the moment preferred as the substituting entity.

A hydrogen ion catalyzed reaction between amine and hypoiodous acid, *i.e.* $-\mathrm{d}x/\mathrm{d}t = k(\text{amine})\cdot(\text{HOI})(\text{H}^+)$, is another possibility which is kinetically identical with, but mechanistically slightly different from, the above. The proton could be visualized as attaching itself to the oxygen atom of hypoiodous acid at the moment of substitution and as weakening, through hydrogen bonding, the oxygen–iodine bond. This picture would not require the actual formation of H_2OI^+ prior to substitution.

The quoted activation energy is composite of the ΔH's for all the pre-equilibria, and is therefore not a true measure of the activation energy for the substitution process. The relatively high negative entropy of activation, which is also a composite value, can be ascribed to the formation of ions (in (3) or (5)) from neutral molecules,[27] and is thus confirmatory evidence for the proposed mechanism. Reactions between neutral molecules and ions should show no salt effect at concentrations at which the limiting law applies. The almost linear relation between k_{obs} and μ is a primary salt effect characteristic of reactions between neutral molecules and ions at very high salt concentration.[28]

Acknowledgment.—The generous help afforded by a Frederick Gardner Cottrell Grant of the Research Corporation is gratefully acknowledged.

[27] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 122 ff.

[28] R. P. Bell, "Acid Base Catalysis," Oxford University Press Oxford, 1941, pp. 32–34.

BRYN MAWR, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT DAVIS]

The Bromination of Polymethylbenzenes in Aqueous Acetic Acid

BY R. M. KEEFER AND L. J. ANDREWS

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The bromination rates of mesitylene, isodurene and pentamethylbenzene in 90 volume % aqueous acetic acid have been measured. The reactions are first order in aromatic hydrocarbon concentration and show mixed first- and second-order dependence on free bromine concentration. Tribromide ion, which accumulates in the media during the course of the reactions, is ineffective as a brominating agent. The rate of the mesitylene reaction is much greater in the aqueous medium than in pure acetic acid. That this difference does not result entirely from the change in dielectric constant of the solvent is suggested by the results of studies of the rate of bromination of mesitylene in chlorobenzene and in acetic-*d* acid.

The effects of perchloric acid on the rate of mesitylene bromination in acetic acid and of light and heavy water on the reaction in carbon tetrachloride also have been investigated.

A series of investigations is in progress in this Laboratory to determine how variations in solvent polarity alter the mechanism of electrophilic aromatic bromination. Previous reports have described kinetic studies of the reaction of bromine and mesitylene in carbon tetrachloride[1] and in pure acetic acid.[2]

In the current investigation similar kinetic studies have been made of the reactions of several polymethylbenzenes, including mesitylene, in aqueous acetic acid (90 volume % acetic acid). The role of the hydroxylic solvent has been examined further by observing the changes in mesitylene bromination rate which occur when acetic-*d* acid or mixtures of acetic-*d* acid and heavy water are substituted for media of normal isotope content. The rates of bromination of mesitylene in chlorobenzene and in acetic acid solutions of perchloric acid also have been investigated, and the relative catalytic effects of light and heavy water in the reaction of bromine with mesitylene in carbon tetrachloride have been measured.

Experimental

Solvents.—Reagent grade acetic acid was further purified and dried by refluxing with chromic anhydride and acetic anhydride.[3] A large batch of 90% acetic acid, for use in rate runs, was prepared by mixing nine volumes of the purified acid with one volume of water.

Sulfur-free carbon tetrachloride (Eastman Organic Chemicals) was dried for several days over freshly ignited Drierite and used without distillation. Chlorobenzene (Eastman Organic Chemicals) was distilled, b.p. 131.1–132.0°, and dried for two days over Drierite.

