must orient dipoles in its vicinity. There will be an orientation of solvent molecules in front of the moving ion and a relaxation to random orientation behind it. The steady state will correspond to a net excess of oriented dipoles behind the moving ion and a deficiency in front, due to the non-zero viscosity of the medium, and the ion therefore carries an electrostatic brake with itself in any polar solvent. This effect is at least part of the reason why $\Lambda_0\eta$ is not a true constant, as it would be if the Stokes model were valid.

Finally, a suspected property of the picrate ion can be deduced from the conductance data. The ion is electrically asymmetrical; to first approximation, we may neglect (as a mutually cancelling vector sum) the dipole moments of the three nitro-groups. The net negative charge is, of course, distributed over the entire structure, but it must be an unsymmetrical distribution, leaving a fairly strong dipole with the negative end at the oxygen atom at position 1. From the J values of systems 1–3, we found $\mathring{a}$ = 5.31. From the slope of Fig. 3, we obtain the smaller value of 3.18, if we assume that K_A is given by equation 1. If, however, a dipole field is also involved, (1) should be replaced[23] by

$$\ln K_A = \alpha + e^2/DkTa + \mu e/DkTd^2 \quad (16)$$

where μ is the dipole moment of the picrate ion and d is the distance parameter in the dipole term in the potential energy at contact of anion and cation. The slope of the log K_A *vs.* $1/D$ plot then is

$$d \log K_A/dD^{-1} = 0.4343(e^2/akT + \mu e/d^2kT) \quad (17)$$

Using the experimental value of 176 for the slope from Fig. 3 and $\mathring{a}$ = 5.31, equation 17 gives 0.61 for the ratio μ_D/d^2_A (moment in debyes, distance in Å.). This ratio appears to be quite reasonable; if the distance from the center of the cation to the center of the dipole in the picrate ion is set equal to 2 Å., for example, we obtain a moment of 2.4 for the latter.

[23] See discussion of sodium bromate, ref. 10.

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The Influence of Solvent on the Rate of Aromatic Chlorination

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RECEIVED JULY 31, 1958

In ethylene dichloride the rate of toluene chlorination is extremely slow at room temperature unless a polar catalyst is present. In the presence of added hydrogen chloride the reaction is first order with respect to each reactant and to the catalyst. The rate of simple bimolecular nuclear chlorination of toluene at 25° varies with solvent in the order, $ClCH_2CH_2Cl \ll (CH_3CO)_2O \sim CH_3COOH \sim CH_3CN < CH_3NO_2$. The activation energies, excluding that for ethylene dichloride which must be very large, fall off in the order $CH_3COOH > (CH_3CO)_2O > CH_3CN > CH_3NO_2$. The activation entropy for the reaction in the hydroxylic solvent, acetic acid, is much less negative than in more polar non-acidic media. The reaction is actually more rapid in acetic acid than in acetic anhydride. The activation energy for aromatic hydrocarbon chlorination in a given solvent varies in the order, benzene > toluene > *m*-xylene. The variation in the entropies of activation in this series is very small.

The activated complex for electrophilic halogenation of the aromatic nucleus is presumed to be an aggregate of molecules of the benzenoid compound, the halogen and an additional substance. The primary function of this additional substance is to assist rupture of the bond between the two atoms of the halogen molecule.[1] In a medium of low polarity, such as carbon tetrachloride, the halogen or hydrogen halide may serve as the third member of the aggregate as evidenced by the fact that the reactions are of higher than first order in halogen or are autocatalytic.[2] When, alternatively, a polar medium is used, the order with respect to halogen may drop to unity and the sensitivity of the reaction to catalysis by extraneous polar substances is reduced. In this case the solvent itself may serve as the third component of the activated complex.

To obtain more detailed information concerning the contribution of a polar solvent to the activation process for aromatic halogenation the energies and entropies of activation for the chlorination of toluene in several different media of widely varying polarity have been determined. Chlorine, rather than another of the halogens, has been used since its reactions with aromatic hydrocarbons are usually first order in halogen and are, except in carbon tetrachloride,[2] insensitive to hydrogen halide.[3] A few measurements to determine the influence of temperature changes on the rate of chlorination of *p*- and *m*-xylenes have been conducted. Comparative values for the activation energies and entropies of halogenation of the entire series of methylbenzenes are potentially of considerable theoretical interest.[4] Because of extreme variations in reactivity of these hydrocarbons, a complete set of such constants was not obtainable by the methods of this investigation.

