[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Relative Rates of Bromination of Benzene and the Methylbenzenes. Partial Rate Factors for the Bromination Reaction[1-3]

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The relative rates of the uncatalyzed bromination of benzene and toluene at 25° in 85% acetic acid have been established as 1.00/605. The isomer distribution in the bromination of toluene under the same conditions is 32.9% *ortho*, 0.3% *meta* and 66.8% *para*. From these results the partial rate factors for the bromination of toluene can be calculated to be o_f = 600, m_f = 5.5 and p_f = 2420. The results are in good agreement with the relationship, $\log p_f = 1.310 \log p_f/m_f$, previously established for other substitution reactions of toluene. The relative rates of bromination of all of the higher methylbenzenes were determined under related conditions. The relative rates calculated by means of the partial rate factors agree with the experimentally observed values with an average deviation of 27.7%.

In 1948, Condon calculated the relative rates of halogenation of the methylbenzenes and compared these values with the then available experimental rates.[4] The same treatment was later applied to the basicity of the methylbenzenes[5] in hydrogen fluoride–boron trifluoride.[6] The existence of a simple linear relationship between the logarithms of the equilibrium constants for the basicity data and the logarithms of the rate data for the chlorination reaction was pointed out[5] and the existence of this relationship was attributed to the similarity in the factors stabilizing the σ-complexes for the protonated aromatic and the chlorination reaction.[7]

In calculating his partial rate factors, Condon was forced to make several major assumptions. First, he used the relative rate data of de la Mare and Robertson on the uncatalyzed chlorination of toluene and benzene in acetic acid.[8] No data were available for the isomer distribution under these conditions. Therefore he adopted Wertyporoch's value of 42% *p*- and 58% *o*-chlorotoluene for the catalyzed chlorination of toluene,[9] and calculated from these data the partial rate factors: p_f 870, o_f 600. A value of m_f of 5 was assumed. The relative rates of chlorination of the various methylbenzenes were then calculated, using these partial rate factors. Since the available chlorination data on the higher methylbenzenes were few, he compared his calculated rates with the relative rates observed in the bromination of these compounds.

The utility of the Condon treatment has been demonstrated in the mercuration of the methylbenzenes.[10] It appeared desirable to obtain experimental data to provide a similar test of its full applicability in the halogenation reactions. Since the bromination reaction appeared to have advantages in a quantitative rate study, we undertook to establish the isomer distribution in the bromination of toluene and the relative rates in the bromination of benzene and the methylbenzenes.

Results

Ideally, the relative rates of bromination of the various aromatics should be established by a direct kinetic study and comparison of the actual rate constants. However, it has been repeatedly established that aromatic bromination in acetic acid exhibits complicated kinetics. Thus, the reaction kinetics most closely approximate third order (second order in bromine),[11,12] complicated by the presence of a second order term (first order in bromine).[13] It has been reported that the specific rate constants are dependent upon the initial concentrations of the aromatic component.[13,14] Moreover, the reaction order appears to alter as the reaction proceeds.[15] In some cases the reaction is retarded by the presence of hydrogen bromide.[12,14] This inhibition was indicated to be greater than could be accounted for on the basis of the formation of hydrogen tribromide.[14]

In order to avoid these kinetic difficulties, previous studies have based the relative reactivities on the time required to achieve 10 and 20% reaction under a standardized set of reaction conditions.[8,11,16,17] We therefore adopted this technique.

Essentially pure acetic acid was utilized as the solvent for the bromination of the higher methylbenzenes. However, in the case of the lower methylbenzenes, the bromination rates were much slower and a concurrent reaction of bromine with the solvent became significant. The rate of bromination of the aromatic is increased by a factor of approximately 150 in 85% aqueous acetic acid. Moreover, the aqueous acid reacts with bromine only moderately faster than the pure acid. Consequently, the aqueous acid possessed considerable advantage for the study of the less active aromatics and it was therefore adopted for that purpose. Both the present study and that of Illuminati and Marino[17] indicate that the reactivity ratios are not

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(1) Directive Effects in Aromatic Substitution. IX.

(2) Supported by the Petroleum Research Fund of the American Chemical Society.

(3) Based upon a thesis submitted by Leon M. Stock in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(4) F. E. Condon, THIS JOURNAL, **70**, 1963 (1948).

(5) F. E. Condon, *ibid.*, **74**, 2528 (1952).

(6) D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951).

