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THE MECHANISM OF HALOGENATION OF ALKENES WITH A QUATERNARY CARBON ATOM AT THE DOUBLE BOND

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I. INTRODUCTION

Millions of tons of various halogen derivatives of hydrocarbons are produced every year over the whole world and used in many branches of industry, agriculture, and everyday life [1].

This review deals with information on the mechanism of the very interesting reactions that occur in the halogenation of unsaturated hydrocarbons with a quaternary carbon atom at the double bond (with 2-methylpropene as a particular example). Up to now there have been different views on the mechanism of these reactions, and we kept this in mind in compiling the review.

It seemed that a critical analysis of the available publications together with a presentation of experimental results obtained by the authors of the review would bring a certain amount of clarity to this problem.

II. EARLY VIEWS ON THE MECHANISM OF ANOMALOUS CHLORINATION

In 1884 Sheshukov found that when chlorine acts on 2-methylpropene, instead of the expected saturated dichloro-derivatives, the main products of the reaction were monochlorides of the allyl and vinyl types [2].

Later L'vov and his students showed [3-8] that trimethylethylene [2-methylbut-2-ene], tetramethylethylene [2,3-dimethylbut-2-ene], and unsymmetrical ethylmethylethylene [pent-2-ene] also react with chlorine in an unusual manner. Subsequently, reactions of this type, which were termed anomalous, were the object of thorough study.

A number of schemes were proposed to explain the formation of allyl and vinyl monochlorides, and also saturated dichlorides, when alkenes are chlorinated.

L'vov and coworkers considered that chlorination reactions of unsaturated hydrocarbons proceed through two successive steps [9-11]:

$$C_nH_{2n} + Cl_2 \rightarrow C_nH_{2n}Cl_2;$$
$$C_nH_{2n}Cl_2 \rightarrow C_nH_{2n-1}Cl + HCl.$$

It was supposed that an unstable dichloride is first formed, which decomposes into hydrogen chloride and an unsaturated monochloride with displacement of the double bond.

This view has been shown to be untenable by thermodynamic [12] and kinetic [13] results on the decomposition of dichlorides, and also by a comparison of the results of dehydrochlorination of saturated dichlorides with unbranched and branched hydrocarbon skeletons.

It is well known that the low-temperature chlorination of ethylene leads to the formation of dichloroethane, and only an insignificant amount of vinyl chloride is obtained as a by-product [14-16]. Under comparable conditions the reaction of chlorine with 2-methylpropene gives mainly unsaturated monochlorides, although the dichlorides of both alkenes are about equally stable.

As one of us has shown [12], the dehydrochlorination of 1,2-dichloroethane with a conversion of 80% is achieved at 400° when the reaction is initiated with molecular chlorine (1%). In the absence of initiators, the analogous conversion of 1,2-dichloroethane into vinyl chloride requires a temperature of 480–500°. [17] According to Striegler [18], 1,2-dichloro-2-methylpropane is also dehydrochlorinated at 500° with 77.5% conversion into 2-methylallyl chloride and dimethylvinyl chloride, which are present in the reaction mixture in the constant ratio of 75 : 25. Moreover, Tishchenko [19] checked the doubtful results of Pauly and Lieck [20], who only obtained an addition product at the carbon–carbon double bond by the action of chlorine on mesityl oxide, and found that when one mole of chlorine acts on two moles of 2-methylpent-2-en-4-one, 60–70% of 3-chloro-2-methylpent-1-en-4-one is obtained. The 2,3-dichloro-2-methylpentan-4-one obtained together with the unsaturated monochloride in this reaction decomposes by the Wagner–Saytzeff rule with liberation of hydrogen chloride to form a mixture of 3-chloro-2-methylpent-1-en-4-one and 3-chloro-2-methylpent-2-en-4-one.

The scheme proposed by Ostromyslenskii [21] for the chlorination of alkenes with a quaternary carbon atom at the double bond has not brought clarity into this field and has the same disadvantages as L'vov's scheme. By the action of chlorine on 2-methylbut-2-ene, the author obtained almost equal amounts of t-pentyl chloride and the unsaturated chloromethylbutene, and explained this by the elimination of a molecule of hydrogen chloride from the saturated dichloride produced. The liberated hydrogen chloride then combines with 2-methylbut-2-ene to give a saturated monochloride, that is, it is assumed that there is an unusual transfer of the elements of hydrogen chloride from the dichloride molecule to the ethylene bond of the initial alkene:

$$C_5H_{10} + Cl_2 \rightarrow C_5H_{10}Cl_2;$$
$$C_5H_{10}Cl_2 + C_5H_{10} \rightarrow C_5H_9Cl + C_5H_{11}Cl.$$

III. HOMOLYTIC MECHANISM OF CHLORINATION

For a long time due attention was not given in world literature to the work of Russian chemists mentioned above, and it was only in the 40's that these investigations

were continued. Deanesly [22] found that the addition of chlorine to alkenes is initiated by the reaction in which hydrogen is replaced by chlorine in alkanes present at the same time. Since that time, American workers have continued the study of the chlorination of alkenes with the object of preparing unsaturated chloro-derivatives [23-27].

Solodar' and Markin [28] have analysed the work of this school (see also Refs. 29 and 30). Furthermore, Smolyan and coworkers [31] have reviewed the mechanism of substituting chlorination, dealing with examples of the halogenation of saturated hydrocarbons under different conditions (initiated, photochemical, thermal, etc.).

American workers who studied the high-temperature and low-temperature chlorination of alkenes used a radical scheme for chlorination by substitution. Thus, Burgin and coworkers [32] proposed a scheme for the chlorination of 2-methylpropene at low temperatures according to which 2-methylallyl chloride is formed by the migration of a hydrogen atom from one of the methyl groups. The formation of unsaturated monochlorides in the non-photochemical chlorination of ethylene [15,16,33,34] at room temperature, and of pent-2-ene [35] in carbon tetrachloride solution was also explained by the direct replacement of hydrogen. Stewart and Weidenbaum attempted to associate a three-atom chlorine molecule with the formation of unsaturated monohalo-derivatives [36]. They suggested that in chlorination, a chlorine radical formed by thermal chain generation reacts by two competing routes.

$$Cl^{\cdot} + Cl_2 \rightarrow Cl_3,$$
$$\text{or } Cl^{\cdot} + C_2H_4 \rightarrow C_2H_4Cl.$$

It was assumed that the active three-atom chlorine molecule reacts preferentially by the addition route.

Groll and Hearne [24], who studied the reaction of alkenes with chlorine at different temperatures, showed that there are certain critical temperatures above which monochlorides are formed preferentially:

	°C
2-Methylpropene	< — 40
Pent-2-ene	125 — 200
But-2-ene	150 — 225
Propene	200 — 350
Ethylene	250 — 350

This temperature "threshold" was found to be lowest for hydrocarbons with a quaternary carbon atom at the double bond. A "threshold" was not established for 2-methylpropene, and this caused the authors to have doubts about the existence of a critical temperature for this hydrocarbon. Only recently, Lishnevskii and Sergeev succeeded in obtaining the addition product (1,2-dichloro-2-methylpropane) in 87% yield by the reaction of frozen layers of 2-methylpropene with chlorine [37]. It was also previously reported [38] that when chlorine is passed through a mixture of pentenes cooled to -17°, the reaction proceeds without the formation of hydrogen chloride, but a slight increase in temperature promoted elimination of the latter. The proportions of the reagents, as well as the temperature, affect the direction of the reaction. A deficiency of chlorine in the reaction zone increases the yield of unsaturated monochlorides [27]. For example, in the chlorination of butenes at 380–390°, the optimal ratio of alkene to chlorine is 3.5 : 1, [39] and for 2-methylpropene the ratio is 1.5–2.0 : 1. [18] The mechanism of substituting chlorination proposed by American workers cannot explain why unsaturated monochlorides of the allyl type are formed and why chlorine does not replace hydrogen in all possible positions.

