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Molecular Complexes in the Liquid-phase Halogenation of Unsaturated Compounds

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Results on the halogenation of unsaturated compounds in the liquid phase are discussed. The possibility is examined that molecular complexes are involved in the polar, molecular, and radical mechanisms of addition. A list of 151 references is included.

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I. INTRODUCTION

Reactions involving the addition of halogens at a multiple bond are important because of their wide distribution and their practical value. The electrophilic addition of halogens at a double bond was surveyed in a monograph [1]. A large amount of factual information has accumulated in recent years, and has been interpreted mainly on the basis of an ionic mechanism. Nevertheless, the existence of halogen–alkene molecular complexes and of complexes of halogens with several compounds used as solvents has been demonstrated experimentally. The role of such complexes in the mechanism of the halogenation of multiple bonds has not been finally established.

The Review analyses, mainly from an energetic point of view, the possibility that complexes are involved in polar, molecular, and radical mechanisms of the liquid-phase halogenation of unsaturated compounds.

The view that carbonium ions of varied structures were reaction intermediates was based on the work of Francis [2] and Roberts and Kimball [3]. The importance of the role of donor–acceptor interactions in reaction mechanisms was noted by Shilov [4,5]. Dewar developed the concept of π-complexes [6]. The theory of charge-transfer complexes was formulated by Mulliken [7].

The structure, physicochemical properties, and methods of studying molecular complexes in systems in which no appreciable chemical reaction is occurring have been

discussed in monographs [8-10]. The formation of halogen–alkene complexes is accompanied by a chemical change in the components, and therefore is especially interesting. The role of molecular complexes in the halogenation of unsaturated compounds has been partly considered in reviews [5,11-13].

II. MOLECULAR COMPLEXES OF HALOGENS WITH ALKENES

Molecular complexes of halogens with alkenes have been investigated mainly spectrophotometrically [14-18]. Charge-transfer bands appear in the spectra when halogens (acceptors) interact with alkenes (donors). The complexes absorb in the range 240–320 nm in the ultraviolet. The charge-transfer band $h\nu$ is related to the ionisation potential I_V of the alkenes by the equations [15] $h\nu(Br_2) = 0.69I_V - 2.09$ and $h\nu(Cl_2) = 0.51I_V + 0.03$.

Table 1. Enthalpies ΔH and equilibrium constants K_C of alkene–halogen complexes in non-polar solvents.

Alkene	I_2		Ref.	Br_2		Ref.	Cl_2		Ref.
	$-\Delta H$, kcal mole^{-1}	$K_C^{298°}$, M^{-1}		$-\Delta H$, kcal mole^{-1}	$K_C^{298°}$, M^{-1}		$-\Delta H$, kcal mole^{-1}	$K_C^{298°}$, M^{-1}	
Hex-1-ene	2.8	0.20	19	3.3	0.145	19	1.7	0.24	17
Cyclohexene	2.3	0.52	18	4.0	0.36	16	2.7	0.33	17
4-Methyl-pent-1-ene	3.3	0.24	19	2.8	0.33	19	—	—	
Hept-3-ene	4.0	0.72	19	4.0	—	19	—	—	
Cyclopentene	2.8	0.43	18	—	—		—	—	
Styrene	2.1		20	—	—		—	—	
trans-Stilbene	1.8	—	20	—	—		—	—	
	2.6								

Inadequate study has been made of the complexes of halogens with alkenes, owing to the experimental difficulties involved in investigations in the reacting systems. Table 1 summarises experimental results on the thermodynamic functions of the complexes of reactive alkenes with halogens. Data have been published also on the complexes of cyclohexene with iodine bromide ($\Delta H = -7.5$ kcal mole^{-1} and $K_C^{298°} = 2.2$ M^{-1}) [16] and of hex-1-ene with iodine chloride (-1.5 kcal mole^{-1} and 2.0 M^{-1}) [19].

Table 1 shows that halogens form weak complexes with alkenes, characterised by low equilibrium constants ($K_C < 1$) and enthalpies of formation ($|\Delta H| < 5$ kcal mole^{-1}). The latter values are comparable with the activation energies of many halogenations of alkenes, and may make an appreciable contribution to the energetics of the process.

Table 2 lists data on the structural and physicochemical properties of the halogens.

Scheme 1 shows the mechanism of the reaction of halogens with alkenes [12]. Initially an internal ion-pair, analogous to Dewar's π-complexes [6] or to σ-complexes in aromatic substitution [23], is formed from a labile halogen–alkene π-complex or directly from the original molecules. This complex then rearranges into the reaction products or else breaks down into solvated ions, whose interaction results in formation of the product. In the termolecular reactions characteristic of the addition of bromine and iodine the anion X^- is replaced by X_3^-. The rate of the reaction is governed by the passage of the system through the transition states (II) (ionisation) and (IV) (separation or migration of the ions in the ion-pair).

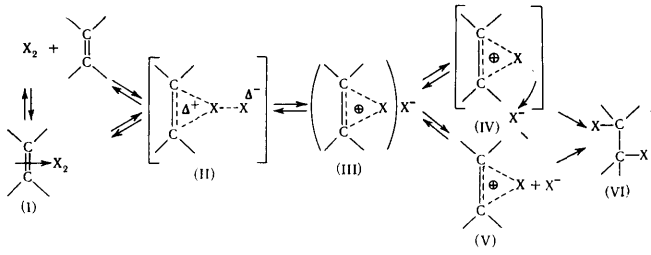
Let us examine the rôle of halogen–alkene complexes (I) in formation of the transition state (II) under conditions such that the contribution by solvation effects can be neglected. This transition state (II) may be established both by collision of activated X_2 molecules with the unsaturated compound and by charge redistribution in the molecular complex (I). The latter follows from a comparison of structures (I) and (II).

Table 2. Some physicochemical properties of halogens [21,22].

Mol.	Internuclear distance, Å	Anionic radius, Å	Dissociation energy at 298°K, kcal mole^{-1}	Electron affinity	
				mol., eV	atom, eV
I_2	2.667	2.20	36.1	2.4	3.29
Br_2	2.283	1.81	46.1	2.6	3.54
Cl_2	1.998	1.06	57.9	1.70	3.76
ClI	2.321	—	50.5	—	—
BrI	—	—	42.5	—	—

Changes occur mainly in two distances—from the halogen molecule to the centre of the double bond rC–X and between the nuclei in the halogen—as the molecule approaches the double bond with formation of an ion-pair.

Scheme 1.



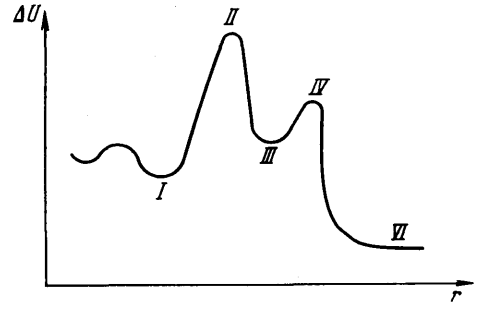


Figure 1. Variation in potential energy along reaction path of heterolytic halogenation.

The former distance rC–X changes from infinity to the halogen–double bond distance in the carbonium ion. The internuclear distance X–X in the bromine molecule, for example, is < 2.3 Å. The X–X distance in the ion-pair can be estimated as the sum of the radii of the negative

ion and of the uncharged atom. For bromine this sum is 3.1 Å, which exceeds the internuclear distance in the molecule by 0.8 Å. Since these distances are the chief variables on formation of an ion-pair, the potential-energy surface of the system can be plotted with r_{C-X} and r_{X-X} as coordinates. The distance r_{C-X} is shorter in the complex than in the initial molecules. X-Ray diffraction has established that the formation of complexes involving halogens leads to some increase in the internuclear distances in the latter molecules[24,25]. Thus

$$(r_{X-X})_{init} < (r_{X-X})_{complex} < (r_{X-X})_{transn.\ state},$$

$$(r_{C-X})_{init} \gg (r_{C-X})_{complex} > (r_{C-X})_{transn.\ state}.$$

Hence the π-complex lies on the reaction path between the initial molecules and the transition state. It can be shown similarly that the σ-complex (internal ion-pair III) also lies on the reaction path between (II) and (IV).

Thus application of the transition-state theory to polar halogenation indicates that halogen-alkene complexes may be involved as intermediate species. Fig. 1 illustrates the variation in the potential energy along the reaction path.

III. POLAR MECHANISM

The energy barriers at individual stages in Scheme 1 can be estimated by means of a model involving electrostatic interactions.

The potential barrier (II) in Scheme 1 is connected with ionisation of the molecular complex. This process is analogous to complete electron transfer from donor to acceptor with energy equal to the difference between the ionisation potential of the donor and the electron affinity of the acceptor. The energy of Coulombic attraction between the oppositely charged ions is gained.