(7) H. C. Brown and J. D. Brady, *ibid.*, **74**, 3570 (1952).

(8) P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 279 (1943).

(9) E. Wertyporoch, *Ann.*, **493**, 153 (1932).

(10) H. C. Brown and C. W. McGary, Jr., THIS JOURNAL, **77**, 2310 (1955).

(11) P. W. Robertson, P. B. D. de la Mare and W. T. G. Johnston, *J. Chem. Soc.*, 276 (1943).

(12) P. W. Robertson, *ibid.*, 1267 (1954).

(13) R. M. Keefer, A. Ottenberg and L. J. Andrews, THIS JOURNAL, **78**, 255 (1956).

(14) R. M. Keefer and L. J. Andrews, *ibid.*, **78**, 3637 (1956).

(15) The explicit cause for this alteration in order is unknown. However, Robertson and co-workers have noted the effect in several instances (ref. 11 and 12). Compare, however, ref. 13 and 14.

(16) P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 1764 (1951).

(17) For a recent application of this procedure, see G. Illuminati and G. Marino, THIS JOURNAL, **78**, 4975 (1956).

significantly altered by such a modification in solvent.

Benzene, the least reactive of the aromatics examined and pentamethylbenzene, the most reactive, differ in reactivity by a factor of approximately 10^9. To cover the entire range required the determination of the reaction times at various concentrations, permitting a direct comparison of a more reactive aromatic with that of a less active under identical reaction conditions.

The experimental results are summarized in Table I.

TABLE I

TIME REQUIRED FOR THE TEN AND TWENTY PER CENT. REACTION IN THE BROMINATION OF THE METHYLBENZENES AT 25°

Compound	Concentration, *M* [ArH]	Concentration, *M* [Br_2]	$t_{10\%}$, min.	$t_{20\%}$, min.
Benzene[a]	0.450	0.0425	77,000	
Toluene[a]	.450	.0425	127	
Toluene[a]	.200	.0200	409	
o-Xylene[a]	.0200	.0100	746	
m-Xylene[a]	.0200	.0100	7.7	
m-Xylene[b]	.0200	.0100	1290	3440
m-Xylene[a]	.00500	.00500	51.2	
p-Xylene[a]	.200	.0200	98	
p-Xylene[a]	.0200	.0100	1572	
Pseudocumene[a]	.00500	.00500	18.4	
Pseudocumene[b]	.0200	.0100	412	
Hemimellitene[b]	.0200	.0100	404	1045
Prehnitene[b]	.0200	.0100	63.4	154
Durene[b]	.0200	.0100	252	586
Mesitylene[b]	.0200	.0100	3.56	9.23
Isodurene[b]	.0200	.0100	1.68	3.97
Pentamethylbenzene[b]	.0200	.0100	0.82	2.16

[a] 85% acetic acid. [b] 100% acetic acid.

The extrapolations utilized, the resulting reactivity ratios, together with the available literature results are summarized in Table II. It is apparent that the agreement with the literature values is satisfactory, within the precision of the method.

Toluene was brominated under identical conditions as those utilized for the determination of the toluene/benzene reactivity ratio. The bromotoluenes were isolated from the reaction mixture, distilled, and analyzed for the isomeric composition by infrared. The results of two duplicate determinations are summarized in Table III.

Discussion

Considerable confidence can be placed in the analysis for the *ortho* and *para* isomers.[18] However, the *meta* isomer involves the determination of a minute amount of product in the presence of large amounts of the other isomers and its analysis, consequently, is on much less certain ground.

Utilizing the toluene/benzene ratio of 605 (Table II) and the yield of 66.8% *p*-bromotoluene, it is possible to calculate the partial rate factor, $p_f = 2420$. We can now employ the relationship previously established for the substitution of toluene[19–21] (1, 2) to calculate the formation of 0.35% of *m*-bromotoluene in this reaction.

