Translated from *Uspekhi Khimii*, 50, 273-295 (1981) U.D.C. 547.311

The Mechanism of the Electrophilic Addition of Halogens to a Multiple Bond

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A systematic account is given of the literature data on the mechanism of the electrophilic halogenation of olefins. Particular attention is devoted to the experimental methods for the investigation of the structures and reactivities of the intermediate unstable adducts produced by the electrophilic addition of the halogen to the multiple bond. The relation between the mechanisms of electrophilic halogenation and other *Ad* reactions is discussed. Certain aspects of the stereochemistry of the addition of halogens and hypohalites to olefins are examined.
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I. INTRODUCTION

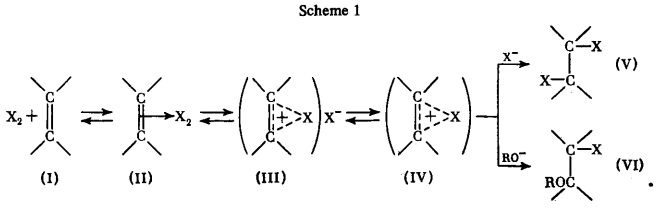
The electrophilic addition of halogens and hypohalites to olefins is a fairly well known reaction[1], but the study of its mechanism is still being continued[2-4]. The present review attempts to give a systematic and critical account of the available data (using studies published up to 1978), mainly from the standpoint of the reaction mechanism, the structure of the intermediates, and the influence of the structure of the reactants on the rate of their interaction. The synthetic aspects of the problem as well as the role of the donor–acceptor complexes are considered briefly, mainly in relation to new data which have not been included in recently published reviews[3-5].

II. THE REACTION MECHANISM. GENERAL KINETIC FEATURES

1. General Consideration of the Mechanism

The mechanisms of the halogenation and coupled halogenation of olefins (I) are closely related, as can be readily seen from Scheme 1 below:

Scheme 1



The first stage involves the formation of a π-complex (II) from the initial reactants, which is then converted into a "close" ion pair (III) (analogous to a σ-complex in aromatic substitution reactions); the latter then dissociates in media with a high solvating capacity into two solvated ions—the anion X^- and the cation (IV).[6-11]. In non-polar weakly solvating media the intermediate is a solvate-separated pair (IV) $\| X^-$.[6,12-14].

The rate-limiting stage of the entire process is ionisation of the π-complex (II) with formation of ion pairs[5,15,16]. Products (V) and (VI) are formed simultaneously, since the ratio of their yields is independent of the extent of reaction and remains constant[17,18]. Depending on specific conditions (the polarity of the medium, the structure of the components, and the reaction temperature), the proposed mechanism can be modified. The rate of formation of the final products depends not only on the rate of conversion of intermediates (III) or (IV) but also on their absolute concentrations. The rates of formation and decomposition of the unstable intermediates have not been determined directly but with the aid of low-temperature infrared, untraviolet, and ^1H NMR spectroscopy it has sometimes been possible to identify the intermediate[19,20] whose structure determines the mode of addition of the reactants and the stereochemistry of the final adducts[21].

On the other hand, during the last 15 years new facts have been observed, which can be regarded as evidence in support of the mechanism described in Scheme 1.

1. An anomaly in the temperature variation consists in the fact that k_{eff} for electrophilic addition either increases slightly[22-24] or actually decreases as the temperature rises[25-27], i.e. the effective activation energy is less than zero. This agrees well with the concept of the reversible formation of the intermediates (III) and (IV) with a considerable energy release. A negative temperature coefficient ($E_{act}^{eff} \leq 0$) was found initially only for chlorination[22] and bromination[27] reactions and was later noted for the addition of mixed halogens[28] and for coupled bromination or chlorination[26,29]. Since it is clear from Scheme 1 that $E_{act}^{eff} = \sum \Delta H + E$, where E is the activation energy for the conversion of (IV) or (III) into (V) and (VI) and $\sum \Delta H$ is the sum of the exothermic heats of the equilibrium stages, it follows that, when $\Delta H \ll 0$, the effective (or apparent) activation energy can become zero or even less than zero. Only one of the components is determined experimentally, namely the enthalpy of formation of the donor–acceptor complex (II), the absolute

value of which varies in the range 2–10 kcal mol^{-1} depending on the nature of the olefin and the halogen[5,30,31].

2. The halogenation of pure *cis*- or *trans*-isomers of olefins takes place stereospecifically. Thus it has been noted for *cis*- or *trans*-but-2-ene[32], d_3-styrene[33], and di-isopropylethylene[34] that the *anti*-addition of the halogen to the olefin takes place to the extent of 99.5%; this forced the investigators[32–34] to postulate that a cyclic halonium ion, with restricted rotation about the carbon bond, is involved exclusively in the reaction. Because of this, pure stereoisomers were isolated as a result of the reaction.

3. In the study of the behaviour of vicinal dihalogenoderivatives in strongly acid media, the ^1H NMR spectra demonstrated unambiguously the existence of intermediates whose interaction with methanol yields mixed adducts of type (VI), equivalent to products obtained in the coupled halogenation of an unsaturated compound in the presence of methanol[35].

It is seen from the evidence presented above that the structure of the intermediate determines the mode and rate of electrophilic addition to the double bond.

The existence of an equilibrium stage preceding the formation of adducts (V) and (VI) has been demonstrated most readily and convincingly with the aid of ultraviolet spectroscopy[30,31]. When equimolar amounts of bromine and cyclohexene are mixed, a 1:1 charge-transfer complex is formed and can be detected by the stopped flow method ($\lambda_{max} = 290$ nm; $\varepsilon \cong 15400$).[31] Similarly charge-transfer complexes have been identified in the chlorination of cyclohexene and hexene ($\lambda_{max} = 248$ and 263 nm; $\varepsilon \cong 1400$ in both cases).[30] The main difficulty arising in the study of the intermediate compound in olefin–halogen systems by ultraviolet spectroscopy arises from the fact that the σ- and π-complexes absorb in approximately the same spectral region; the initial molecules and electrophilic adducts as a rule also absorb in this region of the spectrum. It is therefore impossible to detect and identify the ultraviolet spectra of the separated and non-separated ion pairs whose concentration determines the mode and rate of electrophilic addition of the halogen.

The thermodynamic parameters of the reversible formation of charge-transfer complexes were found from the temperature variation of the equilibrium constants. The enthalpy of formation of the bromine–cyclohexene complex ($\Delta H \cong -4$ kcal mol^{-1}) [31] proved to be greater in absolute magnitude than for the chlorine complexes of hexene and cyclohexene ($\Delta H = -1.7$ and -2.7 kcal mol^{-1} respectively),[30] which indicates a lower stability of the olefin—chlorine complexes and is associated with a weaker polarisability of chlorine compared with bromine. The influence of the structure of the olefin on the thermodynamic parameters of the complex is related to the ionisation potential of the unsaturated compound (I) and the σ constants of the substituents[12,36]; the observed linear relations are described by the equations $h\nu_{eV} = 0.56I + 2.39$ and $\lg(k/k_0) = -3.16\sigma$.

