160 ± 1 and 0 ± 0.1; 0 ± 0.1 and 305 ± 7. Extinction coefficients tabulated above for the deuterium compounds are for the pure materials. The figures were obtained from the data on the mixtures of deuterium and protium compounds actually used by assuming that the "pure" deuterium compound absorbed only negligibly at at least one of the maxima for the protium compound.[27] From this assumption the percentage of deuteration of the actual haloform sample was calculated as follows: $CDCl_2I$ 85.1%, $CDBr_2Cl$ 93.0%, CDBrClF 95.9%, $CDBr_3$ 99.4% and CDI_3 55.7%. These values are minima and will be higher if the assumption is wrong. While the correctness of the assumption can influence the values of k obtained with bromochlorofluoromethane, it is obvious that the assumption cannot be wrong by more than 4% in this case. Furthermore, if the assumption were seriously in error the values of k should show a large drift with time. For those haloforms whose hydrolysis occurs at a rate negligible compared to that of the deuterium exchange, the following argument shows that the values of k obtained are completely independent of the validity of the assumption that the pure deuterium compound does not absorb at the protium maximum. If the assumption is incorrect the calculated fraction of deuteration of haloform will be in error. Let us denote this calculated fraction as p/r, where p is the true value. Since our values of p/r and of ϵ^{CDX_3} are obtained from measurements on samples of known total haloform concentration $(H + D)$ they are related to the optical density as

optical density =

$$l\left[\frac{p}{r}\,\epsilon^{CDX_3}(H + D) + \left(1 - \frac{p}{r}\right)\epsilon^{CHX_3}(H + D)\right]$$

The optical density may also be expressed in terms of ϵ^{CDX_3*}, the *true* extinction coefficient for the deuterohaloform.

optical density =

$$l\,[p\epsilon^{CDX_3*}(H + D) + (1 - p)\epsilon^{CHX_3}(H + D)]$$

Eliminating the optical density between these two equations and solving for r

$$r = \frac{\epsilon^{CDX_3} - \epsilon^{CHX_3}}{\epsilon^{CDX_3*} - \epsilon^{CHX_3}}$$

This shows that r, the ratio of the true fraction of deuteration to the value we used, is a constant, independent of the haloform concentration and of p. In equation 1 we have the term

$$\log\left(p_0 + p_0\frac{H}{D}\right)$$

which can be written $\log (p_0/p)$. Instead of this we have been using $\log (p_0/r)/(p/r)$ which is, of course, identical.

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[27] This means that the *apparent* extinction coefficient of the deutero compound is the negative of the *actual* extinction coefficient of the solvent.

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

The Reaction of Alkylbenzenes with Iodine Monochloride in Carbon Tetrachloride and in Trifluoroacetic Acid

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The kinetics of nuclear iodination of methylbenzenes with iodine monochloride in carbon tetrachloride and in trifluoroacetic acid have been compared. In carbon tetrachloride mesitylene and pentamethylbenzene react by a process which is third order in halogen. The activation energies for both reactions are slightly negative. In trifluoroacetic acid the reactions of toluene and p-xylene are first order in halogen. The activation energy of the toluene reaction is 12.7 kcal. The reactions in this solvent are accompanied by consecutive reactions in which the aromatic iodide is subject to further halogenation. The transition state intermediate for the reaction in trifluoroacetic acid undoubtedly includes solvent molecules which assist the rupture of the iodine–chlorine bond of the substituting halogen molecule. It seems probable that in carbon tetrachloride an aggregate of halogen molecules has a similar function.