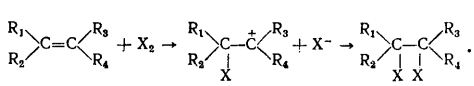
The active state postulated by Hass [40] for hydrogen atoms linked with carbon atoms in the α-position to the double bond also does not explain these contradictions. Indeed, in substituting chlorination, the probability of replacement of hydrogen by chlorine is the same for any position [41-43].

The formation of unsaturated monochloro-derivatives in high-temperature halogenation may occur partly by L'vov's scheme. Thus, a study of the chlorination of ethylene in a reactor with a moving heat carrier at 400–500° showed that vinyl chloride is partly formed through 1,2-dichloroethane with subsequent dehydrochlorination [44]. Moreover, as Reeve and coworkers have shown [45,46], in the gas-phase chlorination of 2-methylpropene containing the tracer carbon isotope ^{14}C (2-methyl-[1-^{14}C]prop-1-ene) at 0°, it is the extreme carbon atom linked to the double bond that is chlorinated, and not the methyl groups. The formation of unsaturated monochloro-derivatives in the low-temperature chlorination of alkenes is accompanied by the displacement of the double bond; according to Azinger, this indicates a heterolytic halogenation process at low temperatures [47]. On the other hand, it is highly probable that the high-temperature chlorination of alkenes in the absence of a thin film [48] proceeds by a homolytic mechanism [49,50]. A proof of this is the reduction of the temperature of gas-phase chlorination in the presence of additives that promote the formation of free radicals [25]. Semenov [51], who examined two competing radical reactions in the chlorination of ethylene — substitution and addition of chlorine with reference to energy factors — established a relation between the rate of substitution and the temperature of the process.

It should be mentioned that the main defect in the interpretation by American workers of the mechanism of chlorination of alkenes with a quaternary atom at the double bond is the unfounded extension of the principles of high-temperature and initiated halogenation to low-temperature chlorination under non-photochemical conditions.

IV. HETEROLYTIC MECHANISM OF HALOGENATION

The action of chlorine on alkenes with a quaternary carbon atom at the double bond is dealt with in greatest detail in the papers of Tishchenko and coworkers [52-56]. A heterolytic mechanism proposed for the halogenation of straight-chain alkenes was used to interpret the experimental results. Francis [57] studied the halogenation of ethylene in dilute aqueous solutions of various salts and observed the formation of mixed addition compounds. The reaction of bromine with ethylene in solutions of sodium chloride or nitrate gives 2-bromo-1-chloroethane or 2-bromoethyl nitrate respectively as the main product; with iodine in sodium chloride solution the main product is 1-chloro-2-iodoethane. The author explained the production of mixed products by the intermediate formation of a carbonium ion of the type $[R\text{–}\overset{|}{C}Br\text{–}\overset{|}{C}R]^{+}$ in the bromination. Ingold [58] and Robinson [59] proposed the following scheme for the mechanism of halogenation of alkenes:



The authors consider that this reaction is electrophilic; the molecule taking part in the addition is first polarised,

and this is followed by attack on the substrate by the positive halide ion, which leads to the formation of an organic cation. The halide anion reacts with the latter to give the final addition product. Ingold used the addition of iodine monochloride to propene to illustrate this scheme[60]. The distribution of electron density in the ICl molecule corresponds[61] to the formula I^+-Cl^-; on the other hand, the electron density of the π bond of propene is displaced because of the positive inductive effect of the CH_3-group[62] (from a calculation of the limiting electron density for divinyl and isoprene molecules carried out by Hayashi), which permits the scheme for this reaction to be represented as follows:

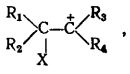
$$H_3C\rightarrow CH=\overset{\delta-}{C}H_2 + Cl^- - I^+ \longrightarrow CH_3-\overset{+}{C}H-CH_2I + Cl^- \longrightarrow CH_3-CHCl-CH_2I.$$

This mechanism is similar to that proposed by Nenitescu for the iodination of alkenes[63].

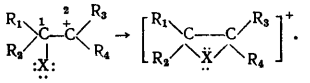
Other workers have also pointed out that an organic cation is formed in the first stage of the reaction of molecular halogens with the ethylene bond[64,65].

Moreover, the existence of various carbonium ions is confirmed by numerous investigations in which NMR spectra[66], ultraviolet spectra[67-74], cryoscopy[75-77], and chemical methods[76,78-80] have been used.

However, the question of the structure of the carbonium ion is still debatable[81]. Thus, it has been noted that the structure of the organic ion proposed by Ingold and Robinson is not in accord with the stereospecificity of the addition[82]. In the hypothetical ion



free rotation is possible round the single C–C bond, which should lead to the formation of *cis*- and *trans*-adducts in equal amounts. Nevertheless, *trans*-products are mainly formed in a number of instances[83]. Since a halogen atom with an unshared pair of electrons in *p*-orbitals is close to the positively charged carbon atom in the intermediate carbonium ion, Roberts and Kimball have suggested that interaction leading to the formation of a bond is possible between the centre of the carbonium ion and halogen atoms[84]. The structure of the intermediate carbonium ion would then be close to a three-membered ring:



The preparation of stable cyclic onium compounds in the aromatic series has confirmed this hypothesis[85].

An analysis of published results made by Bethell and Gold[81] is also in favour of the cyclic cation of Roberts and Kimball.

We shall see below that this hypothesis provides a fairly good interpretation of addition to a multiple bond, although it is subject to the criticism that considerable bond strain is required for the formation of a three-membered ring[86].

However, the formation of *cis*- and *trans*-adducts in additions, at least to the ethylene bond, cannot be unambiguously related to the structure of the intermediate complex.

It is well known that the internal rotation of groups of molecules relative to one another has several potential energy minima for a complete rotation round a single bond. It has been shown by various physical methods that for molecules of the general formulae XH_2C-CH_2X and XH_2C-CH_2Y (X and Y = Cl, Br, I, CH_3, OH, etc.) the *trans*-configuration is the most stable[87-89].

Less stable forms, which have been found together with the *trans*-isomer in a study of the liquid and gaseous states of 1,2-dihaloethanes, are gauche conformations, obtained from the *trans*-form by rotation of one of the CH_2X-groups of the molecule through an angle of $\pm 120°$.[90,91]

The *cis*-form of the rotational isomers is the least stable of known conformations[91]. The stability of *trans*-isomers may be the main reason for the preferential formation of *trans*-adducts in the addition of halogens to alkenes.

Later a new interpretation was put forward for the structure of the intermediate addition complex, which Dewar termed a π complex[92,93]. With both aromatic compounds[94-96] and unsaturated aliphatic compounds[97], the formation of complexes by halogen molecules, which are electron donors, is due to the presence of low antibonding orbitals in iodine, bromine, and chlorine molecules[98] and their considerable polarisability[96]. Freed and Sancier[97] studied the spectra of frozen solutions of iodine in alkenes and their solutions in propane at temperatures from -196° to -43°; the authors assumed that cooling to a low temperature would reduce the rate of addition of halogen to alkenes and increase the concentration of pre-reaction complexes. This assumption was recently confirmed by a thermographic investigation of the propene–bromine system, in which it was shown by the use of low temperatures and special freezing-out procedures that the complex-formation and final-product stages could be separated, and the intermediate complex could be accumulated[99]. In propane, iodine gives only a visible band at 520 nm, with no bands right down to 210 nm. The addition of propene displaces the visible band and produces an intense band with a maximum at 280 nm, similar to that observed in aromatic complexes.

