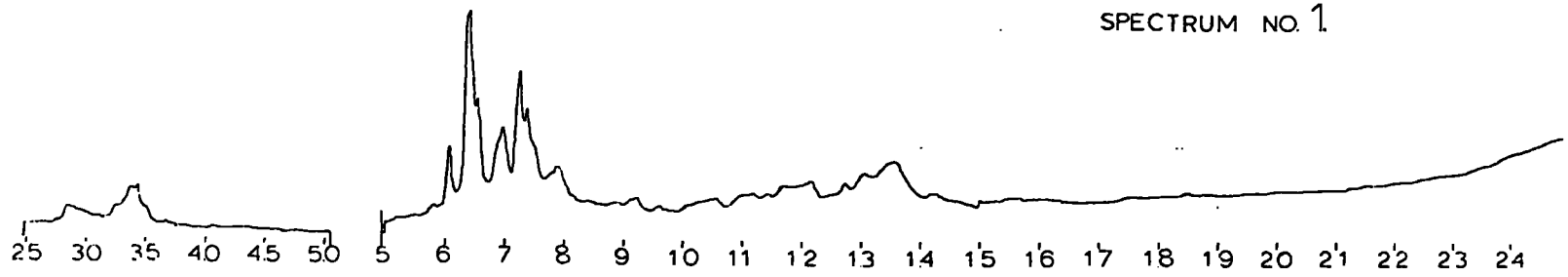
Spectrum No.2. White solid IV from 3-chloropropene and nitrous acid (potassium bromide disc).

Spectrum No.3. Green oil V from 3-chloropropene and nitrous acid (contact film).

Spectrum No.4. White solid IV from 3-chloropropene and dinitrogen trioxide (potassium bromide disc).

Spectrum No.5. 3-chloro-2-hydroxy-2-methylpropionic acid (potassium bromide disc).

Spectrum No.6. Chloroacetic acid (potassium bromide disc).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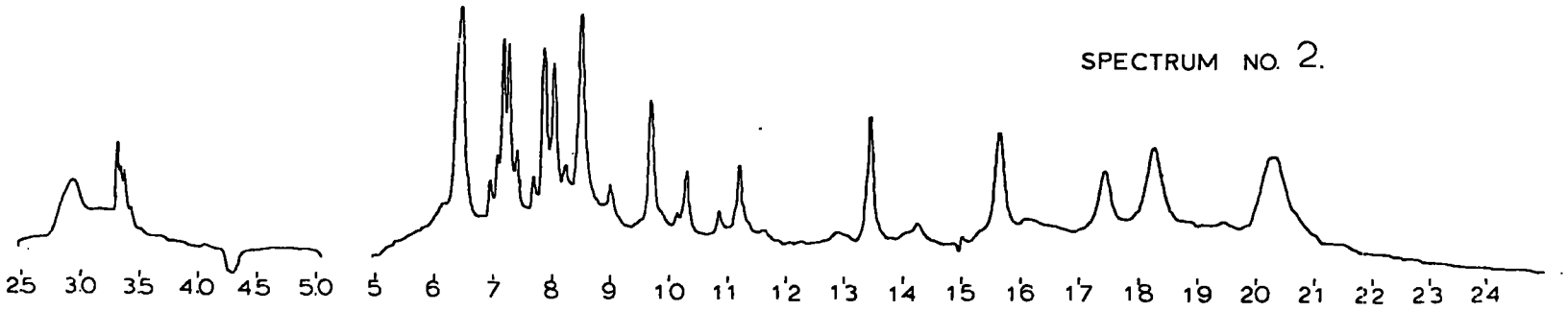
2'5 3'0 3'5 4'0 4'5 5'0 5 6 7 8 9 1'0 1'1 1'2 1'3 1'4 1'5 1'6 1'7 1'8 1'9 2'0 2'1 2'2 2'3 2'4


