carbinol–dye interaction will have time to occur to a significant extent and abnormal rates will be observed. Figure 11, showing k vs. C_{-OH} data for M. G.,[33] and for C.V. with various salt concentra-

(33) R. H. Dinegar, private communication, unpublished data.

tions, shows that deviations from normal behavior persist to higher alkali concentrations the greater the salt concentrations; i.e., the lower the rate constant.

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Kinetics of Iodine-catalyzed Aromatic Bromination. I. A New Rate Expression

BY TEIJI TSURUTA, KEN-ICHI SASAKI AND JUNJI FURUKAWA

Previous interpretations of data on the rate of the iodine-catalyzed bromination of aromatic derivatives are not satisfactory. The experimental data of Bruner have been recalculated through the use of a new expression for the rate law, in which it is assumed that the rate-determining step is the loss of hydrogen bromide from a 1:1 aromatic–bromine complex. This step is proportional in rate to some power, about three in the case of benzene, of the concentration of the BrI present. The new rate expression and mechanism account for both the iodine catalysis of the bromination and for the optimum rates observed with increasing amounts of iodine.

Detailed experimental data on the iodine-catalyzed bromination of benzene have been presented by Bruner.[1] Price[2] suggested that Bruner's measurements corresponded to the rate law

$$d[C_6H_5Br]/dt = k[C_6H_6][Br_2]^{3/2}[I_2]^{5/2} \quad (A)$$

He assumed such higher order of the rate expression (A) might be due to some sequence of reactions involving, e.g., $IBr_2^{(-)}$ or I_3Br.[3]

Suppose his mechanism were valid, but recalculation according to it leads to equation (B) instead of equation (A).

$$d[C_6H_5Br]/dt = k[C_6H_6][Br_2]^{3/2}[I_2]^{5/2}/[I_3^{(-)}] [I^{(+)}] \quad (B)$$

In equation (B), [Br₂] and [I₂] should be the concentrations of free bromine and iodine, respectively. On the other hand, since Price calculated the experimental results taking the total unreacted bromide as [Br₂], it is obvious that his [Br₂] included not only free bromine but BrI, I₃Br and other bromides which appeared in his mechanism. As [I₂], he took the total quantity of iodine added, but on account of large equilibrium constant for BrI formation there should remain only an extremely small quantity of free iodine when iodine was mixed with excess of bromine.
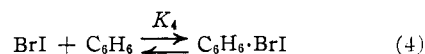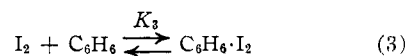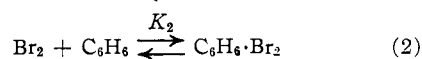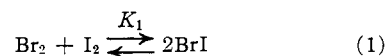
Further, according to equation (A) the greater the quantity of iodine used, the greater is the reaction rate; however, Bruner's data show an optimum in it. Iodine in excess of a given amount decreases the rate of reaction.

Robertson and his co-workers,[4] who used mesitylene as the reactant and carbon tetrachloride or chloroform as solvent, criticized Price's work and established other rate expressions. In order to account for the experimental results they assumed complicated successive and competing paths which involved the assumed existence of such complexes as Br_4, IBr_3, IBr_5 and I_2Br_4. Recently evidence has been presented in favor of 1:1 complexes between several halogens and a variety of benzene deriva-

tives[5-9]; these are formed rapidly and equilibrium constants for their formation have been measured in some cases. The present paper presents a reinterpretation of Bruner's results, which is based upon a simple rate law and utilizes this new information as to the molecular species present in the reacting system.

Derivation of a New Rate Expression

As stated above, in a solution of bromine, iodine and an aromatic compound in an inert solvent, the following equilibria exist

$$Br_2 + I_2 \underset{}{\overset{K_1}{\rightleftharpoons}} 2BrI \quad (1)$$

$$Br_2 + C_6H_6 \underset{}{\overset{K_2}{\rightleftharpoons}} C_6H_6 \cdot Br_2 \quad (2)$$

$$I_2 + C_6H_6 \underset{}{\overset{K_3}{\rightleftharpoons}} C_6H_6 \cdot I_2 \quad (3)$$

$$BrI + C_6H_6 \underset{}{\overset{K_4}{\rightleftharpoons}} C_6H_6 \cdot BrI \quad (4)$$

where K_1, K_2, K_3 and K_4 are equilibrium constants. As Robertson[4] has already indicated, the order of the rate law in aromatic bromination depends upon a number of factors, such as the nature of the aromatic derivative, the concentrations of the reagents and the solvent. He attributed this variation in order mainly to the differences in capacity for 1:1 complex formation of the aromatic ring against the halogen.[10]

In the present analysis, on the other hand, a single kind of aromatic–halogen complex (1:1) is assumed in accordance with the work cited above, and any requirement for higher orders probably referred to the process of removal of hydrogen bro-

(1) L. Bruner, Z. physik. Chem., 41, 514 (1902).

