

550. *The Kinetics of Halogen Addition to Unsaturated Compounds.*
Part XXI. The Mechanisms of Addition Reactions.

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By altering the structure of the olefinic substance and the conditions of reaction, various mechanisms available for halogen addition have been identified, namely: (i) Electrophilic chlorine and bromine addition; (ii) electrophilic bromine addition catalysed by anions; (iii) nucleophilic bromine addition, catalysed by anions, and involving attack by ions of the type Br_2X^- ; (iv) nucleophilic chlorine and bromine addition, catalysed by acids, and involving attack by halogen molecules, or more usually Br_2X^- ions, on cations of the type $^+\text{CHR}\cdot\text{CH}\cdot\text{A}\cdot\text{BH}$, formed by co-ordination of a proton with a ($-T$) group $\cdot\text{A}\cdot\text{B}$ which is conjugated with a double link. Reactions of type (iii) predominate over types (i) and (ii) only for rather unreactive olefins containing a powerfully deactivating ($-I$) group; and those of type (iv) are important only in solvents which are poor proton acceptors (*e.g.*, acetic acid), are more readily observed for bromine than for chlorine addition, and depend to a considerable extent on the basicity of the group $\cdot\text{A}\cdot\text{B}$, the groups $\text{CHO} \approx \text{COPh} > \text{CN} \approx \text{NO}_2 > \text{SO}_2\text{R}$ being in order of decreasing effectiveness in promoting reaction by this mechanism.

OUR views concerning the detailed nature of halogen addition have, as the result of experimental development, gradually become modified since the first paper of this series (*J.*, 1937, 335). In particular, it has been discovered that the $\alpha\beta$ -unsaturated sulphones may react with bromine by a particularly simple nucleophilic mechanism. It seems useful, therefore, to summarise, in conjunction with the preceding group of experimental papers, our present views concerning the various mechanisms available for these reactions of halogens, giving special emphasis to the nucleophilic processes (*i.e.*, those in which the halogenating agent is nucleophilic in character), which until recently have been imperfectly characterised. The results to which reference is made in the present paper have been determined in acetic acid as solvent, and are quoted as second-order rate coefficients ($\text{l. g.}\cdot\text{mol.}^{-1} \text{ min.}^{-1}$), for $x = 20\%$ absorption of halogen, reactants $m/80$, at 25° , except where otherwise specified.

Electrophilic Addition.—(a) *Uncatalysed chlorine and bromine addition.* Chlorine addition, except in special circumstances, proceeds by a second-order process, and is subject to a small positive ionic-strength effect, electrolytes having a slight catalytic power for the reaction. The effect of structure on the rate of chlorine addition is consistent with the view that the reaction involves electrophilic attack by chlorine on the olefinic compound. Concerning the details of those stages of the mechanism which follow the initial attack by the chlorine molecule,* little is known, except that nucleophilic substances appear to be able to intervene in the addition process to give products other than the dichloro-compound. The intermediate involved in the reaction must, therefore, possess a carbonium centre, but it has not so far been ascertained with certainty whether a fully charged ionic intermediate is produced.

The comparative simplicity of chlorine addition has led us to use this process, wherever possible, as a standard of comparison for the study of constitutional effects. Bromine addition to all but the most unreactive olefins, in the concentration region $m/40$ at 25° , is of the first order with respect to the olefinic compound and of the second order with respect to bromine. Under the specified conditions, the rate ratio for chlorine to bromine addition is about 250, and is not very critically determined by the reactivity of the olefinic compound or by its structure. It is fairly certain, therefore, that the fundamental reaction involves again electrophilic attack by halogen, the function of the second molecule of bromine being, in all probability, that of assisting to break the Br—Br link in the attacking molecule (thus, in effect, forming Br_3^-), though whether this second molecule intervenes before or after the initial electrophilic attack is not determined. Intervention of nucleophilic substances to form mixed products also accompanies these third-order additions of bromine, and at still greater concentrations, reactions of a higher order with respect to halogen begin to take control, suggesting the participation of Br_4 molecules. In the reactions with bromine there is, as for chlorine, a small positive ionic-strength effect, as discussed in Part XIV (*J.*, 1949, 294).