SPECTRUM NO. 2.
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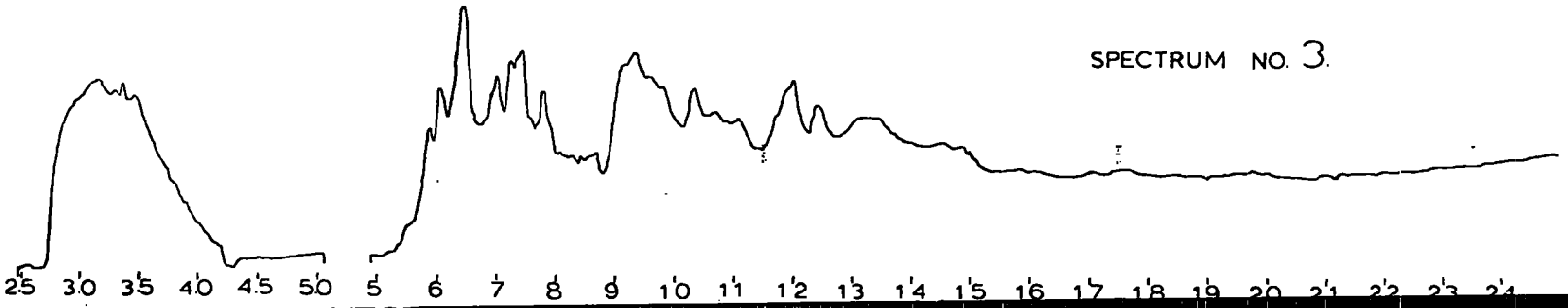
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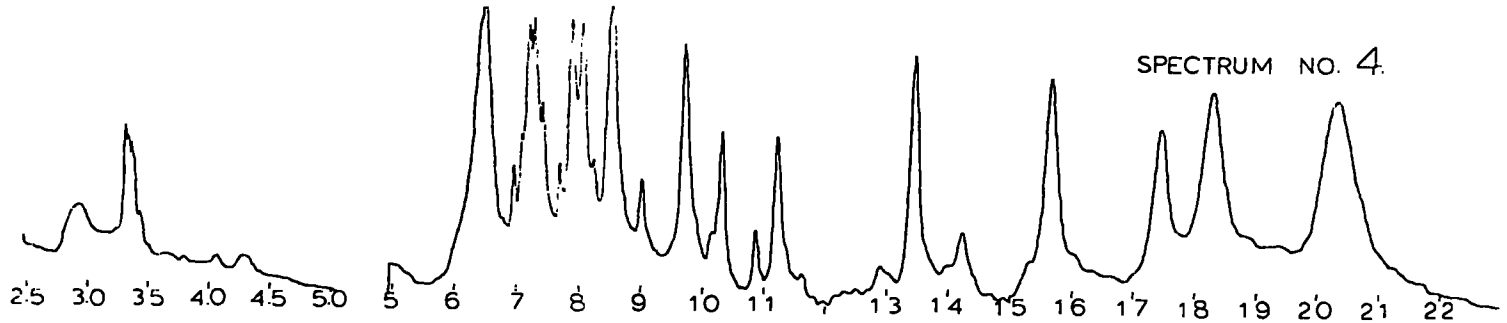
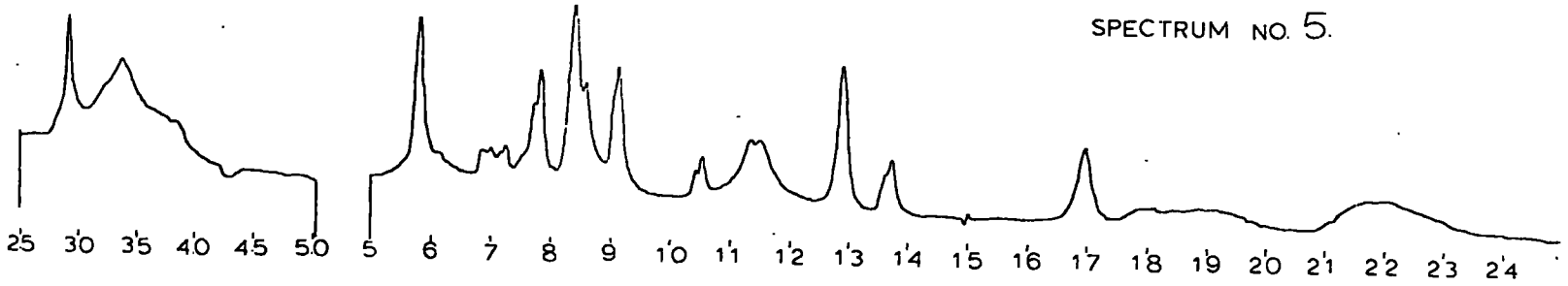
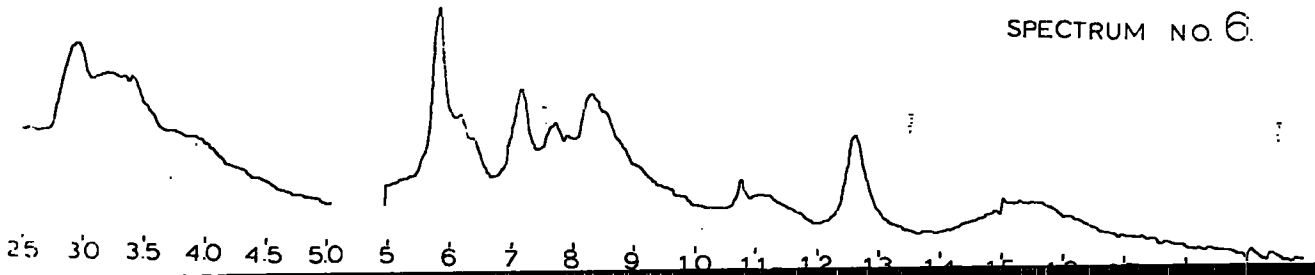