Experimental

Materials.—The aromatic hydrocarbons were obtained from commercial sources and were purified as described previously.[5] Procedures used in preparing hydrogen chloride and dry acetic acid have been reported earlier.[3a]

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[1] For recent pertinent discussions see (a) P. W. Robertson, *J. Chem. Soc.*, 1267 (1954); (b) H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 6292 (1953); (c) R. M. Keefer, A. Ottenberg and L. J. Andrews, *ibid.*, **78**, 255 (1956); (d) E. Berliner and M. C. Beckett, *ibid.*, **79**, 1425 (1957).

[2] See, for example, L. J. Andrews and R. M. Keefer, *ibid.*, **79**, 1412, 5169 (1957).

[3] (a) R. M. Keefer and L. J. Andrews, *ibid.*, **79**, 4348 (1957); (b) H. C. Brown and L. M. Stock, *ibid.*, **79**, 5175 (1957).

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

[5] N. Ogimachi, L. J. Andrews and R. M. Keefer, *ibid.*, **78**, 2210 (1956).

All solvents other than acetic acid were pretreated with chlorine to remove reactive impurities. Eastman Organic Chemicals nitromethane which had stood overnight after gassing with chlorine was distilled twice through a two foot Vigreux column, and early fractions were rejected. The chlorine free distillate was fractionated through a four foot column packed with glass helices, b.p. 101.2° (754 mm.). A similar procedure was used in purifying Eastman Organic Chemicals spectro grade nitromethane, b.p. 82.0° (760 mm.), and Baker and Adamson reagent grade acetic anhydride, b.p. 138.5–139.0° (760 mm.). The same method was used in purifying Matheson Co. ethylene dichloride, b.p. 83.5–83.7° (762 mm.), except that unreacted chlorine was removed by shaking the solvent with aqueous potassium iodide and then with a dilute sodium thiosulfate solution. The solvent was dried over calcium chloride before fractionation.

Some batches of the various solvents were exposed to ignited (300°) Drierite for at least a week before use to reduce the trace water content.

The Kinetic Studies.—The rates of chlorination of the hydrocarbons were followed spectrophotometrically using paraffin sealed 1 cm. or 10 cm. glass stoppered silica absorption cells as the reaction vessels. The chlorine concentrations of the reaction mixtures during the course of the runs were determined from optical density measurements at a fixed wave length (340–380 mμ) against the solvent as a blank. The wave lengths were chosen to provide initial readings between 1.0–0.25.

A number of simulated runs were conducted to check temperature variations which occurred within the cells during the actual rate experiments. The test results indicated that recorded run temperatures were generally accurate to ±0.1° except for runs with *m*-xylene in 10 cm. cells in the 40° region, which were accurate to ±0.2°.

Most runs were followed to completion. Recorded optical densities were corrected for any small absorption by the aromatic hydrocarbon as deduced from readings at infinite time or by separate measurements of hydrocarbon solutions. Except as later noted the optical densities of dilute solutions of chlorine of concentrations comparable to those used in the rate work changed negligibly over the time intervals of even the longest runs.

In runs with ethylene dichloride in which hydrogen chloride was initially present, the concentration of the catalyst was obtained by base titration of samples removed from the absorption cell at termination of reaction. Separate test showed that hydrogen chloride had no effect on the optical density of solutions of chlorine in ethylene dichloride in the wave length region used in this work.

In some solvents the extinction coefficients of chlorine were somewhat enhanced when the aromatic hydrocarbon concentration was increased to high values (0.5–1 *M*). In runs in which this phenomenon was observed the hydrocarbon concentration was always much greater than that of the chlorine and remained essentially constant during the run. The measured optical densities were, therefore, directly proportional to the chlorine concentrations throughout the runs. Other pertinent details are given in an earlier publication.[3]

The Reaction Products.—Although the chlorotoluenes were not isolated in the pure state, the products of reaction of chlorine and toluene in the various solvents were examined to determine the extent to which side chain as opposed to nuclear halogenation occurred under conditions approaching those used in the rate runs. The reaction in acetic acid was not investigated since it previously has been reported to provide good yields of monochlorotoluenes containing small quantities of benzyl chloride.[3b]

In a typical experiment a solution of toluene (1.62 *M*), chlorine (0.159 *M*) and hydrogen chloride (0.10 *M*) in a total volume of 58 ml. in ethylene dichloride was stored in the dark for three days. The solution was then washed with water and dilute aqueous sodium bicarbonate and dried over calcium chloride. The solution was freed of ethylene dichloride by slow fractionation through a small Vigreux column. The last fraction of the distillate, b.p. 95–111°, was mainly toluene and gave only a faint precipitate when treated with hot alcoholic silver nitrate. The boiler residue was heated with alcoholic silver nitrate, and the precipitated silver chloride, which was presumed to derive from side chain halogenation product, was collected and weighed.