It is noteworthy that the effects of substituents on these electrophilic processes show marked analogy with the effects of the same substituents on aromatic substitutions, and are in complete accord with the well-known classification of substituent groups given by Ingold. It is considered by Dewar ("Discussions of the Faraday Society," 1947, 2, 51) that some olefinic substances are likely to react through " π -complex" intermediates (*e.g.*, the simplest ethylenes), whilst others form intermediates of another type (*e.g.*, butadiene, styrene, and related compounds). No such theoretical division of olefinic compounds into different categories has been revealed by our studies of the rates and mechanisms of halogen-addition reactions.

(b) *Anion-catalysed electrophilic bromine addition.* Another reaction process, the character of which has been reasonably well defined, involves, instead of participation of a second bromine molecule in the kinetics of the reaction, the intervention of an anion, giving such rate expressions as $-\text{d}[\text{Br}_2]/\text{dt} = k[\text{A}][\text{Br}_2][\text{Cl}^-]$, or $-\text{d}[\text{Br}_2]/\text{dt} = k[\text{A}][\text{Br}_2][\text{Br}^-] = k[\text{A}][\text{Br}_3^-]$. With excess of bromide ion, the reaction reaches a maximum rate, which is nearly identical for lithium bromide and for hydrogen bromide, when substantially all the bromine has been converted into Br_3^- . This mechanism is of greatest importance for compounds of the type $\text{CHR}:\text{CH}_2$, in which R is an atom or group having a (+T, -I) effect.

In this type of reaction it is highly unlikely that Br_3^- or similar ions are the actual reactive halogenating species, as is shown by the effect of structure on the rate of reaction, in the following comparison:

Compound.	$\text{CH}_2:\text{CH}\cdot\text{CH}_2\text{Cl}$.	$\text{CH}_2:\text{CH}\cdot\text{CH}_2\text{CN}$.	$\text{CH}_2:\text{CHBr}$.
Rate (Br_2)	1.6	0.23	0.001
Rate ($\text{Br}_2 + m/20\text{-LiCl}$)	10	2.4	0.007

The total rate both of the catalysed and of the uncatalysed reaction decreases markedly as we proceed from allyl chloride to the many times less reactive vinyl bromide. If the ClBr_2^- ion were the effective reagent in the catalysed reaction, then this ion would be required to react as a powerfully electrophilic reagent, judged by the effect of structure on reactivity. Such a hypothesis is rather unlikely. It is believed, therefore, that in the catalysed, as in the uncatalysed reaction, attack is initiated rather by the bromine molecule acting as an electrophilic reagent, the chloride ion rendering a subsequent stage in the addition process (which may actually be the completion of addition to form the chlorobromide of the olefinic compound) partially rate-determining.

If correction is made for the decreased concentration of free bromine in solutions containing also bromide ion, it is discovered that the catalytic power of different ions falls in the order

* Not, in these circumstances, the Cl^+ ion.

$\text{Br}^- > \text{Cl}^- > \text{OAc}^-$, the last being almost ineffective in catalysing addition by this mechanism. This is consistent with the experimentally observed order of the nucleophilic power of these ions in attacking some alkyl halides (cf. Bither, Sturtevant, and Thomas, *J. Amer. Chem. Soc.*, 1945, **67**, 1562; Olson and Long, *ibid.*, 1936, **58**, 393; Young and Olson, *ibid.*, p. 1157; Beste and Hammett, *ibid.*, 1940, **62**, 2481).

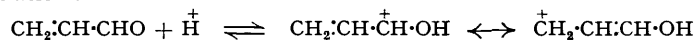
Nucleophilic Addition.—(a) *Anion-catalysed nucleophilic addition.* For compounds in which the ethylenic link is deactivated, as far as attack by electrophilic reagents is concerned, by a substituent with a negative inductive effect (*e.g.*, for methyl vinyl sulphone), a different type of anion-catalysed addition has been observed. Addition of bromine to such compounds has been found to become more (instead of many times less) rapid than chlorine addition, and sodium acetate becomes a good catalyst for bromine addition, lithium chloride and, especially, lithium bromide being still better. The following table summarises these relationships:

Compound.	Cl_2 .	Br_2 .	$\text{Br}_2 + \text{NaOAc}$.	$\text{Br}_2 + \text{LiCl}$.	$\text{Br}_2 + \text{LiBr}$.
$\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{Cl}$	ca. 450	1.6	ca. 2	10	3.8
$\text{CH}_2\text{:CHBr}$	0.38	0.001	ca. 0.001	0.007	0.012
$\text{CH}_2\text{:CH}\cdot\text{SO}_2\text{Me}$	0.0001	0.001	0.005	0.023	0.09