SPECTRUM NO. 4.
2·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 1·0 1·1 1·3 1·4 1·5 1·6 1·7 1·8 1·9 2·0 2·1 2·2


SPECTRUM NO. 5.
2·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 1·0 1·1 1·2 1·3 1·4 1·5 1·6 1·7 1·8 1·9 2·0 2·1 2·2 2·3 2·4


SPECTRUM NO. 6.
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Appendix 2.

Mass spectra of the addition compounds of

nitrous acid and olefins

A2.1. Mass Spectra of Organic Nitroso, Nitro and Nitrito Compounds

A2.1.(a) Nitroso Compounds

Very little information is available in the literature concerning mass spectra of aliphatic nitroso compounds. The mass spectrum of the dimer of nitroso methane has been investigated.[99] The most characteristic trait of the mass spectrum is the strong peak at mass 90 (11% of mass 30 peak), corresponding to the dimer. The ion at mass 45 is much more abundant (70% of mass 30 peak). This corresponds to the monomer of nitroso methane, which may have been formed in the ionisation chamber. A peak appears at mass 60 (5%) which was shown to be due to $(CH_3)_2NO^+$. This indicates the structure of the dimer cannot be

The peak at mass 30 is, however, the base peak and this corresponds to NO^+.

Aromatic nitroso compounds have been rather more widely discussed in the literature.[99,142] The mass spectrum of nitroso benzene exhibits a prominent molecular ion (14%) which fragments by successive loss of $NO^{\cdot}$ (to M77, 100%) and C_2H_2 (to M51, 93%), as indicated by appropriate metastable ions. The facile loss of a nitroso radical is a general feature of all the aromatic C-nitroso compounds studied, and may be compared with the expulsion of $NO_2^{\cdot}$ from nitrobenzene upon electron impact.[143]

A2.1.(b) Nitro compounds

In contrast to nitroso compounds the mass spectra of aliphatic nitro compounds have been quite widely studied.[144,145,146] The mass spectra of aliphatic nitro compounds appear to fall into three categories:

i) that of nitromethane, which is unique

ii) that of primary aliphatic nitro compounds, which show a quite wide variety of behaviour due to change of chain length,

iii) that of tertiary aliphatic nitro compounds, which show quite different behaviour from the other two categories.

In general isomerisation of the nitro compounds to the corresponding nitrites is not significant, in contrast to the behaviour of aromatic nitro compounds.

The spectrum of nitromethane is relatively simple. An abundant molecular ion is accompanied by CH_3^+, NO_2^+ and NO^+ ions representing the most important daughter species, while loss of an oxygen atom to give CH_3NO^+((m/e) 45) is of minor importance. The molecular ion is of low intensity for nitroethane and becomes indiscernible in the spectra of the higher nitroalkanes. α-Cleavage of the hydrocarbon chain, which is an important feature with alkyl nitrites, is essentially absent in the case of nitro compounds. The observed mass spectra of isomeric nitro alkanes are generally quite similar and differ only in the relative abundance of some fragment ions.

The NO_2^+ ion is of low abundance from nitroethane onwards and the NO^+ ion declines gradually in its importance with increasing molecular weight.

The loss of an $NO_2^{\cdot}$ radical to yield the appropriate $C_nH_{2n+1}^+$ ion is a prominent process and can be of diagnostic utility except for higher alkyl ionswhich are very prone to fragment further, especially to thevery stable C_3 and C_4 fragments.