Deuterium oxide (99.59 ± 0.1%) was obtained from the Stuart Oxygen Co. on allocation from the Atomic Energy Commission. For use in comparative rate runs on protium- and deuterium-containing solvents, samples of acetic acid and of acetic-*d* acid were prepared from acetic anhydride[4] by identical procedures. To 107.5 g. (1.051 moles) portions of distilled (b.p. 137–139°) reagent grade acetic anhydride were added 1.02 moles of deuterium oxide (20.43 g.) or water (18.43 g.). The mixtures were refluxed one hour and were distilled through a short Vigreux column. The first 4 ml. of each distillate was collected separately, and the next 100 ml. of distillate was retained for rate work.

Salts and Perchloric Acid.—Reagent grade sodium bromide and sodium acetate trihydrate were dried at 140° overnight.

A solution of perchloric acid in acetic acid was prepared by passing hydrogen chloride gas into a solution of 5.15 g. of silver perchlorate (prepared by drying the monohydrate, G. Frederick Smith Chemical Co., for four days at 120°) until silver chloride precipitation was complete. The solution was then flushed with nitrogen until it gave only faint turbidity on testing with aqueous silver perchlorate. The hydrogen chloride was generated by dropping concentrated sulfuric acid into concentrated hydrochloric acid. The gases were passed through scrubbing chambers of concentrated sulfuric acid and acetic acid before they were passed into the perchlorate solution. The solution thus prepared was 0.488 *M* in perchloric acid, as was established

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[1] (a) R. M. Keefer, J. H. Blake and L. J. Andrews, THIS JOURNAL, **76**, 3062 (1954); (b) J. H. Blake and R. M. Keefer, *ibid.*, **77**, 3707 (1955).

[2] R. M. Keefer, A. Ottenberg and L. J. Andrews, *ibid.*, **78**, 255 (1956).

[3] K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.*, **983** (1927).

[4] J. D. Roberts, C. M. Regan and I. Allen, THIS JOURNAL, **74**, 3683 (1952).

by titration with standard potassium acid phosphate solution using methyl violet as the indicator.

The Aromatic Hydrocarbons.—Samples of materials purified for use in an earlier investigation[5] were used.

The Rate Measurements.—The procedures described previously[2] for studying the rates of aromatic brominations in acetic acid were used, with no substantial revision, to follow the reactions in aqueous acetic acid. The disappearance of bromine from the solutions was followed by making optical density measurements at 448 or 450 mμ (using 2 cm. absorption cells and acetic acid as a blank). At these wave lengths the molecular extinction coefficients of bromine in 90% acetic acid (121 at 448 mμ and 118 at 450 mμ) are insensitive to the bromide ion concentration of the medium.

The rate of mesitylene bromination in chlorobenzene was followed spectrophotometrically using 1-cm. absorption cells and a chlorobenzene blank. In all runs mesitylene was present in large excess. Rate constants for the reactions, which were second order in bromine, were calculated using the slopes of plots of the reciprocals of the total halogen concentrations of the solutions *versus* time. The extinction coefficients of halogen, required for these calculations, were determined from the known halogen concentrations and the optical densities (found by extrapolation) of the freshly prepared solutions.

For the runs in carbon tetrachloride, four solutions of 5γ (added by micropipet) of water in 50 ml. of carbon tetrachloride were prepared. Two of these contained light water and the other two contained heavy water. To 8 ml. of each of these were added 1 ml. of mesitylene and 1 ml. of 8.78×10^{-2} *M* bromine in carbon tetrachloride. All measurements were made by pipet. The disappearance of bromine from these solutions was followed spectrophotometrically at 520 mμ by procedures described previously.[1]

The Products of Bromination of Mesitylene and of Pentamethylbenzene in 90% Acetic Acid.—These products were isolated from reaction mixtures in which the initial concentrations of reactants were similar to those used in the rate runs.

