130. *The Kinetics of Halogen Addition to Unsaturated Compounds. Part VII. Bromine Addition in Carbon Tetrachloride, Chlorobenzene, and Chloroform.*

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In the addition of bromine to allyl benzoate in carbon tetrachloride, a high-order homogeneous reaction occurs concurrently with a lower-order surface-catalysed reaction, which becomes relatively more prominent at lower concentrations. The homogeneous reaction is accelerated by water and retarded by oxygen, and appears to proceed by an activated-molecule chain mechanism. In the addition of bromine to allyl benzoate in chlorobenzene and chloroform there is no surface catalysis; the reactions show third-order kinetics changing towards second-order at lower concentrations. The third-order reaction in chlorobenzene has a temperature coefficient of unity. Competitive experiments indicate that addition of bromine to allyl benzoate in chlorobenzene induces that of bromine to cinnamic acid.

Addition of bromine to olefins in carbon tetrachloride solution may show a high reaction order and heterogeneous effects (Part I, J., 1937, 335), and the simultaneous absorption of oxygen during such addition has been demonstrated by Bockemuller and Pfeuffer (*Annalen*, 1939, **537**, 178). It has also been found that the rate of addition of bromine to cinnamic acid in carbon tetrachloride is reduced by oxygen (Bauer and Daniels, *J. Amer. Chem. Soc.*, 1934, **56**, 378; Urushiba and Takabayashi, *Bull. Chem. Soc. Japan*, 1937, **356**, 499). The catalytic effect of water on bromine addition in carbon tetrachloride had been previously shown by Davis (*J. Amer. Chem. Soc.*, 1928, **50**, 2769).

The kinetics of addition of bromine to allyl benzoate in carbon tetrachloride and other solvents have now been examined in an atmosphere of dry nitrogen. It became apparent during the course of these experiments that the technique of rate measurement (stopping reaction with potassium iodide, and titrating the iodine with sodium thiosulphate) employed by previous investigators and ourselves was liable to considerable error. A new method (stopping the reaction with sodium arsenite and back titration with iodine) was found to give reliable results.

The following values were obtained for the dark reaction at 24° between allyl benzoate and bromine in carbon tetrachloride, the solvent being saturated with dry nitrogen:

	M/5.	M/10.	M/20.	M/40.
Time, mins. ($x = 20$)	3·6	40	200	950
Time, mins. ($x = 20$), with beads *	—	27	—	250

* Sufficient to expose a three-fold surface.

The course of individual reactions is shown as second-order coefficients, and also the influence of oxygen (as dry air) and of water (solvent saturation):

x.	10.	20.	30.	40.	50.
k_2 (M/5)	0·50	0·35	0·28	0·21	0·15 *
k_2 (M/10)	0·089	0·064	0·054	0·049	0·043 *
k_2 (M/10), with O_2	0·053	0·045	0·041	0·037	0·033
k_2 (M/10), with H_2O	0·28	0·25	0·24	0·22	0·22

* For M/5-benzoate + M/10-Br_2, $k_2 = 0·062$.

These results reveal the general nature of bromine addition to allyl benzoate in carbon tetrachloride solution. As the acceleration due to packing with beads becomes relatively less as the concentration is increased, the high order cannot be ascribed to heterogeneous effects, as was formerly considered (Part I). The observed kinetics can be explained by the participation of two simultaneous reactions, a high-order ($n = \sim 4$) homogeneous reaction becoming dominant in the concentration region M/5, and a lower-order surface-catalysed reaction, the relative contribution of which becomes progressively greater as the concentration is diminished. The heterogeneous reaction is dependent on the polar nature of the surface, and it was found that a layer of barium sulphate in the reaction vessel increased the rate about 50-fold. Other polar substances such as manganese dioxide and lead dioxide caused a similar large acceleration. With regard to the high-order homogeneous reaction, the falling off in rate as revealed by the decrease in k_2 values from $x = 10$ to $x = 50$ at M/5 indicates that the course of the reaction is in accord with the reaction order calculated from the initial rates; *i.e.*, the high order observed is not due to any effect such as branching chains or autocatalysis. A possible autocatalyst for the reaction, *viz.*, hydrogen bromide produced by simultaneous substitution, was found by experiment to be absent at the end of the reaction. The relative contributions of allyl benzoate and bromine to the high-order reaction were determined from experiments with different amounts of each. The result quoted above for M/5-benzoate and M/10-bromine indicates that in the homogeneous reaction ($n = \sim 4$) the contribution of the bromine is considerably greater than that of the allyl benzoate.

