Addition reactions of Hypohalous acids and halogens with halogen-substituted - olefins

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ADDITION REACTIONS OF HYPOHALOUS ACIDS AND HALOGENS WITH HALOGEN—SUBSTITUTED-OLEFINS

A thesis submitted for the degree of
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in the
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ABSTRACT

The reaction between hypochlorous acid and 2-chloropropene was studied. The products were analysed as chloroacetone (85%) and 2,3-dichloropropene (15%). The absence of any 2,2-dichloropropanol, formed by nucleophilic attack of water at the terminal carbon atom, is discussed in terms of polarisation of the molecule caused by electron-release from the 2-chloro substituent. The formation of 2,3-dichloropropene by proton-loss in the carbonium ion from C-3 (rather than of 1,2-dichloropropene formed by loss from C-1) is explained in terms of steric strain.

The effect of silver ions on the course of the reaction was also studied. A product analysis revealed no change in the yield of chloroacetone, nor any sign of any unusual products. The kinetics were also unaffected by the presence of silver ions. This behaviour contrasts with that of 2,3-dichloropropene, where silver ions have been found to cause autocatalytic behaviour, and to be responsible for abnormal products. The kinetics of 2-chloroprop-2-en-1-ol were studied, and found to show characteristics midway between the other 2-chloro compounds.

When radioactively labelled hypochlorous acid was used in the addition reaction, the chloroacetone produced was found to contain less than the full activity, showing that some chlorine exchange takes place. The extent of the exchange was found to be reduced by the presence of increasing concentrations of silver ions. In a series of experiments in aqueous acid solution, chloride, bromide and iodide ions were added to hypochlorous acid in the presence of silver ions. Exchange was found to occur, to an increasing extent along the series chloride - bromide - iodide, and to a decreasing extent with increasing silver ion concentration. The rate of exchange between hypochlorous acid and silver chloride was found to be slow, of the same order as that between chloride ion and silver chloride. There was very little exchange between chloride ion and hypobromous acid. The 2,3-dichloropropene produced in the reaction between hypochlorous acid and 2-chloropropene was found to be of the same specific activity as the chloroacetone, and to be exclusively 3-labelled. The conclusion was reached that the chlorine exchange in the addition reaction proceeded by an <u>inter</u>- rather than an <u>intra</u>-molecular mechanism. The addition of hypochlorous acid to 2-bromopropene resulted in the production of some bromoacetone, as expected.

The kinetics of the addition of iodine in aqueous solution to the series of terminally substituted 1- alkenes $CH_2 = CH(CH_2)_nBr$ were followed. A rate maximum at n = 3 appeared to indicate bromine participation in a 5-membered ring, although calculations based on the fall-off of inductive effect with the progressive removal of the bromo substituent from the reaction centre showed the effect not to be very large.

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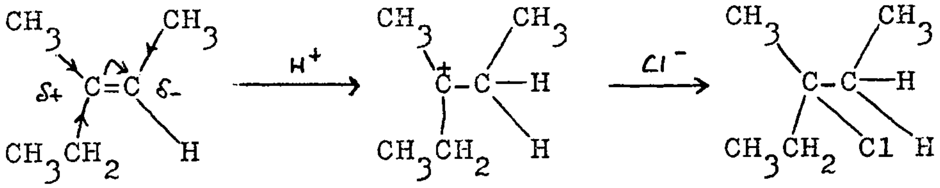
CHAPTER 1

INTRODUCTION

A Addition of various halogen species

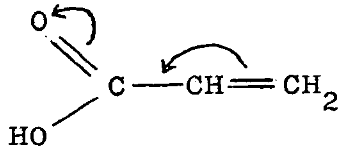
(a) Addition of hydrogen halides

The addition of hydrogen halides to olefins is considered to be initiated by attack of a proton on the more negatively polarisable end of the C=C bond, which in turn is determined by the inductive, mesomeric or hyperconjugative effects of the substituents in the olefin molecule. This initial electrophilic attack is followed by nucleophilic attack by the halide ion on the carbonium ionic centre thus formed. For example, the addition of hydrogen chloride to 3-methylpent-2-ene gives exclusively 3-chloro-3-methylpentane, since the double bond is polarised by the electron-repelling methyl groups in the sense shown:

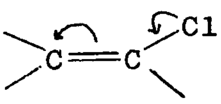


An alternative description of the observed orientation is that the proton will attach itself to the olefin molecule in such a way as to form the more stable of the possible carbonium ionic intermediates. Calculations by Bodot and Jullien[1] of electron densities at each carbon atom in an unsymmetrically substituted ethylene derivative have shown that although in some cases the carbon atom attacked by the electrophile is the more negative one, in others it is the more positive end that is attacked. The same workers calculated the relative energies of the two possible carbonium ions and find that the one of lower energy corresponds to the product actually formed. In other words, the orientation of the initial electrophilic attack is such as to produce the more stable carbonium ion.

Generally, tertiary carbonium ions are more stable than secondary, which in turn are more stable than primary carbonium ions. This is the basis of the Markovnikov rule, which states that in the addition of HX to an olefin, X becomes bound to the more highly substituted of the carbon atoms.[2] Apparent exceptions to this rule can be explained in terms of the electronic movements within the molecule. For example, acrylic acid yields the so-called anti-Markovnikov product,[3] while a proper consideration of the system shows the carboxylate group to be electron-withdrawing, and hence the polarisation of the double bond will be as shown:



It may be noted here that a 2-halo substituent is found to polarise the bond in the scheme shown in I (below), presumably due to the existence of canonical forms such as II, where the carbon-halogen bond has double bond character and the halogen atom takes a positive charge:



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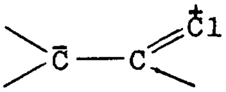
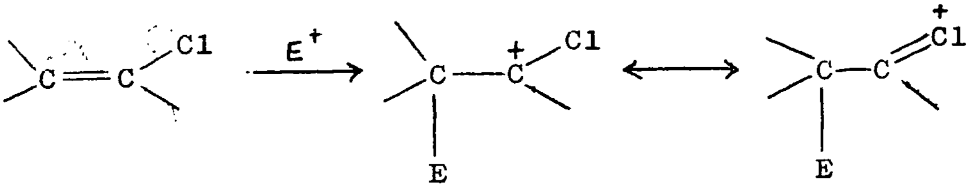


II

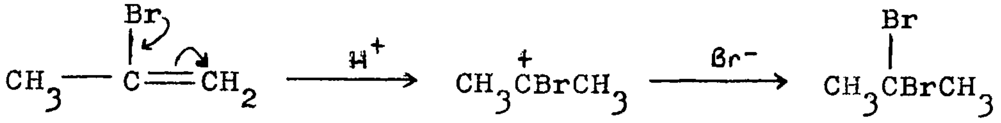
Alternatively, the 2-halo substituent can be thought of as conferring an added stability on the carbonium ion, formed when the electrophile is attached to carbon 1, by a contribution to the structure by the canonical form IV. i.e. by



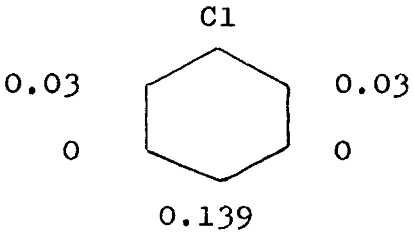
III

IV

a delocalisation of the positive charge. Thus in the addition of hydrogen bromide to 2-halopropenes, 2-bromopropene yields 2,2-dibromopropane and 2-chloropropene yields 2-bromo-2-chloropropane.[4]

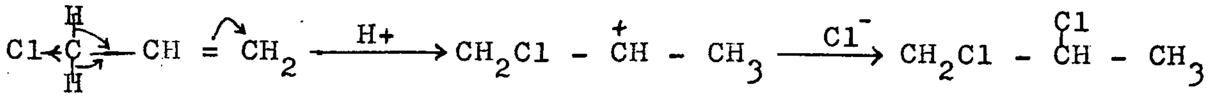


This behaviour is similar to the effect of a chloro substituent on the orientation and rate of electrophilic aromatic substitution. Thus the partial rate factors (i.e. the rate of substitution compared to that in benzene) for the o- and p- positions in chlorobenzene are as follows:[5a]



Note, however, that while the chloro-substituent directs electrons into the o- and p- positions, the overall effect is one of deactivation.

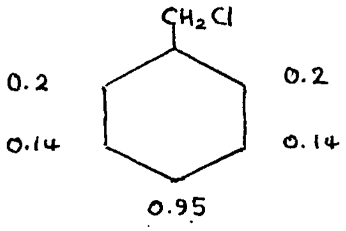
Also, the CH_2Cl- group is found to polarise a double bond in the same sense as does a single chorine atom. Thus various allyl halides, e.g. allyl chloride,[6] 2-methyl-3-chloropropene[7] all give "Markovnikov products"[8] with HCl, showing that hyperconjugative electron release by the hydrogen atoms of the $-CH_2Cl$ group supervenes over the inductive effect of the chlorine atom, polarising the double bond in the sense shown:



$$Cl \leftarrow \overset{H}{\underset{H}{C}} - CH = CH_2 \xrightarrow{H+} CH_2Cl - \overset{+}{C}H - CH_3 \xrightarrow{Cl^-} CH_2Cl - \overset{Cl}{C}H - CH_3$$

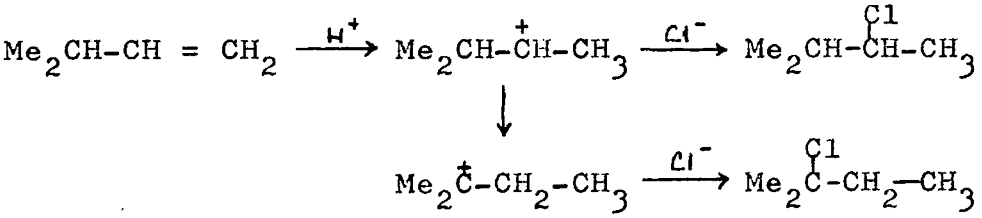
The CH_2Cl- group, however, has the effect of deactivating the molecule towards electrophilic attack. Thus bromination of ethylene in methanol takes place some 14 times faster than bromination of allyl chloride under the same conditions.[9,10]

The CH_2Cl- group also is o-p- directing in electrophilic aromatic substitution. The partial rate factors are as follows:[5b]



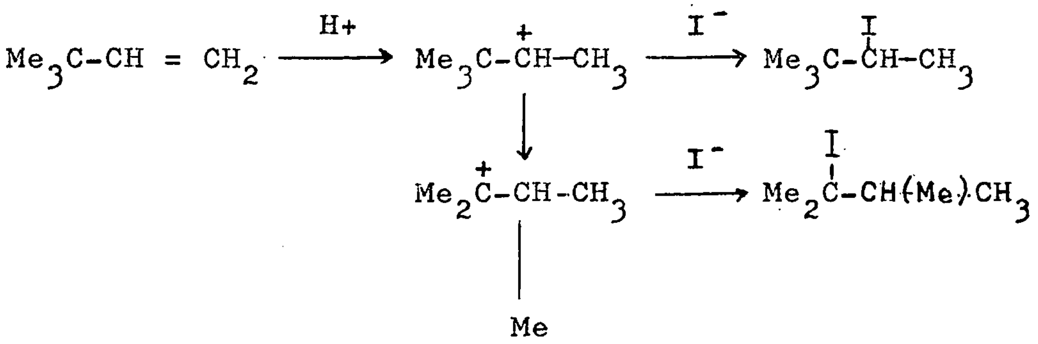
However, consideration of these figures shows the CH_2Cl- group to be neither so deactivating nor so exclusively o-p- directing as the Cl-substituent.

The stepwise nature of the addition reactions is well-established, since rearrangement may accompany the reaction, under conditions where neither the adduct nor the olefin could rearrange. Thus, the addition of hydrogen chloride to 3-methylbutene yields 2-chloro-2-methyl butane as well as the expected 2-chloro-3-methylbutane.[11] The rearrangement to give the tertiary chloride presumably results from the migration of a proton in the intermediate carbonium-ion, as shown below.

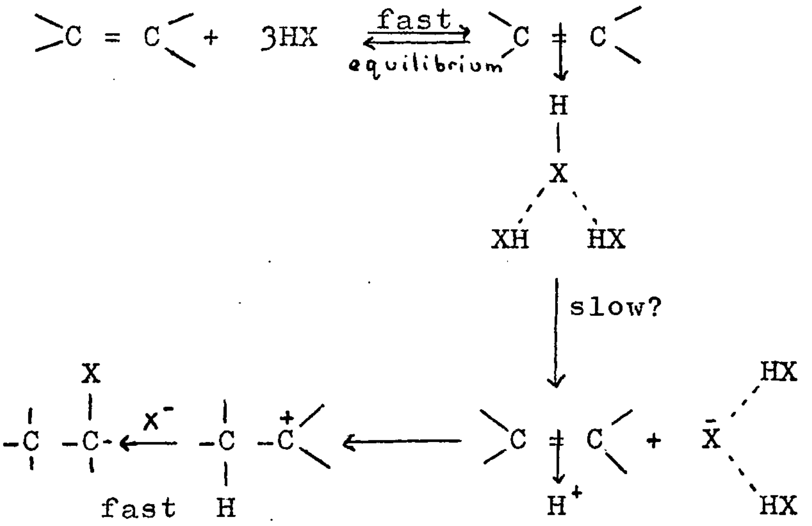


$$\begin{tikzcd} Me_2CH\text{-}CH = CH_2 \arrow[r, "H^+"] & Me_2CH\text{-}\overset{+}{C}H\text{-}CH_3 \arrow[r, "Cl^-"] \arrow[d] & Me_2CH\text{-}\overset{Cl}{C}H\text{-}CH_3 \\ & Me_2\overset{+}{C}\text{-}CH_2\text{-}CH_3 \arrow[r, "Cl^-"] & Me_2\overset{Cl}{C}\text{-}CH_2\text{-}CH_3 \end{tikzcd}$$

A similar example is the production of both 2-iodo-2,3-dimethylbutane and 2-iddo-3,3-dimethylbutane from the addition of hydrogen iodide to 3,3-dimethylbutene.[12] The former product is held to result from a rearrangement of the initially produced secondary carbonium ion into the more stable tertiary carbonium ion, as shown:



The addition of hydrogen halides to double bonds is not conveniently studied in hydroxylic solvents, since hydrogen halides are largely dissociated in such media, and acid-catalysed hydration (or alcoholation, etc.) of the olefins will compete with and possibly overshadow the desired addition. The kinetics of such reactions in non-ionising solvents are rather complex. For instance, the addition of hydrogen chloride to isobutene and that of hydrogen bromide to propene (both in pentane) have been observed to be first order in olefin and of indefinite order (about three) in hydrogen halides.[13] This seems to indicate that besides the HX molecule actually involved in the addition, two or more extra molecules of HX cluster around the activated complex for the slow step. Thus the polarity of the medium in the immediate vicinity of the reaction site would be increased, facilitating heterolysis of the attacking HX molecule. The extra molecules may even directly attack the halogen atom in the attacking molecule, thus further assisting heterolysis, as shown below:



The addition of hydrogen chloride to isobutene in nitromethane, however, has been found to be first order in olefin and second order in hydrogen chloride.[14] The following mechanism is proposed, in which the rate determining step involves attack of HCl_2^- ions (which are stable in nitromethane[15]) on the carbonium ion formed by initial attack of a proton.

$$Me_2C = CH_2 + H+ \rightleftarrows Me_3C+$$

$$Me_3C+ + HCl_2^- \longrightarrow Me_3CCl + HCl$$

(b) Addition of halogens[16]

The addition of halogens to olefins is considered to be initiated by electrophilic halogen attack at the more negatively polarisable of the unsaturated carbon atoms, followed by nucleophilic halide ion attack at the carbonium ionic centre.

The electrophilic nature of the additions is evident from the fact that reaction is facilitated by electron-release to the reaction centre and retarded by electron-withdrawal. Some data are presented in the following tables.[17-24]

Thus, the rate of halogen addition to $CH_2 = CHR$ is increased where R = phenyl or allyl and decreased when R = CH_2Cl, CH_2CN, etc., as shown in Table 1.[16] Also, it will be noted that in the series $RCH = CHCO_2H$, two methyl groups are superior to a phenyl group in promoting reactivity, while the latter is superior to a single methyl group.

Table 1

Relative Rates* of Addition Reactions in Acetic Acid at 24°C.

Compound	Cl_2 addition	Br_2 addition
$CH_2 = CH_2$		84
$C_4H_9CH = CH_2$		2,000
$PhCH = CH_2$		11,000
$CH_2 = CHCH_2Cl$		1.6
$CH_2 = CHCH_2Br$		1.0

$CH_2 = CHCH_2CN$		0.23
$CH_2 = CH(CH_2Cl)_2$		0.019
$CH_2 = CHCHCl_2$	0.60	
$CH_2 = CHBr$	0.28	0.0011
$CH_2 = CHCCl_3$	0.006	
$CH_2 = CHCO_2H$	0.018	
cis $HO_2C.CH = CHCO_2H$	0.00011	
trans $Me.CH = CHCO_2H$	0.62	
trans $Ph.CH = CHCO_2H$	4.9	
$Me_2C = CHCO_2H$	51	

* k_2 (litre mole^{-1} min^{-1})

The marked increase in rate due to a methyl group, whether it is attached directly to the double bond or through a conjugated system is evident from Table 2. Electron-withdrawing groups greatly *decrease* the rate; for example the introduction of a *p*-nitro group into cinnamic acid reduces the rate by a factor of 1000.

Table 2

Values of k_2 for Cl_2 addition

	R = p-Me	H	p-Cl	m-NO_2	p-NO_2
$R.C_6H_4.CH = CHCOPh$	800	61	23	0.23	-
$R.C_6H_4.CH = CHCO_2H$	103	4.9	-	0.011	0.0049

Table 3 shows electron-withdrawing groups arranged in order of effectiveness in reducing reactivity:

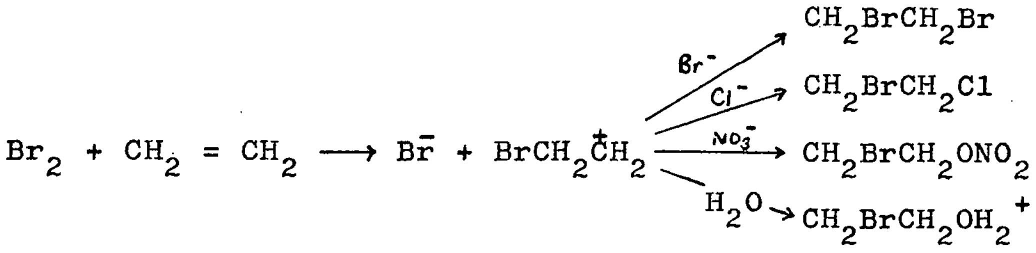
Table 3

Values of k_2 for Cl_2 addition to Ph.CH = CHR.

R	k_2	R	k_2
H	very rapid*	CHO	1.8
COPh	61	CN	0.022
CO_2Et	10	NO_2	0.020
CO_2H	4.9	SO_2Cl	0.001

* By analogy with the rate of bromination, probably $\sim 10.^7$

That the addition is a two-step process, the first step being electrophilic addition to yield a carbonium ion, is demonstrated by carrying out the bromination of ethylene in the presence of sodium chloride or sodium nitrate.[25] In addition to the expected dibromoethane, a bromochloride or a bromonitrate is produced:



Since direct substitution by nitrate ion, etc. on dibromoethane, and also reaction <u>via</u> the BrCl or $BrONO_2$ species can be ruled out, the clear inference is that the reaction proceeds <u>via</u> a carbonium ionic intermediate.

Further, the bromination of stilbene in methanol yields stilbene methoxybromide as well as stilbene dibromide.[26] Again, direct addition by methyl hypobromite is ruled out, since the rate of reaction is found to be independent of the acidity, while the equilibrium shown below would be dependent on the hydrogen ion concentration.

$$Br_2 + MeOH \rightleftharpoons MeOBr + H+ + Br^-$$

The kinetics of halogen addition to unsaturated linkages in non-polar solvents is extremely complicated, the additions being catalysed by light, small quantities of polar substances, or glass surfaces.

In hydroxylic solvents, however, the kinetic picture is much simpler, and most of the information known at present is based on studies in such solvents, particularly water and alcohol.

The reactions are found to be first order in both olefin and halogen.[27]

$$\text{e.g.} \qquad \frac{-d(Cl_2)}{dt} = k_2\,(\text{olefin})\,(Cl_2)$$

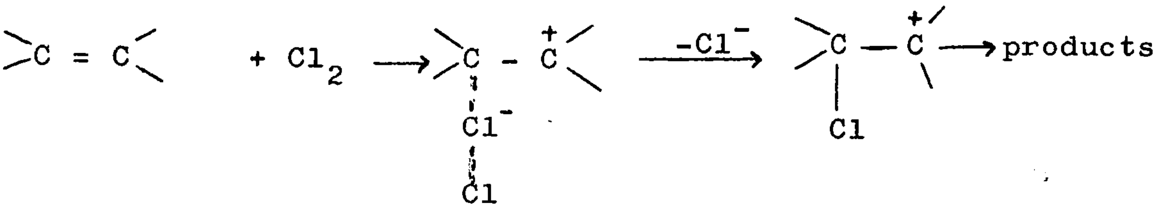
This kinetic form establishes that the transition state for the rate-determining step contains the olefin and the electrophile. It has been shown that added chloride ion, added hydrogen chloride, and added sodium acetate affect the rate of addition only slightly and through a salt effect.[18,21] So it is most unlikely that either Cl^+, $ClOAcH^+$, or ClOAc is the true electrophile, since the following equilibria would be powerfully affected by the presence of hydrogen chloride or sodium acetate:

$$Cl_2 + HOAc \rightleftharpoons ClOAc + HCl$$

$$Cl_2 + HOAc \rightleftharpoons ClOAcH^+ + Cl^-$$

$$Cl_2 \rightleftharpoons Cl^+ + Cl^-$$

It seems probable therefore that the transition state relevant to the rate-determining stage of the reaction contains both the electrophilic and the nucleophilic fragment of the attacking halogen. As for aromatic substitution, therefore,[28] it is reasonable to describe the reaction path as follows:



The effect of change in solvent on the rate of reaction is consistent with this view of the reaction path, and can be interpreted in terms of the Hughes-Ingold theory of solvent action.[29] In this theory, the initial and transition stages are considered differentially. In a reaction, such as this one, in which initially neutral or slightly dipolar molecules form a transition state involving much development of charge, the rate of reaction must be greatly facilitated by increasing the ionising power of the medium. So chlorination in non-polar solvents is less rapid than in acetic acid, and addition of water to acetic acid markedly increases the rate of reaction.[18]

Added electrolytes also facilitate addition in acetic acid, usually by virtue of a primary salt effect.[18] The results suggest, however, that chloride ions have also a special effect in these reactions, introducing a new kinetic form:[18,30]

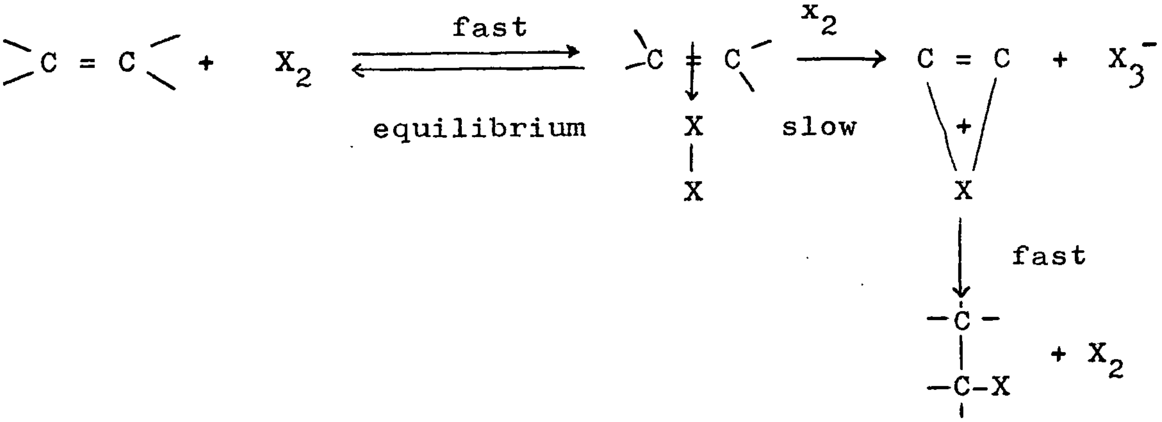
$$\frac{-d(\mathrm{Cl}_2)}{dt} = (\text{olefin})\ (\mathrm{Cl}_2)\ (\mathrm{Cl}^-)$$

A similar form seems established also for bromine addition, though the function of the halide ion is not known.

For additions of Br_2, I_2 and the interhalogens BrCl, IBr and ICl in poorly ionising solvents such as acetic acid and nitrobenzene another term, second order in halogen, must be included in the rate equation, and becomes predominant at moderate halogen concentrations.[31]

$$\frac{-d(X_2)}{dt} = k_2\ (\text{olefin})\ (X_2) + k_3\ (\text{olefin})\ (X_2)^2$$

The second term could be interpreted in the same way as for addition of HX in non-polar solvents. In poorly ionising media, the formation of the presumed halogenonium-ion intermediate, requiring charge separation is difficult, but is aided by a second molecule of halogen which helps to disperse the negative charge by formation of the large trihalide, X_3^-.



In keeping with this suggestion, no third order term has been found for the additions of chlorine, which forms the Cl_3^- ion only with extreme difficulty.[32]

The individual rate constants for attack by the bromine molecule and the tribromide anion Br_3^- can easily be obtained from the variation of the observed composite rate constant with the concentration of added bromide ion.[33]

(c) Addition of hypohalous acids

In considering the addition of a hypohalous acid HOX to an unsaturated linkage, the HOX is thought to be polarised in the sense:

$$\overset{\delta+}{X}\text{- - - - -}\overset{\delta-}{OH}$$

The evidence for this comes from a study of the products of addition of hypohalous acids to various olefins. Thus, the reaction of propene with hypochlorous acid yields 1-chloropropan-2-ol as the main product.[31]

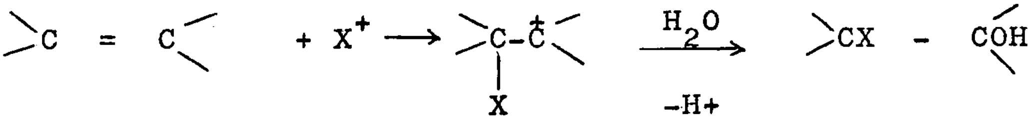
$$CH_3\text{-}CH = CH_2 \xrightarrow{ClOH} CH_3CH(OH)CH_2Cl$$

Comparing this with the addition of hydrogen chloride to the same compound:

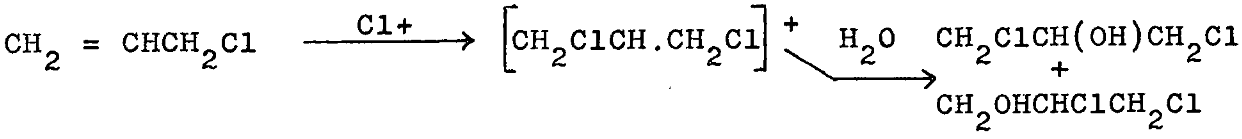
$$CH_3CH = CH_2 \xrightarrow{HCl} CH_3CHClCH_3$$

the halogen atom of ClOH is seen to attack the same carbon atom as does the proton of hydrogen chloride and is therefore the electrophilic moiety of the molecule.

