KINETICS OF THERMAL ADDITION OF HALOGENS TO OLEFINIC COMPOUNDS

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The literature concerning the mechanisms of addition of halogens to olefins is involved and confusing. Complex kinetics and the occurrence of side reactions have considerably hindered experimental study, but a certain clarification has of recent years become apparent, since it has been realised that various mechanisms are available for such additions. The contrasting and to some extent contradictory opinions expressed in recent reviews [1, 2] emphasise, however, the lack of general agreement. It has been thought useful, therefore, to attempt to survey the situation as it now appears. The discussion will be confined mainly to "thermal" (non-photochemical) additions in hydroxylic solvents; for although the products of the reaction are simpler in non-dissociating solvents such as carbon tetrachloride, the kinetics are on the whole more difficult to interpret, and furthermore the experimental work is less detailed, and therefore does not permit extensive generalisation.

1. The General Nature of the Addition Process.—The most familiar addition processes with which we shall be concerned involve electrophilic attack by the halogen, which must become at least partly polarised in the sense $\overset{\delta+}{\mathrm{Br}}\text{- - -}\overset{\delta-}{\mathrm{Br}}$. Two theoretical considerations would lead one to expect that the positively, rather than the negatively, charged end of the halogen molecule would usually initiate addition. First, carbonium cations seem to be more stable entities than carbanions, whereas the bromide ion is better characterised than the Br^+ ion. The energy of the transition state leading to addition should, therefore, be made less (and the addition should be facilitated) if in the transition state any incipient carbanionic centre is effectively destroyed by the developing positive bromine. Secondly, nucleophilic attack by negative ions on the ethylenic carbon atoms is hindered by the screen of unsaturation electrons, which are themselves vulnerable to electrophilic reagents.[3]

The experimental evidence in favour of the electrophilic character of halogen additions has been summarised by Williams.[1] Various workers have shown [4, 5, 6] that halogens in aqueous and alcoholic solutions react with olefins by a two-stage process, wherein either the anion derived from the reagent, or any extraneous nucleophilic anions, or even the weakly

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[1] G. Williams, *Trans. Faraday Soc.*, 1941, **37**, 749.
[2] S. V. Anantakrishnan and R. Venkataraman, *Chem. Reviews*, 1943, **33**, 27.
[3] Cf. A. G. Catchpole, E. D. Hughes, and C. K. Ingold, *J.*, 1948, 8.
[4] A. W. Francis, *J. Amer. Chem. Soc.*, 1925, **47**, 2340.
[5] E. M. Terry and L. Eichelberger, *ibid.*, p. 1067.
[6] P. D. Bartlett and D. S. Tarbell, *ibid.*, 1936, **58**, 466.

nucleophilic solvent molecules may complete the addition, thus:

$$CH_2{:}CH_2 + Br_2 \rightarrow \overset{+}{C}H_2{\cdot}CH_2Br + Br^- ;$$

$$\begin{array}{lll} \overset{+}{C}H_2{\cdot}CH_2Br & + Br^- & \rightarrow CH_2Br{\cdot}CH_2Br \\ \quad ,, & + Cl^- & \rightarrow CH_2Cl{\cdot}CH_2Br \\ \quad ,, & + H_2O & \rightarrow CH_2(OH){\cdot}CH_2Br + H^+ \end{array}$$

Yet it might be argued [7] that the reaction may proceed in the reverse way, *e.g.*, in the presence of sodium chloride, by a nucleophilic attack by the chloride ion, followed by interaction with a bromine molecule, with the resulting liberation of a bromide ion. Thus the orientation of the products of the unsymmetrical addition of iodine chloride (*e.g.*, $Me{\cdot}CHCl{\cdot}CH_2I$ from propylene, and $CH_2Cl{\cdot}CHI{\cdot}CO_2H$ from acrylic acid [8]) is not an unambiguous diagnostic of the course of the reaction. On the other hand, the principles which govern the production of isomeric (1 : 2 and 1 : 4) mono-addition products from halogens and conjugated dienes are intelligibly correlated with the facts known about the mobility of anionotropic systems,[9, 10] suggesting that similar intermediates are involved, and therefore that addition of the anionic part of the reagent is the second, rather than the first, stage of the addition process. Proof that the electrophilic attack by the reagent usually determines the course of the reaction is derived from the effects of substituent groups on the rates of addition to substituted ethylenes. Ingold *et al.*[11, 12] showed by a competition method that electron-donating groups (such as CH_3 or C_6H_5) favour the addition of bromine, which is inhibited by electron-withdrawing groups (such as Br or CO_2H). Correspondingly, an actual charge on the molecule is important in determining the rate. Thus the ion $CH_2{:}CH{\cdot}CO_2^-$ is more reactive than the undissociated acid [13]; and when an otherwise reactive unsaturated group is part of a positive ion, as in $R_3\overset{+}{N}{\cdot}CH_2{\cdot}CH{:}CH{\cdot}\overset{+}{N}R_3$, no addition of bromine will take place.[11, 14] Further discussion and exemplification of the detailed theory due to Ingold and Ingold [11] can better be given below, since the reagent and mechanism operating in their experiments are not yet certain.

2. Second-order Halogen Addition.—A. Berthoud and M. Mosset showed [15] that, in water, bromine addition to maleic and fumaric acids proceeds with rate proportional to $[A][X_2]$, where A is the unsaturated compound and X_2 the halogen. Kinetically similar are the additions of iodine to allyl alcohol in water,[15] of bromine to stilbene in methyl alcohol,[6] and of bromine to *cis*-cinnamic acid and to acrylic acid in aqueous acetic acid and in water.[13] Trihalide ions were found to be less reactive than

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[7] Cf. R. A. Ogg, *ibid.*, 1935, **57**, 2727; 1939, **61**, 1946.

[8] C. K. Ingold and H. G. Smith, *J.*, 1931, 2742.

[9] H. Burton and C. K. Ingold, *J.*, 1928, 910.

[10] P. B. D. de la Mare, E. D. Hughes, and C. K. Ingold, *J.*, 1948, 17.

[11] C. K. Ingold and E. H. Ingold, *J.*, 1931, 2354.

[12] S. V. Anantakrishnan and C. K. Ingold, *J.*, 1935, 984, 1396.

[13] P. W. Robertson, N. T. Clare, K. J. McNaught, and G. W. Paul, *J.*, 1937, 335; I. K. Walker and P. W. Robertson, *J.*, 1939, 1515.

[14] C. K. Ingold and E. Rothstein, *J.*, 1931, 1666.

