

200. *The Kinetics of Aromatic Halogen Substitution. Part VI. Iodine-catalysed Bromination.*

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The iodine-catalysed bromination of hydrocarbons such as mesitylene in carbon tetrachloride solution proceeds by simultaneous reactions, of different order with respect to iodine for the same bromine concentration. There are maximum rates with added iodine, and a graphical interpretation shows that the positions of the maxima correspond with those required for the proposed simultaneous reactions. The rate measurements by Bruner (1902) for the iodine-catalysed bromination of benzene are also analysed by this method. Theoretical considerations indicate that the experimental results are consistent with a reaction proceeding in two stages, in each of which the iodine, as either its tribromide or its bromide, may participate.

THE efficiency of iodine as a catalyst in bromine substitution has long been known, and the first to make a kinetic study of the reaction was Bruner (*Z. physikal. Chem.*, 1902, **41**, 514). He examined especially the bromination of benzene, without the addition of a solvent, varying the amounts of bromine and iodine. The results corresponded with fourth-order kinetics, *i.e.*, for the total halogen, and approximately bimolecular rates were found for the individual runs. Bruner endeavoured to explain these results by a theory involving formation of bromine atoms from iodine bromide, but it was not indicated how the proposed mechanism accorded with other characteristics of the reaction, the maximum velocity with added iodine, and the rapid fall in rate in the individual reactions when the amount of iodine was considerable.

A further investigation of the nature of the iodine catalysis of bromination was made by Price, who used phenanthrene as the reactant, and carbon tetrachloride as solvent (*J. Amer. Chem. Soc.*, 1936, **58**, 2101; 1938, **60**, 2835; *Chem. Reviews*, 1941, **29**, 37). He concluded that the rate is given by the expression $-d[\text{Br}_2]/dt = k[\text{A}][\text{Br}_2]^{3/2}[\text{I}_2]^{1/2}$, and by a selection of certain of Bruner's measurements decided that the bromination of benzene showed similar kinetics. Thereupon he proposed a mechanism for aromatic substitution, involving an attack by BrI_3 to give an intermediate which then reacted with IBr_2^- ions formed from $(\text{IBr})_2$. In the evaluation of the rate-expression it was assumed that $[\text{IBr}]^2$ is proportional to $[\text{I}_2]$ and $[\text{Br}_2]$, which is permissible only if IBr is considerably dissociated; this is not the case, as IBr is dissociated only to the extent of 9% in carbon tetrachloride solution at 25° (Yost *et al.*, *J. Amer. Chem. Soc.*, 1933, **55**, 3876). Further, in this formulation bromine plays no part in the reaction other than to give iodine bromide, so that the proposed mechanism cannot explain the attainment of a maximum rate with increasing amounts of iodine, which is a characteristic feature of these reactions.

The compounds hitherto selected for the investigation of the iodine catalysis of bromination have not been especially suitable. Since the reaction with benzene is very slow, high concentrations of bromine have to be used for the measurements. Likewise phenanthrene is not a favourable compound, because bromine substitution tends to be accompanied by addition (cf. Kharasch, White, and Mayo, *J. Org. Chem.*, 1938, **2**, 574). Measurements that we have made with phenanthrene in carbon tetrachloride solution showed that it was not possible to obtain reproducible results, even in an atmosphere of dry nitrogen. Traces of oxygen appear to react with the hydrogen bromide present and initiate a bromine atom-chain addition. In chloroform solution, on the other hand, the substitution reaction is relatively favoured and more reproducible results were obtained, and it was found that with $m/40$ -reactants the order with respect to iodine, when present at low concentrations, was ~ 1.5 .

Iodine-catalysed bromination is conveniently studied with a more rapidly reacting hydrocarbon such as mesitylene. Measurements have been made in carbon tetrachloride and chloroform solution, and the results found to conform with those obtained for iodine-catalysed bromine addition (Waters, Caverhill, and Robertson, *J.*, 1947, 1168), the order being dependent on the amount of added iodine.

The simplest method of determining the kinetics of these reactions is to measure the rates on

changing the concentrations of the reactants separately. This is illustrated for the bromination of mesitylene in carbon tetrachloride, at 24° :

	[I ₂] = 0.	M/800.	M/400.
M/40-A + M/40-Br ₂ , time (mins., $\alpha = 10$)	72	14	6.5
<i>n</i> (IBr) corr.	—	1.1	—
M/80-A + M/80-Br ₂ , time (mins., $\alpha = 10$)	—	45	21
<i>n</i> (IBr) corr.	—	1.1	—
<i>n</i> (A + Br ₂)	—	2.7	2.7

The results for the same reaction in chloroform, M/80-reactants, at 24°, are now given :