Reaction is considered to proceed in two stages, as in the other electrophilic additions so far studied. The first stage involves electrophilic halogen attack to form a carbonium ion, the second, nucleophilic attack by water on this carbonium ion, to give a chlorohydrin.



Unsymmetrical olefins often yield a mixture of both possible isomeric products. For example, allyl chloride yields 70% 2,3-dichloropropanol and 30% 1,3-dichloropropan-2-ol.[34,35]



$$CH_2=CHCH_2Cl \xrightarrow{Cl+} [CH_2ClCH.CH_2Cl]^+ \xrightarrow{H_2O} CH_2ClCH(OH)CH_2Cl + CH_2OHCHClCH_2Cl$$

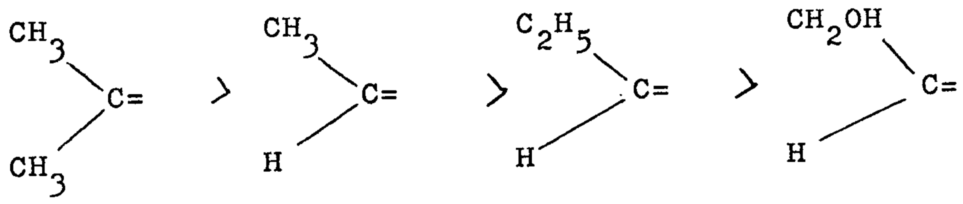
It has been established that the ratio of isomeric chlorohydrins is little affected by the nature of the halogenating species.[34,35] That is to say, chlorination under conditions where the active species is presumed to be Cl+ or H_2OCl+, yields the same ratio of products as chlorination by Cl_2 or Cl_2O.

The products of addition of hypochlorous acid to some olefins are given in Table 4.

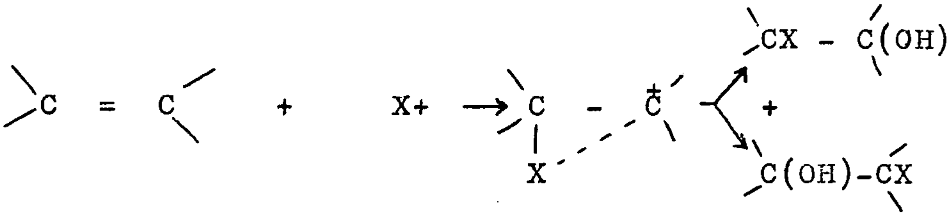
Table 4

	Olefin	α-Chlorohydrin		β-Chlorohydrin		Ref
(1)	$(CH_3)_2C=CH_2$	$(CH_3)_2C(OH)CH_2Cl$	100%	$(CH_3)_2CClCH_2OH$	0%	36
(2)	$CH_3CH=CH_2$	$CH_3CH(OH)CH_2Cl$	95%	$CH_3CHClCH_2OH$	5%	36
(3)	$C_2H_5CH=CH_2$	$C_2H_5CH(OH)CH_2Cl$	85%	$C_2H_5CHClCH_2OH$	15%	36
(4)	$CH_2OHCH=CH_2$	$CH_2OHCH(OH)CH_2Cl$	75%	$CH_2ClCHClCH_2OH$	25%	34,37
(5)	$CH_2ClCH=CH_2$	$CH_2ClCH(OH)CH_2Cl$	30%	$CH_2ClCHClCH_2OH$	70%	34,35
(6)	$CH_2BrCH=CH_2$	$CH_2BrCH(OH)CH_2Cl$	32%	$CH_2BrCHClCH_2OH$	40%	38a
(7)	$CH_2ClCMe=CH_2$	$CH_2ClCMe(OH)CH_2Cl$	84%	$CH_2ClCMeClCH_2OH$	6%	39
(8)	$CH_2ClCCl=CH_2$	$CH_2ClCOCH_2Cl$	97%	$CH_2ClCCl_2CH_2OH$	3%	40

Reactions (1) - (4) appear to accord with the idea of initial attack by positive chlorine at the terminal carbon, which is negatively polarisable due to electron-repulsion by the substituted methyl groups. The decrease in the proportion of terminally halogenated isomer in the product on going from (1) to (4), and the corresponding increase in 2-chloro isomer, is explained by the decrease of electron-releasing capacity of the substituted groups. The electron-releasing ability of these groups is in the following order:



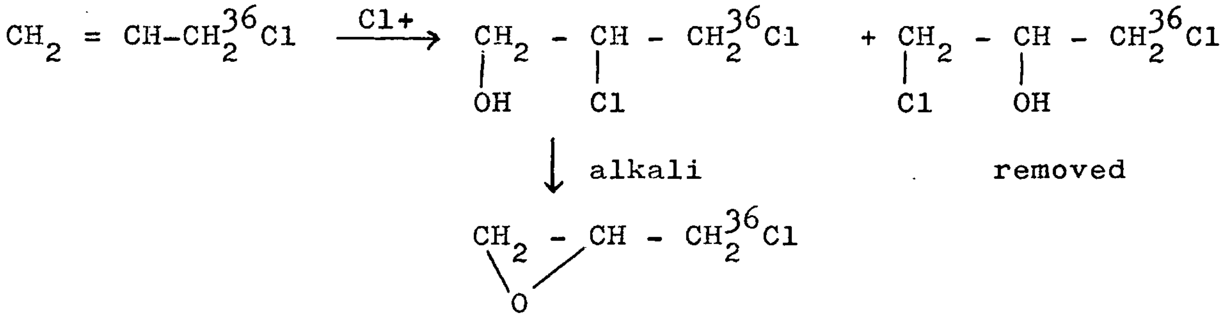
The preponderance of 2-chloro over 1-chloro isomer in reactions (5) and (6), however, appears at first sight to be anomalous, since the CH_2Cl group is also regarded as electron-releasing as discussed in hydrogen halide additions earlier. The interpretation of this behaviour will be discussed later. Briefly, the incoming halogen is thought to interact with the carbonium ionic centre, giving an intermediate such as shown below. Subsequent nucleophilic attack on such an intermediate would occur, by analogy with ring-cleavage of epoxides, principally at the terminal carbon atom;



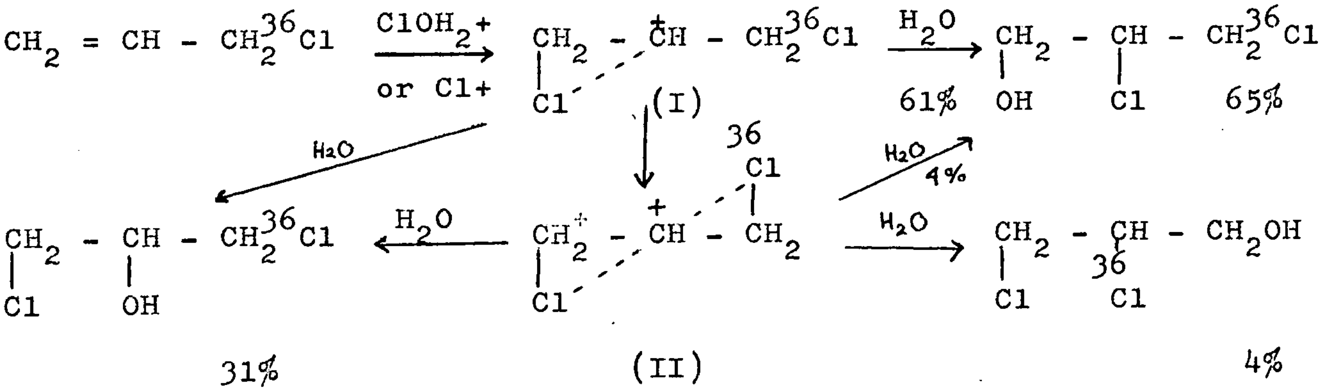
Reaction (7) indicates that the electron-release of the methyl group in β-methyl allyl chloride so strongly reinforces the polarisation of the double bond that the orientation of addition is completely reversed compared with allyl chloride, the "normal" (Markovnikov) addition product completely predominating.

The inclusion of a β-chloro substituent has likewise the effect of strongly polarising the double bond so that the positive halogen species becomes very firmly attached to C-1, with correspondingly less interaction with the carbonium ionic centre, and hence little production of 2,2,3-trichloropropanol from 2,3-dichloropropene (8).

In a product analysis of the reaction between ClOH and allyl chloride labelled with ^{36}Cl, de la Mare and Pritchard isolated and measured the radioactivity of the 2,3 dichloropropanol produced.[41] This was then converted to the epichlorohydrin, which was found to contain only ca.94% of the activity of the chlorohydrin.



The authors concluded that about 4% of the chlorine originally in the 3-position in allyl chloride had migrated to the 2-position in the 2,3-dichloropropanol product, and therefore that 12% of the 2,3-dichloro isomer was derived from a symmetrical intermediate such as II in the scheme set out below.



It was suggested that the major proportion of the products was yielded by nucleophilic attack of water on the initially formed intermediate (I), before it could become completely symmetrical (II).

The extent of rearrangement due to allylic halogen migration is summarised for the other allylic halides in the following table:

Table 5

Percentages of addition products yielded by the addition of ClOH

Compound	Markovnikov Product	Anti-Markovnikov	Rearranged Anti-M.	Refs.
$CH_2{=}CHCH_2Cl^*$	$CH_2ClCH(OH)CH_2Cl^*$ (31)	$CH_2OHCHClCH_2Cl''$ (65)	$CH_2ClCHCl^*CH_2OH$ (4)	41
$CH_2{=}CHCH_2Br$	$CH_2ClCH(OH)CH_2Br$ (32)	$CH_2OHCHClCH_2Br$ (40)	$CH_2ClCHBrCH_2OH$ (28)	38a
$CH_2{=}CHCH_2I$	$CH_2ClCH(OH)CH_2I$ (30)	$CH_2OHCHClCH_2I$ (22)	$CH_2ClCHICH_2OH$ (48)	38b

cont. below

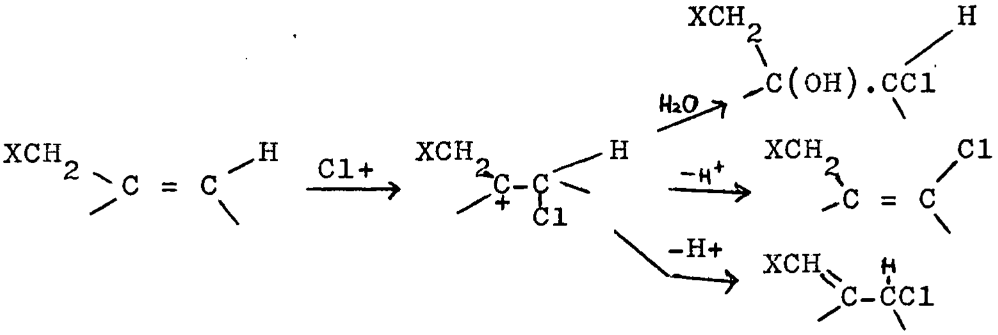
The extent of rearrangement is seen to increase with the known migrating ability of the halogen atoms: Cl < Br < I. It is to be expected that this ability will depend on both the neighbouring group interaction of the halogen and the ease of heterolysis of the carbon-halogen bond, and will be discussed more fully later.

The rather complex kinetics of chlorination by hypochlorous acid have been studied extensively by Shilov <u>et.al.</u> and by Israel <u>et.al.</u>[42], and will be discussed in Section E. The reactive halogenating species in a dilute solution of hypochlorous acid in the presence of strong acid is believed to be the hypochlorous acidium ion H_2OCl^+ and/or the chlorinium ion Cl^+, as well as the hypochlorous acid molecule itself.

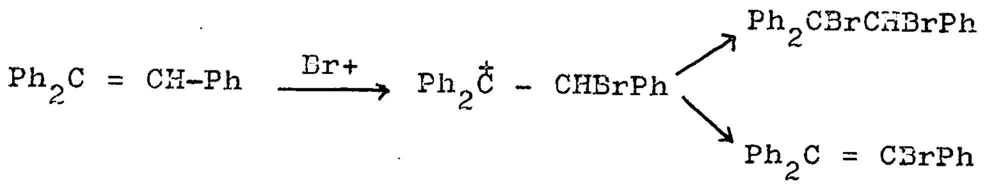
B Substitution accompanying addition

It is a well-established fact that elimination reactions from certain allyl halides (viz.E_1 reactions) involve proton-loss from carbonium ions. By analogy with this mechanism, any reaction proceeding through a carbonium ion could give olefinic products by proton-loss, as well as the products of nucleophilic attack on the carbonium ion. For unsymmetrical structures a number of different isomeric olefins could theoretically be formed.

Thus in the case of the addition of halogens or hypohalous acids to olefins, we have the possibility of addition or of overall substitution by the halogen.

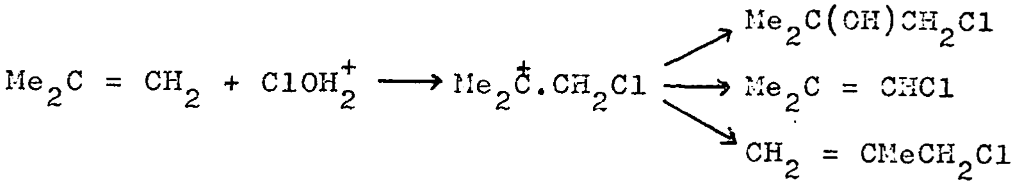


For example, the bromination of triphenylethylene gives, depending on the conditions, mainly the product of addition, 1,2-dibromotriphenylethane, or of substitution, bromotriphenylethylene.[43]



$$\mathrm{Ph_2C = CH{-}Ph \xrightarrow{Br+} Ph_2\overset{+}{C} - CHBrPh} \begin{array}{l} \nearrow \mathrm{Ph_2CBrCHBrPh} \\ \searrow \mathrm{Ph_2C = CBrPh} \end{array}$$

Also, one of the products of chlorination of isobutene was found to be 3-chloro-2-methylpropene.[7,44,45]

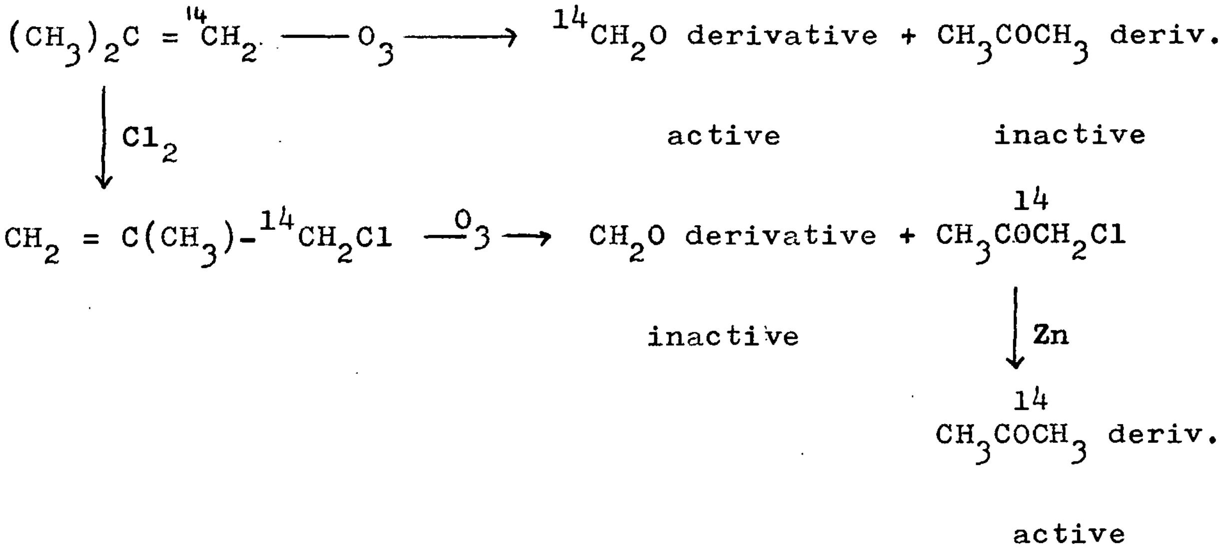


$$\mathrm{Me_2C = CH_2 + ClOH_2^+ \longrightarrow Me_2\overset{+}{C}.CH_2Cl} \begin{array}{l} \nearrow \mathrm{Me_2C(OH)CH_2Cl} \\ \longrightarrow \mathrm{Me_2C = CHCl} \\ \searrow \mathrm{CH_2 = CMeCH_2Cl} \end{array}$$

Other workers investigated similar reactions[46] and the general conclusion drawn was that olefins which reacted readily with mineral acids (i.e. those capable of forming tertiary halides), gave substitution as well as, or instead of, addition products. Another observation was that the ratio of substitution to addition products was increased for a given reaction by raising the temperature.

Tischenko showed, by examination of addition of chlorine to many substituted ethylenes, that the reaction leading to a chloro-substituted olefin was not one of simple substitution by chlorine, but that a shift of a double bond was taking place.[47]

Reeve, Chambers and Prickett[48] confirmed this by labelling isobutene (at 0°C) in the 1- position with ^{14}C. Both the starting material and the product were treated with ozone. The starting material was found to give inactive acetone and active formaldehyde, while the product, 3-chloro-2-methylpropene, yielded active acetone and inactive formaldehyde.



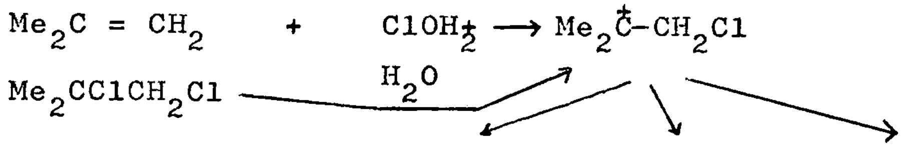
$$(CH_3)_2C={}^{14}CH_2 \xrightarrow{O_3} {}^{14}CH_2O \text{ derivative} + CH_3COCH_3 \text{ deriv.}$$

$$CH_2=C(CH_3)-{}^{14}CH_2Cl \xrightarrow{O_3} CH_2O \text{ derivative} + CH_3\overset{14}{C}OCH_2Cl$$

$$CH_3\overset{14}{C}OCH_2Cl \xrightarrow{Zn} CH_3\overset{14}{C}OCH_3 \text{ deriv.}$$

(The formaldehyde was converted to its dimedone derivative for counting, and acetone to its 2,4-dinitrophenylhydrazone). These results indicate that the mechanism is not one of direct attack by Cl_2 on one of the methyl groups, but involves electrophilic attack by chlorine on the terminal carbon atom, followed by proton-loss from one of the methyl groups of the carbonium ion formed.

Further evidence for the two-stage carbonium ion mechanism for halogen substitution accompanying addition reactions is provided by a comparison of the products in aqueous solution of the chlorination of isobutene and of the hydrolysis of 1,2-dichloro-2-methylpropane. These were found by de la Mare and Salama to be produced in essentially the same proportions.[49] It is assumed therefore that the two reactions proceed via a common carbonium ionic intermediate, the reaction scheme being set down as follows:



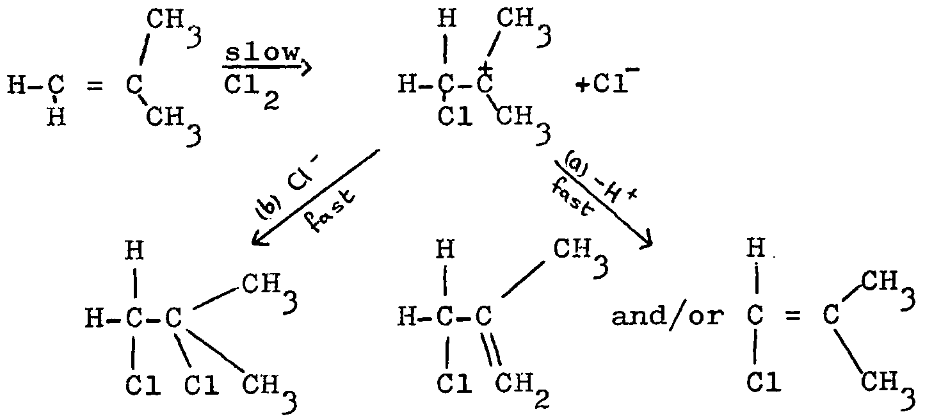
	$Me_2C = CHCl$	$CH_2 = CMe.CH_2Cl$	$Me_2C(OH)CH_2Cl$
Hydrolysis	6%	10%	84%
Addition	0.4%	12%	87.6%

To summarise, then, the chlorination of olefins, as suggested by Taft,[50] appears to proceed in two stages:

(1) the rate-determining addition of positive halogen to form the carbonium ion;

(2) two distinct fast reactions of the carbonium ion to give (a) substitution and/or (b) addition products.

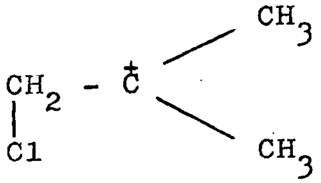
Setting out such a scheme in full:



The ratio of addition products to substitution products was found to bear a rough relationship to the number of hydrogen atoms on the carbon atom adjacent to the positive carbonic centre. Generally speaking the greater the number of such α-hydrogen atoms, the higher the substitution: addition ratio. The reason suggested was that the greater the number of hydrogen atoms in the molecule, the greater the number of resonance structures that can be written for the intermediate carbonium ion, and hence the greater the extent to which the positive charge is delocalised. The charge density at carbon-2 is therefore reduced and the proportion of nucleophilic attack accordingly lessened.

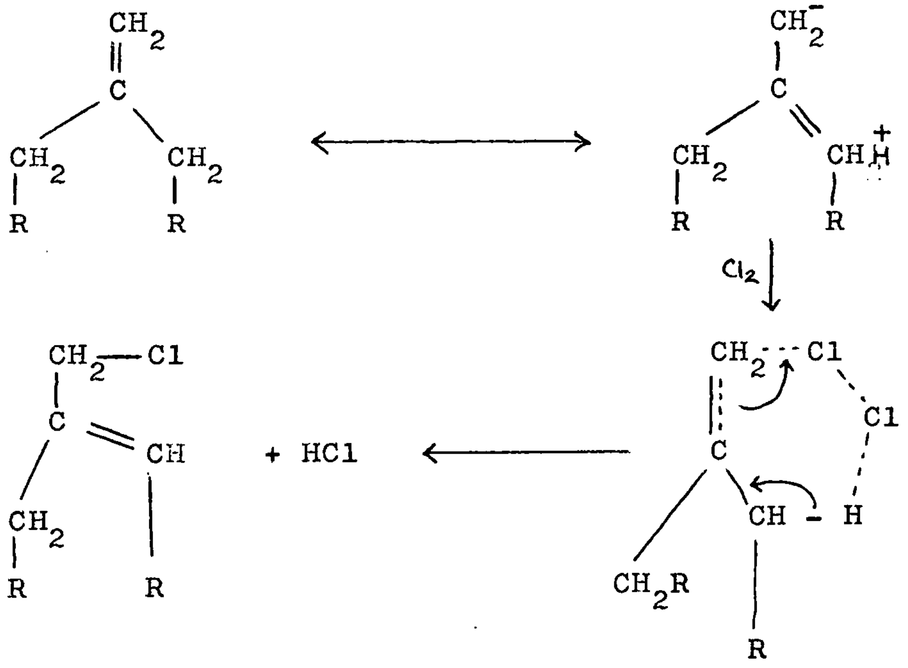
The orientation of elimination, that is, the direction of proton loss, has given rise to some speculation.

Taft, for example, suggested that the orientation would be determined by the polar effects of the substituents attached to the carbonium ionic centre.[45] For example, the ion below, produced by the addition of Cl_2 to isobutene, has greater electron density around the carbon atom of the methyl group than around the carbon atom of the chloromethyl group, because of the inductive effect of the chlorine atom. This suggests that proton-loss would take place from the chloromethyl group rather than from the methyl group.

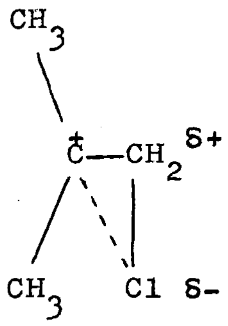


Further, the electromeric effect of this chlorine atom also would increase the tendency to form a double bond between the carbonium ionic centre and the carbon atom of the chleromethyl group. These predictions, however, are contrary to the experimental findings, which are that 3-chloro-2-methylpropene is formed in much greater quantities than the isomeric 1-chloro-2-methylpropene.[44]

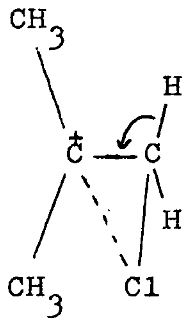
Arnold and Lee, from their work on the chlorination of methylene cyclohexane,[51] suggested that a cyclic transition state was involved in the formation of allylic monochlorides from isobutenes. In this mechanism, the attachment of a chlorine atom, elimination of hydrogen chloride, and rearrangement of the double bond all take place simultaneously.



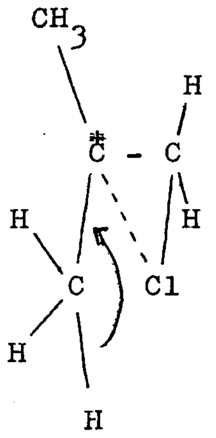
de la Mare and Salama put forward a theory based on stereochemical grounds to explain the predominant loss from the methyl group in the addition of hypochlorous acid to isobutene described earlier. They suggested that there was some distortion towards a three-numbered ring in the chloromethyl group produced by interaction between the C-Cl dipole and the carbonium ionic centre.



I



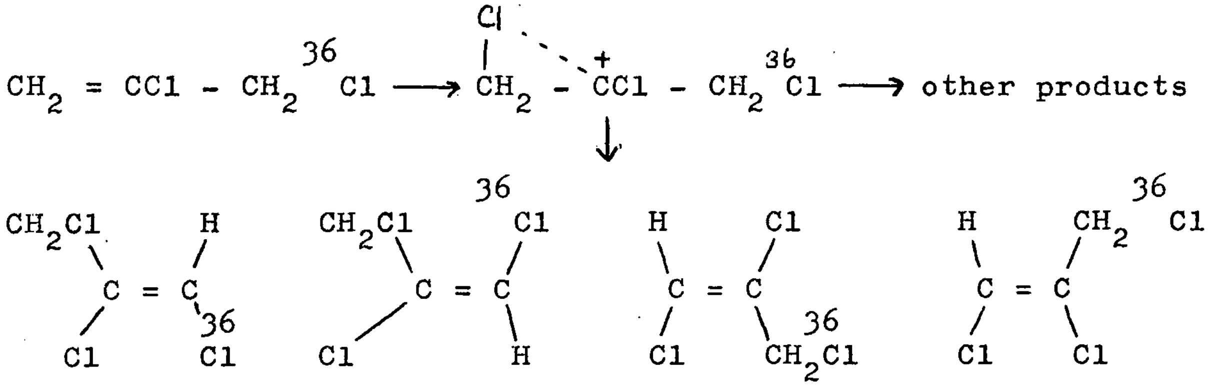
II



III

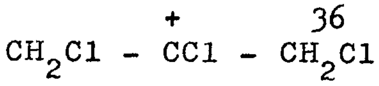
This distortion was considered to be stereochemically unfavourable for proton-loss from this chloromethyl group as in II, but not to affect the ease of proton-loss from one of the methyl groups as shown in III.