Analysis of published data[100,101] indicates that the new ultraviolet absorption band is due to a complex formed by donor–acceptor interaction between halogen molecules and unsaturated compounds, which is also called a charge-transfer complex[101].

The heats of formation of complexes of iodine with aromatic compounds are estimated at 1 kcal $mole^{-1}$.[102] For alkenes this value is somewhat less than 1 kcal $mole^{-1}$, with the exception of the 2-methylpropene complex, the heat of formation of which is somewhat higher[100].

In spite of such low intermolecular bond energies in associations of halogens with unsaturated hydrocarbons, a review of published information shows that these are not associations of a purely cohesion type. This is indicated by the results of a thermographic investigation of the propene–bromine system[99], evaluation of which showed that the heat of formation of the propene–bromine complex is not less than 5 kcal $mole^{-1}$.

A study[96] of the infrared absorption spectra of the cyclohexene–iodine system showed a reduction in the vibrational frequency of the C=C bond from 1650 to 1524 cm^{-1}, which was considered to be due to the formation of a cyclohexene–iodine π complex.

A reduction of the vibrational frequency of chlorine dissolved in benzene and its derivatives has also been observed; the reduction in frequency increases with increasing electron density in the ring.

According to Mulliken[98,103], the most probable structure for the complex is that in which the halogen molecule is symmetrically arranged in a plane parallel to the benzene ring, because this ensures maximum overlap of selected orbitals[98,103].

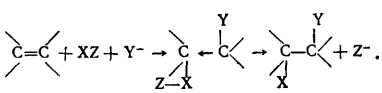
If the molecule of alkene or aromatic compound is unsymmetrical, then the electron density of the bond between the donor and acceptor in the π complex does not have a plane of symmetry perpendicular to the C–C bond. The positively charged halogen atom in such a π complex is situated closest to the carbon atom with the highest electron density[104].

Terenin[100], developing the intermolecular-complex hypothesis, concluded that in the formation of the complex its components are partially ionised, for example, $C_6^{+\delta}H_6.I_2^{-\delta}$, that is, part of the charge is transferred to the iodine molecule, which becomes negatively charged.

Later it was shown[101] that the degree of electron transfer from the donor to the acceptor may vary from zero to complete transfer; in the latter instance, neutral molecules are converted into ion-radicals.

According to Reutov[104], in the course of chemical reaction the π complex can assume the structure of Roberts and Kimball's carbonium ion[84].

Shilov and coworkers[86,105-110] showed that the π complex hypothesis is in good agreement with the kinetics of heterolytic addition reactions; in particular, it explains the emergence of termolecular kinetic equations. If the reaction is of the ionic type, a termolecular addition mechanism operates:



The molecule XZ behaves as an electron acceptor and Y^- behaves as a donor.

Shilov called this a termolecular acceptor–donor mechanism[106]. In the general case a termolecular heterolytic mechanism leads to a termolecular kinetic equation

$$v = k[A][XZ][Y^-],$$

where [A] is the concentration of unsaturated compound. This form of kinetic equation has been established for many addition reactions[111-113].

It is assumed that in electrophilic addition the unsaturated molecule A forms a complex with the electron acceptor XZ in the equilibrium state (constant R), which then reacts with the donor Y^- (nucleophilic reagent).

The reaction rate is then given by the equation

$$v = RC_{AXZ}C_Y = RkC_AC_{XZ}C_Y.$$

A number of reactions are also known in which halogenation of unsaturated hydrocarbons in solvents with a certain polarity, particularly acetic acid, is a second-order reaction[114-118]:

$$v = k[A][Hal_2].$$

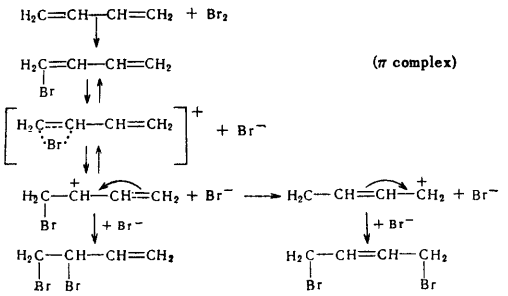
However, the addition of bromine to alkenes in solvents that are no more polar than acetic acid, or in acetic acid over a certain concentration range (0.025 M), is third-order[119-122]:

$$v = k[A][Hal_2]^2.$$

Dilution, increase in temperature, or addition of water reduces the order of reaction from third to second.

The results of these kinetic investigations show that the agent attacking the double bond is a halogen molecule, which acts on alkenes as an electrophilic reagent[123].

Petrov adduces sufficiently convincing facts in favour of the two-stage mechanism for electrophilic 1,2- and 1,4--addition to 1,3-diene compounds[124]. He considers the π complex to be the first combination with the diene; this complex is then converted into a carbonium ion:



The idea of association of the halogen with the π bond of the alkene, and of the charge-transfer complex[100,101], and the results of a thermographic study[99] are in agreement with this scheme.

In explaining the mechanism of chlorination of alkenes with a quaternary carbon atom at the double bond, Tishchenko[52-56] considered that the process is initiated by the addition of the positive end of the halogen molecule, as in all electrophilic additions to the carbon atom with the maximal electron density. The polarisation of the multiple bond in asymmetrical disubstituted and trisubstituted ethylenes is achieved by the positive inductive effect of alkyl groups[62,125].

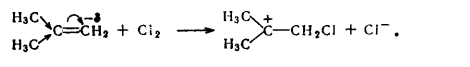
Because of the displacement of four electron pairs to the double bond, symmetrical tetrasubstituted ethylenes have a large inductomeric effect, which is brought into play under the influence of approaching ions or polar molecules at the moment of reaction. This statement is confirmed by the increase in the relative rates of bromine addition to ethylene and its methylated derivatives[126]:

Alkene	$CH_2=CH_2$	$CH_3CH=CH_2$	$(CH_3)_2C=CH_2$	$C(CH_3)_2=CHCH_3$	$(CH_3)_2C=C(CH_3)_2$.
Rate of addition	1.0	2.0	5.5	10.4	14.0

The ionisation potentials decrease in parallel[127,128]:

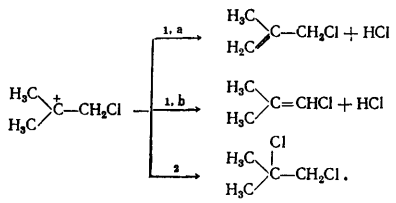
Alkene	$CH_2=CH_2$	$CH_3CH=CH_2$	$(CH_3)_2C=CH_2$	$CH_3CH=C(CH_3)_2$	$(CH_3)_2C=C(CH_3)_2$.
Ionisation potential	10.62	9.84	9.35	8.85	8.45

For 2-methylpropene, the first stage of chlorination may be represented by the following scheme:



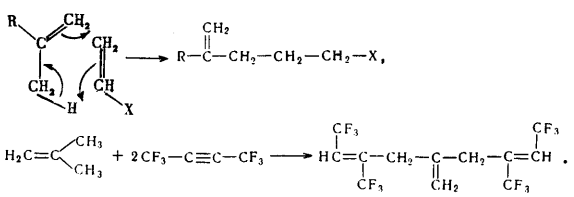
The intermediate carbonium ion is then stabilised in two main ways: (1) by elimination of a proton from adjacent alkyl groups with the formation of unsaturated monochlorides and the separation of a molecule of hydrogen chloride;

(2) by addition of a negative chloride ion to the positive centre of the carbonium ion with the formation of a saturated dichloride



Stabilisation of the carbonium ion in the first way is energetically less favoured by about 8 kcal mole^{-1}.[30] However, when there is a quaternary carbon atom at the double bond, this is the predominating route; according to Tishchenko, the approach of the Cl^- ion to the centre of the carbonium ion is sterically hindered, and this reduces the probability of stabilisation of the organic ion by the second route. In addition to an unsaturated monochloride of the allyl type, the reaction mixture always contains a small quantity of monochloride of the vinyl type. Tishchenko ascribes the preferential formation of the former to the high "proton-likeness" of the primary hydrogen of the methyl group.

