

liquor. This ultimately gave 8 g. of ester, m.p. 97–98°, $[\alpha]^{25D} + 22.70^\circ$ (c 1.5 in acetone), $[\alpha]^{25D} + 22.00^\circ$ (c 1.5 in nitrobenzene).

Anal. Calcd. for $C_{16}H_{20}O_2SI$: C, 47.26; H, 5.68; S, 7.89; I, 31.35. Found: C, 47.26; H, 5.08; S, 8.11; I, 31.50.

Although the esters appeared to be quite stable, they were kept in a desiccator in the dark.

Kinetic Measurements.—The kinetics of the epimerization reactions were determined at $25.00 \pm 0.05^\circ$ as reported previously.³

For the ethanolysis reactions, stock solutions of sodium ethoxide were prepared by dissolving sodium, cleaned and weighed under dry ether, in dry ethanol³⁰ and transfer of the supernatant solution from traces of undissolved material

to a polyethylene bottle that was stored in a desiccator in the dark. The solution was standardized just before use by addition of an aliquot to an excess of standard acid and back titration with standard sodium hydroxide solution. The ethoxide solutions were discarded after two weeks of use.

To carry out a kinetic run, ester was weighed into a volumetric flask and dissolved in anhydrous ethanol. This solution, as well as the other reagents, was then thermostated at the appropriate temperature for 30 minutes. The sodium ethoxide solution, standardized at the temperature of use, was added to the flask to start the reaction and the flask was immediately filled to the mark with anhydrous ethanol. After mixing, the solution was transferred to a thermostated polarimeter tube. Determination of the water temperature at the inlet and outlet of the thermostating jacket of the tubes showed that the maximum temperature variation was $\pm 0.05^\circ$.

(30) E. L. Smith, *J. Chem. Soc.*, 1288 (1927).

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

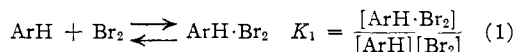
The Kinetics of Bromination of Polymethylbenzenes in Chloroform. Catalysis by Iodine Bromide

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In chloroform, as contrasted to carbon tetrachloride, polymethylbenzenes are subject to uncatalyzed nuclear bromination. The reactions are second order in halogen. In the presence of iodine bromide as a catalyst these reactions are first order in bromine and first order in the catalyst. The corresponding reactions in carbon tetrachloride are second order with respect to the catalyst. At moderately high concentrations of aromatic hydrocarbon the observed third-order rate constants diminish with increasing hydrocarbon concentration. Some of this decrease is attributable to the formation of molecular complexes and some of it results because of the change in the polar character of the medium. The activation energies for the reactions in chloroform are very small or slightly negative. These results are discussed in terms of the probable mechanism for polar aromatic halogenations.

In acetic acid mesitylene undergoes nuclear bromination by a third-order process (first order in mesitylene and second order in bromine).^{1,2} At very low bromine concentrations a term which is first order in halogen also makes a significant contribution to the over-all rate law. The two reactants show an appreciable tendency to interact to form a molecular complex (eq. 1) in acetic acid. Even at moderate mesitylene concentrations



the extent of the interaction is sufficient so that the difference between the total $[\text{Br}_2]_T$ and free bromine concentration of the medium is appreciable (eq. 2). It should follow, therefore, that if

$$[\text{Br}_2]_T = [\text{Br}_2] + [\text{ArH} \cdot \text{Br}_2] \quad (2)$$

the rate-determining step of the third-order reaction involves one mesitylene and two free bromine molecules (or a bromine molecule and the 1:1 complex), the experimental k_1 values for that third-order reaction which are based on eq. 3 should diminish according to eq. 4 with increasing mesitylene concentration of the medium. Actually the

$$-d[\text{Br}_2]_T/dt = k_1[\text{ArH}][\text{Br}_2]_T^2 \quad (3)$$

$$k_1 = k_a/(1 + K_1[\text{ArH}])^2 \quad (4)$$

depression in k_1 with increases in mesitylene concentration is much larger than predicted on the basis of the experimental value for K_1 . Presumably, then, the dilution of the polar solvent with even

relatively small amounts of the non-polar aromatic hydrocarbon has a significantly unfavorable "medium effect" on the polar bromination process.

