

**218.** *The Kinetics of Halogen Addition to Unsaturated Compounds.  
Part XII. Iodine Catalysis of Chlorine and Bromine Addition to  
Ethyl Cinnamate.*

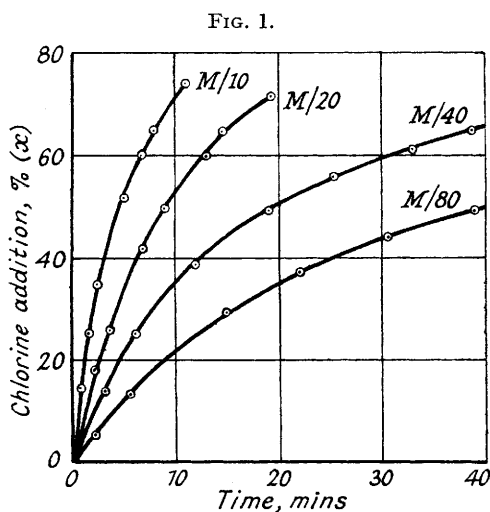
By H. D. C. WATERS, A. R. CAVERHILL, and P. W. ROBERTSON.

Iodine-catalysed addition of chlorine to ethyl cinnamate in carbon tetrachloride solution proceeds according to the expression  $-d[\text{Cl}_2]/dt = k[\text{A}][\text{Cl}_2][\text{ICl}]$ , and in the corresponding bromine reaction,  $-d[\text{Br}_2]/dt = k[\text{A}][\text{Br}_2]^2[\text{IBr}]$ . At higher concentrations of added iodine,

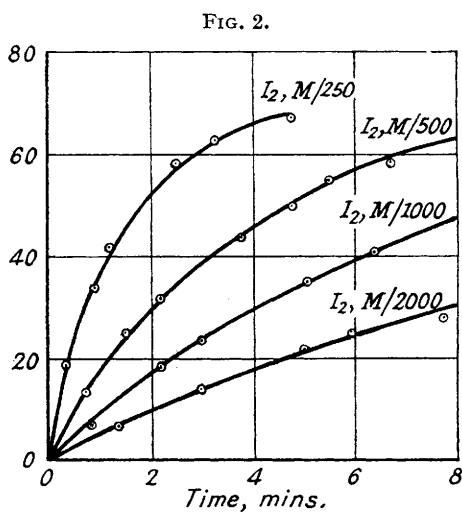
the order for the chloride and the bromide becomes greater than unity. In the polar solvents chloroform and *o*-dichlorobenzene, the overall rate is one order less than in carbon tetrachloride, as for uncatalysed bromine addition. A general theory is proposed to explain the phenomenon of *trans*-halogen addition with inversion.

THE influence of iodine as a catalyst for bromine addition has long been recognised (Hertz and Mylius, *Ber.*, 1906, **39**, 3816; Bruner and Fischler, *A.*, 1914, ii, 260), but such rate measurements as have been made are insufficient to establish the kinetics of the reaction. Although iodine is known to catalyse chlorine addition to unsaturated compounds, there appears to be no record of any kinetic investigation of such reactions. However, Slator (*J.*, 1903, **83**, 729) has studied the kinetics of the reaction,  $C_6H_6 + Cl_2$ , in benzene as a solvent or diluted with carbon tetrachloride, with added iodine. The reaction proceeds with 70% substitution and 30% chlorine addition at a rate given by the expression,  $-d[Cl_2]/dt = k[A][Cl_2][ICl]^2$ , but the reaction was examined over only a limited iodine chloride concentration range.

Just as the chlorination of benzene does not proceed in the absence of iodine, chlorine adds to ethyl cinnamate in dry carbon tetrachloride at a rate too slow to be measured, but with a small amount of added iodine the change goes rapidly to completion. At the end of the reaction the original amount of iodine is left, as is indicated by tintometric observation or titration of the



Ethyl cinnamate-chlorine, with  $I_2$ ,  $M/1000$ .