The enthalpies of formation of the complexes obtained do not exceed 7.5 kcal mol^{-1} (for bromine iodide) and cannot explain the anomalous temperature variation of the rate constants for the electrophilic halogenation and coupled reactions, for which a negative temperature coefficient has been frequently observed[22,26,27,29,37]. It is logical to postulate the existence of at least yet another exothermic process[33,39] whose contribution would account for the decrease of the apparent activation energy to negative values. At the present time there is no unanimous view concerning the equilibrium which gives rise to the additional energy. A number of workers believe that the initially formed π-complexes rearrange to more closely linked "internal" complexes characterised by a higher degree of charge transfer[37]; the concept of the "internal" complex is apparently equivalent to the σ-complex and that of the "external" complex is equivalent to the π-complex.

Different exothermic processes are important for the mechanism of the electrophilic reaction: the formation of 2:1 halogen–olefin complexes[27,38] and the formation of complexes between the reactants and the solvents, including weakly polar solvents[39]. In polar solvents, particularly those which contain a heteroatom and are effective *n*-donors, the halogen forms a complex with the solvent. The enthalpy of formation of halogen–*n*-donor complexes is frequently higher[40] than that for olefin–halogen complexes. For example, $\Delta H = -8$ kcal mol^{-1} for the complex of epoxycyclohexane and bromine[41], which is twice as high as the enthalpy of formation of a complex between cyclohexene and bromine[31]. *n*-Donors are in fact most frequently involved in a coupled electrophilic reaction leading to the formation of mixed adducts, which have been established for α- and β-oxides[37,42–47], alcohols[48], and aliphatic[49–51] and acyclic[52,53] esters and anhydrides[54].

The reversible reaction between halogens and oxygen-containing *n*-donors can proceed via a two-well kinetic model[41,55] (like the interaction of a halogen with olefins) with conversion of the "external" complex formed initially into an "internal" complex[41]. The high exothermic heat of formation of complexes between *n*-donors and halogens is responsible for the occurrence of side reactions involving the isomerisation and polymerisation of the oxygen-containing donors; thus, depending on temperature and other conditions, in the case of an epoxide different amounts of dioxans and epoxide polymers were detected in the reaction mixture as well as the product of addition to the double bond[56].

Electrophilic halogenation begins with a series of reversible stages, including the formation of π- and σ-complexes. The problem therefore arises whether these two intermediate species, separated by a transition state with a low energy level, are in a state of equilibrium or whether their transformation is irreversible. The salt effect can serve as an indirect characteristic of the position of the equilibrium between intermediates (II) and (III). The addition of an electrolyte containing an anion common to the reactants increases the rate of conversion of the π- or σ-complex as a result of an increased concentration of the nucleophile attacking the intermediate; this phenomenon will be considered in detail below. The introduction of neutral electrolytes, without anions common to the reactants, into the electrophilic addition reaction will have an effect only in those cases where a solvate-separated ion pair (σ-complex) arises as an intermediate or individual ions are formed[57,58]. The positive salt effect is explained in this case by the fact that the electrolyte increases the degree of charge separation in the intermediate (III) and stabilises the latter as a result of association; the changes enumerated above lower the apparent activation energy for the entire electrophilic halogenation process. In the chlorination of *trans*-cinnamic acid the reaction rate constant increases by a factor of three in the presence of 0.1 M $LiClO_4$.[10]

The introduction of a neutral salt prevents the association of the separated ion pair into a non-separated pair (Scheme 1) and therefore displaces the equilibrium towards the more reactive σ-complex, so that the reaction rate constant increases. Added electrolyte increases the rate constant for the bromination of styrene by a factor of seven[57]. The increase in the degree of charge separation in the intermediate should increase the sensitivity of the halonium ion to the influence of substituents and the reaction rate constant should therefore increase in absolute magnitude. With

increase of the $LiClO_4$ concentration from 0 to 10^{-1} M in the acetoxy-bromination of R-styrene (Fig.1), the reaction rate constant increases owing to the increased dipole moment of the intermediate; the intersection of the two relations at the point corresponding to *m*-nitrostyrene can be explained only by the fact that the bromination involves the existence of only a solvate-separated ion pair whose state does not change with increase of the electrolyte concentration[57].

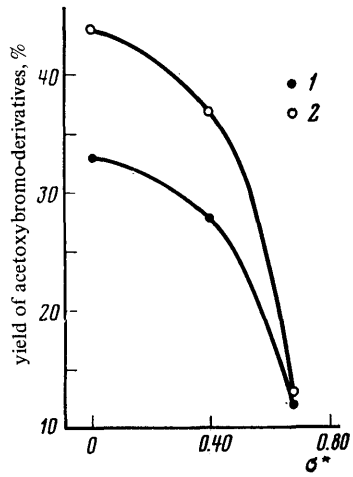


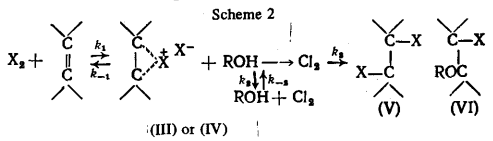
Figure 1. Dependence of the yield of the acetoxybromo-derivative in the bromination of R-styrene in acetic acid on the σ^+ constants of the substituents: *1*) acetic acid; *2*) acetic acid + 0.10 M $LiClO_4$.

2. The Ratio of the Rates of Individual Stages

Since the interaction of a halogen with an olefin proceeds at a high rate, it is frequently assumed that the electrophilic addition is irreversible. On the other hand, a number of facts are presented above confirming the formation of intermediates which are subsequently converted into the reaction products (V) or (VI). The entire reaction involving the electrophilic addition of a halogen to an olefin proceeds under pseudostationary conditions, so that the intermediates do not accumulate in large amounts. It is not possible to detect the intermediate species, because the rate of their formation is comparable to the rate of their conversion into the reaction products. The rate constant for the rate-limiting stage of a complex process involving the formation of products from an intermediate (III) or (IV) is close to the apparent rate constant for the entire process determined experimentally. The absolute value of k_{eff} varies within broad limits, depending on the structure of the olefin; thus k_{eff} varies in the range from 5×10^{-2} to 5×10^5 litre mol^{-1} s^{-1} in the bromination of *cis*- and *trans*-substituted olefins at 25 °C.[34,59]

In the coupled reaction the formation of a second donor–acceptor complex is no less important than the formation of the halogen–olefin σ-complex (Scheme 2):

Scheme 2



The exothermic heat of the two reversible processes lowers the effective activation energy for the electrophilic reaction. The addition of π- and *n*-donors not involved directly in the electrophilic addition reaction should have a catalytic effect owing to the formation of donor–acceptor complexes with the halogen. Thus, in the study of the electrophilic addition of chlorine to hexene in CCl_4, an increase of the rate constant and a change of the kinetic equation were observed in the presence of benzene or dioxan; on passing from CCl_4 to an electron-donating solvent, the rate constant changes from 1.7 litre mol^{-1} min^{-1} to 4800 $litre^2$ mol^{-2} min^{-1}.[60] Analogous results have been obtained also for other electron-donating solvents (diethyl and dibutyl ethers) which do not enter directly into the reaction under the experimental conditions[61].