In moist carbon tetrachloride mesitylene undergoes hydrogen bromide-catalyzed bromination by a process which is first order with respect to each reactant and half order with respect to the catalyst.³ As should be the case if a mesitylene molecule and a free bromine molecule (or a 1:1 mesitylene-bromine complex) are involved in the rate-determining step, the experimental rate constants, k_{obs} , diminish with increasing mesitylene concentration as predicted by eq. 5. That is, in

$$\frac{-d[\text{Br}_2]_T}{dt} = k_{\text{obs}} [\text{Br}_2]_T [\text{ArH}] [\text{HBr}]^{1/2} = \frac{k' [\text{Br}_2]_T [\text{ArH}] [\text{HBr}]^{1/2}}{1 + K_1 [\text{ArH}]} \quad (5)$$

contrast to what is observed for reaction in acetic acid, no significant rate effects attributable to changes in character of the medium with changes in the aromatic hydrocarbon content are found for the reaction in carbon tetrachloride.

The bromination of mesitylene in carbon tetrachloride is also catalyzed by iodine bromide.^{4,5} The reaction is first order in total bromine and second order with respect to the catalyst. Iodine bromide, as well as bromine, interacts with mesitylene in carbon tetrachloride, and the equilibrium

(3) R. M. Keefer, J. H. Blake and L. J. Andrews, *J. Am. Chem. Soc.*, **76**, 3062 (1954).

(4) P. W. Robertson, J. E. Allan, K. N. Haldane and M. G. Simmers, *J. Chem. Soc.*, 933 (1949).

(5) J. H. Blake and R. M. Keefer, *J. Am. Chem. Soc.*, **77**, 3707 (1955).

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

(2) P. W. Robertson, *J. Chem. Soc.*, 1267 (1954).

constant, K_2 , is substantially larger than K_1 in carbon tetrachloride. If, then, the rate-determining step for the iodine bromide-catalyzed reaction involves the attack of two free iodine bromide mole-

$$K_2 = [\text{ArH}\cdot\text{IBr}]/[\text{ArH}][\text{IBr}] \quad (6)$$

cules on a 1:1 mesitylene-bromine complex, the k_{obs} values should diminish with increasing aromatic hydrocarbon concentration as predicted by eq. 7. Actually⁵ the diminution in k_{obs} is approximately predicted by eq. 7 if the second term

$$-d[\text{Br}_2]_{\text{T}}/dt = k_{\text{obs}}[\text{ArH}][\text{Br}_2]_{\text{T}}[\text{IBr}]_{\text{T}}^2 = \frac{k''[\text{ArH}][\text{Br}_2]_{\text{T}}[\text{IBr}]_{\text{T}}^2}{[1 + K_1(\text{ArH})][1 + K_2(\text{ArH})]^2} \quad (7)$$

in the denominator is one. It appears that iodine bromide is equally effective as a catalyst whether it is in the free or complexed form.

It has seemed of interest to extend the previous investigations of polymethylbenzene bromination kinetics to include a study of the reactions in chloroform, a non-hydroxylic solvent which resembles acetic acid more than carbon tetrachloride in its polarity (as measured by its dielectric constant,⁶ $\epsilon = 5.05$ at 20°). The uncatalyzed reactions of bromine with mesitylene and pentamethylbenzene and the iodine bromide-catalyzed reaction of bromine with these two hydrocarbons and with durene have been investigated. Particular attention has been given to determining the nature of the effect on the experimental rate constants (medium effect *vs.* complexing effect) of increasing the aromatic hydrocarbon content of the reaction mixtures.