Formation of a bridging halogenonium cation of the type



is accompanied by partial dehybridisation of the double-bonded carbon atoms and the appearance of incompletely covalent C–X bonds. Quantum-mechanical calculation of the relative stabilities of ions differing in structure enables the contribution of these two factors to be estimated[26]. With ethylene, chloronium and bromonium bridges are more stable than the corresponding classical carbonium ions of type



by 28.4 and 26 kcal mole^{-1} respectively. The carbonium ion involves complete rupture of the double bond and formation of a C–X bond, and the heat of reaction can be estimated as the difference between the corresponding energy changes. Adding 28.4 or 26 kcal mole^{-1} to the result yields the stabilisation energy of the ion E_{st} due to formation of new bonds. Depending on the alkene E_{st} = 45–49 and 31–35 kcal mole^{-1} for chlorine and bromine respectively. On the assumption that an iodonium bridge is 20 kcal mole^{-1} more stable than the open system we obtain $E_{st} \simeq 7$–11 kcal mole^{-1}.

Thus the energy of the system during conversion of the π-complex into an ion-pair is described by the formula

$$U = e(I - E_x) - \sum_{ij} \frac{e_i e_j}{r_{ij}} - E_{st} \qquad (1)$$

where I is the ionisation potential of the donor, E_X the electron affinity of the acceptor, r_{ij} the distance between the centres of i and j atoms bearing charges e_i and e_j respectively, $e = \Sigma e_i$ the total transferred charge, and E_{st} the stabilisation energy of the carbonium cation, which depends on the fraction of the charge transferred. Quantum-mechanical calculation of the structures of ethylene–chloronium and ethylene–bromonium cations shows that up to 30–40% of unit positive charge is concentrated on the halogen atom[26,27]. Hence the charge is uniformly distributed among all the vertices of the triangle. Calculations indicate[26] that the radius of the halogen atom in the cation can be regarded as equal to its covalent radius. Formula (1) can be used to estimate the heat of transition of the complex into the ionised state. In the series of complexes of chlorine, bromine, and iodine with ethylene, hex-1-ene, and cyclohexene the iodine–ethylene ion-pair had the largest heat of formation, and chlorine–cyclohexene the smallest (110 and 30 kcal mole^{-1} respectively).

The heat absorbed on complete charge transfer is not necessarily identical with the activation energy. The first term in Eqn. (1) varies linearly with the amount of charge transferred, and the second term is a quadratic function, so that $U(e_i, r_i)$ may reach a maximum even with incomplete charge transfer. This implies that partial transfer of the electronic charge may prove sufficient in the reactive systems, and further charge separation requires no further energy consumption, but occurs readily as a spontaneous process. The degree of charge transfer at which the potential energy reaches a maximum can be estimated by means of Eqn. (1). If we suppose that internuclear distances cease to depend on the degree of ionisation at charge transfers exceeding $0.5e$, we can then find the value of x corresponding to U_{max} from the condition for a maximum $dU/dx = 0$ (where x is the degree of transfer).

Table 3. Activation energies (kcal mole^{-1}) of formation of ion-pairs.

Alkene	Halogen		
	Cl	Br	I
Ethylene	69	73	110
Hex-1-ene	48	50	84
Cyclohexene	39	40	70

Specific values for I, E_X, E_{st}, and r_{ii} yield values for x_{max} from 0.6–0.7 (cyclohexene and hexene with chlorine) to 1.0 (systems containing iodine and ethylene–bromine). From the values of x_{max} we can calculate U_{max}, i.e. the activation energy of formation of ion-pairs. The results listed in Table 3 exceed those obtained on the basis of a four-membered transition state and the postulate that formation of a hemi-ionic pair is sufficient for reaction[28]. The values in Table 3 give the correct sequence of reactivity for the halogens $Cl_2 > Br_2 \gg I_2$,[1] whereas the opposite sequence was obtained in Ref. 28.

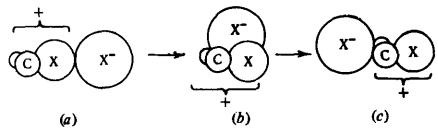
Considering now the probable structure and energetics of the σ-complex, we note that an ion-pair with a linear arrangement of the atoms

$$\overset{\oplus}{>}X....X^-$$

is in a state of unstable equilibrium. Any displacement of

the anion X^- from the plane of the cyclic cation in the direction of the double bond involves a gain in energy. In the stable state of the ion-pair the halide anion is situated above the plane of the carbonium cation, the C–X and X–X distances being minima (Scheme 2).

Scheme 2.



Structure (*b*) is also a σ-complex, the gain in energy on its formation from the unstable ion-pair (*a*) being the depth of the potential well (III) in Fig. 1). To estimate this gain we assume that the radii of atoms and ions in (*a*) and (*b*) are identical. Calculation of the energy of electrostatic attraction in (*b*) shows that (*a*) and (*b*) differ in energy by 38–42 kcal mole^{-1} for all the halogens.

In the last stage of the reaction the anion X^- again passes into the plane of the carbonium cation, but from the side opposite to the second atom (structure *c*). The height of the potential barrier to the transition (*b*) → (*c*) can be estimated as the difference between the Coulombic energies of attraction. Calculation shows it to be small, from 8 to 12 kcal mole^{-1} for iodine and chlorine respectively. Hence it may be expected that the σ-complex will pass readily into the product. The situation is different if this change is impeded, e.g. by steric hindrance. In fact stable complexes, having the character of internal ion-pairs, are formed by the interaction of bromine with sterically hindered alkenes at −78°C [29]. The above estimates show that the limiting step in the reaction is ionisation of the π-complex with formation of an ion-pair (σ-complex).

Table 4. Calculated activation energies (kcal mole^{-1}) in solutions.

Dielectric constant of solvent	Reactants								
	ethylene			hex-1-ene			cyclohexene		
	Cl_2	Br_2	I_2	Cl_2	Br_2	I_2	Cl_2	Br_2	I_2
2.2	39	40	64	28	28	47	22	22	38
4.5	33	35	54	24	25	38	19	20	33
8.0	31	31	51	22	23	36	16	18	30
20.0	28	28	49	18	20	34	15	16	28

1. Effect of Non-specific Solvation on Reaction Velocity

When a polar reaction takes place in a solvent of dielectric constant ε and incapable of specific solvation either of the starting materials or of the transition state, the ion-pair can be regarded as a dipole, and its energy of non-specific solvation can be estimated by means of Kirkwood's formula. We assume that the length of the dipole is the distance between the centre of the anion and the geometric centre in the carbonium cation. The radius of the dipole is the mean of the dimensions of the ion-pair parallel and perpendicular to the axis of the dipole. Solvation energies may reach several tens of kilocalories. Thus the consumption of energy required for ionisation should be appreciably smaller in the liquid phase than in the gas. The potential energy reaches its maximum value with incomplete charge transfer, as in the gas phase. We can find U_{max} by adding in Eqn. (1) a solvation term calculated by means of Kirkwood's formula. The estimated activation energies are given in Table 4.

In sufficiently polar solvents the difference between the activation energies of (*a*) and (*b*) (Scheme 2) plays no appreciable part, and the potential barrier (IV) should not be very high. Traversing the barrier, the reaction system forms the product by continuous passage of the halide anion to the side of the double bond opposite that on which the second X atom is located. Fig. 2 shows the change in the potential-energy profile on passing from the gas phase to a solvent having ε = 8 (for the reaction of chlorine with hex-1-ene). The activation energies for bimolecular polar reactions should be a few tens and 10–20 kcal mole^{-1} in media of low and high dielectric constant respectively.

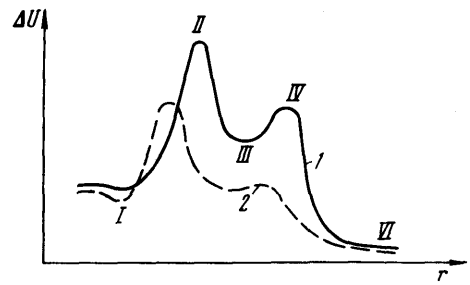


Figure 2. Variation of potential energy along reaction path of hex-1-ene with chlorine in: 1) gas phase; 2) solvent of dielectric constant 8.

The polar character of transition states and intermediate species in halogenation has been confirmed for several alkenes in various solvents by measuring the electrical conductivity during bromination [30]. The conductivity is determined by the degree of charge separation established in the alkene–halogen system. The effect of the solvent varies in parallel with its dielectric constant and its ability to solvate polar and ionic species. Alkenes form a sequence according to their reactivity towards bromination. The conductivity is small in carbon tetrachloride, phenyl bromide, and chloroform, which indicates the absence of ionic states.

The rate of bromination of pent-1-ene has been investigated in water, alcohols, acetic acid, dioxan, Freon, aqueous methanol, and other solvents [31,32]. The second-order rate constant varies widely, from 0.07 to 1.5×10^{-9} M^{-1} min^{-1} in Freon-113 and water respectively. It increases with the dielectric constant of the medium, and is given by the equation $\lg k = 5.40 - 1.164 \lg (k_S/k_0)$, where k_S and k_0 are the solvolysis rate constants for t-butyl chloride at 25°C in the given solvent and in 80% aqueous ethanol respectively.

A qualitative correspondence between the rate constant and the dielectric constant of the medium has been established[33] for the bromination of octene, vinyl acetate, and certain other unsaturated compounds. Direct proportionality of the rate constant to the dielectric constant of the medium was observed also in the chlorination of 3-chloro-1-phenylprop-1-ene in benzene to which more polar solvents had been added[34]. Rates of bromination in a 70:30 methanol–water mixture at 25°C may vary by factors of $\sim 10^4$ depending on the structure of the unsaturated molecule. On passing to methanol itself the rate falls roughly equally for all alkenes, in conformity with the equation $\lg k_{mixt} = 2.6 + 0.9 \lg k_{CH_3OH}$, which suggests that the reaction mechanism remains unchanged[35].