However, a whole series of donors react with the halogen–olefin π-complex, forming mixed adducts[23,24,26,29,62]. The formation of donor–acceptor complexes of *n*-donors with chlorine has been indicated in kinetic studies by an increase in the reaction order with respect to the halogen in coupled reactions[23,24,63] and by the necessity for an excess of the oxygen-containing donor for the reaction to occur at a high rate. A decrease of the concentration of both chlorine and the *n*-donor inhibits the coupled reaction; in this case the kinetic curve acquires the S-shape characteristic of auto-catalytic reactions. The induction period of the auto-catalytic reaction is associated with the need to accumulate a considerable amount of the intermediate[64]. The presence of an induction period has been noted, for example, in the coupled bromination of cyclohexene in the presence of epoxycyclohexane[37].

With increase of temperature, the specific rate constants corresponding to the elementary stages of the process shown in Scheme 2 increase unequally; the dependence of the effective rate constant for the coupled halogenation on temperature is therefore anomalous—the absolute value of the effective rate constant decreases with increase of temperature[29,37]. Analysis of the process in Scheme 2 readily shows that an *n*-donor concentration higher than the stoichiometric value is necessary for the practical realisation of the coupled reaction. Reactions involving the coupled chlorination of allyl chloride together with α-oxides[29] and β-oxides[63] as well as 2-chloroethanol[24] take place in precisely this manner in the presence of an excess of the oxygen-containing compound.

If an appreciable charge separation takes place in the intermediate of the electrophilic reaction and the intermediate acquires the character of a solvate-separated ion pair, an increase in the concentration of the common halide ion should increase the rate of the electrophilic addition of the halogen to the multiple bond, i.e. a positive salt effect should be observed. Stimulation of the electrophilic bromination of olefins in methanol under the influence of NaBr has been most widely studied[65–67]. An increase of the concentration of the nucleophile increases (as a result of the dissociation of the electrolyte) not only the rate of the electrophilic reaction but also the fraction of *trans*-addition to the double bond. Nucleophilic attack on the carbon atom does not require in this case either a reorientation of the nucleophilic bromine or rotation about the carbon–carbon bond in the intermediate. With increase of the LiBr concentration in the bromination of styrene from 0 to 0.1 M, the fraction of *trans*-addition increases from 72 to 95%.[68]

The positive salt effect of the halide anion is described by a third-order kinetic equation incorporating the concentrations of both the halogen and the halide anion[69]. Electrophilic addition to an olefin in the presence of metal halides is a process which proceeds via two bimolecular collisions; the effective activation energy for this reaction is reduced,

since the energy expended on the dissociation of the halogen–halogen bond is compensated by the energy of formation of the halogen–carbon bond[70,71].

In those cases where the intermediate in the electrophilic addition of a halogen to a multiple bond acquires the character of a close ion pair (a π-complex) the addition of metal halides does not alter either the rate of reaction or the proportions of the *cis*- and *trans*-additions. In the chlorination of phenanthrene the addition of LiCl does not effect the stereochemistry of the halogen addition products[72]. An increase of the chloride ion concentration does not change the rate constants for the chlorination of *trans*-cinnamaldehyde[10] and *trans*-cinnamic acid[11]. In the study of salt effects it is important to take into account the formation of mixed adducts with protic solvents, since in this case hydrogen chloride is generated, increasing the rate of the electrophilic reaction by a factor of 10–12, which makes the addition of the halogen to the multiple bond autocatalytic[10,73].

The kinetic equation for the electrophilic addition of bromine to olefins is more complex: the reaction proceeds via two parallel competing pathways[58,59,74,75], involving the interaction of the olefin with molecular bromine (k_1) and with the tribromide anion (k_3); the latter interaction is described by the equation

$$Br_2 + Br^- \rightleftarrows Br_3^-$$

$$-\frac{d[Br_2]}{dt} = k_1\,[\text{olefin}]\,[Br_2] + k_3\,[\text{olefin}]\,[Br_3^-] \ .$$

The equilibrium constant for the formation of the tribromide anion has a high absolute value, so that minimal amounts of the common ion produced in the dissociation of the electrolyte shift the equilibrium towards the tribromide anion and reduce the contribution of the "molecular" reaction pathway. The equilibrium constant K_{2S} depends on temperature, the source of the counterion, and the solvent. Thus, on passing from acetic acid to methanol, the equilibrium constant changes from 92 litre mol^{-1} (Rolston and Yates[57]) to 177 litre mol^{-1} (Dubois et al.[8]). The equilibrium constant changes even more when the nature of the electrolyte is altered; thus in the presence of HBr the equilibrium constant is 125 litre mol^{-1}, which is 2.5 times more than in the presence of added NaBr (53 litre mol^{-1}).[57,75] The equilibrium constant in the formation of the tribromide anion increases also with increase of the $LiClO_4$ concentration[57].

The relative contributions of the two parallel pathways are usually described by the ratio $Q = k_{Br_2}/k_{Br_3^-}$, which varies from 0.01 (Yates and Wright[58]) to 85 (Dubois et al.[8]). The change in the relative contributions of the competing pathways can be accounted for by the change in the bromide anion–tribromide anion equilibrium constant under the influence of the factors enumerated above. However, in all cases, ranging from dominant bromination by the tribromide anion ($Q < 1$) [58,74] to virtually complete absence of the reaction with the tribromide anion ($Q \gg 1$),[8,76–78] the rate of reaction of Br_3^- is higher than that of Br_2. The anomalously high values of Q observed by Dubois et al.[8] can be explained by the steric hindrance in the diphenylethylene being brominated and also by the autocatalytic effect of HBr, which is evolved on formation of mixed adducts with the solvent.

The interaction with the trichloride anion is less characteristic of chlorination owing to the low value of the equilibrium constant for the formation of the Cl_3^- anion[5,79,80]. On the whole, as in the cases enumerated above, the exothermic reversible formation of the trihalide ion exhibits a catalytic effect on the conversion of the intermediate into the reaction product; a change of temperature can alter the rate-limiting stage of the process, the rate constant for the reversible stage involving the formation of a π- or σ-complex being smallest.

III. PHYSICOCHEMICAL METHODS FOR DETECTING THE INTERMEDIATE SPECIES INVOLVED IN ELECTROPHILIC ADDITION REACTIONS

The electrophilic addition of a halogen usually takes place under pseudostationary conditions, so that the intermediate does not accumulate in considerable amounts, which hinders its detection by physicochemical methods. By carrying out the reaction at reduced temperatures, it is possible to separate the reversible and irreversible stages of the process (Scheme 1) and to investigate the structure of the unstable intermediates.

