

The Bromination of Aromatic Compounds with a Mixture of Peroxyacetic Acid and Bromine in Acetic Acid

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It is well known that the bromination of aromatic compounds with molecular bromine is catalyzed by some electrophilic reagents such as ferric bromide and that, without these catalysts, the bromination of benzene is very slow. In the course of our study of some reactions using peroxycarboxylic acid, we discovered that peroxyacetic acid could accelerate the bromination of benzene. Although the yield of bromobenzene was not high (56%), the probable mechanism and attacking species of this reaction is of interest since the reaction mixture constitutes a homogeneous system suitable for a kinetic study. Thus far there have seemed to be two mechanisms for the bromination of aromatics; i. e., one is the rate-determining abstraction of bromide ions from the π -complex between an aromatic molecule and a bromine molecule, followed by the rapid elimination of the proton to give brominated aromatics;¹⁾ the other is an attack of the bromonium ions formed from bromine and the electrophilic reagent on aromatics.²⁾ The present paper summarizes our data on the mechanism of bromination by a mixture of peroxyacetic acid and bromine in acetic acid. The data suggest a mechanism which involves the intermediary formation of acetyl hypobromite, CH_3COOBr . The mechanism was studied kinetically and, in addition, by the spectrophotometric detection of acetyl hypobromite.

Experimental

Materials.—Peroxyacetic acid was prepared by the reaction of acetic anhydride with hydrogen peroxide³⁾ and was stored as an acetic acid solution. Acetyl peroxide was prepared by dropping water into a suspension of sodium peroxide in an ethereal solution of acetic anhydride;⁴⁾ the ether was evaporated after the addition of acetic acid to prepare an acetic acid solution of acetyl peroxide for

safe storage. Aqueous hypobromous acid was prepared by the addition of aqueous bromine to a suspension of an excess of mercuric oxide in water.⁵⁾ Acetyl hypobromite⁷⁾ was prepared by mixing an acetic acid solution of bromine and a suspension of silver acetate in acetic acid.

The Preparation of Bromobenzene.—An acetic acid solution of peroxyacetic acid was added slowly to a solution containing acetic acid, bromine and benzene. Aqueous sodium hydroxide was added to the resulting solution to remove unreacted bromine; the benzene layer was washed with water, dried and then distilled, yielding bromobenzene (b. p. 156–157°C). The trace of α -benzene hexabromide which was identified in the product is probably formed by the photochemical reaction. The results, including those of the other brominations, are shown in Table I. The yields were calculated on the basis of the original bromine.

Reaction Products Criterion.—Bromobenzene (b. p. 156–157°C) was identified by gas chromatography in comparison with an authentic sample. *p*-Chlorobromobenzene and *p*-dibromobenzene were identified by mixed melting point determinations with authentic samples; m. p. and mixture m. p., 66°C and 84°C, respectively. α -Benzene hexabromide was identified by a mixed m. p. determination (m. p. and mixture m. p. 214°C), together with a comparison of its infrared spectrum with that of an authentic sample prepared by the photochemical bromination of benzene.

A Typical Procedure for the Rate Measurements.—An acetic acid solution containing known amounts of benzene, peroxyacetic acid and sulfuric acid was brought to the constant temperature of 60°C. A known amount of an acetic acid solution of bromine was then added to the solution to start the reaction. Aliquots (each 5 ml.) were pipetted out at regular intervals and poured into ice-cooled aqueous 0.04 M phenol (50 ml.) to remove the bromine. After a few minutes, 5% aqueous potassium iodide (5 ml.) was added. The iodine liberated by peroxyacetic acid was titrated with 0.005 N aqueous sodium thiosulfate.

It was preliminarily confirmed that no appreciable reaction occurred between phenol and peroxyacetic acid under these conditions. The concentration of peroxyacetic acid was corrected by a blank test which estimated the extent of the decomposition of peroxyacetic acid alone (3–4% at 60°C for 100 min.).

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

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

3) M. W. C. Smit, *Rec. trav. chim.*, **49**, 674 (1930).