A better test of Taft's theory was the examination of proton-loss from a formally symmetrical intermediate, such as that produced from hypochlorous acid and 2,3-dichloropropene. Ballinger, de la Mare and Williams found the following proportions of isomeric substitution products.[52]



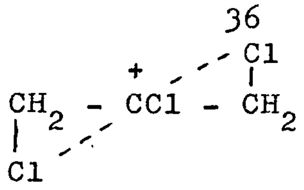
cis,vinylically labelled	*trans*,vinylically labelled	*trans*,allylically labelled	*cis*,allylically labelled
2.9%	3.8%	0.5%	0.8%

Thus, about 84% of the substitution products is vinylically labelled, that is, derived from proton-loss from the $CH_2{}^{36}Cl$ already present in the olefin molecule. Since equal amounts of proton-loss do not occur from the two possible branches of the carbonium ion, it is apparent that the intermediate involved in this reaction cannot be completely symmetrical about the central carbon atom. Thus both the classical carbonium ion (I) and also an intermediate in which both 1- and 3- substituted chlorine atoms interact equally with the central carbon atom (II) are ruled out. An intermediate such as III is suggested, in which the C-Cl dipole of C_1 interacts with the positive centre, producing a strained configuration, which stereochemically hinders the loss of a proton from the attacked carbon atom. The main product would then be the vinylically labelled isomer.

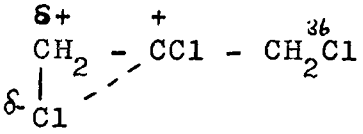


$CH_2Cl-\overset{+}{C}Cl-CH_2{}^{36}Cl$

I

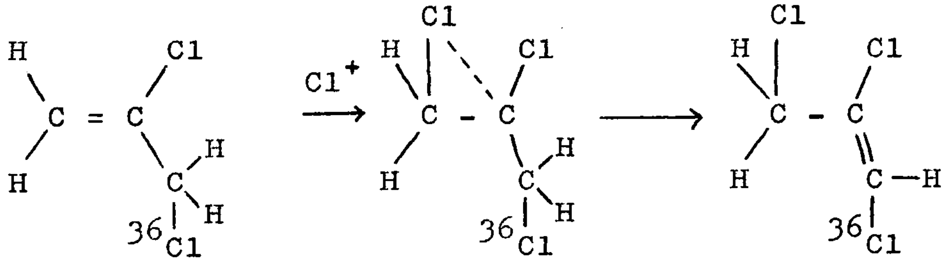


II

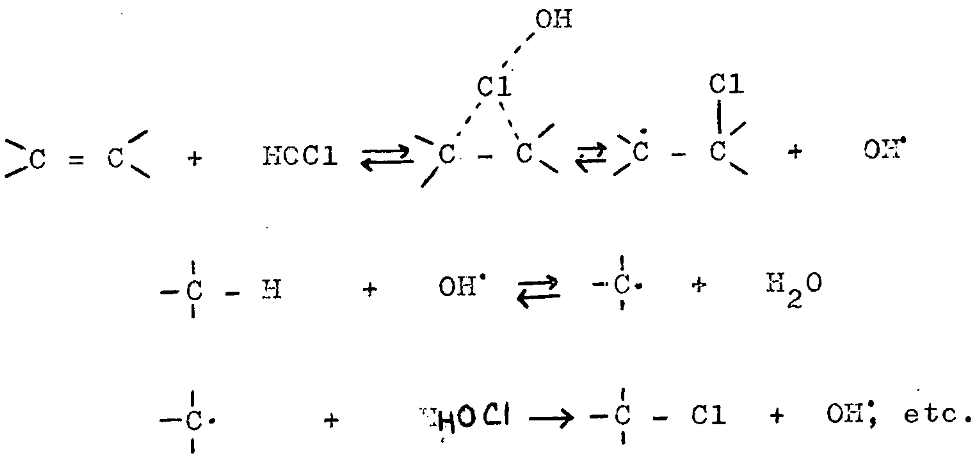


III

It will be noted that in the formation of the main product, i.e. the vinylically labelled trichloropropene, the *trans* isomer is formed in predominant amount. This suggests a tendency for the chlorine atoms on carbons 2 and 3 to take up a conformation so that they are as far apart as possible, to minimise the repulsions of the dipoles of the C-Cl bonds. Proton-loss is then more likely to take place in such a way as to leave these two chlorine atoms *trans*- to each other in the product i.e. to favour the formation of *trans*-$(1-{}^{36}Cl)$ 1,2,3-trichloropropene.



Marmor and Maroski advance the theory that the addition of HOCl to olefins involves a free-radical process.[53] They found that in the addition of HOCl to various hindered olefins, such as *unsym* - dineopentylethylene and 3,3,5,5,-tetramethylmethylenecyclohexane, substitution was the main or only reaction, with the double bond remaining in the original position. Since direct halogenation of alkanes is believed to occur <u>via</u> a free-radical process, they say that it is reasonable to assume that substitution accompanying addition in reactions of alkenes with halogens is also due to a free radical process. They propose that the concept of "molecule-induced homolysis" (first put forward by Martin and Drew <u>et</u>.<u>al</u>.[54]) is operative in reactions of HOCl with olefins. The HOCl molecule is largely undissociated in aqueous solution, and as such it is analogous to a chlorine molecule. Furthermore, it has been established that HOCl can and does react with unsaturated ketones, in the presence of peroxides, <u>via</u> a free-radical mechanism. It is being assumed, therefore, that some of the HOCl undergoes homolysis, with the generation of chain-propagating radicals. The fact that no C-OH structures are formed is explained on the basis of the greater stability of the OH radical as compared with the Cl radical. (In the free-radical reaction of HOCl with quinones and unsaturated ketones no hydroxy compounds were observed in the products either.[55]) The following scheme is proposed as a representation of the possible mechanism:



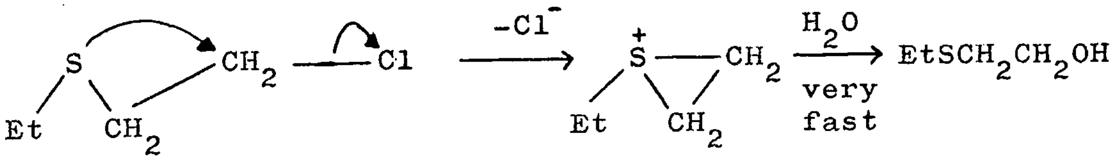
Marmor and Maroski also studied the reaction of hypochlorous acid with a mixture of dineopentylethylene and cyclohexane. Chlorocyclohexane was formed, indicating that free radicals were generated if we are to assume that substitution of H by Cl proceeds only by a free radical mechanism.

These results, however, can also be interpreted by the usual ionic mechanism. The preponderance of substitution products arises simply because in these hindered olefins there is steric hinderance to nucleophilic attack by the solvent on the carbonium ion.

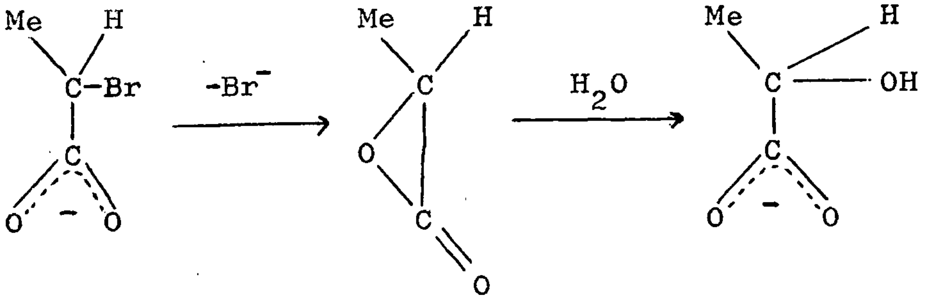
C Neighbouring group participation

Winstein[57] termed the phenomenon of interaction between a substituent and a developing carbonium ionic centre the neighbouring group effect. There are three principal types of evidence which point towards neighbouring group participation.

First, if such participation occurs during the rate-determining step, the reaction is almost certain to be significantly faster than other reactions which are similar but do not involve such participation. Typically, the β-chloro sulphide CH_2ClCH_2SEt is hydrolysed over 10,000 times as rapidly as is the corresponding ether $ClCH_2CH_2OEt$ (in aqueous dioxan).[58] This rate difference is far too great to be attributed to differences in inductive, conjugative, or steric effects, but suggests rather that the hydrolysis of the sulphide (but not the ether) proceeds through a cyclic 'onium ion (in this case, sulphonium ion). The intermediate, because of the strained three-membered ring, is readily hydrolysed to the observed products.



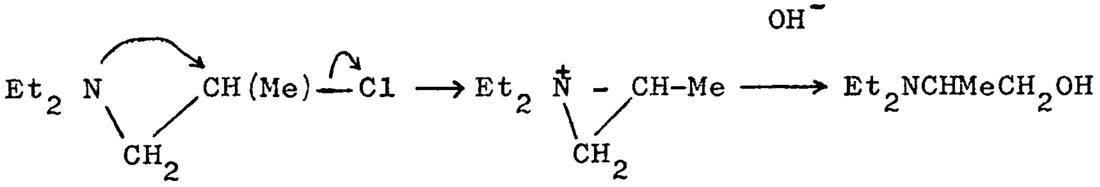
Second, sometimes the stereochemistry of a reaction suggests that neighbouring groups become involved. Thus the hydrolysis of α-bromopropionate ion in water or dilute base yields lactate with retention of configuration about the α-carbon atom.[59] Since nucleophilic displacements at secondary carbon atoms almost invariably result in partial or complete inversion of configuration, it was assumed that two displacements were actually involved: the first a displacement of bromide by the neighbouring carboxylate group to form the non-isolatable α-lactone, the second a very rapid cleavage of the lactone by water. Inversion presumably occurred in both displacements, the second inversion "nullifying" the first.



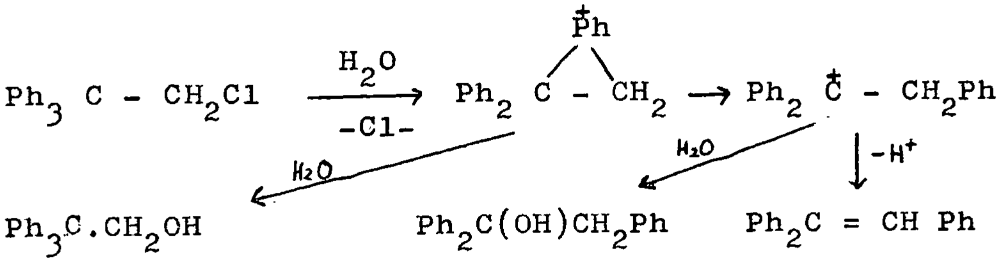
Evidence for this mechanism comes from a study of the relative rates of solvolysis of α-bromopropionate[60] and isopropyl bromide.[61] In methanol, α-bromopropionate is the faster by a factor of 20, while in water, the relative rates are reversed. It is found that α-bromopropionate is not sensitive to solvent and salt effects. Since S_N1 reactions involving ionisation typically depend markedly on solvent effects, it is apparent that such a mechanism is not involved here. The evidence strongly suggests that the rate-determining step involves a direct intramolecular displacement by the carboxylate group.

<u>Finally</u>, neighbouring group participation may lead to rearranged or cyclic products. The neighbouring group remains attached to the reaction centre and either breaks away from the atom to which it was originally attached in the substrate, yielding a rearranged product, or remains bonded to both, yielding a cyclic product.

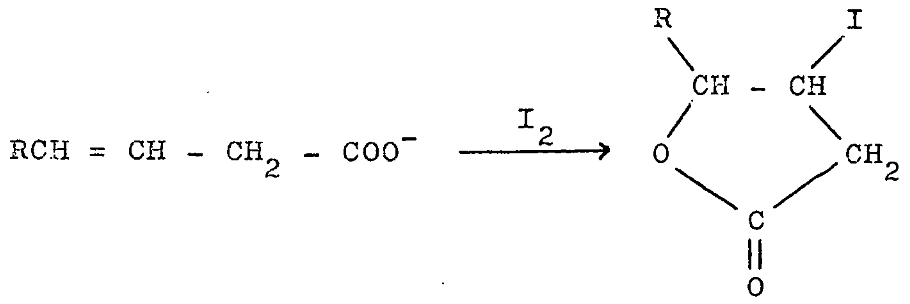
As an example of the former type, 2-chloro-<u>n</u>-propyldiethylamine yields on basic hydrolysis a rearranged aminohydrin, presumably because the intermediate imonium ion is attacked preferentially at the α-carbon atom.[62]



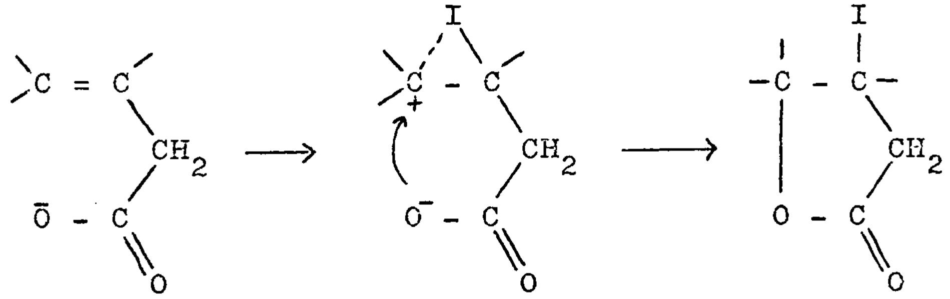
The hydrolysis in formic acid of $Ph_3C.CH_2Cl$ yields in addition to the solvolysis products, a rearranged olefin, formed by migration of a phenyl group in the carbonium ionic intermediate:[63]



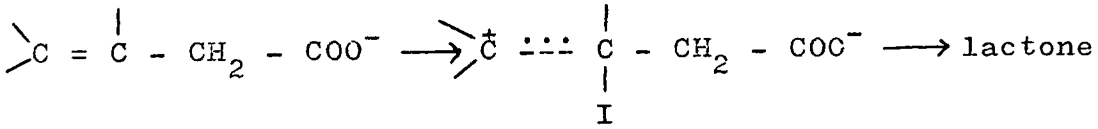
Neighbouring group interaction is also found in carbonium ions produced by electrophilic additions to olefinic double bonds. For example Tamelen and Shamma found that the addition of iodine to unsaturated carboxylate ions yields iodolactones.[64]



The authors suggest that iodolactonisation proceeds by way of an initial positive iodine attack on the double bond followed by carboxylate ion displacement on the resulting iodonium portion of the intermediate zwitterion.



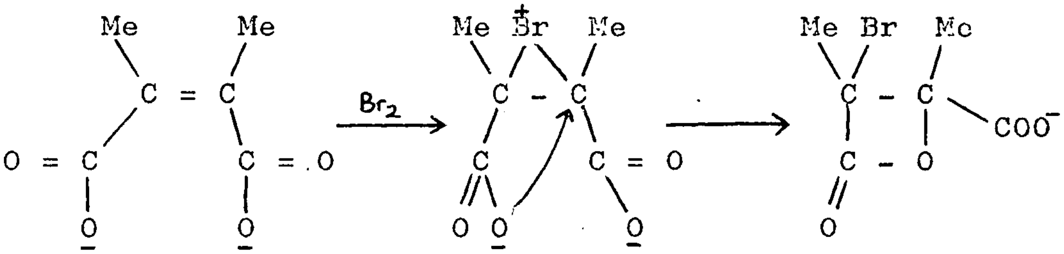
They point out that the view of Linstead,[65] who visualizes an acyclic intermediate which subsequently lactonizes, is essentially the same.



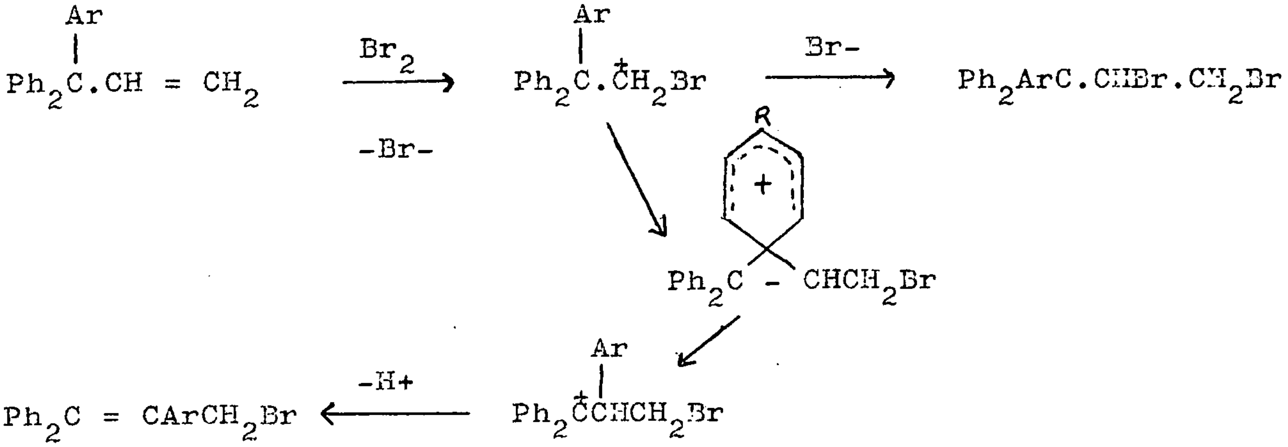
$$>C = \overset{|}{C} - CH_2 - COO^- \longrightarrow >\overset{+}{C} \cdots \underset{I}{\overset{|}{C}} - CH_2 - COO^- \longrightarrow \text{lactone}$$

It was further found that 5- and 6- membered rings were favoured in these iodolactone formations, and that the double bond must be isolated, i.e. not conjugated.

Bartlett and Tarbell found similar lactone formation in the addition of bromine to dimethylmaleic acid.[66]

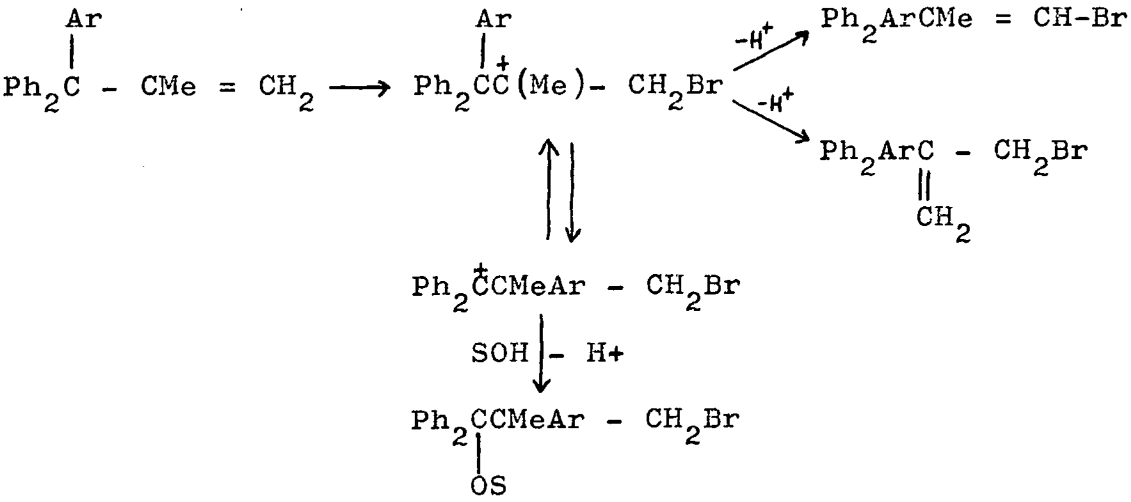


More recently Norman and Thomas found that addition of Br_2 to $Ph_2C(Ar)CH = CH_2$ involved migration of the aryl group.[67] They described the sequence as follows:



The ratio of rearrangement product to dibromide was found to increase with the change from Ar = phenyl to Ar = anisyl, and also with an increase in the polarity of the solvent. These increases are attributed in the first case to an increase in the electron-releasing ability of the p-MeO.C_6H_4 - group as compared to C_6H_5-, and in the second case to an increase in the lifetime of the carbonium ionic intermediate, thus allowing greater participation by the neighbouring group. The same changes were also found to increase the rate of the reaction, as would be expected.

Reaction of $Ph_2ArCCMe = CH_2$ with Br_2 produced similar results. Here, however, there are two possible directions of proton loss from the carbonium ionic intermediate, leading to isomeric products.



The allylic bromide was found to predominate over the vinylic isomer. This is interpreted in terms of the steric strain involved in proton loss from the CH_2Br group, as discussed earlier.

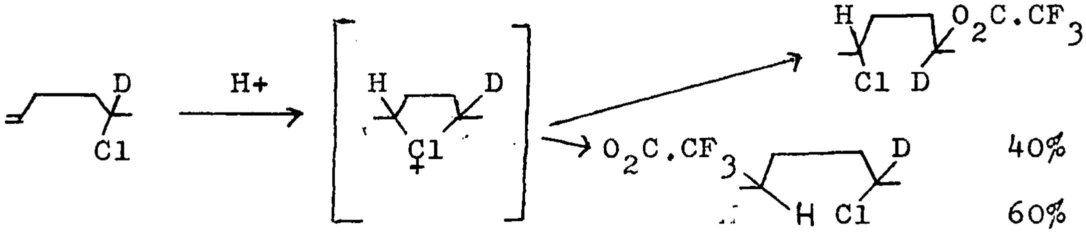
Internal competition by halogen, giving rise to rearranged products, has been described by de la Mare and others in electrophilic addition to allyl halides.[38] The following table gives the percentage of 2-G product yielded by the addition of ClOH to $CH_2 = CRCH_2G$.

Table 6

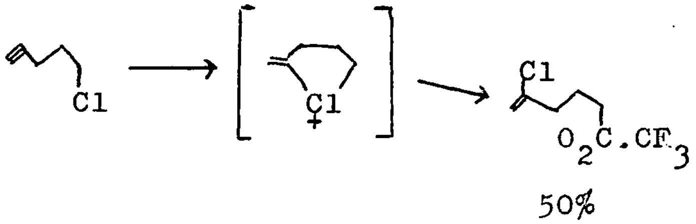
R	H	Me	Cl	H	H	H	H	H	H	H	H
G	Cl	Cl	Cl	Br	Br	Br	I	I	I	OH	H
Solvent	H_2O	H_2O	H_2O	H_2O	40% dioxan	70% dioxan	H_2O	40% dioxan	dioxan 70%	H_2O	
% rearrangement	4	2	0	28	18	11	48	30	18	0	
% Markownikoff Orientation	30	94	96	32	37	39	30	31	32	73	91
% Anti-M. Orientation	66	4	4	40	45	50	22	39	50	27	

These results indicate increasing neighbouring group participation in the order I>Br>Cl. The increase in migration with increase in solvent polarity is interpreted in terms of the greater stability of carbonium ions in more polar solvents, leading to increased opportunity for neighbouring group interaction.

More recent evidence for neighbouring halogen participation in electrophilic reactions is given by Peterson <u>et.al</u>. Thus, addition of trifluoroacetic acid to 5-chlorohexene proceeds some 7 to 10 times faster than would be expected, and also involves a 1, 4 chlorine shift to yield a rearranged product.[68a]



A similar 1, 4-chlorine shift was observed in the addition of CF_3CO_2H to 5-chloropent-1-yne.[62b]

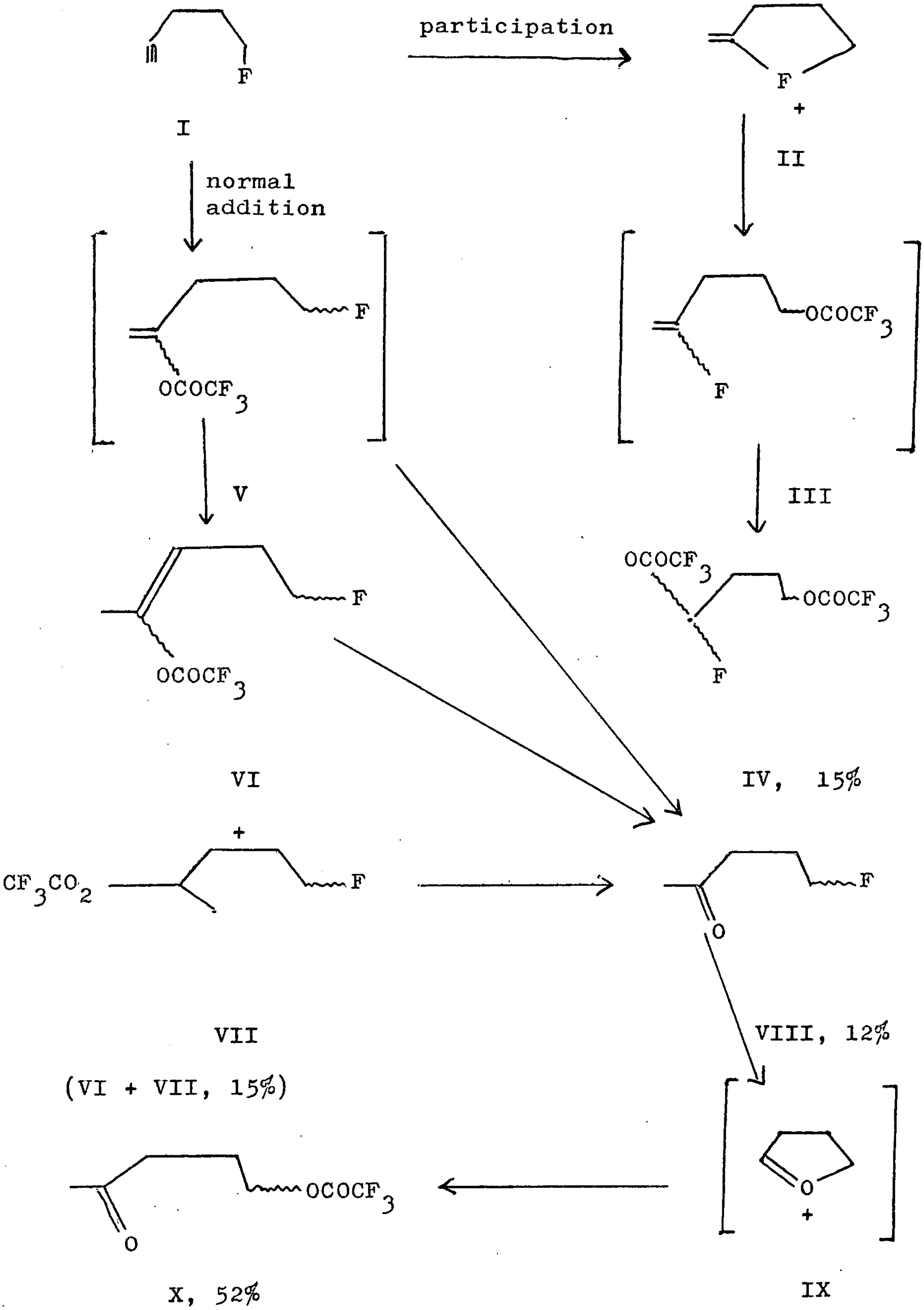


Further, in a study of the rates of addition to a series of 5-substituted 1-hexenes, the 5-Cl,-Br, and -I compounds were found to react several times faster than would be expected merely by a consideration of their inductive effects.[69] It was assumed that internal assistance by the halogens largely offset their inductive effect.

Moreover, the rates of addition of CF_3COOH to 5-bromopentene and 6-bromohexene respectively were found to be very similar, again indicating neighbouring group interaction by halogen counteracting its inductive effect.