It has been shown[20,81–86] by low temperature infrared spectroscopy that, when an olefin and a halogen are sputtered onto a cooled (~–200 °C) cryostat support under molecular beam conditions, the spectrum shows initially only bands characteristic of the parent compounds. Heating of the cryostat support to between −180 °C and −165 °C leads to the mutual diffusion of the components and to the appearance in the infrared spectrum of a group of new bands which are not characteristic of either the initial compound or the reaction product[82,83,85].

The changes occurring in the infrared spectra can be explained solely by the formation of intermediates of the olefin–halogen type, which are converted on heating into dihalogeno-derivatives[81]. The decrease of the vibration frequency of the multiple bond suggests a decrease of its electron density compared with the initial olefin[83,84]. Analysis of the frequencies and modes of the normal vibrations shows that the olefin–halogen complexes have C_{2v} symmetry, which is characteristic of three-membered heterocycles[81]. Simultaneously with the structure, the equimolecular composition of the unstable intermediate was demonstrated[81–84]. In the presence of an excess of bromine an intermediate containing two bromine molecules per olefin molecule was detected[87]. In a mixture of bromine and propene the disproportionation of a 1 : 1 complex to give a 2 : 1 complex and free propene, identified in a mixture of complexes, was noted[84].

The conclusions reached in the study of the low-temperature spectra of halogen–olefin complexes were confirmed by quantum-mechanical calculations. The formation of the open-chain carbonium ion (VII)

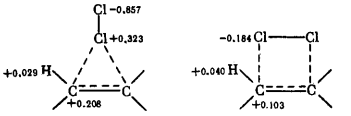


(VII)

incorporating an sp^3-hybridised carbon atom and a covalent carbon–carbon bond of normal length (1.53 Å), is unlikely; the existence of the carbonium ion is possible only when it is stabilised by the attacking nucleophiles[88,89]. Theoretically, the structure of the centrosymmetric halonium ion (IV) with a partially rehybridised carbon atom and altered valence angles is energetically most favourable[90,91]. The changes occurring on formation of intermediates can be followed in the infrared spectra of solid solutions of chlorine in olefins; the observed effects can be accounted for by a decrease of the electron density in the multiple bond and by the formation of partial C—Cl bonds.

For 1 : 1 donor–acceptor complexes of C_{2v} symmetry, two structures can be postulated[91,92]. The first is the axial structure (VIII) in which the halogen molecule is located on the symmetry axis of ethylene perpendicular to the carbon–carbon bond. In the alternative structure (IX) the halogen–halogen bond is parallel to the plane of the carbon–carbon bond. The complex (IX) presupposes the formation of a four-centre transition state and the *cis*-addition of a halogen

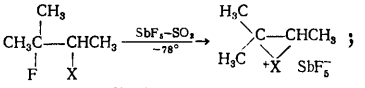
molecule to the multiple bond. Comparison of the distributions of electron density in the intermediates (VIII) and (IX) in the reaction involving chlorine shows that the former is energetically favoured, since it involves a greater charge separation[90].



(VIII) (IX)

According to quantum-mechanical calculations[90], the stability of the intermediate complexes decreases in the sequence Br > Cl > F, which agrees well with experiment[93]. The cyclic structure of the intermediate ion makes it possible to explain the *trans*-specificity of the electrophilic halogenation in non-polar media, associated with the inhibition of the free rotation about the carbon–carbon bond in the cyclic ion (VIII), compared with the open-chain carbonium ion (VII).[94,95] In polar media where there is a possibility of the formation of solvate-separated ion pairs, the open-chain ion may be stabilised† and the stereospecificity of the reaction may be infringed[96]; *cis*-addition to the multiple bond is possible only when there is rotation about the carbon–carbon bond in the intermediate. α-Substitution in the olefin molecule distorts the symmetrical distribution of electron density on the carbon atoms and in the limiting case such an intermediate may become open-chain[98–100]. Quantum-mechanical calculations have now been made only for the simplest olefins (ethylene and propene); the stabilising influence of the solvent on the charge distribution in halonium ions has been taken into account only indirectly[99]. The latter factor precludes an unambiguous utilisation of the quantum-chemical results for the consideration of the mechanism of electrophilic halogenation.

NMR has been widely used in recent years in the study of labile intermediates. A major achievement of NMR has been direct detection of non-classical cyclic halonium ions. Olah and coworkers frequently detected the formation of a cyclic intermediate from the corresponding vicinal dihalides when the latter were dissolved in superacids at low temperatures[35,93,101–108]. The dissolution of 3-chloro-, 3-bromo-, or 3-iodo-2-fluoro-2-methylbutane in an SbF_5–SO_2 mixture at −78 °C leads to the formation of the stable trimethylethylene–halonium ion (X):[104]

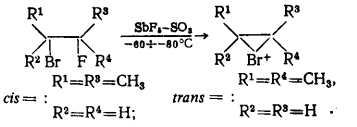


X=C , Br, or I.

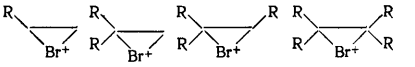
(X)

In the case of symmetrical ethylenehalonium ions[103,109] the conclusion that the ion had a bridged structure is based mainly on three pieces of evidence: the detection of a singlet signal due to the methylene protons in the ^1H NMR spectra, the upfield shift of the signal of the α-carbon atoms (to 40 ppm.) [105] relative to the spectra of typical open-chain ions[93], and the stereoselective methanolysis of the halonium ion generated from the optically active vicinal dihalides[93]. The presence of even insignificant amounts of a classical carbonium ion containing an sp^3-hybridised carbon atom should lead to the non-equivalence of the signals of the methylene protons and to the formation of racemates on solvolysis[102,103,162].

When *erythro*- and *threo*-3-fluoro-2-iodobutanes were ionised in superacids, the *trans*- and *cis*-iodonium ions were obtained, their reactions with CH_3OH proceeding stereospecifically with formation of *erythro*- and *threo-dl*-2-iodo-3-methoxybutanes respectively[35]. Indeed, if the non-classical halonium ions are three-membered cyclic species, they should have both *cis*- and *trans*-isomers. In a study of the low-temperature ^{13}C NMR spectrum of *erythro-dl*- and *threo-dl*-2-bromo-3-fluorobutanes in superacids both the *trans*-isomer ($\delta_{C_1} = \delta_{C_2} = 85.0$ ppm., $\delta_{CH_3} = 175.4$ ppm.) and the *cis*-isomer ($\delta_{C_1} = \delta_{C_2} = 82.9$ ppm., $\delta_{CH_3} = 174.4$ ppm.) of the dimethylethylenebromonium ion were identified[107]:



The introduction of alkyl substituents at the α-carbon atom stabilises the bridged ion; this has been demonstrated not only by NMR [103,107] but also by special thermochemical studies in superacids at −60 °C. The heat of formation of methyl-substituted bromonium ions varies in the following sequence[110]:

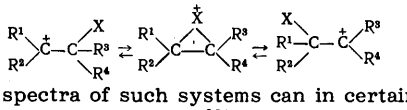


ΔH, kcal mol^{-1} — 3.29 — 8.39 — 13.5 —22.5 .