TABLE II

RELATIVE BROMINATION RATES

Aromatic	This study: [ArH] 0.45[a] / [Br_2] 0.045	0.20[a] / 0.02	0.02[a] / 0.01	0.005[a] / 0.005	0.02[b] / 0.01	Rel. rates	Lit. values, rel. rates: Ref. 8, 16[c]	Ref. 14[d]	Ref. 17[e]
Benzene	1.00					1.00			
Toluene	605	1.00				605			
p-Xylene		4.17	1.00			2.52×10^3			
o-Xylene			2.11			5.32×10^3			
m-Xylene			204	1.00	1.00[f]	5.14×10^5	4.99×10^5		
Hemimellitene					3.24[f]	1.67×10^6			
Pseudocumene				2.78	3.13	1.52×10^6	1.60×10^6		
Mesitylene					368[f]	1.89×10^8	2.10×10^8		1.78×10^8
Prehnitene					21.3[f]	1.10×10^7			
Isodurene					817[f]	0.42×10^9		0.41×10^9	0.32×10^9
Durene					5.50[f]	2.83×10^6	2.95×10^6		
Pentamethylbenzene					1580[f]	0.81×10^9	0.89×10^9	1.46×10^9	

[a] 85% acetic acid. [b] 100% acetic acid. [c] In 99.9% acetic acid, *o*-xylene assumed to be 5.32×10^3. [d] In 90% acetic acid containing 0.1 *M* sodium acetate, reported k_2 values were utilized; mesitylene assumed to be 1.89×10^8. [e] In 100% acetic acid, durene assumed to be 2.83×10^6. [f] Based on average of $t_{10\%}$ and $t_{20\%}$ values.

TABLE III

ISOMERIC DISTRIBUTION IN THE BROMINATION OF TOLUENE AT 25°

	Bromotoluenes, %: *ortho*	*meta*	*para*
Detmn. A	32.7	0.24	67.0
Detmn. B	33.1	.32	66.6
Average	32.9	.3	66.8

$$\log p_f = 1.310\, S_f \qquad (1)$$

$$\log p_f = 1.310 \log (\%\ para \times 2/\%\ meta) \qquad (2)$$

Finally, Robertson has estimated m_f from the relative rates of bromination of mesitylene and pentamethylbenzene.[12] Utilizing a toluene/benzene ratio of 480, he estimated the formation of 0.3% *meta*. If we utilize the toluene/benzene value of 605 as determined in this study, the calculated quantity of the *meta* isomer becomes 0.24%. In view of the essential agreement in these different

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[18] Under similar experimental conditions the formation of 31% *o*- and 69% *p*-bromotoluene has been reported. An isotopic dilution technique was used for the analysis; P. W. Robertson, P. B. D. de la Mare and B. E. Swedlund, *J. Chem. Soc.*, 782 (1953).

[19] H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 6292 (1953).

[20] H. C. Brown and C. W. McGary, Jr., *ibid.*, **77**, 2300 (1955).

[21] H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956).

approaches, some confidence can be placed in the experimental value of 0.3%.

From the toluene/benzene rate ratio (k_T/k_B = 605) and the isomer distribution (*o*- 32.9, *m*- 0.3, *p*- 66.8), the partial rate factors are calculated to be o_f 600, m_f 5.5, p_f 2420. These factors have been used to calculate the relative rates of bromination of all of the methylbenzenes. The results are summarized in Table IV.

TABLE IV

CALCULATED AND EXPERIMENTAL RELATIVE RATES OF BROMINATION AT 25°

Compound	Calculated	Experimental
Benzene	1.00	1.00
Toluene	605	605
o-Xylene	5.54×10^3	5.32×10^3
m-Xylene	5.44×10^5	5.14×10^5
p-Xylene	2.20×10^3	2.52×10^3
Hemimellitene	2.67×10^6	1.67×10^6
Pseudocumene	1.66×10^6	1.52×10^6
Mesitylene	4.36×10^8	1.89×10^8
Prehnitene	1.46×10^7	1.10×10^7
Isodurene	1.60×10^9	0.42×10^9
Durene	3.63×10^6	2.83×10^6
Pentamethylbenzene	4.39×10^9	0.81×10^9

The average deviation between the calculated and the experimental values is 28%. In view of the vast range of reactivities in this series of compounds (10^9), the agreement between the two sets of values must be considered to be highly satisfactory.

Without minimizing the experimental difficulties in a series of extrapolations of the kind used here, it is our opinion that the deviations are real and not the result of any uncertainties in the experimental data. Thus the differences between the measurements of various workers (Table II) is considerably smaller than the differences between the calculated and experimental values for mesitylene, isodurene and pentamethylbenzene.