Peterson bases his calculations of the "expected" rate constant for electrophilic addition to a terminally substituted polymethylene 1-alkene or 1-alkyne on the observation that the inductive effect exerted by the substituent at the reaction centre falls off by a constant factor per methylene group (see Chapter 2).[70]

Evidence has been obtained by Peterson and Bopp for fluoronium ion intermediates in the reaction of trifluoroacetic acid with 5-fluoropentyne and 5-fluoro-2-pentyl tosylate.[71.] In the former case the reaction scheme proposed is:


participation
normal addition
F
I
F
+
II
OCOCF3
F
OCOCF3
F
OCOCF3
V
III
F
OCOCF3
OCOCF3
OCOCF3
F
VI
IV, 15%
+
CF3CO2
F
F
O
VII
VIII, 12%
(VI + VII, 15%)
OCOCF3
O
O
+
X, 52%
IX

Their evidence for fluorine participation in solvolysis in CF_3COOH of 5-fluoro-2-pentyl Tosylate is obtained from comparison of the rates of various $\underline{\omega}$-fluoroalkyl tosylates. There is an increase over the expected (unassisted) rate by a factor of 2.4

Hydroxyl participation in electrophilic addition reactions has been established by Williams, who studied the initial rates of addition of iodine to the series of unsaturated alcohols $CH_2 = CH(CH_2)_nOH$.[72] The rate constants for n = 1-4 were found to be 0.011, 0.023, 2.2 and 0.38 $l.mole^{-1}min^{-1}$ respectively. Clearly OH -5 and OH -6 participation are involved, with the 5-membered ring particularly favoured.

The bromination of the series of alcohols $CH_2 = CH(CH_2)_nOH$ in water and in methanol[73] also demonstrates participation by the -OH group, particularly for n = 3, although the effects are considerably smaller than for the corresponding iodinations. The rate constants for n = 1,2,3 and 4 for the bromination in methanol are 284,525,2630 and 1730 $l.mole^{-1}min^{-1}$ respectively. Cyclic products, tetrahydrofuran derivatives for n = 3 and tetrahydropyran derivatives for n = 4 were isolated from the reaction mixtures. The more effective participation by the OH-group in iodination than in bromination was thought to arise from the greater selectivity of the less reactive iodine molecule. Approximate calculations show that for iodination the ratio of rate constants for the assisted reaction to that for the unassisted reaction (k_Δ / k_s) is 60 for n = 3 and 8 for n = 4 whereas for bromination in methanol the

corresponding ratios are 1.5 and 0.2.

A similar result for hydroxyl participation is found for the hydrolysis in water of the series of chlorohydrins $Cl(CH_2)_nOH$.[74] A rate maximum and also the formation of a cyclic product occurred for n = 4.

Further, a study of the reaction of I_2 with the sodium salts of olefinic carboxylic acids reveals a rate maximum corresponding to O^--5 participation.[75]

The rates of addition of Br_2 to the series of w-Br-1-alkenes, $CH_2 = CH(CH_2)_nBr$, in methanol, has also been studied, but here there is no clear indication of a particular ring size being favoured : for n = 1-4, k_2 = 1.5,75,500 and 1170 $l.mole^{-1}min^{-1}$ respectively.[73]

The optimum ring size for neighbouring group interaction is determined by the interplay of several quantities.[56,76]

(1) Formation of a ring results in loss of rotational freedom and hence is accompanied by an entropy decrease. With increasing length of the chain that is closed, the loss of rotational freedom increases. Hence there is an increasing unfavourable loss of entropy on ring closure, with increasing ring size.

(2) There is an unfavourable strain factor on ring formation, which decreases on going from a three- to a six-membered ring, then increases with ring size up to nine members and decreases again with rings of larger size.

(3) Since most leaving and neighbouring groups are electron withdrawing inductively, the electronic effects of these groups on one
(in nucleophilic substitution reactions)

another act to decrease the nucleophilicity of the latter and to decrease the tendency of the former to depart. They therefore tend to decrease the rate of ring formation, the decrease being greatest for three-membered rings, when leaving and neighbouring groups are attached to neighbouring carbon atoms, and decreasing with increasing ring size.

With ring closures of unsubstituted polymethylene chains involving an intramolecular nucleophilic attack on a saturated carbon centre, five-membered ring formation is most highly favoured when the element of the nucleophilic group is oxygen or nitrogen. With the more highly polarisable thioether group, the ring strain factor and the electronic effect appear to be relatively less important, since the three-membered ring is most readily formed.

Winstein made a study of the effect of various neighbouring groups on the rates of replacement reactions.[57b] Allowance having been made for inductive effects, the free energy of activation contributed by the neighbouring group to reduce the overall free energy of activation could be calculated. This was termed the <u>driving force</u> resulting from neighbouring group participation.

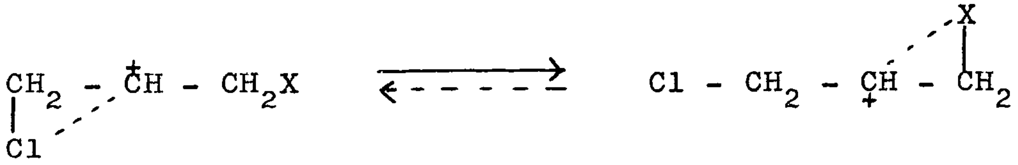
Table 7

Driving force estimated for neighbouring group (G) participation in solvolysis of $G.CH_2.CH_2X$ in acetic acid.

Neighbouring Group	I	NH_2	O^-	Br	OH	Cl	$S(CH_2)_2OH$
Driving force (kcal/mole)	9	8	6	5	1	0	13

Different numerical values would be obtained for different systems but those above do provide a sequence (I>Br>OH>Cl) for relative importance of neighbouring group interaction which will prove significant in later discussions.

Also, the existence of neighbouring group phenomena can be useful in certain cases in defining the lifetime of intermediates. Thus, if a carbonium ion is formed, where two neighbouring groups could participate, such as Cl and X in $ClCH_2\overset{+}{C}HCH_2X$, where X is a much better participator than Cl, and the ion exists long enough for the most stable configuration to be adopted, then structure II rather than I will be taken up.



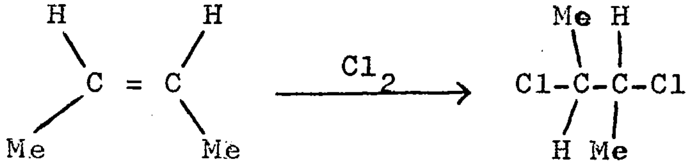
I

II

If, however, the nature of the products indicates that the reaction has occurred through intermediate I rather than II, the deduction is that the ion did not last long enough to establish the above equilibrium, and also that the geometry of the ion at the moment of production more closely resembled I than II.

D The nature of the intermediate

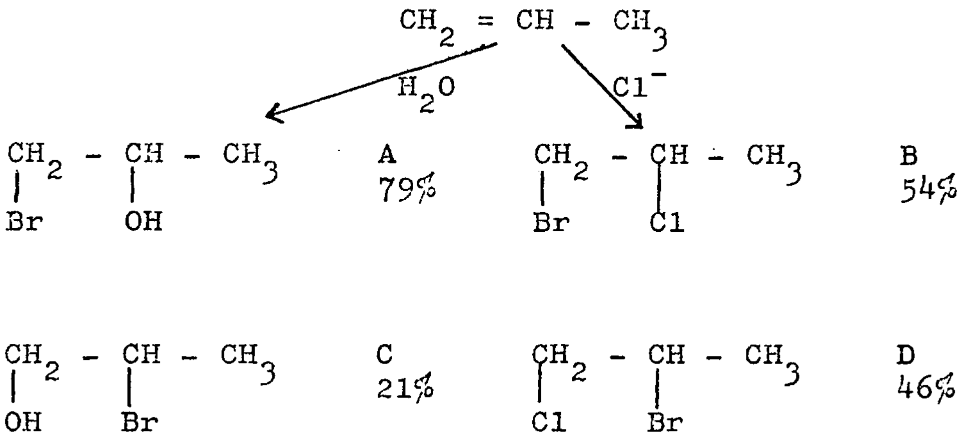
It is well known that addition to olefins initiated by electrophilic halogen often proceeds in the trans sense.[77] Thus, the addition of chlorine to cis-but-2-ene gives the racemic (±)2,3-dichlorobutane, whereas the trans-isomer gives the meso-isomer.[78]



Similarly, addition of hypochlorous acid to cyclohexene gives sterospecifically trans-2-chlorocyclohexanol.[79]

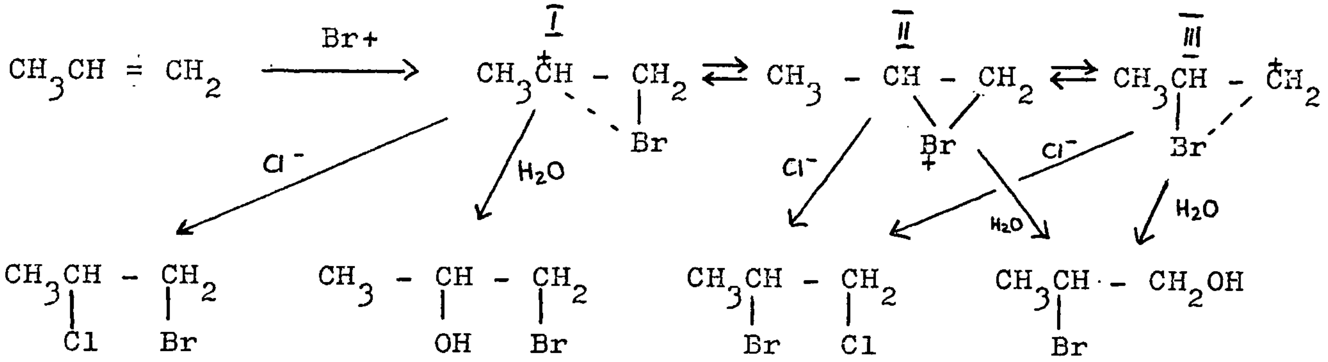
Clearly, then, the halogen atom in the carbonium ion is bound in such a way that the configuration of the system is retained. The "classical" carbonium ion, with the halogen attached specifically to one carbon atom, as in $\overset{+}{C}H_2$-CH_2Cl, and free rotation about the C-C bond, does not provide an explanation of this phenomenon.

Further, the results of addition of bromine chloride to propene in water in the presence of chloride ions,[80] make it apparent that some intermediate with considerable interaction between the entering halogen and the carbonium ionic centre is involved. The following figures were obtained:



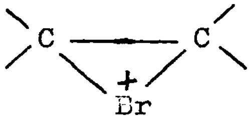
Since no dichloride or chlorohydrin was produced, despite the excess of chloride ions present, the possibility of reaction through free chlorine can be ruled out. For the same reason we can rule out attack on the olefin molecule of BrCl polarised in the sense $\overset{\delta-}{Br}\ldots\overset{\delta+}{Cl}$. Spectrophotometric evidence appears to establish that BrCl prepared from mixtures of Br_2 and Cl_2 reacts in addition reactions as if it were polarised in the sense $\overset{\delta+}{Br}{-}{-}{-}\overset{\delta-}{Cl}$.[81]

The fact that the ratio of chloride to water nucleophilic attack at the terminal carbon atom (i.e.D:C) differs from the ratio of chloride to water attack at the central carbon atom (i.e.B:A), indicates the necessity of postulating at least two (I and II) and possibly three (I, II and III) intermediates.



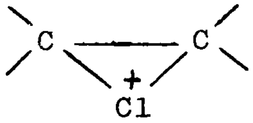
Thus, the 1-bromo isomers are derived from intermediate I and the 2-bromo isomers from II and/or III. It is reasonable to suppose that intermediates I and II/III should <u>differ</u> in the ratios in which they react with chloride and water.

It was Roberts and Kimball[82] who first interpreted <u>trans</u>-addition of bromine in terms of "bromonium structures":



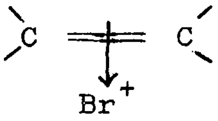
In any intermediate of this type, the interaction between halogen and the carbonium ionic centre would prevent rotation about the original C= C double bond, and would ensure that the entering nucleophile attacked from the side of the double bond opposite to that on which the electrophile had become attached.

This theory was extended to addition initiated by chlorine by Lucas and Gould,[78] "chloronium" structure being proposed for the addition of chlorine to but-2-enes.



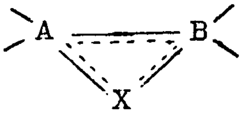
Winstein[83] supported the idea of cyclic 'onium structures for intermediates in these addition reactions, and suggested that they could be regarded as resonance hybrids involving the following four canonical forms:

Dewar[84] described the intermediates as π-complexes, in which the bond is formed from the bonding p-orbitals of the unsaturated carbon atoms and the s-and p-orbitals of the acceptor ion.



This in fact is equivalent to Winstein's fourth canonical form above. It may be important in explaining the formation of complexes with heavy metal ions, e.g. Ag^+. However, Dewar[85] has since shown that for the addition of deuterium halides to acenaphthalene, indene and <u>cis</u> and <u>trans</u> 1-phenylpropene in methylene chloride solvent that neither π-complexes nor free carbonium ions are involved.

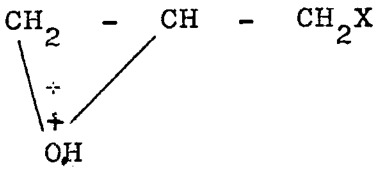
Of the various other speculations on this topic should be noted that of Arcus,[86] who suggested a ternary bond where the three atoms are bonded by one electron pair (besides the normal bond between A and B):



and of Walsh,[87] who suggested that it was not necessarily the non-bonding electron pair which contributed to the coordinate link, but possibly also the bonding electrons.

It is instructive to compare the three-membered cyclic intermediate halonium ions postulated earlier with the stable three-membered cyclic compounds, the epoxides, and to consider the mechanism of the ring-opening of these compounds.

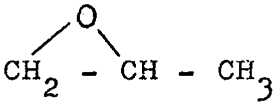
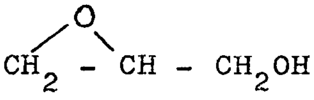
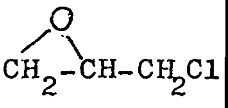
It seems generally agreed[88] that anion-catalysed ring openings involve nucleophilic attack on the oxide molecule, with, correspondingly, the expected orientation of attack at the primary position. The HCl- calysed ring openings generally have the kinetic form: rate $\propto$ (oxide) . (H+) . (Cl$^-$) ; on the whole they preserve orientation involving nucleophilic attack at the primary carbon atom, and they are therefore considered to involve to a predominant extent nucleophilic attack on the oxonium cation shown below. The proportion of



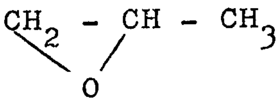
the other isomeric product formed under acid conditions is thought to indicate partial reaction through the "linear" classical carboniu ion. Ring opening in this direction will be facilitated by increasing electron release from the CH_2X group, as exemplified in the horizontal comparisons of Table 8.[34,35,132-135]

Table 8

Percentage of nucleophilic attack on the central carbon atom in ring openings of substituted ethylene oxides.

Compound				
Reagent:	OR^-	2	0	0
	HCl	25	10	0
	$ROH - H_2SO_4$	50	22	ca.2

In the addition reactions, as compared with the oxide ring openings, there is always formed a much greater proportion of the isomer derived by nucleophilic attack at the central carbon atom. (See corresponding compounds in Table 2). If then, the oxide (I) and the oxonium cation (II) undergo ring-opening by nucleophilic attack at the terminal carbon atom,



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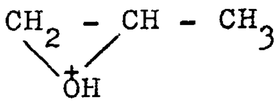
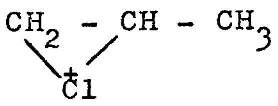
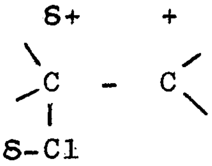


II



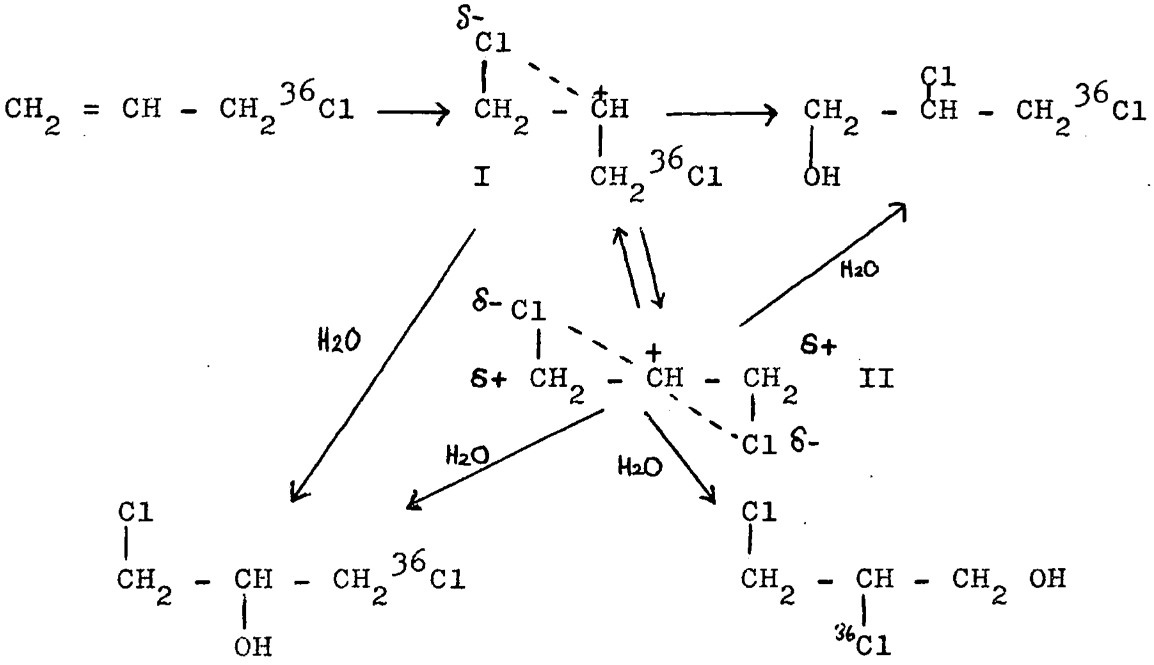
III

there appears to be no reason why the intermediate (III) should undergo ring opening in the opposite direction. Various authors have recognised this point, and proposed various descriptions of the intermediate.[89] de la Mare[35] has suggested that the best representation of the intermediate is a structure where the entering halogen is attached by a bond to the carbon atom usually attacked by electrophiles, at the same time allowing electrostatic ion-dipole interactio with the carbonium ionic centre.



Interaction of this type is consistent with retention of configuratio

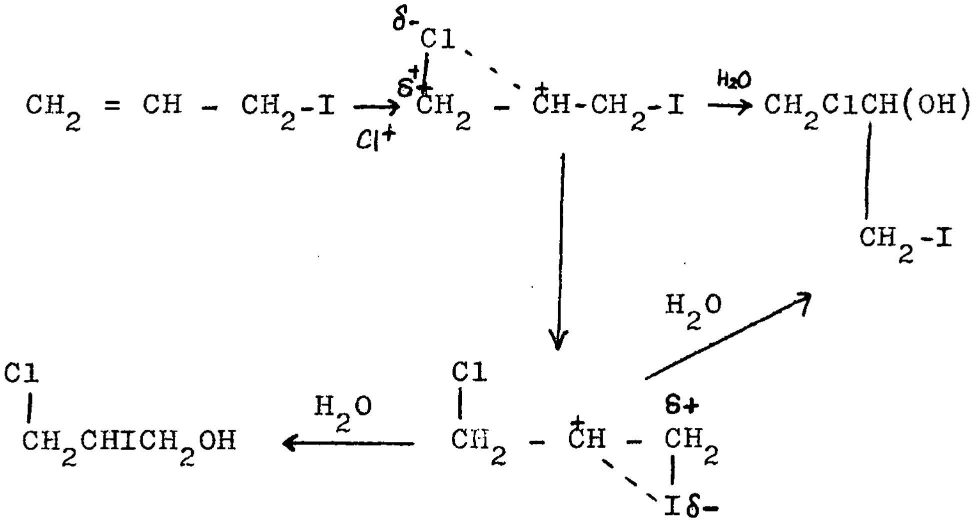
de la Mare and Pritchard[87] also discuss the possible intermediates involved in additions to allyl compounds. Migration of the allylic substituent, giving rise to rearranged products (Table 6) clearly indicates interaction between the allylic substituent and the carbonium ionic centre in the intermediate. The authors suggest the following scheme for the reaction of ClOH with allyl chloride.



They suggest that I is very quickly attacked by nucleophiles, and that only a small proportion of the reaction goes through II.

As seen in Table 6, the proportion of migration of halogen increases with increasing "driving force" of the halogen (Table 7). The absence of migration of the hydroxyl group in addition to allyl alcohol, however, indicates that the ease of heterolysis of the bond between carbon and the neighbouring group also plays a part in determining the possibility of migration.

It is apparent from the products of addition of ClOH to allyl iodide that the lifetime of the carbonium ion is not long enough for its most stable form to be adopted, as otherwise iodine, a much better participator than chlorine, would gain complete control of the carbonium ionic centre, as in II below, leading to almost complete predominance of rearrangement in the anti-Markovnikov product:



The effect of solvent variation on the extent of rearrangement of allyl bromide and allyl iodide also supports the theory that the extent of migration of a group will depend, other things being equal, on the lifetime of the carbonium ionic intermediate. Table 6 shows the decreasing amount of rearrangement with decreasing polarity of solvent, i.e. with decreasing stability of the carbonium ion.

Further, it is observed that a greater proportion of rearrangement in the anti-Markownikoff product occurs with 3-chloro-2-methylpropene than with allyl chloride. This is presumed to be due to an increase in the lifetime of the carbonium ionic intermediate owing to delocalisation of the positive charge by the methyl group.

It is also of interest to consider the effect of variation of the entering halogen on the proportion of the product resulting from attachment of the positive halogen species to the terminal carbon atom. Table 9 compares the results of addition of ClOH and BrOH to a series of olefins.[34,51,80,90,91,92]

Table 9

The percentage of products resulting from the attachment of the positive halogen species to the terminal carbon atom.

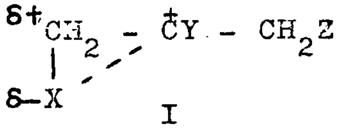
	$MeCH = CH_2$	$OHCH_2CH = CH_2$	$ClCH_2CH = CH_2$	$BrCH_2CH = CH_2$
ClOH	91	73	30	32
BrOH	79	66	26	20

Thus, on changing the electrophile from positive chlorine to the better participating positive bromine, there is an increase in the amount of product which has the electrophile attached to the 2-carbon atom. Also, the C-Br bond is more easily broken than the C-Cl bond. This result confirms the ideas outlined earlier on neighbouring group interaction.

However, it must be pointed out, as Clarke and Williams have realised, that the dependence of the course of the reaction on the entering halogen is not very marked.[93] This may be because the entering halogen, being so favourably situated for interaction with the developing carbonium ionic centre, probably attaches itself simultaneously to carbon-1 and carbon-2. This appears to be borne out by the fact that in the addition of HOX to various olefins, the relative amounts of 1-X and 2-X adducts are not markedly dependent on solvent composition. This indicates that the rate-determining step does not involve development of a high charge density, as would be the case in the formation of a classical carbonium ion.

The theory for electrophilic additions to allylic systems may be summarised as follows:

An electrophilic reagent $X^{\delta+}$ or X^{+} attacks the terminal carbon atom of the double bond in the allylic compound $CH_2 = CYCH_2Z$ to give the carbonium ion (I), with interaction as shown between X and the carbonium ionic centre. The completion of reaction by nucleophilic attack of water on the carbonium ion is thought to occur very rapidly after this electrophilic attack.



I

The following factors then decide the relative amounts of products formed.

(1) The greater the neighbouring group participation of X, the greater the percentage of 2-X isomer formed.

(2) As the electron-releasing property of the $-CH_2Z$ group decreases ($-CH_3 > -CH_2OH > -CH_2Cl > -CH_2Br$) the double bond becomes <u>less</u> polarised in the sense $\underset{\delta-}{\overset{\curvearrowleft}{CH_2}} = \underset{\delta+}{CY}.CH_2Z$; therefore X is less firmly attached to the terminal carbon atom, and a greater amount of 2-X product results.

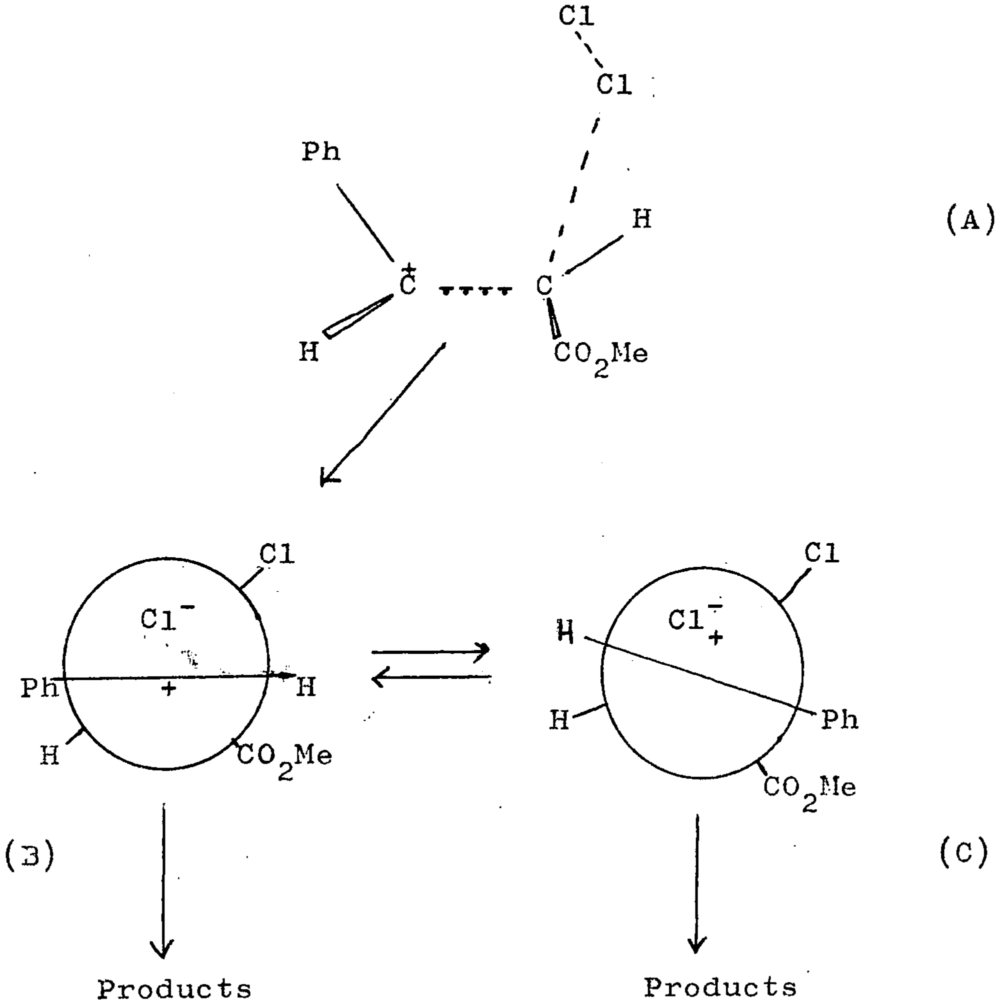
(3) The introduction of an electron-repelling group Y (e.g. CH_3 or

Cl conjugated to the double bond) reinforces the polarisation of the double bond (by - CH_2Z), thus giving rise to a greater amount of 1-X isomer.