The tetramethylbromonium ion proved to be the most stable, in agreement with conclusions which follow from spectroscopic studies[108]. The halonium ions of olefins substituted in the α-position by bulky alicyclic groups, for example, the adamantane ring, are particularly stable and can be isolated at the usual temperatures[111,112]. The structure of the adamantylbromonium ion has been confirmed mass-spectrometrically[111].

The substitution of the protons at the α-carbon atom of the olefin by arene rings leads to the destabilisation of the cyclic halonium ion and to the appearance of considerable amounts of an open-chain halonium ion; the presence of the latter has been demonstrated not only by NMR but also by the formation of a mixture of isomers in the solvolysis reaction[105,106].

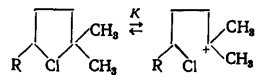
The stability of the cyclic ions increases in the following sequence of halogens: F < Cl < Br ≪ I,[107] which corresponds to the increase of the ionic radius and the polarisability of the atoms. The formation of a non-classical ion from fluorine is doubtful[113]. Bridged (butene[103] and ethylene[109]) and open-chain (propene[102]) ions are apparently characteristic of chlorine. It is logical to suppose that both forms under consideration are in a state of dynamic equilibrium:



The ^1H NMR spectra of such systems can in certain cases show a broadened singlet signal[114], which hinders its assignment to a specific type of ion. The problem can be solved using the temperature variation of the ^1H NMR spectra, which provides an unambiguous answer to the question whether or not a reversible reaction of the ions takes place in the given case. Such a temperature dependence has now

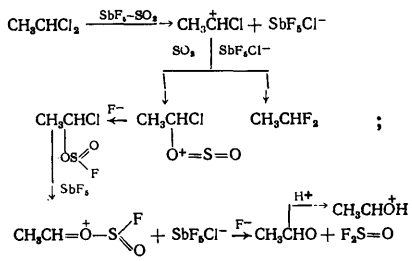
†According to quantum-mechanical calculations, the open-chain form $CH_3CH_2^+$ of the cation $C_2H_5^+$ is more stable than the cyclic form by 6.7 kcal mol^{-1}.[97]

been investigated only for the substituted tetramethylene-chloronium ion, whose stability is higher than that of the ethylenehalonium ion[115]. The predominance of the open-chain form of the ion over the cyclic form has been noted; the equilibrium constants K are 0.31 litre mol^{-1} in SO_2ClF and 0.21 litre mol^{-1} in SO_2.[115] An increase of temperature from −100° to −33 °C increases the content of the cyclic form from 10.5 to 25%:[115]



An increase of the size of the ring for the same number of methyl substituents in the α-position relative to the halogen atom greatly increases the stability of penta- and hexa-methylenechloronium ions[116] compared with ethylenehalonium ions[110,117]. The available information about the trimethylene-halonium ion is contradictory[113,116]; the attempts to detect this ion proved unsuccessful owing to its rapid isomerisation to an ethylenehalonium ion[113]. In terms of their reactivities, the five- and six-membered halonium ions are analogous to ethylenehalonium ions[76,115,118–120].

The data concerning the formation of non-classical bridged ions, obtained with the aid of low-temperature NMR, cannot be transfered mechanically to the consideration of different aspects of electrophilic reactions, since highly ionising media (SbF_5–SO_2 and SO_2ClF–SO_2) and a low temperature have a stabilising influence on the unstable intermediates. The conversion of the latter on heating does not always proceed solely with the electrophilic addition of the halogen to the multiple bond, with formation of an adduct, but can be complicated by a whole series of side reactions. An example of degradative decomposition is provided by the conversion of the cation obtained from 1,1-dichloroethane in the SbF_5–SO_2 medium[35]; in this case only the products of the conversion of the initially formed ion were identified in the reaction mixture[35]:

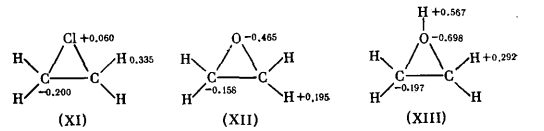


The formation of the ethylenechloronium ion in SO_2ClF is complicated by the 1,2-hydride shift[109].

Overall, the study of the NMR spectra of dihalides at low temperatures confirms the validity of the concept of cyclic halonium ions, because *cis–trans*-isomerism has been observed, the solvolysis proceeds stereoselectively, and the absolute values of the chemical shifts are not characteristic of classical carbonium ions.

IV. THE *Ad* MECHANISM OF THE ADDITION OF A HALOGEN TO A MULTIPLE BOND

If it is assumed that a bridged non-classical ion is involved in the electrophilic addition of a halogen to a multiple bond in non-polar media, then the conversion of the ion into products is a typical *Ad* reaction[18,121], the kinetics of which are common to other analogous reactions, for example, those involving the opening of the ring in epoxides under the influence of nucleophiles[122]. The principal objection to the proposed analogy is the nature of the distribution of electron density in the "bridged" ion (XI)—the intermediate in the electrophilic reaction[97]—and in the epoxide (XII):[123]



(XI) (XII) (XIII)

Systematic study of the quantitative characteristics of the opening of the epoxide ring under the influence of nucleophiles showed that the species which usually reacts is the protonated epoxide (XIII),[123,124] where the distribution of electron density differs significantly from that known for the epoxide (XII). The reactions of epoxides with nucleophiles under the conditions of both acid[125–129] and base[130,131] catalysis proceed via a trimolecular transition state incorporating both the nucleophile and the proton donor molecule. Protonation of epoxides increases the polarisation of the C–O bond, which facilitates its dissociation; the nature of the distribution of electron density in the intermediates (XI) and (XIII), formed respectively in the electrophilic addition of the halogen and in the opening of an epoxide, is the same, as has been frequently confirmed by quantum-mechanical calculations[98,123].

The chemical shifts (δ, ppm.) of the protons of protonated epoxides and certain halonium ions[132].