No systematic study has been made of the effect of the dielectric constant of the medium on the activation energy of halogenation. In the bromination of certain aliphatic alkenes in water E_{act} = 8–11 kcal mole^{-1}.[36] The activation energy for the bromination of 1,3-alkenynes in acetic acid varies from 3 to 8.5 kcal mole^{-1}.[37] The bromination of styrene in acetic acid has activation enthalpies of 8–11 kcal mole^{-1} and negative entropies of activation of 27–33 kcal mole^{-1} deg^{-1}.[38] The bimolecular bromination of cinnamic acid in methanol has an activation energy of 9.2 kcal mole^{-1},[39] and 6.1 kcal mole^{-1} is required for the bromination of allyl acetate in acetic acid[40]. The activation energy for the bromination of various alkenes in methanol varies from 7 to 11 kcal mole^{-1}.[41] The activation energies for the chlorination of allyltrimethylammonium perchlorate and 2,3-dichloropropene in acetic acid are 7.4 and 11.2 kcal mole^{-1} respectively[42].

Thus activation energies in polar media vary in the range 5–15 kcal mole^{-1}. This corresponds to the above estimates for a polar mechanism with the rate constant depending on the polarity of the medium.

The ionisation potential is a component of the activation energy and, according to the reaction mechanism assumed (Scheme 1), determines the reactivity of the alkene in the polar medium. A linear dependence of the logarithm of the rate constant on the ionisation potential may be expected in polar media.

2. Dependence of Reaction Velocity on Structure of Alkene

The dependence of the rate of bromination on the structure of the alkene is summarised in the form of correlation equations. Those containing the Taft σ^* [43] and Brown σ^+ [44] parameters are of the form (Table 5)

$$\lg k = \rho \sum \sigma + \text{const}. \qquad (2)$$

A term proportional to the sum of the steric parameters ΣE_S is sometimes detached from the constant in Eqn. (2) [46,47].

Table 5 shows that the parameters ρ have negative values typical of electrophilic reactions. These yield certain conclusions as to the structure of the transition state. Large negative values of ρ probably indicate considerable separation of charges in the transition state with polar solvents. The rate of bromination of tetrasubstituted alkenes correlates with the sum of the Taft σ^* parameters. This suggests that the positive charge in the transition state is uniformly distributed between the two carbon atoms, so that bromination of these compounds involves an intermediate structure of the bridged cation type[46]. As the agent becomes less electrophilic, e.g. on passing from Br_2 to Br_3^-, the value of ρ decreases. The corresponding values for the bromination of substituted stilbenes in acetic acid are −4.21 and −2.02.[52] Correlation equations for chlorination have been obtained only in Ref. 54.

Correlation equations have been published also linking the reaction velocity with parameters other than σ. A linear relation has been found between Γ, representing the electrostatic energy of the halogen–alkene complex in the excited state, and the rate constant for bromination in water: $\Gamma = b + a \lg k_2$.[15] The parameter Γ in turn correlates with the ionisation potential of the alkene: e.g. for bromine complexes $\Gamma = 0.31 I_V + b'$.

Table 5. Correlation equations for liquid-phase polar halogenations.

Alkenes	Halogenating agent	Solvent	Equation	Ref.
RCH = CHR′R″ (R, R′, R″ = alk)	Br_2	MeOH	$\lg k = -5.299\,\Sigma\sigma^* + 0.914\,\Sigma E_s + 7.414$	45
RR′C=CR″R‴ (R, R′, R″, R‴ — Alk)	Br_2	MeOH	$\lg k = -5.221\,\Sigma\sigma^* + 0.896\,\Sigma E_s + 7.381$	46
$CH_2 = CH - CH_2X$ (x = Alk, OH^-, Ph, Cl)	Br_2	MeOH	$\lg k = -3.10\,\Sigma\sigma^* + 8.8$	47
$CH_2 = CH - CHXX'$ (X,X = Alk)	Br_2	MeOH	$\lg k = -2.99\,\Sigma\sigma^* + 7.61$	48
(X,X′ — CH_2OH, CH_2Cl, CH_2OEt)	Br_2	0.2 M NaBr	$\lg k = -2.4\,\Sigma\sigma^* + \text{const}$	50
$X - C_6H_4 - CH = CH_2$ (X = Various solvents)	Br_2	ditto	$\lg k = -4.3\,\Sigma\sigma^* + \text{const}$	49
(X = Hal, NO_2)	Br_2	MeCOOH	$\lg k = -4.71\,\Sigma\sigma^* + \text{const}$	53
(X = Hal, NO_2)	Br_2	MeCOOH	$\lg k = -4.21\,\Sigma\sigma^* + \text{const}$	52
(X = Hal, NO_2)	Br_3^-	MeCOOH	$\lg k = -2.02\,\Sigma\sigma^* + \text{const}$	52
$R - C_6H_4 - CH = CH - Ph$	Br_2	MeOH 0.2 M NaBr	$\lg k = -1.53\,\Sigma\sigma^+ + \text{const}$	51
(R = Acceptor) (R = Donor)	Br_2	ditto	$\lg k = -5.05\,\Sigma\sigma^+ + \text{const}$	51
$CH_2 = CH - C \equiv C - R$ (R = Alk)	Br_2	MeCOOH	$\lg k = -1.35\,\Sigma\sigma^* + \text{const}$	37
$X - C_6H_4 - C \equiv CH$	Br_2	MeCOOH	$\lg k = -5.17\,\Sigma\sigma^+ + \text{const}$	40
RR′C = CH — COOH	Cl_2	MeCOOH	$\lg k = -5.5\,\Sigma\sigma^+ + \text{const}$	54
$R - C_6H_4 - CH = CH -$ —COOH	Cl_2	MeCOOH	$\lg k = -3.9\,\Sigma\sigma^+ + \text{const}$	54

A linear relation has been established also between this parameter and $\Sigma\sigma^*$.[55] If two quantities are linearly related to a third, the relation between them is also linear. The application of this principle to the linear relationships involving free energy was discussed in Pal'm's monograph[56]. In the case of halogenation the principle implies that the above correlation equations represent the dependence of the rate of reaction on the ionisation potential of the alkene. The ionisation potential in turn determines the properties of the halogen–alkene molecular complexes. In this sense the correlation equations in Table 5 can be regarded as indicating a connection between reaction velocity and the properties of the complex.

3. Halogenating Agents in Polar Media

The reactivity of the halogens increases in the sequence $I_2 < Br_2 < Cl_2$. This differs from the sequence of increasing electron affinity (Table 2) and also from that of the increase in acid strength of the halogens ($I_2 > Br_2 > Cl_2$). Table 6 lists parameters representing the acidity of the halogens—free energies of formation of the corresponding trihalide ions ΔG, [57] the $X^- + X_2 \rightleftharpoons X_3^-$ equilibrium constants $K_{eq}(X_3^-)$ in sulpholan [58], and the equilibrium constants for forming the molecular complexes with benzene $K_{eq}(C_6H_6X_2)$. [59]

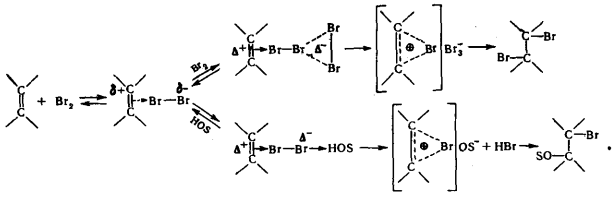
Table 6. Acidity parameters of halogens [57-59].

Hal	$-\Delta G$, kcal mole^{-1}	$K_{eq}(X_3^-)$ in sulpholan, M^{-1}	$K_{eq}(C_6H_6X_2)$, mole fractions
I_2	3.89	$10^{7.4}$	1.72
Br_2	1.67	$10^{2.8}$	1.04
Cl_2	−2.70	$10^{2.1}$	0.33

The reactivity sequence of the halogens can be explained by the participation of their cations in the reaction. The latter become more strongly electrophilic on passing from iodine to bromine and then to chlorine. The view has hitherto been held that X^+ ions act as halogenating agents in the reaction [60], but kinetic investigations have made the existence of such species improbable [61,62]. This conclusion is supported by a review on halogen cations [63]. Only cations of composition from X_2^+ to X_7^+ can exist in strongly acid media. Thus, in the absence of external additions, the only possible halogenating agents are the halogen molecules.

The reactivity of a halogen is determined by its electron affinity and molecular size. Increase in the latter weakens the Coulombic forces of attraction and prevents solvation of the transition state. The most favourable combination of these factors (Table 4) occurs with chlorine, and the least favourable with iodine. These conclusions are consistent with the observed reactivity sequence of the halogens.