(2) (a) C. C. Price, THIS JOURNAL, 58, 1834, 2102 (1936); (b) C. C. Price and C. E. Arntzen, ibid., 60, 2835 (1938).

(3) C. C. Price, Chem. Revs., 29, 42 (1941).

(4) P. W. Robertson, J. E. Allan, K. N. Haldane and M. G. Simmers, J. Chem. Soc., 933 (1949).

(5) F. Fairbrother, Nature, 160, 87 (1947); J. Chem. Soc., 1051 (1948).

(6) J. Kleinberg and A. W. Davidson, Chem. Revs., 42, 601 (1948).

(7) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, 70, 2832, 3978 (1948); 71, 2703 (1949).

(8) N. S. Bayliss, Nature, 163, 764 (1949).

(9) (a) R. M. Keefer and L. J. Andrews, THIS JOURNAL, 72, 4677, 5170 (1950); (b) R. M. Keefer and L. J. Andrews, ibid., 73, 462 (1951).

(10) Robertson assumed in his mechanism the 1:1 complex as an intermediate. But he considered that this complex was formed through the complicated successive reactions and the variation in order of the rate law was mainly attributed to these reactions.

mide. When a reactive aromatic hydrocarbon, e.g., mesitylene, is used as a reactant, removal of hydrogen bromide from the complex takes place so readily that a catalyst would not be needed. With benzene, this is not the case; bromobenzene is formed in the dark only with the aid of catalysts. In Bruner's experiments in which bromine is in excess compared to iodine it is reasonable to assume that BrI is the only catalyst present for removal of hydrogen bromide.

We therefore assume the mechanism

$$C_6H_6 \cdot Br_2 + mBrI \xrightarrow{k} C_6H_5 \cdot Br + HBr + mBrI \quad (1')$$
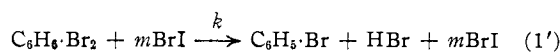
where k is a rate constant of reaction $(1')$ and m is a constant which is determined in response to the sorts of reactant and the other experimental conditions. The way in which IBr reacts to remove hydrogen bromide cannot be detailed, but it is reasonably assumed that the less reactive compounds will demand more molecules of IBr than the more reactive ones do.

In the rate study, the only experimental observation is the titration for total halogen present; its rate of decrease denotes the rate (v) of formation of bromobenzene. If a, b, $\ldots$, f and ϕ denote the concentrations (moles per ml.) of the following reactants when reaction has attained to a steady state: $[Br_2] = a$, $[I_2] = b$, $[BrI] = c$, $[C_6H_6 \cdot Br_2] = d$, $[C_6H_6 \cdot I_2] = e$, $[C_6H_6 \cdot BrI] = f$, and $[C_6H_6] = \phi$, the reaction rate v would be given by

$$v = kdc^m \quad (5)$$

and from the equilibrium relations of (1)–(4) it follows that

$$K_1 = c^2/(ab) \quad (6)$$
$$K_2 = d/(a\phi) \quad (7)$$
$$K_3 = c/(b\phi) \quad (8)$$
$$K_4 = f/(c\phi) \quad (9)$$

The titers of total bromine X (moles per ml.) and of total iodine Y (moles per ml.) are given by

$$2X = 2a + c + 2d + f \quad (10)$$
$$2Y = 2b + c + 2e + f \quad (11)$$

From equations (6)–(11) the following relations are easily obtained

$$a = (2X - \gamma c)/2\alpha \quad (12)$$
$$b = (2Y - \gamma c)/2\beta \quad (13)$$

and

$$c = \{-K_1(X + Y)\gamma + \sqrt{K_1^2(X + Y)^2\gamma^2 + 4K_1XY(4\alpha\beta - K_1\gamma^2)}\}/ (4\alpha\beta - K_1\gamma^2) \quad (14)$$

where $\alpha = 1 + K_2\phi$, $\beta = 1 + K_3\phi$ and $\gamma = 1 + K_4\phi$.