Further evidence that the discrepancies are real is provided by a comparison of the relative rates for durene and pentamethylbenzene (3). This leads directly to a numerical value for p_f (4)

$$\frac{k_{\text{Mes}}}{k_{\text{Dur}}} = \frac{p_f m_f^2\, o_f^2}{2m_f^2\, o_f^2} = \frac{0.81 \times 10^9}{2.83 \times 10^6} \qquad (3)$$

$$p_f = 572 \qquad (4)$$

The discrepancy between this value of p_f and the value calculated from the data on benzene and toluene is so large that it cannot be attributed to minor uncertainties in the data.

Steric effects may provide an explanation. The partial rate factor, o_f, calculated on the assumption of no steric factor,[21] leads to a value of 1740, far greater than the experimental value. This suggests that bromination by molecular bromine involves a large steric factor.[22] Mesitylene, isodurene and pentamethylbenzene, which exhibit the largest discrepancies, require substitution between two *o*-methyl groups and should therefore exhibit a magnified steric effect. However, durene which should also exhibit this effect, appears to behave normally (Table IV).

Another possible basis for these deviations lies in the formation of relatively stable π-complexes between the halogen and the higher methyl aromatics.[23] The relative stabilities of the π-complexes do not parallel the stabilities of the σ-complexes.[7,23]

In this discussion of possible causes for the deviations, it should not be forgotten that the agreement between the experimental and the calculated values must be considered excellent and the deviations relatively minor in view of the 10^9 range in relative reactivities.

The relative rate data for the three xylenes permit the formulation of a set of three simultaneous equations in o_f, m_f, p_f. Solution of these equations led to the values: o_f 640, m_f 5.8, p_f 2075. These are in satisfactory agreement with the partial rate factors based on the isomer distribution.[24]

The success of this approach led us to apply it to the calculation of the partial rate factors for the uncatalyzed chlorination reaction utilizing the available relative rate data for the chlorination of benzene, toluene, *o*- and *p*-xylene[8] (5–7).

$$\frac{2o_f + 2m_f + p_f}{6} = \frac{k_T}{k_B} = 350 \qquad (5)$$

$$\frac{2o_f m_f + 2m_f p_f}{6} = \frac{k_{o-xy}}{k_B} = 4600 \qquad (6)$$

$$\frac{4o_f m_f}{6} = \frac{k_{p-xy}}{k_B} = 2200 \qquad (7)$$

Solution of this set of simultaneous equations leads to the values o_f 402, m_f 8.2 and p_f 1280. These values disagree seriously with those estimated by Condon.[4] Consequently, we are undertaking an experimental determination of the partial rate factors for the chlorination reaction. In spite of the present uncertainty in the precise values for the chlorination partial rate factors, there is little doubt that these must differ considerably from the bromination factors. Consequently, the common practice of treating both bromination and chlorination with a common set of partial rate factors should be avoided.

The various partial rate factors are summarized in Table V to facilitate ready reference and comparison. The extent of the agreement with the Selectivity Relationship is indicated in Fig. 1.

It was predicted previously that in an electrophilic substitution, such as the bromination reaction, the use of catalysts of increasing electrophilic characteristics should lead to a decrease in the toluene/benzene rate ratio and in the *para/meta* product ratio.[20] In the present study, the toluene/benzene relative rate has been determined to be 605 for the uncatalyzed bromination reaction at 25°. A value of 465 has been reported previously for the iodine-catalyzed reaction,[25] whereas a value

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[22] A. F. Holleman [*Chem. Revs.*, **1**, 218 (1924)] noted that there is a decrease in the *ortho* isomer from 45% to 12% in the chlorination and bromination of chlorobenzene.

[23] L. J. Andrews and R. M. Keefer, THIS JOURNAL, **74**, 4500 (1952); R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 4677 (1950).

[24] Partial rate factors can also be calculated from sets of simultaneous equations set up for the tri- and tetramethylbenzenes. However, the results do not agree with each other or with the consistent results obtained from the isomer distribution, the three xylenes, or from the selectivity factor, S_f[21] (m_f and p_f). Presumably, the difficulty in the case of the tri- and tetramethylbenzenes arises from the double steric factor, or from complications caused by the formation of relatively stable π-complexes, as previously discussed.

[25] E. Berliner and F. J. Bondhus, THIS JOURNAL, **70**, 854 (1948).

