319. *The Kinetics of Bromine Addition to Olefinic Compounds. Part II. The Homogeneous Mechanisms.*

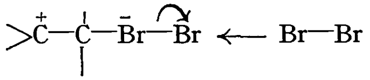
By I. K. Walker and P. W. Robertson.

The termolecular addition of bromine to olefins in acetic acid, dominant at 25° in the concentration region M/40, is accompanied to a small extent by bimolecular addition. The bimolecular reaction becomes established at low concentration, *ca.* M/1000, for allyl derivatives, and also when the ionising power of the solvent is increased, *e.g.*, by addition of water to the acetic acid. Rise in temperature also favours the bimolecular mechanism, which has a higher heat of activation.

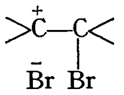
In Part I (J., **1937**, 335) it was shown that bromine addition in solution may proceed by a termolecular mechanism. Since then Williams (*Trans. Faraday Soc.*, **1938**, **34**, 1144) has found that vinyl bromide and bromine in the gas phase give a surface reaction of the third order. This behaviour is explained as due to the formation of a complex, C_2H_3Br,Br_2, which then reacts with a second molecule of bromine. From experiments on the photochemical addition of bromine to bromobenzene in carbon tetrachloride, Hammick, Hutson, and Jenkins (J., 1938, 1959) conclude that the first step may be the formation of a complex, C_6H_5Br,Br_2, from activated bromine molecules.

A general theory of halogen addition in dissociating solvents has been proposed in the preceding communication, depending on the ability of bromine or iodine to expand its outer ring of electrons, so that an addition product, *e.g.*, A,Br_2, is first formed, and on collision with another bromine molecule it gives the product (I). There is, however, no reason to believe that addition of bromine may not also proceed by the direct bimolecular mechanism (II).

(I.)



$>\overset{+}{C}-\underset{|}{\overset{|}{C}}-\overset{-}{Br}-Br \longleftarrow Br-Br$



$>\underset{\overset{-}{Br}}{\overset{+}{C}}-\underset{\underset{Br}{|}}{C}<$

(II.)

In acetic acid in the concentration region M/40, kinetic measurements have shown that the reaction at 25° is predominantly termolecular : for the compounds previously examined (Part I) the average value of n, the order of reaction, for the range M/20—M/40 at 25° was 3·0. The contribution of the bimolecular addition to the total reaction at this concentration must therefore be slight. If, however, addition can take place by two simultaneous mechanisms, it should be possible to alter the experimental conditions in such a way that the bimolecular process may be isolated. One method would be to measure the reaction in a region of very low concentration, as the frequency of termolecular collisions is decreased on dilution relatively more rapidly than that of bimolecular. Another method would be to increase the ionising power of the solvent medium by the addition of a second solvent such as water, so as to favour the more direct mechanism. Both these expectations have been realised. The following values show the effect of concentration on the reaction, in the dark, between equivalent amounts of allyl acetate and bromine in acetic acid at 25°.

The velocity coefficients are calculated for the half-reaction time, the k_2 values in l. g.-mol.$^{-1}$ min.$^{-1}$, and the k_3 values in l. g.-mol.$^{-1}$ min.$^{-2}$ by the formula previously employed (J., 1937, 336).

	M/40.	M/80.	M/200.	M/400.	M/800.	M/2000.	M/3000.
k_2	17·2	10·2	5·8	4·7	3·9	3·8	3·7
$k_3 \times 10^{-3}$	4·1	4·9	6·9	11·3	18·9	45	67
E, cals.	3600	4500	6500	7700	8300	9100	—

Corresponding results have been obtained for allyl succinate in acetic acid at 25° at different concentrations. The k_2 and k_3 values are calculated on the assumption that 1 mol. of the ester reacts as if it were two separate molecules, each with an allyl group.

	M/40.	M/80.	M/160.	M/400.	M/800.	M/2000.
k_2	16·8	9·3	5·5	3·3	2·8	2·6
$k_3 \times 10^{-3}$	4·0	4·5	5·3	8·0	13·6	31·3
E, cals.	2700	3800	6200	7000	7800	8500

Actually only the k_3 values at the upper concentration, and the k_2 values at the lower concentration, are real; the other values, although fictitious, indicate how the reaction gradually changes its order as the concentration of reactants is altered. The k_3 coefficients are constant throughout the reaction at M/40, and the k_2 at M/800, as illustrated by the following figures.

