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The Acid-catalyzed Bromination of Aromatic Compounds with Potassium Bromate in Aqueous Acetic Acid

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Bromobenzene is obtained in a 64% yield when an aqueous acetic acid solution containing a catalytic amount of sulfuric acid is slowly added to an aqueous acetic acid solution of benzene and potassium bromate at 60°C. It seems, according to the synthetic data, that the formation of bromobenzene is accelerated by an electron-releasing group. The rate of the consumption of active oxygen has been expressed as follows:

$$v=k_2[\mathrm{BrO_3}^-][\mathrm{C_6H_6}] + k_3[\mathrm{BrO_3}^-][\mathrm{C_6H_6}]^2$$

Here, both k_2 and k_3 gave a straight line against $-\log(C_{\mathrm{BH^+}}/C_{\mathrm{B}})$, with a slope of *ca.* -2. The reaction is accelerated by sulfuric acid and does not occur at all in the absence of the acid. The evolution of oxygen gas was not observed during the reaction, but the presence of peroxyacetic acid and/or acetyl peroxide in the reaction mixture was indicated by paper chromatography. A mechanism which involves the rate-determining attack of protonated hypobromous acid and/or protonated acetyl hypobromite on benzene has been suggested.

The heterogeneous bromination of benzene with potassium bromate in the presence of sulfuric acid is well-known[1]; however, no kinetical study has yet been made. We now wish to describe some findings regarding the mechanism of this reaction in a homogeneous system, using 50 vol% aqueous acetic acid as the solvent.

It is well known that there are two theories[2,3] as to the bromination of aromatic ring with molecular bromine in the presence of an electrophilic reagent. In the present reaction, however, the attacking species is not the bromine cation but protonated hypobromous acid and/or acetylbromite.

Experimental

Materials. The Potassium bromate was recrystallized twice from hot water and dried at 120°C for 2 hr. The benzene[4] was treated with concentrated sulfuric acid and diluted aqueous sodium hydroxide, washed with water, and then rectified after drying on phosphorus pentoxide; bp 80.0°C. The acetic acid was rectified; bp 117—119°C. The sulfuric acid used was of a guaranteed grade. Peroxyacetic acid was prepared by the reaction of acetic anhydride with hydrogen peroxide.[5] Acetyl peroxide was prepared by dropping water into a suspension of sodium peroxide in an ethereal solution of acetic anhydride.[6] Aqueous hypobromous acid was prepared by the addition of an aqueous solution of bromine to an excess of mercuric oxide suspended in water.[7] Acetyl hypobromite was prepared by mixing an acetic acid solution of bromine and a suspension of silver acetate in acetic acid.[8]

Preparation of Bromobenzenes. An aqueous acetic acid solution containing a catalytic amount of sulfuric acid was added slowly to an aqueous acetic acid solution of benzene and potassium bromate kept below 60°C; the heating was continued at the same temperature until the total reaction time reached 3.5 hr. The organic layer separated was washed with diluted aqueous sodium hydroxide and water, dried on calcium chloride, and then distilled, yielding bromobenzene, bp 156—157°C. The results, including those of the other brominations, are shown in Table 1. The yields were calculated on the basis of the original potassium bromate.

Reaction Products Criterion. Bromobenzene was identified by gas chromatography in comparison with an authentic sample. *p*-Chlorobromo- and *p*-dibromobenzene were identified by mixed melting point determinations; mp and mmp, 67°C and 89°C respectively.

A Typical Procedure for the Rate Measurements. A 50% aqueous acetic acid solution containing known amounts of benzene and potassium bromate was brought to a temperature equilibrium at 50°C. A known amount of the same aqueous acetic acid solution of sulfuric acid was then poured into the solution in order to start the reaction. Aliquots (1 m*l* each) were pipetted out at

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[1] F. Krafft, *Ber.*, **8**, 1044 (1875).

[2] R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **78**, 255, 4549 (1956).

[3] P. B. D. de la Mare and J. T. Harvey, *J. Chem. Soc.*, **1956**, 36; **1957**, 131, 923.

[4] C. A. Kraus and R. A. Vingee, *J. Am. Chem. Soc.*, **56**, 511 (1934).

