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The Iodine Bromide Catalyzed Reaction of Bromine with Mesitylene in Carbon Tetrachloride Solution

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The reaction between mesitylene and bromine in carbon tetrachloride solution is catalyzed by iodine bromide. At low concentrations of mesitylene the rate of disappearance of bromine is second order in iodine bromide, first order in bromine and first order in mesitylene. At concentrations of mesitylene above 1 *M* the effect of increasing mesitylene concentration on the rate of reaction may be explained on the basis that both free and complexed iodine bromide act as a catalyst for the conversion of a 1–1 mesitylene–bromine complex to ring substituted bromomesitylene.

Bruner's[1] data on the iodine-catalyzed bromination of benzene have been reinterpreted by several different workers.[2] Robertson[2b] and co-workers state that the data may be explained by two simultaneous reactions both of which are fourth order in halogen. In addition they present data for the iodine bromide catalyzed bromination of mesitylene in carbon tetrachloride solution which they treat in terms of two simultaneous reactions that are third order in halogen. Tsuruta[2c] and co-workers interpret Bruner's data in terms of a single reaction which is third order in iodine bromide and first order in bromine. This is in agreement with calculations carried out in this Laboratory. In a later publication Tsuruta[3] and co-workers have shown that the rate of bromination of toluene in carbon tetrachloride is third order in iodine bromide, first order in bromine and first order in toluene. However, the reactions which they investigated were subject to an induction period. This fact suggests that an appreciable fraction of the bromination proceeded by a hydrogen bromide catalyzed reaction of the type reported for mesitylene.[4] Thus their conclusions as to the order of the reaction with respect to iodine bromide may not be valid. Therefore an investigation of the iodine bromide catalyzed reaction of bromine with mesitylene was undertaken.

The Effects of Changes in Reaction Conditions.—In carbon tetrachloride solutions containing excess bromine, iodine is almost completely converted to iodine bromide.[5] On adding excess mesitylene to such solutions bromination of the mesitylene takes place until the excess bromine is used up and the reaction then practically stops. Thus the rate of reaction of iodine bromide with mesitylene in carbon tetrachloride solution is negligible compared to the iodine bromide catalyzed bromination reaction.

In a previous communication[4] it was shown that carbon tetrachloride solutions of mesitylene could be brominated using hydrogen bromide as a catalyst only when water also was present.

To minimize the amount of the reaction proceeding by hydrogen bromide catalysis all solutions used in the rate runs were stored over freshly regenerated "Drierite" and all glassware was coated with Desicote. Even after these precautions were taken there was a noticeable autocatalytic effect when the iodine bromide concentration was less than 0.5×10^{-3} *M*, however, there was no evidence of an induction period. The solutions of bromine and mesitylene in the presence of iodine bromide were much less photosensitive than corresponding solutions without the iodine bromide. The brominated mesitylene from several of the rate runs was found to have 99% of the bromine attached to the ring thus indicating a negligible amount of side chain bromination.

Kinetic Studies.—Carbon tetrachloride solutions of iodine, bromine and mesitylene were mixed and the bromine concentration of the reaction mixture was determined spectrophotometrically at 520 mμ at various times. In these runs the mesitylene concentration was at least ten times that of bromine so that the mesitylene concentration remained nearly constant throughout the reaction. Under these conditions the individual runs were found to be first order in bromine

$$-\frac{d(Br_2)_T}{dt} = k_1(Br_2)_T \qquad (1)$$

The first-order rate constants, k_1, reported in the upper part of Table I were calculated from the slopes of the straight lines obtained by plotting log $(Br_2)_T$ *versus* time in minutes. The term $(Br_2)_T$ refers to the bromine in excess of the amount required to form iodine bromide. The first-order dependence of the rate of reaction on the bromine concentration is demonstrated by the constancy of the calculated k_1 values over a tenfold variation in initial bromine concentration (first four runs).

The order of the reaction with respect to mesityl-

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(1) L. Bruner, *Z. physik. Chem.*, **41**, 415 (1902).

(2) (a) C. C. Price, THIS JOURNAL, **58**, 2101 (1936); (b) P. W. Robertson, J. E. Allan, K. N. Haldane and M. G. Simmons, *J. Chem. Soc.*, 933 (1949); (c) T. Tsuruta, K. Sasaki and J. Furukawa, THIS JOURNAL, **74**, 5995 (1952).