To promote the electrophilic attack of halogen on an aromatic molecule in a non-aqueous solvent a third reactant, the function of which is to weaken the halogen–halogen bond, seems commonly to be required. In non-polar solvents an aggregate of several halogen molecules must fill this role, since reaction orders with respect to halogen are ordinarily high in such media.[1] Indeed the iodine bromide catalyzed bromination of mesitylene in carbon tetrachloride appears to be exactly third (first in bromine and second in catalyst) order with respect to halogen.[2,3] In acetic acid mesitylene reacts with bromine and with iodine monochloride by processes which are second order in halogen.[4] In this solvent the over-all bromination reaction receives small contribution from a reaction which is first order in bromine and in which acetic acid itself probably functions as the required third reactant. This first-order term becomes tremendously more important when small amounts of water are added to the medium.[5] It seems likely that the water, as does zinc chloride in acetic acid,[4c,6] also enhances the first-order reaction by direct participation in the rate-determining step rather than solely through the imposition of a favorable dielectric effect.[7]

Studies of this strong dependence of halogen order in aromatic substitution reactions on the nature of the solvent have now been extended to in-

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[1] (a) L. Bruner, *Z. physik. Chem.*, **41**, 415 (1902); (b) P. W. Robertson, J. E. Allen, K. N. Haldane and M. G. Simmers, *J. Chem. Soc.*, 933 (1949); (c) T. Tsuruta, K. Sasaki and J. Furukawa, THIS JOURNAL, **76**, 994 (1954).

[2] J. H. Blake and R. M. Keefer, *ibid.*, **77**, 3707 (1955).

[3] Bromine itself seems incapable of more than first-order participation in an aromatic substitution in carbon tetrachloride. Reaction does not occur unless traces of water are present. See R. M. Keefer, J. H. Blake and L. J. Andrews, *ibid.*, **76**, 3062 (1954).

[4] (a) L. J. Lambourne and P. W. Robertson, *J. Chem. Soc.*, 1167 (1947); (b) R. M. Keefer, A. Ottenberg and L. J. Andrews, THIS JOURNAL, **78**, 255 (1956); (c) R. M. Keefer and L. J. Andrews, *ibid.*, **89**, 5623 (1956).

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

[6] L. J. Andrews and R. M. Keefer, *ibid.*, **78**, 4549 (1956).

[7] The kinetics of aromatic halogenations in *pure* water as solvent have been studied in detail in recent years. See E. Berliner, THIS JOURNAL, **72**, 4003 (1950); **73**, 4307 (1951); **78**, 3632 (1956), for a series of interesting papers on the subject.

clude iodinations with iodine monochloride in both carbon tetrachloride and trifluoroacetic acid. The reactions of mesitylene and pentamethylbenzene in the former solvent have been investigated to verify the halogen order of three, observed for the iodine bromide catalyzed bromination of mesitylene in carbon tetrachloride, under the kinetically less complex condition that only one type of halogen is present in the medium. Trifluoroacetic acid has been used as a solvent for the reactions of toluene and *p*-xylene to determine the effect of a moderately acidic[8] medium of relatively low dielectric constant[9] on the halogenation rate law.

Experimental

Materials.—The aromatic hydrocarbons and iodine monochloride samples were prepared and purified as indicated previously.[4c] A freshly opened bottle of Eastman Organic Chemicals sulfur-free carbon tetrachloride was used without further purification. Eastman Organic Chemicals trifluoroacetic acid was purified by a procedure described elsewhere.[10] A sample of 2-iodo-1,4-dimethylbenzene, also from Eastman Organic Chemicals, was distilled, b.p. 78–81° (3 mm.), before use.

Reaction Rates in Carbon Tetrachloride.—The rates of reaction of iodine monochloride with mesitylene and pentamethylbenzene in carbon tetrachloride were followed spectrophotometrically. Rate samples, prepared from stock solutions held at the temperature of the runs, were placed (in 1 cm. absorption cells) in the housing of the Beckman spectrophotometer. Temperatures during the runs were controlled to ±0.1°. In most cases the runs were followed to at least 70% of completion. In runs at 45.7 and 1.6° the samples were allowed five minutes to equilibrate to the housing temperature before rate measurements were made. Measurements of the optical densities of the solutions as a function of time were made at two wave lengths, 450 and 520 mμ. This procedure was necessary to establish the changes in iodine monochloride concentrations during the course of the runs, since small amounts of iodine produced during the runs absorbed in the region of the spectrum measurements. The iodine monochloride concentrations at any given time were calculated from measured optical densities d_{450} and d_{520}, using equations 1 and 2.