One very interesting feature of the mass spectra of nitroalkanes is the occurrence of oxygen-free CHN fragments. They start formally with HCN, but higher homologues can also be observed (e.g. CH_3CN, M41).

The spectra of several tertiary nitroalkanes have been examined. The main feature is the loss of HNO_2 giving rise to the highest discernible peak in the various spectra. The subsequent fragmentation pattern corresponds to the combination of the decomposition modes of the possible olefins, with the exception of an abundant NO^+ ion and a small amount of CH_3CN^+ (m/e 41).

A2.1.(c) Aliphatic Nitrites

The mass spectra of simple aliphatic nitrites have been studied very thoroughly.[147] One of the most characteric features of these mass spectra is the large abundance of NO^+ (M30). The parent molecular ion is very weak from ethyl nitrite upwards, due to the weakness of the RO-NO bond, known from thermolysis and photolysis studies. α-fission to give CH_2ONO is significant in normal alkyl nitrites, but not in branched chain nitrites. Molecular rearrangement is virtually unknown in alkyl nitrites, as shown by the appearance of the fragment CH_2ONO only in the molecules which are able to yield it by α-fission. Thus in normal and iso propyl nitrites

the following peaks are observed: M60 (CH_2ONO) important in n-C_3H_7ONO but negligible in i-C_3H_7ONO, whereas M74 (CH_3CHONO) is important for i-C_3H_7ONO and (CH_2CH_2ONO) is negligible for n-C_3H_7ONO.

The different behaviour of the nitrites on electron bombardment due to changes of the carbon chain are best seen in the case of the butyl nitrites. Normal and isobutyl nitrites show significant peaks at M60 due to CH_2ONO and then strong hydrocarbon peaks in the region of M43 and M29. Secondary butyl nitrite has a peak at M74, due to loss of the C_2H_5 fragment, no peak at M60 and strong hydrocarbon peaks at M57, M43 and M29. Tertiary butyl nitrite has a peak at M88, due to loss of a CH_3 fragment and strong hydrocarbon peaks as above. All the nitrites show a very strong peak at M30 (NO^+).

Changes in mass spectra due to alteration of the carbon chain are very pronounced. Thus it is very difficult to differentiate between nitro and nitrito compounds. The peak at mass 31 appears in the spectra of nitrito compounds and not in those of nitro compounds.[148] This peak, to which the assignment of either the rearrangement peak CH_3O or NOH can be given, is thus a fairly good characteristic of nitrite esters.

A2.2. Mass spectra of the addition compounds

A2.2.(a) 3-chloro-2-methyl-2-nitrito-1-nitrosopropane

The spectrum was recorded at 70 eV. The base peak was M30 (NO^+) and no molecular ion peak was present. The highest mass peak occurred at

M90/92 ($P-N_2O_3$; 21%:7%). The peaks are shown in Table A2.1.

Table A2.1.

M	Composition
90/92	$P-N_2O_3$; 21% : 7%
89/91	$P-HN_2O_3$; 27% : 9%
75/77	$P-CH_3N_2O_3$; 9% ; 3%
55	$P-ClN_2O_3$; 60%
41	$P-CH_2ClN_2O_3$; 29%
39	$P-CH_4ClN_2O_3$; 44%
30	NO; 100%
27	$P-C_2H_4ClN_2O_3$; 40%