If the aromatic compound is used in sufficient excess, its concentration (ϕ) and hence α, β and γ may be considered as constants. Since a, b and c have been all expressed in terms of X, Y and constants, it would appear possible to test equation (5). But because the form of equation (14) is not proper for further calculations, it is desired to simplify by expanding in a power series. Thus

$$\sqrt{K_1^2(X + Y)^2\gamma^2 + 4K_1XY(4\alpha\beta - K_1\gamma^2)} = K_1(X + Y)\gamma\{1 + (\frac{1}{2})(L/K_1)4XY/(X + Y)^2 - (\frac{1}{8})(L/K_1)^216X^2Y^2/(X + Y)^4 + \ldots\} \quad (15)$$

where $L = (4\alpha\beta/\gamma^2) - K_1$.

If X is not equal to Y, it follows that $0 < 4XY/(X + Y)^2 < 1$. Since $\alpha\beta/\gamma^2$ is always larger than zero and L is negative in the present case owing to a comparable magnitude of γ to α or β and a larger value of K_1[11], it follows that $|L/K_1| < 1$ and hence $|(L/K_1)4XY/(X + Y)^2| < 1$.

Therefore, if bromine is present in excess compared to iodine, neglecting terms below the fourth of equation (15), the following approximation is possible

$$c = 2[\{XY/(X + Y)\} - \{(L/K_1)X^2Y^2/(X + Y)^3\}]/\gamma \quad (16)$$

Therefore it follows that

$$a = [\{X^2/(X + Y)\} + \{(L/K_1)X^2Y^2/(X + Y)^3\}]/\alpha \quad (17)$$
$$b = [\{Y^2/(X + Y)\} + \{(L/K_1)X^2Y^2/(X + Y)^3\}]/\beta \quad (18)$$

and

$$d = K_2\phi[\{X^2/(X + Y)\} + \{(L/K_1)X^2Y^2/(X + Y)^3\}]/\alpha \quad (19)$$

Inserting equations (16) and (19) into equation (5), it follows that

$$v = Muw^m \quad (20)$$

where

$$M = (2/\gamma)^m K_2 k\phi/\alpha$$
$$u = \{X^2/(X + Y)\} + \{(L/K_1)X^2Y^2/(X + Y)^3\}$$

and

$$w = \{XY/(X + Y)\} - \{(L/K_1)X^2Y^2/(X + Y)^3\}$$

Hence

$$\log (v/u) = \log M + m \log w \quad (21)$$

Since M and m are constants, equation (21) indicates that there should be a linear relation between $\log (v/u)$ and $\log w$. Even if the exact value of L/K_1 cannot be known, it may be considered to be almost equal to -1, because K_1 is large (about 400[11]). Thus the authors have assumed $L/K_1 = -1$ in their calculations. Bruner's results on benzene have verified the linear relation demanded in equation (21) as it is seen in Fig. 1. In the case of benzene, from the inclination in Fig. 1, the authors found that m was equal to three.

Therefore, for benzene, equation (20) is transformed into equation $(20')$

$$v = Muw^3 \quad (20')$$

The validity of equation $(20')$ can be ascertained in Table I.

The authors have so far discussed about the validity only of equation (5). However, if Bruner's data fit equation (5), they will also fit the following equations as well as any combination of these, because Bruner's measurements were all held in benzene without any added solvent.

$$v = kac^m \quad (22)$$
$$v = k'af^m \quad (23)$$

and

$$v = k''df^m \quad (24)$$

where k's are rate constants.

Therefore, it is impossible to determine which is the most probable mechanism among these equations; so, from Bruner's data themselves, we can only indicate that equation (5) is one of the possible mechanisms. Experiments which give us infor-

(11) D. M. Yost, T. F. Anderson and F. Skoog, THIS JOURNAL, 55, 552 (1933).