This hypothesis was later confirmed experimentally by Morton and coworkers[129], who proposed a method for determining the relative acidity of unsaturated hydrocarbons and of the most "proton-like" hydrogen atom in the alkene. Moreover, the mobility of the allyl hydrogen has been confirmed by reactions in which monoalkenes are added to various activated unsaturated compounds[130-133].



A study of the microwave spectrum of 2-methylpropene[134] showed that the ordinary C–C bond in the latter is appreciably shortened in comparison with saturated compounds, which also indicates the acidity of the allyl hydrogen.

As a result of thorough investigations, Tishchenko[52-56] established that the presence of a quaternary carbon atom and polarisation of the double bond by substituents are necessary conditions for the anomalous chlorination of alkenes at low temperatures; using the reaction of phosphorus(V) chloride with ketones as an example, he confirmed these conclusions[53].

With the object of eliminating side-reactions due to the liberated hydrogen chloride (addition to the initial and final products[56]), a method of chlorination in the presence of sodium hydrogen carbonate, which readily reacts with hydrogen chloride, has been proposed[54,56]. Aschan's hypothesis[135] that sodium hydrogen carbonate catalytically promotes the elimination of hydrogen chloride from the initial dichloride has been disproved[56]. For example, 2,3-dichloro-2-methylbutane does not react with the hydrogen carbonate even at 135°. The mechanism of low-temperature chlorination proposed by Tishchenko was later accepted also by advocates of "substituting" chlorination[136]. The work of Tishchenko and coworkers on the chlorination of terpenes[30,137-140], many of which contain a quaternary carbon atom at a double bond, provided convincing proof of the views he developed on the mechanism of anomalous chlorination of alkenes.

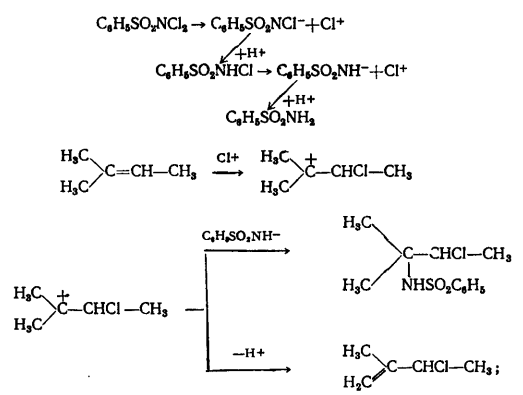
Other papers also show that schemes based on the heterolytic mechanism are widely applicable[141].

Some workers have expressed doubts about the Ingold–Tishchenko mechanism for the chlorination of alkenes[142,143], at least as applied to the chlorination of alkenes in non-polar media, where it was considered there were no grounds for assuming the existence of carbonium ions and ions of the halogenating agent.

The results of mass-spectrometric determinations of ionisation potentials of various compounds in solutions and gases show that this criticism is not valid[144]. Moreover, the heterolytic mechanism does not require that the addend should be ionised before the reaction[145].

Tishchenko's hypothesis that there is steric hindrance to the approach of the chloride anion to the centre of the carbonium ion has been denied without proof by Esafov[142]. Results of later investigations in this field[37] have shown that this criticism is not valid; the rapid addition of chlorine to alkenes (ethylene, propene, 2-methylpropene, styrene, and cyclohexene) at low temperatures in a condensed phase was explained by a reduction in steric hindrance.

Impressive arguments in favour of the steric-hindrance hypothesis in anomalous halogenation reactions have also been put forward by Isagulyants and Balashova[146-148], who studied the chlorination of alkenes with a quaternary carbon atom at the double bond by molecular chlorine and *NN*-dichlorobenzenesulphonamide. They showed that the yield of the anomalous chlorination product depends on the size of the halogenating-agent anion. Thus, in the chlorination of 2-methylbut-2-ene with *NN*-dichlorobenzenesulphonamide[147], the mechanism may be represented as follows:

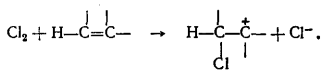


the main reaction product is the unsaturated 2-chloro-3-methylbut-2-ene. Because of the large bulk of the anion of the chloroamide compared with the chloride anion, only 1% of the 2-methylbut-2-ene reacts to form an addition product with the chloroamide, that is, 10–15 times less than with molecular chlorine[42]. Under the same conditions, the action of *NN*-dichlorobenzenesulphonamide on normal pentenes leads mainly to addition products[147].

The results of the chlorination of 3-chloro-2-methylbut-1-ene with *NN*-dichlorobenzenesulphonamide in a mixture

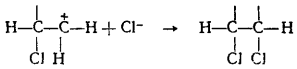
of methyl and ethyl alcohols are also satisfactorily interpreted by the steric-hindrance hypothesis [147].

Taft [145] presents a somewhat different scheme for the heterolytic mechanism in the anomalous chlorination of alkenes. According to Taft, the first stage, which determines the reaction rate, is electrophilic attack on the alkene with the formation of a carbonium cation and a chloride anion as in the Ingold–Tishchenko scheme,

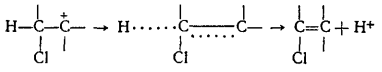


The intermediate carbonium ion reacts by two routes:

a. with the addition of a chloride anion



b. with elimination of a proton



The ratio of the amount of addition products to the amount of unsaturated monochlorides is determined by factors that affect the rates of addition and substitution. This ratio depends on the structure of the intermediate carbonium ion, and also on the reaction medium and the temperature.

Using published experimental results on the chlorination of various alkenes, Taft [145] established a relationship between the yield of unsaturated chloro-derivatives and the number of hydrogen atoms attached to carbon atoms in the α-position to the centre of the carbonium ion (Table 1).

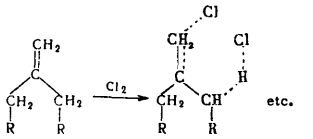
According to Taft, the dependence of the ratio of addition products to substitution products on the number of hydrogen atoms results from a hyperconjugation type of resonance [149,150]. The greater number of possible resonance structure in the chlorination of 2-methylpropene compared with ethylene means that the carbonium ion formed from 2-methylpropene may be more effectively transformed into a stable state than the ion obtained from ethylene. By analogy [151], this should reduce the ratio of the rates of addition and substitution, that is, at low temperatures the chlorination of 2-methylpropene leads to the formation of large amounts of unsaturated monochloride but ethylene mainly reacts to add on chlorine. This hypothesis of Taft on anomalous reactions is not confirmed by the general principles of electrophilic addition to alkenes.