Ion	δ_{CH}	δ_{CH_2}	δ_{CH_2}
CH_2-CH_2 $\diagdown\ /$ I^+	—	5.77	—
CH_2-CH_2 $\diagdown\ /$ Br^+	—	5.53	—
CH_2-CH_2 $\diagdown\ /$ OH^+	—	5.00	—
CH_2-CH_2 $\diagdown\ /$ SH^+	—	3.63	—
CH_3CH-CH_2 $\diagdown\ /$ I^+	7.73	5.77	3.32
CH_3CH-CH_2 $\diagdown\ /$ Br^+	7.48	5.86	2.98
CH_3CH-CH_2 $\diagdown\ /$ OH^+	5.80	5.20	1.53
CH_3CH-CH_2 $\diagdown\ /$ SH^+	4.40	3.66	1.63
$(CH_3)_2C-CH_2$ $\diagdown\ /$ I^+	—	5.72	3.43
$(CH_3)_2C-CH_2$ $\diagdown\ /$ Br^+	—	5.55	3.32
$(CH_3)_2C-CH_2$ $\diagdown\ /$ OH^+	—	5.20	1.63

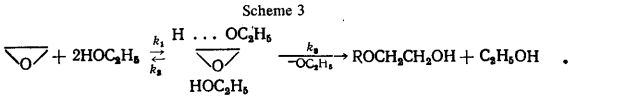
The genetic relation between the intermediates in reactions proceeding via the *Ad* mechanism has been demonstrated experimentally; Olan and Szilagy[132] established that the chemical shifts of the protons of the methylene groups in protonated epoxides and thiirans are similar to those of the cyclic halonium ions (see Table). It is easy to see that the change in the electronegativity of the heteroatom required

an increase of the chemical shifts of the methylene protons giving the following sequence: O > Br > S ≅ C > I.[133] The breakdown of this sequence can be accounted by the different directions of the shifts of electron density in the three-membered heterocycle: if the electronegativity of the heteroatom (Br, Cl, O) is greater than that of carbon, the electron shifts to a centre of the antibonding type (the carbon atom); if the heteroatom is less electronegative than carbon, the electron density of the carbon–heteroatom bond shifts in the opposite direction[99]. A second factor which distorts the sequence of the changes in the chemical shifts arising from the electronegativity series of heteroatoms, is protonation of the heteroatom.

The isotypical distribution of electron density in three-membered protonated heterocycles and in cyclic halonium ions, presupposes a close relationship between the mechanisms of the electrophilic halogenation and the opening of the epoxide rings under the influence of nucleophiles, which is shown particularly clearly in relation to coupled electrophilic reactions.

The π- or σ-complex formed in the first stage of the electrophilic addition is converted into an ether under the influence of the alcohol anion (Scheme 1);[23,24] the protonation of the epoxide under the influence of an alkoxide[124,130] or a phenoxide[126] (Scheme 3) proceeds in exactly the same way:

Scheme 3



The involvement in the transition state of the opening of the epoxide rings of at least two molecules—one proton donor molecule and one nucleophile molecule—has been confirmed by the high kinetic orders of the reactions of epoxides with phenols[126,134] and alcohols[125,135]. The high kinetic orders observed for the electrophilic addition of a halogen to an olefin ($n = 3$) [14,136] and for the coupled reaction[23,24,26] ($n \geq 3$) presuppose the formation of a trimolecular transition state via two bimolecular processes.

The identical characteristics of the charge distribution in the unstable intermediate adducts suggest the identical influence of the ionic strength of the solution on the rates of the two reactions. A positive salt effect has been noted for the opening of the epoxyethane ring under the conditions of acid catalysis[128] for the electrophilic addition of chlorine[71] or bromine[51] to a multiple bond.

The energy profiles of the reactions compared (Fig. 2) are identical[5,7,13], which permits the conclusion that the formation of the unstable oxiran–catalyst (or alcohol) adduct[124,131] is equivalent, from the standpoint of thermodynamics, to the formation of a σ- or π-complex in electrophilic halogenation. The exothermicity of the pre-reaction donor–acceptor interaction lowers the experimental apparent activation energy.

A decrease of the concentration of one of the initial reactants (Schemes 1, 2, and 3) or an increase of temperature leads to a shift of the pre-reaction equilibrium towards the initial reactants in accordance with the Le Chatelier principle, which lowers the concentration of the intermediate and the rate of the process as a whole. The inhibition of the reaction leads to the S-shape of the kinetic relation characteristic of an autocatalytic reaction[137]. Such relations, with an induction period, have been found for the reactions of epoxides with alcohols[130] and for coupled reactions[37].

The formation of cyclic halonium ions in electrophilic halogenation reactions in non-polar media inhibits the rotation about the carbon–carbon bond and increases the percentage of the *trans*-addition to the multiple bond[32,68]. In substituted epoxides, where rotation about the C–C bond is impossible, the probability of the *trans*-opening of the epoxide ring reaches 100%.[129]

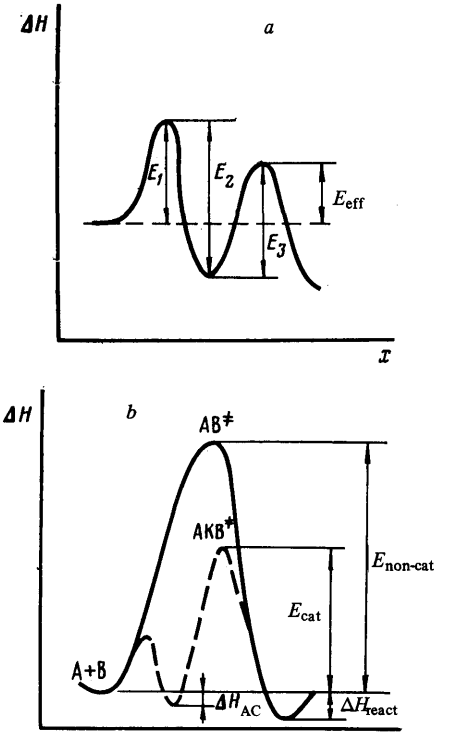


Figure 2. Variation of the potential energy along the reaction coordinate x: *a*) for the coupled halogenation of olefins:

olefin + halogen ⇄ olefin.halogen → mixed adducts / dihalogeno-derivatives;

b) for non-catalytic and homogeneous-catalytic reactions of an epoxide with alcohols:

epoxide + alcohol $\xrightarrow{\text{catalyst}}$ epoxide.alcohol.catalyst → products.
(A) (B)

V. STEREOCHEMICAL ASPECTS OF ELECTROPHILIC HALOGENATION

1. The Influence of the Structure of the Halonium Ion on the Stereochemistry of Electrophilic Halogenation

The study of the stereochemistry of the addition of halogens and hypohalites yields important information about the structure of the intermediate, the degree of ionisation, and the symmetry of the distribution of electron density between carbon atoms. In those cases where the intermediate is a typical halonium ion, the electrophilic reaction proceeds stereoselectively with the formation only of the products of *trans*-addition to the multiple bond[138]. The chlorination of butenes[21,95] and the bromination of ethylenes[21,34] can serve as examples of the stereoselective *trans*-addition.

The addition of mixed reagents, for example bromo- and chloro-acetoxylation, proceeds stereoselectively[34,139]. The stability of a cyclic halonium ion increases with increased atomic radius of the halogen; the stereoselectivity of the addition of a halogen to allyl ethers increases in precisely this sequence[21].