$$d_{450} = \epsilon_{\mathrm{ICl}}(\mathrm{ICl}) + \epsilon_{\mathrm{I_2}}(\mathrm{I_2}) \qquad (1)$$

$$d_{520} = \epsilon'_{\mathrm{ICl}}(\mathrm{ICl}) + \epsilon'_{\mathrm{I_2}}(\mathrm{I_2}) \qquad (2)$$

In general the aromatic hydrocarbon concentration was in large excess over the halogen concentration. The extinction coefficients, ϵ and ϵ', for the two halogens at the two wave lengths varied somewhat with the aromatic hydrocarbon content of the solutions. A few runs were made in which initial reactant concentrations were equal but small enough so that the extinction coefficients of the halogens in hydrocarbon-free solutions could be used in interpreting the rate data by equations 1 and 2.

In runs with mesitylene at 25°, about 3.2% of the iodine monochloride was converted to iodine. In the runs with pentamethylbenzene at 25° about 18% of the reacting halogen was converted to iodine. The fraction of the reacting halogen which appeared as iodine did not vary appreciably during the course of individual runs nor did it change with changes in initial reactant concentrations.

One run on mesitylene was duplicated using as the solvent a sample of carbon tetrachloride which had been equilibrated with water. The rates of the two runs were the same within experimental error.

Reaction Rates in Trifluoroacetic Acid.—The general procedures for the runs with toluene and *p*-xylene were similar to those described for following iodinations in carbon tetrachloride. The changes in iodine monochloride concentration with time were established by making optical density measurements at 460 mμ. Under the conditions of the rate runs less than 5% of the iodine monochloride reacted to produce iodine. This figure is based on the measured optical densities of the product solutions at 520 mμ. In calculating iodine monochloride concentrations during the course of the runs from optical density data corrections for the absorption by iodine were, where necessary, made by procedures similar to those described for the runs in carbon tetrachloride.

Although the formation of trihalide ion (or $\mathrm{HICl_2}$) as hydrogen chloride accumulates in the medium leads to a marked reduction in the reactivity of iodine monochloride as an iodinating agent in acetic acid,[4c] no such complication was observed for the runs in trifluoroacetic acid. Apparently trihalide ion formation does not occur in this medium, since the visible and near ultraviolet spectrum of a 4×10^{-3} *M* solution of iodine monochloride in trifluoroacetic acid is not markedly changed by the introduction of gaseous hydrogen chloride (0.09 *M* HCl) in the solution. It has been reported previously[11] that $\mathrm{ICl_2^-}$ dissociates completely in trifluoroacetic acid.

The Benzene–Iodine Monochloride Complex in Trifluoroacetic Acid.—The equilibrium constant for the formation of the 1:1 benzene–iodine monochloride complex in trifluoroacetic acid at 25.4° was determined spectrophotometrically by the usual[12] procedure. A series of solutions in which the benzene concentration varied from 0.05–0.4 *M* and the iodine monochloride varied from 0.8×10^{-3} to 4×10^{-3} *M* were prepared and measured against a trifluoroacetic acid blank at 284 mμ. The complex absorbs intensely in this region. Since the optical densities of the solutions changed slowly with time, each solution was measured several times during a short interval immediately following its preparation. The optical densities of the solutions at the time of mixing were then determined by extrapolation procedures. These values were corrected for the slight absorption of free benzene. A value for the equilibrium constant, $K = (\mathrm{C_6H_6{\cdot}ICl})/(\mathrm{C_6H_6})(\mathrm{ICl})$, of 0.53 l./mole and an extinction coefficient for the complex at 284 mμ of 9100 were calculated from the experimental data.