Ingold [152], in analysing a communication of Robertson, concluded that in additions to alkenes the inductive effect of alkyl groups, and not the Baker–Nathan effect with participation of hydrogen, has the greatest influence on the reaction rate. Moreover, results have been published that do not generally favour the hyperconjugation effect [153–156].

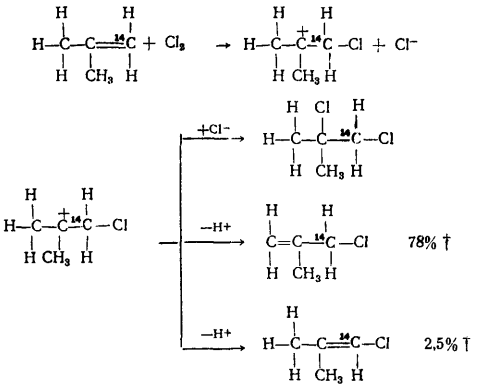
TABLE 1.

No. of hydrogen atoms	Substitution, %	Addition, %
2—3	0—35	60—100
4—5	10—60	40—90
6—7	70—85	10—30
8	93	7

In addition to the mechanisms given above for the chlorination of alkenes with a quaternary carbon atom at the double bond, synchronous cyclic and non-cyclic type mechanisms have been proposed, in which attack on the alkene molecule by a positively charged chlorine atom is accompanied simultaneously by reaction of a negatively charged chlorine atom with a protonated hydrogen atom [157,158]:



The papers of Reeve and coworkers mentioned above are of great interest for the elucidation of the mechanism of anomalous chlorination [45,46]. Their experimental results lead to a mechanism for the chlorination of 2-methylpropene similar to Tishchenko's mechanism:



The results of kinetic studies of the low-temperature chlorination of individual branched and straight-chain alkenes and their mixtures also indicate that these reactions are heterolytic [158–160].

Analysis of the kinetic results shows that substitution and addition reactions of chlorine with alkenes are parallel reactions of the same order and with the same common polar intermediate complex.

V. REACTION OF ALKENES CONTAINING A QUATERNARY CARBON ATOM WITH HYPOHALOGEN ACIDS

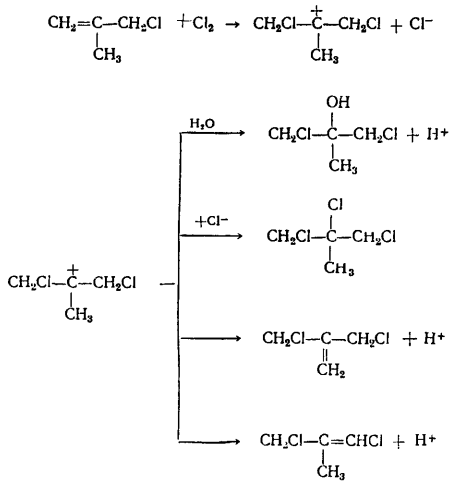
The addition of hypochlorous acid to unsaturated hydrocarbons was first studied by Markovnikov, who established the rule that bears his name [161]. Saytzeff [162], who studied the reaction of hypochlorous acid with butene, also found that the halogen adds to the carbon atom with the greatest number of hydrogen atoms, and the hydroxy-group to the carbon atom with the least number. On the other hand, Henry found that hypochlorous acid adds to propene and 2-methylpropene in the reverse manner [163]. Butlerov [164], who assumed that the product of the reaction of 2-methylpropene with hypochlorous acid was 2-chloro-2-methylpropan-1-ol, confirmed Henry's results, which were later shown to be erroneous.

Michael [165] repeated Henry's experiments and showed that the product of the reaction of hypochlorous acid with propene is 1-chloro-propan-2-ol, thus confirming the

† Yield based on chlorine.

validity of Markovnikov's rule. This conclusion was confirmed by Krasuskii [166,167], who showed that propene chlorhydrin contains ~ 68% of 1-chloropropen-2-ol, and 2-methylpropene chlorhydrin, not less than 78% of 1-chloro-2-methylpropan-2-ol. Quantitatively, these results differ somewhat from those reported by other workers for the addition of hypochlorous acid to propene [168] and 2-methylpropene [169-172].

Later papers are mainly devoted to a study of the mechanism of these reactions. Burgin and coworkers [136], who studied the action of chlorine water on 2-methylallyl chloride, explained the composition of the final products by the initial formation of a positively charged carbonium ion complex, which is then stabilised in several ways:



At 30° the yield of 1,3-dichloro-2-methylpropan-2-ol is 70%, and 10% of allyl and vinyl substitution products is formed. Other nucleophilic solvents may be used as the "active" medium instead of water. Thus, the action of chlorine [173] and bromine [174] on ethylene hydrocarbons in the presence of ethylene oxide leads mainly to the formation of $\beta\beta'$-dichloro- and $\beta\beta'$-dibromo-substituted ethers [173,174], Besides these ethers, other products are obtained which indicate that the mechanism of this reaction is in principle similar to the mechanism for the chlorination of alkenes in an aqueous medium.

By means of the reaction of aromatic compounds with hypobromous acid, it has been shown that a bromine cation participates in brominations in aqueous solutions [175-177]; the rate of these reactions is proportional to the concentration of hydronium ions [108].

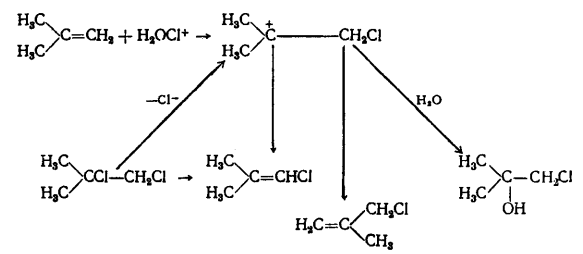
$$\frac{d[\mathrm{BrOH}]}{dt} = k[\mathrm{A}][\mathrm{BrOH}][\mathrm{H_3\overset{+}{O}}],$$

where [A] is the concentration of the organic compound. The concentration of the bromine cation is related to [BrOH] by the equation:

$$k_p[\mathrm{BrOH}][\mathrm{H_3O}] = [\mathrm{BrOH_2^+}].$$

The existence of a bromine cation was deduced from kinetic results obtained in the chlorination with hypochlorous acid of organic compounds [178,179]. Later, the experimental results on which the hypothesis of a chlorine cation is based were subjected to criticism [180].

Using an isotope dilution method at 45°, de la Mare and coworkers [181] separated 11.9% of 3-chloro-2-methylprop-1-ene and 0.4% of 1-chloro-2-methylprop-1-ene from the reaction products obtained by the action of hypochlorous acid on 2-methylpropene. A somewhat larger total of unsaturated monochloro-derivatives (16%) was obtained by the hydrolysis of 1,2-dichloro-2-methylpropane under comparable conditions. From these results the authors conclude that identical carbonium ions are formed as intermediates when hypochlorous acid acts on 2-methylpropene and in the hydrolysis of 1,2-dichloro-2-methylpropane:



on hydrolysis	6%	10%	84%
on addition	0.4%	12%	87.6%

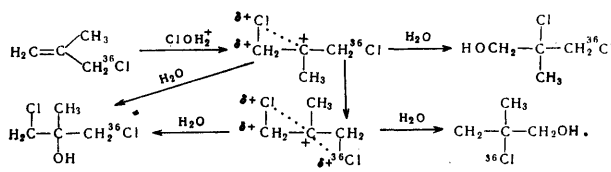
This hypothesis is in good agreement with the results of spectrographic [74,182] and cryoscopic studies [75] on solutions of tertiary alcohols and the corresponding alkenes in sulphuric acid. Thus, Gold and coworkers [74,75,183] showed that when $\alpha\alpha$-diphenylethylene is dissolved in sulphuric acid, a carbonium ion is formed identical with that obtained by similar treatment of 1,1-diphenylethanol:

$$(\mathrm{C_6H_5})_2\mathrm{C{=}CH_2} + \mathrm{H_2SO_4} \rightarrow (\mathrm{C_6H_5})_2\mathrm{CH_3C^+} + \mathrm{HSO_4^-},$$
$$(\mathrm{C_6H_5})_2\mathrm{CH_3COH} + 2\,\mathrm{H_2SO_4} \rightarrow (\mathrm{C_6H_5})_2\mathrm{CH_3C^+} + \mathrm{H_3O^+} + 2\,\mathrm{HSO_4^-}.$$