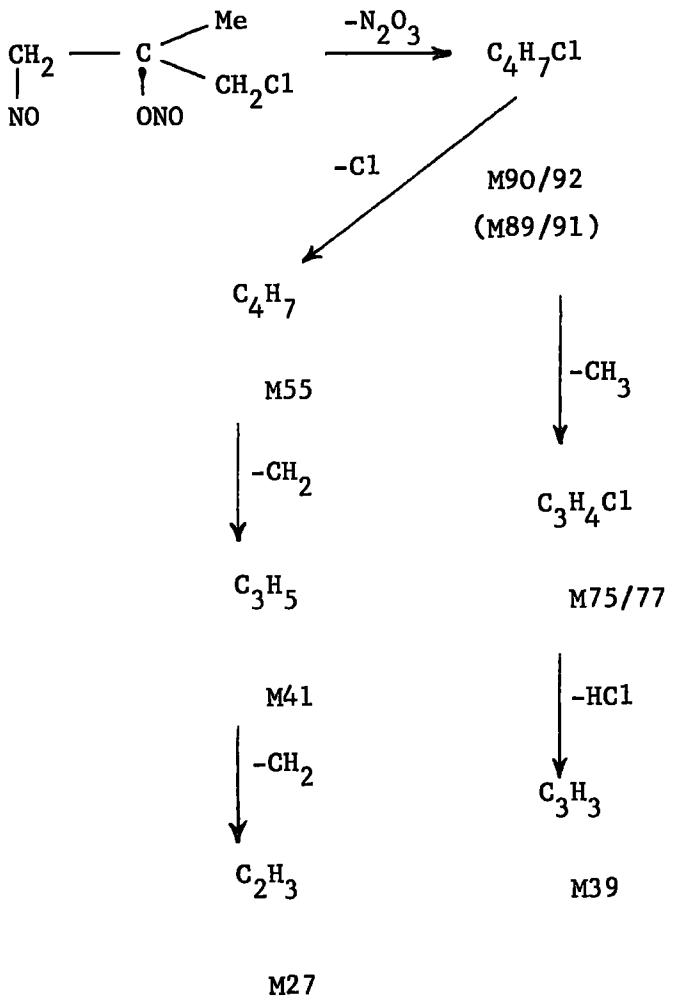
The fragmentation is represented in Scheme A2.1.

A2.2.(b) 3-chloro-2-nitroso-nitritopropane

The base peak was M30 (NO^+) and no molecular-ion peak was present. The most intense peak occurred at M75/77 ($P-HN_2O_3$) whilst the highest mass peak was M106/108 ($P-NO_2$). Other prominent peaks were M49/51 (CH_2Cl), M40 ($P-HClN_2O_3$) and M27 ($P-CH_2ClN_2O_3$).

A2.2.(c) The addition compound of dinitrogen trioxide and 2-methylpropene

The liquid and solid products had essentially the same mass spectrum.



Scheme A2.1.

The base peak was M28 (C_2H_4) and there was no molecular-ion peak. The following peaks were also present in the mass spectrum at M101 (P-HNO), M86 (P-NO_2), M55 (P-HN_2O_3) and M40 (P-$CH_4N_2O_3$).

A2.2.(d). The addition compound of dinitrogen trioxide with propene

Once more the liquid and solid products had the same mass spectrum. The base peak occurred at M28 (C_2H_4) and there was no molecular-ion peak. The other prominent peaks present were at M104 (P-CH_2), M87 (P-HNO), M58 (P-CH_2NO_2), M41 (P-HN_2O_3) and M28 (P-$CH_2N_2O_3$).

Discussion

The peak common to all the mass spectra is that at mass 30, corresponding to NO. It is more significant for the chlorinated olefins, where it becomes the base peak. The peak at mass 31, which is characteristic for the mass spectra of nitrite esters, is present in all the mass spectra of the addition compounds.

A molecular ion peak was never observed for any of the addition compounds and in general the highest mass peak observed was that corresponding to the hydrocarbon chain. Typical hydrocarbon fragmentation was observed. This was particularly obvious in the mass spectra of the chlorinated compounds.

Appendix 3.

Kinetic Analysis of mixed first and second order reactions

In the diazotisation of aromatic amines concurrent first and second order processes were identified at intermediate acidity but it was possible study nitrosation by just one of the processes by suitably changing the experimental conditions. Thus, by studying an aromatic amine of much lower basicity than aniline at intermediate acidity in the presence of a low concentration of molecular nitrous acid, nitrosation was shown to be a pure first order process.[40]

In the nitrosation of 2,3-dimethyl-2-butene a similar procedure was used but there still existed a range of acidity within which nitrosation was a mixed first and second order process with respect to nitrous acid. With 2-methyl-2-butene, however, only a pure second order process was observed at very low acidity alongwith a non-integral order as the acidity was increased to 0·1M perchloric acid.

Evidence for non-integral order behaviour was obtained from first and second order rate plots, neither of which was a straight line. Also, observed first order rate constants tended to decrease as the run progressed, whilst second order rate constants would increase. Fig.A3.01 shows the first and second order rate plots for the nitrosation of 2,3-dimethyl-2-butene at $4{\cdot}28 \times 10^{-4}$M perchloric acid, whilst Table A3.1 shows the variation of the observed first and second order rate coefficients as the reaction progresses in the nitrosation of 2-methyl-2-butene in 0·031M perchloric acid.