The Products of Reaction of Mesitylene and Pentamethylbenzene with Iodine Monochloride in Carbon Tetrachloride.—To establish the nature of the reaction products formed under experimental conditions which approximated those of the rate runs, the following experiments were performed:

To a solution of 1.48 g. (0.010 mole) of pentamethylbenzene in 50 ml. of carbon tetrachloride was added 1.62 g. (0.010 mole) of iodine monochloride. The addition was carried out in subdued light, and the resultant solution was stored in the dark overnight. The solution was then washed with water, freed of iodine by treatment with sodium thiosulfate solution and dried over calcium chloride. The carbon tetrachloride was removed under reduced pressure. The remaining yellow powder weighed 2.0 g. and melted over a wide range ending at about 115°. This material was recrystallized from ethanol to yield 1.33 g. of white crystals of m.p. 134–136° and mixed m.p. of 134–137° with an authentic sample[4c] of 6-iodo-1,2,3,4,5-pentamethylbenzene. An additional 0.2 g. of product was obtained by adding water to the mother liquor from the recrystallization. The over-all yield of purified product was 56%.

The reaction of 1.20 g. (0.010 mole) of mesitylene with 1.62 g. (0.10 mole) of iodine monochloride in carbon tetrachloride was carried out in essentially the same manner as was the pentamethylbenzene reaction. After washing and drying the solution of products (much less iodine was formed than with pentamethylbenzene), the carbon tetrachloride was evaporated under reduced pressure. The resultant mushy yellow crystals, after drying in a vacuum desiccator, weighed 1.14 g. (yield of crude product 46.4%). This material, after recrystallization from aqueous acetic acid, melted from 29–30° and gave a mixed m.p. of 29–30° with an authentic sample[4c] of 2-iodomesitylene.

The Product of Reaction of Mesitylene with Iodine Monochloride.—Iodine monochloride has a very low solubility in trifluoroacetic acid. For this reason it proved expedient to plan an experiment leading to an easily recognized solid, rather than a liquid product, in establishing that ring rather than side chain iodination occurs in this solvent. Therefore mesitylene, rather than the toluene or *p*-xylene used in the rate work, was chosen as the starting material.

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(8) J. E. B. Randles and J. M. Tedder, *J. Chem. Soc.*, **55**, 1218 (1955).

(9) W. Dannhauser and R. H. Cole, THIS JOURNAL, **74**, 6105 (1952).

(10) R. E. Buckles and J. F. Mills, *ibid.*, **75**, 552 (1953).

(11) R. E. Buckles and J. F. Mills, *ibid.*, **76**, 1845 (1954).

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

To a solution of 0.49 g. (4.1×10^{-3} mole) of mesitylene in 10 ml. of trifluoroacetic acid 50 ml. of 0.083 *M* iodine monochloride in trifluoroacetic acid was added dropwise with shaking over a one-half hour period. The reaction flask was wrapped to exclude light. The solution of the product, which was faintly pink because it contained traces of iodine, was then poured into 500 ml. of ice-water. The precipitated solid was filtered and dissolved in 50 ml. of ether. The ether solution was dried with calcium chloride and evaporated to dryness. The resultant white crystals, which weighed 0.67 g. (67% yield), melted at 31° and gave a mixed m.p. of 30-31° with 2-iodomesitylene.