(3) T. Tsuruta, K. Sasaki and J. Furukawa, *ibid.*, **76**, 994 (1954).

(4) R. M. Keefer, J. H. Blake, III, and L. J. Andrews, *ibid.*, **76**, 3062 (1954).

(5) A. I. Popov, K. C. Brinker, L. Campanaro and R. W. Rinehart, *ibid.*, **73**, 514 (1951).

ene may be determined from the series of runs at a constant iodine bromide concentration of 0.84 × 10^{-3} *M*. The values[6] of $k_1/(\mathrm{M})(\mathrm{IBr})_\mathrm{T}^2$ in the last column of Table I do not vary markedly with changes in the mesitylene concentration thus indicating that the reaction is first order in mesitylene in the region of 0.02 to 0.7 *M* mesitylene. That the reaction is second order in iodine bromide is indicated by the constancy of $k/(\mathrm{M})(\mathrm{IBr})_\mathrm{T}^2$ over a fivefold change in iodine bromide concentration.

TABLE I

RATE CONSTANTS AT 25.2° FOR THE IODINE BROMIDE CATALYZED REACTION OF BROMINE WITH MESITYLENE IN CARBON TETRACHLORIDE SOLUTION

(M), mole/l.	(IBr), mole/l. × 10^3	$(\mathrm{Br})_2$, mole/l. × 10^3	$10^3 k_1$, min.$^{-1}$	$10^{-4}k_1/(\mathrm{M})(\mathrm{IBr})_\mathrm{T}^2$, mole^{-3} l.^{3} min.$^{-1}$
0.204	0.840	2.03	7.79	5 4
.204	.840	4.48	7.53	5.2
.204	.840	9.37	7.65	5.4
.204	.840	19.16	7.9	5.5
.102	.840	9.37	4.25	5.9
.712	.840	9.37	22.0	4.4
1.424	.840	8.89	33.2	3.3
2.85	.840	8.89	43.2	2.15
0.204	.420	9.58	2.10	5.8
0.204	2.00	8.76	37.3	4.7
			k_2	$10^{-4}k_2/(\mathrm{IBr})_\mathrm{T}^2$
0.0544	2.42	6.46	0.36	6.1
.0257	3.84	6.31	.83	5.6
.0240	5.04	6.12	1.34	5.3
.0429	5.02	5.70	1.44	5.7

The last four rate runs reported in Table I were designed to test the above rate law at lower concentrations of mesitylene and higher iodine bromide concentrations. In these rate runs the bromine concentration was determined at various times by iodometric titration of an aliquot of the reaction mixture. Since mesitylene was not present in large excess in these runs, the rate law was formulated as

$$-\frac{\mathrm{d}(\mathrm{Br}_2)_\mathrm{T}}{\mathrm{d}t} = k_2(\mathrm{M})(\mathrm{Br}_2)_\mathrm{T} \qquad (2)$$

This equation may be integrated to give eq. 3 where $(\mathrm{M})_\mathrm{i}$ and $(\mathrm{Br}_2)_\mathrm{i}$ are the concentrations of mesitylene and bromine at zero time.

$$\log \frac{(\mathrm{M})}{(\mathrm{Br}_2)_\mathrm{T}} = [(\mathrm{M})_\mathrm{i} - (\mathrm{Br}_2)_\mathrm{i}]\; k_2 t/2.303 + \text{constant} \qquad (3)$$

Thus a plot of log $(\mathrm{M})/(\mathrm{Br}_2)_\mathrm{T}$ against time should give a straight line from the slope of which the value of k_2 may be calculated. Values of k_2 calculated from straight line plots are given in Table I. The good agreement between the values of $k_2/(\mathrm{IBr})_\mathrm{T}^2$ and the values of $k_1/(\mathrm{M})(\mathrm{IBr})_\mathrm{T}^2$ in Table I constitutes further evidence that the reaction is first order in mesitylene and second order in iodine bromide.