TABLE I

	X^a × 10^4, moles/ml.	Y^a × 10^4, moles/ml.	uw^3 × 10^{16}, (moles/ml.)^4	v × 10^4, moles/ml. day	$M = v/uw^3$ × 10^{-12}, (mol./moles)^3 (1/day)
1A	7.88	2.14	44.60	55.50	1.24
1A	5.70	2.14	24.70	28.20	1.14
1B	5.73	1.42	10.12	11.57	1.14
1B	4.19	1.42	5.95	6.45	1.08
1B	3.26	1.42	3.58	3.96	1.11
1B	2.66	1.42	2.25	2.72	1.21
1C	4.07	1.07	2.95	3.36	1.14
1C	2.90	1.07	1.50	1.81	1.21
1D	3.58	0.86	1.40	1.52	1.08
1D	2.54	.86	0.78	0.86	1.11
1D	1.92	.86	0.44	0.41	0.93
2A	6.15	1.44	11.73	13.60	1.16
2A	3.62	1.44	4.69	4.94	1.05
2A	2.54	1.44	2.02	2.46	1.24
2B	4.53	0.90	2.28	2.53	1.11
2B	3.62	.90	1.62	1.67	1.03
2B	3.17	.90	1.32	1.56	1.18
2B	2.58	.90	0.90	0.83	0.92
2C	3.97	.71	1.05	1.14	1.09
2C	2.98	.71	0.68	0.77	1.14
2C	2.16	.71	.39	.38	0.98
3A	2.51	.71	.51	.53	1.04
3A	2.04	.71	.34	.36	1.07
3A	1.72	.71	.24	.29	1.20
3A	1.50	.71	.19	.23	1.24
3A	1.33	.71	.14	.16	1.14
3B	2.31	1.06	.99	.91	0.92
3B	1.90	1.06	.60	.72	1.20
3B	1.63	1.06	.43	.48	1.13
4A	7.25	2.04	33.80	40.70	1.20
4A	4.84	2.04	15.73	16.40	1.04
4A	3.53	2.04	7.63	9.05	1.18
4B	8.32	1.50	20.20	24.00	1.19
4B	5.89	1.50	12.43	14.90	1.20
4B	3.63	1.50	3.30	4.44	1.34
4C	9.60	1.14	11.75	13.80	1.17
4C	6.79	1.14	7.45	11.30	1.52[b]
4C	5.25	1.14	5.17	5.25	1.01
4C	4.08	1.14	3.37	4.07	1.20
4E	7.80	0.79	3.31	4.53	1.37
4E	3.90	0.79	1.31	1.45	1.11

Mean [1.13 ± 0.068]

[a] X and Y were calculated from the Bruner data.
[b] This value was omitted from the mean.

mation as to the dependence of the concentration of aromatic compound upon the reaction rate, would afford an approach to a unique mechanism.

It is seen that equation (21) is in good accord with the experimental results provided the ratio of bromine to iodine (X/Y) is not too small. In this paper evaluation of equation (21) has been limited to those experiments in which the ratio $X:Y$ was at least 3. When the titer of bromine falls to be equivalent to that of iodine, i.e., $X = Y$, equation (14) can be simplified without any approximation; and hence, for benzene, the following expression can be immediately derived from equations (5), (7), (12) and (14)

$$v = MUW^3X^4 \qquad (25)$$

where

$$M = (2/\gamma)^3K_2k\phi/\alpha$$
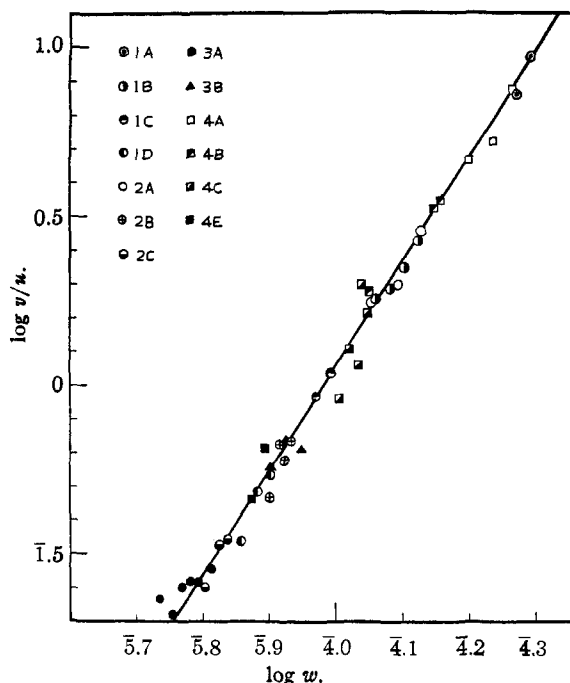$$U = (2\sqrt{\alpha\beta}/\gamma)/\{(2\sqrt{\alpha\beta}/\gamma) + \sqrt{K_1}\}$$

Fig. 1.—log v/u vs. log w. 3C, 3D and 3E, where Y/X is too large, and 4D, which involves some questionable data, have been neglected.

and

$$W = \sqrt{K_1}/\{(2\sqrt{\alpha\beta}/\gamma) + \sqrt{K_1}\}$$

The rate of reaction at $X = Y$, is hard to estimate from Bruner's data, owing to the extremely small value of the tangent at $X = Y$ except for a few examples, but it is not necessarily difficult to estimate the range in which the value lies. At Bruner's experiment 3D and 3E, however, velocity v can be obtained with a tolerable accuracy. The mean value of MUW^3 in 3D and 3E was about (1.74 × 10^{10}) (ml./moles)^3 (1/day).