(4) Increase in the neighbouring group participation of Z, and increasing ease of the heterolysis of the C-Z bond results in the formation of more of the rearranged 2-Z isomer in the products.

Recently, an increasing number of addition reactions giving high yields of products derived through cis-addition have been studied, for example, addition to phenanthrene[94] (56% of total addition products[95]), naphthalene[96] (90% of the addition products may be formed by at least one cis-addition of chlorine), and the phenylpropenes[97] (cis, 48-50%; trans, 38-39% of total addition products). Such cis-addition, it is suggested, is the result of the internal capture of an incipient chloride ion by a developing carbionic centre in a highly polarised structure[94,96] or the collapse of an ion-pair[94,96,97] (see below). Other products are assumed to be formed by capture of ions or of ion pairs by solvent and by chloride ion.[94,96,97]

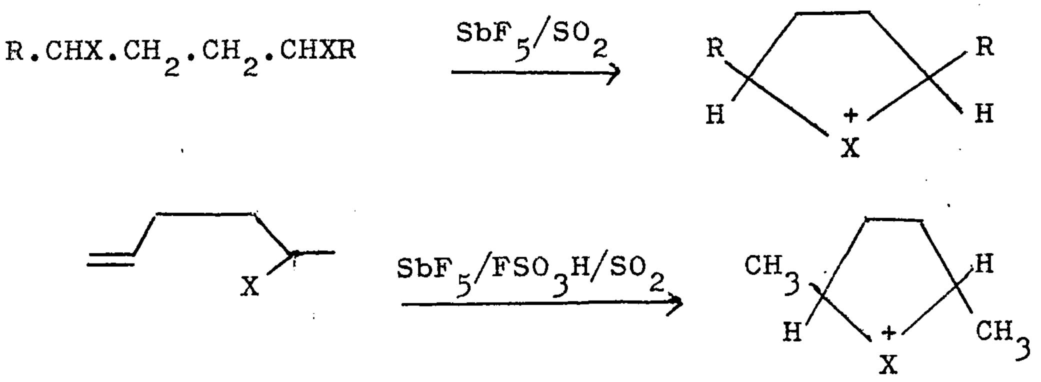
More recently, Johnson and Cabaleiro have studied the kinetics and products of the chlorination in acetic acid of methyl trans-cinnamate.[98] It was concluded that the rate-determining step involved a highly polarised transition state involving both the chlorine molecule and the olefin. This transition state is written as (A) below, based on evidence that the chloride ion is present until a very late stage in the reaction.[94,96,97,99,100] It is not, however, necessarily an exact description of the transition state.



The *threo* dichloride is produced in high yield. This product of *cis*-addition is thought to result from the collapse of an ion pair such as (C), before the Cl$^-$ ion can escape from the vicinity of the substrate, rather than by subsequent capture of the ion-pair by liberated chloride. The *erythro*-isomer is thought to come from (B) a conformational isomer of (C).

The high yields of *cis*-addition products formed in the reactions of chlorine with some cyclic olefinic systems (higher than in the reactions with open systems) are thought to be due at least in part to the inability of the ion-pairs to undergo conformational isomerisation other than by migration of chloride ion from one side of the carbonium ion to the other.

Very recently, five-membered halonium ions have been observed by n.m.r. spectroscopy.[101] These have been generated by ionisation of 1,4-dihalobutanes and also by protonation of 5-halo-hex-1-enes as shown below.



E The kinetics of hypochlorous acid addition

The kinetics of addition of ClOH to certain olefins was first studied by Shilov and co-workers.[102] They found the rate equation to be approximately:

$$\frac{-d(\mathrm{ClOH})}{dt} = k_2(\mathrm{ClOH})^2$$

(k_2 was not quite independent of the olefin concentration). This is consistent with attack on the olefin by chlorine monoxide,

$$2\mathrm{ClOH} \longrightarrow \mathrm{Cl_2O} + \mathrm{H_2O}$$

which is known to be about 10^6 times more reactive than ClOH as a halogenating agent.[103b]

The chlorination of phenol by neutral ClOH was shown to be represented by the rate equation:

$$\frac{-d(\mathrm{ClOH})}{dt} = k(\mathrm{ClOH})(\mathrm{OPh}^-)$$

which suggests that chlorination involves molecular ClOH as the electrophile.[104] The rate of reaction was increased by the addition of hydrochloric acid but not other mineral acids, indicating that molecular chlorine (produced from hypochlorous acid and chloride ions) is a more effective electrophile than ClOH.

The rate of aromatic chlorination by ClOH, under conditions excluding the possibility of formation of Cl_2O or Cl_2 (i.e. in the presence of perchloric acid and silver perchlorate), was found for various compounds to be represented by the equation

$$\frac{-d(\text{ClOH})}{dt} = k.(\text{ClOH}).(\text{H}^+)$$

k being independent of the concentration and nature of the aromatic substrate.[105] This suggests that the rate-determining step is the formation of the chlorinium ion from the hypochlorous acidium ion.

In the rate equation for chlorination of methyl p-tolyl ether, a second term appears:

$$\frac{-d(\text{ClOH})}{dt} = k.(\text{ClOH}) + k^1.(\text{ClOH}).(\text{H}^+)$$ [106]

This represents rate-determining formation of Cl+ directly from ClOH, and is outweighed by the other term at moderately high acid concentrations.

For less reactive hydrocarbons, and as the concentration of the aromatic compound is increased, a further term appears in the rate equation:

$$\frac{-d(\text{ClOH})}{dt} = k.(\text{ClOH}) + k'(\text{ClOH}).(\text{H+}) + k''(\text{ClOH})$$ [107]

This expression, at concentrations of ClOH of 5×10^{-4}M and less, approximates to a first order rate equation

$$\frac{-d\,(\mathrm{ClOH})}{dt} = k_o\,(\mathrm{ClOH})$$

It has been suggested that as the reactivity of the aromatic compound increases, the following reactions become rate-determining in turn.

(1) Bimolecular reaction between the chlorinium ion and the aromatic compound.

(2) Formation of the chlorinium ion (ArH term disappears).

(3) Bimolecular attack of the hypochlorous acidium ion on the aromatic compound (ArH reappears).

(4) Formation of the hypochlorous acidium ion.

The rates of reaction of ClOH with allyl chloride and allyl methyl ether have been measured, in the presence of perchloric acid and silver perchlorate.[108] Extrapolation of the rate to zero olefin concentration gave the same value as for the reaction with methyl tolyl ether and phenol. Clearly the mechanisms of addition reactions and aromatic substitution reactions are built up of similar steps.

Arotsky and Symons,[109] however, have questioned the strength of the evidence for the participation of halogen cations in many addition reactions of hypochlorous acid in aqueous solution. They claim that the thermodynamic calculations of Bell and Gelles,[110] even allowing for increased solvation energy of the halogen cations, arising from their incomplete outer shell,[111] make the participation of Cl cations in reactions in aqueous media very improbable. But since kinetic evidence for chlorination by Cl+ in certain ClOH reactions is very strong, it has become generally assumed that Cl+ is the <u>usual</u> agent in aqueous acidic media.[112] A summary of the evidence, however,[111] shows it to be based on the significant observation that the rate equation for relatively unreactive aromatic compounds is of the form:

$$\frac{-d\ (\mathrm{ClOH})}{dt} = k_1(\mathrm{HOCl}) + k_2(\mathrm{HOCl})\ (\mathrm{H}^+)$$

This is interpreted (as described earlier in this section) in terms of a rate-determining heterolysis of the O-Cl bond, followed by rapid attack of the resulting Cl+ cations on the aromatic compound. Accordingly, there is an increase in rate when D_2O is used as the solvent.[106] This has been accepted as good evidence for the transient formation of Cl+ cations in solution. The authors take the view, however, that the large excess of silver perchlorate present in these reactions[106,107] (to suppress the reaction $Cl^- + H_2OCl^+ \longrightarrow Cl_2 + H_2O$) is significant, although it has been concluded that since the rates are unaffected by small changes in the concentration of silver perchlorate, silver ions are not involved in the reaction whose rate was measured. There is strong evidence, however, that AgI_2^+ is of considerable stability and is a powerful iodinating agent.[113] There is also some evidence from spectrophotometric, solubility and conductometric studies for the formation of $AgBr_2^+$ and

Ag Cl_2^+,[114] and hence for the participation of $AgCl_2^+$ in the addition reactions.

The steps involved would then be:

$$AgCl(s) + H_2OCl^+ \underset{}{\overset{k_1}{\rightleftarrows}} AgCl_2^+ + H_2O \qquad (1)$$

$$AgCl_2^+ + ArH \xrightarrow{k_2} ArCl + AgCl(s) + H^+ \qquad (2)$$

Agreement with the kinetic data requires that $k_2 \gg k_1$ and $(AgCl_2^+) \gg (Cl_2)$ Since the forward reaction of (1) is the rate-determining step, the overall rate is independent of (Ag^+) and of (ArH.)

Further, the authors suggest that doubtless several other mechanisms could be found which would accommodate the kinetic data for these complex systems.

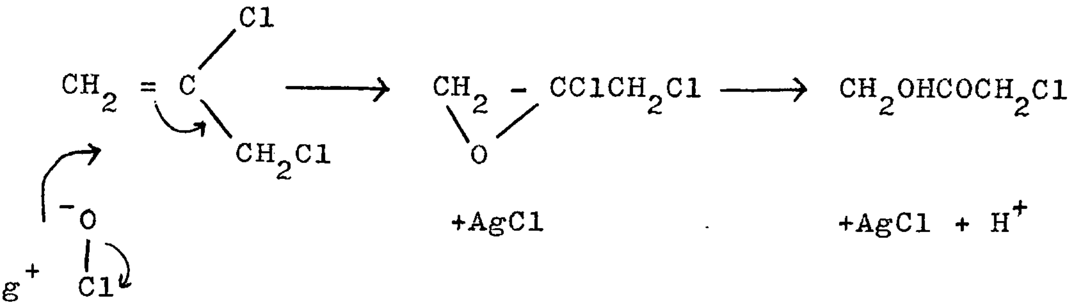
Williams has studied the effect of silver ion concentration on the products and kinetics of hypochlorous acid addition to 2,3-dichloropropene.[40,115] In the absence of silver ion the reaction is very fast, occurring <u>via</u> free chlorine, and the products are 1,3-dichloroacetone (76%), 2,2,3-trichloropropanol (3%) and 1,2,3-trichloropropene (<u>cis</u> + <u>trans</u>, 22%), together with chloride ion (80%). To study the kinetics of the reaction it is necessary to have excess silver ion present, to remove chloride and hence prevent the reaction going <u>via</u> free chlorine. With the concentration of hypochlorous acid below 10^{-3}<u>M</u>, a bare excess of silver ions, mineral acid present and olefin in ten times excess, good first order (in HOCl) kinetics were obtained. There was also a linear dependence on mineral acid concentration, and the graph of the first order rate constant, k_{obs}, (at constant olefin concentration) against (acid) gave an intercept showing that there is a non-acid-catalysed component in the rate equation. The reaction order in olefin was approximately unity, giving as the rate equation

$$\text{rate} = k_2'(\text{ClOH})(\text{olefin}) + k_2''(\text{ClOH})(\text{H}^+)(\text{olefin})$$

This suggests rate determining attack by both ClOH and $ClOH_2^+$.

On studying the kinetics of this reaction at high concentrations of silver ion, however, Williams discovered auto-catalytic behaviour. This behaviour was shown to be markedly dependent on the reactant concentrations, being more apparent at low mineral acid and high silver ion and HOCl concentrations. The products of the reaction were redetermined at various silver concentrations. The yield of 1,3-dichloroacetone was found to decrease from 76% at zero silver concentration to 38% at 0.02 M Ag^+ and to 7% at 0.09 M Ag^+. The yield of 1,2,3-trichloropropene also fell with increasing silver concentration, the amount of silver chloride precipitated increased, and a ketol, $CH_2OHCOCH_2Cl$ was formed.

Clearly, another reaction is competing with the normal electrophilic reaction, and the author suggests that the results are consistent with nucleophilic attack by hypochlorite ion on the olefin, giving an epoxide, which undergoes ring opening to give the observed ketol product.



This mechanism is consistent with many of the observed facts viz.

(1) the nature of the products;

(2) catalysis by silver ion; and

(3) increased rates as the effective hypochlorite ion concentration is increased, both by decreasing the acidity and by increasing the initial hypochlorous acid concentration.

Several possibilities can be ruled out:-

(1) the reaction is not catalysed by the final products, since the same kinetic form was observed in the presence of the products;

(2) no rate determining sequence involving the olefin and silver ion only can be involved, since again the same kinetic pattern was obtained after a solution containing both the olefin and the silver salt had been allowed to stand before the run;

(3) similarly, no rate determining sequence involving the hypochlorous acid and the silver ion only is possible since again the same kinetic form was found after a solution containing hypochlorous acid and silver ion had been left to stand;

(4) since the precipitation of silver chloride by the addition of a

sodium chloride solution during the early stages of the run had only little effect on the kinetics it seems unlikely that solid silver chloride (possible colloidal) can be the agent responsible for the autocatalysis.

It is suggested that the mechanism is probably of a chain type: $A \rightarrow B$ and $A + B \rightarrow$ products (slow) and probably involving several stages. A possible sequence would be:

$$\begin{aligned}
&\mathrm{ClOH} + \rangle C = C\langle \longrightarrow \text{Complex I}\\
&\text{Complex I} + Ag^{+} \longrightarrow \text{Complex II}\\
&\text{Complex II} + \mathrm{ClO}^{-} \longrightarrow \text{Epoxide} \longrightarrow \text{Ketol}
\end{aligned}$$

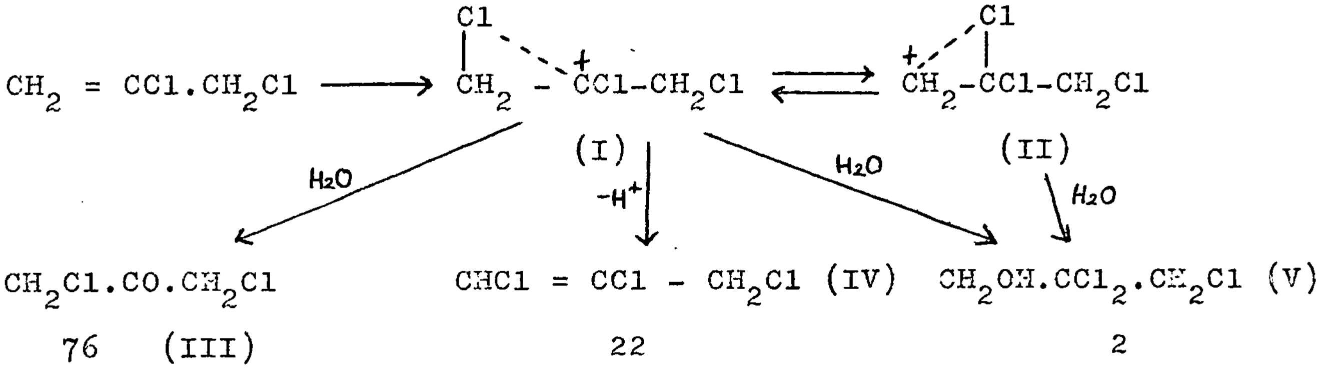
Possibly the attacking reagent is not the hypochlorite ion itself, but some species derived from it.

CHAPTER 2

THE PRESENT WORK

A Selection of topics for investigation

During a study of the addition of hypochlorous acid to 2,3-dichloropropene, Williams reported a curious effect of silver ions on the course of the reaction.[40] In the absence of silver ions, the products were analysed as follows: 1,3-dichloroacetone (III)(76%)1, 2,3-trichloropropene (III)(22%) and 2,2,3-trichloropropanol (IV)(2%), as set out in the scheme below.



When silver ions were present, however, to prevent the reaction proceeding via free chlorine, produced in the reaction Cl + H_2OCl^+ Cl_2 + H_2O, a marked change in the amounts of the various products occurred. The yield of chloride ion produced (as silver chloride) was greatly increased, while the yields of III and IV dropped to 33% and 8% respectively, and a further product, VI, was isolated, and identified as 1-hydroxy-3-chloroacetone. On increasing the initial concentration of silver perchlorate, the yields of III and IV dropped markedly, whilst that of VI increased (to about 90% at 0.12M silver).

The formation of this unexpected product was shown to be connected with an unusual accelerating effect when the rate of this reaction was measured.[115] This effect was markedly dependent on the reaction conditions, being favoured at low mineral acid, high silver ion and high ClOH concentrations.

Now since no such interference by silver ions had been observed in the corresponding reactions of allyl chloride, 3-chloro-2-methylpropene, or isobutene, it was suggested that the substitution of a 2-chloro- (or, generally, a 2-halogeno-) atom in the olefin molecule played some important part in this anomalous reaction. It was concluded that the reactions of 2-chloropropene with hypochlorous acid would be of interest.

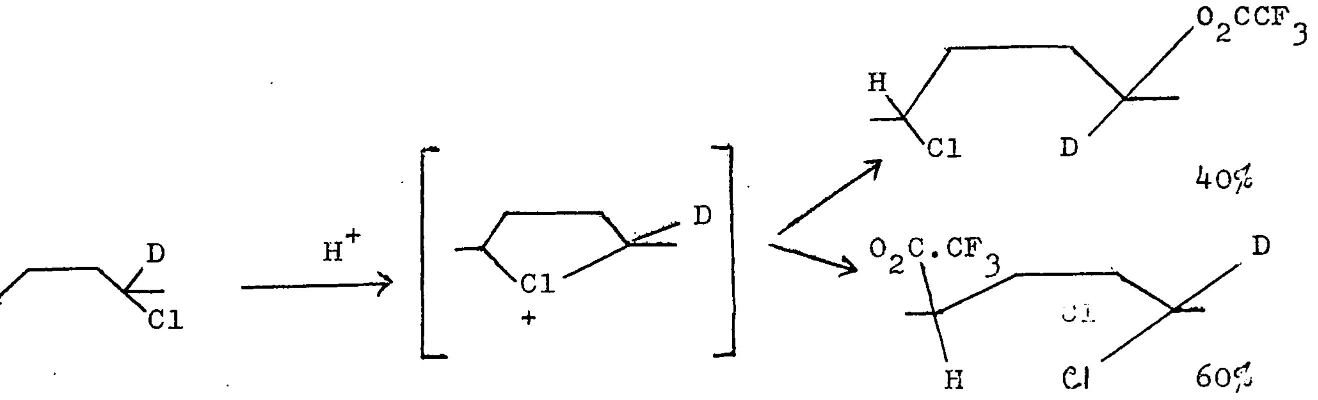
The aims of the present investigation were: firstly, to establish the products of the reaction, and interpret them in the light of the factors discussed in Chapter 1, viz the influence of the substituent on the orientation of addition and of substitution. Secondly, it was hoped to detect any unusual effect of silver ions in the course and/or the rate of the reaction.

During the course of these investigations, it was discovered that when ClOH labelled with radioactive ^{36}Cl was added to 2-chloropropene, the full activity of the $^{36}ClOH$ was not retained in the product. The nature of the mechanism of this chlorine exchange reaction, and the effect of the concentration of silver ions on its extent were therefore also studied. In particular it was hoped to establish whether this loss of activity took place by some intra-molecular exchange process involving bridged carbonium ions or whether the loss of radioactivity could be accounted for by some inter-molecular process involving chlorine exchange between the hypochlorous acid and some other chlorine-containing species, during the course of the reaction. Most of the detailed product analyses (including the radioactive work) and rate were done with 2-chloropropene but the investigation was extended to cover the addition to 2-bromopropene, while kinetic measurements of hypochlorous acid addition were carried out with 2-chloropropene, 2,3-dichloropropene (to confirm the original observations) and 2-chloroprop-2-en-1-ol.

Fairly extensive kinetic investigations of neighbouring group participation accompanying electrophilic addition reactions have been made. For example, hydroxyl participation has been established by Williams, who obtained rates for addition of iodine to the series of unsaturated alcohols $CH_2 = CH(CH_2)_nOH$.[72] The rate constant was greatest for n = 3, indicating particularly strong participation by OH in a 5-membered ring. This compares with the results of the hydrolysis in water of the series of chlorohydrins $Cl(CH_2)_nOH$, where a rate maximum and formation of a cyclic product occurred at n = 4.[74] Further, a study of the reaction of iodine with the sodium salts of olefinic carboxylic acids reveals a rate maximum corresponding to O^- - 5 participation.[75]

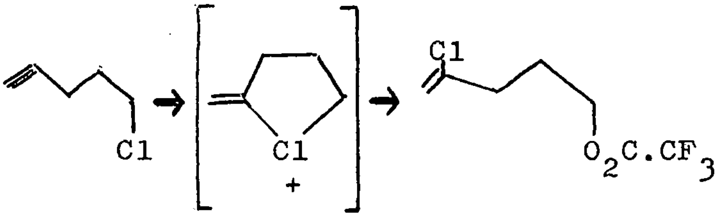
The picture with halogen participation, however, is less clear. de la Mare et.al. have described internal competition by halogen in the electrophilic additions to allyl halides,[38] which resulted in the formation of rearranged 2-halo-products. The extent of this rearrangement was greatest for the iodo substituent and the sequence I>Br>Cl was observed, as expected from the decreasing nucleophilicity. Also, rearrangement occurred to a lesser extent in less polar solvents (dioxan-water mixtures). This was interpreted as being due to the decreased stability of the carbonium ion in the less polar medium, allowing less time for the neighbouring group interaction by the allylic halogen to become established.

More recently, Peterson et.al. have established halogen participation in a 5-membered ring. Addition of CF_3COOH to $CH_2 = CH(CH_2)_2CHCl.CH_3$ proceeds some 7-10 times faster than expected and also a rearranged product resulting from a 1,4 Cl shift is obtained.[68a]



A 1,4 Cl shift can also be observed in the addition of CF_3COOH

to 5-chlorohex-1-yne.[68b]



Further, Peterson found that in a series of 5-substituted 1-hexenes, the 5-Cl, 5-Br and 5-I compounds reacted several times faster than would be expected merely by consideration of their inductive effects. It was assumed that the inductive effect was being offset by internal participation by the halogen atoms.

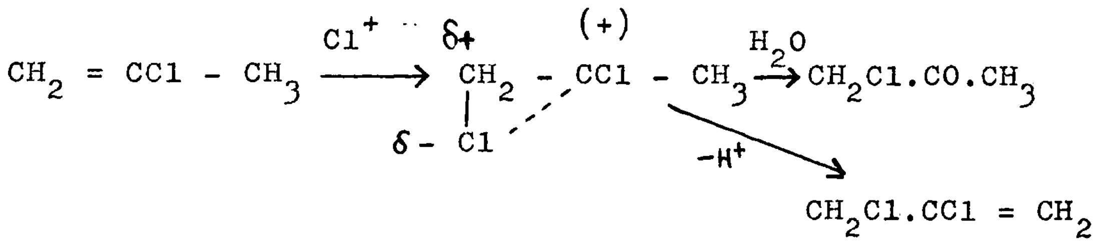
Again, the rate of electrophilic addition to 5-bromopentene and 6-bromohexene respectively were found to be very similar, indicating that greater participation by bromine in the 5-bromopentene (<u>via</u> a 5-membered ring) tended to counteract its inductive effect.

The rates of addition of bromine in methanol to the series of unsaturated alcohols $CH_2 = CH(CH_2)_nOH$[73a] and bromides $CH_2 = CH(CH_2)_n Br$[73b] have been measured. For the alcohols the rate constants were 284,525,2630 and 1730 $l.mole^{-1}$ min^{-1} for n = 1,2,3 and 4 respectivel This indicates a measure of OH -5 participation (at n = 3), which was confirmed by the isolation from the reaction product of 2-bromomethyltetrahydrofuran. Clearly, the participation is much less than for the iodination reactions. For the series of bromo compounds, the rate constants were 1.5,75,500 and 1170 $l.mole^{-1}$ min^{-1} for n = 1,2,3 and 4 respectively. Calculations, similar to those carried out by Peterson <u>et</u>.<u>al</u>.,[70] based on a regular fall off of the inductive effect of the bromo substituent show that there is no evidence at all for any rate enhancements, which are generally thought to indicate participation in the rate determining step by a neighbouring group. In the present work the rates of addition of iodine to a series of unsaturated bromides, $CH_2 = CH(CH_2)_nBr$, were measured, in order to determine whether participation by a five (or other)-membered bromonium ion is kinetically detectable. Iodine was used as the electrophile in preference to chlorine or bromine, as its slower rate of reaction would show up the difference in rate between the various bromides more clearly.

The evidence from Peterson's work in trifluoroacetic acid[68-71] is that halogen-5 participation is possible in this system, although the magnitudes of the effect are not large.

B The addition of hypochlorous acid to 2-chloropropene

The products of this reaction, carried out in aqueous acid solution, were identified as chloroacetone and 2,3-dichloropropene. The amounts were estimated by isotope dilution analysis and found to be 85% and 15% respectively, based on the amount of ClOH used (the olefin being in excess). The other possible product of addition, 2,2-dichloropropan-1-ol, was not detected. The course of the reaction can be described by the following scheme:



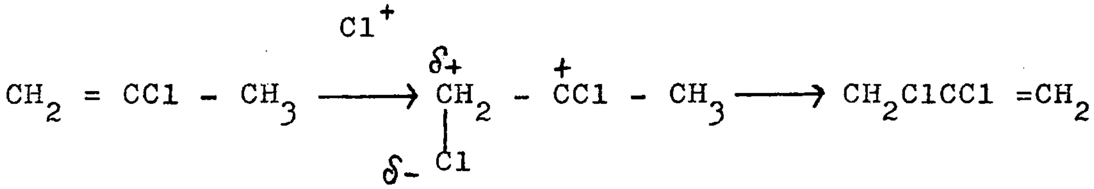
$$CH_2 = CCl - CH_3 \xrightarrow{Cl^+} \underset{\delta-\ Cl}{\overset{\delta+}{CH_2}} - \overset{(+)}{CCl} - CH_3 \xrightarrow{H_2O} CH_2Cl.CO.CH_3$$

$$\xrightarrow{-H^+} CH_2Cl.CCl = CH_2$$

The absence of any of the isomer produced by nucleophilic attack by water at the terminal carbon atom is consistent with the work discussed in Chapter 1. Thus, addition of ClOH to allyl chloride yielded 70% 1,2-dichloropropan-3-ol and 30% of the isomer resulting from nucleophilic attack at the centre carbon atom. This was attributed to interaction by the incoming chlorine atom with the carbonium ionic centre, facilitating attack by the nucleophile at C-1 (but not to the extent found in the epoxides, where nucleophilic attack is <u>almost exclusively</u> at the primary carbon atom). 3-chloro-2-methylpropene, isobutene and 2,3-dichloropropene, however, all gave upwards of 96% of the 2-OH isomer. In these cases, it was suggested, electron-release from the 2-substituent makes the C-1 more negatively polarisable, and hence the incoming Cl^+ becomes firmly attached here, with consequently less interaction with C-2. With 2-chloropropene, likewise, it is to be expected that nucleophilic attack will take place predominantly at the centre carbon atom, giving the observed product, chloroacetone.