The non-radical liquid-phase addition of chlorine is described by a second-order kinetic equation. Bromination in water and in methanol is also represented by a bimolecular equation, but in acetic acid third-order kinetics is observed. A termolecular equation applies in less polar media. Iodination in the absence of catalysts has a total order of three or four [1,64]. With chlorine reaction takes place readily in polar media by a simple bimolecular scheme, and does not require the action of a third particle. With bromine and especially iodine a second halogen molecule or a molecule of a hydroxylated solvent HOS is required. The gain in energy due to delocalisation of the negative charge on these particles lowers the activation energy and facilitates the reaction:



Addition of halide and other anions promotes the reactions in polar media [1]. Shilov's explanation [65] of anionic catalysis and of the action of nucleophilic solvent molecules is that the termolecular donor–acceptor mechanism involves halogenation via a transition complex in which the unsaturated molecule is subjected simultaneously to the action of electrophilic and nucleophilic reagents. The mechanism is represented by the general scheme $D \rightarrow (M \rightarrow A)$, where $(M \rightarrow A)$ is the donor–acceptor complex of unsaturated compound and acceptor (halogen) molecule, while D is an electron-donor. The transition state in the chlorination of ethylene in the presence of the chloride ion is



The simultaneous addition and removal of a chloride ion lowers the activation energy: the energy consumed in rupturing the Cl–Cl bond is balanced by the energy of formation of the C–Cl bond (Table 7).

Table 7. Activation energies for the chlorination and bromination of unsaturated compounds in acetic acid containing added lithium chloride.

Reactant	Trimethylammonium perchlorate with chlorine (Ref.42)		2,3-Dimethylpent-2-en-4-yne with bromine (Ref.66)		
LiCl, M	0	0.1	0	0.01	0.05
E_{act}, kcal mole^{-1}	7.3	4.9	7.16	6.69	5.53

The involvement of halide anions as component of the halogenating agent changes the rate law [42]. For chlorination in the presence of the chloride ion we have $W = k_3[Un][Cl_2][Cl^-]$ where Un is the unsaturated compound. Analogous equations have been established for bromination [1] and iodination [67].

Acceleration of the reaction in the presence of salts is a general feature of chlorination, and the catalytic strength of the anions is independent of their nucleophilic character [42]. The iodination of allyl alcohol in water exhibited the sequence $I^- > CNS^- > Br^- > Cl^-$. [67] Bromination is also accelerated by the addition of anions with the exception of the bromide ion, which sometimes accelerates but at other times slows down the reaction. The latter effect is explained by the binding of bromine into the tribromide anion, which is less strongly electrophilic than the free molecule. In the bromination of *trans*-stilbene in methanol the reactivity of free bromine exceeds that of the tribromide ion by a factor of 43 [68]. The ratio of their reactivities towards brominated alkenes under the same conditions varies from 5.7 to 25. [69] The activation energy for the bromination of 1,3-alkenynes is significantly higher with the tribromide ion than with molecular bromine [37]. Whereas the addition of bromide ions lowers the rate of the process with reactive alkenes, a catalytic effect is more characteristic of relatively unreactive alkenes [52,70,71]. In the bromination of several alkenes of reactivity varying by a factor of 10^7 correlations enabled anion catalysis by the bromide ion with unreactive alkenes to be separated

from inhibition of reaction due to formation of the tribromide ion with highly reactive unsaturated compounds [72]. Inhibition of chlorination by the chloride ion could not be observed because of the small equilibrium formation constant of the trichloride ion (Table 6). Thus a mechanism of polar halogenation allowing for termolecular donor–acceptor interaction provides a good explanation of the reactivities of different halogenating agents.

4. Products of Polar Halogenation

Three types of compounds—dihalides, mixed adducts (reaction involving the solvent), and monohalides (substitution)—are formed by the reaction of halogens with alkenes in polar media. Data on the composition and yields of substitution products obtained by halogenation, covering the period to 1965, were assembled in an exhaustive review by Bodrikov and Smolyan [73]. Bodrikov and his coworkers then studied the dependence of the yield and rate of formation of anomalous halogenation products on the nature of the alkene and the halogen, the temperature, the nature of the solvent, and other factors [74–77]. It was found in particular that the ratio of addition to substitution depended on the degree of charge separation in the polar transition state.

The tendency to form *trans*-dihalides falls in the sequence $I_2 > Br_2 > Cl_2$. The addition of bromine to *cis*-1-phenylpropene yields mainly the *trans*-dibromide, whereas chlorine forms a mixture of nearly equal quantities of *cis*- and *trans*-addition products [78]. The bromination of acenaphthene and phenanthrene produces the *trans*-dihalides [79,80]; chlorination gives a substantial quantity of the *cis*-adduct together with the *trans*-isomer [79,81]. Such variation is explained in terms of polar addition by the stronger tendency of bromine to form bridged structures in the cation [26]. Furthermore, the large size of iodine and bromine atoms may prevent formation of the *cis*-isomers.

Table 8. Effect of solvent on stereospecificity of bromination.

Solvnet	CCl_4	CS_2	MeCOOH	CH_2Cl_2	CCl_3COOMe	PhCN	CCl_3CN	$PhNO_2$	MeCN	H_2O
Dielectric constant ε	2.2	2.2	6.2	9.1	—	25.2	—	34.8	37.5	78.5
Percentage of *trans*-dibromide on bromination of *cis*-stilbene (Ref.88)	100	90	50	50	—	40	—	10	30	20
trans-stilbene (Ref.89)	77	31.4	—	—	51	34	34	29.5	—	—

The structure of intermediate species and of the transition state—and hence the stereochemistry of the products—depend on the nature of the unsaturated compound. Bridged structures and hence *trans*-dihalides are most probable with aliphatic alkenes. In fact the chlorination of butenes and allyl chloride in non-polar media [82] and in acetic acid [83] and the bromination of but-2-enes in acetic acid [84] are *trans*-stereospecific. Quantum-mechanical calculations show that an open carbonium ion structure is more probable for alkenes having aromatic substituents [27,85], in which stereospecificity may break down owing to stabilisation of the localised charge in the open carbonium ion. Mixtures of *cis*- and *trans*-dihalides are obtained in the chlorination of stilbenes in dichloroethane [86] and in chloroform [87], in the chlorination of 1-phenylpropenes [78], and in the bromination of substituted styrenes in acetic acid [84].

A polar mechanism provides an explanation also of the dependence of the stereochemistry of the halogenation products on the nature of the solvent. Table 8 shows that the *trans*-stereospecificity of bromination diminishes as the solvent becomes more polar. A polar solvent favours separation of charges and stabilisation of the open carbonium ion, since the energy of solvation of the latter is greater than that of the bridged structure. This leads to a decrease in the proportion of *trans*-addition.

Specific solvation may change the stereochemistry of the addition products. Thus the bromination of *cis*-β-methylstyrene in dioxan gives 80% of the *cis*-dibromide as a result of stabilisation of the unsymmetrical structure in the ion-pair by dioxan [90]. The chlorination of diphenylacetylene in benzene–pyridine mixtures yields solely *cis*-dichlorostilbene, which is explained by the cyclic structure of the transition state [91].

Table 9. Effect of solvent on relative yield of mixed chlorination products.

Solvent	ε	Ratio of yields of mixed products to dichlorides					
		pent-2-ene (Ref.92)		pent-1-ene (Ref.92)	1-phenylpropene (Ref.83)		methyl vinylacetate (Ref.93)
		cis	*trans*		*cis*	*trans*	
H_2O	78.5	—	—	—	—	—	Mixed product ∞ only
HCOOH	57.9	3.6	1.6	3.4	—	—	—
MeOH	32	10.7	5.4	11.2	4.9	4.9	—
EtOH	26.4	4.3	2.3	3.9	—	—	—
BuOH	12.3	1.0	0.45	1.4	—	—	—
CF_3COOH	8.2	0.2	0.095	0.2	—	—	0.25
MeCOOH	6.2	0.87	0.3	0.85	0.48	0.43	2.34

Halogenation results in mixed adducts when dissociated solvents (water, methanol, acetic acid) and anions of added salts are involved. Table 9 shows that the yield of mixed adducts is strongly dependent on the solvent. The quantity of mixed adducts does not correlate with the dielectric constant, and only qualitative dependence of the yield on the nucleophilic strength of the solvent is observed. It is difficult to interpret the combined effect of these two properties of the solvent. The yield of mixed products obtained by the chlorination of several unsaturated compounds [92,93] and substituted cinnamic esters [94] in acetic acid increases as the unsaturated component becomes less reactive.

According Shilov's views [5] a third component (solvent or added anion) will have an insignificant effect on the reaction if the transition state approaches an ion-pair in character. On the other hand, the less ionised the transition state the more significant the effect of the third component. In polar halogenation energy is consumed mainly in converting the π-complex into an ionised state, and in this case the involvement of a donor component, e.g. an anion, is less significant. In conformity with this,

in the presence of 1 M lithium chloride the yield of *trans*-dichloride increases in parallel with the decrease in reactivity of the double bond[94]. The predominant formation of *trans*-isomers with mixed products is connected with the synchronous action of acceptor (halogen molecule) and donor (solvent or anion) on the multiple bond. Thus kinetic examination based on the effect of non-specific solvation, the structure of the alkene, the nature of halogenating agents and third components, and also the composition of the products shows that a mechanism involving molecular complexes provides a good description of aspects of the halogenation of unsaturated compounds in polar media.