Experimental

Materials.—Reagent grade chloroform was freed of the stabilizing ethanol by the method of Fieser⁷ before it was used in rate runs. The purified material, b.p. 60.7–61.3°, was prepared in small batches and stored in the dark. Samples which were so stored were discarded as soon as they were found to liberate iodine from aqueous potassium iodide. In some instances the chloroform was further dried, after distillation, with freshly roasted calcium sulfate. The optical density of solutions of bromine in purified chloroform remained constant over a period of 3 hours which is about the reaction time of the slowest rate runs.

Eastman Organic Chemicals durene, m.p. 79–80°, and pentamethylbenzene, m.p. 51.0–52.2°, were recrystallized from aqueous ethanol. Eastman Organic Chemicals mesitylene was purified through sulfonation⁸ and fractionated, b.p. 166.5–167°.

Reagent grade bromine (J. T. Baker Chemical Co.) and iodine (Mallinckrodt Chemical Works) were used without further treatment.

Kinetics of the Uncatalyzed Reactions.—The reactions of the aromatic hydrocarbons and bromine were followed spectrophotometrically. In all cases the hydrocarbon concentration was in substantial excess of that of the halogen. To start a run known volumes of chloroform solutions (of known concentrations) of the two reactants were mixed at the temperature of the rate measurements. A sample of the resultant solution was transferred to a 1-cm. glass stoppered absorption cell contained in a temperature-controlled housing ($\pm 0.1^\circ$) of a Beckman model DU spectrophotometer. The change in bromine concentration of the cell contents was determined through measurement of the optical density of the reaction mixture, against a chloroform blank, as a function of time at a wave length such that the initial readings were usually of the order of 0.4–1.0. Wave lengths of 440, 500 and 530 $m\mu$ were used in runs with

mesitylene, and the runs with pentamethylbenzene were followed at 460 $m\mu$. The corresponding extinction coefficients for bromine in chloroform are 173, 88.3, 47.0 and 144. These values are subject to some variation, the magnitude of which depends on the identity and concentration of the aromatic hydrocarbon which is present in the solution. The exact extinction coefficients which were used in calculating bromine concentrations from optical densities during the course of individual rate runs were based on the optical densities of the reaction mixtures at the time of preparation (as estimated by extrapolation of the experimental data).

Kinetics of the Iodine Bromide-catalyzed Brominations.—The experimental procedure was essentially the same as that described for the uncatalyzed reactions except that iodine was included in the reaction mixtures (at a concentration substantially less than the initial bromine concentration). It was assumed, as is approximately correct even when the two halogens are present in equimolar quantity (see below), that the iodine was completely converted to iodine bromide. The reactions were followed until the excess bromine (over iodine) was consumed, and the optical density readings no longer changed at an appreciable rate. The bromine concentrations of the reaction mixtures were calculated from the measured optical densities after subtracting out the final readings. Wave lengths of 440, 460 and 490 $m\mu$ were used in following the reactions spectrophotometrically. The extinction coefficient of bromine at the last wave length is 104.

The Degree of Association of Iodine Bromide in Chloroform.—A procedure similar to that applied in determining the degree of association of iodine bromide in carbon tetrachloride⁹ was used. Equal volumes of solutions of equal concentrations, $[C]$, of iodine and bromine were mixed, and the optical density, d , of the resultant solution was measured against a chloroform blank in a 1-cm. absorption cell at an appropriate wave length in the visible region. The iodine bromide concentration of the halogen mixture was calculated using eq. 8. The extinction coefficients of the

$[\text{IBr}] = d - [C](\epsilon_{\text{Br}_2} + \epsilon_{\text{I}_2})/[\epsilon_{\text{IBr}} - (\epsilon_{\text{Br}_2} + \epsilon_{\text{I}_2})/2] \quad (8)$

elemental halogens were established by separate measurements. That of iodine bromide was obtained through measuring the absorption of solutions in which one of the halogens was present in twofold molar excess of the other; it was assumed that the elemental halogen present in smaller amount was converted quantitatively to iodine bromide under these conditions. Typical results are listed in Table I.