Later, the trimethylmethylium ion was obtained from 2-methylpropene and t-butyl alcohol by analogous methods [182]:

$$(\mathrm{CH_3})_2\mathrm{C{=}CH_2} \xrightarrow{+\mathrm{H^+}} (\mathrm{CH_3})_3\mathrm{C^+} \xleftarrow[(-\mathrm{H_2O})]{+\mathrm{H^+}} (\mathrm{CH_3})_3\mathrm{COH}.$$

The preferential formation of unsaturated chloro-derivatives of the allyl type in comparison with vinyl derivatives (30 : 1) by the action of hypochlorous acid is explained [184] by internal interaction between the centre of the carbonium ion and the chlorine atom, as described by Roberts and Kimball [84]. Ballinger and de la Mare [185] studied the addition of hypochlorous acid to 2-methylallyl chloride containing the labelled atom ^{36}Cl and confirmed the hypothesis that the centre of the carbonium ion interacts with the halogen on the adjacent carbon atom by the partial displacement of ^{36}Cl from position 3 to position 2:



A similar migration of the chlorine atom was also observed in the reaction of hypochlorous acid with allyl chloride [186]. However, in the chlorination of allyl alcohol with molecular chlorine, the assumed interaction of the hydroxyl group with the positively charged carbon atom was not accomplished by migration of the hydroxyl group

to the centre of the carbonium ion [187], although that such a migration is possible in principle has been shown by the rearrangement of 1-phenylallyl alcohol to 3-phenylallyl alcohol in a mixture of dioxan and water (60 : 40 vol.%) in the presence of perchloric acid at 0°. [188]

The observations of de la Mare and coworkers [189] are important in considering the reasons for the elimination of a proton from alkyl groups adjacent to the centre of the carbonium ion with the formation of anomalous products; these workers found that treatment of [3-^{36}Cl]-2,3-dichloroprop-1-ene with hypochlorous acid leads to the formation of substitution products (3.7% of *cis*- and 4.3% of *trans*-1,2,3-trichloropropene). These results are in agreement with an earlier statement [53] that anomalous products are formed in chlorination not only by alkenes with a quaternary carbon atom at the double bond, but also by unsaturated compounds in which only one of the carbon atoms at the double bond does not have a hydrogen atom.

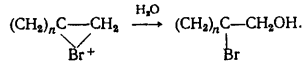
This analogy indicates the similarity between the mechanisms of chlorination and hypochlorination of alkenes, at least in the first stage when a carbonium ion is formed. This has been confirmed by other examples [47,191,192]. It is well known that normal alkenes react with chlorine at ordinary or slightly increased temperature to form only addition products. The action of hypochlorous acid on but-2-ene [190] and 2-methylpent-3-ene [191] also leads to addition at the double bond, but under similar conditions 2,4-dimethylpent-2-ene and diisobutylene give unsaturated monochlorides as the main products [191]. Umnova [191] explained the mechanism of the formation of substitution products in these reactions by L'vov's scheme, which includes initial additions of hypochlorous acid to the double bond followed by elimination of a molecule of water. We have dealt with the defects of this scheme in the section above on the chlorination of alkenes.

The action of hypobromous acid on acyclic unsaturated hydrocarbons leads to the formation of bromhydrins; the order of addition is mainly the same as that in hypochlorination. For example, the reaction of hypobromous acid with 2-methylpropene gave an addition product in 77% yield containing not less than 97% of 1-bromo-2-methylpropan-2-ol and 3% of the isomer, 2-bromo-2-methylpropan-1-ol [192,193].

A comparative study of the reaction of hypochlorous acid with allyl bromide and the reaction of hypobromous acid with allyl chloride [194] in a water–dioxan mixture showed that the solvent materially affects the composition of the products of the reaction, in which a halogen atom of the starting alkene migrates to the central carbon atom. The change in the composition of the reaction products can be explained fairly satisfactorily by a mechanism based on the formation of an intermediate carbonium ion.

Bodot and Jullien give an interesting theoretical explanation of orientation in the addition of electrophilic agents to alkenes [195]; using the method of Smith and coworkers [196], they calculated the relative stability of possible carbonium ions and showed, for example, that in the reaction of hypochlorous acid with 2-methylpropene the carbonium ion structure $(CH_3)_2\overset{+}{C}CH_2Cl$ is energetically more favoured than the structure $(CH_3)_2CClCH_2$.

However, in the hypohalogenation of cycloalkenes the order of addition is, as a rule, not so rigid as in the electrophilic addition of HOX to acyclic unsaturated compounds. Thus, in the hypobromination of methylenecycloalkenes the order of addition is reversed [192,193]. Traynham and Pascual [193] attempted to explain this orientation in the addition of hypobromous acid to methylenecycloalkenes by the formation of a bromonium ion with subsequent attack of a water molecule on the secondary carbon atom:



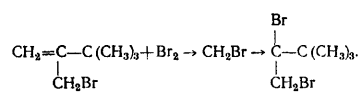
VI. REACTIONS OF ALKENES BRANCHED AT THE DOUBLE BOND WITH BROMINE AND INTERHALOGEN COMPOUNDS

The action of bromine, iodine, and interhalogen compounds on alkene compounds has mainly been studied with reference to normal compounds [113-122,197-202].

In a review [203], Dombrovskii lists the substitution reactions that occur in the halogenation, sulphonation, nitration, alkylation, acylation, and azo-coupling of both alkenes and aromatic compounds. In this review, the reactions of bromine and interhalogen compounds with unsaturated compounds having a quaternary carbon atom at the double bond are compared with the corresponding chlorination reactions.

As early as 1879, Butlerov observed the liberation of hydrogen bromide, and therefore the formation of substitution products, in the bromination of triisobutylene [204].

Hydrolysis of the products of the reaction of bromine with 2-methylbut-2-ene also showed the presence of unsaturated monobromides in the reaction mixture [205,206]. Later, Favorskii [207] established that the reaction mixture obtained by the bromination of isopentene contains t-pentyl bromide, with dibromo- and tribromo-derivatives of 2-methylbut-2-ene. With increase of bromination temperature, unsaturated bromo-derivatives of methylbutene were formed [208]. The dibromo- and tribromo-derivatives were the main products of the action of bromine on 2,3,3-trimethylbut-1-ene, when the reagents were cooled with an ice–salt mixture [207]. However, a mixture of saturated and unsaturated monobromides were separated from the low-boiling fractions. The formation of unsaturated monobromides was explained by L'vov's scheme for anomalous chlorination [9-11]. The formation of tribromo-derivatives was considered to be due to the reaction of bromine with the unsaturated monobromide which is partly formed:



It was also noted that *unsym*-dineopentylethylene [4,4-dimethyl-2-neopentylpent-1-ene] reacts with bromine with liberation of hydrogen bromide [209].

