

117. The Kinetics of Halogen Addition to Unsaturated Compounds. Part XI. The Halogeno-ethylenes.

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Whereas bromine addition to vinyl bromide in acetic acid solution is catalysed by both hydrogen bromide and lithium chloride, $\text{CHPh}\cdot\text{CHBr}$ and $\text{CMe}_2\cdot\text{CHCl}$ behave differently, bromine addition being decelerated by hydrogen bromide and accelerated by lithium chloride to a relatively small extent. This is further evidence that electrophilic addition of HBr_3 may take place to compounds in which there is considerable electron-accession to the ethylenic system. The rates of chlorine addition to *cis*- and *trans*-1:2-dichloroethylene and to trichloroethylene have been measured in aqueous acetic acid solution. The velocity of bromine addition to *s*-dichloroisobutylene is low owing to steric hindrance, and with this compound there is very marked catalysis by hydrogen bromide and lithium chloride. The theoretical significance of these various results is discussed.

REFERENCE was first made to the hydrogen bromide catalysis of bromine addition to vinyl bromide in acetic acid solution in Part I of this series (Robertson *et al.*, *J.*, 1937, 335), and was later confirmed by Nozaki and Ogg (*J. Amer. Chem. Soc.*, 1942, 64, 697), who also showed that the reaction was greatly accelerated by lithium chloride. These authors considered that such catalysis was characteristic of bromine addition generally, and accordingly formulated a special theory of bromine addition. It has since been demonstrated by us that these effects are not obtained with certain allyl derivatives (Swedlund and Robertson, *J.*, 1944, 131). A similar result is now found for vinyl compounds containing electron-contributing groups, as is evident from the following ratios for catalysed to uncatalysed reactions, reactants $m/80$, in acetic acid solution:

	$\text{CH}_2\cdot\text{CHBr}$ ($k_3 = 0.42$).	$\text{CHPh}\cdot\text{CHBr}$ ($k_3 = 52$).	$\text{CMe}_2\cdot\text{CHCl}$ ($k_3 = 220$).
LiCl (3.2 mols.)	7.0	1.5	2.2
HBr (8 mols.)	10.5	0.49	0.64

Included in the table are the termolecular rates of bromine addition. These are higher than the velocities for the corresponding acids, $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, $k_3 = 5.0$, and $\text{CMe}_2\cdot\text{CH}\cdot\text{CO}_2\text{H}$, $k_3 = 47$, indicating that the carboxyl group is more efficient in reducing the electrophilic rate of halogen addition than chlorine or bromine.

As was found for the allyl halides (Part VI), when there is a small lithium chloride acceleration, hydrogen bromide has a decelerating influence on the rate of bromine addition. Whereas the acceleration caused by lithium chloride increases with its concentration, the effect due to hydrogen bromide becomes constant with excess of catalyst, indicating that HBr_3 is the reactive compound. A nucleophilic mechanism is considered to operate for HBr_3 addition to vinyl bromide, and an electrophilic mechanism for the other two compounds, where there is considerable electron-accession to the ethylene system. Hydrogen bromide causes a change from third- to second-order kinetics, so if hydrogen bromide has a decelerating influence on the rate of bromine addition, this effect becomes relatively greater when the initial concentration of the reactants increases. This is illustrated by the rates of bromine addition to $\text{CMe}_2\cdot\text{CHCl}$, quoted below as bimolecular coefficients, in acetic acid at 24° :

	$m/40$.		$m/80$.
k_2 ($x = 50$)	0.98	($n = 3.1$)	0.46
+ $8[\text{HBr}]$, k_2 ($x = 50$)	0.30	($n = 2.0$)	0.29

The present investigation has been extended to include rate measurements with chloroethylenes containing more than one atom of chlorine. The rate of chlorine addition to *cis*- and *trans*-dichloroethylene under the influence of light has been measured by Chavanne (*Bull. Soc. chim. Belg.*, 1914, 28, 234). It was found that the relative rates were *trans* > *cis*,

but such measurements with pure compounds are not strictly comparable, as a change in solvent is in effect involved. Chlorine addition to *cis*- and *trans*-dichloroethylene in acetic acid in the dark was inconveniently slow, but measurable rates were obtained in the mixed solvent, HOAc 80% + H₂O 20%, at 24° :

x	10	20	30	40	50
k_2 (<i>cis</i>)	0.016	0.014	0.012	0.011	0.011
k_2 (<i>trans</i>)	0.0053	0.0054	0.0054	0.0053	0.0051

The normal relative order, *cis* > *trans*, as for other compounds of the general type CH₂:CHb, is now found for these stereoisomers, the ratio for the initial rates being 3 : 1. The *trans*-compound gives constant bimolecular coefficients, but for *cis*-dichloroethylene there is a fall in rate as the reaction proceeds; this is attributed to a partial conversion into the more slowly reacting *trans*-isomer during the course of the reaction. Jones and Taylor (*J. Amer. Chem. Soc.*, 1940, **62**, 3480) have shown that bromine in the dark can cause a partial change from *trans*- to *cis*-dichloroethylene.