TABLE I
DEGREE OF ASSOCIATION OF IBr IN CHLOROFORM (25.0°)

Wave length of measurement, $m\mu$	$10^3[\text{IBr}]$, mole/l.	Optical density ^a	Association, %
540	1.90	0.670	96
550	1.90	.514	95
540	0.948	.345	93
550	0.948	.257	94
530	1.00	.476	92
540	1.00	.370	92

Av.^b 94 \pm 1.5%

^a The extinction coefficients of the halogens in chloroform at 530, 540 and 550 $m\mu$ are, respectively, 47.0, 34.6, and 25.5 for bromine; 842, 722 and 597 for iodine and 226, 168 and 125 for iodine bromide. ^b Based on 17 measurements.

Equilibrium Constants for the Iodine Bromide-Durene and the Bromine-Mesitylene Complexes.—The equilibrium constants for the formation of these 1:1 complexes in chloroform at 25.0° were determined spectrophotometrically by the usual procedures.¹⁰ A series of solutions of each of the two types of complexes, in which the aromatic hydrocarbon concentrations varied from about 0.1 to 1.0 M and the halogen concentrations ranged from 1×10^{-4} to $20 \times 10^{-4} M$, were prepared. The optical densities of the fresh solutions were measured, against blanks of corresponding

(6) "International Critical Tables," Vol. VI, First Edition, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p. 83.

(7) L. F. Fieser, "Experiments in Organic Chemistry," Third Edition, D. C. Heath and Co., Boston, Mass., 1955, p. 283.

(8) L. I. Smith and O. W. Cass, *J. Am. Chem. Soc.*, **54**, 1603 (1932).

(9) A. Popov, K. Brinker, L. Campanaro and R. Rinehart, *ibid.*, **73**, 514 (1951).

(10) See for example, N. Ogimachi, L. J. Andrews and R. M. Keefer, *ibid.*, **77**, 4202 (1955).

concentrations of the hydrocarbon, at a series of wave lengths in the 320-350 $m\mu$ region at which the complexes absorb strongly. The measurements were conducted rapidly enough so that no errors resulting from consumption of halogen by aromatic substitution occurred. The extinction coefficients of the free halogens in chloroform at the wave lengths of the measurements were determined by spectrophotometric study of hydrocarbon free solutions (at 320 $m\mu$ $\epsilon_{I_2} = 33.5$ and $\epsilon_{Br_2} = 3.1$). The average values of the equilibrium constants obtained by graphical analysis of data recorded at the several wave lengths were $K_1 = 0.25$ mole⁻¹ l. for the bromine-mesitylene complex and $K_2 = 1.1$ mole⁻¹ l. for the iodine bromide-durene complex at 25.0°.

The Bromination Reaction Products.—The product of both the uncatalyzed and the iodine bromide-catalyzed reaction of bromine and pentamethylbenzene, as formed under experimental conditions similar to those used in the rate runs, was isolated to ascertain that nuclear rather than side chain bromination was the dominant process. In one experiment a solution of 2.96 g. (0.02 mole) of pentamethylbenzene in 100 ml. of chloroform was treated with a total of 1 ml. of bromine (0.0182 mole). The halogen was added in 100- λ portions, and the color of bromine was allowed to disappear from the reaction mixture between successive additions. The solvent was then removed on the steam-bath, and the residue was taken up in 30 ml. of boiling ethanol. When the resultant solution was cooled, 3.68 g. (93% yield) of 6-bromo-1,2,3,4,5-pentamethylbenzene was obtained, m.p. 157-160° (lit.¹¹ m.p. 160°).