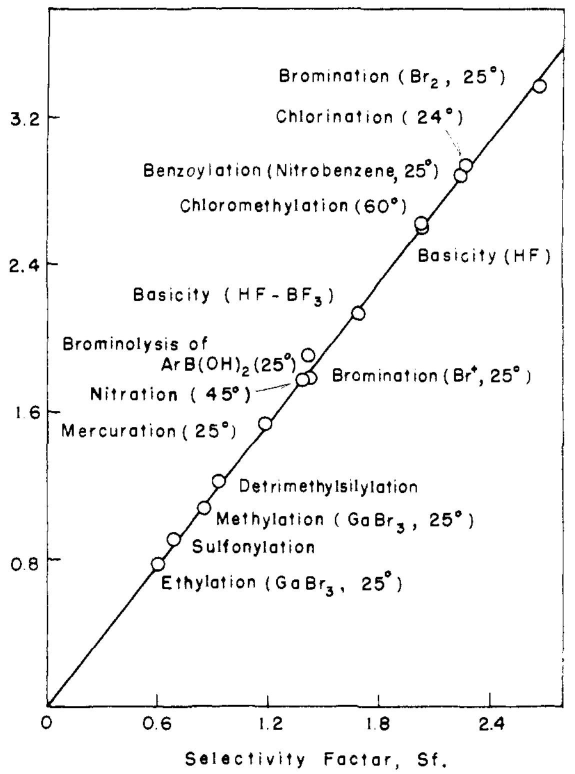

Fig. 1.—Substitution reactions of toluene in the selectivity relationship.

of 150 has been noted in the zinc chloride-catalyzed bromination.[26] These changes are clearly in accord with the increasing electrophilic character of iodine and zinc chloride as catalysts.

TABLE V

SUMMARY OF PARTIAL RATE FACTORS FOR AROMATIC HALOGENATION

Reaction	Partial rate factors o_f	m_f	p_f	Selectivity factor, S_f
Chlorination (Cl_2)	600^a	5.0^a	870^a	2.240
	402^b	8.2^b	1280^b	
	532^c	4.96^c	870^c	
Bromination (Br_2)	600^d	5.5^d	2420^d	2.648
	640^e	5.8^e	2075^e	
	1740^f	6.6^f	2940^f	

[a] Condon's values (ref. 4). [b] Calculated from relative rates of chlorination (ref. 8). [c] Assuming p_f = 870 and then applying the relationships: $\log p_f = 1.310S_f$, $\log m_f = 0.309S_f$, $\log o_f = 1.215S_f$, ref. 21. [d] From toluene/benzene rates and isomer distribution in toluene. [e] From relative rates of bromination of xylenes. [f] From Selectivity Relationships (ref. 21) assuming no steric factor.

Experimental Part

Materials.—With two exceptions all aromatic hydrocarbons were samples available from previous work with purities exceeding 99.5 mole %. Prehnitene, prepared by a Jacobsen rearrangement, was carefully fractionated (b.p. 202.5–203° (742 mm.), $n^{20}D$ 1.5190), and pentamethylbenzene was recrystallized from purified benzene to a constant m.p. of 53.0–53.6°.[27]

The bromotoluenes utilized as infrared standards were all carefully purified by rectification (and the *meta* isomer by fractional crystallization). All purities were determined by analysis of the cooling curves.[28] The following properties and purities (in mole %) were noted: *o*-bromotoluene, b.p. 180.5° (750 mm.), $n^{20}D$ 1.5562, 99.53%; *m*-bromotoluene, b.p. 183° (754 mm.), $n^{20}D$ 1.5527, 99.80%; *p*-bromotoluene, m.p. 26.74°, 99.81%.

Carbon disulfide was distilled from mercuric chloride and dried over calcium hydride. Bromine (J. T. Baker purified grade) was purified by extraction with aqueous sodium hydroxide, followed by distillation over phosphorus pentoxide.[29] After experiment revealed that identical results were realized with unpurified bromine, the halogen was used directly in the later experiments.

Acetic acid was distilled, followed by a vacuum sublimation. This procedure yielded acid of f.p. 16.585°, indicating a purity of 99.89 mole %. An analysis of the water content by Karl Fischer reagent following its use for the rate measurements indicated the presence of 0.15 mole % water. Acetic acid for the 85% solvent was first distilled from chromium trioxide, fractionally crystallized at 0°, followed by fractional crystallization under vacuum at 0°.[30]

Kinetic Measurements. A. In 85% Acetic Acid.—In applying the procedure of Berliner and Berliner,[31] our results exhibited considerable scatter. The error appeared to arise from volatilization of bromine during sampling. The use of sealed ampules avoided this difficulty and gave highly consistent results.