Esafov [210] observed considerable liberation of hydrogen bromide in the determination of the bromine numbers of di- and tri-isobutylene, and also of diene hydrocarbons with branching at the double bond. A thorough analysis of the bromination products of 2-methylpropene at 0° was first carried out by Pogorzhel'skii [211]. The main reaction product was 1,2-dibromo-2-methylpropane, that is, the addition product; t-butyl bromide and polybromo-derivatives of 2-methylpropene were also separated. Saponification of the fraction boiling below 100° failed to convert 0.3 g of bromo-derivatives (out of 4.4 g) into alcohols, and this

portion was assumed to consist of unsaturated monobromide. In later papers on the bromination of 2-methylpropene to obtain dibromo-derivatives, the formation of unsaturated monobromides is not mentioned[212,213]. However, since t-butyl bromide is formed, it may be assumed that the bromination of 2-methylpropene[210] is accompanied by the formation of 2-methylallyl bromide or dimethylvinyl bromide and hydrogen bromide. The latter further reacts with the starting 2-methylpropene.

The liberation of hydrogen bromide has also been noted in the bromination of 2-methylpropene in the presence of calcium halide, which catalyses additions to alkenes[214].

It was later shown[215] that bromination of an excess of liquid 2-methylpropene at -10°, either directly or in the presence of a non-polar solvent, is accompanied by the formation of up to 20% of allyl and vinyl substitution products. The yield of unsaturated monobromides falls to 5.5–6% if the experiment is carried out with stoichiometric quantities of the reagents.

If this reaction is carried out at a very low temperature (-154°), as in the chlorination of 2-methylpropene in a condensed phase[37], only addition products are formed[216].

In the gas-phase bromination of 2-methylpropene at 300–350° in an atmosphere of nitrogen, up to 50% of 2-methylallyl bromide and 20% of dimethylvinyl bromide are formed[18]; the remaining products are t-butyl bromide (7%) and polybromides (20%).[18] Under these conditions the reaction is probably of the free-radical type, and a sharp increase in the yield of 2-methylallyl bromide and dimethylvinyl bromide is probably due to replacement of hydrogen atoms according to Semenov[51]. It is well known, for example, that in the halogenation of alkenes with *N*-bromosuccinimide[217] and *N*-bromoacetamide[218,219], hydrogen in methyl and methylene groups is readily replaced by bromine. These reactions are accelerated by heat and by ultraviolet light[220], and also by the addition of peroxides[221]; the presence of peroxides promotes the formation of unsaturated monobromo-derivatives, while 4-t-butylpyrocatechol, an inhibitor of radical reactions, increases the yield of addition products.

Although the halogenation of alkenes by *N*-bromoacetamide is carried out in the presence of hydrobromic acid, like low-temperature bromination, the reaction is heterolytic, since here the double bond of the alkene is attacked by molecular bromine[219]:

$$AcNHBr + HBr \rightleftarrows AcNH_2Br^+ + Br^-;$$
$$AcNH_2Br^+ + Br^- \rightleftarrows AcNH_2 + Br_2.$$

Novikov and coworkers[222] examined published information on the halogenating properties of organic compounds containing positive halogen and concluded that *N*-bromosuccinimide can react with alkenes both by an ionic and by a homolytic mechanism.

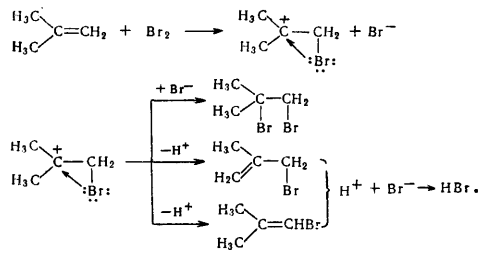
Tishchenko and Yarzhemskaya[223] studied the bromination of 2-methylbut-2-ene and 3-chloro-2-methylbut-2-ene at low temperatures in the presence of sodium hydrogen carbonate; they showed that, in contrast to chlorinations[41], only a small part of the bromine reacts to form unsaturated monobromides.

Comparison of published information on low-temperature chlorination[42,46] and bromination[215,223] of alkenes with branching at the double bond shows that while chlorination leads mainly to the formation of anomalous products, in bromination the predominating reaction is addition (Table 2).

TABLE 2.

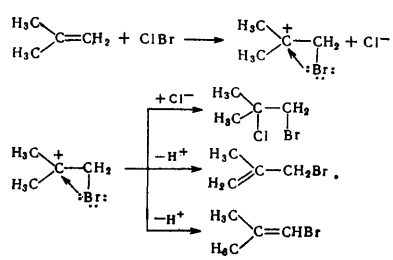
Alkene		Yield of anomalous products, %	Yield of normal products, %	References
$(H_3C)_2C{=}CH{-}CH_3$	chlorination	70—80	10—15	42
	bromination	15	85	223
$(H_3C)_2C{=}CCl{-}CH_3$	chlorination	80	10	42
	bromination	15	85	223
$(H_3C)_2C{=}CH_2$	chlorination	82.4	17.6	46
	bromination	20	60	215

The mechanism of the reaction of bromine with alkenes containing a quaternary carbon atom may be represented by the Ingold–Tishchenko scheme, a halogen atom reacting internally with a carbonium centre:



According to Temnikova[224], the composition of the reaction products of halogens with alkenes having a quaternary carbon atom is determined by the nature of the nucleophilic component of the halogenating agent. However, the results of low-temperature bromination and chlorobromination of liquid 2-methylpropene have shown that the nucleophilic properties of the halogen have no appreciable effect on the yield of anomalous chlorination products[215].

Published information[225–229] shows that bromine chloride adds to unsaturated compounds by an ionic mechanism; Br^+ attacks the double bond of alkenes to form an intermediate carbonium ion. The mechanism of chlorobromination may thus be represented by the following scheme:



Comparison of the scheme for the mechanism of bromination of 2-methylpropene with this scheme for chlorobromination shows that both reactions proceed through an identical intermediate carbonium ion. If it is assumed that the nucleophilic centre of the halogen plays a predominating part in anomalous halogenation reactions, then the yield of monobromides should be higher in chlorobromination than in bromination. However, experimental results show that in both the yield of unsaturated monobromo-derivatives is ~ 20%.

In the gas-phase chlorobromination of 2-methylpropene at 150° in a flow-through system[230], the yield of 2-methylallyl bromide is 41.5%, that is, somewhat lower than in the

gas-phase bromination of 2-methylpropene at 300°.[18] From this it follows that the anionic centre of the halogen has no appreciable effect on the composition of the products of halogenation of alkenes with a quaternary carbon atom at the double bond.

The authors of the present review[231] have put forward the hypothesis that the main reason for the elimination of a proton from alkyl groups in the α-position to the carbonium ion centre, and therefore for the formation of anomalous halogenation products, is the high degree of localisation of the positive charge at the centre of the organic cation formed as a result of electrophilic attack on the alkene[231]. On the other hand, delocalisation of the positive charge, due to the high polarisability of the electrophilic part of the reagent attached to the carbon atom in the α-position to the centre of the organic cation, hinders the elimination of a proton; as a result, the carbonium ion is stabilised by the addition of a halide ion to the positively charged carbon, and dihalo-derivatives are formed as final adducts. Here the reaction rate also depends on the nucleophilic properties of the halide anion[115].