In a similar experiment a solution of 0.74 g. (0.005 mole) of pentamethylbenzene and 1.2 mg. of iodine in 50 ml. of chloroform ($1 \times 10^{-4}M$ iodine solution) was treated in 50- λ increments with a total of 300 λ (0.005 mole) of bromine. The solution was allowed to stand for 5 hours after the final addition, and then the excess halogens were removed with sodium bisulfite solution. A total of 1.02 g. (89.5%) of 6-bromo-1,2,3,4,5-pentamethylbenzene, m.p. 159-162°, was recovered from the solution by the procedure used in recovering the product of the uncatalyzed reaction.

Results

The Uncatalyzed Reactions.—The reactions of mesitylene and pentamethylbenzene in the absence of added iodine were found to be second order in bromine. The aromatic hydrocarbon concentration was essentially invariant during the rate runs which were made. Values of $k_1(\text{ArH})$, as defined by the experimental rate law (eq. 3), were therefore calculated from the product of the bromine extinction coefficient and the slope of the straight line obtained by plotting the reciprocal of the optical density of the reaction mixture as a function of time. In runs with pentamethylbenzene in which the solvent was not dried over calcium sulfate before it was used, the apparent rate constants, $k_1(\text{ArH})$, were found to drift upward to some degree after anywhere from 40 to 70% of the bromine was consumed. When the dried solvent was used, this drift was not observed even up to 80% of completion of the reaction. The rate constants based on the early phases (first 50%) of reactions in the wet solvent are in good agreement with those obtained from duplicate runs using calcium sulfate-dried solvent. In runs with mesitylene these drifts were noted in later phases of the reactions (over 50% of completion) even when calcium sulfate-dried solvent was used. Apparently these reactions are subject to mild catalysis by the hydrogen bromide which forms as a reaction product. As in the case of the mesitylene bromination reaction in carbon tetrachloride,³ the activity of the catalyst is enhanced as the trace water content

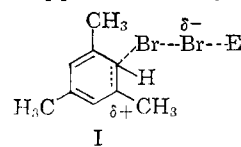
of the medium increases. The specific contribution of hydrogen bromide to the over-all rate law was not investigated. The experimental rate constants k_1 for reactions in the absence of iodine, which are based on those phases of the runs in which hydrogen bromide catalysis was not observed, are summarized in Table II.

TABLE II
RATE CONSTANTS FOR THE UNCATALYZED REACTIONS OF BROMINE WITH AROMATIC COMPOUNDS IN CHLOROFORM^a

[ArH], mole l. ⁻¹	10 ³ [Br ₂], ^b moles l. ⁻¹	No. of runs ^c	k_1 , mole ⁻² l. ² sec. ⁻¹
Pentamethylbenzene, at 25.0°			
0.040	3.8	2	2.01 ± 0.25
.050	3.8	3	1.75 ± .12
.080	3.5	1	1.81
.100	1.8-6.2	6	1.80 ± .15
.160	3.1-3.6	2	1.87 ± .29
.200	2.8	2	1.74 ± .31
.250	3.1-3.9	2	1.73 ± .23
At 9.7°			
0.102	3.7	2	1.43 ± 0.04
At 44.6°			
0.100	3.7	2	1.68 ± 0.04
Mesitylene, 25.0°			
0.072	3.58	1	0.233
.144	3.58	1	.199
.216	3.9-17.9	3	.204 ± 0.14
.360	3.90	1	.178
.720	3.90	1	.129
At 12.9°			
0.219	3.84	4	0.210 ± 0.05
At 44.4°			
0.212	3.57	2	0.238 ± 0.12

^a In all runs chloroform which had been purified and dried according to the directions of Fieser⁷ was used. In all but the runs on pentamethylbenzene at 25.0° the solvent which was used had been subjected to additional drying over freshly roasted calcium sulfate. ^b Initial bromine concentration. ^c In some instances several runs at the same concentration of the aromatic hydrocarbon were made. In such cases reported k_1 values are the averages of those for the several runs.