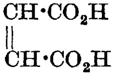
[15] *J. Chim. physique*, 1936, **33**, 272.

the parent halogen molecules ; in studying additions to organic acids, it was necessary to ensure, by adding mineral acid in order to suppress ionisation, that the addition did not proceed *via* the very reactive unsaturated carboxylate ion. In one of the above investigations, that of Bartlett and Tarbell,[6] careful kinetic study eliminated the possibility that, in methyl alcohol as solvent, the true brominating agent was MeOBr, an erroneous view held by K. Meinel ; [16] the evidence that such compounds, formed by equilibrium with the solvent ($X_2 + R{\cdot}OH \rightleftharpoons H^+ + X^- + RO{\cdot}X$), are not generally intermediates in addition reactions in hydroxylic solvents, is given by Williams.[1]

E. P. White and P. W. Robertson [17] investigated the kinetics of chlorine addition to *cis*-cinnamic acid and other olefinic compounds in acetic acid as solvent. The reaction followed a second-order course, as has been confirmed in later investigations by Robertson and co-workers [18–23] for olefins of widely varying reactivity. The second-order velocity constants obtained in these investigations are collected in the Appendix and are quoted without further reference hereafter. Ingold and Ingold [11] had observed that when two or more polar groups are attached to an ethenoid centre, their interaction may complicate the resulting effect on the rate. When one such group only is varied, however, the changes in rate are consistent with the view that electron accession to the double bond increases the rate of reaction. Thus the methyl group, when attached to the ethylenic carbon either directly or through a conjugated system, increases the rate of chlorine addition by a factor of more than 10 ; similarly, electron-withdrawing groups reduce the rate, the nitro-group producing a change in velocity of addition by a factor of 10^4 :

Parent compound.	R = *p*-Me.	H.	*p*-Cl.	*m*-NO_2.	*p*-NO_2.
$R{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}COPh$ *	k_2 = *ca.* 800	61	23	0·23	—
$R{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2H$	k_2 = 103	4·9	—	0·011	0·0049

Two methyl groups are superior to a phenyl group in promoting reactivity, the latter being more effective than a single methyl group :

$CMe_2{:}CH{\cdot}CO_2H$	*trans*-$CHPh{:}CH{\cdot}CO_2H$	*trans*-$CHMe{:}CH{\cdot}CO_2H$
$k_2 = 51$	4·9	0·62
	$CH_2{:}CH{\cdot}CO_2H$	 $\begin{array}{l}CH{\cdot}CO_2H\\ \Vert\\ CH{\cdot}CO_2H\end{array}$
	0·018	0·00011

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[16] *Annalen*, 1935, **516**, 231.

[17] *J.*, 1939, 1509.

[18] I. D. Morton and P. W. Robertson, *J.*, 1945, 129.

[19] P. B. D. de la Mare and P. W. Robertson, *ibid.*, p. 888.

[20] I. Hartmann and P. W. Robertson, *ibid.*, p. 891.

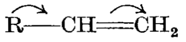
[21] I. Ting and P. W. Robertson, *J.*, 1947, 628.

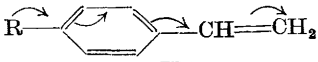
[22] B. E. Swedlund and P. W. Robertson, *ibid.*, p. 630.

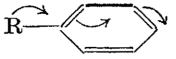
[23] H. P. Rothbaum, I. Ting, and P. W. Robertson, *J.*, 1948, 980.

* Substituents in the PhCO group, as compared with the Ph′ group, of $CHPh'{:}CH{\cdot}COPh$ are much less effective in altering the rate of addition—as would be expected, since the carbonyl group breaks the conjugation between the substituent and the double bond.

The types of electron displacement which favour halogen addition to a double link are those which would favour aromatic substitution :


(I.)

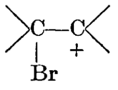

(II.)

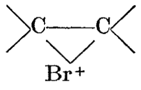

(III.)

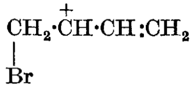
It is not surprising, therefore, that the effect of R in promoting addition of chlorine to (I) and (II) is similar to that of the same substituent on the chlorination of (III), as shown by the following values of k_2 :

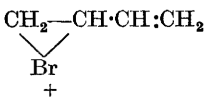
	R = COPh.	CO_2Et.	CO_2Me.	CO_2H.	CHO.	CN.	NO_2.	SO_2Cl.
Cl_2 addition to Ph·CH:CH·R :	61	10	10	4·9	1·8	0·022	0·020	0·001
Cl_2 substitution in p-MeO·C_6H_4R, relative rate : [24]	29	19	16	10	—	—	0·07	—

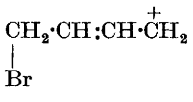
Sufficient evidence has been given to illustrate that electrophilic attack by the halogen molecule is the rate-determining stage of these additions. It has already been pointed out, however, that the intervention of solvent and of added ions in the completion of the reaction demonstrates that the whole process of addition involves at least two stages. Neither the kinetics nor the effect of structure on the rate throws light on the exact nature of the intermediates involved. In particular, it is not known whether the halogen–halogen link in the molecule which initiates reaction is broken in the first (rate-determining) stage of the process. It is commonly supposed that such a structure as (I*a*) is formed by attack of halogen on the olefinic compound ; and it is now usually thought that structure (I*b*) [25] contributes to the resulting resonance hybrid, and accounts for the familiar trans-addition of halogen.*

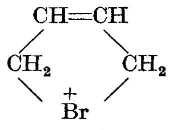

(I*a*.)


(I*b*.)


(II*a*.)


(II*b*.)


(III*a*.)


(III*b*.)

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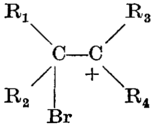
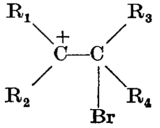
[24] A. E. Bradfield and B. Jones, *Trans. Faraday Soc.*, 1941, **37**, 726.

[25] I. Roberts and G. E. Kimball, *J. Amer. Chem. Soc.*, 1937, **57**, 947.

* The π-complex formulation (cf. Dewar [26]) is perhaps an equivalent method of writing a complex between a Br^+ ion and an olefin ; but the former type of representation appears to indicate more clearly that the two alternative forms



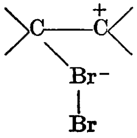
and



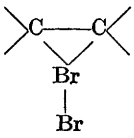
do not in general contribute equally to the resulting resonance hybrid.

In an extension, due to Burton and Ingold,[9, (cf. 10)] of the above theory, the coexistence of 1 : 2- and 1 : 4-addition to conjugated systems is associated with the distribution of charge due to mesomeric electron shift in the cation of an anionotropic system. Thus the mesomeric cation involved in the reaction between butadiene and bromine would be written as a resonance hybrid of structures (II*a*) and (III*a*) ; and this can then take up an anion at either the 2- or the 4-position. Either of the ring structures (II*b*) and (III*b*) could theoretically contribute also, but since they involve different geometrical relationships of atomic nuclei, they cannot both contribute appreciably to the same resonance hybrid. If, however, the facts necessitated the postulation of all four types of structure, (II*a*), (II*b*), (III*a*), (III*b*), then this might be accommodated by assuming a tautomeric equilibrium between a hybrid of (II*a*), (II*b*), (III*a*) and one of (II*a*), (III*a*), (III*b*).

Although these true carbonium ions are plausible intermediates in addition reactions, the known facts could equally be explained in terms of intermediates such as (IV*a*) and (IV*b*) [cf. 1, 27] which also constitute a possible resonance hybrid. Although a carbonium ionic centre is present in such a structure, thus permitting, in an ionising solvent, stabilisation by solvation forces, the resulting complexes are dipolar rather than fully ionic. Such a view would seem to approach that held by Sir R. Robinson,[28] but is as yet neither necessitated nor disproved. A more detailed study of the products of addition as related to reaction kinetics in the presence of added salts may help to elucidate this problem.



(IV*a*.)



(IV*b*.)

3. Third-order Bromine Addition.—It was first established by Robertson, Clare, McNaught, and Paul,[13] and has since been confirmed for olefins of widely different reactivity,[21, 23] that in the concentration region M/40 in pure acetic acid, addition of bromine to unsaturated compounds proceeds by third-order kinetics, the rate being proportional to $[A][Br_2]^2$. Dilution, increase of temperature, or dilution of the solvent with water was shown to result in the gradual dominance of a second-order reaction with a higher heat of activation. Similar behaviour was observed [29] for bromination of aromatic substances in the same solvent.

The effects of substituents on the rates of reaction by this mechanism are collected, as relative rates, in the Appendix. For several compounds, comparison may be made of the rate ratio of second-order chlorine to third-order bromine addition, as follows :

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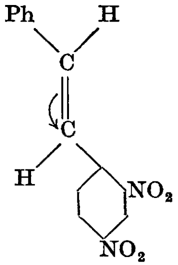
[26] M. J. S. Dewar, *J.*, 1946, 406, 777.