Vinyl bromide, as compared with methyl vinyl sulphone, for example, reacts some 10^3 times more rapidly when the reagent is chlorine, but less rapidly with bromine in the presence of lithium bromide. In the latter case, therefore, the reagent appears to be nucleophilic, and it is considered that the ions Br_2OAc^- , Br_2Cl^- , and Br_3^- are the active reagents in catalysed bromine addition to methyl vinyl sulphone. The existence of the first of these ions has not, as far as we are aware, been recognised, whereas Br_2Cl^- is known, and Br_3^- is still more stable (cf. Sidgwick, "The Chemical Elements and their Compounds," Oxford Univ. Press, 1950, Vol. II, p. 1193). It is consistent with the above that the order of catalytic power for reaction by this mechanism increases in the order $\text{NaOAc} < \text{LiCl} < \text{LiBr}$.

(b) *Acid-catalysed nucleophilic addition.* In the first paper of this series (*J.*, 1937, 335), it was shown that bromine addition to acrylic acid and to vinyl bromide is kinetically distinct from addition to other olefinic compounds such as allyl acetate, in that uncatalysed addition in acetic acid was autocatalytic, owing to the production of hydrogen bromide in the course of the reaction. Subsequent investigations by Anantakrishnan and his co-workers (*J.*, 1939, 224; *Chem. Reviews*, 1943, **33**, 27; *Proc. Indian Acad. Sci.*, 1946, **23**, A, 307, 312, 319; 1948, **27**, A, 184) extended our knowledge of the range of compounds for which this type of mechanism is available, without contributing significantly to our understanding of the nature of the catalysed reaction. Nozaki and Ogg (*J. Amer. Chem. Soc.*, 1942, **64**, 697, 704, 709) showed that the case of vinyl bromide must be considered separately from that of acrylic or maleic acid, the experimental distinction being that addition to vinyl bromide is catalysed equally by hydrogen and by lithium bromide. Addition to $\alpha\beta$ -unsaturated acids, however, is very much more powerfully catalysed by hydrogen bromide than by lithium bromide. For these compounds, therefore, a proton appears to be required for the addition process. In the present series of papers, the importance of this mechanism of addition has been established for quinones, $\alpha\beta$ -unsaturated ketones (*J.*, 1948, 980), acids (*J.*, 1945, 129), aldehydes (*J.*, 1945, 888), nitro-compounds (*J.*, 1947, 628), and nitriles (*J.*, 1950, 2834).

Numerous examples in which the order of reactivity with electrophilic reagents is reversed under conditions of acid catalysis (cf. *J.*, 1945, 129) show that these reactions involve attack by some nucleophilic halogenating agent. The specific influence of ($-T$) groups conjugated with the double link in promoting acid-catalysis shows, however, that the nucleophilic halogenating agent is attacking, not the olefinic compound itself, but rather the ion produced by attachment of a proton to the substituent to form a mesomeric carbonium cation, as in the following formulation:



This first stage of the reaction is favoured by electron-repelling substituents attached to the olefinic centre, *e.g.*, as in $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$, whereas the subsequent nucleophilic attack by halogen on the resulting carbonium cation is hindered by such substituents. The balanced electronic requirements of the two stages make prediction in any particular instance difficult, but the experimental results now accumulated allow us to make certain generalisations concerning the relationship between constitution and the rate of acid-catalysed addition. In compounds of the type $\text{CH}_2\text{:CHX}$, the introduction of an alkyl or aryl group to form $\text{CHR}\cdot\text{CHX}$ results in a decrease in rate, the stage of the reaction involving nucleophilic attack on the cation being predominant. On the other hand, in compounds of the type $\text{CH}_2\text{:CHX}$ and $\text{CHR}\cdot\text{CHX}$,

when X is varied, it is found that the basicity of the group and its capacity for conjugation become important factors. Thus the groups $\text{COR} > \text{NO}_2 > \text{SO}_2\text{Me}$ diminish in effectiveness as the basic character becomes less; the SO_2Me group is particularly ineffective, being, as discussed in Part XX (*J.*, 1950, 2836), inefficiently conjugated with the double linking.