In contrast to the requirements for aromatic bromination in carbon tetrachloride, the presence of a strongly polar catalyst is not essential for reaction in chloroform. Rather, the solvent itself has a sufficiently high dielectric constant so that it provides a suitable environment for the separation of charge which must occur in the activation process. The second-order dependence of reaction rate on bromine concentration in chloroform is reasonably explained on the assumption that in the rate-determining step the bromine-bromine bond of a 1:1 aromatic-halogen complex (eq. 1) is weakened through electrophilic attack by a second bromine molecule.⁴ The activated complex for this reaction, where E represents the second bromine molecule, can be approximated by the structure I.



(11) 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.

In the case of aromatic bromination in acetic acid that phase of the reaction which is second order in halogen may be presumed to involve a similar activated complex. It should be noted that the rate constants k_1 for reaction in acetic acid are over ten times larger than in chloroform. The difference is probably due largely to the differences in the dielectric properties of the two solvents. That phase of the reaction in acetic acid which is first order in bromine is presumed to proceed through an activated complex similar to I in which an acetic acid molecule functions as the reagent E by hydrogen bonding to departing bromide ion. A reaction which is first order in aromatic hydrocarbon and first order in halogen is not to be expected (and apparently does not occur) in chloroform since this solvent cannot assume the specific role played by acetic acid in promoting the bromine-bromine bond break.

The rate constants k_1 for bromination of mesitylene in chloroform were found to diminish as the mesitylene concentration was increased. That this effect is not entirely the result of a lowering of the concentration of free bromine, as predicted by eq. 4, was established by plotting the reciprocals of the square roots of the experimental values of k_1 for the runs on mesitylene (see Table II) against the corresponding hydrocarbon concentrations. From the slope and intercept of the resultant straight line a figure of $K_1 = 0.56 \text{ mole}^{-1} \text{ l.}$ for the bromine-mesitylene complex was calculated. This figure is substantially higher than the value, $K_1 = 0.25 \text{ mole}^{-1} \text{ l.}$, obtained by direct evaluation of the equilibrium concentration of the complex in solution at 25.0° . Apparently an appreciable share of the decrease in k_1 values with increasing mesitylene concentration must (like the corresponding decrease observed for reaction in acetic acid) be attributed to the reduction in the polar character of the medium which results when its aromatic hydrocarbon content is increased.

The runs involving pentamethylbenzene were conducted at a sufficiently low concentration of the hydrocarbon so that neither medium effects nor complexing effects were noticeably reflected in the experimental k_1 values.

The Iodine Bromide-catalyzed Reaction.—In the presence of iodine bromide the reactions of pentamethylbenzene, mesitylene and durene in large excess, with bromine in chloroform are (as suggested by the results of an earlier study⁴) first order with respect to the concentrations of bromine and of the catalyst. Values of the third-order rate constant k_2 , defined by the rate law given in eq. 9,

$$-d[\text{Br}_2]_{\text{T}}/dt = k_2[\text{ArH}][\text{Br}_2]_{\text{T}}[\text{IBr}]_{\text{T}} \quad (9)$$

are listed in Table III. The values of $k_2[\text{ArH}][\text{IBr}]_{\text{T}}$ for individual runs, on which the reported k_2 values are based, were calculated from the slopes of plots of the logarithms of the optical densities of the reaction mixture (corrected for the absorption of the catalyst) against time. In general such plots were linear to better than 70% of completion of the reaction.