[5] M. W. C. Smit, *Rec. trav. chim.*, **49**, 674 (1930).

[6] J. R. Slagle and H. J. Shine, *J. Org. Chem.*, **24**, 107 (1959).

[7] M. Christen and Hch. Zollinger, *Helv. Chim. Acta*, **45**, 2057 (1962).

[8] M. Anber and J. Dostrovsky, *J. Chem. Soc.*, **1954**, 1105.

appropriate time intervals and poured into an ice-cooled aqueous solution of 50 m*l* of 0.02 N potassium iodide containing 1 N sulfuric acid. The iodine liberated by active oxygen was quickly titrated with a 0.01 N sodium thiosulfate solution.

Paper Chromatography of Reaction Mixture. A solution of the reaction products was developed with a mixture of diethyl ether and ethyl acetate (2 : 3 in vol) on acetylated Toyo Filter paper No. 54.[9] Two pink spots were observed upon spraying with a methanolic solution of 3% *p*-dimethylaminoaniline dihydrochloride. The values of R_f were found to be 0.64 and 0.83; these values agreed with those for authentic samples of peroxyacetic acid (0.66) and acetyl peroxide (0.82) respectively.

Measurement of the Isotope Effect. The rate constants, k_2 and k_3, were obtained from the plot of $k_{2\,\mathrm{obs}}$ *vs.* the concentration of benzene on the reaction of various concentrations of benzene with 0.025 M potassium bromate in the presence of 3.0 N sulfuric acid in 50% acetic acid at 50°C. These constants, k_2 and k_3, were expressed as $k_{2\mathrm{H}}$ and $k_{3\mathrm{H}}$ for usual benzene, and as $k_{2\mathrm{D}}$ and $k_{3\mathrm{D}}$ for deuterobenzene, respectively.

Results and Discussion

Synthetic Results. The results of the bromination of benzene with potassium bromate in the presence of sulfuric acid are shown in Table 1. The substituent effect seems to suggest that the acid-catalyzed bromination involves an electrophilic attack on the benzene ring. The absence of sulfuric acid resulted in the complete recovery of benzene.

TABLE 1. BROMINATION OF SUBSTITUTED BENZENES IN AQUEOUS ACETIC ACID

Molar ratio, $C_6H_5X : KBrO_3 = 1.0 : 0.1$
Final concn. of sulfuric acid, 3.0 N
Solvent, 250 m*l* of aqueous acetic acid (50% in vol.)
Reaction temp., 60±2°C
Reaction time, 3—3.5 hr

Substituted group of C_6H_5X	Product	Yield, %
H[a]	—	0.0
H	C_6H_5Br	64.1
CH_3	CH_3-C_6H_4-Br[b]	70.1
Br	*p*-Br-C_6H_4-Br	36.0
Cl	*p*-Cl-C_6H_4-Br	28.7
NO_2	—	0.0

a) Without sulfuric acid
b) A mixture of *o*- and *p*-bromotoluenes

Kinetic Data. The bromination rate of benzene was followed by the iodometrical titration of the potassium bromate remaining in a reaction mixture. The initial rate data (up to 40—50% consumption) satisfied the following equation, as shown in Table 2.

TABLE 2. THE RATE DATA FOR THE CONSUMPTION OF ACTIVE OXYGEN IN THE ACID-CATALYZED BROMINATION OF BENZENE WITH POTASSIUM BROMATE IN 50% AQUEOUS ACETIC ACID AT 50°C

Initial concn. of $KBrO_3$, 2.48×10^{-2} M; C_6H_6, 4.00×10^{-2} M Concn. of sulfuric acid, 3.0 N