Appropriate modifications in this technique were made to analyze the reaction products in other solvents. The results are summarized in Table I.

TABLE I

SIDE CHAIN HALOGENATION IN THE CHLORINATION OF TOLUENE

Solvent	$(\mathrm{Cl_2})_i$, mole/l.	(Toluene)$_i$, mole/l.	Side chain halogenation,[a] %
Ethylene dichloride	0.159	1.62[b]	20
Nitromethane	.120	0.87	15
Nitromethane	.124	.87	11[c]
Acetonitrile	.123	.85	3
Acetic anhydride	.142	.85	6

[a] Moles AgCl × 100/moles of initial chlorine. [b] $(\mathrm{HCl})_i$ = 0.10 *M*. [c] Reaction carried out at 0°. All other reactions were at room temperature.

Results

The Chlorination of Toluene in Ethylene Dichloride.—Ethylene dichloride is significantly more polar[6] than carbon tetrachloride and presumably should be a more effective medium for promotion of electrophilic aromatic halogenation than the tetrahalide. However, as was noted for the reaction of pentamethylbenzene and chlorine in carbon tetrachloride, the rate of chlorination of toluene in ethylene dichloride is strongly dependent on the availability of a polar substance to serve as a catalyst.

In ethylene dichloride which had been subjected to no accessory drying procedures the rate of disappearance of chlorine from a solution containing a large excess of toluene remained essentially constant over the first 50% of reaction (which took 10 hr.). In a run which was identical except that the solvent had been exposed to calcium sulfate (Drierite) before use, less than 10% of the chlorine disappeared over a 12 hr. period. Presumably traces of water induce a side reaction to form hydrogen chloride, which functions as a catalyst. When hydrogen chloride was present at high concentrations (0.1 *M*) at the start of the reaction, the chlorination rate was extremely rapid and was the same in duplicate runs using dried and undried solvent.

A series of more quantitative runs were made in which hydrogen chloride was present initially in large excess over chlorine in the reaction mixtures. Rate constants were calculated assuming the integral rate law

$$\frac{kt}{2.3} = \frac{1}{(\mathrm{ArH})_i - (\mathrm{Cl_2})_i} \log \frac{(\mathrm{Cl_2})_i(\mathrm{ArH})}{(\mathrm{ArH})_i(\mathrm{Cl_2})} \qquad (1)$$

which generally held to well over 50% of complete reaction in individual runs. Values of $k/(\mathrm{HCl})_f$, where $(\mathrm{HCl})_f$ represents the concentration of hydrogen chloride at the end of a run, were relatively independent of the initial concentrations of the reactants. In other words the chlorination of toluene in ethylene dichloride is first order with respect to halogen, to hydrocarbon and to the catalyst. A summary of rate constants for the hydrogen chloride catalyzed runs at 25° and at 1.6° is given in Table II. The rate of reaction is not markedly in-

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(6) The dielectric constants of ethylene dichloride and of carbon tetrachloride are, respectively, 10.65 and 2.24 at 20°; see J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 43.

TABLE II

THE HYDROGEN CHLORIDE CATALYZED CHLORINATION OF TOLUENE IN ETHYLENE DICHLORIDE

(Toluene), mole/l.	$10^3(Cl_2)_i$, mole/l.	$(HCl)_f$, mole/l.	$10^3k/(HCl)_f$, l.^{2} mole^{-2} sec.$^{-1}$
	25.0°		
0.730	9.49	0.122	4.3
.730	9.40	.127	4.4[a]
.730	5.10	.091	4.4
.730	5.05	.0456	4.1
.730	4.52	.121	4.2[a]
.730	4.12	.109	4.4
.730	2.26	.111	4.5[a]
.730	1.77	.106	4.3
.723	1.51	.0268	3.6[a]
.362	6.41	.114	5.05[a]
.181	6.54	.115	5.45[a]
	1.6°		
.744	5.89	.133	2.54[a]
.372	5.91	.130	2.82[a]
.186	5.78	.126	3.01[a]

[a] Runs in which the solvent had been exposed to Drierite.

fluenced by temperature as is the case for other catalyzed aromatic chlorination and bromination reactions in non-polar solvents.