Allyl succinate + bromine in acetic acid at 25°.

x, %	10	20	30	40	50	60
$k_3 \times 10^{-3}$ (M/40)	3·8	3·8	3·7	3·8	4·0	4·0
k_2 (M/800)	3·0	2·9	2·9	2·9	2·8	2·9

The heats of activation (*E*) were calculated from measurements at 17°, 25°, and 40°. As the points on the log k–$1/T$ curves (the results being independent of whether k_2 or k_3 values were used) fell well on straight lines, *E* can be regarded as constant within this somewhat restricted temperature interval. The measurements reveal, then, that the termolecular addition dominant at M/40, with its characteristically low heat of activation, is gradually replaced at lower concentrations by a bimolecular addition process, which has a considerably higher heat of activation, the change-over being practically complete at M/1000.

The influence of water on the rate of bromine addition at 25° varies with the concentration: 1% of water accelerates the reaction between allyl acetate and bromine in acetic acid by 90% at M/80 and 130% at M/1000. As the acceleration is greater for the k_2 mechanism, the effect of adding water to the solvent in the higher concentration regions must be ultimately to make the bimolecular addition predominant; but this is only attained by addition of a considerable proportion of water. The velocities for allyl acetate in aqueous acetic acid are too rapid for satisfactory kinetic measurements, but figures are available for the more slowly reacting *cis*-cinnamic acid (J., 1931, 341). These results show that the bimolecular reaction becomes dominant on the addition of *ca.* 25% of water, and that there is an accompanying change in *E* from 5800 to 8500. The inadequacy of the term " catalysis " to describe the effect of water in such circumstances now becomes apparent; it is a special solvent effect in which water preferentially accelerates the mode of reaction in a dual mechanism process.

There is a third factor, the temperature, which also has an influence in determining the relative contributions of the dual reaction mechanisms of bromine addition. As the bimolecular reaction, which becomes established at the lower concentration, increases in rate with the temperature more rapidly than the termolecular change, the termolecular reaction must be gradually replaced by the bimolecular reaction with rise in temperature. Owing to the restricted range of temperatures under observation, this change is not reflected in the *E* values at the two temperature intervals measured. The change, however, may be illustrated by comparing the values of *n* (the order of reaction) for the same concentration interval at the different temperatures:

Temp.	17°	25°	40°
Allyl acetate, *n* (M/80—M/160)	2·8	2·7	2·5
Allyl succinate, ,,	2·9	2·7	2·6
Allyl malonate, ,,	2·9	2·8	2·7

EXPERIMENTAL.

The acetic acid and bromine were purified as previously described; the allyl acetate, succinate, and malonate were prepared by the action of the acid chlorides on pure allyl alcohol, and purified by low-pressure distillation. These compounds were analysed and gave the theoretical bromine absorption. In the slow reactions, at concentrations less than M/400, there was a slight volatility loss (cf. previous communications), for which corrections were accordingly introduced.

The following are the experimental details of two experiments, with added data to show the reproducibility of the results.

M/80-*Allyl acetate* + M/80-*bromine in acetic acid at* 25°.

Reaction mixture, 50 ml.; 5-ml. samples titrated with N/80-$Na_2S_2O_3$.

Time (mins.)	0	1	2	3	5	8	12	17
Titre, ml.	9·90	8·70	7·68	6·91	5·92	4·90	4·10	3·40

From curve : at $x = 30\%$, $t = 2·95$; $x = 50\%$, $t = 7·85$.
Second expt. : at $x = 30\%$, $t = 3·0$; $x = 50\%$, $t = 7·8$.

M/2000-*Allyl acetate* + M/2000-*bromine in acetic acid at* 25°.

Reaction mixture, 100 ml.; 10-ml. samples titrated with N/1000-$Na_2S_2O_3$.

Time (mins.)	0	90	150	390	620	810
Titre, ml.	9·90	8·62	8·00	5·79	4·40	3·60
Volatility correction	0	0	0·02	0·06	0·11	0·16

From curve : at $x = 30\%$, $t = 264$; $x = 50\%$, $t = 538$.
Second expt. : at $x = 30\%$, $t = 270$; $x = 50\%$, $t = 542$.

The following E values were recalculated for the two ranges 17—25° and 25—40°, for allyl acetate at different concentrations: M/40, 3500, 3600; M/80, 4800, 4300; M/200, 6500, 6600; M/800, 8300, 8200; M/2000, 9000, 9300; these values are in agreement with those previously recorded, which were obtained by the graphical method.