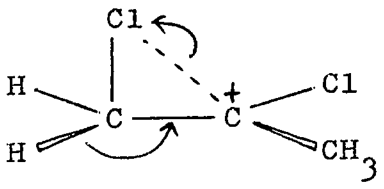
C Substitution accompanying the addition of hypochlorous acid to 2-chloropropene

The sole olefinic product of the reaction was identified by V.p.c. and infra-red spectra as 2,3-dichloropropene.

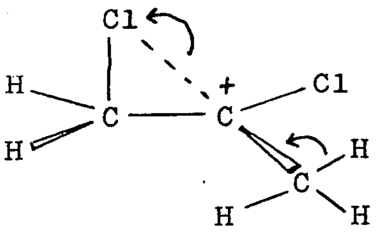


$$CH_2 = CCl - CH_3 \xrightarrow{Cl^+} \underset{\delta- \, Cl}{\overset{\delta+}{CH_2}} - \overset{+}{C}Cl - CH_3 \longrightarrow CH_2ClCCl = CH_2$$

Of the two possible sites for proton-loss, then, only C-3 is involved. This is consistent with the view of de la Mare and Salama,[49] who point out that if the entering Cl atom is interacting with C-2, then in the transition state (I) for elimination from C-1 it is particularly strained relative to the final position of the atoms in the product. The unaffected H atoms of the CH_3 group, however, are able to adopt relatively unstrained positions in the required transition state for elimination from C-3(II), and the distortion in the CH_2Cl group does not adversely affect the geometrical requirements of the double bond.



I



II

Hence, the observed olefinic product of the reaction is 2,3-dichloropropene, the 1,3 isomer being produced in very low yield or not at all.

D The effect of silver ions on the products of the reaction between hypochlorous acid and 2-chloropropene

The curious effect of silver ions on the course of the reaction (i.e. on both products and kinetics) between hypochlorous acid and 2,3-dichloropropene was described earlier in the present chapter. The "normal" products, $CH_2ClCOCH_2Cl$ and $CH_2Cl.CCl = CHCl$ (which together account for 97% of the products of the reaction when carried out in the absence of silver) are obtained in greatly reduced yield in the presence of excess silver ions, and a further product has been isolated, and identified as $CH_2OHCOCH_2Cl$.[40] As no such interference by Ag^+ ions is observed in the corresponding reactions of allyl chloride, 2-methyl-3-chloropropene or isobutene, it was inferred that the 2-chloro substituent played some important rôle. The corresponding reaction of 2-chloropropene might therefore be expected to suffer similar interference by silver ions.

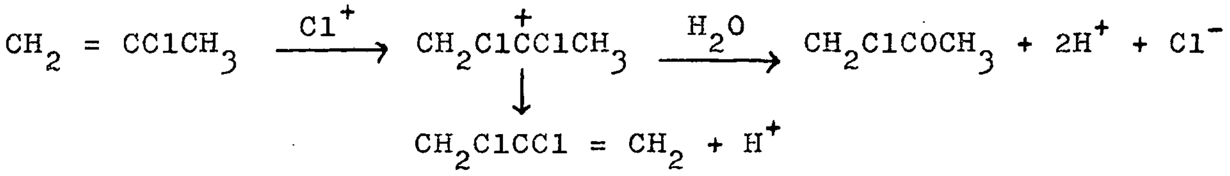
In the present work, the reaction between ClOH (0.011 M) and 2-chloropropene (0.022 M) was carried out in the presence of perchloric acid (0.12 M) and excess (0.05 M) silver perchlorate. After reaction the solution was analysed for chloride ion, which was found to be 113% of the chlorine originally present in the ClOH. The yield of chloroacetone was determined by isotope dilution analysis, and represented 83% of the ClOH used.

The yield of chloroacetone is only slightly less than that obtained in the absence of silver, indicating that this considerable excess of silver ions has no significant effect on the course of the reaction.

On the other hand, the high yield of chloride ion suggests that some sort of hydroxylation reaction is taking place, which we could represent as

$$CH_2 = CClCH_3 \xrightarrow[H_2O]{HOCl} CH_2OHCCl(OH)CH_3 \longrightarrow CH_2OHCOCH_3$$
$$+ H^+ + Cl^- \qquad\qquad + H^+ + Cl^-$$

in addition to the usual scheme:



$$CH_2 = CClCH_3 \xrightarrow{Cl^+} CH_2Cl\overset{+}{C}ClCH_3 \xrightarrow{H_2O} CH_2ClCOCH_3 + 2H^+ + Cl^-$$
$$\downarrow$$
$$CH_2ClCCl = CH_2 + H^+$$

However, this postulate would require that the ketol $CH_2OHCOCH_3$ or some other hydroxylation product be yielded in appreciable quantities.

It should be noted that the chloride produced is computed as the difference between the amount of silver present in solution before and after the reaction. Since the silver is in high excess over the HOCl, only a small proportion is used up, and therefore the error in silver determination is greatly magnified.

2-chloropropene was again added to an aqueous acidic solution of hypochlorous acid, this time 0.10 M in silver. The reaction solution was extracted by continuous ether extraction, and the resulting product analysed by vapour phase chromotography. Two peaks only were detected, one corresponding to chloroacetone, the other to 2,3-dichloropropene. The complete absence of any further product at this fairly high concentration of silver strongly suggests the absence of any unusual effect of silver ions on the products of the reaction.

The kinetics of the reaction are discussed in the following section.

E Kinetics of the addition of hypochlorous acid to 2-chloropropene : possible anomalous effect of silver ions

When the kinetics of the reaction between hypochlorous acid and 2,3-dichloropropene were followed in the presence of silver ions, the observed rate constants showed a sudden and substantial increase during the course of the reaction.[115] This effect was markedly increased by raising the silver ion and hypochlorous acid concentrations and lowering the mineral acid concentration.

In the present work, this reaction was again followed under similar conditions, and the accelerating effect of silver ions confirmed.

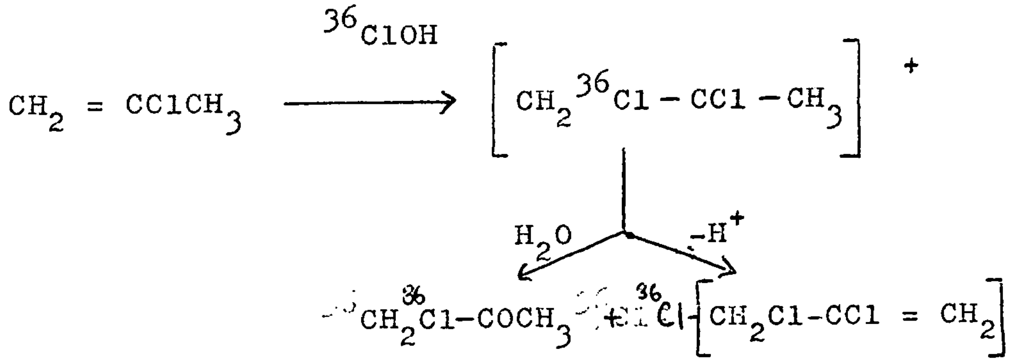
Then the kinetics of the reaction between hypochlorous acid and 2-chloropropene were followed, to discover whether or not such a phenomenon occurred in this case. Initially several runs were done at low (about 0.002 M) concentrations of hypochlorous acid. If any higher concentrations were used (which would have been desirable in view of the difficulty in obtaining accurate end-points at these low concentrations), an appreciable amount of Cl_2O is formed, giving rise to some second order reaction, when a downward drift of the rate "constants" is observed. At 0.002 M hypochlorous acid, with a ten or more fold excess of 2-chloropropene, quite good first order kinetics were obtained. The mean value of k_1 was 5.46×10^{-4} ($sec.^{-1}$) at an olefin concentration of 0.026 M, and mineral acid concentration 0.02 M. This compares with an extrapolated value[115] of 3.3×10^{-5} ($sec.^{-1}$) for 2,3-dichloropropene at the same acid strength. The presence of the 3-chloro substituent therefore decreases the rate constant by a factor of ca.17.

In order to look for the silver-accelerated reaction in 2-chloropropene, the mineral acid concentration was reduced to zero, the silver ion concentration raised to 0.11 M (previously 0.036 M) and the hypochlorous acid concentration increased to 0.005 M. However, no sign of acceleration by silver was observed under these conditions, where in the case of 2,3-dichloropropene the reaction would go almost exclusively by the anomalous mechanism.

However, since 2-chloropropene is much more reactive than the dichloro compound towards electrophilic addition, it is possible that the reaction whereby the silver ions interfere may be slower than the addition reaction of the former. Williams[115] suggests that the interfering reaction involves nucleophilic attack by hypochlorite ion, competing with electrophilic attack by Cl^+ or $ClOH_2^+$. The kinetics of the addition of hypochlorous acid to 2-chloroprop-2-en-1-ol were also studied. Here, no increase in the rate constants during the course of the reaction was observed, even at a hypochlorous acid concentration of 7×10^{-3} M and silver ion concentration of 0.05 M. But, increasing the silver concentration to 0.20 M resulted in a marked increase in the rate constant (see Chapter 3). Clearly, then, the reaction is silver-catalysed to a certain extent. It should be noted that at this concentration of hypochlorous acid, the reaction is no longer first order, since reaction via Cl_2O is now important, but can be analysed by a graphical method into first and second order components. Although the autocatalytic type of behaviour observed with 2,3-dichloropropene is not observed with 2-chloroprop-2-en-1-ol, the fact that an increase in silver concentration increases the reaction rate, suggests that it may just be starting to creep in at this stage, i.e. at a reactivity intermediate between 2-chloropropene and 2,3-dichloropropene. It would be of interest to extend the range of reactivity further, say to 1,1-dichloroethylene and possibly to cyano substituted olefins.

F Chlorine exchange accompanying the reaction between hypochlorous acid and 2-chloropropene

The chloroacetone produced by the addition of hypochlorous acid labelled with ^{36}Cl to 2-chloropropene was isolated and its specific activity measured. It was found to contain only 50-60% of the radioactivity of the initial ^{36}ClOH.



The percentage of reactivity retained was increased by the inclusion of excess silver ions in the reaction mixture, but still did not reach 100%.

The same phenomenon had earlier been observed in the case of ^{36}ClOH addition to 2,3-dichloropropene.[116]

Clearly, some exchange has taken place between the entering chlorine atom and the chlorine substituent in the 2-position in the olefin molecule. This exchange reaction takes place in the presence and in the absence of silver ions, and several experiments were done to establish the relation between the initial concentration of silver ions and the specific activity of the chloroacetone produced.

In each case labelled ^{36}ClOH of known specific activity was added to an aqueous acid solution containing excess 2-chloropropene. After the reaction the chloroacetone was extracted with ether, and after removal of the solvent was converted to its 2,4-dinitrophenylhydrazone. The specific activity of the derivative was then measured in acetone, and correction made for variation in counting rate with solvent. The results of several experiments are presented in Table 10, where the specific activities are represented as percentages of the initial ^{36}ClOH activity:

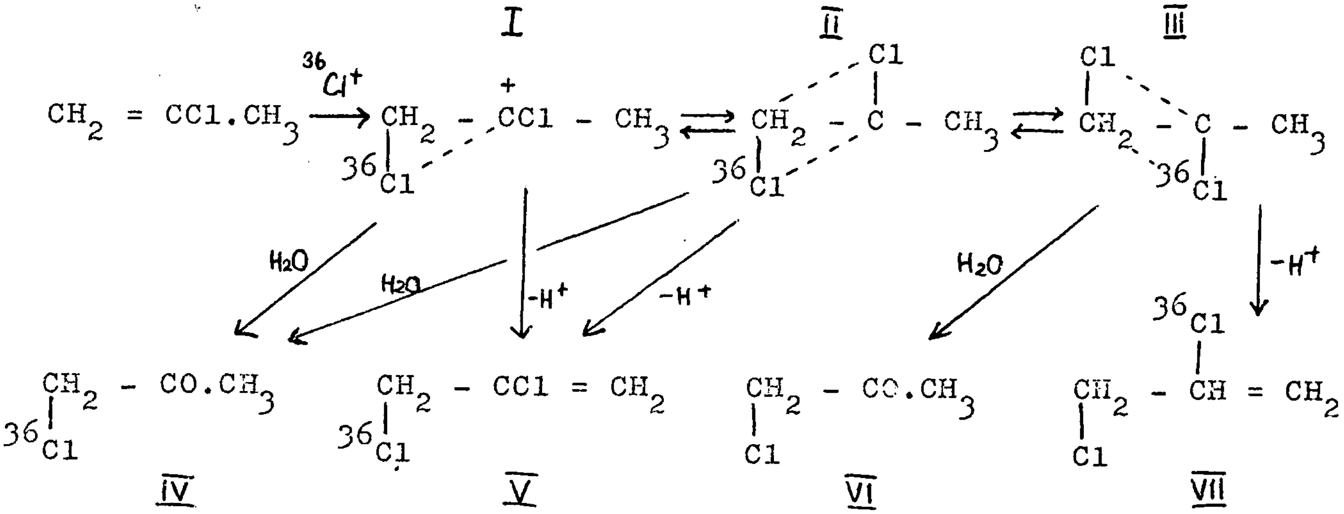
Table 10

Initial silver ion concentration (moles litre^{-1})	Specific Activity of the chloroacetone produced (% of initial HOCl)	Experiment Number
0	62, 59	5, 7
0.01	64	5
0.025 - 0.05	86	9
0.04	91	7
0.05	83	5
0.10	84	6

Apparently an initial silver ion concentration of less than about 0.015 M allows about 35% exchange, while a concentration greater than 0.025 M reduces the extent of exchange to 20% or less.

Two possible types of mechanism can be envisaged for this exchange reaction:

(a) An intra-molecular mechanism, in which the entering chlorine atom interacts with the carbonium ionic centre, while at the same time the 2-chlorine substituent interacts with carbon-1 (II). The two chlorine atoms could then become equivalent and finally exchange, as in III.



This mechanism could account for the reduced specific activity of the chloroacetone compared to the hypochlorous acid. Further, it would predict (i) that some of the 2,3-dichloropropene produced would be labelled in the 2- and some in the 3- position, and (ii) that it would retain the full activity of the hypochlorous acid. These conclusions were subsequently tested.

(b) An intermolecular exchange, between the $^{36}ClOH$ and the inactive chloride ion released from the 2-position of the olefin molecule.

$$^{36}ClOH + Cl^- \rightleftarrows ClOH + {}^{36}Cl^-$$

The labelled chloride ions would then be precipitated by silver ions, and the unlabelled hypochlorous acid would react with the olefin, yielding a product of diminished activity. It may seem surprising that the exchange process could conceivably proceed at a rate comparable to that of the reaction of silver with chloride ion. This point will be discussed later with regard to the formation of solid silver chloride. It might also be considered a possibility that the hypochlorous acid could exchange chlorine with the solid silver chloride as well as with any organic chloride present in solution. These last possibilities are discounted by the experimental evidence, as will be seen later.

A necessary requirement of the intermolecular mechanism would be that the 2,3-dichloropropene produced would be of the same activity as the chloroacetone produced, and would be labelled exclusively in the 3-position.

Determination of the specific activity of and the position of labelling in 2,3-dichloropropene produced by the addition of ^{36}Cl-OH to 2-chloropropene

An aqueous solution of hypochlorous acid labelled with ^{36}Cl was added to an aqueous acidic solution of 2-chloropropene containing an excess of silver perchlorate. After reaction, the solution was extracted with pentane, then with ether. The pentane extract was evaporated down, and the radioactivity of the remaining, 2,3-dichloropropene measured in alcohol. The specific activity of the chloroacetone isolated from the ether extract was also measured, after conversion to the 2,4-dinitrophenylhydrazone, in acetone. After making corrections for the variation of the counting rate with solvent, the specific activities of the two products were found to be identical within experimental error (about 88% of the initial ClOH).

Now, it has been shown that the S-allyl thiouronium picrate of $CH_2 = CCl.CH_2{}^{36}Cl$ has zero activity, within experimental error.[47] This derivative was made of the active 2,3-dichloropropene produced in the reaction, and was found to retain about 1% of the activity of the olefin. The 2,3-dichloropropene produced must therefore be almost exclusively 3-labelled.

Both of these results, viz the specific activity of the 2,3-dichloropropene produced being the same as that of the chloroacetone and the exclusive 3-labelling, argue against the acceptance of an intra-molecular exchange mechanism.

It was then attempted to gain direct evidence for mechanism(b).

Exchange reactions between chloride ions and hypochlorous acid in the presence of excess silver ions

A solution was made up about 0.01 M in labelled hypochlorous acid, 0.1 M in perchloric acid, and of a known excess concentration of silver perchlorate. The specific activity of the ClOH, computed as counts per minute divided by titre against standard sodium thiosulphate solution, was measured, then a known amount of chloride, slightly in excess over the ClOH, was added in the form of sodium chloride solution. After filtering off the precipitated silver chloride, the specific activity of the solution was measured.

The experiment was repeated with different excess concentrations of silver and also without silver; it was also carried out for the other halide ions, bromide and iodide.

The results, which were obtained in duplicate with very good agreement, are presented in Table 11.

Table 11

Halide Ion	% Exchange		
	Zero Ag+	.0175 M Ag+	.0350 M Ag+
Chloride	55	35	21
Bromide		42	23
Iodide		94	36

Clearly, then, exchange between ClOH and chloride ions can indeed occur in the presence of excess silver ions.

It should be noted that the added amount of chloride was about 1.2 times that of ClOH and therefore the figure of 55% exchange in the absence of silver corresponds to full equilibration:

$$\text{Cl} + {}^{36}\text{ClOH} \rightleftarrows {}^{36}\text{Cl} + \text{ClOH}$$

with an equilibrium constant, K, equal to unity:

$$K = \frac{({}^{36}\text{Cl})\ (\text{ClOH})}{(\text{Cl})({}^{36}\text{ClOH})} = 1$$

Further, the extent of exchange for a given silver concentration corresponds quite closely to the percentage loss of activity in the production of chloroacetone in the addition reaction, as will be seen by a comparison of Tables 10 and 11.

The extent of the exchange varies, as would be expected, with variation in the nucleophilicity of the added anion. Specifically, the nucleophilic power of the halide ions increase in the order Cl $<$ Br $<$ I, and therefore the equilibrium

$$X^- + {}^{36}ClOH \rightleftarrows XOH + {}^{36}Cl^-$$

lies increasingly over to the right. The converse of this was also checked by the addition of labelled chloride to hypobromous acid. Very little exchange occurred.

The inference of this series of experiments is that mechanism (b) is operative in the addition of ClOH to 2-halo-olefins.

This conclusion was confirmed further by the addition of ClOH to 2-bromopropene, when bromoacetone was detected in the products (see next section).

Two further experiments were done in an attempt to clarify the precise nature of this exchange reaction.

(i) Chloride ion (as sodium chloride solution) of known specific activity was precipitated by the addition of excess silver ions. Inactive hypochlorous acid was then added, and the solution, containing the precipitated silver chloride, well shaken. Samples of the solution were drawn off from time to time, and their specific activity measured. The solution was observed to become slowly active. But the rate of exchange was many times slower than the very fast exchanges with which we are concerned. For example, the ClOH reached about 20% of the initial activity of the chloride in about 15 hours.

(ii) Labelled chloride ion was again precipitated by silver, and then this time inactive <u>chloride</u> <u>ion</u> was added. The rate of increase in the radioactivity of the solution was again followed, and found to be of the same order as the reaction in (i).

These results throw light on the possibility that the $AgCl_2^+$ species may be involved in the exchange reaction. As described in Chapter 1, there is evidence[117] for the existence and stability of AgI_2^+, and Arotsky and Symons[109] argued that the species $AgCl_2^+$ might be the chlorinating agent in electrophilic aromatic chlorination:

$$AgCl(s) + H_2OCl^+ \rightleftharpoons AgCl_2^+ + H_2O \qquad (1)$$

$$AgCl_2^+ + ArH \longrightarrow ArCl + H^+ + AgCl(s) \qquad (2)$$

It might be argued that step (1) would account for the observed chlorine-exchanges. However, reaction (i) above clearly shows that AgCl/HOCl exchange is very much slower than the exchange between HOCl and Cl^- in the presence of excess Ag^+. It would appear therefore that the latter must take place in solution.

Also, result (ii) shows that AgCl/HOCl exchange takes place at much the same rate as $AgCl/Cl^-$ exchange. Since the latter could take place <u>via</u> initial solution and ionisation of the AgCl, followed by chloride-exchange in solution; it seems likely that the former does not involve positive chlorine exchange. However, a heterogeneous process cannot be ruled out.

Anbar <u>et</u>.<u>al</u>.[118] have measured the rate of exchange between chloride ion and hypochlorous acid by chlorine-36 labelling and by carrying out the reaction in an alkaline medium, thus reducing the concentration of free HOCl, which was thought to be the entity taking part in the exchange. The rate was given by the expression

$$\text{Rate} = k(\text{HCCl})(\text{Cl}^-)(\text{H}^+)$$

and k was found to be $5.3 \times 10^{11}\ \text{M}^{-1}\ \text{Sec.}^{-1}$. In neutral solution we might write

$$\text{Rate} = k^1(\text{HOCl})(\text{Cl}^-)$$

where $k = 5.3 \times 10^{4}\ \text{M}^{-1}\ \text{Sec.}^{-1}$.

Now the collision rate for

$$\text{Ag}^+ + \text{Cl}^- \longrightarrow \text{AgCl}$$

may be calculated from the Debye expression.[119]

$$k = \frac{4\pi N Z_1 Z_2\, e_o^2 (D_1 + D_2)}{10^3 \epsilon k T \left\{ \exp\,(Z_1 Z_2 e_o^2/\epsilon k T \sigma) - 1 \right\}}$$

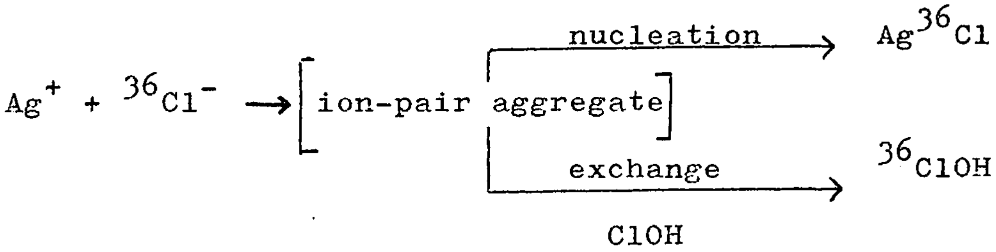
where D_1 and D_2 are the diffusion coefficients of the two ions. By use of the value of 7.5Å for σ, the effective reaction distance (although k is fairly insensitive to the choice of σ), and values of D_1 and D_2 obtained from ionic mobilities, the value of 3.2×10^{10} M^{-1} $sec.^{-1}$ is calculated for the encounter rate constant.[120]

Since in the experiments described the concentrations of Ag^+ and ClOH were of the same order, the exchange reaction is apparently not just a simple matter of competition between Ag^+ and HOCl for the capture of Cl^-, since the precipitation reaction would be approximately 10^6 faster.

However, Neilsen has found, by the use of a flow technique, that on mixing Ag^+ and Cl^- ions, there is an induction period before visible precipitation of silver chloride.[121] This induction period, t, was greatest at low salt concentration and from a plot of log t against log (salt) the number of ions in the critical nucleus could be calculated. In the case of silver chloride this was found to be five.

Also, Davies and Jones have studied the rate of precipitation by conductivity measurements.[122] After mixing Ag^+ and Cl^- ions, the conductance of a solution decreased until it reached a steady value. The rate of precipitation was highly dependent on the initial concentrations of the electrolytes, being greater for higher concentrations. The work suggested that $Ag^+ - Cl^-$ pairs aggregated in multi-ion pairs, which have a significant lifetime before nucleation takes place and silver chloride is precipitated.

The present work could be interpreted, therefore, in terms of formation of these ion-pair aggregates, which could then exchange chlorine with an HOCl molecule. The competition is thus between nucleation of the aggregate to form solid silver chloride, and exchange within the aggregate of Cl-36 with a hypochlorous acid molecule.



Since an increase in the concentration of silver ions in solution leads to an increase in the rate of nucleation, less exchange would be expected at higher silver concentrations, as is observed.

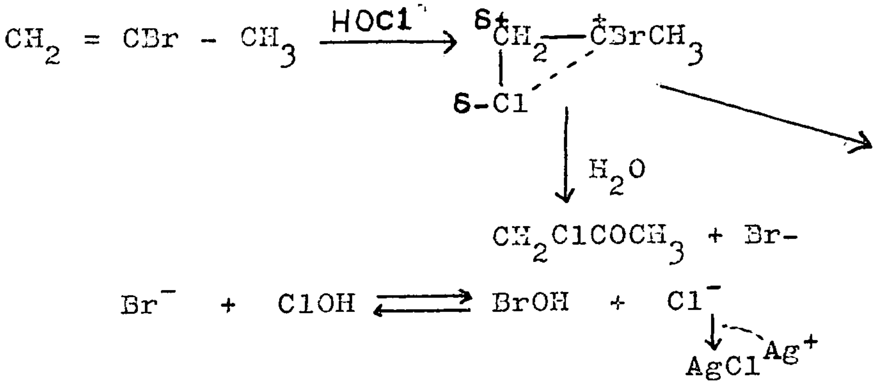
G The addition of hypochlorous acid to 2-bromopropene

The reaction was carried out in aqueous solution in the presence of 0.04 M silver perchlorate. After reaction, the solution was subjected to continuous ether extraction, which, it was assumed, would extract all possible products.

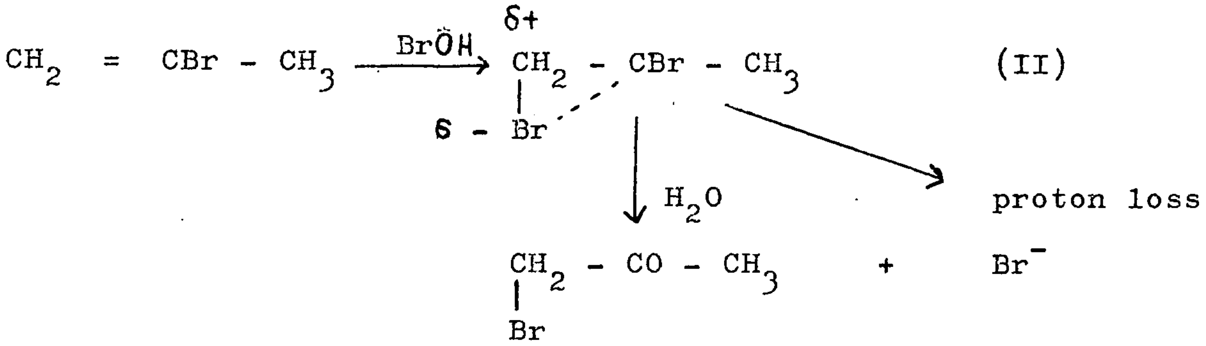
The resulting mixture of products was examined by vapour phase chromatography. Two peaks corresponding respectively to chloroacetone and bromoacetone were obtained, as well as a third, which could not be identified. The proportions were calculated by measurement of the areas of the peaks obtained : assuming that this area is proportional to the weight of the compound injected, the composition of the product mixture was calculated as : chloroacetone, 82.5%; bromoacetone, 11.0%; unidentified compound, 6.5%.

The production of bromoacetone fulfills the expectation that bromide ion released from C-2 in 2-bromopropene should exchange with HOCl to give BrOH, which then adds to the olefin giving the bromoketone.