A solution of 2.0 g. (0.0135 mole) of pentamethylbenzene in 1 l. of 90 volume % acetic acid was treated with 13.6 g. of sodium acetate trihydrate (0.1 mole) and 2.16 g. (0.0135 mole) of bromine. The solution, after decolorization, was concentrated to half its original volume under reduced pressure and was then treated with 500 ml. of water. The fluffy white precipitate which formed, after washing with water and drying, weighed 2.44 g. (77% yield). The m.p. 159–161°, agreed with that reported for 6-bromo-1,2,3,4,5-pentamethylbenzene.[6]

The reaction of 5.0 g. (0.042 mole) of mesitylene and 6.72 g. (0.042 mole) of bromine in 1 l. of 0.1 *M* sodium acetate in 90% acetic acid was carried out in similar fashion. The decolorized solution was concentrated to about 250 ml. and was treated with 1 l. of water. The oil which separated was extracted with two 50-ml. portions of carbon disulfide. The extract was washed with dilute alkali and dried over calcium chloride. From the extract 3.30 g. (40% yield) of 2-bromomesitylene, b.p. 87–88° (5 mm.), was isolated. Substantial losses in yield were sustained in the concentration of the aqueous solution of the product.

Neither of the two bromination products gave precipitates on boiling in alcoholic silver nitrate solution. In other words, they contained no side-chain brominated material.

The Equilibrium Constant for Tribromide Ion Formation in 90% Acetic Acid.—A series of solutions of varying concentrations of sodium bromide (0.005–0.05 *M*) and of bromine (1.8–3.5×10^{-4} *M*) in 90% acetic acid were prepared. These solutions all contained sufficient sodium acetate to provide a total salt concentration of 0.10 *M*. These solutions were measured on the spectrophotometer at 25.4 ± 0.2° in 2-cm. absorption cells against an acetic acid blank. Optical densities were recorded at several wave lengths between 340 and 370 mμ, a region in which the absorption of tribromide ion is intense and that of free bromine is weak. The data at each wave length were analyzed graphically[7] according to equation 1. In this equation $\epsilon_{\mathrm{Br_{2T}}}$ represents the experimentally measured

$$\frac{1}{(\epsilon_{\mathrm{Br_{2T}}} - \epsilon_{\mathrm{Br_2}})} = \frac{1}{(\mathrm{Br}^-)}\,\frac{1}{K(\epsilon_{\mathrm{Br_3}^-} - \epsilon_{\mathrm{Br_2}})} + \frac{1}{(\epsilon_{\mathrm{Br_3}^-} - \epsilon_{\mathrm{Br_2}})} \qquad (1)$$

apparent extinction coefficient of bromine (both free and complexed). The terms $\epsilon_{\mathrm{Br_2}}$ (measured independently) and $\epsilon_{\mathrm{Br_3}^-}$ are the extinction coefficients of free bromine and tribromide ion; and K is the equilibrium constant for tribromide ion formation (equation 2).

$$K = (\mathrm{Br_3}^-)/(\mathrm{Br}^-)(\mathrm{Br_2}) \qquad (2)$$

The K and $\epsilon_{\mathrm{Br_3}^-}$ values at each wave length, as determined from the linear plots of $1/(\epsilon_{\mathrm{Br_{2T}}} - \epsilon_{\mathrm{Br_2}})$ against $1/(\mathrm{Br}^-)$, are

mμ	K	$\epsilon_{\mathrm{Br_3}^-}$
340	149	2200
345	145	1740
350	146	1360
360	150	940

These values for K appear reasonable in the light of reported[8,9] equilibrium constants for tribromide ion formation in acetic acid solutions of somewhat higher water concentration.