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

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

Results and Discussion

Synthetic Experiments.—The results on the synthetic bromination of benzene are shown

TABLE I. BROMINATION OF SUBSTITUTED BENZENES

Molar ratio, $C_6H_5X : Br_2 : CH_3CO_2H =$

1.28 : 0.11 : 0.27

Reaction temp., 80~85°C

Reaction time, 2.5~4 hr.

Substituted group of C_6H_5X	Product	Yield, %
H	$\begin{cases} C_6H_5Br \\ \alpha\text{-Benzene hexa-} \\ \text{bromide} \end{cases}$	$\begin{cases} 31.1 \\ \text{a small amount} \end{cases}$
H(H_2SO_4) ^{a)}	C_6H_5Br	56.0
H ^{b)}	C_6H_5Br	18.5
Cl	$p\text{-Cl-C}_6H_4\text{-Br}$	5.0
Br	$p\text{-Br-C}_6H_4\text{-Br}$	7.6
NO_2	—	0.0
CN	—	0.0

Molar ratio are as follows:

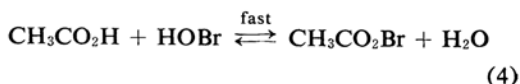
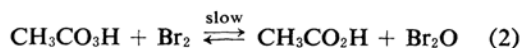
a) $C_6H_6 : Br_2 : CH_3CO_2H : H_2SO_4 : CH_3CO_2H =$
1.0 : 0.1 : 0.14 : 0.135 : 0.5b) $C_6H_6 : Br_2 : CH_3CO_2H : CH_3CO_2H =$
1.0 : 0.1 : 0.14 : 1.0

in Table I. The data show that the addition of a small quantity of sulfuric acid increases the yield of bromobenzene, and that the reaction is an electrophilic substitution. The formation of a small amount of α -benzene hexabromide suggests a radical attack in part; its formation is not due to the presence of diacetyl peroxide,⁶⁾ because no hexabromide was formed upon the addition of acetyl peroxide to the corresponding benzene solution of bromine.

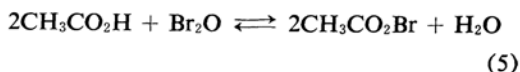
Kinetics.—The rate data are shown in Table II. The table indicates that the rate is expressed as

$$-d[CH_3CO_2H]/dt = k_2 [CH_3CO_2H] [Br_2] \quad (1)$$

where k_2 is independent of the concentration of benzene and also independent of the acidity of the solution. Hence, the rate-determining step is the reaction of bromine and peroxyacetic acid to form reactive species which can react rapidly with benzene. It is known that bromine reacts with some oxidizing agents, e. g., mercuric oxide, to give bromine monoxide Br_2O , which may be formed in this reaction, but it should react rapidly with acetic acid or water to form acetyl hypobromite or hypobromous acid as follows:



or



The rate-determining formation of bromine monoxide, followed by the rapid attack of acetyl hypobromite on benzene, was supported by the determination of the rate of the bromination of benzene with authentic acetyl hypobromite; i. e., the second-order rate constant was $3.20 \times 10^{-2} M^{-1} sec^{-1}$ at 60°C, which was ca. 20 times as high as the rate constant of bromination with a mixture of bromine and peroxyacetic acid.

A Discussion of Active Attacking Species.—

The ultraviolet spectrum of bromine showed a maximum at 266 $m\mu$ both in water (Fig. 1, curve 4) and in anhydrous acetic acid (curve 2), but neither an aqueous hypobromous acid solution (curve 5) nor an acetic acid solution of acetyl hypobromite (curve 3) showed a maximum at a wavelength longer than 250 $m\mu$. The apparent maxima at ca. 243 $m\mu$ (curves 3 and 6 in Fig. 1) were found to be caused by the high absorption and, hence, too wide a slit width, which prevented scanning of the spectrophotometer, because the maxima shifted by changing the thickness of the layer for measurements and the maximum disappeared in a pure ethereal solution of acetyl hypobromite (curve 7). Hence, the maximum at 324 $m\mu$ for acetyl hypobromite reported by by Anber and Dostrovsky⁷⁾ is doubtful.

The molar extinction coefficient at 250 $m\mu$ for acetyl hypobromite is higher than that of hypobromous acid (curves 3 and 6 in Fig. 1); the extinction for acetyl hypobromite is comparatively stable, but that for hypobromous acid is decreased rapidly by the decomposition of the acid.