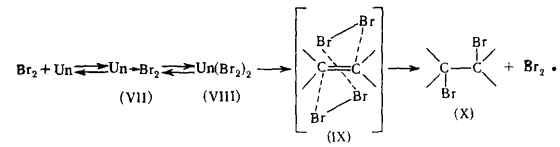
IV. MOLECULAR MECHANISM

On passing from polar to non-polar solvents the composition of the products and the kinetics of the reaction change. We must therefore examine in greater detail the mechanism of halogenation in non-polar media.

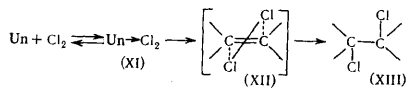
If we assume that a polar mechanism is feasible even in media of low dielectric constant, we would then expect a similar strong dependence on the structure of the alkene, since the energy barrier to a polar reaction is a linear function of the ionisation potential of the alkene. However, the rates of bromination of cyclohexene and hex-1-ene differ by a factor of 27 in methanol methanol[42], but only 4 in carbon tetrachloride[19]. The weakening of the dependence of the rate on the structure of the unsaturated compound leads to a decrease in the values of ρ in the correlation equations for non-polar media: the slope is a few negative units (Table 5) for polar media, but −0.67 for carbon tetrachloride[95]. The observed difference is inconsistent with the view that the same mechanism operates in the two cases.

A wide range of reactions in non-polar media have negative activation energies[19,96-101]: the observed values for several alkenes vary from zero to −10 kcal mole^{-1}. On the assumption that the reaction has a polar mechanism the energy barrier should be higher in such solvents as hexane and carbon tetrachloride than in polar media, but this is contradicted by experiment.

It is supposed that the bromination of ethylenic compounds can take place without the intermediate formation of ionic or strongly polar compounds[102]. Two halogen molecules and one alkene molecule are assumed to form a 2:1 complex, which can rearrange into a non-polar six-membered ring containing 4 Br + 2 C. Constructing molecular models shows that such a ring can be formed without significant distortion of the C=C and Br—Br bond lengths. Carbon and bromine atoms approach one another until relatively close to the C—Br covalent bond length, and bromine atoms from different molecules to distances close to the Br—Br bond length in the Br_2 molecule. The dibromide is formed by simultaneous rupture of two Br—Br bonds and formation of two C—Br bonds together with a new Br—Br molecule. The energy of rupture of the bonds is immediately balanced by the energy evolved on formation of the new bonds. The overall process of bromination is exothermic, so that formation of the product does not require the consumption of energy. The free-energy barrier is determined by the entropy term. If the solvent is disregarded, the hypothetical transition state contains three oriented reactant molecules, and several degrees of freedom are eliminated, so that the transition state has a large negative entropy. The product is formed from the complex by simultaneous rupture and formation of bonds. Such a reaction mechanism can be termed molecular, and represented in general by the scheme



Such a mechanism is impossible for chlorination, and the size of the chlorine molecule does not ensure formation of a structure (IX): the Cl—Cl distances in a structure similar to (IX) are so large that formation of a new chlorine molecule simultaneously with the rupture of old bonds and the formation of C—Cl bonds is not feasible. However, direct rearrangement of the complex (XI) into the reaction product is possible during chlorination:



Since the suggested chlorination transition state contains only two molecules, and its structure is less rigid than that of (IX), a lower entropy of activation and a higher rate must be expected than with bromination.

The ultraviolet spectra of mixtures of bromine with cyclohexene indicate the existence of a 2:1 complex[103], which has been demonstrated also by low-temperature infrared spectroscopy[104]. When a mixture of bromine and cyclohexene vapours is sprayed as a molecular beam on to a surface cooled in liquid nitrogen, bands due to vibrations of the double bond in 1:1 and 2:1 complexes are observed on a background of a weak band due to deformation vibration of this bond. The composition of the complexes was proved by studying the dependence of absorption on the ratio of the reactants. The displacement of the band due to the double bond is greater in the 2:1 than in the 1:1 complex, and the former has a larger heat of formation. Solid-phase conversion of the 2:1 complex into a dibromoalkane was observed when the temperature rose to −160°C. Reactants not combined in the complex are not involved in the process. A 2:1 complex has been observed also when solutions of bromine and biadamantylidene in carbon tetrachloride are mixed[105].

Table 10 lists kinetic parameters for several halogenations in non-polar media. The data for stilbenes and several other alkenes containing aromatic substituents contrast sharply with results for the remaining reactions. This is probably due to stabilisation of the positive charge by the aryl substituents, which lowers the energy of formation of the ion-pair. Since the entropy of activation of the polar reaction is numerically smaller, a polar process having an activation energy of 5–15 kcal mole^{-1} is able to compete with the molecular process. Small and negative activation energies in non-polar media correlate with the occurrence of the reactions at very low temperatures[106]. The chlorination and the bromination of cyclohexene in the absence of a solvent takes place at −175°C.[107] The chlorination of ethylene in propane takes place with considerable velocities between −140° and −150°C.[108]

A negative temperature coefficient is a general feature of the addition of halogens to alkenes in non-polar media. It is not connected with the temperature dependence of the pre-exponential factor. The activation energy observed for an elementary termolecular reaction is given by the difference between the true height of the barrier and $4RT$, and the appearance of this difference is associated with

the pre-exponential factor. At 300°K we have $4RT \simeq 2.4$ kcal mole^{-1}, which does not explain the experimental values of the negative temperature coefficient.

Table 10. Kinetic parameters of some halogenations in carbon tetrachloride at 25°C.

Alkene	Hal	Overall order	Rate constant	Activation energy, kcal mole^{-1}	Ref.
Cyclohexene	Br_2	3	8 M^{-2} s^{-1}	-8.0	19
Hex-1-ene	Br_2	3	1.5 M^{-2} s^{-1}	-4.1	19
4-Methylpent-1-ene	Br_2	3	1.5 M^{-2} s^{-1}	-3.5	19
Diphenylalkenes	Br_2	3	20-150 M^{-2} s^{-1}	0--5	100
Hex-1-ene	Cl_2	2	0.013 M^{-1} s^{-1}	0	99
Cyclohexene	Cl_2	2	0.15 M^{-1} s^{-1}	-1.7	99
Cyclohexene	IBr	3	45 M^{-2} s^{-1}	-8.2	98
cis-Stilbene	Br_2	3	-	+6.5	12
trans-Stilbene	Br_2	3	0.032 M^{-2} s^{-1}	+13.9	12

The observation of negative activation energies may be evidence that molecular complexes are involved in the reaction mechanism. If the kinetic equations for a scheme of the type $Un + X_2 \rightleftharpoons \pi$, $Un + X_2 \rightarrow P$ (where π is the complex and P the product) with parallel formation of the complex are differentiated with respect to the reciprocal of the temperature, the resulting equation is

$$E_{obs} = -R\frac{\partial \ln k_{obs}}{\partial T^{-1}} = -R\frac{\partial \ln k_2}{\partial T^{-1}} + R\frac{\partial}{\partial T^{-1}}(1 + K_{eq}[Un] = \\ = E_2 + \frac{K_{eq}[Un]}{1+K_{eq}[Un]}|\Delta H| > 0 \quad (3)$$

where E_{obs} is the experimental activation energy, E_2 the true activation energy of the bimolecular reaction between halogen and alkene, $|\Delta H|$ the numerical value of the enthalpy, and K_{eq} the equilibrium constant of complex formation. Equation (3) shows that, at sufficiently high alkene concentrations [Un], the observed activation energy increases from E_2 to $E_2 + |\Delta H|$ with increase in this concentration. A similar increase is observed on passing from high temperatures ($K_{eq} \rightarrow 0$) to low temperatures ($K_{eq} \gg 1$). Thus increase in K_{eq}[Un] should be accompanied by a gradual increase in the activation energy, and

$$E_{obs}^{max} - E_{obs}^{min} = |\Delta H| \ . \quad (4)$$

For a termolecular scheme not involving the complex we have

$$E_{obs} = E_3 + \frac{2K_{eq}[Un]}{1+K_{eq}[Un]}|\Delta H| > 0 \\ \text{and } E_{obs}^{max} - E_{obs}^{min} = 2|\Delta H| \ . \quad (5)$$

For the simplest bimolecular scheme involving a π-complex we find that

$$E_{obs} = E_2 - |\Delta H| + \frac{K_{eq}[Un]}{1+K_{eq}[Un]}|\Delta H| \ . \quad (6)$$

If $E_2 > |\Delta H|$, this case is identical with the parallel scheme. But when $E_2 < |\Delta H|$, a negative temperature coefficient must be expected in the region of small values of the product K_{eq}[Un] (low concentrations and not too low temperatures). The numerical value of this coefficient will decrease at low temperatures and with increase in [Un], and at some point the coefficient will become positive. Here, as before, Eqn. (4) holds. Fig. 3 illustrates various forms of temperature dependence of the rate constant for the given scheme.

