Bromination of Halobenzenes[1]

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The ratios of ortho, meta and para isomers produced in the aluminum bromide-catalyzed bromination of fluorobenzene, chlorobenzene and bromobenzene, and the relative rates of bromination of these halobenzenes with respect to benzene have been determined in carbon disulfide. Photochemical catalysis gives markedly different results from which it is concluded that the aluminum bromide-catalyzed bromination does not take place by a homolytic mechanism. All analyses were made by infrared spectrophotometry.

Introduction

Aromatic nitration has been investigated very exhaustively over the past 75 years and its mechanism is understood quite well.[3] Most of our ideas about aromatic substitution were formed from nitration studies and only by experiment could it be determined to what extent they hold true for halogenation. Recent studies reveal that nitration and halogenation may take place by different mechanisms and this fact has drawn considerable attention in the post-war years.[4,5] Furthermore, it has become increasingly more evident that the nature of the attacking agent in aromatic substitution should be considered.[5] For these reasons, a study of aromatic halogenation was begun in this Laboratory. It was decided to start with the halobenzenes since they form a related series and, for convenience, bromination was chosen as the reaction. Consequently, this report describes a study of the aluminum bromide-catalyzed bromination of fluorobenzene, chlorobenzene and bromobenzene in carbon disulfide using infrared spectrophotometry as the analytical tool.[6]

Experimental

a. **Chemicals.**—Carbon disulfide, benzene, fluorobenzene, chlorobenzene, bromobenzene, p-fluorobromobenzene, p-chlorobromobenzene and p-dibromobenzene were Eimer and Amend highest purity products, redistilled or sublimed to reasonable purity. The following compounds were synthesized by conventional methods from the respective anilines: o-fluorobromobenzene, b.p. 151° (755 mm.); m-fluorobromobenzene, b.p. 150° (755 mm.); o-chlorobromobenzene, b.p. 54–56° (4 mm.); m-chlorobromobenzene, b.p. 56° (5 mm.); o-dibromobenzene, b.p. 70° (5 mm.); m-dibromobenzene, b.p. 66–67° (5 mm.).

b. **Orientation Studies.**—A solvent was used in order to have moderate control over the reaction and CS₂ was chosen as one that does not react appreciably with bromine nor interfere with the spectroscopic analyses. To illustrate

the actual procedure, a typical bromination was carried out as follows: Twenty-nine grams (ca. 0.25 mole) of chlorobenzene, 0.5 g. of aluminum powder and 100 ml. of CS₂ were placed in a one-liter, ground-glass, three-necked flask which was fitted with a mercury-sealed stirrer, a glass plug and a Friedrich condenser. This mixture was stirred continuously with a mechanical stirrer and brought to the desired reaction temperature, 54–57°. Then a solution of 10 g. (ca. 0.05 mole) of bromine in 20 ml. of solvent was added by drops over a 45-minute period down the condenser from a dropping funnel. The evolution of hydrogen bromide was evident about 15 to 20 minutes after the initial addition of bromine. To ensure complete reaction and to expel most of the hydrogen bromide, the reaction mixtures were refluxed with constant stirring for eight hours, refluxed 10 hours more without stirring, cooled, filtered and diluted as necessary for analysis. Tests made for unreacted bromine before the final reflux period were always negative.

The reaction products ranged in color from almost colorless to light amber. Not all of the aluminum was changed into AlBr₃ and it swirled around quite vigorously during the reaction.

c. **Relative Bromination Rates.**—The procedure was to mix two halobenzenes, or a halobenzene and benzene, in equimolar proportions and to brominate them simultaneously with a small amount of bromine. The initial and final amounts of halobenzene and benzene in the reaction vessel were determined spectrophotometrically. The experimental ratios in which the two compounds were found to have undergone bromination were then corrected as suggested by Ingold and Smith[7] for the fact that one compound reacts faster than the other and after the reaction starts the two are no longer present in equimolar amounts. The reactions were set up in the same manner as in the orientation studies except that twofold quantities were used.

d. **Spectrophotometric Analyses.**—The spectrophotometric work was done using a Perkin–Elmer, Model 12c spectrophotometer. A rocksalt optical system was used with slit widths of 0.3–0.5 mm. and fixed cell thicknesses of 0.2 mm. Concentrations were adjusted by dilution so that the per cent. transmissions read would give optical densities between 0.15 and 0.4. All readings were corrected for the small difference in cell thicknesses, which was determined by measuring the transmissions with just solvent in both cells. The general procedure for the spectrophotometric analyses and calculations has been reported previously.[8] Wave lengths used for the various analyses appear in parentheses beside the respective components.

Discussion

The first point of interest is the fractions of isomers produced in the bromination of the halobenzenes. The experimental results are given in Table I. To verify that the values obtained were reaction–product ratios and not equilibrium compositions, owing to isomerization, synthetic mixtures of a halobenzene plus its bromination products were made up and heated in the presence of aluminum bromide in carbon disulfide and then analyzed. It was found that essentially no isomerization occurs under the conditions used in this study.

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(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chap. IV.

(4) P. W. Robertson and P. B. D. de la Mare and co-workers, J. Chem. Soc., 782 (1953); 294, 933 (1949); T. Tsuruta, K. Sasaki and J. Furukawa, THIS JOURNAL, 74, 5995 (1952); Bull. Inst. Chem. Res. Kyoto Univ., 28, 71 (1952); A. E. Bradfield, G. I. Davies and E. Long. J. Chem. Soc., 1389 (1949).