It seems likely that the catalyst can function much more effectively than bromine as the electrophilic reagent E (see structure I) in assisting

TABLE III
RATE CONSTANTS FOR THE IODINE BROMIDE-CATALYZED REACTIONS OF BROMINE WITH AROMATIC COMPOUNDS IN CHLOROFORM^a

[ArH], mole l. ⁻¹	10 ³ [IBr] _T , moles l. ⁻¹	10 ³ [Br ₂] _T , ^b moles l. ⁻¹	No. of runs ^c	k_2 , mole ⁻² l. ³ sec. ⁻¹
Pentamethylbenzene, at 25.0°				
0.060	5.06	3.0	1	597
.080	5.06	3.0	1	581
.100	5.0-20.0	1.0-4.0	5	566 ± 28
.200	5.00	3.0	1	465
At 12.3°				
0.102	4.10	3.0	2	668 ± 36
At 42.1°				
0.098	3.96	3.0	2	483 ± 38
Mesitylene, at 25.0°				
0.072	10.2-52.6	2.0-8.0	3	104 ± 4
.144	10.2	4.0	1	96
.216	2.5-10.1	4.0	3	95 ± 4
.216 ^d	10.4	4.0	1	67
.216 ^e	10.4	4.0	1	52
.360	7.62	4.0	1	69
.720	3.08	4.0	1	50
.936	10.4	4.0	1	38
1.44	3.08	4.0	1	27
At 12.8°				
0.219	5.86	4.0	2	112 ± 5
At 44.2°				
0.212	6.08	4.0	2	69 ± 0.5
Durene, at 25.0°				
0.10	84.4	4.0	1	2.61
.20	84.4	4.0	1	2.42
.40	36.6-342	4.0-8.0	6	1.96 ± 0.10
.50	84.0	4.0	1	1.89
.70	84.4	4.0	1	1.30
At 10.5°				
0.409	80.2	4.0	2	1.82 ± 0.05
At 44.6°				
0.394	75.2	4.0	2	2.41 ± 0.02

^a Purified chloroform⁷ which was dried over freshly roasted calcium sulfate was used. ^b Initial bromine concentration.

^c In some instances several runs at the same concentration of aromatic hydrocarbon were made. In such cases reported k_2 values are the averages of those for the several runs. ^d The solvent was 10 volume % benzene. ^e The solvent was 10 volume % CCl₄.

the bromine-bromine bond break in the activation process. It is interesting to recall that in the catalyzed reaction in carbon tetrachloride two iodine bromine molecules, rather than a single one, are included in the activated complex. It is probable that in this case E is an iodine bromide dimer, which in the absence of a polar medium capable of contributing electrostatically, provides a several atom center for dispersal of the negative charge developing in the activation process.

If, as is assumed, a free iodine bromide molecule attacks a 1:1 aromatic-bromine complex in the rate-determining step of the catalyzed reaction, the observed rate constant k_2 should be related to equilibrium constants K_1 and K_2 as shown in eq. 10. That is, k_2 should drop with increasing