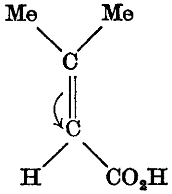
[27] H. D. C. Waters, A. R. Caverhill, and P. W. Robertson, *J.*, 1947, 1168.

[28] *Ibid.*, p. 1294.

[29] P. W. Robertson, P. B. D. de la Mare, and W. T. G. Johnston, *J.*, 1943, 276.



t_{Br_2}/t_{Cl_2} * = 450



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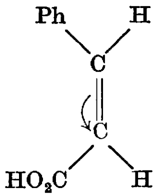

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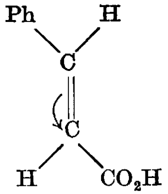

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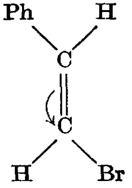
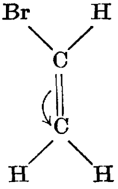


t_{Br_2}/t_{Cl_2} * = 270



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Small variations in the rate ratio are not unexpected ; for in third-order bromination, when as compared with second-order chlorination one additional molecule must be accommodated in the transition state in the vicinity of the double bond, larger steric effects might be anticipated. In fact, although the absolute reactivities of these compounds cover a large range, the rate ratios differ by a factor of less than 2, illustrating that the electronic requirements of the two reactions are similar. Table I exemplifies that electron-withdrawing substituents (R) retard, whereas the phenyl group, and more powerfully two methyl groups, accelerate the addition.

TABLE I

Effects of substituents on the rate of third-order bromine addition

Parent compound.	Relative rate of addition.		
	R = CH_2Cl.	R = Hal.	R = CO_2H.
CMe_2:CHR	—	0·5	0·15
trans-CHPh:CHR . .	77	0·1	0·017
CH_2:CHR.	1·6	0·001	—

At this stage, attention should be drawn to an apparent irregularity. The rate of bromine addition to stilbene (*trans*-CHPh:CHPh), as compared with styrene (CHPh:CH_2), is unexpectedly small, although several examples have already been given (*e.g.*, in Table I) of the considerable effect of the phenyl group in facilitating addition. Ingold and Ingold [11] gave an explanation of this point, referring particularly to the small reactivity of tetra-

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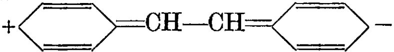
* t_{X_2} = time for 20% disappearance of halogen (reactants initially M/80 at 24° in acetic acid).

phenylethylene. The second phenyl group in stilbene is conjugated with the first phenyl group, which in styrene makes electrons available at the attacked olefinic carbon atom ($\mathrm{Ph{-}CH{=}CH_2}$). Electrons supplied by one phenyl group, therefore, are absorbed by the other (structures such as  making a substantial contribution to the stability of the molecule), instead of becoming available for co-ordination with the attacking halogen. This effect will contribute to the relative unreactivity of any olefin in which an electron-donating group is similarly conjugated with one which can withdraw electrons.

The groups CH_2Cl and CH_2Br are electron-attracting in character, as shown, for third-order bromine addition, by the following comparison :

$CH_2{:}CH{\cdot}CH_2{\cdot}O{\cdot}COPh$	$CH_2{:}CH{\cdot}CH_2Cl$	$CH_2{:}CH{\cdot}CH_2Br$	$CH_2{:}CH(CH_2Cl)_2$	$CH_2{:}CHBr$
14	1·6	1·0	0·019	0·0011

The greater reactivity of allyl chloride than of allyl bromide (the opposite would be expected, because chlorine is more powerfully electron-attracting than bromine) is not at present understood, and awaits more detailed study of the effect of halogen substituents on the rate of addition. The inclusion of vinyl bromide in the above series emphasises the importance of the inductive effect in deactivating the unsaturated compound, even though, as in the halogenobenzenes, the electron-releasing potentiality of the halogen controls the orientation of attack by electrophilic reagents.[30]

The effects of substituents (Me, Br, CO_2H) on the rate of addition as determined by the competition method of Ingold *et al.*[11, 12] were much smaller than those indicated by the above kinetic experiments. The difference is partly explained by the difference in conditions ; it is probably also relevant that bromine addition to allyl benzoate in chlorobenzene as solvent may induce addition to the much more slowly reacting cinnamic acid.[31] Indeed, it appears, in the comparison on p. 129, that substituents influence the rate of halogen addition to ethylene more powerfully than they affect the rate of aromatic halogen substitution.

The following are rates of uncatalysed addition to *cis*-ethylenic derivatives relative to the rate for the corresponding *trans*-isomer, the halogen and solvent being given in parentheses :

cis-Dichloroethylene . . .	3·0	(Cl_2, aqueous acetic acid)
cis-Cinnamic acid . . .	3·8	(Br_2, acetic acid)
	3·0	(Cl_2, acetic acid)
Maleic acid	2·3	(Br_2, aqueous acetic acid)
Citraconic acid . . .	2·8	(Br_2, aqueous acetic acid)

A greater reactivity of *cis*- than of *trans*-compounds is, therefore, characteristic of these reactions in which halogen is an electrophilic reagent ; though the same is not true of addition by other mechanisms.

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[30] M. S. Kharasch, M. C. McNab, and F. R. Mayo, *J. Amer. Chem. Soc.*, 1933, **55,** 2521, 2531.

[31] P. B. D. de la Mare, R. A. Scott, and P. W. Robertson, *J.*, 1945, 509.

It is also noteworthy that electrophilic attack by halogens on olefins appears to be more rapid than similar attack on the corresponding acetylenes. Thus we have the following relative rates:

	trans-Cinnamic acid.	Phenylpropiolic acid.
Second-order chlorine addition in acetic acid:	4·9	2·4
Third-order bromine addition in acetic acid:	0·017	0·0053

Similarly phenylacetylene as compared with styrene is very much less reactive towards bromine. No satisfactory explanation of this result seems to have been given; it is unexpected, on various grounds, namely: (*a*) in acetylenes, as compared with ethylenes, there must exist a greater density of unsaturation electrons available for attack; (*b*) steric considerations must, if anything, favour the reaction of the acetylene, rather than that of the olefin; (*c*) the addition of one halogen molecule to an acetylene is probably more exothermic than the addition of one halogen molecule to the corresponding olefin, as judged, at least, from the related heats of hydrogenation [32]; (*d*) the triple bond is apparently more polarisable than the double bond, since, in vinylacetylene, attack by hydrochloric acid is initiated by H^+ at the acetylenic rather than the olefinic terminal carbon atom.[10, 33]

As compared with second-order halogen addition (rate $\propto [A][X_2]$), even less is known about the intermediates concerned in third-order bromine addition (rate $\propto [A][Br_2]^2$). There is complete lack of evidence concerning whether third-order addition always produces a dibromide, or whether instead the mechanism is so complex that anions or solvent molecules may still participate in a stage of the reaction which is not rate-determining. It is unlikely that Br^+ formed in a pre-equilibrium (*e.g.*, $Br_2 + Br_2 \rightleftharpoons Br^+ + Br_3^-$) takes part in the reaction, since then the addition of negative ions would greatly reduce the rate of addition (*e.g.*, $Br^+ + OAc^- \rightleftharpoons BrOAc$). The kinetics make it clear that the presence of hydrobromic acid or a similar catalyst is not essential for the addition of bromine, despite the contrary earlier opinion held by Anantakrishnan and Venkataraman.[2] Thus the presence of sodium acetate, which should in acetic acid act as a base and reduce the rate of acid-catalysed addition, actually slightly facilitates the addition, *e.g.*, of bromine to ω-bromostyrene. It is not intended to imply that hydrobromic acid cannot intervene in addition; but merely that the reactions which have been described above are essentially those found in the absence of hydrobromic acid.