Results

Iodination in Carbon Tetrachloride—The data for individual runs on the reactions of mesitylene and pentamethylbenzene with iodine monochloride in carbon tetrachloride conformed to the rate law

$$-d(\mathrm{ICl})_T/dt = k_{\mathrm{obs}}(\mathrm{ArH})(\mathrm{ICl})_T^3 \qquad (3)$$

The term $(\mathrm{ICl})_T$ is the sum of free and complexed iodine monochloride (equation 4).

$$(\mathrm{ICl})_T = (\mathrm{ICl}) + (\mathrm{ArH{\cdot}ICl}) \qquad (4)$$

For runs in which the aromatic hydrocarbon concentration was in large excess over the original iodine monochloride concentration plots of $(\mathrm{ICl})_T^{-2}$ *vs.* time were found to give straight lines. The slopes of these lines were measured as $k_{\mathrm{obs}}(\mathrm{ArH})/2$. For runs in which the initial concentrations of hydrocarbon and halogen were equal, plots of $(\mathrm{ICl})_T^{-3}$ *vs.* time also gave straight lines, the slopes of which were measured as $k_{\mathrm{obs}}/3$.

Figure 1, line 1, shows a plot of $(\mathrm{ICl})_T^{-2}$ *vs.* time for one of the runs with a large excess of mesitylene. That this run does not show a lower than third-order dependence on halogen is indicated by the non-linearity of a plot, shown in line 2 of Fig. 1, of $1/(\mathrm{ICl})_T$ *vs.* time.

The rate constants for the several runs on the two hydrocarbons are summarized in Table I.

TABLE I

RATE CONSTANTS FOR IODINATION IN CARBON TETRACHLORIDE

$10^3(\mathrm{ArH})_i$, mole/l.	$10^3(\mathrm{ICl})_{T_i}$, mole/l.	k_{obs}, mole^{-3} l.^{3} sec.$^{-1}$
Mesitylene, $t = 25.2°$		
712	2.58	7.37
712	5.16	7.40
712	10.32	7.34
356	5.26	21.6
142	5.26	57.6
71.2	2.63	93.4
10.2	10.2	188
$t = 45.6°$		
9.89	9.89	121
Pentamethylbenzene, $t = 25.2°$		
244	5.3	49.2
97.4	5.3	146
96.6	1.79	169
96.6	3.6	162
96.6	7.2	161
48.7	2.67	318
8.64	8.70	628
8.64	8.70	612
$t = 45.7°$		
8.35	8.41	512
8.35	8.41	532

Values of k_{obs} for runs of the same hydrocarbon concentration but with varying initial halogen concentration are generally in good agreement. These rate constants do, however, diminish with increasing hydrocarbon concentration of the solutions. This behavior is characteristic of aromatic halogenations in which the halogen engages in molecular complex formation with the aromatic reactant.[2,3] In the present case the variation in k_{obs} with (ArH) may be explained semi-quantitatively on the assumption that the iodination reaction proceeds by the mechanism[13,14] indicated in equations 5 and 6.

$$\mathrm{ArH} + \mathrm{ICl} \underset{}{\overset{K_1}{\rightleftarrows}} \mathrm{ArH{\cdot}ICl} \qquad K_1 = \frac{(\mathrm{ArH{\cdot}ICl})}{(\mathrm{ArH})(\mathrm{ICl})} \quad (5)$$

$$\mathrm{ArH{\cdot}ICl} + 2\mathrm{ICl} \xrightarrow{k_1} \mathrm{ArI} + \mathrm{HCl} + 2\mathrm{ICl} \quad (6)$$

Two molecules of halogen and a 1:1 aromatic–halogen complex are shown as the reactants in the rate-determining step (equation 6). This step might equally well be represented with iodine monochloride dimer, in place of two halogen molecules, as a reactant with only minor alteration in the discussion which immediately follows.[15] Equations 5 and 6 correspond to a rate law of the form

$$-d(\mathrm{ICl})_T/dt = k_1K_1(\mathrm{ArH})(\mathrm{ICl})_T^3/[1 + K_1(\mathrm{ArH})]^3 \quad (7)$$

The validity of equation 7 as an explanation of the experimental data was tested by solving for n in equation 8 using the observed rate constants (Table I) for both mesitylene and pentamethylbenzene.