The addition of peroxyacetic acid to an acetic acid solution of bromine gave rise to an increase in extinction corresponding to that of acetyl hypobromite, the extinction being increased as the reaction proceeded.

The addition of water to an acetic acid solution of acetyl hypobromite results in a decrease in the extinction at 250 $m\mu$ (Figs. 1 and 2) and also in the appearance of a maximum at 266 $m\mu$ (bromine). These phenomena indicate the hydrolysis of acetyl hypobromite

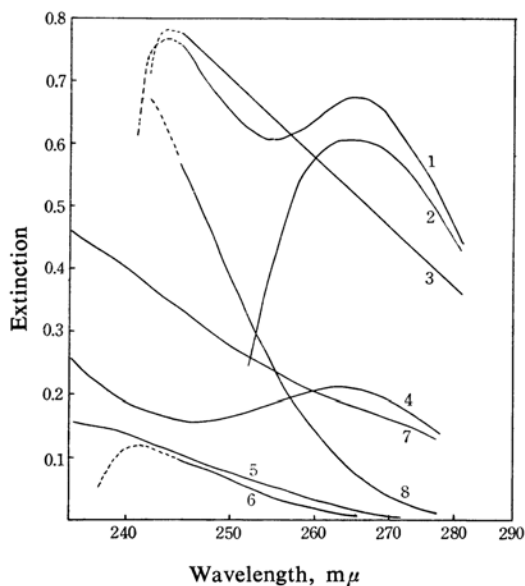
6) Y. Ogata, Y. Furuya, J. Maekawa and K. Okano, *J. Am. Chem. Soc.*, **85**, 961 (1963).

7) M. Anber and J. Dostrovsky, *J. Chem. Soc.*, **1954**, 1105; Cf. P. B. D. de la Mare, I. C. Hilton and C. A. Vernon, *ibid.*, **1960**, 4039.

TABLE II. THE RATE DATA FOR THE CONSUMPTION OF PEROXYACETIC ACID WITH A MIXTURE OF BROMINE AND PEROXYACETIC ACID AT 60°C

Catalyst: Sulfuric acid

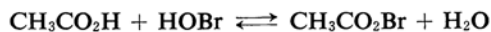
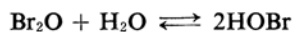
[CH ₃ CO ₃ H] M	[Br ₂] M	[C ₆ H ₆] M	[H ₂ SO ₄] M	H ₀ ^{a)}	k ₂ × 10 ³ M ⁻¹ sec ⁻¹
0.0113	0.0118	0.05	0	—	1.55
0.0241	0.0114	0.05	0	—	1.66
0.0091	0.0056	—	0.036	-1.13	1.60
0.0188	0.0056	0.05	0.036	-1.13	1.64
0.0093	0.0056	0.05	0.036	-1.13	1.66
0.0123	0.0056	0.05	0.063	-1.39	1.64
0.0115	0.0056	0.05	0.117	-1.68	1.44
0.0114	0.0056	—	0.117	-1.68	1.43

a) N. F. Hall and W. F. Spengeman, *J. Am. Chem. Soc.*, **62**, 2487 (1940).Fig. 1. Ultraviolet spectra of probable attacking species in the bromination of aromatic compounds.^{a, b)}