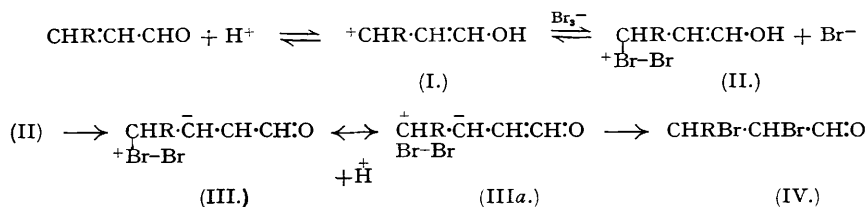
Acid catalysis is absent, therefore for such compounds as allyl chloride, in which there is no basic group to attract a proton.* Acid catalysis may also be obscured when a powerfully electron-donating substituent is attached to the double link. In the case of cinnamic acid, for instance, the rate of electrophilic addition of bromine is sufficiently large to make catalysis of addition by added hydrobromic acid rather small, and difficult to distinguish from the alternatively available anion-catalysed reactions, whereas acrylic acid, owing to its low rate of electrophilic addition, shows very large acid catalysis.

The form in which the halogen takes part in acid-catalysed addition is shown by the catalytic power of different acids. Thus addition of bromine to cinnamaldehyde with different catalysts, $m/320$, arranged in order of decreasing conductivity in acetic acid, follows the following rate sequence (*J.*, 1945, 888):

Catalyst.	HClO_4 .	HBr .	H_2SO_4 .	HCl .	HNO_3 .
Rate	7.3	ca. 300	3.4	24	ca. 0.8

The abnormal effectiveness of hydrogen chloride and especially of hydrogen bromide in relation to their acid strengths indicates that, although molecular bromine can, *e.g.*, in the presence of perchloric acid, act as a nucleophilic halogenating agent for a carbonium cation, yet the Br_3^- and the Br_2Cl^- ions are more powerful nucleophilic brominating agents, as indeed would be expected.

In earlier communications (*e.g.*, *J.*, 1945, 129), we considered the possibility that the active reagent in addition catalysed by hydrogen bromide might be the HBr_3 molecule, acting as a 1:4-brominating agent, and attacking simultaneously the unsaturated ($-T$) substituent and the double link. The establishment of similar catalysis of addition to $\alpha\beta$ -unsaturated nitriles (*J.*, 1950, 2834), for which compounds steric considerations render unlikely such bimolecular addition of HBr_3 to an olefinic compound, suggests that this special mechanism is unnecessary. The following type of formulation, illustrated for an aldehyde, accords with the kinetics of the reaction for compounds with a $-I$, $-T$ group attached to the ethylene system:



Nucleophilic attack by Br_3^- on the organic cation (I) forms the intermediate (II), which then changes, by the removal of a proton, to form (III). An alternative resonance structure of (III) is (IIIa). What happens, in effect, is that the nucleophilic mechanism brings a bromine molecule into a position favourable sterically for the final electrophilic attack, and correspondingly there is *trans*-addition of bromine to the olefinic compound (cf. Nozaki and Ogg, *loc. cit.*), whereas *cis*-addition would be expected for a one-stage nucleophilic addition.

The proton required in the first stage of the reaction can be supplied either by the solvent or by any acid present in solution. Although the reaction is sensitive to small traces of hydrogen ions, being strongly decelerated by sodium acetate, large concentrations become unfavourable by maintaining a proton on the intermediate (II). The kinetics of the reaction thus correspond, for a given amount of acid catalyst, with the rate expression $-\text{d}[\text{Br}_2]/\text{d}t = k[\text{A}][\text{Br}_2]$, and the rate reaches a maximum value with added acids. Water added to the acetic acid solvent decreases the importance of this mechanism, by virtue of the greater stability of H_3O^+ than of H_2OAc^+ , whereby protons become less readily available to form the reactive intermediate. Even for quite powerfully catalysed compounds, 25% of water in the solvent is sufficient almost completely to eliminate acid-catalysed bromination in favour of the electrophilic mechanism.

Chlorine addition can be forced to proceed by nucleophilic processes only in the most favourable circumstances. Certain $\alpha\beta$ -unsaturated aldehydes, *e.g.*, cinnamaldehyde, with

* The ethylenic link itself is negligibly basic, even in acetic acid, despite the contrary view held by Anantkrishnan and his co-workers (*loc. cit.*).

chlorine and hydrochloric acid give evidence of acid catalysis. The rates of these catalysed additions, corrected for any concurrent electrophilic addition, are less than those of the corresponding acid-catalysed bromine additions, and this difference between the electrophilic and the nucleophilic process is an additional diagnostic of mechanism.

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[Received, June 8th, 1950.]