Uncatalyzed Reactions in Other Solvents.—The activation energy for uncatalyzed chlorination of toluene in ethylene dichloride apparently is much too high for reaction to occur at a significant rate at room temperature. In acetic acid, acetic anhydride, acetonitrile or nitromethane the simple second-order reaction occurs relatively rapidly. A summary of rate constants, k (see equation 1), for reactions of toluene and a few other aromatic hydrocarbons in these solvents are summarized in Table III.

TABLE III

SECOND-ORDER RATE CONSTANTS[a] FOR CHLORINATION OF AROMATIC COMPOUNDS IN VARIOUS SOLVENTS

$10^3(ArH)_i$, mole/l.	$10^3(Cl_2)_i$, mole/l.	Temp., °C.	10^3k, l. mole^{-1} sec.$^{-1}$
	Toluene in acetic acid		
406	7.75	25.2	0.70
203	7.73	25.2	.82
101.5	7.73	25.2	.88
398	7.96	45.4	3.04
199	8.04	45.4	3.60
99.5	7.76	45.4	3.74
	m-Xylene in acetic acid		
3.12	0.651	26.0	421
1.56	.657	25.8	375
3.06	.690	43.1	996
1.53	.711	43.3	896
	Toluene in acetic anhydride		
723	13.42	25.0	0.30
723	6.39	25.0	.29
723	3.12	25.0	.28
362	6.50	25.0	.35
181	6.42	25.0	.39
90.5	6.15	25.0	.44
710	12.5	45.4	.80
710	6.04	45.4	.77
710	2.98	45.4	.77
358	7.61	45.4	.94
96	7.31	45.4	1.16
	Benzene in acetonitrile		
657	12.92	25.0	0.00091
328	12.88	25.0	0.00090
	Toluene in acetonitrile		
727	16.4	25.0	1.30
727	7.09	25.0	1.16
727	3.51	25.0	1.12
745	18.7	25.0	1.24[b]
373	18.4	25.0	1.58[b]
364	16.3	25.0	1.49
182	16.2	25.0	1.64
710	17.8	45.4	3.00
710	6.78	45.4	2.80
710	3.57	45.4	2.71
355	18.2	45.4	3.50
177	15.1	45.4	3.72
	p-Xylene in acetonitrile		
79.5	14.44	25.0	10.6
79.5	7.11	25.0	9.3
40.0	7.32	25.0	9.8
20.0	7.45	25.0	9.9
77.9	15.58	45.4	24.3
77.9	6.94	45.4	21.4
39.0	7.82	45.4	22.5
19.5	7.14	45.4	25.2
	m-Xylene in acetonitrile		
11.00	5.44	25.1	1730
2.28	0.505	25.2	1530
1.14	.511	25.1	1590
2.24	.525	41.9	2240
1.12	.540	42.5	2530
	Toluene in nitromethane		
732	35.8	25.0	9.6
724	32.8	25.0	10.0[b]
362	33.8	25.0	11.4[b]
366	69.4	25.0	10.8
366	35.4	25.0	10.4
366	18.0	25.0	10.6
183	32.8	25.0	12.4
373	37.4	1.5	4.9
187	35.6	1.5	5.3
93.5	35.0	1.5	5.5
	Benzene in nitromethane		
662	28.9	25.0	0.0068
662	28.6	25.0	.0054
331	13.4	25.0	.0075

[a] $-d(Cl_2)/dt = k(ArH)(Cl_2)$. [b] The solvent was exposed to Drierite for one week before use.

With the exception of the reactions in nitromethane the individual rate runs followed equation 1 to very high percentages of completion. The reaction in nitromethane at 25° must be somewhat susceptible to hydrogen chloride catalysis since in some runs, particularly those with high initial concentrations of chlorine, the constants increased somewhat with time. This behavior was not encountered at 1.5°. Rate constants reported for runs in this medium at the higher temperature are actually based on data taken up to about 50% of completion of reaction.

The rate constants for chlorination of toluene and *m*-xylene in acetic acid at 25° are slightly higher than those reported previously.[3] Presumably the differences result from slight differences in water content of the solvent used in the several sets of experiments. A few runs in nitromethane and in acetonitrile were made using solvent which had been exposed to Drierite before use. Within the limits of error the observed rate constants agreed with those for runs with solvent which had not been treated with the drying agent.

As described in details in the Experimental section the products of toluene chlorination in the various solvents were examined to establish that nuclear rather than side chain halogenation was the predominant reaction occurring under the conditions of the rate runs. Generally speaking the percentages of benzyl halide in the product were small, although the figure rose to 20% in the case of the hydrogen chloride catalyzed reaction in ethylene dichloride.