Time min	$[KBrO_3]$ $a-x$ $\times10^2$ M	$[C_6H_6]$ $b-x$ $\times10^2$ M	$\log\frac{a-x}{b-x}$	$k_{2\,\mathrm{obs}}$ $\times10^3$ M^{-1} sec^{-1}
0	2.477	4.000	−0.2082	
30	2.015	3.538	−0.2445	3.05
50	1.735	3.258	−0.2738	3.31
80	1.427	2.950	−0.3154	3.38
120	1.142	2.665	−0.3680	3.36
150	0.969	2.492	−0.4103	3.40
180	0.854	2.377	−0.4445	3.31
				Av. 3.30

$$v=k_{2\,\mathrm{obs}}[C_6H_6][BrO_3^-] \tag{1}$$

The apparent activation energy and entropy for the reaction in 50% acetic acid were calculated to be 22.3 kcal/mol and −4.01 e.u. respectively from the following average values of $k_{2\,\mathrm{obs}}\times10^3$ $\mathrm{M}^{-1}\mathrm{sec}^{-1}$: 40°C, 0.833; 50°C, 2.85; and 60°C, 7.11, where the initial concentrations of benzene and potassium bromate were both 2.5×10^{-2} M and that of sulfuric acid was 3.0 N.

Under a definite initial concentration of benzene, the apparent second-order rate constant, $k_{2\,\mathrm{obs}}$, slightly decreased with an increase in the initial concentration of potassium bromate, as is indicated in Table 3. Such a decrease in the rate may result from a decrease in the effective acidity in the reaction medium[10] with an increase in the concentration of potassium bromate, as is indicated

TABLE 3. THE CONSTANCY OF THE APPARENT SECOND-ORDER RATE CONSTANT WITH VARIOUS CONCENTRATION OF POTASSIUM BROMATE IN THE REACTION MIXTURE WITH 0.025 M BENZENE AND 3.0 N SULFURIC ACID AT 50°C

$[KBrO_3]$ $\times10^2$ M	$k_{2\,\mathrm{obs}}$ $\times10^3$ M^{-1} sec^{-1}
1.99	2.94
2.50	2.85
3.03	2.82
4.05	2.78
5.02	2.68

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[9] J. Janoušek, *Faserforsch. u. Textiltech.*, **8**, 339 (1957).

[10] To get experimental support for such an explanation, we tried to measure the acidity function (by the indicator method) for a given medium containing potassium bromate. However, this attempt was unsuccessful because of the fading of the indicator.

by the following equation:

$$\ln K_a = \ln K_c - 2A\mu^{1/2} + b\mu$$

Here, K_a and K_c are dissociation constants expressed by, respectively, activity and concentration in an equilibrium, $AH \rightleftarrows H^+ + A^-$; μ is the ionic strength of the medium, and A and b are constants. Hence, it is considered that the $k_{2\,\mathrm{obs}}$ rate constant does not contain the concentration of potassium bromate.

On the other hand, the plot of $k_{2\,\mathrm{obs}}$ against the initial concentration of benzene gave a straight line, with a definite slope which did not pass through the point of origin, as is shown in Fig. 1. Thus the rate equation would be given by:

$$v = \{k_2 + k_3[C_6H_6]\}[C_6H_6][BrO_3^-] \qquad (2)$$

The rate was also affected by the concentration of the acid catalyst. To obtain some information on the effective acidity, the indicator ratio (C_{BH^+}/C_B) at 415 mμ for each medium (without the bromate) were determined spectrophotometrically using *o*-nitroaniline. Since no accurate pK_a value

$$H_0 = pK_a - \log(C_{BH^+}/C_B) \qquad (3)$$

of *o*-nitroaniline in 50% acetic acid is available, we have plotted the values of $\log k_{2\,\mathrm{obs}}$ against those of $-\log(C_{BH^+}/C_B)$ instead of H_0. As is illustrated in Fig. 2, a linear relationship with a slope of -1.81 was obtained. Therefore, both the k_2 and k_3 rate constants should involve the term of a square of proton activity. Thus, two corresponding paths yielding bromobenzene should involve protonation twice before each rate-determining step. On the other hand, the plots of $\log k_{2\,\mathrm{obs}}$ *vs.* J_0[11] gave a straight line with a slope of -1.43. Thus, the attacking species are protonated hypobromous acid and protonated acetyl hypobromite, not the bromine cation.