The increase of the degree of charge separation in the intermediate, due to external factors such as the polarity of the solvent[69,140] and the addition of salts[10], increases the probability of the formation of an "open-chain" ion and the stereoselectivity of the electrophilic addition of the halogen is then limited. An increase of solvent polarity in the bromination of *cis*-β-methylstyrene in the series from carbon tetrachloride to nitrobenzene reduces the percentage *trans*-addition from 70 to 45%; for *trans*-β-methylstyrenes, the effect of the change in solvent polarity is less pronounced (71% *trans*-addition for dioxan and 82% for nitrobenzene).[68]

The positive salt effect observed in the electrophilic addition of a halogen was discussed above[57]; the addition of an electrolyte alters not only the reaction rate constant but also the stereoselectivity of the process. The ability of the salt to stabilise the solvate-separated ion pair as a result of electrostatic interaction increases the probability of rotation about the carbon–carbon bond and infringes the stereospecificity of the electrophilic addition of a halogen to a multiple bond. In the chlorination of acrylic acid derivatives the yield of the *trans*-addition product is reduced by 30–35% in the presence of added $LiClO_4$.[9-11] In those cases where the electrophilic addition of a halogen in non-polar media proceeds with participation of a close ion pair, the influence of added electrolytes on the stereochemistry of the addition reaction should be minimal[32,68].

The comparatively simple postulates explaining the proportions of the *cis*- and *trans*-addition of a halogen to a multiple bond are distorted when the molecular reaction pathway is accompanied by a significant contribution by the radical non-stereospecific pathway[141], which is especially characteristic of reactions involving chlorine[142,143]. In the chlorination of *trans*-but-2-enes the contribution of the radical reaction increases as the olefin concentration is reduced and the number of alkyl substituents in the olefin is decreased[94]. The probability of the radical reaction changes in the sequence which is the opposite of that based on the stabilities of cyclic halonium ions (Cl > Br > I); for the addition of bromine to a multiple bond, the contribution of the free-radical reaction pathway is small[144].

In connection with the difficulty of determining the angle of rotation in the intermediate, which is rapidly converted into the reaction products, the stereochemistry of the electrophilic addition of a halogen to the multiple bonds of acyclic compounds, where rotation in the intermediate labile complex is impossible, acquires particular importance[72,145]. The interaction of chlorine with unsubstituted cyclohexene proceeds stereoselectively[72], while the addition of chlorine to acenaphthylene and phenanthrene results in a mixture of stereoisomers[72]. The absence of a definite stereospecificity for the electrophilic addition of chlorine to a multiple bond can be explained by the contribution of a free-radical process, which has been confirmed by the detection in the reaction mass of different amounts of radical-substitution products[145,146]. The principle, according to which an increase of the reactivity of the reagent reduces the selectivity of the reaction, holds for the electrophilic addition of a halogen to unsaturated acyclic compounds[147].

The high absolute rates preclude at the present time the estimation of the relative rates of rotation in the open-chain ion and of the addition of a halogen to the intermediate cation, but it is possible to estimate the thermodynamic parameters of these two processes. The thermodynamic parameters of the electrophilic reaction involving the geometrical isomers of olefins have been compared[57,68,148,149] with the enthalpies of their *cis*–*trans* isomerisation, estimated as differences between the heats of combustion of the *cis*- and *trans*-isomers. It is postulated[148] that, when the activated complex resembles an "open-chain" ion, the interaction of bulky alkyl substituents at the sp^3- and sp^2-hybridised atoms of the intermediate will be weakened as a result of the rotation; the difference between the enthalpies of the electrophilic halogenation of *cis*- and *trans*-isomers will then decrease relative to the enthalpies of isomerisation of the same geometrical isomers. In those cases where the activated complex has the structure of a halonium ion the steric influence of the bulky substituents is more pronounced; the difference between the enthalpies of the electrophilic addition reactions involving geometrical isomers therefore increases compared with the enthalpy of their isomerisation. The energy profiles of the bromination reactions of *cis*- and *trans*-stilbenes (Fig.3) show that the enthalpy difference in the transition state is greater than in the initial state, which corresponds to a cyclic bromonium ion and not an open-chain ion[148].

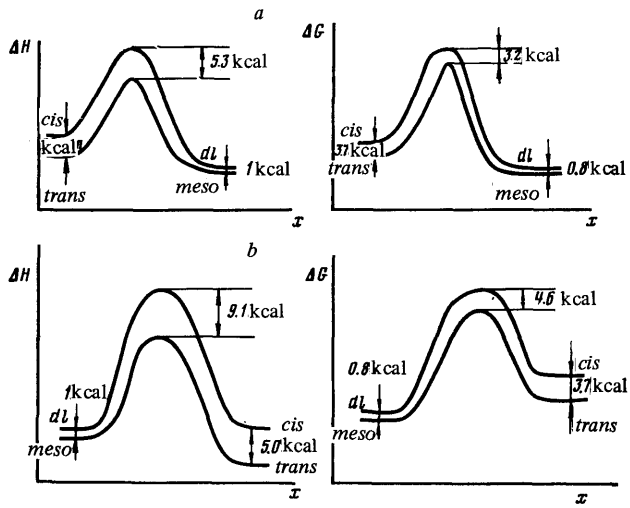


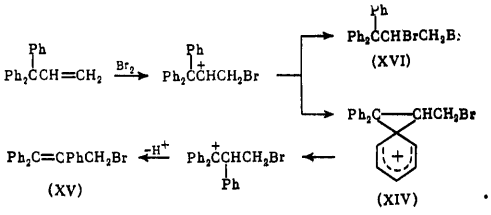
Figure 3. Variation of the enthalpy and free energy along the reaction coordinate for the bromination of *cis*- and *trans*-stilbenes in acetic acid[148] (*a*) and for the debromination of *dl*- and *meso*-stilbene dibromides in dimethylformamide catalysed by lithium bromide[151] (*b*).

Examination of the nature of the variation of the enthalpy along the reaction coordinate explains the higher rate constant for the electrophilic reaction involving the *trans*-olefins than for the *cis*-olefins, usually observed, since the potential barrier to the latter reaction is greater (Fig.3*a*) than the barrier to the former[69,138,150]. The difference between the energetic parameters of the electrophilic addition reaction agrees satisfactorily with the difference between the enthalpies of the debromination of the *dl*- and *meso*-dibromo-derivatives in dimethylformamide (Fig.3*b*) which apparently also proceeds via a stage involving the formation of a bromonium ion[151–153].

The joint study of the thermochemistry, kinetics, and stereochemistry of the addition of a halogen to the *cis*- and *trans*-isomers of an olefin yields the most complete information about the structure of the intermediate species.

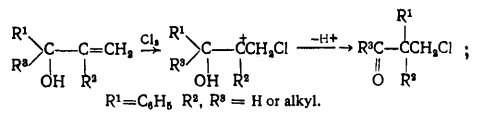
2. The Effect of the Involvement of Neighbouring Groups

The introduction of several substituents at one carbon atom alters the charge distribution in the intermediate[154], infringes the additivity of the influence of the substituents[155-158], and causes additional stabilisation of the charge on the cationic centre[159,160] due to interaction with the electron-donating groups located at the α-atoms of the carbon chain, which permits the migration of one of the substituents to an unsubstituted carbon atom of the olefin[161,162]. A characteristic example of the rearrangement of the carbon skeleton is the migration of the arene ring on bromination of 3,3,3-triphenylpropene[161]:



The presence of unduly bulky substituents at the carbon atom in 3,3,3-triphenylpropene, together with the stabilisation of the charge on the intermediate cation in the reaction with bromine, permits a direct interaction of the carbonium centre with one of the benzene rings. The intermediate phenonium ion has much in common with halonium ions; thus, when the reaction is carried out in methanol, a mixed adduct, incorporating the solvent, is obtained, apart from the rearrangement of product (XV) and the dibromide (XVI), as in other electrophilic reactions[161]. The bromination of 4-allylanisole leads to the formation of a mixture of a dibromide and a rearranged product, which are formed via two parallel pathways with participation of the bromonium and phenonium ions respectively[163]. The substitution of the benzene rings in 3,3,3-triphenylpropene with methyl groups increases the steric hindrance and makes the addition of a second bromine atom to the double bond more difficult; only the rearranged product is isolated from the reaction mixture in this case[161].