Fig A 3·01

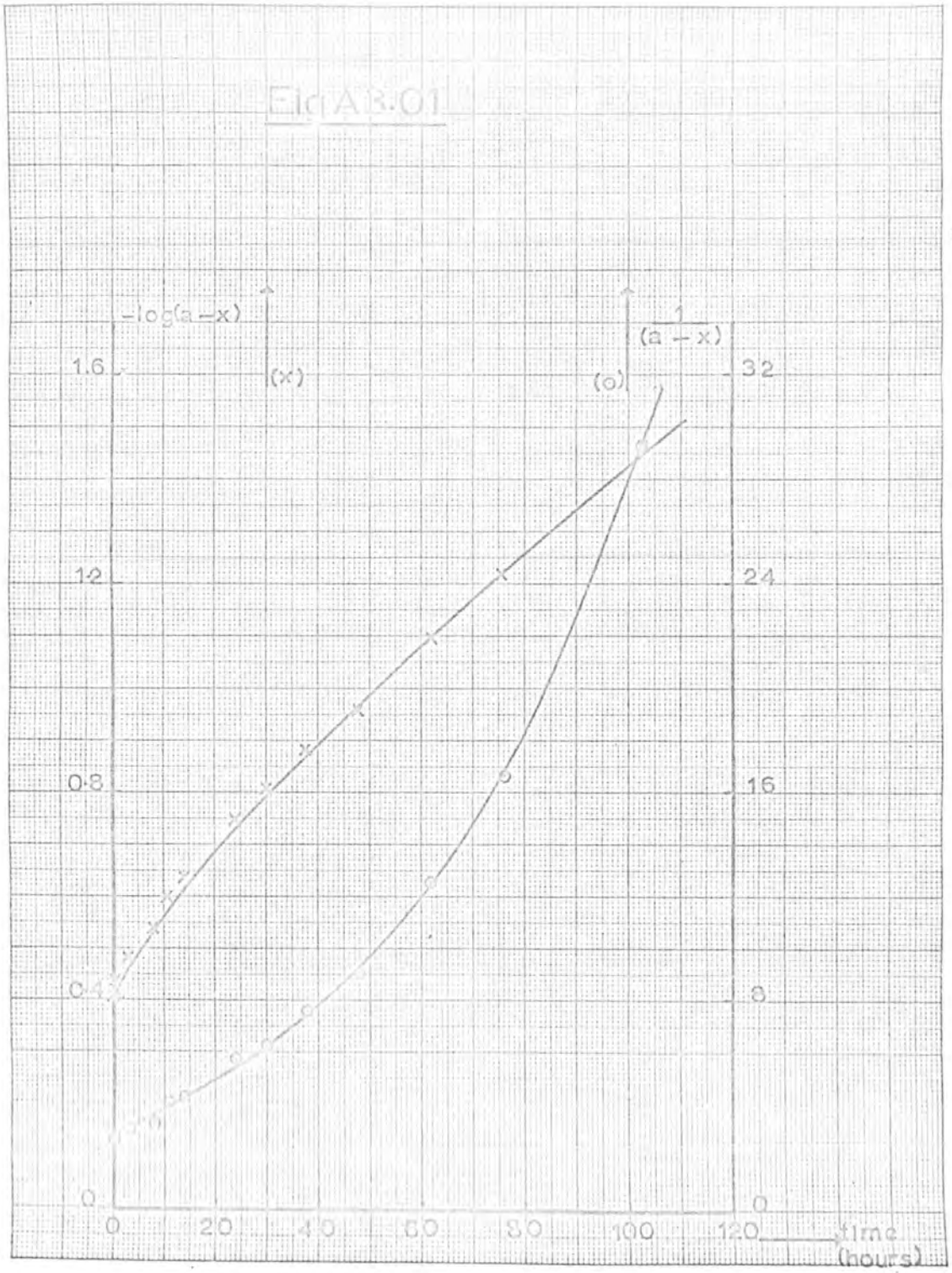

−log(a−x)
(x)
1.6
1·2
0·8
0·4
0
1/(a−x)
(o)
32
24
16
8
0
0
20
40
60
80
100
120
time (hours)

Table A3.1.