Allyl malonate also was investigated (in acetic acid at 25°) to ascertain whether the proximity of the two allyl groups had any influence on the rate of bromine addition. These experiments could not be carried to such a low concentration, for a back-reaction liberating iodine interfered with the titrations in the more dilute solutions. The values obtained correspond in general magnitude with those of allyl succinate, both in rate and in heat of activation, but the termolecular reaction tends to persist to a lower concentration: M/40, $k_3 \times 10^{-3} = 1·9$, $E = 3400$; M/80, $k_3 \times 10^{-3} = 2·0$, $E = 3800$.

An unexpected observation was made on illumination of M/800-allyl acetate + M/800-bromine in acetic acid at 25° in a clear-glass bottle with a 200-watt lamp suspended 10 inches above it:

Time (mins.)	50	100	200	400	800	1200	1600
A, dark reaction; x, %, Br_2 absorbed	21	38	56	78	89	95	97
B, light ,, ; ,,	21	31	44	58	65	66	66
C, light ,, ; ,,	21	31	41	53	63	64	64

C was a repetition of B with different samples, reagents, and solvent.

Hence, under the influence of light the reaction at this dilution follows a course involving incomplete bromine absorption. This effect could be explained by the dimerisation, or polymerisation, of a portion of the ethylene compound under the influence of bromine. A similar photo-dimerisation has been reported by Berthoud (*Helv. Chim. Acta*, 1930, **13**, 385) for α-phenylcinnamonitrile.

[*Note, added June 27th,* 1939, by P. W. ROBERTSON.] Anantakrishnan and Venkataraman (this vol., p. 224) have reported that addition of bromine to crotonic and tiglic acids shows an induction period, the reactions being catalysed by hydrogen bromide. In their discussion they overlook the conclusions of Part I of this series (*loc. cit.*), *viz.*, that bromine addition in acetic acid may proceed by two different mechanisms: (*a*) for allyl esters and *cis*-cinnamic acid, a termolecular reaction not catalysed by hydrogen bromide; (*b*) for vinyl bromide and acrylic acid, a slow reaction showing an induction period and catalysed by hydrogen bromide. They also overlook the observation that there may be stereo-conversion during addition of bromine, this change being catalysed by hydrogen bromide. We investigated *trans*-crotonic acid, but as it was difficult to separate the stereo-conversion effect from the independent hydrogen bromide acceleration catalysis, acrylic acid was examined in detail, and we concluded (*loc. cit.*, p. 339) that, in the presence of hydrogen bromide, " the reaction is truly bimolecular and the hydrogen bromide activates the bromine and not the ethylenic compound."

To explain the behaviour of crotonic acid, Anantakrishnan and Venkataraman propose a chain mechanism, involving the hypothetical complex A,HBr and activated bromine; but such a mechanism is not the only possible means of explaining a period of induction, and the effect observed. Evidence is accumulating from independent observers that bromine addition proceeds by way of an addition complex : (i) $A + Br_2 \longrightarrow A,Br_2$; (ii) $A, Br_2 + Br_2 \longrightarrow ABrBr + Br_2$. If reaction (i) is very slow, it will take an interval for sufficient A,Br_2 to accumulate for reaction (ii) to be perceptible, *i.e.*, there is an induction period. Further, if hydrogen bromide accelerates either (i) or (ii), this period will be shortened and the over-all reaction will become bimolecular.

Finally, a set of values, obtained by N. T. Clare and not recorded in Part I, is given for *cis*-cinnamic acid :

M/80-cis-*Cinnamic acid* + M/80-*bromine in acetic acid at* 25°.

x, %	10	20	30	40	50	60
k_3	21	20	20	20	21	20
$k_2 \times 10^3$	67	63	54	48	38	30

Although, as in the corresponding reaction for crotonic acid (which proceeds with rising k_2 values owing to hydrogen bromide catalysis) hydrogen bromide is also formed in small quantities, the k_2 coefficients nevertheless continue to fall. The reaction is, in fact, termolecular, with constant k_3 values, which are the same as at M/40.

This termolecular addition, which is found not only for bromine, but also for iodine, iodine chloride and bromine chloride with olefinic compounds, holds also for bromine addition to acetylenic compounds. Values obtained by D. R. Currie are recorded for phenylpropiolic acid :

Phenylpropiolic acid + bromine in acetic acid (+ 5% *of water*) *at* 25°.

x, %	10	20	30	40	50	60
$k_3 \times 10^{-2}$ (M/40)	—	1·6	1·6	1·6	1·7	1·7
,, (M/80)	1·5	1·6	1·5	1·5	1·5	1·7
,, (M/160)	1·7	1·7	1·7	1·7	1·7	1·7

Similarly the reaction in nitrobenzene is termolecular.

VICTORIA UNIVERSITY COLLEGE, WELLINGTON, N.Z.

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