The experimental results are consistent with the following reaction scheme:



(I)



(II)

It is to be expected from previous discussion that only the products from 2-attack of H_2O and of proton loss from C - 3 in both I and II will be formed. If this is the case, the unknown compound would most likely be $CH_2Cl.CBr = CH_2$. Another possibility is that some hydroxylation reaction, catalysed by silver ions, takes place. However, the product in this case would probably be hydroxyacetone, a possibility which has been ruled out by comparison of the retention time of the peak with that of a sample of this ketone.

It should be noted that here a mechanism involving *intra*-molecular bromine-exchange has not been directly ruled out as in the case of 2-chloropropene; however, there does not appear to be any necessity to postulate such a mechanism, as it has been shown in the present work that bromide ions exchange to a considerable extent with hypochlorous acid in the presence of excess silver ions.

H Possible bromine atom participation in electrophilic addition to bromo-alkenes

The following rate constants were obtained for the addition of iodine in aqueous solution to the series $CH_2 = CH(CH_2)_nBr$.

Table 13

Value of n in $CH_2 = CH(CH_2)_nBr$	k_2(mole.$^{-1}$l.min.$^{-1}$)
1	0.042
2	0.68
3	3.3
4	2.3

Simple inspection of the rate constants gives some indication that we have a rate enhancement for n = 3, since we have a rate maximum here, whereas one would expect an increase throughout the series n = 1 to n = 4 since the inductive effect of the bromo-substituent becomes less effective as it is removed successively further from the reaction centre. The rate constants for bromination of the same series of compounds increase steadily from n = 1 to n = 4 and can be satisfactorily analysed by assuming that the inductive effect falls off by a constant factor (ϵ) per methylene group.[73b]

If we write the inductive effect as

$$\Delta \log k = \log k_H - \log k_X$$

where k_H and k_X are the rate constants for the unsubstituted and substituted compounds respectively, then

$$\Delta \log k_n = \epsilon^{n-m} (\Delta \log k_m)$$

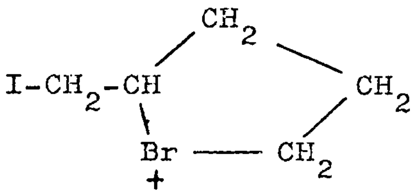
whence

$$\log (\Delta \log k_n) = (n-m) \log \epsilon + \log (\Delta \log k_m)$$

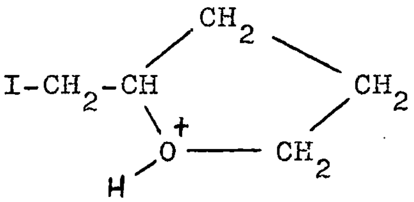
A plot of $\log (\Delta \log k_n)$ against the number of carbon atoms in the chain should give a straight line of slope $\log \epsilon$. Any rate enhancements can be picked out if the points lie substantially below the line. This method has been used extensively by Peterson et.al. for chain lengths up to 10 or more carbon atoms.[70] For the bromination of the series $CH_2 = CH(CH_2)_nBr$ in methanol, a good straight line is obtained, from which $\epsilon = 0.42$, indicating no rate enhancement due to neighbouring group participation.[73b] Similar calculations for the $CH_2 = CH(CH_2)_nOH$ series showed a definite rate enhancement for $n = 3$ for bromination,[73a] and k_Δ/ks (the ratio of the rate constant of the assisted to that of the non-assisted reaction) was calculated to be 1.5. For the iodination of this series,[72] k_Δ/ks for $n = 3$ was ca.60. The values of k_{Δ}/k_s were smaller at n = 4, showing clearly that OH-5 participation is more favoured in this system than OH-6 participation.

No figures are available for the iodination of the unsubstituted olefins $CH_2 = CH(CH_2)_nH$ and so the calculations cannot be carried out in the same way. If, however, one assumes that k_H does not vary much with n (there are only small changes in the rates of bromination[73a] and that there is no participation for n = 1 and n = 2 and additionally that $\epsilon = 0.58$ as found for bromination of the alcohol series in water, then estimates can be made for ks (unassisted rate constants) for n = 3 and n = 4. The values calculated are 3.4 and 7.6 $l.mole^{-1} min.^{-1}$ respectively, i.e. the rate for n = 4 is actually calculated to be larger than the observed value. If one uses $\epsilon = 0.42$ (as in bromination of the bromide series in methanol) the corresponding values are 2.1 and 3.5 $l.mole.^{-1} min.^{-1}$ Obviously the data on the iodination of the bromide series in water cannot be satisfactorily analysed in this way. It is clear that if there <u>is</u> any Br-5 participation (as suggested by the rate maximum at n = 3) then the magnitude of the effect is small - certainly very much smaller than the corresponding OH-5 participation - and with such small effects the assumptions made in the treatment cannot be justified to the degree of accuracy required to enable any quantitative estimation of the effect.

In conclusion one can say that there is evidence from the rates of iodination that the five-membered bromonium ion~~s~~:



is involved in the reaction of iodine with 5-bromopentene, although it is probable that only a small part of the overall reaction proceeds via this ion, in contrast to OH-5 participation, which in iodination is the dominant reaction, virtually 100% involving the oxonium ion:



It is likely that participation by neighbouring halogen substituents becomes increasingly important as the nucleophilicity of the solvent is reduced, consequently it would be of interest to examine the iodination and bromination of the series $CH_2 = CH(CH_2)_nHal.$ in solvents such as acetic acid or better still trifluoroacetic acid.

CHAPTER 3.

EXPERIMENTAL

PART I. PREPARATION OF MATERIALS

1. Hypochlorous Acid[107]

Mercuric oxide was prepared in a freshly precipitated form by disolving yellow mercuric oxide in concentrated nitric acid, then neutralising with caustic soda solution. The precipitate was washed several times with distilled water, the appropriate volume of water added, and chlorine gas bubbled through until the resulting chlorine water was approximately 0.15 molar. Standardisation was by addition of excess potassium iodide to an aliquot of the solution and titration of the liberated iodine with standard 0.1 N sodium thiosulphate solution. The chlorine water was then distilled direct from the mercuric oxide under reduced pressure, at about 35°C, using an iced-water condenser, and collected in a flask surrounded by ice. A rotary evaporator was used so as to reduce bumping. It was advisable to use the hypochlorous acid very shortly after preparation, as even at 0°C some decomposition to chlorine took place. (However, the Cl_2 could be removed from a solution of HOCl by shaking up with more freshly precipitated mercuric oxide and decanting.)

Hypochlorous acid labelled with ^{36}Cl can be prepared by adding $H^{36}Cl$ solution (commercially available) to the chlorine water before distillation.

2. Hypobromous Acid[123]

Silver phosphate (Ag_3PO_4) was precipitated from solution by the addition of a solution of disodium hydrogen phosphate (Na_2HPO_4 - 70 grams) to a solution of silver nitrate (30 grams). This yellow precipitate was washed thoroughly, six or seven times, with distilled water. 500 mls. of water were then added, followed by 7 mls. of liquid bromine. The mixture was then distilled under reduced pressure from a waterbath at about 32°C, using a rotary evaporator. As with hypochlorous acid, iced water was circulated through the condenser, and ice was used to surround the collecting vessel. The concentration of the hypobromous acid distilled over - determined by titration with standard sodium thiosulphate - was about 0.15 molar.

3. 2-chloropropene

(a) The action of PCl_5 on acetone.[124] Analar acetone was added from a dropping funnel on to phosphorus pentachloride. A vigorous reaction took place, and the 2-chloropropene evolved distilled over without the need for external heat. Ice-cold water was circulated through the condenser, and the product was collected in chilled water. It was washed with water several times, then with sodium bicarbonate solution to remove HCl, dried over anhydrous magnesium sulphate, and fractionated. The fraction boiling at 22 - 23° was collected and stored in a well-stoppered flask at -10°. Great care should be taken to keep this compound at as low a temperature as possible, because of its high volatility.

(b) <u>The action of alkali on 2,2-dichloropropane.</u>[125] A weighed amount of potassium was dissolved in small amounts in allyl alcohol in an atmosphere of nitrogen. The solution was heated till boiling (168°), when 2,2-dichloropropane (b.pt.70°) was added in more amyl alcohol. The 2-chloropropene produced was allowed to distil up through a reflux condenser surrounded by water at about 40°, so as to condense out the reactant and the solvent. The product (b.pt.23°) was collected in a chilled flask; the yield was about 65% of the theoretical. It was then fractionated, again into a chilled flask, a drying tube being attached to the air outlet to avoid the condensation of water on to the product.

(c) <u>The action of potassium hydroxide on 1,2-dichloropropane.</u>[126] A 3-necked IL. flask was fitted with a mechanical stirrer, a dropping funnel and a column about 70 cm. long with a side-arm to which was attached an iced-water condenser leading to a collecting flask surrounded by ice. About 225 gm. of potassium hydroxide were put in the flask, and about 225 gm. of ordinary alcohol ("meths"). The mixture was stirred, and 300 gm. of 1,2-dichloropropane gradually added. At first, not all the potassium hydroxide dissolved, as there was insufficient alcohol, but it dissolved as the reaction proceeded. Heat was applied to the reaction vessel; at about 40°C, crystals of potassium chloride first appeared, and at 60-65° the reaction was observed to be proceeding quite vigorously. Towards the end of the reaction, when all the 1,2-dichloropropane had been added, the temperature was raised to approximately 75°C to remove all the product. The temperature of the distillate varied between 23°C and 40°C. The total yield of mixed chloropropenes (2-chloropropene and the isomers of 1-chloropropene) was 158 grams. On attempting a separation of the chloropropenes on a fractionating column, the distillate came over at a high and not very steady temperature. This may have been due to inefficient packing of the column, as glass helices of a suitable size were not at that time available. Separation was therefore achieved by the use of a preparative scale vapour phase chromatographie machine (the Perkin Elmer 'Autoprep'). The ultimate yield of pure product was rather small, and it was not thought that either method (b) or (c) had proved themselves any superior to the usual method (a).

4. <u>2-bromopropene</u>.[127]

Firstly, sodium phenate was prepared by the addition of caustic soda (in aqueous solution) to an equivalent quantity of phenol. The latter dissolves readily, and the water was distilled off under reduced pressure on the rotary evaporator. The residual white solid was washed several times with acetone on a Buchner funnel.

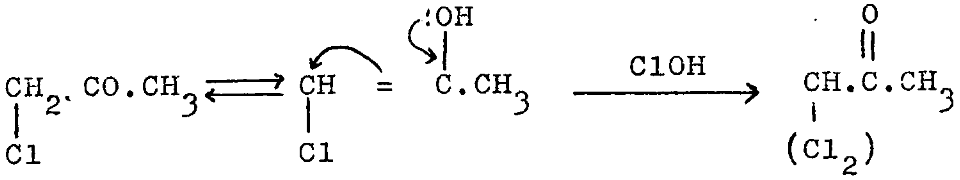
100 grams of sodium phenate were then taken, and dissolved as far as possible in 500 mls. of ethanol. 100 grams of 1,2-dibromopropane, also in ethanol, were added, and the mixture refluxed for 4 hours.

Product distilled over at 48-50°, and proved on examination by vapour phase chromatography to be a mixture of 1- and 2-bromopropenes.

This was dried over anhydrous magnesium sulphate, then carefully fractionated from an oil bath, using a long column packed with small glass helices. 2-bromopropene was collected at 48°C at one-tenth of the reflux rate and proved to be almost completely free from 1-bromopropene, as shown by vapour phase chromatographic analysis.

5. (^{36}Cl) - chloroacetone.

All methods of preparation of chloroacetone (b.pt.119°) by chlorination of acetone invariably lead to the production of a significant quantity of 1,1-dichloroacetone (b.pt.120°), which is difficult to separate from the monochloro compound. The dichloro compound is presumably formed by the further chlorination of the very reactive enol form of chloroacetone:



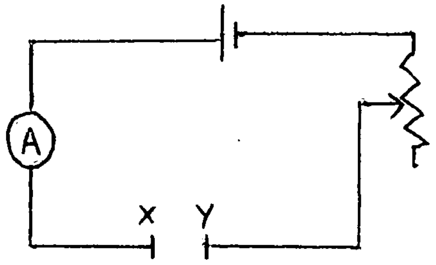
$$\underset{\text{Cl}}{\text{CH}_2}\text{.CO.CH}_3 \rightleftharpoons \underset{\text{Cl}}{\text{CH}} = \overset{\text{OH}}{\text{C}}\text{.CH}_3 \xrightarrow{\text{ClOH}} \underset{(\text{Cl}_2)}{\text{CH}}\text{.}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{.CH}_3$$

The following four methods of preparation were attempted, with varying degrees of success.

(a) The action of chlorine water on acetone. 2.5 L. of distilled water were saturated with chlorine (about 0.1 M), and 3 ml. of a solution of ^{36}Cl - labelled hydrochloric acid (2.24N, specific activity 142 microcuries per gm. of chlorine) added. The solution was acidified with 25 ml. conc. sulphuric acid, and an excess of AnalaR acetone added. The colour of chlorine disappeared after two or three days, when the solution was saturated with sodium sulphate and extracted with ether. The solvent layer was dried over anhydrous magnesium sulphate, and distilled through a Vigreux column. After the ether had distilled (35°), excess acetone came over (56°). The remaining product was fractionated and collected at 119-121°. Analysis on a Perkin Elmer Vapour Phase Gas Chromatograph showed two components (identified by comparison with authentic samples), chloroacetone (about 95%) and 1,1-dichloroacetone (about 5%). Separation of these compounds was possible by use of a preparative scale chromatograph, in this case the Perkin Elmer Autoprep, but recovery of material was very low, about 35%.

(b) The addition of chlorine to 2-chloropropene. Chlorine gas was passed into distilled water, with vigorous shaking to aid solution, until the concentration was about 0.1 molar. The solution was standardised by the addition of excess potassium iodide to an aliquot, and titration with standard 0.1 N thiosulphate. Labelled hydrochloric acid was added. The chlorine water (labelled with ^{36}Cl) was then added from a dropping funnel on to a solution of an excess amount of 2-chloropropene in water, which was chilled, so as to reduce evaporation. The flask used for the reaction was also fitted with a drying pistol filled with solid carbon dioxide, in order to prevent evaporation of the olefin as far as possible. After salting out with sodium sulphate, the aqueous solution was continuously extracted with ether for about 15 hours. Prior removal of the 2,3-dichloropropene also produced in the reaction was attempted, using hexane, but it was found that rather too much chloroacetone is extracted at the same time. The ether and water layers were then separated, the ether layer dried, and the ether distilled off. Since distillation of the chloroacetone at atmospheric pressure tended to produce charring, the product was distilled under reduced pressure. The lower boiling point (about 50°C at 3 cm.Hg pressure) here did not cause charring, and chloroacetone was obtained in an almost pure state, as shown by the vapour phase chromatograph traces.

(c) Electrolysis of HCl in acetone.[128] A circuit was set up as shown, with current passing between platinum electrodes through a solution containing concentrated hydrogen chloride, active hydrochloric acid and excess Analar acetone. Since only small electrodes (surface area about 1 cm.^{2}) were available, and the recommended current density was 0.1 amp.cm.$^{-2}$, six electrodes were connected in parallel at X, and six at Y, so as to increase the rate of production of chloroacetone. The rheostat was used to adjust the current to 0.6 amp., and the reaction left for about 30 hours, with occasional addition of acetone to replace that which was probably lost by evaporation caused by the heat developed during the electrolysis.



The solution was extracted with ether, and the ether extract dried over anhydrous magnesium sulphate. The ether was distilled off, and then the product was distilled over, proving to be very pure.

(d) Hydration of (3-^{36}Cl)-2,3-dichloropropene.[129] Six parts of concentrated hydrochloric acid were added to one part of $CH_2 = CCl.CH_2{}^{36}Cl$ (prepared as described later). Care was taken during this addition, as fumes were rather violently evolved. This reactant solution was then cautiously added, with shaking, to a fairly large excess of an aqueous solution of silver sulphate. After leaving for an hour or so, the solution was salted out and extracted with ether. The ether was distilled off, and the chloroacetone distilled at about 40° under a pressure of about 20 mm. The product was over 99% pure.

Measurement of Radioactivity

All measurements were carried out using a Geiger-Müller counter with a tube designed for liquid counting. Radioactivity is expressed as the "specific activity", in counts $min.^{-1}$ $mole.^{-1}$ litre. The counting rate in all cases has been corrected for background radiation and for the change of solvent, where appropriate. Usually, of the order of 10,000 counts were made, giving a ± 1% statistical error in the specific activity.

6. Bromoacetone

Acetone was brominated by an equivalent quantity of bromine in the presence of mineral acid. The product was extracted into ether after salting out with sodium sulphate. The ether solution was dried over anhydrous magnesium sulphate, and the ether distilled off under reduced pressure on the rotary evaporator. The resulting bromoacetone was distilled under reduced pressure, and a VPC trace showed it to be pure.

7. 3-(^{36}Cl) - 2,3-dichloropropene[52]

Unlabelled olefin, which is available commercially, was refluxed in pure, dried acetone (prepared by refluxing over potassium permanganate and potassium hydroxide and then distilling) containing Li^{36}Cl (the latter was prepared by adding an excess of lithium carbonate to the commercially available H^{36}Cl until the solution is neutral). After refluxing for about 40 hours, the lithium chloride and most of the acetone were extracted with ice-cold water. The olefin was then shaken with ferrous sulphate, washed with water, dried over anhydrous magnesium sulphate, and fractionated. The boiling point at atmospheric pressure was 93°C.

8. Conversion of labelled hypochlorous acid to a derivative suitable for determining the counting rate

(a) Conversion to 2,4-dinitrophenylhydrazone of chloroacetone. A sample of the HO^{36}Cl was acidified, and a slight excess of Analar acetone was added. The solution was allowed to stand, with occasional shaking, till the smell of chlorine had disappeared, which took about two days. The chloroacetone was extracted from the acetone with ether, then the ether distilled off. Then a solution was made up of 2 grams.of 2,4-dinitrophenylhydrazine in 10 mls. of concentrated sulphuric acid, and added to a mixture of 50 mls. ethanol and 125 mls. water. This was filtered, and 1 gram of chloroacetone was added to the filtrate. On standing overnight, a yellow precipitate was obtained, which was recrystallised from alcohol. The specific activity was then measured in acetone.

(b) Conversion to lithium chloride. A small excess of lithium carbonate was added to a portion of the hypochlorous acid and sulphur dioxide passed until effervescence ceased. The water was then removed on a rotary evaporator, and the remaining lithium chloride extracted into alcohol, in which solvent the activity was measured. The chloride ion was determined by titration (Volhard's method).

(c) Conversion to silver chloride. The unexpectedly low recovery of lithium chloride in the above experiment suggested that not all the chlorine was being converted to the chloride species. Accordingly, sulphur dioxide was passed into a solution of the hypochlorous acid containing excess silver nitrate and acidified with nitric acid. The precipitated silver chloride was filtered off on a Buchner funnel, washed with water, dissolved in 0.880 ammonia, and reprecipitated with dilute nitric acid. The precipitate was again filtered on a Buchner funnel, and washed successively with water, ethanol, and acetone.

It was then dried and a standard solution made up in 0.880 ammonia, to determine the specific activity.

In order to relate the counting rate in ammonia to that in water, a portion of the silver chloride was converted to sodium chloride by means of sodium fusion. The resulting sodium chloride was dissolved in water, the chloride content analysed by titration, and the radioactivity measured.

9. Allyl bromide

This is available commercially; it was purified on a preparative scale vapour phase chromatograph before use.

10. 4-bromobutene

This is also available commercially, and was purified before use on a preparative scale v.p.c.

11. 5-bromopentene[130]

133 gm. (1.55 mole) of 1-penten-5-ol and 35 gm. (0.44 mole) of pyridine were mixed in a flask surrounded by an ethanol $-CO_2$ bath (-25° to -30°). 174 gm. (0.64 mole) of phosphorous tribromide was added dropwise over a period of 4 hours to the flask, which was fitted with a stirrer. The stirrer was then replaced by a condenser and the product distilled from an oil-bath. Caution is required at this stage, as the vapours tend to ignite spontaneously, especially towards the end. The product was washed twice with water, once with caustic soda, and dried over calcium chloride. The yield of product boiling between 127° and 130° was 180 gm. (78%). It was purified by v.p.c. before use.

12. 6-bromohexene[131]

The corresponding alcohol $CH_2 = CH(CH_2)_4OH$ was treated with phosphorus tribromide in pyridine, the same relative proportions of reactants being used as in the bromopentene preparation. The boiling point at 16 mm. was 47-51°, yield 53%.

PART II. DESCRIPTION OF EXPERIMENTS

Experiment 1

Analysis of the products of the reaction between hypochlorous acid and 2-chloropropene

2-chloropropene (11 gms.) was added in small portions, shaking well in between additions, to an aqueous solution of hypochlorous acid (1l., 0.0820 M) containing perchloric acid (0.040 N). The reaction mixture was left overnight. No hypochlorous acid was left in the morning, as shown by the absence of iodine when a sample was added to a potassium iodide solution. The chloride ion liberated was determined by titration (Volhard's method) and represented 83% of the amount of hypochlorous acid used up.

Isotope dilution experiments were then carried out on both of the expected products of the reaction, chloroacetone and 2,3-dichloropropene. Chloroacetone labelled with ^{36}Cl (2.5522 gm., specific activity in acetone 11,225) and 2,3-dichloropropene labelled in the 3-position with ^{36}Cl (6.2367 gm., specific activity in ethanol 14,547) were added to the reaction mixture and the whole thoroughly mixed. The solution was extracted first with pentane, the extract dried, and the pentane removed. 2,3-dichloropropene was distilled from the residue (b.pt. 94-95°) and was shown to be pure by vapour phase chromatography. A standard solution was made up in ethanol and the specific activity determined as 11,692.

If Wo gm. is the weight of 2,3-dichloropropene formed in the reaction then the isotope dilution expression is

$$\frac{6.2367}{Wo + 6.2367} = \frac{11,692}{14,547}$$

$$Wo = \frac{6.2367 \times 2,855}{11,692}$$

$$= 1.524$$

Therefore the percentage yield, based on the hypochlorous acid used up $= \frac{1.524 \times 100}{0.0820 \times 111} = 17 \pm 1\ \%$.

After the pentane extraction, the solution was saturated with sodium sulphate and extracted with three portions of ether. The extract was dried and the ether removed, rather slowly at reduced pressure, since the chloroacetone tended to char. The residual oil was shown to be pure chloroacetone by v.p.c. analysis but because of the difficulty of obtaining a clear liquid by distillation the ketone was converted directly into its 2,4-dinitrophenylhydrazone derivative for counting purposes. 2,4-dinitrophenylhydrazine (24 gm.) was dissolved in concentrated sulphuric acid (120 ml.) and the solution added cautiously to a mixture of ethanol (225 ml.) and water (600 ml.). Insoluble material was filtered off and to the reagent solution was added an equivalent quantity of chloroacetone. A yellow precipitate began to form immediately but the solution was left overnight to allow complete precipitation. The precipitate was filtered and recrystallised from alcohol to constant specific activity, 3182 in acetone. Again, if Wo gm. of chloroacetone is formed in the reaction,

$$\frac{2.5522}{Wo + 2.5522} = \frac{3182}{11,225}$$

$$Wo = \frac{2.5522 \times 8043}{3182}$$

$$= 6.451$$

Therefore the yield of chloroacetone based on the amount of hypochlorous acid used up $= \frac{6.451 \times 100}{92.5 \times 0.0820}$

$$= 85 \pm 2 \ \%$$

Experiment 2

Investigation of the effect of silver ions on the yield of chloroacetone in the reaction between hypochlorous acid and 2-chloropropene

2-chloropropene (2 gm.) was added to an aqueous solution (1070 ml.) containing hypochlorous acid (0.0105 M), perchloric acid (0.112 M) and silver perchlorate (0.0491 M). The reaction mixture was shaken well and left overnight, when all the hypochlorous acid was used up. The chloride ion liberated was determined by Volhard's method, and represented 113% of the hypochlorous acid used.

Active chloroacetone (1.1524 gm., specific activity in acetone 15,910) was added to the solution, which was vigorously shaken. The ketone was extracted into ether as in Experiment 1 and converted into its 2,4-dinitrophenylhydrazone, whose specific activity in acetone was found to be 9,131.

$$\frac{1.1524}{Wo + 1.1524} = \frac{9,131}{15,910}$$

$$Wo = 0.8557$$

Therefore the yield of chloroacetone, based on the amount of hypochlorous acid used up $= \dfrac{0.8557 \times 100}{92.5 \times .01124}$

$$= 83 \pm 2 \quad \%$$

Experiment 3

Identification of the products of the addition of hypochlorous acid to 2-chloropropene in the presence of a large excess of silver ions

1-gm. quantities of 2-chloropropene were added to an aqueous solution (IL) of hypochlorous acid (0.045 M) and silver perchlorate (0.095 M). Each addition was shaken vigorously till the olefin dissolved. After the addition of about 6 gm., it was difficult to get further olefin to dissolve, and the solution no longer smelled of hypochlorous acid. The solution was saturated with sodium sulphate and the silver chloride and the excess salt filtered off. The organic products were removed into ether by continuous extraction (about 30 hrs.). The ether was cautiously distilled off, and the residual oil examined by vapour phase chromatography. Only two peaks were produced (apart from ether), which were shown by comparison with authentic samples to represent chloroacetone and 2,3-dichloropropene.

Experiment 4

The kinetics of the reaction between hypochlorous acid and 2-chloropropene

A Determination of the rate constant under "normal" conditions.

An aqueous solution (250 ml.) of hypochlorous acid (0.002 M), silver perchlorate (0.036 M) and perchloric acid (0.02 M) was allowed to attain ambient temperature in a 25°C thermostat. Slightly over 0.5 gm. 2-chloropropene (sufficient to saturate this volume of solution) was added with vigorous shaking. 5 ml. samples of the solution were taken and run into an excess of chilled potassium iodide solution containing dilute sulphuric acid and saturated with nitrogen. The time was invariably noted when the liquid began to run from the pipette into the flask. The released iodine was titrated again 0.001 N sodium thiosulphate.

Now since the olefin is in large excess over the hypochlorous acid, its concentration remains effectively constant, and so we may use the following form of the rate expression

$$k_2 = \frac{2.303}{t.b} \log \frac{a}{a - x}$$

where

a = concentration of hypochlorous acid initially

a - x = concentration of hypochlorous acid at time <u>t</u> seconds

b = concentration of 2-chloropropene

To determine b, a known excess of standard bromide-bromate solution was added to a saturated solution of the olefin, acidified, and the released excess bromine determined by using it to liberate iodine from potassium iodide, followed by thiosulphate titration. The solubility of 2-chloropropene in water at room temperature was found to be 0.0260 moles per litre. The following tables present the results of three runs at 25°, with k_1 computed as $\frac{2.030}{t} \log \frac{a}{a - x}$. The mean value for the rate constant, k_2, is then calculated by dividing the mean value of k_1 by 0.026.