Results

The Rates in 90% Acetic Acid.—As was observed for the reaction in pure acetic acid, the initial rate of bromination of mesitylene in 90% acetic acid increased as the initial bromine concentration was increased. Accordingly the kinetic data for the reaction of mesitylene in aqueous acetic acid were tested for correspondence to the same rate law (equation 3) which applied to the reaction in the non-aqueous solution.[2] The term $(\mathrm{Br_2})_{\mathrm{T}}$ includes, in addition to free halogen, any bromine which is

$$R = -\mathrm{d}(\mathrm{Br_2})_{\mathrm{T}}/\mathrm{d}t = k_1(\mathrm{ArH})(\mathrm{Br_2}) + k_2(\mathrm{ArH})(\mathrm{Br_2})^2 \qquad (3)$$

bound in the form of a molecular complex with the hydrocarbon or is associated with bromide ion or hydrogen bromide. In the present series of experiments the concentration of aromatic hydrocarbon was kept sufficiently low so that the concentration of molecular complex should have been very small.

Although the reactivity of bromine in the runs in pure acetic acid apparently was not diminished through the formation of $\mathrm{HBr_3}$ or $\mathrm{Br_3}^-$ during the course of the reaction,[2] values of $R/(\mathrm{ArH})(\mathrm{Br_2})_{\mathrm{T}}$ calculated for the runs in 90% acetic acid at any fixed value of $(\mathrm{Br_2})_{\mathrm{T}}$ dropped with increasing hydrogen bromide content of the medium. This drop can be explained on the assumption that only free bromine but not tribromide ion in the medium is effective as a bromination agent. Values of $R/(\mathrm{ArH})(\mathrm{Br_2})$ at any fixed free bromine concentration, within the limits of error, have been found to be independent of the bromide ion concentration of the medium. The preceding discussion is summarized in Fig. 1, which presents data for two rate runs at different initial bromine concentrations.

The equilibrium constant K for tribromide ion formation in solutions of sodium bromide and

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(5) N. Ogimachi, L. J. Andrews and R. M. Keefer, This Journal, **77**, 4202 (1955).

(6) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds, Order I," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 502.

(7) J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit and W. Dzcubas, *Rec. trav. chim.*, **71**, 1104 (1952).

(8) W. J. Jones, *J. Chem. Soc.*, **99**, 392 (1911).

(9) (a) A. E. Bradfield, G. I. Davies and E. Long, *ibid.*, **1389** (1949); (b) E. Grovenstein, Jr., and U. V. Henderson, Jr., This Journal, **78**, 569 (1956).

bromine in acetic acid (with sodium acetate added to adjust the total salt concentration to 0.1—see Experimental section) has been used in estimating the free bromine concentrations of the dilute hydrogen bromide solutions. In making these estimates equation 4 (in which $(Br_T^-) = (Br_3^-) + (Br^-)$

$$(Br^-) = (Br^-)_T/(1 + [K(Br_2)_T - (Br_T^-) + (Br^-)]) \quad (4)$$

(Br^-) and $(Br_2)_T = (Br_2) + (Br_3^-)$) has been solved by approximation procedures.

Since the equilibrium constant K (average value 148) was actually determined using sodium bromide rather than hydrogen bromide as the source of halide ion and since sodium acetate was also present in the solutions prepared for equilibrium study, several rate runs were also made in which sodium acetate and, in some cases, sodium bromide were added to the reaction mixtures. Rate constants k_1 and k_2 calculated for these runs were in reasonably good agreement with those obtained in runs without added salt.[10] These constants were obtained respectively from the intercepts and slopes of the straight lines obtained by plotting $R/(M)(Br_2)$ values against the corresponding free bromine concentrations. The R values were measured from plots of $(Br_2)_T$ against time.

The rate constants obtained for the several runs with varying initial concentrations of mesitylene, bromine and added salts are listed in Table I. This table also summarizes the results of bromination rate runs on isodurene and pentamethylbenzene, which may also be interpreted satisfactorily by equation 3. The general rate picture for the reactions of these hydrocarbons is the same as that reported for bromination of *p*-chlorophenyl ethers in 75% acetic acid.[9a] No experimental evidence to support the contention of Robertson[11] that the first-order (in bromine) reaction of mesitylene is "catalyzed" by hydrogen bromide has been obtained. It should be noted, however, that Robertson's conclusions are based on experiments in which large excesses of hydrogen bromide were present initially in the reaction medium.