The influence of temperature on the high-order homogeneous reaction was also examined: for M/5-solutions at 42°, time for $x = 20$ was 2·4 mins., giving $k_{35°}/k_{25°} = 1·2$. There is thus a small temperature coefficient, and the lowering of rate with temperature previously observed (Part I) is attributed to a variation in the water content of the reaction mixtures.

The addition of bromine in the dark to allyl benzoate in chlorobenzene solution under dry nitrogen gave the following results, reaction times being expressed in mins.:

	M/10.		M/20.		M/40.		M/80.
Time ($x = 50$) at 24°	2·4		10·8		39		142 *
$n =$		3·1		3·0		2·8	
Time ($x = 50$) at 42°	2·3		—		—		110

* With beads, $t = 142$; with a layer of barium sulphate, $t = 23$.

This reaction is similar to bromine addition in acetic acid solution, showing third-order kinetics in the region M/10—M/40, with a concomitant second-order reaction becoming apparent when the concentration is further reduced. In this polar solvent there is no catalysis by a glass surface, but the more strongly polar barium sulphate causes an acceleration. Iodine [with 0·02 mol. and M/10-solutions, t ($x = 50$) was 0·73] is a catalyst in chlorobenzene solution, but oxygen (air) and water (solvent saturation) had no influence on the rate. The reaction in M/10-solutions has a temperature coefficient of unity, increasing with the incursion of the second-order reaction, as indicated by measurements on M/80-solutions. A similar effect was found in acetic acid solution, in which solvent there is a small temperature coefficient for termolecular bromine addition, increasing in magnitude with the establishment of the bimolecular reaction in dilute solutions (J., 1939, 1515).

Addition of bromine to cinnamic acid at 24° in chlorobenzene also showed third-order kinetics: M/10—M/20 (M/10, $x = 25$, time = 820); since, for allyl benzoate, M/10, $x = 25$, time = 0·66, this gives the relative rate of bromine addition to the two compounds as 1240 : 1. The corresponding ratio obtained by a competitive method in the same solvent is very much smaller (~7 : 1).

The competitive method for addition of bromine has been investigated in dichloromethane solution (Ingold and Ingold, J., 1931, 2354; Anantakrishnan and Ingold, J., 1935, 984, 1396). One pair of compounds chosen for examination was propylene and crotonic acid (rate ratio, competition method, 8 : 1). Addition of bromine to propylene is too rapid for convenient measurement, but the relative rate of addition of iodine to this compound and to allyl benzoate is 15 : 1 (J., 1938, 179); addition of bromine to crotonic acid is very slow and autocatalytic, but the relative rate of chlorine addition to this compound and to cinnamic acid is 1 : 9 (J., 1939, 1509). By combining these values and the value quoted above for allyl benzoate and cinnamic acid, it may be concluded that the kinetic rate ratio for propylene and for crotonic acid for electrophilic halogen addition is of the order 10^5 : 1. It appears therefore from these results that a fast addition of bromine may have an inducing effect on a slower reaction of the same type. A similar effect has been reported by Stewart and Hanson (*J. Amer. Chem. Soc.*, 1931, **53**, 1121), who have shown that addition of chlorine to ethylene induces that to benzene.

The polar compound chloroform (D = 1·1), in its behaviour as a solvent for the reaction between allyl benzoate and bromine, is very similar to chlorobenzene (D = 1·6), reacting at about the same rate and showing third-order kinetics in the concentration region M/10—M/20; at 24°:

	M/10.		M/20.		M 40.
Time (mins.), $x = 20$	0·63		2·4		7·4
$n =$		2·9		2·7	

Similarly the reaction shows no acceleration with glass beads and is catalysed by iodine.

EXPERIMENTAL.

Bromine (Baker's "Analysed"), after being boiled under reflux with potassium bromide, was distilled from an all-glass apparatus, and the middle fraction collected; it was free from iodine and hydrogen bromide. Carbon tetrachloride was purified by treatment with Fehling's solution and alcoholic potash (Ingold and Powell, J., 1921, **119**, 122). Chlorobenzene was a B.D.H. sample redistilled; b. p. 132·5°/757 mm. Chloroform ("AnalaR") was distilled in and preserved in an atmosphere of nitrogen; b. p. 60·5°/762 mm. Allyl benzoate, b. p. 115°/15 mm., was used in preference to allyl acetate as it can be more readily purified. The cinnamic acid had m. p. 132°.