Two possible two-stage mechanisms would lead to third order kinetics as found, namely:

$$A + Br_2 \rightleftharpoons A,Br_2;\quad A,Br_2 + Br_2 \longrightarrow \text{products} \qquad \text{(i)}$$
$$Br_2 + Br_2 \rightleftharpoons Br_4;\quad A + Br_4 \longrightarrow \text{products} \qquad \text{(ii)}$$

The first was that favoured by White and Robertson,[17] and accepted by Williams [1]; but the kinetics do not distinguish between the two, since either

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[32] J. B. Conn, G. B. Kistiakowsky, and E. A. Smith, *J. Amer. Chem. Soc.*, 1939, **61,** 1868.

[33] W. H. Carothers, G. J. Berchet, and A. M. Collins, *ibid.*, 1932, **54,** 4066.

would be expected to have a low temperature coefficient, and would be supplanted by a concomitant second-order process on dilution, or at high temperatures.

4. Third-order Addition of Other Halogens.—The additions of iodine chloride and of iodine bromide to double bonds are the bases respectively of the Wijs and the Hanus method of determining quantitatively the unsaturation of fats, oils, and related compounds. Few measurements of rates and kinetics of these reactions of interhalogen compounds have, however, been made. White and Robertson [17] showed that, with reactants in the concentration region M/40, iodine chloride addition is a reaction of the third order in acetic acid. Hydrochloric acid retarded addition, presumably by formation of the unreactive $HClI_2$. The compounds examined were undecenoic acid, allyl acetate, cinnamic acid, and *o*-methoxycinnamic acid ; extension of the measurements to include less reactive olefins would be instructive. Bromine chloride and iodine bromide additions were also found to be kinetically of the third order, but the dissociation of these compounds is sufficient to necessitate correction for the concomitant addition of the more reactive halogen component. An estimate was made of the relative reactivity of the various halogens by the third-order mechanism ; it is as follows :

Halogen	I_2	IBr	Br_2	ICl	BrCl
Relative rate of addition	1	3×10^3	10^4	10^5	4×10^6

The increasing reactivity in the series I_2, IBr, ICl, may be associated with the increasing electron withdrawal from the point of initiation of addition (*i.e.*, with increasing polarity in the sense $\overset{\delta+}{\mathrm{I}}\text{—}\overset{\delta-}{\mathrm{I}} < \overset{\delta+}{\mathrm{I}}\text{—}\overset{\delta-}{\mathrm{Br}} < \overset{\delta+}{\mathrm{I}}\text{—}\overset{\delta-}{\mathrm{Cl}}$). It is difficult to avoid the conclusion, however, that the stability of the final product is partly responsible for the rate differences, particularly in the unpolarised halogens themselves, the additive reactivities of which increase in the order $I_2 < Br_2$. Quite a different situation arises in the substitution reactions between halide ions and alkyl halides ; in acetone, for example, alkyl iodides are attacked more rapidly by iodide ions than by bromide ions.[cf. 34, 35]

The addition of iodine to ethylenes differs from that of other halogens in that it is reversible. N. J. Bythell and P. W. Robertson [36] isolated the forward reaction by keeping the olefin in excess and measuring only the initial stages of the reaction. The kinetics appeared to be similar to those of the addition of bromine, except in that water added to the acetic acid solvent had a markedly less powerful effect in accelerating the rate of the reaction. Constitutive effects indicated that iodine acts as an electrophilic reagent ; the work of K. Nozaki and R. A. Ogg,[37] however, suggests that a re-examination of iodine addition in acetic acid would be desirable.

5. Fourth-order Bromine Addition.—The large variation in rate with

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[34] L. Fowden, E. D. Hughes, and C. K. Ingold, unpublished work.

[35] E. D. Hughes, F. Juliusberger, S. Masterman, B. Topley, and J. Weiss, *J.*, 1935, 1525.

[36] *J.*, 1938, 179.

[37] *J. Amer. Chem. Soc.*, 1942, **64**, 697, 704, 709.

initial concentration of reactants makes it difficult to follow these reactions over a wide concentration range. Nozaki and Ogg [37] produced evidence for the existence of a reaction of the kinetic form $dx/dt = k[A][Br_2]^n$ in the addition of bromine to allyl halides, though B. E. Swedlund and P. W. Robertson [38] were unable quantitatively to confirm their findings. The latter authors, however,[22] later showed that, in addition of bromine to slowly reacting olefins (*e.g.*, ω-bromostyrene, M/5—M/10), a reaction of kinetic order higher than 3 appears. A similar phenomenon was observed in an examination of the kinetics of bromination of aromatic compounds.[29, 39] The following sequence of reactions was regarded as providing a plausible explanation of these unusual kinetics :

$$Br_2 + Br_2 \rightleftharpoons Br_4 ; \quad A + Br_4 \rightleftharpoons A,Br_2 + Br_2 ; \quad A,Br_2 + Br_2 \longrightarrow \text{products}$$

The possibility was considered that the previously described third-order additions in the concentration region M/40 could be explained, as Nozaki and Ogg apparently believed, by a roughly equal contribution of second- and fourth-order addition. If this were so, however, there would be expected a much more rapid variation in reaction order with concentration than is actually observed.[cf. 29, 39]

6. Bromine Addition Catalysed by Halide Ions.—(a) *Catalysis by chloride ions.* Nozaki and Ogg [37] observed that halide ions may act as catalysts for bromine additions in acetic acid ; for instance addition to allyl chloride and to vinyl bromide is considerably catalysed by lithium chloride. The results were consistent with the contribution to the rate of a term $-d[Br_2]/dt = k[A][Br_2][Cl^-]$, and these authors proposed that such a mechanism is of general availability for bromine addition.

Subsequent investigations, particularly by Swedlund and Robertson,[22, 38] have confirmed that lithium chloride does, in general, catalyse bromine addition to olefins, as shown by the results summarised in Table II.

TABLE II

Halide-ion catalysis of bromine addition in acetic acid

Compound.	Relative rate of third-order uncatalysed bromine addition.	Ratio of catalysed rate to uncatalysed rate, reactants initially M/80, $x = 20\%$ reaction at 24° with catalyst :	
		LiCl, M/25.	HBr, M/20.
CHPh:CHPh	18	1·6	0·43
CH_2:CH·CH_2Cl	1·6	6·3	2·4
CH_2:CH·CH_2Br	1·0	5·5	2·2
CMe_2:CHCl	0·5	2·2	0·64
CHPh:CHBr	0·1	1·5	0·64
CH_2:C$(CH_2Cl)_2$	0·019	18	8·9
CHBr:CH_2	0·0011	7·0	10·5

Analogy with the two possibilities considered for third-order un-

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[38] *J.*, 1945, 131. [39] P. B. D. de la Mare and P. W. Robertson, *J.*, 1948, 100

catalysed addition [equations (i) and (ii)] suggests the two alternatives for additions catalysed by chloride ions :

$$A + Br_2 \rightleftharpoons A,Br_2;\quad A,Br_2 + Cl^- \longrightarrow \text{products} \qquad . \quad . \text{ (iii)}$$
$$Br_2 + Cl^- \rightleftharpoons ClBr_2^-;\quad A + ClBr_2^- \longrightarrow \text{products} \qquad . \quad . \text{ (iv)}$$

Equation (iv) can, the Reviewer believes, hardly be significant in addition to allyl chloride, for the following reason. A negative ion, such as the $ClBr_2^-$ ion, should act as a nucleophilic reagent ; yet the relative rates of the catalysed additions to allyl chloride and to vinyl bromide require this anion to be acting as an electrophilic reagent, seeing that the extent of the catalysis is much the same for these two compounds whose reactivities towards electrophilic halogen differ by three powers of 10. It is not meant to imply that the mechanism represented by equation (iv) is never available for addition of bromine. In a later section, evidence will be presented of a rapid nucleophilic attack by $ClBr_2^-$ on olefinic cations such as $R{\cdot}\overset{+}{C}H{\cdot}CH{:}CH{\cdot}OH$; and some evidence exists[40] that attack by $ClBr_2^-$ is also possible in additions to such olefins as maleic acid, in which electron regression from the double link is considerable.