The rates of bromination in 90% acetic acid of several less reactive hydrocarbons including durene and some polyethylbenzenes were also investigated. These reactions appeared to be inhibited by hydrogen bromide to a much greater degree than could be accounted for on the basis of tribromide ion formation. It is possible that the reactions of these compounds are complicated by a back reaction (equation 5) of bromide ion and reactive intermediate (possibly $ArHBr^+$).

$$ArHBr^+ + Br^- \longrightarrow ArH + Br_2 \quad (5)$$

No satisfactory kinetic analysis of these runs has as yet been made. Obviously any detailed analysis of variations in halogenation rate with structure of the polyalkylbenzenes cannot safely be made unless the rate law for each hydrocarbon is very clearly established. The practice of comparing reactivities of aromatic hydrocarbons by determining times for 10% bromination in acetic acid[12] is of particularly limited value, since there is no assurance that the relative contributions of terms of different order (in halogen) to the mixed order rate law are independent of the structure of the hydrocarbon. The ratios of k_2/k_1 for mesitylene, isodurene and pentamethylbenzene found in the present series of experiments are, respectively, 685, 605 and 1030 (based on runs in 0.1 *M* sodium acetate solution). Much wider variations in second- and first-order bromination rate constants have been reported[9a] for *p*- and *o*-chlorophenyl ethers. However, the relative halogenation rates for mesitylene (1), isodurene (3) and pentamethylbenzene (4.5) predicted by Condon from the distribution of isomers on chlorination of toluene[13] are in surprisingly good agreement with the relative k_1 values (1, 2.3, 4.8) found in the present study.

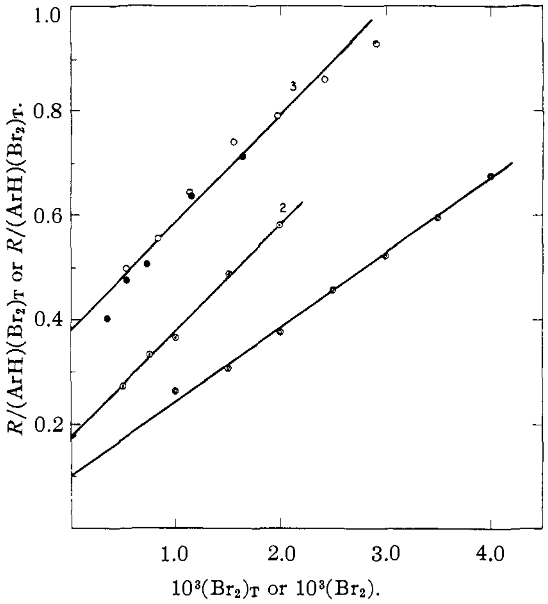

Fig. 1.—The influence of bromine and bromide ion concentrations on the rate of bromination of mesitylene in 90% acetic acid (25.4°). Lines 1 and 2 are plots of $R/(ArH)\cdot(Br_2)_T$ against $10^3(Br_2)_T$. In line 1, $(Br_2)_i = 0.0076$ *M* and $(ArH)_i = 0.0095$ *M*. In line 2, $(Br_2)_i = 0.00387$ *M* and $(ArH)_i = 0.0095$ *M*. In line 3 these same data are analyzed by plotting $R/(ArH)(Br_2)$ against $10^3(Br_2)$; the open circles are based on the data used to plot line 1 and the filled circles are based on the data of line 2.

Solvent Effects on Bromination Rates.—The bromination of mesitylene in 90% acetic acid is apparently more subject to inhibition by hydrogen bromide than is the reaction in pure acetic acid. Solutions of hydrogen bromide and bromine in pure acetic acid, like those of the halogen and hydrogen halide in 90% acetic acid, show the characteristic spectrum of tribromide ion in the near ultraviolet region.[14] By spectrophotometric methods it has been shown that the equilibrium constants for tribromide formation in these two solvents are of the same order of magnitude. An earlier report indicates that interaction to form the

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[10] Actually the k_1 values for the runs with added sodium bromide are somewhat higher than those for runs in the absence of this salt (see Table II). This discrepancy may result from a slight overestimation of the tribromide ion concentration of the solutions.