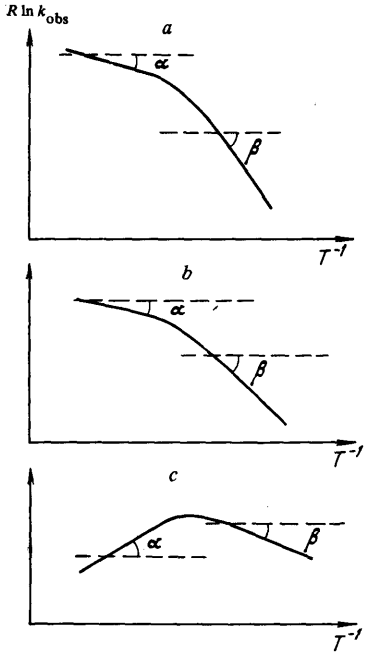


Figure 3. Possible forms of temperature dependence of the effective rate constant of bimolecular halogenation.

For the corresponding termolecular scheme we have

$$E_{obs} = E_3 - |\Delta H| + \frac{2K_{eq}[Un]}{1+K_{eq}[Un]}|\Delta H| \ . \quad (7)$$

With $E_3 < |\Delta H|$, low concentrations [Un], and sufficiently high temperatures a negative temperature coefficient may be expected even for termolecular reactions. Maximum and minimum values of the activation energy are connected by the relations (5).

The negative temperature coefficient may increase when two types of complexes (e.g. 1 : 1 and 2 : 1) are involved in the reaction. For a termolecular scheme and a steady state with respect to both complexes we have $E_{obs} = E_3 - (|\Delta H| + |\Delta H'|)$, where $|\Delta H'|$ is the enthalpy of formation of the 2 : 1 complex. The difference between maximum and minimum values of the observed activation energy is $2(|\Delta H| + |\Delta H'|)$. If a steady state with respect to the second complex is established slowly, the situation is more complicated. The product will accumulate in conformity with an autocatalytic law, and a negative temperature coefficient may not be observed under these conditions even when $E_3 < (|\Delta H| + |\Delta H'|)$.

Thus schemes that involve parallel formation of a molecular complex are unable to explain the appearance of a negative temperature coefficient. Such a possibility is feasible with a complex as a reaction intermediate. A negative activation energy therefore provides kinetic evidence that complexes are involved. Negative activation

energies indicate that the potential energy of the transition state during halogenation lies below that of the initial molecules. According to the theory of the activated complex maximum free and potential energy corresponds to the transition state. Fig. 4 shows possible changes in potential and free energy along the reaction path for the halogenation of alkenes in non-polar media. In the case illustrated the potential energy has a maximum in the transition state, but is lower than in the initial molecules. This means that the formal activation energy in the Arrhenius equation becomes less than zero for the effective rate constant. Observed activation energies close to zero can be expected for chlorination. Large negative values are possible for the entropy of activation, especially in the case of bromination, and reaction velocities will be low. All the above features are in fact confirmed by experimental data [19,102].

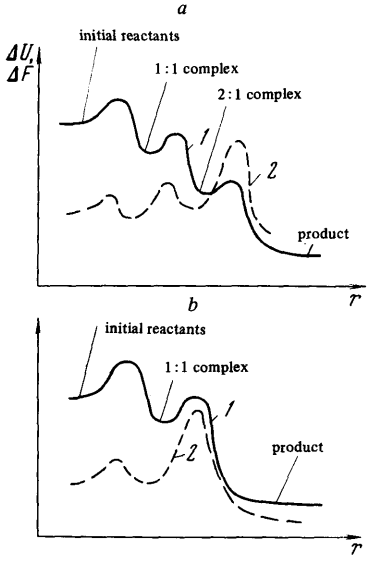


Figure 4. Variation of: 1) potential energy; 2) free energy along path of molecular reaction: *a*) bromination; *b*) chlorination.

Specific solvation of starting materials and transition state should play an important part in a molecular mechanism. The formation of complexes with halogens is typical of several compounds used as solvents (Table 11). Crystalline molecular compounds of carbon tetrachloride with chlorine are known [119]. A charge-transfer band between carbon tetrachloride and bromine in perfluoropentane solution has been detected spectrophotometrically [120].

The dissolution of any substance A in a solvent S is accompanied by solvation and the formation of a solvate complex of mean composition AS_n:

$$(A)_{S,L,G} + nS \rightleftarrows AS_n .$$

Strictly speaking, all the substance A is present in solution as such a solvate complex AS_n. The formation in solution of a complex of a halogen with a donor, e.g. an alkene, can be represented:

$$X_2S_n + D \overset{K_{eq}}{\rightleftarrows} X_2{\cdot}D + nS \qquad K_{eq} = \frac{[X_2D][S]^n}{[X_2S_n][D]} . \qquad (8)$$

Table 11. Enthalpies of formation ($-\Delta H$, kcal mole^{-1}) of molecular complexes of halogens with certain donor solvents.

Hal	Benzene	Toluene	Methanol	Dioxan	Dimethyl sulphoxide	Oxolan	Pyridine	Diethyl ether
I_2	1.3[109]	1.8[109]	1.9[110]	3.3[111]	3.7[114]	5.3[115]	7.8[116]	4.3[117]
Br_2	—	—	—	2.0[112]	—	3.5[112]	—	5.5[118]
Cl_2	—	—	—	2.1[113]	—	2.5[113]	4.3[113]	—

The applicability of Eqn. (8) has been shown [121] for the ternary systems formed by iodine and hexane with benzene, tetrachloroethylene, carbon tetrachloride, and allyl bromide and by iodine with benzene and carbon tetrachloride. In all cases 1 : 1 complexes are formed, which confirms the type of interaction between halogens and solvents.

Reaction may be prevented by formation of a halogen–solvent donor–acceptor bond. The acceptor and electrophilic properties of a halogen become weaker when it is bound into a complex. Formation of the complex $X_2.Un$ by the exchange reaction (8) is impeded by the presence of a bond with the solvent. Increase in the donor strength of the solvent is accompanied by a rise in the potential barrier to complex formation: for example, the enthalpy of interaction of bromine with dimethyl sulphide is -9 kcal mole^{-1}, [112] and up to 10 kcal mole^{-1} is absorbed by reaction (8) in this case. In such solvents the formation of complexes may become the limiting stage, and the reaction velocity may be lower than in weakly complexing solvents such as carbon tetrachloride. In fact, hardly any bromination of alkenes occurs in dimethyl sulphide [118]. Donor solvents are able to solvate not only the halogens but also the transition state. The role of such solvation in effecting the reaction has been noted several times by Shilov [5,65]. Solvation of the transition state, like that of the initial molecules, depends on the donor strength of the solvents. Cases are probable in which solvation of the transition state will exceed that of the reactants. The reaction velocity may increase in such solvents. The relative strength of solvation effects in the reaction can be assessed from the enthalpy of the various processes involved in complex formation, and the reaction velocity may be expected to pass through a maximum depending on the stability of the halogen–solvent complex. This phenomenon has been observed in the bromination of cyclohexene and hex-1-ene in solvents that form complexes with bromine [118] (Fig. 5). The maximum rate of reaction is found in dioxan. A similar relation has been obtained for iodination–cyclisation [122], where the iodine–benzene complex exhibited the maximum rate.

A molecular mechanism should yield *trans*-addition products, which has been confirmed experimentally [99,102,123]. Breakdown of stereospecificity on passing to more polar media has been reported [78,88], and is probably due to a diminution in the contribution by the molecular mechanism.

In several cases specific solvation effects are as important as the dielectric constant of the medium. The concentration of added bromobenzene appears in the rate equation for the bromination of stilbenes in carbon tetrachloride, and the activation energy falls from 13.9 to 8 kcal mole^{-1} on the addition of 10% of bromobenzene [124].

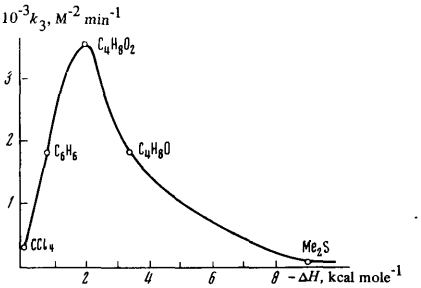


Figure 5. Dependence of rate constant for the bromination of hex-1-ene on enthalpy of formation of bromine–solvent molecular complex.

In mixtures of carbon tetrachloride and nitrobenzene the chlorination rate constant increases considerably more rapidly than might be expected from the variation in the dielectric constant of the medium [125]; this is explained by specific solvation of chlorine by nitrobenzene. This polarises the chlorine molecule, which facilitates electrophilic attack on the double bond. Catalysis of chlorination in carbon tetrachloride and benzene by carboxylic acids is also related to specific solvation [91], and becomes greater as the acid becomes stronger. Only the monomeric forms of the acids are active. A probable mechanism for the action of carboxylic acids is solvation of the anionoid part of the transition state by the proton.

Thus the halogenation of alkenes in non-polar media is characterised by negative effective activation energies and high kinetic orders. The reaction velocity depends on the specific solvation of the halogens. All these facts are consistent with the view that various donor–acceptor complexes are involved in the reaction, and are converted into the reaction products by a molecular mechanism.