Equation (iii) as the mechanism of additions catalysed by halide ions is consistent with the observation that chlorine addition, for which the third-order uncatalysed mechanism does not seem to be available, is little influenced by the presence of lithium chloride.* A difficulty arises, however, in that the extent of the catalysis seems to be selectively dependent on the nature of the olefin. It would have been expected that the rate of such a catalysed addition would follow, and decrease less rapidly than, the rate of uncatalysed addition, as the structure of the olefin became progressively less favourable towards electrophilic attack by halogen, and correspondingly more favourable toward attack by a nucleophilic ion. In other words, catalysis should be greatest for the least rapidly reacting olefins.

The data of Table II indicate considerable deviations from such a simple hypothesis : for example, catalysis of addition to ω-bromostyrene is less than that of addition either to stilbene (which, without catalysts, is very much more reactive), or to vinyl bromide (which is many times less reactive in addition reactions). Such considerations led Swedlund and Robertson [22, 38] to propose a special mechanism for these additions ; it may be, on the other hand, that some special steric or polar consideration affecting the rate of the attack by halide ions is causing deviations from the simple predictions of equation (iii). Further examination over a wider range of compounds of the catalytic effects of halide and other ions, together with detailed knowledge of the equilibria present in solutions of bromine in the presence of these ions, seems necessary to clarify the position.

(b) *Catalysis by bromide ions.* The last column in Table II gives the rate ratios for hydrogen bromide-catalysed to uncatalysed addition of bromine in acetic acid.[21, 22, 23] Since these are very near the limiting values for

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[40] P. W. Robertson and co-workers, unpublished work.

* Iodine addition, on the other hand, is catalysed by halide ions, but the reaction is complicated by the considerable stability of such complex ions as ClI_2^-.

excess of hydrogen bromide, it is presumed that they include negligible contributions from uncatalysed third-order addition, the rate of which ($\propto[A][Br_2]^2$) is very critically determined by the concentration of free bromine. The results are, therefore, consistent with the rate expression $-d[Br_2]/dt = k[A][HBr_3] = k[A][Br_2][Br^-]$.[37, 38] The equilibrium $HBr + Br_2 \rightleftharpoons HBr_3$ in acetic acid lies well to the right, but the equilibrium constants as determined by W. J. Jones [41] vary with concentration, though they correspond roughly with the value obtained by Nozaki and Ogg [37] for the equilibrium between lithium bromide and bromine in the same solvent. The presence of hydrobromic acid or of lithium bromide in a solution of bromine in acetic acid will, therefore, considerably reduce the concentration of free bromine in the mixture. Bromide ions, however, like chloride ions, should act as catalysts for additions of bromine to olefins. Accordingly, as shown by the last column of Table II, the presence of excess of hydrobromic acid actually retards the rate of bromine addition to those olefins, addition to which is not much catalysed by lithium chloride; for the other compounds, both lithium chloride and hydrobromic acid act as catalysts.

It would seem reasonable, then, to suppose that, for addition to these olefins, lithium chloride and hydrobromic acid have a similar catalytic function. Further evidence was given by Nozaki and Ogg, who showed that hydrobromic acid and lithium bromide are equally effective as catalysts for addition to allyl chloride and to vinyl bromide. Swedlund and Robertson [22, 38] proposed the alternative view, which is also permitted by the kinetics, that in addition catalysed by hydrogen bromide, the electrophilic reagent is the hydrogen tribromide molecule. Their reason for adopting this view is essentially as follows. The basicity of the reagent is usually (cf. E. D. Hughes [42]) regarded as the most important factor determining the nucleophilic reactivity of ions. One would, therefore, be tempted to predict that, since the dissociation of acids increases in the order $HOAc < HCl < HBr$,[43] the corresponding ions should decrease in the order $OAc^- > Cl^- > Br^-$ in their efficiency as nucleophilic catalysts for addition. The opposite is, in fact, the case; for, when allowance has been made for the disturbance of the concentration of free bromine in solutions containing hydrobromic acid, bromide ions appear to be about 20 times as effective as chloride ions in catalysing addition of bromine; and the catalytic power of acetate ions, though perhaps not zero, is certainly almost negligible as compared with that of chloride ions.

There exists, however, some evidence that basicity does not always give a satisfactory measure of the relative nucleophilic power of anions. For example, measurements of the rates of bimolecular nucleophilic reactions with bromide ions and with chloride ions of a number of substituted alkyl halides [44, 45, 46] indicate that bromide ion is at least 5 times as reactive as

[41] *J.*, 1911, **99**, 392.

[42] *Trans. Faraday Soc.*, 1938, **34**, 185.

[43] I. M. Kolthoff and A. Willmann, *J. Amer. Chem. Soc.*, 1934, **56**, 1007.

[44] T. A. Bither, J. M. Sturtevant, and H. C. Thomas, *ibid.*, 1945, **67**, 1562.

[45] A. R. Olson and F. A. Long, *ibid.*, 1936, **58**, 393.

[46] M. J. Young and A. R. Olson, *ibid.*, p. 1157.

chloride ion. Similar comparisons and conclusions can be reached in other cases,[47] though data for reactions in acetic acid do not seem to be available. The factors determining the rates even of these simple substitutions are not yet fully understood, but it is satisfactory that the order of reactivity for nucleophilic substitution, $Br^- > Cl^-$, appears to be the same as the order of catalytic efficiency in addition.

The fact [37] that water added to the acetic acid solvent reduces the efficiency of halide ions as catalysts for bromine addition is to be expected, and is of no help in further elucidating the mechanism. An increase in the solvating power of the solvent should stabilise the polarised transition state of uncatalysed addition relative to the formally neutral reactants, thus accelerating addition by this mechanism; [48] but such a solvent change should still more stabilise the fully ionic halide ions, and should thus diminish their catalytic activity. As compared with addition in acetic acid, addition in strongly solvating solvents such as methanol should not be greatly catalysed by halide ions.

7. Nucleophilic Halogen Addition.—(a) *Catalysis by sulphuric acid and by perchloric acid.* In the reactions considered so far, the effects of structure on the rate of halogen addition indicate that the halogen molecule acts as an electrophilic reagent. It was first predicted by Ingold and Ingold,[11] however, that if the ethylene link were polarised by a sufficiently strongly electron-demanding group, an addition involving nucleophilic attack by halogen might be realisable. Experimental evidence for the existence of such a mode of addition is most strikingly given by the reactions of $\alpha\beta$-unsaturated aldehydes and ketones in acetic acid.[19, 23]

Addition of bromine to cinnamaldehyde (reactants M/80) in the absence of catalysts is very slow at first, but after about 10 minutes begins to increase autocatalytically, and reaches 70% in about 30 minutes. In the presence of sodium acetate (M/20) the autocatalysis is repressed, and the reaction proceeds slowly without an induction period, at a rate less than that of addition to cinnamic acid under the same conditions. In the presence of perchloric or sulphuric acid, however, addition is rapid, and with acid concentration constant, the initial rate of addition is proportional to the concentration of olefin and of bromine. Water reduces the rate of the acid-catalysed reaction. Perchloric acid, a stronger acid in this solvent, is more effective as a catalyst than sulphuric acid, and nitric acid, relatively a very weak acid, has very little catalytic power.