Trichloroethylene adds chlorine more slowly than the dichloroethylenes, and its rate was measured in acetic acid containing 40% of water; tetrachloroethylene was found not to react in the dark in this solvent at a measurable rate. The following table shows the relative rates of halogen addition to certain halogen derivatives of ethylene. The ratio measured for the first and second compounds is for iodine addition, for the second and third bromine addition, and for the third, fourth, and fifth compounds chlorine addition.

CH ₂ :CH ₂ .	CH ₂ :CH-CH ₂ Br.	CH ₂ :CHBr.	CHCl:CHCl (<i>cis</i>).	CHCl:CCl ₂ .
1	3 × 10 ⁻¹	3 × 10 ⁻⁴	1 × 10 ⁻⁷	3 × 10 ⁻¹⁰

The decelerating influence of halogen atoms on the rate of addition to ethylenic compounds is thus illustrated. In tri- and tetra-chloroethylene a steric effect, in addition to the electron-attracting power of the chlorine atoms, is probably an additional cause of the low reactivity.

Another type of ethylenic compound which shows steric hindrance to halogen addition is *s*-dichloroisobutylene, as is evident from the relative rates :

CH ₂ :CH ₂ .	CH ₂ :CH-CH ₂ Cl.	CH ₂ :C(CH ₂ Cl) ₂ .
1	0.45	0.0055

In the CH₂Cl group the electron-attracting and electron-repelling power tend to neutralise each other, so that one such group attached to an ethylene carbon atom should not be expected to have a large influence on the electrophilic rate. Actually, there is a small reduction in rate, and this effect should be expected to be greater in *s*-dichloroisobutylene, but not to the very large extent experimentally found. According to the theory proposed by Roberts and Kimball (*J. Amer. Chem. Soc.*, 1937, **59**, 947) the two-phase process of halogen addition is completed by the approach of a negative halogen ion to the positive carbon atom, which approach in this compound is hindered by the screen of CH₂Cl groups. An additional effect is possible in this type of compound, namely, a repulsion of the approaching halogen ion by the outer electrons of the chlorine atoms in the CH₂Cl groups, thus tending still further to reduce the rate.

A single CH₂Cl in 3-chloropropylene by its electron-attracting power produces the condition favourable for the nucleophilic mechanism, *i.e.*, hydrogen bromide or lithium chloride catalysis. With *s*-dichloroisobutylene there is similarly catalysis by both, as illustrated by the ratios of the rates of catalysed reactions, m/80-reagents in acetic acid, to the uncatalysed reactions in acetic acid at 24° : 8[HBr], 5.8 : 1, 6.4[LiCl], 35 : 1.

EXPERIMENTAL.

The following compounds were used in this investigation : vinyl bromide, b. p. 16°/760 mm.; *cis*-dichloroethylene, b. p. 59—60°/750 mm.; *trans*-dichloroethylene, b. p. 48—49°/750 mm. (these two compounds from commercial dichloroethylene); trichloroethylene, b. p. 85.7—85.8°/756 mm.; 1-chloroisobutylene, b. p. 67.3—67.9°/754 mm.; ω -bromostyrene, b. p. 110—112°/25 mm. The *s*-dichloroisobutylene, CH₂:C(CH₂Cl)₂ (*J. Amer. Chem. Soc.*, 1945, **67**, 942), was kindly provided by Professor J. B. Cloke, Troy, N. Y.

The reaction velocities were measured in duplicate or triplicate, as previously described, with specially ground and tested stoppered bottles well shielded from light. In the chlorine experiments the established technique for volatility corrections was used. The measurements with di- and tri-chloroethylene were made in an atmosphere of nitrogen. Herewith is a typical rate determination :

CH₂:CHBr, m/10 + Br₂, m/80 in HOAc, 24°; reaction mixture, 10 ml., 1-ml. samples titrated with KI and n/160-Na₂S₂O₃ :

Time (mins.)	0	660	1590	2850	0	1210	1980	2660
Titre (ml.)	3.99	3.72	3.42	2.87	3.99	3.53	3.26	2.98

From combined curve, $x = 10$, $t = 1050$; $x = 20$, $t = 2160$.