When data were available (Table III), the energies and entropies of activation were calculated.[7] These are summarized in Table IV. For reactions at high concentrations of aromatic substance (those of toluene in nitromethane, acetic acid, acetic anhydride and acetonitrile) the rate constants varied somewhat with changing hydrocarbon concentration. In these cases the activation energies were calculated using k values obtained at two temperatures for runs of the same aromatic hydrocarbon concentration. Values of E_a which were so obtained were independent of the aromatic hydrocarbon concentration within the limits of error. The corresponding entropies of activation were calculated using extrapolated values of $k_{25°}$ for the reactions at infinite dilution of the hydrocarbon.[8]

TABLE IV

ACTIVATION ENERGIES AND ENTROPIES FOR AROMATIC HYDROCARBON CHLORINATION

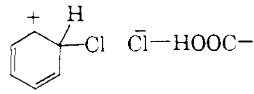
Aromatic	Solvent[a]	$10^3 k_{25°}$, l. mole sec.$^{-1}$	E_a, kcal./mole	$-\Delta S^‡$, e.u.
Toluene	Ethylene dichloride (10.65)	Very small[b]	Large[b]	..
Toluene	Acetic acid (6.15)	0.8	13.0	30.4
Toluene	Acetic anhydride (20)	0.3	9.1	45.0
Toluene	Acetonitrile (37.5)	1.5	7.9	46
Toluene	Nitromethane (37.5)	10	5.6	50
m-Xylene	Acetonitrile	1600	4.6	43
p-Xylene	Acetonitrile	10	7.7	44
m-Xylene	Acetic acid	400	9.4	30.6
Benzene[c]	Trifluoroacetic acid (8.5)[d]	7	11.4	32

[a] Figures in parentheses are the solvent dielectric constants at 20°; values are from Hine's book[6] unless other wise stated. [b] For the uncatalyzed reaction. [c] From t data of ref. 2. [d] F. E. Harris and C. T. O'Konski, THIS JOURNAL, 76, 4317 (1954).

It has been stated that the activation energies for halogenations increase as the polarity of the medium is increased.[2] This is true only when one compares values for reactions such as the hydrogen chloride catalyzed aromatic hydrocarbon chlorination in carbon tetrachloride and the simple second-order chlorination of hydrocarbons in acetic acid. The results reported in Table IV indicate that the activation energy for the uncatalyzed reaction diminishes appreciably as the dielectric constant of the solvent increases. This is reasonable for a reaction in which the activated complex is more polar than the reactants.[9]

The activation energy for toluene chlorination in acetic acid must be considerably less than that in ethylene dichloride, and yet the latter solvent has a somewhat higher dielectric constant than the acid. This is in accord with the generalization that hydroxylic solvents are usually good electrostatic solvating agents.[10] Trifluoroacetic acid, which is not significantly more polar than acetic acid, must serve even more effectively in solvation of the activated complex, since the activation energy for benzene chlorination in the fluorinated solvent is of the order of 2 kcal./mole less than that for toluene chlorination in the unsubstituted acid. The difference in the activation energies for chlorination of toluene in these two solvents would undoubtedly be larger than this figure.

As has been noted previously[2] the superiority of the moderately strong[11] fluorinated acid as a solvent very likely results from its capacity to share protons with the departing halide ion in the activated complex, as depicted below.



The activation energy for toluene chlorination decreases (by 4 kcal./mole) as the solvent is changed from acetic acid to acetic anhydride. Yet the rate constant at 25° is slightly lower for the anhydride medium than for the free acid. The process of solvation of the activated complex by the more polar solvent is accompanied by an entropy loss which is sufficiently large to offset completely the favorable influence of the lower activation energy on the rate.

The entropies of activation for this reaction in acetonitrile and nitromethane are also highly negative. The activation energy in nitromethane is, however, low enough so that the rate is considerably faster at 25° than in any of the other solvents.

The E_a value for reaction in acetonitrile is over 2 kcal./mole greater than that for reaction in nitromethane although the dielectric constants for the two media are the same. Even if one discounts the hydrogen bonding type solvents, it seems likely that as for other polar processes the effects of medium changes on activation energies are only qualitatively explained on the basis of simple electrostatic considerations.[12] One may question whether this activation energy difference is of real significance since in the reaction in nitromethane, like that in ethylene dichloride, the extent of side chain halogenation is appreciable (about 15% at room temperature). However, in the reaction at 0° the extent of side chain halogenation is approximately the same (11%—see Table I). Therefore even if nuclear and side chain substituted products are

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(7) The equations $E_a = [2.3RT_1T_2/(T_2 - T_1)] \log k_2/k_1$ and $\Delta S^‡ = 2.3R(\log k_{25°} - \log 6.21 \times 10^{12} + E_a/2.3RT - 1/2.3)$ were used in determining energies and entropies of activation.