[11] P. W. Robertson, *J. Chem. Soc.*, 1267 (1954).

[12] E. Berliner and F. Berliner, THIS JOURNAL, **71**, 1195 (1949).

[13] F. E. Condon, *ibid.*, **70**, 1963 (1948).

[14] L. J. Andrews and R. M. Keefer, unpublished work.

Table I

Rate Constants for Bromination of Polyalkylbenzenes in 90% Acetic Acid (25.4°)

(ArH), 10^3 moles/l.	$(Br_2)_T$, 10^3 moles/l.	Salt	k_1, mole^{-1} sec.$^{-1}$ l.	k_2, mole^{-2} sec.$^{-1}$ l.
		Mesitylene[a]		
5.76	4.01	0.1 *M* NaOAc	0.372	241
9.50	3.87	...	.345	238
9.50	7.60	...	.370	234
11.52	0.98	.1 *M* NaOAc	.423	328
11.52	1.96	.1 *M* NaOAc	.385	277
11.52	3.92	.1 *M* NaOAc	.373	227
11.52	3.92	.1 *M* NaOAc .005 *M* NaBr	.415	210
11.52	3.92	.09 *M* NaOAc .01 *M* NaBr	.415	210
11.52	3.92	.08 *M* NaOAc .02 *M* NaBr	.450	260
19.00	1.92	...	.310	180
19.00	3.88	...	.352	192
19.00	5.67	...	.348	217
19.00	7.69	...	.359	237
23.04	4.01	0.1 *M* NaOAc	.372	241
38.00	5.76	...	.364	191
		Isodurene[b]		
2.44	1.83	0.1 *M* NaOAc	0.86	520
4.88	0.913	.1 *M* NaOAc		
4.88	1.83	.1 *M* NaOAc		
4.88	3.65	.1 *M* NaOAc		
9.75	1.83	.1 *M* NaOAc		
		Pentamethylbenzene[b]		
2.74	1.93	0.1 *M* NaOAc	1.81	1860
5.48	0.965	.1 *M* NaOAc		
5.48	1.93	.1 *M* NaOAc		
5.48	3.86	.1 *M* NaOAc		
10.96	1.93	.1 *M* NaOAc		

[a] The five runs on mesitylene in 0.1 *M* NaOAc solutions in the absence of added sodium bromide were plotted separately. The average deviations of k_1 and k_2 values from the mean for these runs were, respectively, 4 and 12%. [b] All runs were summarized on a single plot of $R/(ArH)(Br_2)$ *versus* (Br_2).

trihalide becomes more extensive as the water concentration of the solvent is decreased.[8] If this is the case, then in pure acetic acid the tribromide species which forms, either[15] un-ionized HBr_3 or the ion pair $H^+Br_3^-$, may compete favorably with bromine as a brominating agent. In the aqueous medium this acid may be sufficiently dissociated so that its effectiveness as a brominating agent is sharply reduced. Further studies of the rate of mesitylene bromination in pure acetic acid in the presence of added hydrogen bromide should serve to test this explanation.

The change in medium for mesitylene bromination from pure to 90% acetic acid results (approximately) in 800-fold and 90-fold increases in k_1 and k_2, respectively. The rate-determining process previously proposed for the reaction in acetic acid (equation 6) is presumed to lead to rupture of the

$$C_6H_3(CH_3)_3{\cdot}Br_2 + E \longrightarrow C_6H_3(CH_3)_3Br^+ + EBr^- \qquad (6)$$

bromine–bromine bond of a 1:1 mesitylene–bromine complex through attack of an electrophilic reagent E. The observed first- and second-order reactions in bromine should, therefore, correspond, respectively, to the functioning of solvent and of bromine as the reagent E. As is the case experimentally, the rates of both reactions should increase as the dielectric constant of the medium increases.