Ethyl cinnamate-chlorine, both  $M/20$ , with  $I_2$ .

residual iodine. The kinetics of the reaction can be conveniently studied by rate determinations (a) with reactants,  $A + Cl_2$ , constant, and different amounts of iodine, or (b) with iodine constant and varying initial concentrations of  $A + Cl_2$ . The results of these experiments are shown in Figs. 1 and 2, the measurements being made in dry carbon tetrachloride under nitrogen at  $24^\circ$ .

The average orders,  $x = 10$  to  $x = 50$ , for  $A + Cl_2$  (Fig. 1) are:  $M/10$ — $M/20$ ,  $n = 2.0$ ;  $M/20$ — $M/40$ ,  $n = 2.0$ ;  $M/40$ — $M/80$ ,  $n = 2.0$ . The reaction is thus bimolecular with respect to  $A + Cl_2$ , and the constancy of the bimolecular coefficients during the separate runs indicates the absence of autocatalytic disturbances. This is shown by a typical measurement, in carbon tetrachloride at  $24^\circ$ :

$x$ .....	10	20	30	40	50
$k_2$ (reactants $M/20$ , $I_2$ $M/1000$ ) .....	2.1	2.1	2.1	2.2	2.2

The average values of  $t_1/t_2$  with different amounts of added iodine (Fig. 2) are:  $M/2000$ — $M/1000$ , 2.0;  $M/1000$ — $M/500$ , 2.0;  $M/500$ — $M/250$ , 2.4. On further addition of iodine the initial rates become too rapid for accurate measurements, but reach a maximum when the iodine chloride concentration is approximately equal to that of the chlorine, and then diminish.

The iodine is present almost entirely as chloride, and when its amount is small it does not appreciably alter the chlorine concentration, so these measurements are in accord with the rate expression

$$-d[Cl_2]/dt = k[A][Cl_2][ICl]$$

The increase in order with respect to iodine, when its amount becomes more considerable, will be discussed later.

The reaction between ethyl cinnamate and bromine in carbon tetrachloride (in nitrogen at 24°) was found to be not accurately reproducible under the conditions of the experiments, a result possibly due to the sensitiveness of this reaction to oxygen (cf. Bauer and Daniels, *J. Amer. Chem. Soc.*, 1934, **56**, 378). Added iodine caused a very considerable acceleration of the rate, and the measurements, now found to be reproducible, were made by varying separately  $A + Br_2$ , and  $I_2$  (Figs. 3 and 4).

The difference in appearance between Figs. 1 and 3 is due to the fact that bromination is a higher-order reaction than chlorination. The average orders,  $\alpha = 20$  to  $\alpha = 50$ , for  $A + Br_2$ , are:  $M/5-M/10$ ,  $n = 2.9$ ;  $M/10-M/20$ ,  $n = 2.9$ ;  $M/20-M/40$ ,  $n = 3.0$ . Special experiments,

FIG. 3.

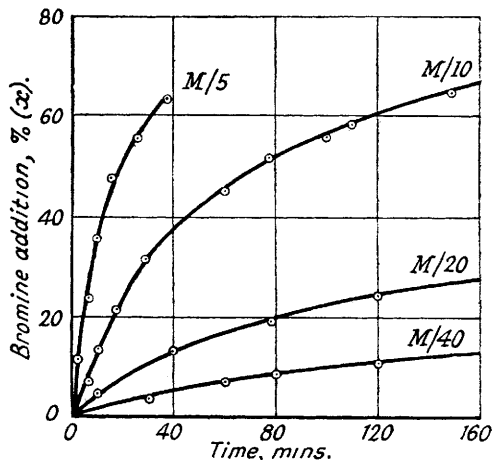
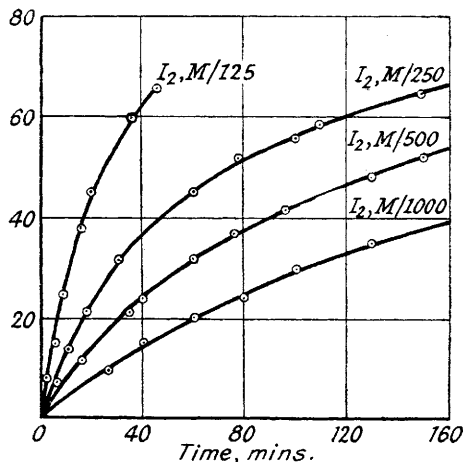
Ethyl cinnamate-bromine, with  $I_2$ ,  $M/250$ .