$$(1 + K_1[\text{ArH}])(1 + K_2[\text{ArH}])k_2 = k_b \quad (10)$$

aromatic hydrocarbon concentration since it is evaluated on the assumption that both the free and complexed halogens are equally capable of participation in rate-determining processes. Such decreases in the experimental rate constant are clearly apparent for runs with mesitylene in which wide variations in the hydrocarbon concentration were made. However, a substantial part of the observed rate depression must result from decreases in medium polarity as the hydrocarbon concentration increases. This conclusion is based on the observation that when other non-polar diluents, benzene or carbon tetrachloride, are added to the medium, substantial decreases in the rate of iodine bromide-catalyzed mesitylene bromination are observed (see Table III). In this regard three runs are of particular interest. For one of these, in which the initial mesitylene concentration was 0.936 *M*, a k_2 value of 38 l.² mole⁻² sec.⁻¹ was obtained. In this case the medium was 13 volume % mesitylene. In the other runs, conducted at 0.216 *M* mesitylene concentration, the amounts of non-polar diluent in the medium were raised to 13 volume % by the addition of benzene ($k_2 = 67$ l.² mole⁻² sec.⁻¹) or carbon tetrachloride ($k_2 = 52$ l.² mole⁻² sec.⁻¹). If it is assumed that the "medium effect" on the magnitude of the rate constant is the same for the run at high mesitylene concentration as for that with added benzene, eq. 10 can be used (along with the measured values of k_2 for the two runs in question and the known value of K_1 for the mesitylene-bromine complex in chloroform) to calculate a value for the mesitylene-iodine bromide complex of $K_2 = 0.82$ mole⁻¹ l. If the k_2 value for the run with added carbon tetrachloride is substituted for that for the run with added benzene in making this calculation, the figure of $K_2 = 0.64$ mole⁻¹ l. is obtained. Actually K_2 could not be determined by direct spectrophotometric study because of the rapidity of reaction of mesitylene with iodine bromide in chloroform at concentrations of the halogen high enough to provide reliable results. The constant should, however, be somewhat greater than that ($K_2 = 1.1$ mole⁻¹ l.) for the durene-iodine bromide complex in chloroform¹² and less than the corresponding constant for the iodine bromide-mesitylene complex in carbon tetrachloride ($K_2 = 1.5$ mole⁻¹ l.).¹³ The values crudely approximated, as described above, from the effects of mesitylene concentration increases on reaction rate are, therefore, somewhat low. It is possible that in chloroform, as has already been noted is the case for reaction in carbon tetrachloride, iodine bromide still may retain some catalytic activity even though it is complexed

(12) Durene is generally a somewhat weaker electron acceptor than mesitylene; cf. L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **74**, 4500 (1952).

(13) Increases in solvent polarity are generally unfavorable to the formation of donor-acceptor type complexes; see R. M. Keefer, A. Ottenberg and L. J. Andrews, *ibid.*, **78**, 255 (1956).

with aromatic hydrocarbon. It is, however, very clear that chloroform, because it is more polar than carbon tetrachloride, can (unlike the latter solvent) play an important role in the activation process for the iodine bromide-catalyzed reaction, as well as for uncatalyzed brominations.

The Energies and Entropies of Activation.—The energies and entropies of activation for the bromination reactions, which were calculated using the appropriate results of Table III, are listed in Table IV. The rates of the uncatalyzed brominations in chloroform were found to be essentially temperature independent. The iodine bromide-catalyzed reactions have slightly negative energies of activation. The entropies of activation for both the catalyzed and uncatalyzed processes are highly negative as is to be expected for reactions which are third order. Very small positive energies of activation have been reported for the reaction of chlorine with aromatic ethers in chloroform.¹⁴ That is, halogenations in chloroform, like those in carbon tetrachloride^{3,5} and like halogen additions to olefins in non-polar media,¹⁵ have very low (or negative) activation energies. The fact that negative activation energies are observed can be attributed to the participation of molecular complexes, the formation of which is mildly exothermic, in rate-determining processes.¹⁶ The third-order bromination of mesitylene (second order in bromine) in acetic acid, in contrast to the corresponding reaction in chloroform, has an appreciable positive activation energy, $E_a = 6.8$ kcal./mole.¹ The fact that this figure for reaction in acetic acid is relatively high may be explained on the assumption that intermolecular attractive forces between solvent molecules must be overcome to a substantial degree in order that the solvent can participate in stabilization of the activated complex. Presumably such forces are considerably higher in acetic acid than in chloroform.

TABLE IV
ACTIVATION ENERGIES AND ENTROPIES FOR THE CATALYZED AND UNCATALYZED REACTIONS IN CHLOROFORM^a

ArH	Uncatalyzed		1Br catalyzed	
	E_a , kcal./mole	ΔS^\ddagger , e.u.	E_a , kcal./mole	ΔS^\ddagger , e.u.
Pentamethylbenzene	0	-59	-1.94	-54
Mesitylene	0	-64	-2.76	-61
Durene	+1.4	-55

^a Based on k_2 values of Table III for runs in which the concentrations of pentamethylbenzene, mesitylene and durene were 0.1, 0.2, and 0.4 *M*, respectively.

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