Temperature Coefficient of the Reaction Rate.—Reaction mixtures for runs at 36 and 14° were prepared in the same manner as the reaction mixtures for the runs followed by spectrophotometric determination of the bromine concentration. The values of the rate constant, k_1, were determined (in the same manner as the values of k_1 in Table I) and are given in column 4 of Table II. Since there is only a slight change in rate constant with temperature, the over all activation energy of the reaction must be very nearly zero.

TABLE II

THE EFFECT OF TEMPERATURE

(M), mole/l.	(IBr), mole/l., × 10^3	(Br_2), mole/l. × 10^3	$\frac{10^{-4}k_1}{(\mathrm{M})(\mathrm{IBr})_\mathrm{T}^2}$ Mole^{-3} l.^{3} min.$^{-1}$	Temp., °C.
0.200	0.95	10.7	4.9	36.0
.208	.97	10.7	5.5	14.1
.204	.84	2–19	5.5[a]	25.2

[a] Average values for first four runs in Table I.

Discussion.—Tsuruta, Sasaki and Furukawa[2c,3] have proposed the following mechanism (eq. 4–6) for the iodine bromide catalyzed reaction of bromine with benzene or toluene. When (AH) ≫ (Br_2)

$$\mathrm{AH} + \mathrm{Br}_2 \overset{K_1}{\rightleftarrows} \mathrm{AH{\cdot}Br_2} \qquad (4)$$

$$\mathrm{AH} + \mathrm{IBr} \overset{K_2}{\rightleftarrows} \mathrm{AH{\cdot}IBr} \qquad (5)$$

$$\mathrm{AH{\cdot}Br_2} + m\mathrm{IBr} \xrightarrow[\text{slow}]{k_3} \mathrm{ABr} + \mathrm{HBr} + m\mathrm{IBr} \qquad (6)$$

the rate law given in eq. 7 may be derived from this mechanism.

$$-\frac{\mathrm{d}(\mathrm{Br}_2)_\mathrm{T}}{\mathrm{d}t} = \frac{k_3K_1(\mathrm{AH})(\mathrm{Br}_2)_\mathrm{T}(\mathrm{IBr})_T^m}{[1 + K_1(\mathrm{AH})][1 + K_2(\mathrm{AH})]^m} \qquad (7)$$

where $(\mathrm{Br}_2)_\mathrm{T} = (\mathrm{Br}_2) + (\mathrm{AH{\cdot}Br_2})$, $(\mathrm{IBr})_\mathrm{T} = (\mathrm{IBr}) + (\mathrm{AH{\cdot}IBr})$. The available data for benzene[2c] and toluene[3] is in agreement with eq. 7 if *m* is 3 except that only qualitative agreement was noted for the effect of high concentrations of toluene upon the rate of reaction.

The iodine bromide catalyzed reaction of bromine with mesitylene is first order in bromine and second order in iodine bromide; thus eq. 7 is in agreement with the experimental results if *m* is 2. Furthermore since the equilibrium constants of the mesitylene complexes[4] are known (K_1 = 0.38 mole^{-1} l.; K_2 = 1.5 mole^{-1} l., see Experimental section), it is possible to test quantitatively the effect of mesitylene concentration on the rate of reaction with the effect predicted by eq. 7. At low concentrations of mesitylene where $K_1(\mathrm{AH})$ and $K_2(\mathrm{AH})$ are small compared to one, the reaction should be first order in mesitylene. This is in agreement with the results reported in Table I. However eq. 7 predicts that the rate of reaction in 1.4 *M* mesitylene would be 1.3 times the rate in 0.102 *M* mesitylene while the experimental ratio is 7.8 (Table I). Therefore it is apparent that the term in the denominator of eq. 7 is too large for high mesitylene concentrations. If only the first term in the denominator is used, the ratio of the rates in 1.4 to 0.102 *M* mesitylene would be 9.4 which is in fair agreement with the experimental value of 7.8. In terms of the mechanism this would mean that both free and complexed iodine bromide would act as the catalyst in eq. 6. It is

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(6) The term $(\mathrm{IBr})_\mathrm{T}$ refers to the sum of the concentrations of the free IBr and of that complexed with mesitylene (see eq. 5).

possible that "medium" effects are involved at the high mesitylene concentrations although such "medium" effects were not apparent at similar mesitylene concentrations in the hydrogen bromide[4] catalyzed bromination of mesitylene.