Other results are expressed as times (mins.) for $x\%$ halogen absorption at 24° in acetic acid, unless otherwise stated. $\text{CH}_2\text{:CHBr}$, $m/10 + \text{Br}_2$, $m/80 + m/20\text{-HBr}$, $x = 20$, $t = 205$; $x = 50$, $t = 690$; $+ m/10\text{-HBr}$, results identical; $+ 0.04M\text{-LiCl}$, $x = 20$, $t = 310$; $x = 50$, $t = 980$; $+ 0.08M\text{-LiCl}$, $x = 20$, $t = 130$, $x = 50$, $t = 490$; $\text{CH}_2\text{:CHBr}$, $m/10 + \text{Cl}_2$, $m/80$; $x = 20$, $t = 8.0$, $x = 50$, $t = 24$; same reactants in $\text{HOAc} + 20\% \text{H}_2\text{O}$, $x = 50$, $t = 0.32$.

CHCl:CHCl (*cis*) (in nitrogen), $m/10 + \text{Cl}_2$, $m/80$, in $\text{HOAc} + 20\% \text{H}_2\text{O}$, $x = 20$, $t = 165$, $x = 50$, $t = 700$; same reactants in $\text{HOAc} + 40\% \text{H}_2\text{O}$, $x = 30$, $t = 7.9$. CHCl:CHCl (*trans*) (in nitrogen), $m/10 + \text{Cl}_2$, $m/80$, in $\text{HOAc} + 20\% \text{H}_2\text{O}$, $x = 20$, $t = 420$, $x = 50$, $t = 1400$.

CHCl:CCl_2 (in nitrogen), $m/10 + \text{Cl}_2$, $m/80$, in $\text{HOAc} + 40\% \text{H}_2\text{O}$, $x = 30$, $t = 2700$.

$\text{CMe}_2\text{:CHCl}$, $m/80 + \text{Br}_2$, $m/80$, $x = 20$, $t = 38.5$, $x = 50$, $t = 175$; $+ m/10\text{-HBr}$, $x = 50$, $t = 275$; $+ 0.08M\text{-LiCl}$, $x = 50$, $t = 78$.

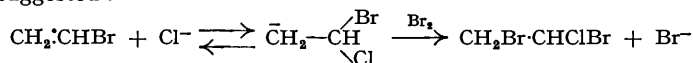
CHPh:CHBr , $m/10 + \text{Br}_2$, $m/80$, $x = 20$, $t = 17.7$, $x = 50$, $t = 63$; $+ m/10\text{-HBr}$, $x = 50$, $t = 127$; $+ 0.08M\text{-LiCl}$, $x = 50$, $t = 30$.

$\text{CH}_2\text{:C}(\text{CH}_2\text{Cl})_2$, $m/80 + \text{Br}_2$; $m/80$, $x = 20$, $t = 1080$, $x = 50$, $t = 3350$; $+ m/10\text{-HBr}$, $x = 20$, $t = 115$; $x = 50$, $t = 580$; $+ 0.08M\text{-LiCl}$, $x = 20$, $t = 14$, $x = 50$, $t = 95$. Ratio of rates ($x = 10$), A , $m/5 + \text{Br}_2$, $m/5$: A , $m/10 + \text{Br}_2$, $m/5 = 1.95$: $n(A) = 1.0$.

Correction.—The results quoted in *J.*, 1945, 131, for $0.05M\text{-}$ and $0.1M\text{-LiCl}$ should read $0.04M\text{-}$ and $0.08M\text{-LiCl}$ respectively.

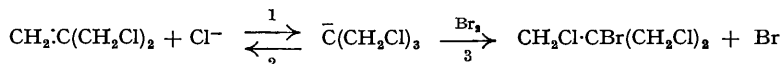
DISCUSSION.

Electrophilic halogen addition to vinyl bromide proceeds by an attack on the β -carbon atom, and the low reaction rate, more than 1000 times slower than for ethylene, is due to the simultaneous operation of the inductive effect of the bromine atom in this bromide. Correspondingly in bromobenzene the bromine atom determines the point of attack (*o*, *p*-positions) and at the same time makes the compound less reactive than benzene. To explain the marked lithium chloride catalysis of bromine addition to vinyl bromide, the following mechanism is suggested:



The initial attack by the halide ion may be regarded as similar to that taking place in the Finkelstein reaction. The negative ion thus produced, even if present to a very small extent, would react rapidly with bromine (by the electrophilic mechanism) to complete the reaction. Replacement of the β -hydrogen atoms by electron-repelling groups would tend to inhibit the initial attack by chloride ion on the α -carbon atom, and consequently prevent the catalysis. For a similar reason, in the Finkelstein reaction, the relative velocities are $\text{CH}_2\text{:CHBr} > \text{CHMe:CHBr}$, with sodium iodide in acetone solution (Juvala, *Ber.*, 1930, **63**, 1998).