$$k_{\mathrm{obs}} = k_1K_1(\mathrm{ArH})/[1 + K_1(\mathrm{ArH})]^n \qquad (8)$$

As is consistent with equation 8, plots of log $[1 + K_1(\mathrm{ArH})]$ *vs.* log $k_{\mathrm{obs}}/(\mathrm{ArH})$ for the two hydrocarbons were found to give straight lines.[16] From the slopes of these lines $(-n)$, n values of 2.4 for mesitylene and 2.9 for pentamethylbenzene were obtained, in fair agreement with the value of 3 which is consistent with equations 3 and 7. This result contrasts with that found for the iodine bromide catalyzed bromination of mesitylene in carbon tetrachloride. In that reaction both free and complexed iodine bromide appear to react with equal effectiveness in the rate-determining step[2] (equation 9).

$$\mathrm{ArH{\cdot}Br_2} + 2(\mathrm{IBr}, \mathrm{ArH{\cdot}IBr}) \xrightarrow{k} \mathrm{Products} \quad (9)$$

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[13] See references 1b and 1c for similar interpretations of high reaction orders in aromatic halogenation.

[14] To be precise an additional equation should be included to account for the small amount of iodine formed as a reaction product. Presumably the reaction to form iodine is also third order in iodine monochloride, since it was observed that the fraction of reacting iodine monochloride which was converted to iodine appeared to be invariant over the entire course of the rate runs (see Experimental section). It is possible that chlorinated aromatic product is formed in this reaction by the rate determining step

$$\mathrm{ArH{\cdot}ICl} + 2\mathrm{ICl} \xrightarrow{k_2} \mathrm{ArCl} + \mathrm{I_2} + \mathrm{HCl} + \mathrm{ICl}$$

Then k_1 of equations 7 and 8 should be represented as $k_1 + k_2$.

[15] There is evidence that solutions of iodine in non-polar media contain small amounts of $\mathrm{I_4}$; *cf.* G. Kortüm and G. Friedheim, *Z. Naturforsch*, **2a**, 20 (1947), and R. M. Keefer and T. L. Allen, *J. Chem. Phys.*, **25**, 1059 (1956).

[16] The equilibrium constants K_1 for mesitylene (3.70 l./mole) and for pentamethylbenzene (6.43 l./mole) at 25° were taken from reference 12.

If the situation were analogous in the iodine monochloride reaction, n would have a value of unity.

Activation energies for the iodination reactions were calculated from k_{obs} values at 25.2 and 45.7° for runs at high dilution (see Table I). The reaction rates diminished with increasing temperature. The observed E_a values were -4.1 kcal. for mesitylene and -1.6 kcal. for pentamethylbenzene. Very low or negative activation energies for aromatic halogenations or for the addition of halogens to olefins in non-polar solvents are frequently reported.[2,3,17] The fact that the activation energies are negative in the present work may be accounted for in part on the assumption that complexes, known to form by mildly exothermic reactions,[12] participate in the rate-determining step.

Iodination in Trifluoroacetic Acid.—When the solvent for methylbenzene iodination was changed from carbon tetrachloride to trifluoroacetic acid, the order of the reaction with respect to halogen dropped from three to one. This fact was established using toluene and *p*-xylene rather than mesitylene and pentamethylbenzene, both of which iodinated almost instantaneously in trifluoroacetic acid. For individual rate runs plots of $-\log (\mathrm{ICl})_T$ *vs.* time gave straight lines, from the slopes of which values of $k'_{obs}(\mathrm{ArH})_i$, as defined in equation 10, were determined.

$$-d(\mathrm{ICl})_T/dt = k'_{obs}(\mathrm{ArH})_i(\mathrm{ICl})_T \qquad (10)$$

These plots were linear to greater than 50% and in some cases to 80% of completion even for runs in which the hydrocarbon as well as the iodine monochloride concentration diminished appreciably during the course of the reaction. For such runs rate constants, which were calculated using the integrated form of a second-order rate law to account for the drop in (ArH) with time, increased as the reaction proceeded.