FIG. 4.

Ethyl cinnamate-bromine, both  $M/10$ , with  $I_2$ .

$A$  being varied and  $Br_2$  kept constant, showed that the reaction was first order for  $A$  and second order for  $Br_2$ . Correspondingly, the bimolecular coefficients fall as the reaction proceeds:

$\alpha$ .....	10	20	30	40	50	60
$k_2$ (reactants $M/10$ , $I_2 M/500$ ) .....	0.16	0.155	0.15	0.145	0.135	0.125

The effect of varying the amount of added iodine is shown in Fig. 4, the average  $t_1/t_2$  ratios being:  $M/1000-M/500$ , 1.9;  $M/500-M/250$ ,  $n = 1.95$ ;  $M/250-M/125$ , 2.7. As for the iodine-catalysed additions of chlorine, the order with respect to iodine is constant for low concentrations of added iodine, and subsequently increases. Iodine with bromine in carbon tetrachloride solution is almost entirely present as  $IBr$ , so these results correspond, for small amounts of iodine bromide, with the rate expression

$$-d[Br_2]/dt = k[A][Br_2]^2[IBr]$$

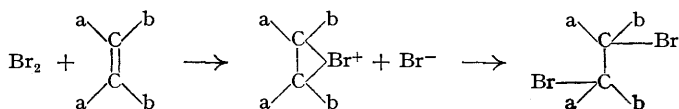
In polar aprotic solvents such as chloroform and *o*-dichlorobenzene, addition of bromine shows third-order kinetics (*J.*, 1945, 509). Added iodine in these solvents causes a relatively smaller catalysis than in carbon tetrachloride, and for small amounts of iodine the rate is given by the expression

$$-d[Br_2]/dt = k[A][Br_2][IBr]$$

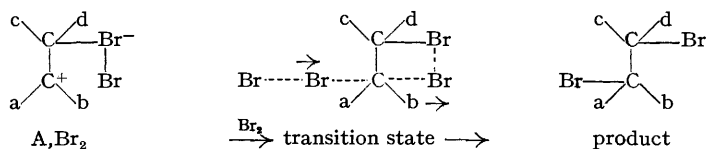
The iodine-catalysed addition of bromine to allyl benzoate in carbon tetrachloride has also been examined, with reactants  $M/10$  and  $M/20$ , and iodine  $M/500$  and  $M/1000$ . The average orders obtained were  $A + Br_2$ ,  $n = 2.8$ ;  $IBr$ ,  $n = 1.3$ , so for this compound also the catalysed reaction can be regarded as a fourth-order reaction with one or more molecules of bromine replaced by iodine bromide. With greater amounts of added catalyst, the order for iodine bromide increases, but the reaction becomes too rapid for accurate measurement.

The addition of halogen to ethylenic compounds is a two-stage process, and to explain the

*trans*-addition with inversion that takes place, Roberts and Kimball (*J. Amer. Chem. Soc.*, 1937, 59, 947) have proposed the mechanism

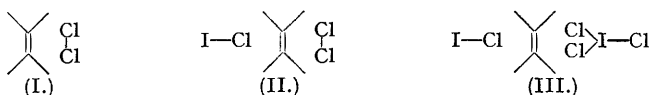


The discovery that addition of bromine may take place by a termolecular mechanism (*J.*, 1937, 335) was not inconsistent with this mode of formulation, as the result could be explained by the reaction proceeding:  $A + Br_2 \longrightarrow A, Br_2 \xrightarrow{Br_2} ABr^+ + Br_3^- \longrightarrow ABrBr + Br_2$  (*J.*, 1943, 276). There are, however, certain formalistic difficulties in connection with Roberts and Kimball's theory. The  $Br^-$  released in the first stage must move to the reverse side of the positive ion to complete the process, and the model of the transition state reveals a condition of considerable strain. An alternative mechanism is now proposed, according to which the initial addition compound forms a four-atom ring (in which the strain is less than in a three-atom ring) and the change is completed by a second molecule of bromine:

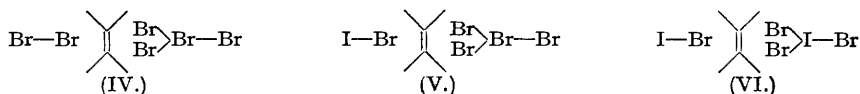


The formation of  $A, Br_2$  is due to the electrophilic attack by  $Br_2$  on  $A$ , and  $A, Br_2$  is represented by one of its possible resonance structures. The dotted lines in the diagram of the transition state indicate bond lengths intermediate between covalent and ionic bonds, as suggested by Dostrovsky, Hughes, and Ingold (*J.*, 1946, 173), and the arrows show the direction of the movement of the bromine atoms. The model thus constructed fulfils the requisite conditions for minimum strain, the bonds C-C, C-a, and C-b all being in one plane, and the direction  $Br-C-Br$  at right angles to this plane. The criticism may be made, however, that with such a mechanism there should be a possibility of *cis*-addition also, and in fact this is actually found, more extensively indeed than suggested in general in writings on this subject. For instance, Liebermann and Finkenbeiner (*Ber.*, 1895, 27, 2235) have shown that addition of chlorine to cinnamic acid in the dark in carbon tetrachloride takes place almost entirely by the *cis*-mechanism, whereas in the light the high m. p. isomer formed by *trans*-addition is obtained. No reference was made to the drying of the solvent, so the reaction appears to have been catalysed by water. In the corresponding addition of bromine to cinnamic acid in the same solvent, in the dark there is 37% *cis*-addition, which becomes reduced to 13% when the reaction takes place in light (Michael, *Ber.*, 1901, 34, 3663). When steric hindrance to addition becomes considerable, e.g., in *o*-nitrostilbene, addition of bromine may take place preferentially by the *cis*-mechanism (Peiffer, *Ber.*, 1915, 48, 1051).

With a small amount of added iodine we find that addition of chlorine to cinnamic acid, in the dark, takes place with the formation chiefly of the *trans*-addition product. These observations suggest the following modes of reaction mechanism for addition of chlorine to ethyl cinnamate: (I), no iodine, *cis*; (II), a small amount of iodine, *trans*; (III), a larger amount of iodine, *trans*, the iodine trichloride being represented by one of its possible resonance structures.



With the higher-order addition of bromine to ethyl cinnamate the process becomes more complicated, one or two molecules of bromine being replaced in the catalysed reactions by iodine bromide. This is illustrated by the following representations: (IV), fourth-order addition of bromine; (V), the same reaction catalysed by a small amount of iodine; and (VI), catalysed by a larger amount of iodine.



It was proposed (de la Mare, Scott, and Robertson, *J.*, 1945, 509) that the high-order bromine additions in the non-polar solvent carbon tetrachloride might be explained by a chain mechanism involving activated molecules, and it was considered that the iodine-catalysed reactions might have diagnostic value. Actually, it is difficult to devise a suitable chain mechanism involving iodine bromide molecules, and the kind of formulation suggested in the present communication appears on the whole a more likely mode of representation than a chain reaction for catalysed as well as uncatalysed bromine addition.

#### EXPERIMENTAL.

The materials and method were as previously described (*J.*, 1945, 511) except that chloramine-T was used instead of iodine in the back titration. Herewith the details of one of the measurements :

Ethyl cinnamate, M/20 + Cl <sub>2</sub> , M/20 + I <sub>2</sub> , M/500 in CCl <sub>4</sub> , at 24°.						
Time (mins.) .....	0.88	1.80	2.73	4.80	9.80	12.20
Titre .....	1.55	1.98	2.34	2.77	3.36	3.61
Back titre .....	0.84	0.85	0.86	0.88	0.94	0.96
Cl <sub>2</sub> absorption, % .....	19	30	38	50	65	71

Our thanks are due to Mr. B. B. Marsh for the measurements in chloroform solution.

VICTORIA UNIVERSITY COLLEGE, WELLINGTON, N.Z.

[Received, November 21st, 1946.]