Run 1

t (sec.)	Titre (ml.)	$\log \frac{a}{a-x}$	$10^4\ k_1(\text{sec.}^{-1})$
0	9.10		
725	6.30	0.1597	5.075
950	5.44	0.2234	5.42
1205	4.86	0.2724	5.21
1680	3.72	0.3885	5.33
2190	2.92	0.4936	5.19
3395	1.49	0.7858	5.33

Run 2

t (sec.)	a - x	$\log \frac{a}{a - x}$	10^4 k_1 (sec.$^{-1}$)
0	9.30		
940	5.45	0.2321	5.69
1215	3.85	0.3830	5.97
1520	3.25	0.4566	5.89
1985	2.60	0.5535	5.63
2500	2.00	0.6675	5.52
3265	1.55	0.7782	5.02

Run 3

t (sec.)	a - x	$\log \frac{a}{a - x}$	10^4 k_1 (sec.$^{-1}$)
0	10.05		
840	6.12	0.2153	5.90
1020	5.63	0.2516	5.68
1440	4.60	0.3393	5.73
2580	2.85	0.5473	5.06
3180	2.10	0.6799	5.06
3840	1.18	0.9302	5.58

The mean value for k_1 obtained is therefore in run 1, 5.26 x 10^{-4}; in run 2, 5.62 x 10^{-4}; and in run 3, 5.50 x 10^{-4} giving an overall mean of 5.46 x 10^{-4}. The rate constant, k_2, is thus 5.46 x 10^{-4} ÷ 0.026 = 0.021 sec.$^{-1}$ mole.$^{-1}$ l.

B Determination of the rate constant under conditions of low mineral acid, high silver and high hypochlorous acid concentrations

(a) 2,3-dichloropropene

The reaction was followed by the same method as for the previously described runs on 2-chloropropene. The concentrations were : hypochlorous acid, 3.13×10^{-3} M; silver perchlorate, 0.0563 M; 2,3-dichloropropene, 0.0342 M; and mineral acid, zero. The results for a representative run are set out below.

t (sec.)	a - x	$\log \frac{a}{a - x}$	$10^5\ k_1 (\text{sec.}^{-1})$
0	11.60		
300	11.25	0.0134	10.3
720	10.80	0.0311	9.95
1140	10.05	0.0624	12.5
1440	7.20	0.2067	33.1
1635	5.05	0.3612	50.9
1770	4.60	0.4013	52.2
1920	3.80	0.4847	58.1
2100	3.05	0.5802	63.6
2340	2.60	0.6495	63.9
2700	2.60	0.6495	55.4
3300	2.25	0.7123	49.7
3900	1.50	0.8884	52.5

(b) 2-chloropropene

The concentrations used were : hypochlorous acid, 5.15×10^{-3} M;

silver perchlorate, 0.109 M; 2-chloropropene, 0.0260 M; and mineral acid, zero.

t (sec.)	a - x	$\log \frac{a}{a - x}$	$10^4\ k_1 (\text{sec.}^{-1})$
0	13.15		
480	8.25	0.2024	9.71
735	7.20	0.2616	8.20
1200	5.30	0.3946	7.58
1440	4.25	0.4905	7.84
1800	3.50	0.5748	7.35
2220	2.60	0.7039	7.30
2700	1.90	0.8401	7.17
3180	1.65	0.9014	6.53

(c) 2-chloroprop-2-en-1-ol

Runs were done at a concentration of (i) 0.050 M silver perchlorate and (ii) 0.200 M silver perchlorate. Both reactions were followed at a perchloric acid concentration of 0.020 M, hypochlorous acid, 7×10^{-3} M, and 2-chloroprop-2-en-1-ol, 0.0307 M.

Run (i)

t (sec.)	a - x	$\log \frac{a}{a-x}$	$10^4 k_1 (sec.^{-1})$
0	15.63		
210	12.78	0.0874	9.59
420	11.62	0.1287	7.06
720	10.20	0.1853	5.93
1140	8.70	0.2544	5.14
1680	7.20	0.3366	4.61
2280	5.99	0.4165	4.21
2820	5.02	0.4932	3.94
3360	4.48	0.5426	3.72
4020	3.80	0.6141	3.52
4620	3.35	0.6689	3.34
5220	2.92	0.7285	3.21

Run (ii)

t (sec.)	a - x	$\log \frac{a}{a-x}$	$10^3 k_1 (sec.^{-1})$
0	16.02		
240	9.31	0.2357	2.26
420	7.60	0.3238	1.78
600	6.61	0.3844	1.48
800	4.70	0.5325	1.46
1065	4.60	0.5418	1.17
1200	4.02	0.6004	1.15
1380	3.52	0.6581	1.10
1560	2.77	0.7621	1.13

Run (ii) cont.

t (sec.)	a - x	$\log \frac{a}{a - x}$	$10^3\ k_1 (\text{sec.}^{-1})$
1740	2.50	0.8067	1.07
1920	2.30	0.8429	1.01
2220	1.71	0.9716	1.01
2400	1.40	1.0585	1.02
2700	1.20	1.1254	0.96

Experiment 5

Determination of the specific activity of the chloroacetone produced by the addition of ^{36}Cl - labelled hypochlorous acid to 2-chloropropene

Three aqueous solutions were made up with the following compositions (in moles per litre)

	(1)	(2)	(3)
Hypochlorous acid	0.0697	0.0474	0.0697
Perchloric acid	0.0990	0.0990	0.1010
Silver perchlorate	-	0.0103	0.0532
Total volume (ml.)	1010	1485	1010

2-chloropropene (8gm.) was added to each, in small quantities, with vigorous shaking. Each solution was saturated with sodium sulphate then filtered. The products were extracted into ether, which was dried and slowly distilled off, the last traces under reduced pressure on a rotary evaporator. Each sample of chloroacetone was converted to its 2,4-dinitrophenylhydrazone, which was recrystallised from ethanol to constant specific activity. The specific activities of the samples in acetone were (1) 17,712 (2) 18,165 (3) 23,724. The specific activity of the hypochlorous acid was 21,919 in water. This corresponds to 21,919 x 1.298 = 28,451 in acetone. The percentage activities were therefore (1) 62.3 (2) 63.8 (3) 83.4. (in all cases ± 1%)

Experiment 6

Determination of the specific activity of the chloroacetone produced by the addition of $HO^{36}Cl$ to a continuous excess of 2-chloropropene

5 gm. of 2-chloropropene (dissolved in 20 ml. alcohol so as to aid dispersion) were added with vigorous shaking to an aqueous solution (3850 mls.) containing silver perchlorate and perchloric acid. 130 ml. of labelled hypochlorous acid (0.020 M, specific activity 31,900) was added. The concentration of the HOCl was therefore 0.0065 M, that of the silver ion, 0.100 M, of mineral acid 0.096 M, and of olefin 0.0163 M.

The solution was worked up for the chloroacetone product as described before. The specific activity of the 2,4-dinitrophenylhydrazone was measured in acetone and found to be 34,781, i.e.

$\frac{34,781}{31,900 \times 1.298} \times 100 = 84 \pm 1\%$ of the specific activity of the $HO^{36}Cl$ used.

Experiment 7

Determination of the specific activity of the chloroacetone produced in the reaction between 2-chloropropene and $HO^{36}Cl$

Hypochlorous acid labelled with ^{36}Cl was prepared, and its specific activity in water determined at 36,182. A sample was also converted to chloride and its specific activity redetermined as follows. To 100 mls. of the solution (0.291 M) lithium carbonate (2.5 gm.) was added and sulphur dioxide passed till effervescence ceased. Silver nitrate (8 gm. in 20 ml. water) was added to the solution, after acidification with nitric acid. The precipitated silver chloride was filtered off, dissolved in 0.880 ammonia, filtered, and reprecipitated by 50 : 50 water : conc. sulphuric acid. It was washed successively with water, ethanol and acetone, and dried in an oven. The silver chloride sample obtained was fused in an ignition tube with an excess of sodium. The tube was dropped into distilled water, ground up, and all insoluble material filtered off. The sodium chloride solution was analysed for chloride content, and its counting rate determined. The specific activity determined by this method was 35,596. The mean of this figure and that obtained by the usual method of simply standardising the hypochlorous acid against thiosulphate was taken to represent the specific activity of the $HO^{36}Cl$ (35,889).

Two solutions, each 0.022 M in HOCl, and 0.096 M in $HClO_4$ were made up (total volume 2L). Solution (2) was made 0.0415 in $AgClO_4$, while (1) contained no silver ions. 10 gm. of 2-chloropropene was added to each, in portions of approximately 1.5 gm., with vigorous shaking. When all the hypochlorous acid had reacted (smell) each solution was worked up to produce a pure sample of chloroacetone, as described before. Derivatives were made and their specific activities determined. As a percentage of the specific activity of the initial HOCl, these were found to be (1) 59 ± 1% and (2) 91 ± 1%.

Experiment 8

Determination of the specific activity of and the position of labelling in the 2,3-dichloropropene produced by the addition of $HO^{36}Cl$ to 2-chloropropene

This addition was carried out on a larger scale than previous experiments, since the 2,3-dichloropropene is produced in only about 15% yield. Stock solutions were made up as follows: 3.6 L., 0.200 M in perchloric acid and 0.193 M in hypochlorous acid (specific activity 22,477); 1.0 L., 1.00 M silver perchlorate.

For ease of handling, the addition reaction was carried out in four 2L. flasks. In each of these (labelled 1,2,3 and 4), 1.0 L. of water was saturated with 2-chloropropene (ca. 1.7 gm.). To each solution, 25 ml. of the silver solution were added (making it ca. 0.025 M), and 50 ml. of the acidified HOCl solution (making it ca. 0.01 M). The flask was shaken up till the smell of HOCl disappeared, when it was resaturated with olefin, and more HOCl added. The process was repeated, olefin being added to keep it always in excess, HOCl as soon as it was used up, and silver so as to keep it always in excess over the HOCl, but never at any time at a concentration above 0.025 M. The following table describes the additions of each reagent to solutions 1,2,3 and 4. The units for the olefin are grams, and for the others, millilitres.

1			2			3			4		
Olefin	Ag^+	HOCl	Olefin	Ag^+	HOCl	Olefin	Ag^+	HOCl	Olefin	Ag^+	HOCl
1.7	25	45	1.7	25	20	1.9	25	50	1.6	25	50
		35			30	2.1		50	1.9		50
2.0					35	2.1	50		1.8	25	50
1.8			2.1	25	50			50			50
		20			15	2.0	25	50	2.0	25	50
	25	65	1.8		50	0.9			0.6		
		35	0.7	25	50	1.8	25	50	1.8	25	50
1.8	25	50	1.9		50	1.8		45	1.8	25	55
		50	1.6	25	50	1.8		45	1.8		55
1.7	25	50	2.1	25	50	1.8		50	1.8		50
		50	1.0		50			25			25
1.6	25	50	1.8	25	50	1.8		50			
1.5		50			50						
1.8	25	50	0.6								
		50	1.8	25	40						
0.8											
1.8	25	60									

Each solution was then extracted with two half-litre portions of pentane. The extracts were dried over anhydrous magnesium sulphate, and the solvent evaporated off. The product samples were bulked, and distilled (b.pt. 94.5°). The retention time on a gas phase chromatograph column was identical to that of a commercial sample of

2,3-dichloropropene. The specific activity was measured in ethanol and found to be 25,300. The specific activity of an active sample of chloroacetone was then determined in ethanol and found to be 0.9553 times the value for the same sample in acetone.

The S - allylthiouronium picrate of the 2,3-dichloropropene was then prepared. To 0.5 gm. of the olefin were added 0.5 gm. thiourea in 10 ml. alcohol, and the mixture refluxed for 40 min. 0.5 gm. picric acid was added, and the mixture refluxed for a further 10 mins. then allowed to cool. A few drops of water were added, when yellow crystals separated out. The derivative was recrystallised from ethanol, m.pt. 171°. The specific activity in ethanol was determined at 294.

The chloroacetone was next recovered by ether extraction of the aqueous solution remaining after the pentane extraction. Solvent was evaporated off and the 2,4-d.n.p. derivative prepared as in Experiment 1. The specific activity in acetone was found to be 24,963.

The activities may be summarised as below, corrected to the same solvent, acetone.

Material	Specific activity in acetone	Specific activity expressed as a percentage
$^{36}ClOH$	29,200	100
$^{36}ClCH_2CO.CH_3$	25,000	85.6
$^{36}ClCH_2CCl=CH_2$	26,500	90.7
$CH_2=CCl.CH_2-X$	308	1.1

Experiment 9

Investigation of halogen exchange in aqueous solution

(a) Solutions were made up (200 ml.) containing hypochlorous acid labelled with ^{36}Cl (ca. 0.01 M), perchloric acid (ca. 0.1 M) and varying amounts of silver perchlorate. The specific activity, defined in this case as the counting rate divided by the titre for 5 ml. of the solution against 0.01 N thiosulphate, was measured. (It was found that with a hypochlorous acid concentration no higher than about 0.01 M, interaction with the silver ions was not significant over a short period of time.) Sodium chloride solution (containing chloride ion in slight excess over the ClOH) was added, the solution shaken, and the precipitated silver chloride filtered off. The specific activity of the remaining solution was determined, and compared with that before the addition of the chloride. The procedure was carried out for two concentrations of silver (each in duplicate) and in the absence of silver. The addition of bromide ion at two silver concentrations (each in duplicate) and of iodide at two silver concentrations was also carried out. The results are set out in the following tables, showing the specific activity of the hypohalous acid after the halide addition expressed as a percentage of that before the addition.

(i) Chloride ion

Molality of:	1	2(a)	2(b)	3(a)	3(b)
ClOH	.00939	.00936	.00938	.00939	.00937
Ag^+	-	.0167	.0168	.0336	.0~~0~~335
Cl^-	.0113	.0123	.0115	.0113	.0121
% activity retained	42.4	64.4	64.2	82.3	82.7

(ii) Bromide ion

Molality of:	1(a)	1(b)	2(a)	2(b)
ClOH	.00951	.00951	.00951	.00952
Ag^+	.0170	.0170	.0340	.0340
Br^-	.0116	.0118	.0116	.0113
% activity retained	60.4	56.2	76.2	76.5

(iii) Iodide ion

Molality of:	1	2
ClOH	.00940	.00940
Ag^+	.0168	.0336
I^-	.0111	.0112
% activity retained	5.69	61.0

(b) A solution of hypobromous acid was made up, and silver perchlorate in excess was added. Radioactive chloride ion of known specific activity was added, the solution shaken, and the precipitated silver halide filtered off. The hypohalous acid solution was standardised against thiosulphate and its activity measured. The specific activity was calculated and compared with that of the added chloride.

Molality of:	
HOBr	.0220
Ag^+	.0400
$^{36}Cl^-$	.0302
% exchange	4.2

(c) Labelled chloride ion was precipitated from solution by an excess of silver ions. A sample of the solution was filtered off and its counting rate measured and used as a background. Then unlabelled hypochlorous acid was added to the main solution, containing the $Ag^{36}Cl$ precipitate. After shaking up, a sample was filtered off and its counting rate and concentration determined. The counting rate was redetermined at intervals of approximately ½ hr., 2 hrs., 3 hrs., and 16 hrs. The specific activity of the chloride used was 86,405, and the concentrations were: chloride ion, 0.0228 M, silver perchlorate, 0.0358 M; perchloric acid, 0.02 M; hypochlorous acid, 0.0196 M. The following table gives the specific activity of the solution at various times.

Time (min.)	0	30	140	205	960
Specific Activity	0	553	2,411	4,588	17,945

(d) Active chloride solution (specific activity 122,384) was precipitated by an excess of silver ions. A filtered sample of solution was counted for use as a background count. Then inactive chloride ions were added to the solution containing the active silver chloride precipitate. The concentration of chloride ions remaining in solution was 0.00904 M. The solution was shaken vigorously, and at intervals samples of the solution were counted.

Time	20 min.	4 hr.	$15\frac{1}{3}$ hr.	$20\frac{1}{3}$ hr.
Specific Activity	1,556	1,811	29,000	32,556

Experiment 10

Analysis of the products of addition of hypochlorous acid to 2-bromopropene in the presence of silver ions

An aqueous solution (IL.) was made up 0.0244 M in hypochlorous acid, 0.0394 M in silver perchlorate and 0.0960 M in perchloric acid. 6 gm. of 2-bromopropene (about a 2-fold excess over the ClOH) was added in small quantities with vigorous shaking. The smell of ClOH disappeared, and the lachrymatory smell typical of halo-acetones was detected. The solution was saturated with sodium sulphate and extracted with ether. The extract was dried over anhydrous magnesium sulphate, filtered, and the solvent slowly distilled off using a Vigreux column. It was not attempted to remove the last traces of ether from the product, which was examined on a Perkin Elmer Vapour Phase Chromatograph. Apart from the ether, three peaks were obtained. These corresponded to chloroacetone, bromoacetone and an unidentified compound. The area under the peak for each compound was measured by means of a planimeter, and assuming that this area is proportional to the weight of the compount injected on to the column, the percentage composition of the product was calculated to be chloroacetone, 82.5; bromoacetone, 11.0; unidentified compount 6.5.

A sample of hydroxyacetone was injected on to the column, and its retention time showed that the third component of the product mixture was not hydroxyacetone.

Experiment 11

The kinetics of the addition of iodine in aqueous solution to allyl bromide, 4-bromobutene, 5-bromopentene and 6-bromohexene

(a) Iodine Solution

A stock solution of iodine was made up by stirring about 25 grams of the solid with one litre of water for about 12 hours. The solution was decanted from undissolved iodine, and made 0.1 molar in potassium iodide. Then the concentration of iodine was determined by standardisation with sodium thiosulphate. A 1 ml. sample was run into 100 mls. of water, dilute nitric acid and 2 ml. of sodium starch glycollate indicator added, then titrated against 0.01 N sodium thiosulphate.

The indicator is made by mixing 5 grams of the finely divided solid with 1-2 mls. ethanol, adding 100 mls. cold water, and boiling for a few minutes with vigorous stirring, to give a faintly opalescent solution. This 5% stock solution is diluted to 0.1% strength as required.

The stock iodine solution was found to be 0.0489 M for the first series of runs, and was restandardised for the bromobutene runs at 0.0473 M.

(b) Allyl Bromide runs

A solution of the olefin was made by dissolving 6 gm. in one litre of water, and standardised by taking a 5 ml. sample, adding dilute sulphuric acid and 10 ml. of 0.1 N potassium bromide/

potassium bromate solution, stoppering well and shaking the flask from time to time to give the bromine released time to react. The excess bromine was estimated by addition to standard potassium iodide solution, then titration against 0.1 N sodium thiosulphate. The concentration was found to be 0.0374 M.

120 mls. of this solution were taken and put into a 20°C thermostat until the ambient temperature was attained. Then 10 mls. of iodine solution were added. Zero time was taken when the iodine solution started to run out from the pipette. 10 ml. samples of the reactant solution were taken at intervals, and run into 100 mls. water, dilute sulphuric acid and 2 mls. indicator added, and titrated against 0.01 N $Na_2S_2O_3$.

Now,

$$\text{Initial olefin concentration} = 0.0374 \times \frac{120}{130} \text{ molar}$$
$$= 0.0345 \text{ molar}$$

and

$$\text{Initial iodine concentration} = 0.0489 \times \frac{10}{130} \text{ molar}$$
$$= 0.00376 \text{ molar}$$

Therefore we can use the following form of the rate equation

$$k_2 = \frac{2.303}{t.b.} \log \frac{a}{a - x}$$

where a = initial concentration of iodine (proportional to titre)

a - x = concentration of iodine at time t minutes (proportional to titre)

b = concentration (assumed constant) of olefin.

The results of the two runs and the calculation of the rate constant are set out below. Time (t) is measured from the taking of the first sample, and <u>a</u> is taken as the first titre.

Run 1

t (min.)	a - x	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$	k_2 (min.$^{-1}$mole.$^{-1}$l.)
0	6.60	1.000		
65	6.03	1.0945	0.0393	0.040
120	5.56	1.187	0.0745	0.041
167	5.10	1.294	0.1120	0.045
217	4.88	1.352	0.1309	0.040
273	4.30	1.535	0.1860	0.046

Run 2

t (min.)	a - x (ml.)	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$	k_2 (min.$^{-1}$mole.$^{-1}$l.)
0	6.71	1.000		
56	6.17	1.0875	0.0365	0.044
111	5.70	1.177	0.0708	0.043
157	5.41	1.240	0.0934	0.040
208	5.07	1.323	0.1216	0.039
264	4.46	1.504	0.1772	0.045

The mean value for k_2 in each run is 0.042.

(c) 4-bromobutene runs

This olefin was considerably less water-soluble than allyl bromide. 150 ml. of a 0.00495 M solution were taken and 10 ml. iodine solution (restandardised at 0.0473 M) added. Since the olefin is now no longer in great excess over the iodine, we use the rate expression

$$k_2 = \frac{2.303}{t(a-b)} \quad \log \quad \frac{b(a-x)}{a(b-x)}$$

where a = initial concentration of olefin

b = initial concentration of iodine

(a-x) and (b-x) are the concentrations of olefin and iodine respectively at time t minutes.

Now b = 0.002956, or $11.83 \times 2.5 \times 10^{-4}$, i.e. 10 ml. of the initial reactant solution would give a titre of 11.83 ml. against 0.01 N thiosulphate. Similarly, a = 0.004640 = $18.56 \times 2.5 \times 10^{-4}$. In the following tables b - x is written as the titre and a - x = b - x + (18.56 - 11.83). The rate expression reduces to

$$k = \frac{1368}{t} \quad \log \quad 0.6374 \quad \frac{a - x}{b - x}$$

Run 1

t (min)	b - x	a - x	$\log \frac{b(a - x)}{a(b - x)}$	k_2 (min.$^{-1}$mole.$^{-1}$l.)
0	11.83 (calc.)			
50	10.16	16.89	0.0248	0.679
75	9.41	16.14	0.0386	0.704
85	9.22	15.95	0.0426	0.686
120	8.37	15.10	0.0607	0.692
140	8.11	14.84	0.0667	0.652
170	7.45	14.18	0.0839	0.675
190	7.32	14.05	0.0875	0.704
210	6.80	13.53	0.1031	0.671
260	6.16	12.89	0.1252	0.659
320	5.60	12.33	0.1473	0.630

The mean value for k_2 is 0.675

Run 2

t (min.)	b - x	a - x	$\log \frac{b(a - x)}{a(b - x)}$	k_2 (min.$^{-1}$mole.$^{-1}$l.)
0	11.83 (calc.)	18.56		
50	10.30	17.03	0.0228	0.624
76	9.39	16.12	0.0390	0.702
86	9.19	15.92	0.0430	0.684
101	8.84	15.57	0.0500	0.677

Run 2 cont.

t (min.)	$b - x$	$a - x$	$\log \frac{b(a-x)}{a(b-x)}$	k_2 (min.$^{-1}$mole.$^{-1}$l.)
120	8.38	15.11	0.0604	0.689
150	7.56	14.29	0.0810	0.739
170	7.42	14.15	0.0849	0.683
191	7.10	13.83	0.0941	0.674
240	6.38	13.11	0.1173	0.669
300	5.50	12.23	0.1517	0.692

Mean value is 0.683 for Run 2. The rate constant for bromobutene is therefore found to be 0.679 min.$^{-1}$mole.$^{-1}$ l.

(d) 5-bromopentene runs

150 ml. of 0.002225 M olefin solution was taken, and 10 ml. of stock iodine solution (0.0473 M) added. ∴ a = initial concentration of iodine = .002956 (= $11.82 \times 2.5 \times 10^{-4}$), and b = initial olefin concentration = 0.002086 (=$8.34 \times 2.5 \times 10^{-4}$), The rate equation thus reduces to

$$k = \frac{2647}{t} \log 0.7057 \frac{a - x}{b - x}$$

Run 1

t (min.)	a - x	b - x	log 0.7051 $\frac{a-x}{b-x}$	k_2 (min.$^{-1}$mole.$^{-1}$l.)
0	11.82 (calc.)	8.34		
7	11.25	7.77	0.0095	3.59
15	10.81	7.33	0.0174	3.07
27	9.85	6.37	0.0378	3.71
31	9.73	6.25	0.0411	3.51
37	9.52	6.04	0.0461	3.30
45	9.22	5.74	0.0543	3.20
55	8.69	5.21	0.0708	3.41
60	8.53	5.05	0.0762	3.36
75	8.16	4.68	0.0902	3.18
90	7.82	4.34	0.1045	3.07
110	7.46	3.98	0.1213	2.92
132	7.05	3.57	0.1442	2.89
161	6.75	3.27	0.1634	2.69

Run 2

t (min.)	a - x	b - x	log $\frac{b(a-x)}{a(b-x)}$	k_2 (min.$^{-1}$mole.$^{-1}$l.)
0	11.82 (calc.)			
20	10.28	6.80	0.0281	3.72
30	9.70	6.22	0.0414	3.65
40	9.15	5.67	0.0566	3.75

Run 2 cont.

t (min.)	$a - x$	$b - x$	$\log \frac{b(a-x)}{a(b-x)}$	k_2 ($\text{min.}^{-1}\text{mole.}^{-1}\text{l.}$)
50	8.84	5.36	0.0660	3.49
63	8.49	5.01	0.0777	3.26
75	8.15	4.67	0.0902	3.18
92	7.75	4.27	0.1075	3.09

The value for k_2 obtained from Run 1 is 3.22, and from Run 2, 3.45. The rate constant for 5-bromopentene is thus 3.34 $\text{mole.}^{-1}\text{l.}\ \text{min.}^{-1}$

(e) 6-bromohexene

This olefin was very sparingly soluble in water. 250 ml. of a 0.0003525 M solution were taken, and 5 ml. of iodine solution. In order to make up the iodide concentration, 12 ml. of a 0.1 N solution of potassium iodide was also added. 20 ml. samples were taken and titrated against 0.002 N sodium thiosulphate.

The titre at time zero was this time estimated by extrapolation of the titre v. time curve, and was 17.52 for Run 1. ∴ $a = 17.52 \times 5 \times 10^{-5} = 0.0008760$. b = initial olefin concentration = 0.0002885 ($= 11.75 \times 5 \times 10^{-5}$). Thus we have for the rate equation:

$$k = \frac{7982}{t} \log 0.6707 \frac{a - x}{b - x}$$

Run 1

t (min.)	a - x	b - x	$\log 0.6707 \frac{a - x}{b - x}$	k_2 ($min.^{-1} mole.^{-1} l.$)
0	17.52 est.	11.75		
30	16.78	11.01	0.0095	2.53
52	16.30	10.53	0.0162	2.49
75	15.93	10.16	0.0220	2.34
100	15.55	9.78	0.0277	2.21
140	14.85	9.08	0.0402	2.29
170	14.34	8.57	0.0500	2.35
213	14.01	8.24	0.0569	2.13
246	13.67	7.90	0.0645	2.09
274	13.55	7.78	0.0674	1.96

Mean value for k_2 from Run 1, 2.27.

For Run 2, by extrapolation $a = 17.46 \times 5 \times 10^{-5} = 0.0008730$. b = initial olefin concentration = 0.0005875 (= $11.75 \times 5 \times 10^{-5}$). The rate equation from which the rate constant is calculated is then

$$k = \frac{8067}{t} \log 0.6730 \frac{a - x}{b - x}$$

Run 2

t (min.)	a - x	b - x	$\log 0.673 \frac{a - x}{b - x}$	k_2 (min.$^{-1}$mole.$^{-1}$l.)
0	17.46 est.	11.75		
1	17.37	11.66	0.0013	10.50
25	16.93	11.22	0.0069	2.23
52	16.30	10.59	0.0154	2.39
70	15.81	10.10	0.0224	2.58
100	15.52	9.81	0.0273	2.20
140	14.77	9.06	0.0402	2.32
180	14.38	8.67	0.0480	2.15
210	13.89	8.18	0.0581	2.23
240	13.66	7.95	0.0629	2.11
270	13.41	7.70	0.0689	2.06

Mean value of k (excluding first reading) is thus 2.25. Therefore the mean rate constant for the two runs on bromohexene is 2.26 min.$^{-1}$mole.$^{-1}$l.

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