It is interesting to consider whether these increases result entirely from dielectric effects or whether they represent in part a medium effect which is related to the hydroxylic character of the solvent. The results of three rate runs on the bromination of mesitylene in chlorobenzene, a solvent with approximately the same dielectric constant as acetic acid,[16] support the latter view. In this solvent the reactions were essentially pure second order in bromine. The constants, k_1, were immeasurably small, and k_2 values (see Table II) were much less than those found earlier[2] for runs in which acetic acid was the solvent. The corresponding values of k_1 and k_2 for the reaction in acetic acid[2] were 0.029 mole^{-1} min.$^{-1}$ l. and 167 mole^{-2} min.$^{-1}$ l.^{2}.

To examine the degree to which the rate of bromination of mesitylene was controlled by the capacity of the solvent to solvate bromide ion through hydrogen bond formation, several runs in deuterated media were made. The runs are summarized and compared with identical runs in deuterium-free solvents in Table III.

Table II

The Bromination of Mesitylene in Chlorobenzene (25.4°)[a]

$(ArH)_i$, 10^3 moles/l.	$(Br_2)_i$, 10^3 moles/l.	k_2, mole^{-2} min.$^{-1}$ l.^{2}
191.2	3.84	14.8
191.2	19.06	17.9
191.2	38.12	18.6

[a] The runs were followed in the order presented by measuring changes in optical densities at 450, 540 and 560 mμ, respectively, as a function of time. Under the conditions of the runs bromine did not react with the solvent.

In general the k_1 values are reduced when the solvent of normal isotope content is replaced by deuterated material. These isotope effects are of the same general order of magnitude as has been observed in studies of the hydrolysis rates of tertiary halides and are large enough to suggest that the H–O bond of the solvent is weakened, but not ruptured, in the rate-determining step.[17]

The observed changes in k_2 with the shifts to deuterated solvents are, except for those for runs with added sodium perchlorate, too small to be of significance. Why this secondary isotope effect on k_2 appears only in the presence of the added salt is not clear. Its appearance, however, is compatible with the observed decrease in k_2 for mesitylene bromination which occurs when the medium is changed from acetic acid to chlorobenzene.

The catalytic effects of light and heavy water on the bromination of mesitylene in carbon tetra-

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(15) See I. M. Kolthoff and S. Bruckenstein, This Journal, 78, 1 (1956).

(16) "International Critical Tables," Vol. VI, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, pp. 84 and 89.

(17) C. G. Swain, R. Cardinaud and A. D. Ketley, This Journal, 77, 934 (1955).

TABLE III

THE BROMINATION OF MESITYLENE IN DEUTERATED AND IN DEUTERIUM-FREE SOLVENTS (25.4°)

$(ArH)_i$, 10^3 moles/l.	$(Br_2)_i$, 10^3 moles/l.	Medium	k_1,[c] mole^{-1} min.$^{-1}$ l.	k_2,[c] mole^{-2} min.$^{-1}$ l.^{2}
193.0	5.71	Acetic-*d* acid	0.008	141
191.2	3.66	Acetic acid	.020	146
48.2	5.71	Acetic-*d* acid[a]	1.20	1150
47.8	3.66	Acetic acid[a]	1.46	1440
			mole^{-1} sec.$^{-1}$ l.	mole^{-2} sec.$^{-1}$ l.^{2}
3.84	12.05	90% acetic-*d* acid 10% D_2O[b]	0.297	205
3.42	12.06	90% acetic acid 10% H_2O[b]	0.385	192

[a] $(NaClO_4)$ = 0.245 *M*. [b] (NaOAc) = 0.099 *M*. [c] In earlier work, reference 2, it was found that the deviations of k_1 and k_2 values from the mean for a series of runs on mesitylene bromination in pure acetic acid were, respectively, 6 and 2% (for runs in which the mesitylene concentrations were all the same). Deviations from the mean of rate constants for runs in 90% acetic acid are listed in the footnote of Table I.