To 5.00 ml. of a standard solution of the aromatic in acetic acid, cooled to −78° in the ampule, was added 5.00 ml. of a standard solution of bromine in the same solvent.[32] The ampules were sealed, warmed to room temperature with constant agitation in a constant temperature bath (25.0 ± 0.05°) in the dark, and allowed to react. At appropriate intervals of time, the ampules were broken under 5% potassium iodide solution and the bromine analysis carried out iodimetrically.

The percentage reaction was plotted against time and the 10% (and 20%) intercept noted. All experiments were carried out in duplicate or triplicate and accompanied by blank samples (containing no aromatic). Since the concentrations unavoidably deviated slightly in experiment to experiment from the desired value, the observed $t_{10\%}$ and $t_{20\%}$ values were corrected to the desired concentration by applying the integrated third-order rate expression. The correction applied in this manner is small. The corrected times are reported in Table I.

B. In 100% Acetic Acid.—Because of the speed of reaction of certain of the higher methylated derivatives, it was necessary to avoid the change in temperature involved in the ampule technique. Accordingly, standard solutions of bromine and aromatic were brought to temperature, mixed in a narrow-necked flask (just wide enough to accommodate the pipet), and samples removed with a fast-delivery pipet. The aliquots were run into 5% potassium iodide and the analysis and data were handled as before.

Bromination of the Solvent.—The extended time required for the bromination of benzene (77,000 min.) resulted in appreciable reaction of the bromine with the solvent. The rate of bromination of acetic acid varies with the water content of the acid.[33] We observed rates at 70° of 2.38×10^{-6} sec.$^{-1}$ for 99.96 mole % acetic and 5.02×10^{-6} for 85% acid. Essentially identical rates were observed at 70° for 85% acetic acid prepared from Baker and Adamson Reagent Grade material (k_1 5.12×10^{-6} sec.$^{-1}$) and from carefully purified acid (k_1 5.02×10^{-6} sec.$^{-1}$). This eliminates the possibility that the loss of bromine arises from the presence of impurities in the solvent. In the case of benzene the reaction of bromine

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(26) L. J. Andrews and R. M. Keefer, THIS JOURNAL, **78**, 4549 (1956).

(27) We are indebted to Dr. B. A. Bolto of this Laboratory for the sample of prehnitene and to Professor L. I. Smith of the University of Minnesota for the sample of pentamethylbenzene.

(28) The procedure was developed by K. L. Nelson.

(29) A. Scott, *J. Chem. Soc.*, **103**, 847 (1913).

(30) We are indebted to Mr. M. Dubeck of this Laboratory who developed these convenient techniques for the purification of the solvent.

(31) E. Berliner and F. Berliner, THIS JOURNAL, **71**, 1195 (1949).

(32) The bromine was pipetted from an all-glass system utilizing nitrogen pressure to fill the pipet. By passing the nitrogen first through an acetic acid solution of bromine, at a concentration approximately 3.5 that of the standard bromine solution, a number of aliquots could be withdrawn without measurable change in the halogen concentration.

(33) K. Ichikawa, *J. Chem. Soc.* (*Japan*), **73**, 415 (1952).

with solvent proceeded at approximately one-fifth the rate of the reaction with the aromatic. The data were corrected for this side-reaction. In all other cases the solvent reaction was negligible.

Isomer Distribution in the Bromination of Toluene.—A. To one liter of 85% acetic acid containing 82.9 g. (0.90 mole) of toluene was added 14.9 g. (0.093 mole) of bromine in one liter of the same solvent. The reaction was allowed to proceed in the dark for 13 hr. at 25.0 ± 0.5°. Analysis indicated that the reaction had proceeded to 39% completion, equivalent to 6.2 g. of bromotoluenes. The reaction mixture was quenched by adding aqueous sodium borohydride, and the organic materials were extracted with carbon disulfide. The extracts were subsequently combined and dried over calcium sulfate and calcium hydride. The carbon disulfide was removed by careful fractionation and triglyme (triethylene glycol dimethyl ether) was added as a chaser. The fraction (b.p. 130–205° (753 mm.)) was taken up in carbon disulfide, washed with water to remove triglyme, dried over calcium hydride, and the resulting solution used for infrared analysis.

B. A duplicate preparation was carried out to 42% completion and the distillation was carried out to include a small quantity of toluene (b.p. 112–212° (746 mm.)).