Corresponding results have been obtained for addition to such $\alpha\beta$-unsaturated ketones as benzylideneacetophenone, CHPh:CH·COPh,[23] the structure of which precludes substitution adjacent to the carbonyl group. The reactions of crotonaldehyde and of acraldehyde are similar, but are too rapid for detailed investigation. Addition of bromine to $\alpha\beta$-unsaturated acids such as acrylic and maleic acids, to maleic anhydride, to ω-cyanostyrene and to ω-nitrostyrene is also catalysed by these mineral acids, but to a much smaller extent. Sulphuric acid does not catalyse addition to ally

[47] Cf. P. B. D. de la Mare, Ph.D. Thesis, University of London, 1948.

[48] Cf. E. D. Hughes, *Trans. Faraday Soc.*, 1941, **37**, 763.

benzoate, and only slightly catalyses addition to ethyl cinnamate and to allyl chloride.

TABLE III

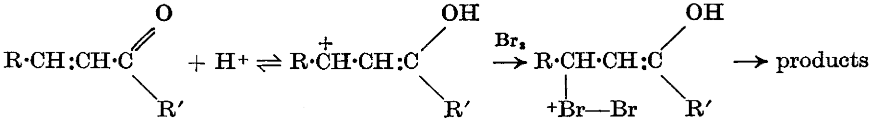
Acid-catalysed addition of bromine in acetic acid (reactants M/80)

Compound.	H_2SO_4-catalysed bromine addition, k_2 (H_2SO_4 = M/80).	H_2SO_4-catalysed chlorine addition, k_2 (H_2SO_4 = M/320).	Uncatalysed chlorine addition (k_2).
Benzylideneacetophenone .	32	—	61
Ethyl cinnamate . . .	$\ngtr$ 0·013 *	—	10
Cinnamaldehyde . . .	27	1·3 *	1·8
trans-Crotonic acid . . .	*ca.* 0·009 *	—	0·62
Crotonaldehyde	> 1000	43	0·41
ω-Nitrostyrene	*ca.* 0·005 *	—	0·020

* Corrected by deduction of the uncatalysed rate.

In Table III, some data for acid-catalysed bromine and chlorine additions are compared with velocity constants for uncatalysed chlorine addition, to emphasise that the effect of structure on the rate of addition is quite different for the two reactions. The very rapid rate of addition to unsaturated aldehydes and ketones as compared with the corresponding acids is suggestive of addition initiated by nucleophilic halogen. The initial polarisation of the olefin is, however, clearly not the only factor concerned in determining the reaction rate, since ω-nitrostyrene as compared with cinnamaldehyde is less reactive under conditions of acid catalysis, despite the greater electron-withdrawing capacity of the NO_2 as compared with the CHO group.

The essential rate-determining stage of acid-catalysed addition is thought, therefore, to involve nucleophilic attack by halogen on the ion † produced by addition of a proton to a group conjugated with the double bond, as in the following sequence [19]:



The stage subsequent to proton-addition is thought to be complex, since the rate of addition is not proportional to the stoicheiometric concentration of acid catalyst. The proposed mechanism accounts for the observed kinetics (including the effect of water, which acts as a base and thus reduces the proton-donating power of the acid catalyst), and is also consistent with the effect of structure on the rate of addition. The electronic requirements of the preliminary addition of a proton to the olefinic derivative are clearly opposite to those of the subsequent nucleophilic attack by halogen, and

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† Such an ion as an intermediate in addition was first suggested by Nozaki and Ogg,[37] but the subsequent stages of their mechanism involved a halide ion, which the Reviewer believes to have, as shown below, quite a different function in such reactions.

therefore the effect of structure on the rate of acid-catalysed addition is complicated. The small magnitude of catalysis in addition to ω-nitrostyrene and to $\alpha\beta$-unsaturated acids, as compared with addition to the corresponding $\alpha\beta$-unsaturated aldehydes and ketones, is almost certainly determined by the greater basicity of the latter compounds. The effect of changing R and R′ (in R·CH:CH·COR′) has been investigated [23] and reveals further the balanced electronic requirements of the two important stages of this type of addition. In certain cases, however, the stage involving nucleophilic attack by halogen predominates, resulting in a reversal of the normal order of reactivity found when halogen acts as an electrophilic reagent. Thus in Table III it is shown that acid-catalysed addition to crotonaldehyde is more rapid than similar addition to cinnamaldehyde. Correspondingly, *p*-xyloquinone as compared with benzoquinone, with sulphuric acid as a catalyst, adds bromine much less rapidly.[23]

Chlorine addition, as is shown in Table III, is less sensitive than bromine addition to the presence of acid catalysts. The chlorine molecule is less polarisable than the bromine molecule, and since nucleophilic attack involves polarisation of the halogen in the sense opposite to that usually effected in this type of reaction, it is perhaps natural that nucleophilic as compared with electrophilic addition is more critically determined by the polarisability of the halogen.

Although sodium acetate usually eliminates autocatalysis of halogen addition in acetic acid, its presence does not always ensure as low a rate of addition as would be expected from the structure of the olefin. Particularly is this the case for such olefins as acraldehyde, addition to which is very sensitive to acid catalysis. The reason for this anomaly is not known for certain. It is possible that the solvent itself acts as a source of protons to catalyse the addition ; alternatively, anion catalysis may be important in electrophilic addition to these compounds.

(b) *Catalysis by halogen acids.* As catalysts for bromine addition, hydrobromic and hydrochloric acids are much more efficient than would be expected from the order of acid strengths in acetic acid, namely : [43]

$$HClO_4 > HBr > H_2SO_4 > HCl > HNO_3$$

Thus the following are relative rates of addition of bromine to cinnamaldehyde, reactants M/80, catalyst M/320 :

$HClO_4$	HBr	H_2SO_4	HCl	HNO_3
7·3	*ca.* 300	3·4	24	*ca.* 0·8

It seems probable that the great catalysis by hydrobromic acid and by hydrochloric acid of halogen addition is attributable to the formation of complex ions (*e.g.*, Br_3^-, $ClBr_2^-$, Cl_3^-). These act as nucleophilic reagents to effect addition of halogen to the olefinic cation (*e.g.*, $\overset{+}{C}HPh{\cdot}CH{:}CH{\cdot}OH$), for which task they are, as would be expected, more active than halogen molecules. The possibility is not excluded that undissociated hydrogen tribromide and similar molecules are the effective reagents. It is unlikely, however, that the olefin itself (rather than the carbonium ion formed by addition of a proton) is attacked ; for Nozaki and Ogg [37] showed that, for this type of addition (exemplified, in their experiments, by bromine addition to maleic acid), the proton plays a specific part in the reaction, hydrobromic acid being much more effective than lithium bromide as a catalyst.* Furthermore, as in addition catalysed by sulphuric acid, addition to ω-nitrostyrene catalysed by hydrogen bromide is much less rapid than similar addition to cinnamaldehyde, though the former should theoretically be more susceptible to attack by a nucleophilic reagent.