The reaction of olefins containing alkyl substituents proceeds in a more complex and more ambiguous manner[162,164,165]. The reactions of alkenylalkylphenylmethanols with halogens and hypohalites have been studied in greatest detail[166-168]:

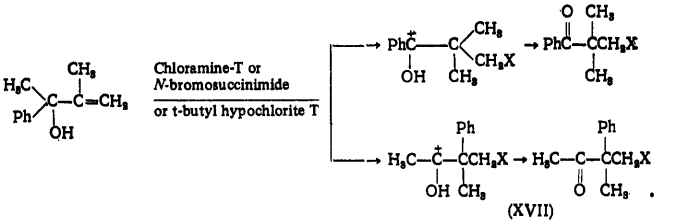


$R^1 = C_6H_5$; R^2, R^3 = H or alkyl.

In the case of acyclic compounds the rearrangement of the carbon skeleton proceeds with ring expansion[169,170]. Thus, for triphenylethylenes[161] in methanol, not only rearranged products and dihalides but also mixed products incorporating the solvent are formed[164,171,172].

The probability of the rearrangement of the halonium ions increases in the sequence Cl << Br < I;[173] the degree of stabilisation of the intermediates in the electrophilic addition reaction increases in precisely the opposite sequence[107].

The degree of delocalisation of the positive charge of the carbonium centre can increase under the influence of electron-donating substituents introduced into the migrating ring, which increases the rate of rearrangement[174]. In order to compare the stabilities of the phenonium, chloronium, and bromonium ions, Kartashov and Bodrikov[173] investigated the rearrangement of isopropenylmethylphenylmethanol under the influence of different agents:



(XVII)

A change in the nature of the halogenating agent does not alter the ratio of the reaction products: in all cases the ketone (XVII)—the product of the migration of the phenyl group—predominates, i.e. the interaction of the positively charged carbonium ion with the aromatic ring is more effective than the interaction with the unshared electron pair of the halogen atom; thus the phenonium ion is more stable than the chloronium or bromonium ion[173].

With decrease of solvent polarity as a result of the destabilisation of the positive charge in the intermediate, the rate of rearrangement increases[175]. Special experiments have shown that the competing reactions—rearrangement, substitution, or addition—are parallel pathways leading to the conversion of the intermediate halonium and phenonium ions[163,176] and that the thermodynamic parameters (enthalpy and entropy) of the rearrangement of the carbon skeleton[177] are similar to those usually observed for the electrophilic halogenation of olefins[178].

VI. THE ELECTROPHILIC PROPERTIES OF THE REACTION CENTRES OF THE INTERMEDIATE

The mode of addition of anions to the halonium ion arising in the intermediate stage of an electrophilic kinetically controlled reaction is determined by the relative electrophilicity of each atom of the intermediate. The reactivity of the latter depends on the basicity and polarisability of each carbon atom of the unstable intermediate and on the electronic nature of the substituents in the α-position relative to the multiple bond[4]. It is impossible to determine independently the basicities and polarisabilities of each reaction centre, because the two atoms are linked into a mesomeric system. The lack of quantitative characteristics necessitates the use of qualitative estimates for each electrophilic atom of the intermediate; Pearson's principle of hard and soft acids and bases (HSAB) [179-183] is most convenient for this purpose. Pearson's empirical principle has been explained on the basis of the quantum theory, where its fundamental concepts (softness and hardness) are related to the different energies of the highest occupied and lowest vacant orbitals[184].

The application of the HSAB principle is particularly effective when the relative amounts of the isomeric products of electrophilic addition to a multiple bond are considered. With increase of the number of methyl substituents at the carbon atom in the series ethylene, propene, isobutene[144,185], the hardness of the cationoid centre increases with a simultaneous increase of the amount of the mixed adduct involving methanol, because the latter is a harder reagent

than the bromide anion. The relative amount of the bromomethoxyalkane varies as a function of the degree of substitution, increasing from 38% for ethylene to 84.7% for isobutene[185]. The degree of formation of mixed adducts increases similarly in the chlorination of olefins in acetic acid[181] and methanol[187].

The addition of the elements of a hypohalite to allyl chloride can also be explained on the basis of the HSAB principle: the hardest reagent (the alkoxide anion) is coordinated to the hardest central atom of the allyl chloride molecule[188-191]. The study of the products of the addition of chlorine and acetate to allyl chloride and hexane showed that the amount of adducts formed in accordance with the Markovnikov rule decreases from 77.5 to 67%, which reflects the increase in the hardness of the carbon atom in the allyl chloride molecule[18].

Pearson's principle can be applied no less successfully when the influence of the solvent is considered; when solvent polarity varies in the sequence carbon tetrachloride < methylene chloride < methanol, the degree of charge separation in the intermediate increases and hence there is an increase in the tendency towards reactions with the harder reagent—an alcohol[190], an acid[17,95], an epoxide[188,189], or a β-oxide[63] rather than a halide anion.

The joint influence of several factors varying simultaneously is more difficult to interpret on the basis of the HSAB principle; thus, when the methyl group of propene is substituted by the benzene ring, the polarisability and hence softness of the carbon atom increase. Nevertheless, in polar media such as acetic acid[95,139,192] and alcohols[122,185] the preferential coordination of the α-phenyl-substituted atom of 1-phenylprop-1-ene to the hard base is observed and mixed adducts are formed; this can be explained by the considerable charge separation in the intermediate under the influence of the polar solvent, which increases the hardness of the system as a whole.

In all cases examined above the factors increasing the hardness and reducing the polarisability of the intermediate lead to the formation of mixed adducts in the electrophilic reaction rather than dihalides.

On the whole, one can conclude that the pre-reaction equilibrium stage in the addition of a halogen to a multiple bond is characteristic of all electrophilic halogenation processes without exception. The structure of the intermediates in the electrophilic halogenation reaction requires further refinement. The low-temperature infrared and NMR spectroscopic methods are the most promising for the solution of this problem. Another important task in the study of the mechanism of the electrophilic reaction is estimation of the partial constants for the multistage process. A detailed investigation of the mechanisms of the electrophilic addition of a halogen to a multiple bond is undoubtedly important for the development of ideas concerning electrophilic reactions.

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