(8) It was found empirically that a plot of log k *vs.* toluene concentration was linear. To eliminate the effect of variations in toluene concentration on rate constants, the intercept of this line at zero molar toluene was used in calculating $\Delta S^‡$.

(9) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 345.

(10) E. Gelles, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2918 (1954).

(11) J. E. B. Randles and J. M. Tedder, *ibid.*, **55**, 1218 (1955).

(12) *Cf.* J. E. Leffler, *J. Org. Chem.*, **20**, 1209 (1955).

formed by different processes, the E_a value for nuclear chlorination of toluene in nitromethane is probably closely represented by the figure given in Table IV, which is based on rate measurements at 1.5 and 25.0°.

The effects of solvent on the rate of toluene chlorination call to mind certain observations concerning the formation of iodobenzene dichloride from the second-order reaction of the halobenzene and chlorine.[13] Dichloride formation is extremely slow in carbon tetrachloride in the absence of a polar catalyst. In trifluoroacetic acid reaction occurs too rapidly for rate measurement at room temperature. In acetic acid and in nitromethane the reaction occurs at conveniently measurable rates which are almost the same. In nitromethane, however, the activation energy and entropy are, respectively, 10 kcal./mole and 34 e.u. less than in acetic acid. As is the case for toluene chlorination in certain strongly polar media the entropy loss attending the electrostatic solvation of the activated complex is sufficiently large so that the qualitative assumption[9] that the activation energy change with change in solvent will dominate the rate picture does not uniformly apply.

Because of the striking similarities in the kinetic influences of changes in media on iodobenzene dichloride formation and aromatic chlorination, it seems likely that the activated complexes for the two reactions must be closely related electronically. The earlier proposal that dichloride formation, as induced by polar solvents or catalysts, occurs through the electrophilic attack of chlorine on the iodine atom of iodobenzene is undoubtedly correct.[14]

Although the supporting evidence is very limited, it appears that the effect of introducing ring methyl substituents on the rate of aromatic hydrocarbon chlorination in a given solvent is controlled almost entirely by activation energy (and not entropy) changes. The rates of chlorination of toluene and *m*-xylene in acetic acid differ by 500-fold but the entropies of activation are virtually identical. It is interesting that these entropies are also in close agreement with that ($\Delta S^{\ddagger} = -29.6$ e.u.) reported for the chlorination of a large number of *para*-substituted phenolic ethers in 99% acetic acid.[15] In addition a value of $E_a = 17.0$ kcal./mole for the chlorination of benzene in 99% acetic acid has been reported.[16] A corresponding value of $\Delta S^{\ddagger} = -30$ e.u. may be calculated from the available data. The same conclusion may be drawn from results obtained with acetonitrile as solvent. The entropies of activation for reaction of toluene, *p*-xylene and *m*-xylene vary over only a 3 e.u. range. Yet the rates of reaction of toluene and *m*-xylene differ by a factor of 10^3.

If the solvent rather than the benzene derivative is changed, both E_a and $\Delta S^{\ddagger}$ may be influenced. As has been noted already, the activation energy for chlorination of toluene in acetic acid is significantly larger than that for reaction in acetic anhydride, acetonitrile or nitromethane; the entropy of activation for reaction in acetic acid is much less negative than for these other solvents. Two alternate explanations seem feasible. Either the reactants and/or the solvent are subject to unusually severe physical restraint in activated complexes which have very small energies of formation or the entropy of activation in the acidic medium is abnormally high because the breakup of solvent dimers precedes the inclusion of acetic acid molecules in the activated complex.

Acknowledgment.—The authors are indebted to the National Science Foundation for a grant in support of this research.

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[13] R. M. Keefer and L. J. Andrews, THIS JOURNAL, **80**, 5350 (1958).

[14] For a detailed discussion of the proposed mechanism for iodobenzene dichloride formation see ref. 13 and preceding papers.

[15] B. Jones, *J. Chem. Soc.*, 418 (1942).

[16] P. B. D. de la Mare and P. W. Robertson, *ibid.*, 279 (1943).