TABLE IV

THE BROMINATION OF MESITYLENE IN CARBON TETRACHLORIDE (25.4°)

$(ArH)_i$, mole/l.	$(Br_2)_i$, 10^3 moles/l.	Added water[a]	*K*, min.$^{-1}$ mole$^{-1/2}$ l.$^{1/2}$
0.712	8.78	H_2O	0.494
.712	8.78	H_2O	.511
.712	8.83	D_2O	.396
.712	8.83	D_2O	.396

[a] In runs with light water, $(H_2O) = 4.42 \times 10^{-3}$ *M*. In runs with heavy water, $(D_2O) = 4.41 \times 10^{-3}$ *M*.

TABLE V

THE BROMINATION OF MESITYLENE IN PERCHLORIC ACID SOLUTIONS OF ACETIC ACID (25.4°)

$(ArH)_i$, 10^3 moles/l.	$(Br_2)_i$, 10^3 moles/l.	$(HClO_4)$, mole/l.	k_1, mole^{-1} min.$^{-1}$ l.	k_2, mole^{-2} min.$^{-1}$ l.^{2}
48.3	3.8	0.049	0.09	715
48.3	3.8	.098	0.53	1180
48.3	3.8	.245	1.64	3750

chloride were also compared. It has been postulated that hydronium ion functions as an electrophilic reagent in assisting the rupture of the bromine-bromine bond of a 1:1 mesitylene-bromine complex in the rate-determining step of the reaction.[1a] The experimental rate law for this reaction in the presence of a large excess of mesitylene is given in equation 7 (the contributions of water and

$$-d(Br_2)_T/dt = k(Br_2)_T(HBr)^{1/2} \qquad (7)$$

mesitylene concentrations to the reaction rate are included in the rate constant *k*). The rate constant for runs at equal concentrations of bromine, mesitylene and light or heavy water, which were evaluated as described previously,[1a] are given in Table IV. Again the reaction is somewhat faster in the deuterium-free medium, but the isotope effect is not large enough to indicate that a hydrogen-oxygen bond of the electrophilic reagent is broken in the rate-determining step.[18] In other words this step cannot be as shown in equation 8.

$$C_6H_3(CH_3)_3\cdot Br_2 + H_3O^+ \longrightarrow C_6H_3(CH_3)_3Br^+ + HBr + H_2O \qquad (8)$$

The Effect of Perchloric Acid on the Rate of Mesitylene Bromination.—Perchloric acid, which apparently is relatively strong in acetic acid,[15,19] enhances the rate of aromatic bromination in acetic acid.[20] To test whether this enhancement results from direct participation of the inorganic acid, which potentially is a much stronger electrophilic reagent than acetic acid in rate-determining processes (equation 6), a series of rate runs on mesitylene bromination in acetic acid containing varying amounts of perchloric acid were made (see Table V). Actually both k_1 and k_2 values were found to increase substantially (as compared to those in the absence of perchloric acid—see Table III), although the enhancement of k_1 was much greater than that of k_2. However, the rate increases produced by perchloric acid are of the same general order of magnitude as those which result from the addition of sodium perchlorate to the reaction mixtures.[2] It seems likely, though not certain, that the effects of sodium perchlorate on the rates are purely electrostatic in origin. The function of hydrogen ion as a direct participant in rate determining processes has not, therefore, been demonstrated.

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[18] Certainly some isotopic exchange between HBr and D_2O occurs during the reactions in the presence of D_2O. In making this interpretation it is assumed that the net concentrations of hydronium ions (H_3O^+ or D_2OH^+, DOH_2^+ and H_3O^+) in the runs in H_2O and D_2O are the same as the same total hydrogen (or deuterium) bromide concentrations.

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