First and second order rate coefficients for

nitrosation of 2-methyl-2-butene

Time (mins)	Optical Density	$\bar{k}_1 \times 10^2$ (min^{-1})	$\bar{k}_2 \times 10^{-2}$ (1 $m^{-1} min^{-1}$)
0·00	0·326	-	-
1·00	0·293	10·61	1·24
2·00	0·255	12·27	1·53
4·00	0·197	12·58	1·79
6·00	0·169	10·94	1·70
9·00	0·128	10·38	1·89
13·00	0·105	8·71	1·78
21·00	0·066	7·61	2·06
34·00	0·037	6·40	2·51
50·00	0·024	5·22	2·77

$[HClO_4]$ = 0·031M; [Olefin] = 0·036M; $[HNO_2] = 1 \times 10^{-4}$N

Temperature = 0°C.

If we consider a general reaction system in which a reactant A can disappear either by a first order process or a second order process, such as:

$$A \xrightarrow{k_1} \text{products}$$

$$A + A \xrightarrow{k_2} \text{products}$$

then the rate is given by the differential expression[149]

$$\frac{dx}{dt} = k_1(a-x) + k_2(a-x)^2 \qquad \text{A3.01.}$$

Expression A3.01 can be integrated:

$$\ln\left(\frac{a}{a-x}\right) = k_1 t + k_2 \int (a-x)dt$$

$$\therefore \quad \frac{1}{t}\ln\left(\frac{a}{a-x}\right) = k_1 + \frac{k_2}{t}\int (a-x)dt$$

$$\therefore \quad k_{obs} = k_1 + k_2 \cdot \frac{I}{t} \qquad \text{A3.02.}$$

where $k_{obs} = \frac{1}{t}\ln\left(\frac{a}{a-x}\right)$, the observed first order rate constant, and $I = \int (a-x)dt$, which can be obtained by measuring the area under a concentration-time curve. The area was determined using a plinimeter and also by counting squares, and no significant difference in the results was observed. k_1 and k_2 were obtained by plotting k_{obs} against $\frac{I}{t}$.

For run 11 at $33{\cdot}3 \times 10^{-4}$M perchloric acid the area was estimated by counting squares. The data obtained are collected in Table A3.2 and are

shown in Fig.A3.02. The plot obtained was not a very good straight line so the slope and intercept were determined by least squares analysis.

Alternatively, equation A3.01 may be treated in its differential form:

$$\frac{\frac{dx}{dt}}{(a-x)} = k_1 + k_2(a-x) \qquad \text{A3.03.}$$

A plot of $\frac{\frac{dx}{dt}}{(a-x)}$ against (a-x) will yield values of k_1 and k_2. $\frac{dx}{dt}$ is the slope of the tangent on the concentration-time curve at a particular value of (a-x). The slope of the tangent was measured using a tangentimeter, built to the specifications of Simons.[150] The results obtained for the nitrosation of 2,3-dimethyl-2-butene in $2{\cdot}14 \times 10^{-4}$M perchloric acid are shown in Table A3.3. Once more the slope and intercept were determined by least squares analysis of the data.