The effects of structure on the rates of addition reactions catalysed by hydrobromic acid have confirmed and extended the conclusions obtainable from the similar reactions catalysed by sulphuric acid. Because the addition of a proton to a basic centre in the olefin is favoured by the presence of suitably placed electron-donor groups in the molecule, whereas the second stage of the reaction, namely nucleophilic attack by Br_3^-, may be decelerated by the same structural influences, the effects of substituents on the rates of these additions are often complex. There are, however, a number of examples [cf. 18] which demonstrate that the normal order of reactivity, found when electrophilic attack by the halogen is the dominant mechanism, may become reversed under conditions of catalysis by hydrobromic acid. Thus we have the following rates:

	$CHMe:CH\cdot CO_2H$.	$CH_2:CH\cdot CO_2H$.
Cl_2 (k_2)	0·62	0·018
Br_2 + HBr (as k_2; reactants M/80, excess HBr) .	0·051	0·44

In a similar way it is found that introduction of a methyl group into maleic, fumaric, or glutaconic acid (thus forming citraconic, mesaconic, or β-methylglutaconic acid, respectively) results in a deceleration of bromine addition in acetic acid when catalysed by hydrobromic acid, but an acceleration of addition in aqueous acetic acid, in which solvent the normal electrophilic reaction of bromine is favoured. Another striking example is the following:

	$CHPh:CH\cdot CO_2H$.	$CHPh:C(CO_2H)_2$.
Br_2 (aqueous HOAc), relative rates	100	1
Br_2 + HBr (HOAc), relative rates	1	250

In benzylidenemalonic acid, it is seen that the presence of two carboxyl groups on the same carbon atom, as compared with that of a single carboxyl group, considerably favours acid-catalysed addition. The presence of two electron-demanding groups on different carbon atoms usually, however, has the opposite effect on addition by this mechanism. Thus bromine in the presense of hydrobromic acid adds to maleic acid at almost the same rate as to acrylic acid. With the same reagent, Ph·CO·CPh:CH·COPh is less reactive than Ph·CH:CH·COPh. It is possible that steric influences are important in these reactions; but a very plausible explanation, due to Hartman and Robertson,[20] of such abnormally low reactivities, is as follows. The normal state, *e.g.*, of the maleic acid molecule involves the contribution of polar structures such as (I). These are unfavourable to the stability of ion (II), as compared with (III), since the presence, in (II), of adjacent

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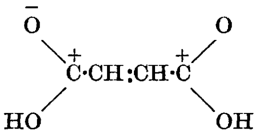
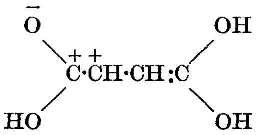
* A part of the LiBr-catalysed addition may, however, in this case involve attack by Br_3^- on the olefinic compound.

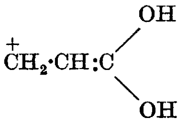
positive poles involves considerable destabilisation. These ions (II) and (III) are involved in acid-catalysed addition to maleic and acrylic acids, respectively, and hence the second carboxyl group in maleic acid hardly facilitates this type of addition. When, however, the second electron-attracting group is separated from the ethylenic carbon atom by a methylene group, this condition no longer applies, and the expected order (*e.g.*, $CO_2H·CH_2·CH{:}CH·CO_2H > CHMe{:}CH·CO_2H$) of reactivity is obtained. Similarly, though the *p*-benzoquinones contain the structure CO·CH:CH·CO, the formation of adjacent positive polarities in the ion may be avoided by resonance, as in (IV), and these compounds add bromine very rapidly under conditions of acid catalysis.



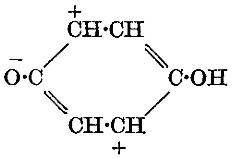
(I.)



(II.)

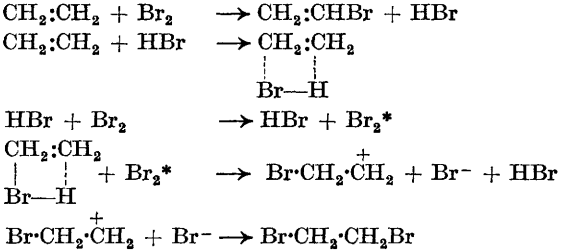


(III.)



(IV.)

Description of acid-catalysed addition as in the above discussion has been challenged by S. V. Anantakrishnan and R. Venkataraman.[2, 49] The mechanism proposed by these authors was originally believed to apply equally to catalysed and uncatalysed addition, and involves the following stages :



$$\begin{aligned}
&CH_2{:}CH_2 + Br_2 \rightarrow CH_2{:}CHBr + HBr\\
&CH_2{:}CH_2 + HBr \rightarrow \underset{Br—H}{CH_2{:}CH_2}\\
&HBr + Br_2 \rightarrow HBr + Br_2^*\\
&\underset{Br—H}{CH_2{:}CH_2} + Br_2^* \rightarrow Br·CH_2·\overset{+}{C}H_2 + Br^- + HBr\\
&Br·CH_2·\overset{+}{C}H_2 + Br^- \rightarrow Br·CH_2·CH_2Br
\end{aligned}$$

It has been shown above that such a mechanism is not responsible for those addition reactions in which bromine acts as an electrophilic reagent ; and, indeed, the existence of uncatalysed third-order bromine addition (rate $\propto [A][Br_2]^2$) has recently been admitted by Anantakrishnan and his co-workers.[50] A scheme such as the above still seems, however, to be supposed to explain acid-catalysed addition ; in particular, these authors

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[49] *Proc. Indian Acad. Sci.*, 1946, **23**, *A*, 307, 312, 319.

[50] *Ibid.*, 1948, **27**, *A*, 184.

still believe that a proton catalyses addition by co-ordination with the ethylenic electrons.

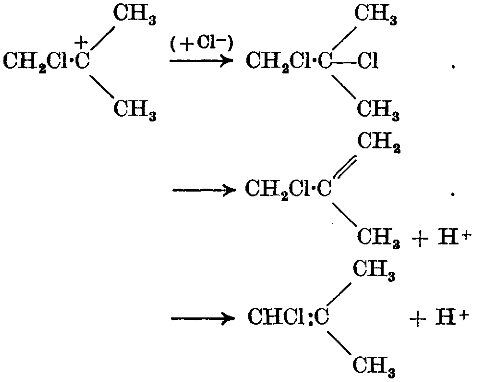
The evidence indicates strongly, in the Reviewer's opinion, that such an attachment, though in some circumstances possible, in no case so far investigated results in catalysis of halogen addition. Two types of addition catalysed by hydrogen bromide have been recognised. In the first (anion-catalysed addition, *e.g.*, to vinyl bromide), the proton plays no part in the reaction. In the second (acid-catalysed addition, *e.g.*, to cinnamaldehyde, acrylic acid, ω-cyanostyrene, or ω-nitrostyrene), an alternative basic centre exists in the molecule which provides, as compared with the double bond, a much more probable site for addition of a proton, and the presence of which in the molecule is essential for substantial catalysis to occur. A third type probably exists, but has not yet been fully established, in which the Br_3^- ion acts as a nucleophilic brominating agent for olefinic compounds containing strongly electron demanding groups.

8. Addition in Non-hydroxylic Solvents.—In hydroxylic solvents, the kinetics of addition reactions, though often complicated, have been shown above to be consistently intelligible, and the effects of structure on the rate of addition can be interpreted in terms of the electronic theory of organic reactions. The exact nature of the intermediates involved, however, remains to be elucidated. It is known that addition is usually initiated by an electrophilic reagent, probably by the halogen molecule ; but details of the subsequent stages are incompletely understood, and an experimental study of the relation between products (determined by these final stages), the presence of added nucleophilic reagents, and the kinetics should prove of value in extending knowledge of the detailed mechanism of this complex reaction.