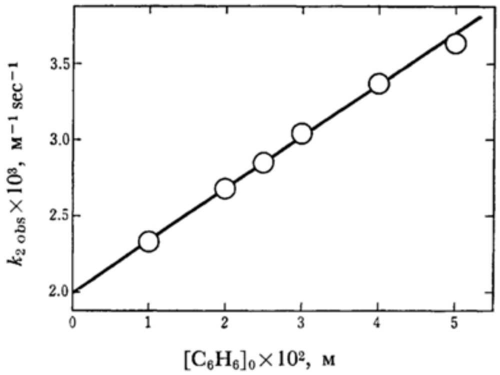

Fig. 1. The plots of $k_{2\,\mathrm{obs}}$ *vs.* initial concentration of benzene in the bromination of benzene with 2.5×10^{-2} M potassium bromate in the presence of 3.0 N sulfuric acid at 50°C.

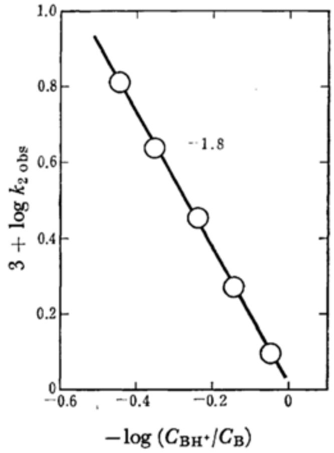

Fig. 2. The plots of $\log k_{2\,\mathrm{obs}}$ *vs.* $-\log(C_{BH^+}/C_B)$ for the acid-catalyzed bromination of benzene with potassium bromate (both, 2.5×10^{-2} M) at 50°C.

The first participation of the proton would be the initial formation of bromic acid from the bromate anion:

$$KBrO_3 \overset{K_4}{\rightleftharpoons} K^+ + BrO_3^- \qquad (4)$$

$$H^+ + BrO_3^- \overset{K_5}{\rightleftharpoons} HBrO_3 \qquad (5)$$

The bromic acid thus formed may decompose to form hypobromous and perbromic acids, and the latter perhaps reacts with acetic acid to afford bromic acid and peroxyacetic acid:

$$3HBrO_3 \overset{K_6}{\rightleftharpoons} HOBr + 2HBrO_4 \qquad (6)$$

$$HBrO_4 + CH_3COOH \overset{K_7}{\rightleftharpoons} CH_3COOOH + HBrO_3 \qquad (7)$$

Acetyl peroxide will be formed by the reaction of peroxyacetic acid with acetic acid in the presence of sulfuric acid.[12] In fact, peroxyacetic acid and acetyl peroxide were detected by the paper chromatographic analysis of a reaction mixture. Unexpectedly, a mixture of the bromate and sulfuric acid in 50% acetic acid did not give any clear spots at the expected positions. This fact could be explained on the assumption that the equilibrium 6 lies too far to the left side. The addition of a substrate being brominated may cause the successive consumption of hypobromous acid, which is formed through Step 6, and the subsequent accumulation of peroxyacetic acid.

Previously, one of the present authors suggested the contribution of acetyl hypobromite as the active attacking species in the bromination of aromatic compounds with a mixture of peroxyacetic acid

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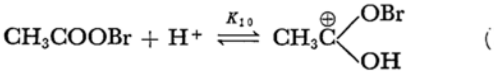
11) These values were calculated from the results of N. C. Deno, J. J. Jaruzelski and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955).

12) Y. Ogata, Y. Furuya, J. Maekawa and K. Okano, *J. Am. Chem. Soc.*, **85**, 961 (1963).

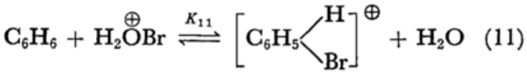
and bromine in acetic acid.[13] A similar attack of acetyl hypobromite, which is thought to be formed from hypobromous and acetic acid, may also be expected in this bromination. Considering the effect of acidity on the rate, an activation of probable attacking species, such as hypobromous acid and acetyl hypobromite, by protonation would be necessary.

$$\mathrm{HOBr} + \mathrm{H^+} \overset{K_8}{\rightleftharpoons} \mathrm{H_2\overset{\oplus}{O}Br} \tag{8}$$

$$\mathrm{CH_3COOH} + \mathrm{HOBr} \overset{K_9}{\rightleftharpoons} \mathrm{CH_3COOBr} + \mathrm{H_2O} \tag{9}$$