(5) P. B. D. de la Mare, A. D. Ketley and C. A. Vernon, Research, 6, No. 2, 128 (1953).

(6) In order to have a homogeneous reaction, iodine was investigated as a catalyst but only traces of chlorobenzene, if any, were brominated in refluxing CS₂. It was intended to include iodobenzene in this study but its aluminum bromide-catalyzed bromination liberated iodine.

(7) C. K. Ingold and M. S. Smith, J. Chem. Soc., 906 (1938).

(8) L. N. Ferguson and A. J. Levant, Anal. Chem., 23, 1510 (1951).

TABLE I

RELATIVE PER CENT. OF ISOMERS PRODUCED IN BROMINATION OF HALOBENZENES IN CARBON DISULFIDE AT 54–57° IN THE PRESENCE OF ALUMINUM BROMIDE

Ortho, %	Mean, %	Meta, %	Mean, %	Para, %	Mean, %
Fluorobenzene (12.45 μ)					
(9.53 μ)		(12.95 μ)		(12.11 μ)	
10.58		0.24		89.19	
11.00		0.28		88.72	
10.57	10.7	0.00	0.2	89.45	89.1
Chlorobenzene[9,10] (13.55 μ)					
(13.40 μ)		(12.96 μ)		(12.28 μ)	
9.6		0.1		90.3	
10.7		0.4		88.9	
11.1		0		88.9	
11.3	10.7	0	0.1	88.7	89.2
Bromobenzene[9,11] (13.78 μ)					
(13.40 μ)		(12.98 μ)		(12.34 μ)	
13.86		0.14		86.00	
13.80		0		86.20	
13.04		0.32		86.64	
12.97	13.4	0	0.1	87.03	86.5

In order to understand the effects of a substituent upon aromatic substitution in terms of such notions as resonance, polarizability, steric relationships, etc., it is necessary to determine the influence of a substituent upon each nuclear carbon atom of a monosubstituted benzene. It is common to express this influence by partial rate factors, calculated from a combination of orientation and relative rates of reaction data. Therefore, the relative rates of reaction of benzene and the halobenzenes were studied by competing two halobenzenes, or a halobenzene and benzene, as described in the experimental section. Several combinations were run, i.e., C_6H_5F vs. C_6H_6, C_6H_5F vs. C_6H_5Cl, C_6H_5Cl

(9) Compare with the results of A. F. Holleman and T. V. Linden who did not use a solvent. They used a thermal method of analysis and their results were not consistent (Rec. trav. chim., 30, 376 (1911)).

(10) These values for chlorobenzene were determined by A. J. Levant, while working on the Office of Naval Research-financed phase of the project, and by P. T. Talbert in his M.S. thesis research at this University.

(11) C. K. Ingold and F. R. Shaw, J. Chem. Soc., 2918 (1927).

vs. C_6H_5Br, etc., from which it was found in each case that the order of decreasing rate of reaction is $C_6H_6 > C_6H_5F > C_6H_5Cl > C_6H_5Br$.[12] In the partial bromination of two halobenzenes, at least six to eight substances are present whose spectroscopic analysis presents a formidable task in calculations. When synthetic mixtures of approximately the composition resulting in the reactions were prepared and analyzed as if only the two original halobenzenes were present, the experimental analyses agreed satisfactorily with the known values for certain pairs but not with others. For example, $C_6H_5Br:C_6H_5F$ and $C_6H_5Cl:C_6H_6$ could be so analyzed, but $C_6H_5Cl:C_6H_5Br$ and $C_6H_5F:C_6H_5Cl$ could not, owing to interference from the bromination products with the spectroscopic analysis. Under these circumstances, relative rates of bromination were found as follows: $C_6H_5F:C_6H_6 \simeq 0.4$ (av. of 12 determinations in the range, 0.14–0.78); $C_6H_5Cl:C_6H_6 \simeq 0.2$ (av. of 8 values in range, 0.12–0.21); $C_6H_5Br:C_6H_5F \simeq 0.24$ (av. of 8 values in range, 0.10–0.37). These give a semiquantitative ratio of $C_6H_6:C_6H_5F:C_6H_5Cl:C_6H_5Br \simeq 1:0.4:0.2:0.1$.

The third point of interest is the mechanism of the reaction. Recent studies[5] reveal that the attacking agent in halogenation may be cationic or molecular halogen, depending upon the experimental conditions. There is little evidence to decide which is the case here. The catalysis in the present study has the additional complication of being heterogeneous. The suggestion[3] that halogenation may be homolytic in polar solvents was examined. Several ultraviolet light-catalyzed brominations of fluorobenzene and chlorobenzene were conducted in carbon disulfide. In some cases, benzoyl peroxide or iodine was added to facilitate free-radical formation. The results in all experiments were drastically different from the AlBr₃-catalyzed brominations to support the view that the latter do not take place by a homolytic mechanism.

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(12) Note that the order for chlorination in acetic acid is $C_6H_5F > C_6H_6 > C_6H_5I > C_6H_5Cl > C_6H_5Br$ (P. W. Robertson, P. B. D. de la Mare and B. E. Swedlund, J. Chem. Soc., 782 (1953)).