C. A synthetic mixture was prepared by dissolving 80.0 g. (0.88 mole) of toluene, 5.02 g. (29.3 mmoles) of *p*-, 2.21 g. (12.9 mmoles) of *o*-, and 0.080 g. (0.47 mmole) of *m*-bromotoluene in 2 l. of acetic acid. To this solution were added in rapid succession 14.0 g. (87.5 mmole) of bromine and 300 ml. of 1% aqueous sodium borohydride. The product was isolated as above.

The solutions were analyzed for the three isomeric bromotoluenes by utilizing the characteristic frequencies of 13.5 μ for *o*-, 13.1 μ for *m*-, and 12.5 μ for *p*-. Preliminary experiments with synthetic mixtures indicated that in order to determine the three components in the range of their expected concentrations, the analysis would have to be made in two parts, by different procedures. The analysis for *o*- and *p*- would utilize relatively dilute solutions (0.2 *M*) while the *m*-bromotoluene would be determined in a more concentrated solution (2 *M*).

Weighed samples of the carbon disulfide solutions (A, B and C above) were diluted with carbon disulfide to give solutions approximately 0.2 *M* in bromotoluenes. No absorption was noted at 13.1 μ for *m*- in solutions A and B, and only slight absorption in C (synthetic composition, 30.3% *o*-, 1.1% *m*-, 68.6% *p*-). The spectra were analyzed by the base line technique:

A. Found: 32.8% *o*-, 67.2% *p*-, 67.2% recovery.
B. Found: 33.2% *o*-, 66.8% *p*-, 75.5% recovery.
C. Found: 31.6% *o*-, 0.4% *m*-, 68.0% *p*-, 80.3% recov.

To determine the *meta* content of solutions A and B, the products were diluted with carbon disulfide to give solutions 2.0 *M* in bromotoluene. A series of standard solutions were prepared, 2 *M* in total bromotoluene with the *p*- to *o*-ratio maintained at 2.1. In these solutions, the *meta* isomer concentration was varied systematically from 0.005 to 0.017 *M*. These solutions gave a sharp absorption at 13.1 μ, in spite of the strong absorption of the high concentrations of the *o*- and *p*-isomers at 13.5 and 12.5 μ. Direct comparison of the spectra from solutions A and B with the spectra from these standard solutions indicated a *meta* content of 0.24% for A and 0.32% for B. These values were normalized with the *o*- and *p*-values and the results are listed in Table III. From the results with numerous test analyses, we believe that the *o*- and *p*-values are accurate to better than ±1.5% of the reported figures and the *m*-value to within ±0.1%.

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[CONTRIBUTION FROM THE MARION EDWARDS PARK LABORATORY OF BRYN MAWR COLLEGE]

Kinetics of Aromatic Halogenation. IV. The Bromination of Naphthalene in 50% Aqueous Acetic Acid[1]

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The bromination of naphthalene by bromine has been studied in 50% by volume aqueous acetic acid in an excess of bromide ion. Unlike in glacial acetic acid, the reaction under these conditions is second-order over-all, first-order in each reactant. The results of the kinetic study are in agreement with a mechanism involving a reaction between free molecular bromine and naphthalene. A very small amount of bromination by the tribromide ion is not excluded.

Aromatic bromination in glacial acetic acid is characterized by two features which complicate its kinetics. According to the extensive work of Robertson and his students,[2] bromination is usually of second and sometimes of third order with regard to bromine, so that the over-all reaction may be third or fourth order. In addition, since bromide ion is formed during the reaction, some of the bromine is continuously removed from the reaction as tribromide ion or HBr_3, which have either no, or only very weak, brominating properties. High-order bromination has also been observed in other solvents of low dielectric constant, such as 75% and 90% aqueous acetic acid,[3,4] carbon tetrachloride,[5] chlorobenzene,[4] methanol[2b] or benzene.[6] Following Robertson,[7] it is customary to regard bromination as a composite reaction of the type

$$-dx/dt = k_1(\mathrm{ArH})(\mathrm{Br_2}) + k_2(\mathrm{ArH})(\mathrm{Br_2})^2 + k_3(\mathrm{ArH})(\mathrm{Br_2})^3 \quad (1)$$

where the exact form of the rate equation and the relative importance of each term depend on various circumstances, such as the medium and the nature and concentration of the reactants.[2]

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