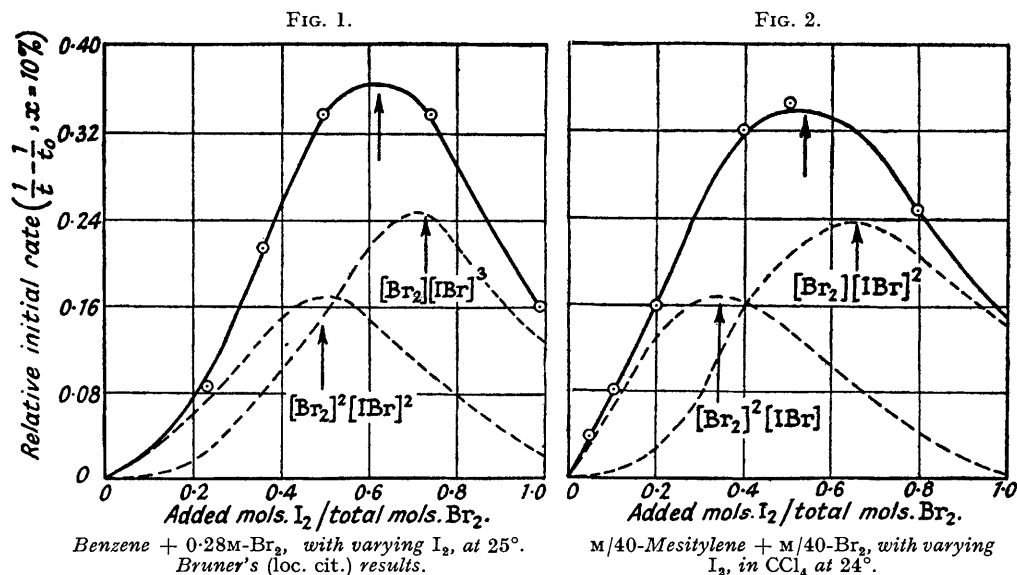
	[I ₂] = 0.	M/1600.	M/800.
Time (mins., $\alpha = 25$)	48	1.80 *	0.77
<i>n</i> (IBr) corr.	—	—	1.2

* Reactants M/40, $t = 0.90$: $n(A + Br_2) = 2.0$.

The *n* values for iodine bromide require a correction (small in the above reactions) (*a*) for the simultaneous uncatalysed reaction and (*b*) for the amount of bromine removed by combination with iodine. These results indicate that for low concentrations of added iodine the order with respect to iodine bromide approaches unity, *i.e.*, when the bromine is in the concentration region M/40. With higher concentrations of bromine, the order for iodine bromide becomes greater even when the amount of added iodine, relative to the bromine, is small, as is shown in the reaction of *o*-xylene with bromine : (M/2-Reactants, at 24°, in carbon tetrachloride solution.)

	[I ₂] = 0.008M.	0.016M.
Time (mins., $\alpha = 20$)	78	18
<i>n</i> (corr.) (IBr)	—	2.0

With greater amounts of iodine an approximate analysis of the experimental results can be made by a graphical method. A similar treatment can also be applied to Bruner's measure-



ments in the bromination of benzene. From his results (Table 3, *loc. cit.*) the relative initial rates, calculated as $1/t$ (since the contribution of the uncatalysed reaction is negligible) may be obtained and are plotted in Fig. 1. The iodine is present chiefly as iodine bromide, and it may be calculated from Bruner's other results (Tables 1 and 2, *loc. cit.*) that at low concentrations of iodine the rate is proportional to $[Br_2]^2[IBr]^2$. A curve representing this reaction is constructed to coincide with the experimental curve at 0.1 mol. of I₂; this is the broken curve showing a maximum at 0.50 mol. of I₂, and there is included a correction, which is small, to allow for the dissociation of the iodine bromide. The difference between this curve and the experimental curve gives a second curve which should correspond with a rate proportional to $[Br_2][IBr]^3$, as the total order of the reaction remains the same and the order for iodine bromide becomes

greater as the iodine is increased. This new curve is found to approximate to the calculated curve for this reaction, and in particular to have its maximum rate at 0.74 mol. of I_2 (calc., 0.75).