In the experiments under nitrogen the solvent was boiled and allowed to cool in a stream of nitrogen dried by sulphuric acid, and subsequent operations were carried out in a current of nitrogen. The reaction bottles were cleaned with chromic acid solution (24 hours), washed with distilled water, and dried at 130°. The stoppers of these bottles were ground until no appreciable loss of solvent occurred at the temperature of the experiments. The reaction bottles were well protected from light, and a dim illumination was maintained in the thermostat room.

The accepted technique of rate measurement for bromine addition (cf. Sudborough and Thomas, J., 1910, **97**, 751, 2450), *viz.*, by running an aliquot of the reaction mixture into aqueous potassium iodide and titrating the liberated iodine, is liable to considerable error for solvents such as carbon tetrachloride. Iodine, which is a catalyst for bromine addition in the solvents employed, may enter the solvent phase before the bromine has been completely extracted by the potassium iodide solution. Catalysed bromine addition takes place, and the measured absorption of bromine is too high by an amount dependent on the time taken for titration and the thoroughness of the shaking. A further error is possible, even in dim illumination, as these reactions are extremely light sensitive, while the aliquot is being withdrawn for titration. In the rapid reactions these errors may become very considerable. In the present investigation separate reaction bottles were used, the whole contents of each being titrated after the reaction had been stopped with bicarbonate-buffered sodium arsenite by vigorous shaking. On back-titrating with iodine it was found that the absorption–time curves showed no initial acceleration and passed smoothly through the point of origin. The following series for 0·1M-allyl benzoate and 0·1M-bromine in carbon tetrachloride under nitrogen at 24° is typical:

1 Ml. 0·200M-A + 1 ml. 0·206M-Br_2: 5 ml. of 0·0984N-Na_2HAsO_3 added to stop reaction: ml. of 0·100N-I_2 required: $t = 0$, 0·80; $t = 2·4$, 0·94; $t = 11·5$, 1·21; $t = 40·0$, 1·64; $t = 117$, 2·34.

From curve, $t\ (x = 30) = 80$; second series, $t\ (x = 30) = 78$.

In the measurements, the initial bromine concentration may vary slightly from that of the ester (as in the experiment quoted), involving a small correction. Each series was repeated at least twice, and for the experiments in chlorobenzene, a different technique (stopping the reaction with standard thiosulphate + potassium iodide) was also employed, and the agreement between separate observers was good. The results of significant measurements have been quoted as times (mins.) or k_2 values (g.-mol.-l.$^{-1}$ min.$^{-1}$) in the text.

In the competition experiments, a deficiency of bromine was added to equimolecular amounts of allyl benzoate (A) and cinnamic acid (X) in chlorobenzene at 24° in a nitrogen atmosphere in the dark, under conditions similar to those prescribed by Ingold and Ingold. The solution after completion of reaction was extracted five times with 10% potassium carbonate solution. The alkaline extract, after three re-extractions with ether, was acidified and extracted twice with ether; the ethereal extracts were washed with water, evaporated, and the residue dried in a vacuum at 100°. The combined mixed acids were weighed, and the composition determined (*a*) by titration with alkali and (*b*) more accurately by estimation of bromine. The weight of mixed acids calculated from the bromine content was the same as the value found within the limits of experimental error. In the measurements summarised below, for which the proportions of A, X, and Br_2 were varied, col. 1 gives the volume of solution after mixing, and cols. 2 and 3 show the molarity of reactants calculated for that solution.

Vol., ml.	A (and X) molarity.	Br_2 molarity.	Acids found (g.).	Acids calc. (g).	Br, %, in acids.	$\frac{[ABr_2]}{[XBr_2]}$.	Relative rate.
50	0·200	0·049	1·58	1·56	4·9	4·0	4·3
50	0·200	0·091	1·55	1·59	6·7	5·8	6·8
60	0·167	0·103	1·56	1·60	7·5	7·5	10·4

A blank measurement was made to test both method and materials: chlorobenzene, containing ester and bromine, was left to completion of reaction, and cinnamic acid added; after 5 days, the acid was extracted and analysed (Found: Br, nil). It was further found experimentally that there was no formation of hydrogen bromide in the reaction A + Br_2, and no decarboxylation of the cinnamic acid in a competition experiment.