The lithium chloride catalysis of addition to *s*-dichloroisobutylene is considered to operate by the mechanism proposed for 3-chloropropylene (Part VI, *J.*, 1945, 131):



By the method of stationary concentrations (if $n = 3$, as is experimentally found)

$$-d[\text{Br}_2]/dt = (k_1/k_2)k_3[A][\text{Br}_2][\text{Cl}^-]$$

Compared with the corresponding reaction with 3-chloropropylene, the inductive effect of the chlorine atoms would cause k_1 to be greater, and k_3 to be less [at the same time the resonance stability due to the symmetry of the ion $\bar{\text{C}}(\text{CH}_2\text{Cl})_3$ would tend to decrease k_2 and k_3], so that the relative velocities of the two compounds cannot be predicted. The especially marked catalysis of bromine addition to *s*-dichloroisobutylene (35 times the rate for 6.4 mols. of LiCl at $m/80$) is due to the fact that the rate of the uncatalysed reaction is low on account of steric hindrance.

With the completion of the present investigation it is now possible to make a critical estimate of the theory of bromine addition elaborated by Nozaki and Ogg in a series of papers (*J. Amer. Chem. Soc.*, 1942, **64**, 697, 704, 709). According to this theory, the addition process may be represented by the rate expression

$$-d[\text{Br}_2]/dt = k_a[A][\text{Br}_2]\text{X}^- + k_b[A][\text{Br}_2] + k_c[A][\text{Br}_2]^2$$

where X^- is an added ion, *e.g.*, Cl^- from lithium chloride.

In support of this theory detailed measurements are made with three compounds, maleic acid, vinyl bromide, and allyl chloride, all of which are found to show considerable catalysis in acetic acid solution, more especially with lithium chloride and bromide and hydrogen bromide. There are less complete observations with allyl acetate, and reference is made to lithium bromide

and hydrogen bromide as catalysts when actually they decelerate bromine addition to this compound. Our study of the kinetics of bromine addition permits a classification of the compounds for which catalysis is to be expected: they are such substances as



in which there is an electron-attracting group, or groups, attached to the ethylenic system, the type of compound especially investigated by Nozaki and Ogg, and by implication regarded as typical. In such compounds the electrophilic rate of bromine addition tends to be low, so any catalytic effect depending on the reverse mechanism is liable to become apparent.

As lithium bromide reduces the bromine concentration by formation of the tribromide, and the last is considered to be inactive, lithium chloride should be superior to the bromide as a catalyst, as is found for $\text{CH}_2\text{:CHBr}$ and $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{Cl}$ (Nozaki and Ogg, *loc. cit.*, pp. 702, 705, 706). A similar result is to be expected for maleic acid, but here measurements only with lithium bromide are recorded. Our experiments reveal that bromine addition to maleic acid in acetic acid is more rapid with added lithium bromide than with the chloride. We find that the latter may even reduce the rate of bromine addition to this type of compound: thus in the reaction, $\text{CHPh}\cdot\text{CH}\cdot\text{COPh} + \text{Br}_2$ in acetic acid at 24° , reactants $M/80$, $k_2 = 10\cdot0$; $+ \text{LiCl}$, $M/20$, $k_2 = 3\cdot1$. The explanation is that lithium chloride acts as a base in acetic acid, and therefore reduces the rate of acid-catalysed nucleophilic addition.

Hydrogen tribromide (and its lithium salt, which forms it by acetolysis with acetic acid) is not an inactive reagent as is claimed by Nozaki and Ogg, but may react rapidly with such compounds as $\alpha\beta$ -unsaturated acids, aldehydes, ketones and nitro-compounds, by a 1:4-addition mechanism. In these reactions the HBr_3 acts as a nucleophilic reagent, since the point of attack is a positive carbon atom. But it appears that HBr_3 may also react by an electrophilic mechanism, *e.g.*, with compounds like allyl benzoate (Part VI) and stilbene (Part X), for which the nucleophilic mode of addition is not to be expected. Therefore, in the reaction between allyl acetate and bromine, the small effect of hydrogen (and lithium) bromide is not because the contribution of the bromine addition reaction is relatively considerable (Nozaki and Ogg, *loc. cit.*, p. 712), but because the bromine addition reaction is eliminated and replaced by an HBr_3 addition reaction, the rate of which, at the concentrations measured, is not considerably different. Such a difference increases, however, as the concentrations become greater, since the orders of the two reactions are not the same, as demonstrated for $\text{CMe}_2\cdot\text{CHCl}$ in the present communication.