Non-hydroxylic solvents, on the other hand, are often used for preparative additions, since the product of the reaction is then substantially the dihalide. Under these conditions, however, the kinetics are often intractable. For instance, in carbon tetrachloride, addition of bromine to allyl benzoate can proceed by a heterogeneous reaction on a polar surface, or, at higher concentrations, by a homogeneous reaction of high kinetic order. The rate of addition is greatly increased by the presence of small amounts of polar catalysts—water, pyridine, hydrobromic acid, or iodine. Dissolved oxygen can also affect the rates of these additions. A kinetic study of iodine-catalysed addition of chlorine and of bromine to ethyl cinnamate [27] has shown that iodine is not used up in the course of the reaction, and that, though the uncatalysed addition of chlorine is very slow, and that of bromine is not reproducible, the presence of iodine renders chlorine addition faster than that of bromine. The kinetics of the two reactions, when the amount of added iodine is small, are consistent with the rate equations $-d[Cl_2]/dt = k[A][Cl_2][ICl]$ and $-d[Br_2]/dt = k[A][Br_2]^2[IBr]$, but the order with respect to iodine halide increases as the amount of added iodine becomes greater.

Similar, though less pronounced catalytic effects persist in the more polar solvents chloroform and chlorobenzene, in which the uncatalysed addition of bromine appears to be similar in kinetic form to that obtained in acetic acid. The effects of structure on the rates of these additions have not, however, been extensively examined by a satisfactory technique, though it is probable that electrophilic attack by halogen is the commonest way in which reaction is initiated. The experiments of Anantakrishnan and Ingold [12] indicate further that nucleophilic attack by some halogenating agent can also be important, when hydrobromic acid acts as a catalyst, in addition of bromine to $\alpha\beta$-unsaturated aldehydes.

The tendency towards over-simplification in discussions of addition in non-ionising solvents is exemplified by the recent work of R. W. Taft,[51] who attempted to explain the varying proportions of substitution and addition in the gas- and liquid-phase chlorination of olefins. Thus *iso*-butylene is supposed to react with Cl^+ to form a carbonium ion which can decompose as follows :



. . . (*a*)

. . . (*b*) (i)

. . (*b*) (ii)

No evidence exists, however, so far as the Reviewer is aware, for such an intermediate in additions under the non-ionising conditions considered. It will be remembered, for example, that chlorine addition to ethyl cinnamate in carbon tetrachloride is certainly more complicated.[27] Detailed deductions from such a mechanism should, therefore, be treated with reserve. The present review has attempted to indicate both what is known and also what is still uncertain in the detailed mechanism of halogen addition reactions, and it will be valuable if some new experimental approach can be found to throw further light on the actual course or courses of these reactions.

The Reviewer has had both valuable comments on this manuscript and access to unpublished experimental findings and theoretical discussions provided by Professor P. W. Robertson, of Victoria University College, Wellington, New Zealand, whose assistance and encouragement are gratefully acknowledged. Advice and help given by Professor C. K. Ingold, D.Sc., F.R.S., and by Professor E. D. Hughes, D.Sc., have also been of great benefit ; and further, the Reviewer thanks Drs. A. Maccoll, R. J. Gillespie, and D. P. Craig for discussion and comment.

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[51] *J. Amer. Chem. Soc.*, 1948, **70**, 3364.

APPENDIX

Relative rates of addition reactions in acetic acid at 24°.*

Compound.	Chlorine addition.	Bromine addition.	Bromine addition catalysed by excess (M/20 or M/10) HBr.
$CHPh{:}CMe_2$	—	v. fast	—
$CHPh{:}CH_2$	—	v. fast	—
$CHPh{:}CH\cdot CH_2Cl$	—	77	16
$CHPh{:}CHPh$	—	18	8
$CH_2{:}CH\cdot CH_2\cdot OAc$	—	10	—
$CH_2{:}CH\cdot CH_2\cdot OBz$	—	14	9
p-$Me\cdot C_6H_4\cdot CH{:}CH\cdot COPh$	*ca.* 800	7·8 †	—
$CH_2{:}CH\cdot CH_2\cdot O\cdot CO\cdot CH_2Cl$	—	6	—
$CH_2{:}CH\cdot CH_2Cl$	—	1·6	3·8
$CH_2{:}CH\cdot CH_2Br$	—	1·0	2·2
$CMe_2{:}CHCl$	—	0·5	0·3
p-$Me\cdot C_6H_4\cdot CH{:}CH\cdot CO_2H$ (*trans*)	103	—	—
$CHPh{:}CH\cdot COPh$	61	0·33 †	> 1000
$CHPh{:}CH\cdot CO\cdot C_6H_4Me$-$p$	61	0·33 †	—
$CMe_2{:}CH\cdot CO_2H$	51	0·15	0·18
p-$Cl\cdot C_6H_4\cdot CH{:}CH\cdot CO\cdot CMe_3$	36	—	—
$CHPh{:}CHBr$	30	0·11	0·07
p-$Cl\cdot C_6H_4\cdot CH{:}CH\cdot COPh$	23	—	—
$CHPh{:}CH\cdot CO_2H$ (*cis*)	22	0·063	0·07
$CHPh{:}CH\cdot CO\cdot C_6H_4(NO_2)$ (*m*)	15	—	—
$CHPh{:}CH\cdot C_6H_3(NO_2)_2$ (2 : 4)	13	0·028	0·03
$CHPh{:}CH\cdot CO_2Me$	10	—	—
$CH_2{:}C(CH_2Cl)_2$	—	0·019	0·17
$CHPh{:}CH\cdot CO_2H$ (*trans*)	4·9	0·017	—
$CPh{\vdots}C\cdot CO_2H$	2·4	0·0053	0·03
$CHPh{:}CH\cdot CHO$	1·8	—	> 1000
$CHMe{:}CH\cdot CO_2H$ (*trans*)	0·62	—	0·051
$CHMe{:}CH\cdot CHO$	0·41	—	> 10,000
$CH_2{:}CHBr$	0·28	0·0011	0·012
m-$NO_2\cdot C_6H_4\cdot CH{:}CH\cdot COPh$	0·23	—	—
$CH_2{:}CH\cdot CO_2Et$	0·026	—	—
$CHPh{:}CH\cdot CN$	0·022	—	4·0
$CHPh{:}CH\cdot NO_2$	0·020	—	*ca.* 1·0
$CH_2{:}CH\cdot CO_2H$	0·018	—	0·44
m-$NO_2\cdot C_6H_4\cdot CH{:}CH\cdot CO_2Me$ (*trans*)	0·011	—	0·006 ‡
p-$NO_2\cdot C_6H_4\cdot CH{:}CH\cdot CO_2Me$ (*trans*)	0·0049	—	0·003 ‡
Coumarin	0·0030	—	—
o-$NO_2\cdot C_6H_4\cdot CH{:}CH\cdot CO_2Me$ (*trans*)	0·0011	—	—
$HO_2C\cdot CH{:}CH\cdot CO_2H$ (*cis*)	0·00011	—	0·56

* As given by Robertson and co-workers.[13, 17–23, 38, 40]

Selection has been made in certain cases between slightly diverging values of different experimenters. The values for chlorine addition are bimolecular velocity constants (min.$^{-1}$ g.-mol.$^{-1}$ l.). Those for bromine addition have been calculated as "bimolecular constants", *i.e.*, if t (mins.) is the time for 20% disappearance of bromine, with olefinic compound and total bromine initially each M/80, then the quoted figure is $20/t$.

† Determined in the presence of excess of sodium acetate.

‡ These values are for the corresponding acids.