Discussion.—Addition of bromine in the vapour phase and in carbon tetrachloride solution at low concentrations is dependent on the polar nature of the surface. As the reactions in chlorobenzene and in chloroform (which are more rapid than in carbon tetrachloride) are not accelerated by a glass surface, it is concluded that in these solvents the rate of addition is determined by the polarity of the solvent. The velocity of the homogeneous reaction in carbon tetrachloride, which on account of the non-polar nature of the solvent would be expected to be slow, becomes, however, considerable at high concentrations. The high reaction order, which determines this rapid rate, is not easy to explain in terms of classical kinetics, but may be due to a mechanism involving reaction chains. Such a theory could also be in accord with the effect of oxygen in carbon tetrachloride, as the function of a negative catalyst is frequently that of a chain-breaker.

Mechanisms involving (*a*) atoms and radicals or (*b*) activated molecules have been proposed to explain the photo-addition of halogens to olefinic compounds. The increase of the photochemical equivalent with the bromine concentration, even in the absence of oxygen, in the photobromination of cinnamic acid in carbon tetrachloride (Bauer and Daniels, *J. Amer. Chem. Soc.*, 1940, **62**, 2821) is difficult to correlate with an atom-chain mechanism, and appears to be related to the high order for bromine found for the dark reactions. The nature of the catalysts for bromine addition in carbon tetrachloride, *viz.*, water, iodine (as iodine bromide), antimony tribromide, and pyridine, is an indication that their function is rather to polarise the bromine molecule than to cause its dissociation into atoms. Actually, iodine has been shown to act as an inhibitor (chain-breaker) in abnormal hydrogen bromide addition, which is considered to proceed by an atom-chain mechanism (Vaughan, Rust, and Evans, *J. Org. Chem.*, 1942, **7**, 477). The formation of bromine-substituted peroxides by the simultaneous action of bromine and oxygen on olefins in carbon tetrachloride (Bockemuller and Pfeuffer, *loc. cit.*) can no longer be considered as evidence for the participation of atoms and radicals in the reaction, as the properties of the products correspond with those of bromo-ketones (Rust and Vaughan, *ibid.*, p. 491).

An extension of the process proposed to explain termolecular bromination in acetic acid solution permits the formulation of a reaction proceeding by active molecule chains :

(1) $A + Br_2 \longrightarrow A,Br_2$
(2) $A,Br_2 + Br_2 \longrightarrow ABrBr + Br_2^*$
(3) $A + Br_2^* \longrightarrow A,Br_2^*$
(4) $A,Br_2^* + Br_2 \longrightarrow ABrBr + Br_2^*$

The chain process, (3) and (4), becomes the same as that suggested for the light reaction by Bauer and Daniels (*loc. cit.*) and afterwards rejected in favour of an atom-chain mechanism (*idem, loc. cit.*, 1940). The kinetics of such a reaction are complex and dependent on the mode of chain-breaking. The effect of oxygen could be explained as due to the deactivation of A,Br_2^* molecules and the consequent breaking of chains (with partial oxidation). A similar proposal was made by Wood and Rideal (J., 1927, 2466) to account for the decelerating influence of oxygen on the photochlorination of *cyclo*hexane.

Bromine addition to allyl benzoate in chlorobenzene solution shows the same kinetic behaviour as for the corresponding reactions in acetic acid. A characteristic of these third-order reactions is their slight sensitivity to temperature change, and in chlorobenzene, at M/10, the reaction investigated has a temperature coefficient of unity. For third-order kinetics (J., 1943, 276), if $A + Br_2 \underset{2}{\overset{1}{\rightleftarrows}} A,Br_2$; $A,Br_2 + Br_2 \xrightarrow{3} ABrBr + Br_2$;

$$- d[A]/dt = Kk_3[A][Br_2]^2 \quad (\text{where } K = k_1/k_2)$$

When the rate does not alter with the temperature, the increase of k_3 is balanced by the decrease of K, or in energy terms, $E - Q = 0$, where Q is the heat of reaction of the reversible reaction, and E the heat of activation of the irreversible reaction.

The inducing effect of the reaction between allyl benzoate and bromine in chlorobenzene on a slower addition of bromine suggests the possibility of a mechanism involving chains. Alternative theories are, however, possible, such as the production of activated molecules without chain formation. Further speculation is withheld pending the extension of this work, in particular to the examination of the kinetics of the catalysed reactions.

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