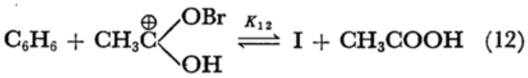


$$\mathrm{CH_3COOBr} + \mathrm{H^+} \overset{K_{10}}{\rightleftharpoons} \mathrm{CH_3\overset{\oplus}{C}}\begin{smallmatrix}\diagup \mathrm{OBr}\\ \diagdown \mathrm{OH}\end{smallmatrix} \tag{10}$$



$$\mathrm{C_6H_6} + \mathrm{H_2\overset{\oplus}{O}Br} \overset{K_{11}}{\rightleftharpoons} \left[\mathrm{C_6H_5}\begin{smallmatrix}\diagup \mathrm{H}\\ \diagdown \mathrm{Br}\end{smallmatrix}\right]^{\oplus} + \mathrm{H_2O} \tag{11}$$

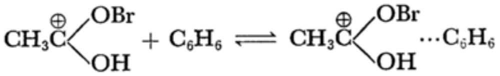
(I)



$$\mathrm{C_6H_6} + \mathrm{CH_3\overset{\oplus}{C}}\begin{smallmatrix}\diagup \mathrm{OBr}\\ \diagdown \mathrm{OH}\end{smallmatrix} \overset{K_{12}}{\rightleftharpoons} \mathrm{I} + \mathrm{CH_3COOH} \tag{12}$$

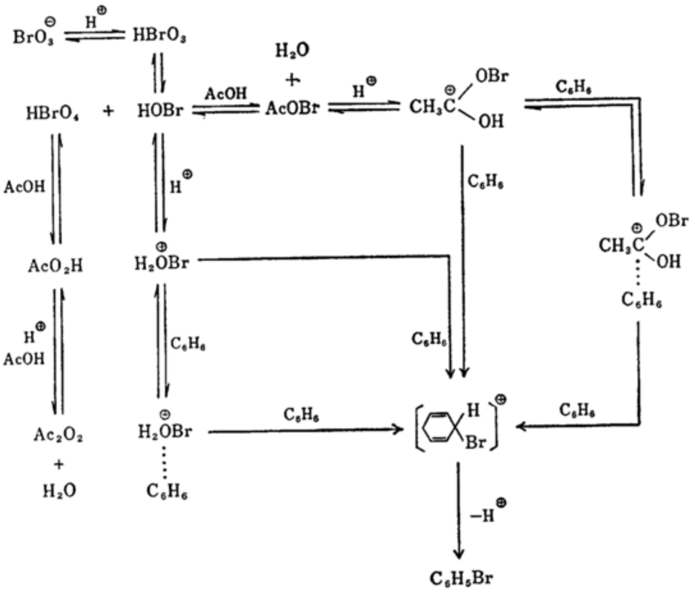
When deuterobenzene was used as the substrate, the isotope effect was not observed for the rate constants, k_2 and k_3. The ratios of $k_{2\mathrm{H}}/k_{2\mathrm{D}}$ and $k_{3\mathrm{H}}/k_{3\mathrm{D}}$ were 1.05 and 1.07 respectively. Hence, the rate-determining step on the reaction is not the step of deprotonation from the σ-complex I, but the forming step of the complex. The reaction expressed by the first term in Rate Equation (2) may consist of Steps 5—12, while the reaction of the second term may involve the rate-determining attacks on benzene by the π-complex of benzene with hypobromous acid and/or acetyl hypobromite, which were formed by the following equilibria:

$$\mathrm{H_2\overset{\oplus}{O}Br} + \mathrm{C_6H_6} \rightleftharpoons \mathrm{H_2\overset{\oplus}{O}Br\cdots C_6H_6} \tag{13}$$



$$\mathrm{CH_3\overset{\oplus}{C}}\begin{smallmatrix}\diagup \mathrm{OBr}\\ \diagdown \mathrm{OH}\end{smallmatrix} + \mathrm{C_6H_6} \rightleftharpoons \mathrm{CH_3\overset{\oplus}{C}}\begin{smallmatrix}\diagup \mathrm{OBr}\\ \diagdown \mathrm{OH}\end{smallmatrix}\cdots\mathrm{C_6H_6} \tag{14}$$

The suggested over-all mechanism can be charted as below:



(Ac=CH₃CH)

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[13] Y. Ogata, Y. Furuya and K. Okano, This Bulletin, **37**, 960 (1964).