V. RADICAL MECHANISM

The gas-phase halogenation of alkenes takes place by a radical–chain mechanism [126]. For a long time no attention was paid to radical halogenation in the liquid phase. The Review discusses radical halogenations taking place at normal temperatures in the absence of illumination and catalysts. Such a reaction (bromination) was first studied in 1951. [127] The process is sharply retarded by inhibitors and by contact with an extended glass surface. Toluene, which is stable towards the short-term action of bromine, reacts with the latter in the presence of an unsaturated compound. The *trans*-addition product is formed under conditions favouring a polar reaction. Nearly equimolecular proportions of *trans*- and *cis*-dibromides are obtained in carbon tetrachloride. Criteria enabling radical halogenations to be identified were formulated [127]—action of inhibitors, nature of products obtained under various reaction conditions, entry into reaction of reactants that are stable towards the halogen in the absence of an unsaturated compound.

The radical chlorination of alkenynes induces benzene and tetrachloroethylene to enter into reaction [128]. Poutsma demonstrated that the chlorination of cyclohexene proceeds partly by a radical mechanism [129]. The postulate of a radical mechanism explained the chlorination of aromatic and saturated hydrocarbons induced by alkenes [130–132]. Radical chlorination is not a consequence of chance external initiation but depends on the chemical nature of the reactants [133]. A radical mechanism is characteristic of the bromination of dienes [134,135], cyclohexene [103], hex-1-ene, and *p*-allylbromobenzene [101].

The proportion of radical processes is determined by the structure of the alkene. An unbranched chain confers the greatest tendency to radical chlorination, but branched alkenes—isobutene, tri- and tetra-methylethylenes, and also styrene—are not characterised by a radical reaction [123]. The reaction mechanism is affected also by the concentration of the alkene: the chlorination of cyclohexene becomes almost exclusively a radical reaction as the concentration of the hydrocarbon increases, and the proportion of the non-radical process increases with decrease in the concentration [133]. A similar phenomenon has been observed in the bromination of hex-1-ene [101], butadiene [135], and *cis*- and *trans*-penta-1,3-dienes [136]. Styrene, which is chlorinated and brominated in conformity with a non-radical scheme, reacts with iodine by a purely radical mechanism [137]. Oxygen inhibits radical chlorination [123], bromination [101,103], and iodination [137]. The scheme

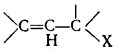
$$\mathrm{StI}^{\cdot} + \mathrm{O_2} \rightarrow \mathrm{StIO_2^{\cdot}},$$

$$2\mathrm{StIO_2^{\cdot}} \rightarrow \mathrm{IStOOStI} + \mathrm{O_2},$$

$$\mathrm{StIO_2^{\cdot}} + \mathrm{StI}^{\cdot} \rightarrow \mathrm{IStOOStI},$$

was suggested [137] for inhibition of the iodination of styrene (St). The action of oxygen is twofold: small additions of oxygen initiate the bromination of tetrachloroethylene, but excess slows it down [138]. Radical halogenation is inhibited also by quinones [137], substituted phenols [136], and cyclohexene oxide [139].

The radical bromination of cyclohexene gives the dibromide in yields exceeding 90%, [103] and hex-1-ene gives a 50% yield [19]. The dihalide is usually the *trans*-product contaminated with the *cis*-isomer. The chlorination of cyclohexene gives more than 95% of the *trans*-dichloride. The bromination of cyclohexene [102] and photochemical iodination of butenes [140] and pentenes [141] are *trans*-stereospecific. In several cases, however, stereospecificity is absent [127,136]. Radical halogenation also yields substitution products, whose proportion sometimes reaches 50%. Substitution products containing an allyl group



are most usual. Allylic compounds are formed in yields of 50%, 27%, and more than 40% in the isobutene–chlorine, cyclohexene–chlorine, and hexene–bromine systems respectively. Vinyl halides, containing halogen at the double bond, are always formed in small amounts (from fractions to 5%). Considerable quantities of the 4-halogeno-derivative are observed in the reaction of chlorine with but-1-ene [123] and in the bromination and chlorination of cyclohexene [103,133]. Products of the latter type are found only in radical halogenation.

Published kinetic data on radical halogenation are collected in Table 12, which shows such reactions to have low and negative effective activation energies, from −15 to 6.5 kcal mole^{-1}. The kinetic equations are extremely diverse. The quantity of data on radical liquid-phase halogenation is limited, and further investigation of these reactions is required.

Table 12. Radical–chain halogenation of alkenes in carbon tetrachloride.

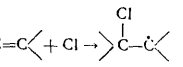
Alkene	Hal	Kinetic equation	Activation energy	Ref
4-Methylpent-1-ene	Br_2	$k[Un]Br_2]^2$	−15	19
Hex-1-ene	Br_2	$k[Un]^2[Br_2]^{3/2}$	−8	19
Cyclohexene	Br_2	$\begin{cases} k[Un][Br_2]^2 \\ k[Un]^2[Br_2] \end{cases}$	−14	19
p-Allylbromobenzene	Br_2	$k[Un]^2[Br_2]$	0	101
Pentenes	I_2	$\frac{k_1[I_2]^{3/2}[Un]}{1+k_2[Un]}$	no data	141
Styrene	I_2	$k[Un]^{3/2}[I_2]$	+6.5	137

Halogenation in the dark is initiated by the alkene, not by thermal breakdown of the halogen molecule into two atoms. Aromatic and saturated hydrocarbons that are inert towards the halogen react in the presence of alkenes [130-132]. If the alkene were not involved in initiation, the rate of initiation would be independent of its presence, and the degree of halogenation of the aromatic or saturated compound would also have been constant. Actually, however, it differs by several orders of magnitude [128], which proves that more halogen atoms are formed in the presence than in the absence of alkenes. Comparison of possible rates of initiation with the observed reaction velocities also shows that the latter cannot be attained with actual chain lengths and with initiation by the dissociation of halogen molecules.

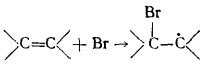
Table 13. Heats of initiation in halogen–alkene systems.

Initiation reaction		Heat of reaction, kcal mole^{-1}	
		bromine	chlorine
$-CH=CH-+X_2 \rightarrow -CHX\dot{C}H+X$	(9)	34	32
$2-CH=CH-+X_2 \rightarrow 2-CHX-\dot{C}H-$	(10)	22	6
$-CH=CH-+2X_2 \rightarrow -CHX-CHX-+2X$	(11)	14	8
$2-CH=CH-+2X_2 \rightarrow -CHX-CHX-+X+$ $+-CHX-\dot{C}H$	(12)	3	−18
$-CH=CH-CH_2-+X_2 \rightarrow HX+X+-CH=$ $=CH-\dot{C}H-$	(13)	32 (35)	29 (32)
$2-CH=CH-CH_2-+X_2 \rightarrow 2HX+2-CH=$ $=CH-\dot{C}H-$	(14)	18 (24)	0 (+6)

With regard to possible schemes of initiation involving the alkene Table 13 gives several mechanisms of radical generation in the presence of bromine and chlorine, together with probable heats of reaction for these processes. The latter were estimated from the energies of rupture of bonds in the halogen molecules (Table 2). The thermal effect of the reaction



was equated to the heat evolved on attachment of a chlorine atom to ethylene, i.e. 26 kcal mole^{-1}. [133] In most compounds the C–Br bond is less stable than the C–Cl bond by 14 kcal mole^{-1}, and for the reaction



it was assumed that ΔH = 12 kcal mole^{-1}. The energies of formation of hydrogen chloride and hydrogen bromide are respectively 103 and 88 kcal mole^{-1}. [21] The heat of detachment of hydrogen in the allyl position was taken [133] to be 74 kcal mole^{-1}, but the values in parentheses in Table 13 are based on the more usual 77 kcal mole^{-1}. The C–Cl and C–Br bond energies are respectively 80 and 66 kcal mole^{-1}. [21]

The results for the heats of reaction enable reactions (10) and (14) to be eliminated for bromine, since both these routes are less favourable than (11). Bimolecular initiation according to (9) and (13) is energetically identical in the case of bromine. Thus three schemes of initiation—bimolecular with ΔH_{13} = 32–35 kcal mole^{-1}, termolecular with ΔH_{11} = 14 kcal mole^{-1}, and formally quadrimolecular with $\Delta H_{12} \simeq 3$ kcal mole^{-1}—can be considered for bromination. A similar analysis for chlorine gives corresponding values of 29–32, < 8, and −12 kcal mole^{-1}. [142] The pre-exponential factors of bimolecular and termolecular reactions can be taken to be 10^{10} M^{-1} s^{-1} and 10^4 M^{-2} s^{-1}. [142] With reactant concentrations each of 0.03 M at 25°C we find that the bimolecular reaction may generate radicals at rates of 10^{-17} and 10^{-14} M s^{-1} for bromine and chlorine respectively, the corresponding rates for the termolecular reaction being 10^{-13} and 10^{-5}. Stage (12) can be regarded as the collision of two molecules of the complex $\cdot X_2.Un$, when rates of initiation may be higher than in the remaining cases. In order that reaction (12) should occur four reactant molecules must be oriented in a certain way, which may lead to great steric hindrance.