In Table II it is seen that any v_0, calculated by inserting (1.74 × 10^{10}) (ml./moles)^3 (1/day) for MUW^3 of equation (25), lies in the range of experimental values, which has been estimated graphically, with a few exceptions. Thus equation (25) also has been verified.

TABLE II[a]

Experimental number of Bruner's	X^4 × 10^{16} (moles/ml.)^4	$v_{obsd.}$ × 10^4, moles/(ml. day)	v_0 × 10^4, moles/ml. day
1A	20.70	52.1—27.2	36.0
1B	4.12	49.5— 7.0	7.2
1C	1.30	7.2— 1.9	2.3
2A	4.25	8.7— 3.6	7.4
3A	0.25	1.2— 0.2	0.4
3B	1.27	5.0— 1.8	2.2
3C	4.00	15.9— 5.5	7.0
3D	20.40	37.8	35.5
3E	64.00	103.5	111.2
4A	16.00	58.3—10.0	27.8

[a] Experiments, which had not been held in the vicinity of $X = Y$ or involve some questionable data, have been neglected in this table.

Moreover, if equations (20') and (25) both hold well, it follows that

$$(MUW^3/M) = (1.74/1.13)(10^{-2}) \quad (26)$$

hence

$$UW^3 = 0.015 \quad (27)$$

If K_1 (the equilibrium constant of reaction (1)) in benzene was assumed to be the same as in carbon tetrachloride, $\sqrt{K_1}$ should be equal to about twenty.[11]

Therefore, from equation (27), it follows that

$$\sqrt{\alpha\beta}/\gamma \doteq 0.15 \quad (28)$$

Referring to Keefer's data,[9b] α and β are easily evaluated

$$\alpha = 1 + K_2\phi = 2.04$$
$$\beta = 1 + K_3\phi = 2.72$$

where $\phi = 1$, $K_2 = 1.04$[12] and $K_3 = 1.72$.[12]

Inserting these values into equation (28), it follows that $\gamma = 15.7$ and hence $K_4 = 14.7$.

Although any data on the equilibrium constant K_4 for the complex formation between benzene and iodine monobromide have never been presented, its value may be much larger than K_2 or K_3, just as that of iodine monochloride has been shown to be several times larger.[9b]

The results of these calculations are of significance in the sense that every series of points plotted in response to the various values of u and w lies on a straight line, regardless of whether this was calculated from the changing values of X during a bromination process in an experiment or from the various initial concentrations of halogens in several experiments.

This is to be expected, but there have been presented not a few rate expressions which have been tested only by the initial velocity of the reaction.

Maximum Point of the Reaction Rate

As Robertson has already indicated, it is one of the characteristics of iodine-catalyzed bromination that there exists a maximum point of the reaction rate with respect to the relative titer of bromine to

(12) There are found some questionable points about the accuracy of the absolute values of K_2 and K_3, but detailed criticism about them should be discussed elsewhere; here the authors adopted the values given in Keefer's paper.[9b]

iodine. The authors' rate expression can account quantitatively for the existence of a maximum point; there, $(\partial v/\partial Y)_X$ should be equal to zero and hence from equation (5)[18]

$$mc^{m-1}/d(\partial c/\partial Y)_X + c^m(\partial d/\partial Y)_X = 0 \quad (29)$$

Therefore, from equations (7), (12) and (14), at the maximum point of reaction rate, the following relation between X and Y is obtained

$$Y = [\{4\alpha\beta/(K_1\gamma^2)\}\{m^2/(m+1)\} + \{m/(m+1)\}]X \quad (30)$$

Equation (30) means that optimum relative titer of iodine with respect to bromine should be influenced not only by the order (m) of reaction of iodine monobromide, but by the equilibrium constants K_1, K_2, K_3 and K_4. Since equilibrium constants are subjected to variation, for instance, by change in temperature or solvent, the optimum relative titer of iodine should change in response to various experimental conditions even if the same aromatic hydrocarbon is used as reactant.

For example, with benzene as reactant, since m is equal to three, equation (30) is transformed to equation (31).

$$Y = [\{4\alpha\beta/(K_1\gamma^2)\}(9/4) + (3/4)]X \quad (31)$$

As it has been seen, $\alpha\beta/\gamma^2$ is less than unity and K_1 is equal to about 400 in an indifferent solvent, so the first term is negligibly small compared with the second when a solvent, in which K_1 is sufficiently large, is used. Therefore, from equation (31) it is expected that the optimum point should exist in the vicinity of $Y = (3/4)X$ which has been observed in Bruner's data.

Results of several series of experiments on the bromination of toluene in the dark, which are in progress at the author's laboratory, will be contributed before long.

(13) The same results are obtained from equations (22), (23) or (24).