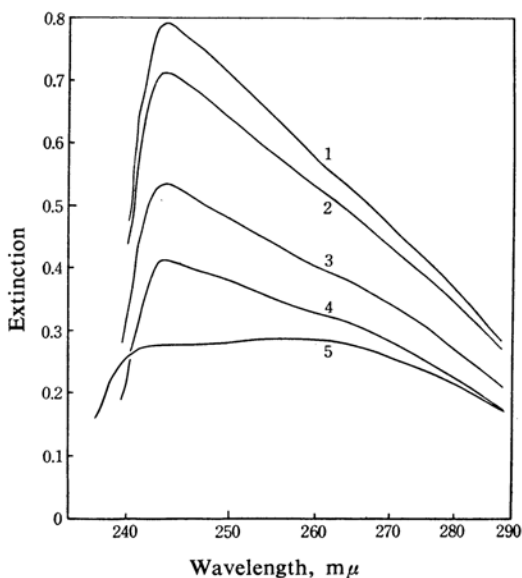
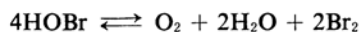
- (1) An acetic acid solution of 5.04×10^{-3} M bromine containing 0.18% water
- (2) An anhydrous acetic acid solution of 2.00×10^{-2} M bromine
- (3) An acetic acid solution of 8.43×10^{-3} M acetyl hypobromite
- (4) An aqueous solution of 4.82×10^{-3} M bromine
- (5) An aqueous solution of 1.36×10^{-3} M hypobromous acid
- (6) An aqueous acetic acid solution of 1.36×10^{-3} M hypobromous acid
- (7) An ethereal solution of 3.6×10^{-4} M acetyl hypobromite
- (8) An aqueous (0.18% water) acetic acid solution of a mixture of 6.23×10^{-2} M bromine and a slight excess of peroxyacetic acid

- a) The thickness of layer: 2 mm. for 1-6, 10 mm. for 7 and 1 mm. for 8
- b) All experiments were done by using corresponding solution as reference.

to hypobromous acid, followed by its rapid decomposition to give bromine. Moreover, the presence of a small percentage of water in an acetic acid solution of bromine gave the extinction corresponding to acetyl hypobromite (compare curves 1 and 2 in Fig. 1). Therefore, the following equilibria are probable:



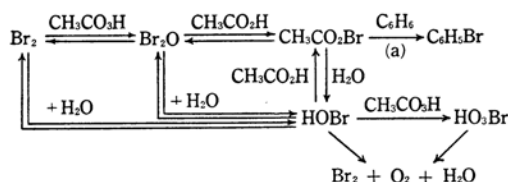
It is well known that bromine monoxide, Br_2O , or hypobromous acid readily decomposes to evolve oxygen and bromine; this must be the main cause of the poor yield of bromobenzene in the present reaction.

Fig. 2. Effect of the water content on the decomposition of 8.43×10^{-3} M acetyl hypobromite in acetic acid at 20°C.

Contents of water (%), (1) 0.18%; (2) 1.18; (3) 5.18; (4) 10.18; (5) 50.18

It was confirmed by gas chromatography (column, molecular sieve, 13X, 80~100 mesh, column temp., 32.5°C; carrier gas, helium 30 ml. min⁻¹) that a mixture of peroxyacetic acid and bromine in acetic acid evolved oxygen. Simultaneously, the mixture liberated bromine which could be titrated with 0.01 N sodium thiosulfate. In this reaction using both reactants in 0.04 M, the titer of peroxyacetic acid decreased to ca. 1/2 after 8 hr. at 50°C, while that of bromine held constant.

Over-all Mechanism. — These findings suggest the following mechanism for the over-all reaction:



A comparison of the electrophilicity of hypobromous acid with that of acetyl hypobromite strongly suggests that acetyl hypobromite, which has the electron-attracting carbonyl group, should be more powerful and a more probable agent for the electrophilic attack on the benzene ring.

The formation of acetyl hypobromite is slower than its reaction with benzene and is little influenced by the acidity of the solution.

However, the addition of sulfuric acid to the reaction mixture appreciably increased the yield of bromobenzene (Table I), which implies that the bromination of benzene (step a) is done by protonated acetyl hypobromite.

Summary

Bromobenzene is obtained in a 56% yield when an acetic acid solution of peroxyacetic acid is slowly added to an acetic acid solution of bromine, benzene and a catalytic amount of sulfuric acid. The rate of the consumption of peroxyacetic acid has been expressed as $v = k_2 [\text{CH}_3\text{CO}_2\text{H}] [\text{Br}_2]$, where k_2 is independent of the concentration of benzene and of the acidity of solution. However, the rate of the formation of bromobenzene is accelerated by sulfuric acid and a more effective use of the attacking species is possible. A mechanism has been suggested which involves the rate-determining formation of bromine monoxide or acetyl hypobromite, followed by its rapid attack on benzene. The rate is slower with benzene substituted with electron-attracting groups. Some evidence for the formation of acetyl hypobromite has been obtained by ultra-violet spectrophotometry.

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