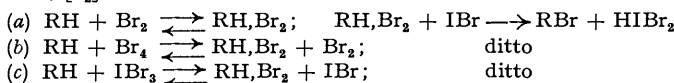
The experimental maximum is between the theoretical maxima, rather more in the direction of the $[Br_2][IBr]^3$ reaction, and correspondingly the relative contribution of this reaction is somewhat greater under these conditions, as shown by the vertical distances in the diagram. The iodine-catalysed bromination of benzene, at high concentrations of bromine, may therefore be represented by

$$-d[Br_2]/dt = k[Br_2]^2[IBr]^3 + k'[Br_2][IBr]^3$$

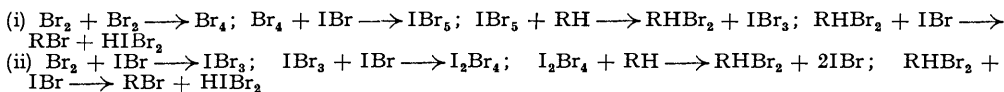
A similar treatment is possible for the iodine-catalysed bromination of mesitylene, *m*/40-reactants, in carbon tetrachloride solution (Fig. 2). A curve for the rate proportional to $[Br_2]^2[IBr]$ is drawn to coincide with the experimental curve at 0.05 mol. of I_2 [when n (IBr) was found to be unity], and has a maximum at 0.35 mol. of I_2 . On subtracting this curve from the experimental curve, a second curve is obtained with maximum at 0.65 mol. of I_2 . This curve has approximately the characteristics of the reaction for which the rate is $k[A][Br_2][IBr]^2$, with a maximum at 0.66 mol. of I_2 . At the experimental maximum rate the contribution of the higher-order reaction (as determined by the vertical distances) is more considerable, and there is a corresponding disposition of this maximum between the maxima of the two contributing reactions. It may be concluded, therefore, that the rate-expression for the iodine-catalysed bromination of mesitylene in carbon tetrachloride, for low concentrations of bromine, is

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

Discussion.—Halogen substitution, like halogen addition, may be formulated as a two-stage process. In bromine substitution the first stage is an electrophilic attack by a bromine molecule polarised by a polar surface, or solvent dipoles, or by a second molecule of bromine, to join with RH forming an addition compound, RH, Br_2 ; the second stage is the anionisation of a bromine atom from this with the simultaneous separation of a hydrogen atom as hydrogen bromide. With added iodine it is suggested that iodine tribromide replaces the bromine in the first stage; its amount present must be small (cf. Morton, *Proc. Royal Soc.*, 1929, *A*, 124, 609) and its concentration therefore proportional to $[Br_2][IBr]$. Like Br_2 , it is favourably polarisable, $[Br^+][IBr_2^-]$, for electrophilic attack. In the second stage of the reaction iodine bromide operates by removal of a bromine atom from RH, Br_2 as the ion IBr_2^- . If the catalytic effect in the first stage is relatively less effective than in the second stage, *i.e.*, occurring to an appreciable extent only when the added iodine becomes considerable, then the bromination of mesitylene may be represented, (a) in chloroform, $[I_2]$ small, (b) in carbon tetrachloride, $[I_2]$ small, (c) in either solvent, $[I_2]$ considerable, as follows:



The explanation of the overall fifth-order reaction measured by Bruner is more doubtful. If, as seems probable, these reactions proceed by a series of bimolecular steps, in each of which one of the reactants is in excess, then the following formulation would be in accord with the observed kinetics of the two simultaneous reactions:



This theory demands the existence of the compounds IBr_5 and I_2Br_4 ; the amounts formed must be small, even at high bromine concentrations, but such compounds may be suitably polarisable for electrophilic attack, towards the structures $[Br^+][IBr_4^-]$ and $[Br^+][I_2Br_3^-]$.

EXPERIMENTAL.

The following compounds were used: mesitylene, b. p. 164°/747 mm.; *o*-xylene, b. p. 143°/756 mm. The technique was as previously described, chloramine-*r* being used instead of iodine for the back titrations (*J.*, 1943, 276). Herewith is a typical set of measurements in detail.

m/40-Mesitylene + *m*/40- Br_2 + *m*/400-iodine, in carbon tetrachloride at 24° under nitrogen; reaction mixture 10 ml.; 1-ml. samples added to *N*/80-sodium arsenite and back-titrated with *N*/80-chloramine-*r*.

Time (mins.).	Titre (ml.).	Br_2 , %, absorbed (x).	Time (mins.).	Titre (ml.).	Br_2 , %, absorbed (x).
0	0.65	0	0	0.56	0
6	1.04	9	5.2	0.90	7.5
12	1.39	17	11.3	1.32	17
19	1.82	27	21	1.81	28

The points lay on a smooth curve from which the value, $t = 6.5$ ($x = 10$) was taken.

The values for M/40-mesitylene + M/40-bromine and different amounts of iodine in carbon tetrachloride at 24° , for $x = 10\%$ bromine absorption (Fig. 2) are as times (minutes) : no I_2 , $t = 72$; M/400- I_2 , $t = 6.5$; M/200- I_2 , $t = 3.4$; M/100- I_2 , $t = 1.8$; M/80- I_2 , $t = 1.65$; M/50- I_2 , $t = 2.4$; M/25- I_2 , $t = 4.7$. Other measurements have been quoted in the text.

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