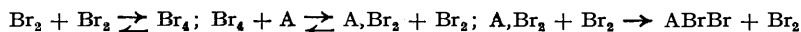
With reference to the second (bimolecular) term in their rate expression, Nozaki and Ogg consider (p. 715) that this involves a simultaneous attack on the unsaturated molecule by bromine and the solvent, which donates acetate ions. This, it is claimed, is in accordance with the experimental finding that the proportion of liberated hydrogen bromide in the reaction between allyl acetate and bromine becomes greater in more dilute solutions (Nozaki and Ogg, *loc. cit.*, p. 712). If, therefore, the reaction rate is dependent on the contribution of acetate ions, sodium acetate, which is considerably dissociated in acetic acid solution, should exert a considerable influence on the rate of bromine addition. Our experiments show that this is not so: for instance, with stilbene, the relative rate ratio of bromine addition at $M/80$, at 24° , with 4 and 1 molecules of added sodium acetate, is only 1:1:1, and with benzoylstilbene, under the same conditions, a still smaller ratio was found. We therefore conclude that the bimolecular rate is determined by the attack of bromine on the unsaturated molecule, and that the production of hydrogen bromide is due to a secondary process which is not rate-determining. Bromine addition in acetic acid is thus similar to its addition in a polar aprotic solvent such as chlorobenzene, in which similar kinetics are observed (Part VII).

Nozaki and Ogg do not discuss the nature of the high-order reaction (the third term in the rate expression) nor do they make any reference to our previous investigation of the allyl acetate-bromine reaction in the concentration range $M/40$ — $M/3000$ (*J.*, 1939, 1515). Concentrations of $\sim M/20$ represent the upper experimental limit for rate measurements with this type of compound, but certain halogenoethylenes have now been investigated at higher concentrations in acetic acid at 24° , with the following results, $x = 50$, times (mins.):

	$M/5$.		$M/10$.		$M/20$.		$M/40$.
$\text{CHPh}\cdot\text{CHBr}$	1.5	($n = 3\cdot6$)	9.1	($n = 3\cdot2$)	4.3	($n = 2\cdot9$)	165
$\text{CH}_2\text{:C}(\text{CH}_2\text{Cl})_2$	8.5	($n = 3\cdot5$)	47	($n = 3\cdot2$)	220		*
		* $n(M/20 - M/80) = 2\cdot9$.					

It seems that a reaction of a higher order than third gradually takes control at the upper concentration. A fourth-order reaction could be explained by the participation of associated

bromine molecules, which, in the polar form $\text{Br}^+-\text{Br}_3^-$, would be reactive. Whilst there is no evidence for the existence of associated bromine molecules in acetic acid solution, a very small concentration might be sufficient to give the effect observed. A quadrimolecular reaction at a measurable rate is inconceivable if it involves a simultaneous collision between four molecules, but it is not impossible if it is regarded as a three-stage process, in each of the stages of which one at least of the reactants is in excess.



Alternatively, the first two stages might be regarded as a three-molecule process, $\text{A} + 2\text{Br}_2$. However, if such a fourth-order reaction does take place, it might be argued that bromine addition in the concentration region $M/40$, where there is third-order kinetics, is due to the equal contribution of the second- and the fourth-order reactions. If this were so, there would be a much more rapid falling off in order than observed with decrease in concentration; it can be calculated that the fourth-order reaction would become virtually eliminated at $M/160$ (when its contribution becomes $1/16$ of that of the bimolecular reaction). But experiment shows that it requires as low a concentration as $M/2000$ to establish the bimolecular rate. We therefore express the velocity of bromine addition by

$$-d[\text{Br}_2]/dt = k_2[\text{A}][\text{Br}_2] + k_3[\text{A}][\text{Br}_2]^2 + k_4[\text{A}][\text{Br}_2]^3$$

the middle term being dominant in the concentration region $M/20$ — $M/80$.

The similarity between addition and substitution by bromine has previously been stressed (*J.*, 1943, 279), and a similar mechanism proposed for the two modes of reaction. Experiments (by P. B. D. de la Mare) now reveal that the order higher than third, found for the bromination of certain hydrocarbons in acetic acid solution, is shown by other compounds also. An account of this work will be given in a future communication.

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