Fig A3.02

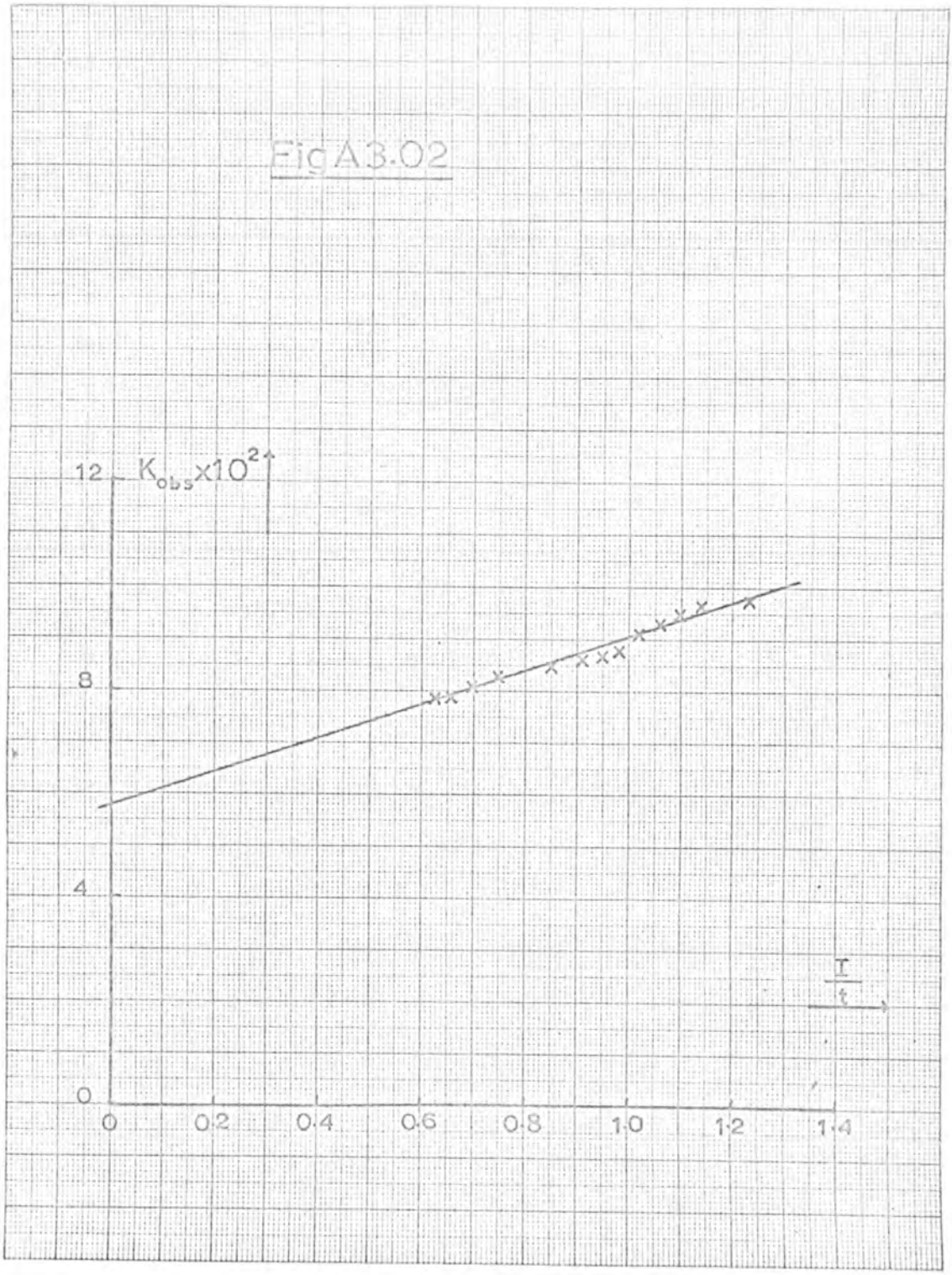


Table A3.2.

Mixed first and second order treatment of Run 11.

Time (mins)	I(squares)	$\frac{I}{t}$ (squares min^{-1})	(a-x) (O.D.)	$k_{obs} \times 10^3$ (min^{-1})
0·00	-	-	0·708	-
30	36·90	1·23	0·527	9·83
40	45·94	1·15	0·480	9·71
50	55·10	1·10	0·440	9·51
60	63·42	1·06	0·405	9·31
70	71·21	1·02	0·375	9·08
80	78·44	0·98	0·350	8·81
90	85·14	0·95	0·323	8·72
100	91·34	0·91	0·300	8·59
120	102·34	0·85	0·255	8·51
140	111·72	0·80	0·215	8·51
160	119·74	0·75	0·187	8·32
180	126·74	0·70	0·165	8·09
200	132·88	0·66	0·145	7·93
220	138·62	0·63	0·125	7·88

$[HClO_4]$ = 33·3 x 10^{-4}M; $[NaNO_2]$ = 2 x 10^{-4}N; Temperature = 0°C

Table A3.3.

Mixed first and second order treatment of the nitrosation of 2,3-diemthyl-2-butene in $2 \cdot 14 \times 10^{-4}$M perchloric acid

$\frac{dx}{dt}$ (O.D. hr^{-1})	$\frac{\frac{dx}{dt}}{(a-x)}$ (hr^{-1})	(a-x)
0·0100	0·029	0·350
0·0089	0·027	0·325
0·0076	0·025	0·300
0·0068	0·025	0·275
0·0061	0·024	0·250
0·0054	0·024	0·225
0·0043	0·022	0·200
0·0031	0·018	0·175
0·0023	0·016	0·150
0·0019	0·015	0·125
0·0014	0·014	0·100
0·0008	0·010	0·075
0·0003	0·006	0·050

Temperature = $0^{\circ}C$; $[NaNO_2] = 1 \times 10^{-4}N$

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