The formation of radicals as a result of the interaction of valency-saturated molecules by bimolecular and termolecular mechanisms has been thoroughly studied in the liquid-phase oxidation of hydrocarbons [143]. A termolecular mechanism predominates with hydrocarbons having weak C–H bonds. It is very likely that termolecular and pseudo-quadrimolecular are more efficient than bimolecular reactions also in the halogenation of alkenes. A review has been devoted to the possible role of molecular complexes in the formation of radicals [144]. Complex formation may weaken the bond in the acceptor molecule. Such a mechanism has been proved for the formation of radicals from tetranitromethane complexes [145]. It has been accepted [133] that the first stage in chlorination is always formation of a complex $Cl_2.Un$, which then breaks down either by a homolytic or by a heterolytic mechanism. The involvement of complexes in the reaction has been assumed also for radical bromination [101,135] and iodination [137]. Hitherto, however, there has been no unambiguous experimental evidence in halogenation reactions that complex formation should precede the formation of radicals.

The participation of complexes in halogenation explains the parallel variation in the reactivity of alkenes in polar, molecular, and radical reactions. If a complex is an

intermediate species in all these processes, the rate constants should actually correlate with the properties of the complex and thus also among themselves. Pseudo-quadrimolecular initiation must be regarded as resulting from pair collisions of 1 : 1 complex molecules.

In radical halogenation chain propagation can be effected by the reactions

$$X + -CH=CH-CH_2- \rightleftarrows -CHX-\dot{C}H-CH_2- , \quad (15)$$

$$X + -CH=CH-CH_2- \rightleftarrows HX + -CH=CH-\dot{C}H- , \quad (15')$$

$$-CHX-\dot{C}H-CH_2- + X_2 \rightarrow -CHX-CHX-CH_2- + X , \quad (16)$$

$$-CH=CH-\dot{C}H- + X_2 \rightarrow -CH=CH-CHX- + X . \quad (16')$$

The activation energies of (15) and (15′) can be estimated by means of the formulae—$E_{act} = 4.3 - 0.1\Delta H$ in an exothermic reaction, and $E_{act} = 4.3 + 0.91\Delta H$ in an endothermic reaction [146]—and in the case of chlorine we have $E_{act} = 2$ kcal mole^{-1} for reaction (15). The pre-exponential factors of the gas-phase reactions of the atoms with the ethylenic compounds amount to 10^{12} M^{-1} s^{-1}, [147]† which gives $k_7 = 10^{10}$ M^{-1} s^{-1}, in good agreement with the experimental $10^{9.9}$ M^{-1} s^{-1}. [148] The heats of reaction of stages (15) and (15′) differ by 2–3 kcal mole^{-1}, and the corresponding rates differ little. As a consequence, the dihalide is accompanied by large quantities of substitution products. In the case of bromine we have $k_7 \simeq 10^8$–10^9 M^{-1} s^{-1} for reactions (15) and (15′). The estimated rates of reactions (16) are of the same order. The rate of (16) may be lower than the calculated value because of steric hindrance to reaction of the halogenalkyl radical with the molecule. The most feasible value in this case is 10^7–10^8 M^{-1} s^{-1}. The rate of reaction (16′) is lower, since its heat of reaction is 5 kcal mole^{-1}. The reversibility of stage (15) is a very important matter, and may affect the kinetics of the process. With chlorine this stage is irreversible, since the reverse reaction is strongly endothermic. With bromine, on the other hand, the decomposition constant of the halogenoalkyl radical is estimated to exceed 10^6 s^{-1}. At a halogen concentration of 0.01 M this decomposition is able to compete with reaction (16).

Halogen atoms, which possess high electron affinities, are very strong acceptors and form complexes with organic donors such as benzene [149]. The enthalpy of formation of such complexes is about double those of complexes of the corresponding molecular halogens [150]. Such complexes should be formed also with alkenes, and the enthalpy can be expected to be 6–12 kcal mole^{-1}. The intermediate species in halogenation may not be classical halogenoalkyl radicals but radical-like complexes



distinguished by the position of the atom and by delocalisation of the free valency over a three-membered ring [103,140]. In fact the heat evolved on formation of a classical radical is smaller with iodine, but with bromine is close to that evolved on formation of the complex. The latter does not require rupture of the double bond, so that formation of such a complex may not have an activation barrier, in contrast to the reaction yielding



A bridged structure for the halogenoalkyl radicals is supported by the *trans*-stereospecificity of the radical addition of bromine and iodine [140]. If the reaction involved the radical



it would not have been completely *trans*-stereospecific with iodine, and with bromine there would have been no advantage at all in formation of a *trans*-product, as is observed e.g. in ionic reactions of the geometrically entirely similar cation [1]



Thus the most probable structure with bromine is



The reversibility of stage (15) can be regarded as a consequence of complex formation between the bromine atom and the unsaturated compound. With chlorine, formation of the complex involves a smaller—and that of the radical a larger—heat of reaction than with bromine, so that the radicals



play the main part in the reaction.

Complex formation explains negative activation energies in radical bromination, since the enthalpy of formation of the radical–complex occurs in the activation energy with a negative sign [116]. A negative activation energy due to reversible formation of a bromoalkyl radical has been reported for the gas-phase hydrobromination of alkenes [151].

Chain termination takes place either by the recombination of atoms and radicals or by reaction with an inhibitor (In):

$$2X \rightarrow X_2 , \quad (17)$$

$$X^{\cdot} + \text{} \rightarrow \text{Products} , \quad (17')$$

$$2\,\text{} \rightarrow \text{Products} , \quad (17'')$$

$$\left.\begin{array}{l} X + In \rightarrow \text{Termination} \\ \text{} + In \rightarrow \text{Termination} \end{array}\right\} . \quad (18)$$

Only the rate constants of reaction (17)—$10^{10.6}$ and $10^{10.3}$ M^{-1} s^{-1} for bromine and iodine [148] respectively—are known for the liquid phase. The rates of reactions (17′) and (17″) are apparently lower owing to steric hindrance. This is supported by data for the gas phase, where $k_{17} = 10^{16}$–10^{17} M^{-1} s^{-1} for chlorine‡, the reaction Cl + C_2H_4Cl gives only 10^{14}, and the recombination of two chloroethyl radicals only 10^{13}. [147] Mechanism (18) is more probable. Furthermore, chain termination may take place on oxygen, which is usually present in solution at concentrations of $\sim 10^{-3}$–10^{-4} M. Radical halogenation is complicated by liberation of the hydrogen halide, which influences the kinetics of the reaction.

†The pre-exponential factors given in Ref. 147 are $\sim 10^{12}$ cm^3 mole^{-1} s^{-1} (Ed. of Translation).

‡This value of k_{17} is in fact the third-order rate constant in cm^6 mole^{-2} s^{-1}, and the two subsequent rate constants are in cm^3 mole^{-1} s^{-1}, although the units are not stated in the Russian text (Ed. of Translation).

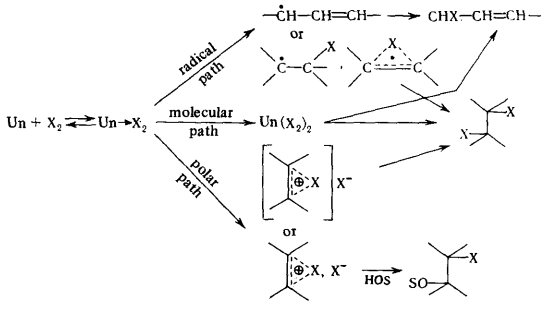
The detailed mechanism of radical halogenation cannot yet be regarded as finally established. Complexes of halogen atoms with alkenes can be assumed to take part in the reaction: without this hypothesis the stereochemistry of the products of radical halogenation becomes incomprehensible.

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Published information on the addition of halogens at a multiple bond shows the attention hitherto devoted to this reaction by research workers. Addition processes occur mainly in organic chemistry. They have formed the basis, in particular, for developing the concepts of carbonium ions, electrophilic and nucleophilic reagents, and π-complexes. The hydrohalogenation of alkenes has played an important part in establishing and developing the chemistry of free radicals.

The Review has considered the halogenation of multiple bonds mainly from the point of view of the possible role of halogen–alkene molecular complexes in this process. The existence of such complexes has been demonstrated experimentally, but their part in halogenation has been inadequately studied. Involvement of molecular complexes in the chemical change enables a unified view to be taken of the mechanism of halogenation. Available information can be summarised by Scheme 3.

Scheme 3.



The concept of complexes will explain the acceleration of the reactions with fall in temperature, the rapidity of the process in non-polar media and at low temperatures, the effect of specific solvation, and several other features of the reaction in systems where donor–acceptor interaction exists between the initial substances, but takes no direct part in the reaction.

The halogenation of multiple bonds shows that, depending on the properties of the medium and the reactants, subsequent changes in the complex can take place by ionic, radical, or molecular mechanisms. The investigation of such processes provides an approach to solving one of the problems of present-day chemical kinetics—elucidating the kinetic role of various types of complexes in chemical reactions. Examination of problems connected with this concept shows the absence of sharp distinctions between ionic and radical reaction mechanisms. Direct conversion of the complexes into the final products is also a possibility. The occurrence of such processes is of fundamental interest.

The halogenations of unsaturated compounds and in particular of alkenes have low activation energies. The reaction can take place in an inert phase over the temperature range 77–400°K, which enables individual stages in the process to be isolated and studied. The fact that the activation energy is comparable with the enthalpy of complex formation makes the halogenation of alkenes a convenient model for studying several general aspects of the effect of complex formation on a chemical process. New opportunities for controlling the rate and enhancing the selectivity of the most diverse processes are opened up by studying complex formation between reactants and paths for the further transformation of the complexes.

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