The rate-determining step (eq. 6) has been formulated as a third-order reaction. It is possible to consider additional equilibria and postulate many different second-order rate determining steps. For example the catalyst might be an iodine bromide dimer[7] which would assist in the removal of bromide from the mesitylene–bromine complex. However because of the large number of molecules involved in the transition state the exact manner in which the iodine bromide functions as a catalyst is not clear.

In view of the complexity of the proposed mechanism it is not possible to estimate the activation energy of the rate-determining step from the over-all activation energy. However since the heats of formation[4,8] of the several complexes involved are on the order of 1.5 to 2.5 kcal. and the over-all activation energy is approximately zero, it is probable that the activation energy of the rate-determining step is only a few kilocalories.

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Experimental

Mesitylene was purified as in previous work.[4] Mallinckrodt bromine and iodine were used without further purification. Eastman Kodak Company sulfur free carbon tetrachloride was used without further purification for the runs followed spectrophotometrically, and was distilled before used in the other runs. Desicote was obtained from the Beckman Instruments Company.

The Rate Measurements.—In the first series of runs the bromine concentration was determined spectrophotometrically. For these runs solutions of iodine, bromine and mesitylene in carbon tetrachloride were prepared from carbon tetrachloride stored over freshly roasted Drierite. The above solutions were also stored over Drierite. All glassware and the spectrophotometer silica cells were coated with Desicote. The reaction mixtures were prepared in Desicote covered flasks and then transferred to one cm. glass stoppered silica cells. The optical density of the mixture was then determined at various times using a Beckman model DU Spectrophotometer. The silica cell was left in the cell housing which was maintained at the desired temperature by circulating water from a constant temperature bath through the cell housing. The initial concentrations of mesitylene, iodine bromide and bromine were determined from the amounts of the solutions of mesitylene, iodine and bromine added. The bromine concentration of the reaction mixture was calculated from the optical density at 520 mμ after subtracting out the contribution due to the iodine bromide. The contribution due to iodine bromide was estimated from the extrapolated value of the optical density at zero time, the initial concentrations of bromine and iodine bromide and the extinction coefficient of bromine (65.3 at 520 mμ).

In the second series of runs the bromine concentration was determined iodometrically. Solutions were prepared as above but were not stored over Drierite.

The Equilibrium Constant for the Iodine Bromide–Mesitylene Complex.—The molar extinction coefficient of iodine bromide in carbon tetrachloride solution was determined and the values obtained at various wave lengths are given in Table III. At corresponding wave lengths the extinction coefficients are in good agreement with those of Popov[5] and co-workers. The optical densities of solutions of mesitylene (0.10 to 1.44 M) and iodine bromide (8.5×10^{-4} to 0.856×10^{-4} M) in carbon tetrachloride were determined at 320, 330 and 340 mμ. Solutions of corresponding mesitylene concentration were used as blanks. Values of the concentration equilibrium constant (eq. 5) were calculated using the methods of previous investigators.[9] The average value of K_2 for the three wave lengths investigated is 1.5 mole^{-1} l.

TABLE III

MOLAR EXTINCTION COEFFICIENTS OF IODINE BROMIDE IN CARBON TETRACHLORIDE

λ, mμ	ϵ_{IBr}, l. mole^{-1} cm.$^{-1}$	λ, mμ	ϵ_{IBr}, l. mole^{-1} cm.$^{-1}$
580	61.2	400	43
560	111	380	13.6
540	197	360	7.5
520	294	340	12.6
500	355	320	30.4
490	361	310	46
480	344	300	67
460	278	290	93
440	191	280	117
420	105	270	135

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[7] Evidence for the association of iodine has been noted in the absorption spectra of iodine vapor and of iodine solutions. See G. Kortüm and G. Friedheim, *Z. Naturforsch.*, **2a**, 20 (1947).

[8] R. M. Keefer and L. J. Andrews, THIS JOURNAL, **77**, 2164 (1955).

[9] J. A. A. Ketelaar, C. Van de Stolpe, A. Goudsmit and W. Dzcubas, *Rec. trav. chim.*, **71**, 1104 (1952).