Interaction of the centre of the carbonium ion with the added halogen probably occurs not in a chain-like manner but spatially, according to Roberts and Kimball[84], or de la Mare and coworkers[184,185]. This hypothesis was checked experimentally by introducing atoms of different inductomeric polarisability into the α-position of the alkene being chlorinated. Results obtained in the chlorination of 2-methylallyl chloride, 2-methylallyl bromide and 2-methylallyl iodide confirm the hypothesis; as the inductomeric polarisability of the halogen atom at the carbon atom in the α-position to the carbonium ion increased, the yield of anomalous chlorination products fell from 50% to 0%[231] (see Table 3).

Internal interaction between a positively charged centre and electronegative or strongly polarised groups at the α-carbon atom may lead to the formation of a new bond. On the basis of the foregoing hypothesis, the formation of halo-lactones when bromine or chlorine acts on the sodium salt of dimethylmaleic or dimethylfumaric acid may be represented by the following scheme[232]:

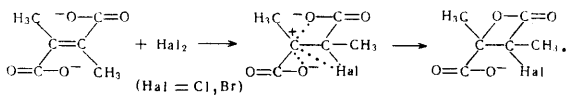
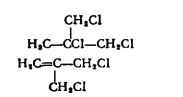
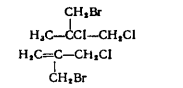
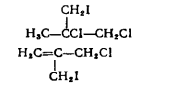


TABLE 3. Results of the low-temperature chlorination of unsaturated monohalo-derivatives of 2-methylpropene.

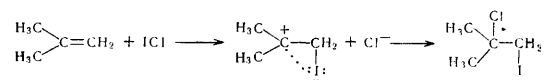
Starting alkene	Proposed structure of intermediate carbonium ion	Possible final adducts*	Yield of reaction products, %
			30 50
			60 11.7
			82.5 0

* The total isomers of unsaturated halo-derivatives are arbitrarily denoted by a single formula.

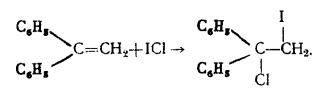
In the first example, because of its greater inductomeric polarisability, the added bromine atom probably partially delocalises the charge on the intermediate organic cation, which further stabilises the latter and thereby prevents the formation of a new lactone bond between the carbon atom and the carboxyl group.

A number of other results are also in good agreement with interpretations that take account of the effect of the polarisability of the electrophilic centre of the reagent.

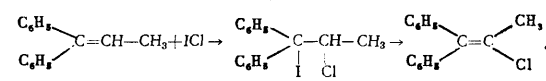
Thus, in the reaction of 2-methylpropene with iodine chloride, the positive charge on the carbon atom is delocalised by the added iodine atom; for this reason, 2-methylallyl iodide was not formed and 2-chloro-1-iodo-2-methylpropane was the sole reaction product[233]:



The addition of iodine chloride to propene[60,234], allyl alcohol and its esters[235], styrene[236], and 1,1-diphenylethylene[237] confirmed the validity of this order of orientation of the iodine chloride molecule, for example:



However, as Temnikova and coworkers have shown, this order may be changed by other substituents[237]. Thus, the production of 2-chloro-1,1-diphenylprop-1-ene when iodine chloride reacts with 1,1-diphenylprop-1-ene was explained by the initial formation of 2-chloro-1-iodo-1,1-diphenylpropane, which eliminates hydrogen chloride at the moment of reaction:



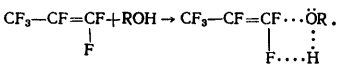
Recently, the effect of the magnitude of the charge on the positively charged carbon atom on the stabilisation route of the carbonium ion was studied in the low-temperature bromination of liquid 2-methylpropene in the following solvents of varying polarity: 2-methylpropene, chloroform, 1,1-dichloroethane, 1,2-dichloroethane, t-butyl chloride, and nitroethane[238]. It was shown that the total yield of 2-methylallyl bromide and dimethylvinyl bromide, and therefore the rate of elimination of a proton from the alkyl groups of the carbonium ion, decreases in proportion to the increasing dipole moment of the solvent; the yield of unsaturated monobromides decreases from 24% with 2-methylpropene to zero with nitromethane in the solvent order given above.

A study of the effect of solvent : alkene ratio on the composition of the products of the low-temperature halogenation of alkenes with a quaternary carbon atom at the double bond showed that a reduction in the concentration of alkene in the solvent leads to a decrease in the yield of allyl and vinyl substitution products[238].

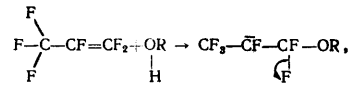
These results show that the ionic charge due to a strongly polar solvent may be reduced by increasing the quantity of less polar solvent while other reaction conditions are kept constant.

An interesting analogy is observed in reactions of alkenes with electrophilic reagents and of fluoroalkenes with nucleophilic compounds[239]. In reactions of perfluoroalkenes with nucleophilic reagents, the difluoromethylene group, which has an induced partial positive charge, is the object of nucleophilic attack; perfluoro-2-methylpropene reacts more readily with nucleophilic agents than perfluoropropene.

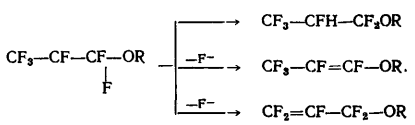
On the other hand, because of the positive inductive effect of alkyl groups, the methylene group of alkenes has excess electron density and is the object of electrophilic attack; the activity of alkenes in reactions with electrophilic reagents increases with the number of methyl groups at the double bond[126]. There is another interesting analogy between the reactions of alkenes and fluoroalkenes. When perfluoroalkenes are subjected to nucleophilic attack, replacement of fluorine atoms in the vinyl, and frequently the allyl, position is observed as well as addition at the double bond[240-245]. It has been suggested[243] that the nucleophilic reagent is linked with the electrophilic perfluoroalkene molecule in a four-membered transition state, which is stabilised by the intramolecular formation of a hydrogen bond[243]:



A somewhat different explanation of the mechanism of these reactions has also been put forward: the initial step in the reaction is considered to be attack by an anion; this leads to the formation of an intermediate carbanion,



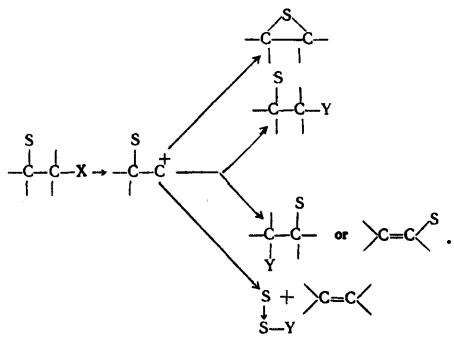
which is then stabilised by the addition of a proton or the elimination of a fluoride anion:



Under the same conditions, the relationship between addition, allyl substitution, and vinyl substitution depends on the structure of the perfluoroalkene and on the mobility of the unshared pair of the nucleophilic agent[239].

The main conditions that determine the stabilisation route of the carbonium ion, and therefore the composition of the products, in the electrophilic low-temperature halogenation of alkenes, are also, as pointed out above[52-56], the structure of the alkene and the mobility of the unshared pair of the attacking electrophilic agent[215,231]. Additions to fluoroalkenes and to alkenes are therefore similar.

A change in the mobility of the electron pairs of atoms at the carbon atom in the α-position to the centre of the carbonium ion, should also affect the composition of the final products in fragmentation reactions, in which the intermediate carbonium ion formed by displacement of some substituent from the organic compound may be stabilised in several ways[246-248]:



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