Values of $k'_{obs}(\mathrm{ArH})_i$, all obtained from the slopes of plots of $-\log(\mathrm{ICl})_T$ as a function of time, are listed in Table II. The k'_{obs} values, also given in Table II, for runs of the same hydrocarbon concentration but with varying initial halogen concentration are in relatively good agreement. In the case of the reaction of toluene, at least, the observed drop in k'_{obs} with increasing hydrocarbon concentration is outside the range of experimental error.

The experimental rate law, equation 10, may be explained in terms of the mechanism outlined in equations 11–13[18]

$$\mathrm{ArH} + \mathrm{ICl} \overset{K_2}{\rightleftarrows} \mathrm{ArH{\cdot}ICl} \qquad (11)$$

$$\mathrm{ArH{\cdot}ICl} \xrightarrow{k_3} \mathrm{ArI} + \mathrm{HCl} \qquad (12)$$

$$\mathrm{ArI} + \mathrm{ICl} \xrightarrow{k_4} \text{diiodide} + \mathrm{HCl} \qquad (13)$$

The rate-determining step for formation of the monoiodide, equation 12, may actually include solvent molecules which assist the removal of chloride ion from the aromatic–halogen complex.

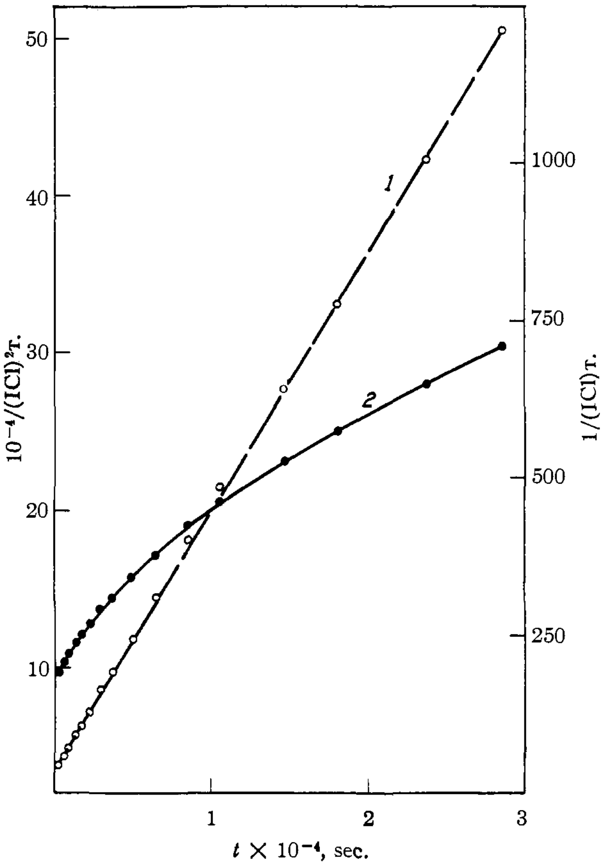

Fig. 1.—Evaluation of the rate constant for the reaction of ICl with mesitylene in $\mathrm{CCl_4}$. $(\mathrm{ICl})_i = 5.26 \times 10^{-3}$ *M*, $(\mathrm{Mes})_i = 0.142$ *M*. Line 1 and ordinate values on the left are for a reaction third order in ICl. Line 2 and ordinate values to the right are for a reaction second order in ICl.

As noted in the introduction, acetic acid is a relatively ineffective medium for iodination by a reaction which is first-order in halogen. The superiority of trifluoroacetic acid in this regard suggests that proton sharing by the solvent may be critical to the formation of the transition state intermediate.

The rate law which is consistent with the proposed mechanism is

$$-d(\mathrm{ICl})_T/dt = [k_3K_2(\mathrm{ArH})(\mathrm{ICl})_T + k_4(\mathrm{ArI})(\mathrm{ICl})_T]/[1 + K_2(\mathrm{ArH})] \qquad (14)$$

The experimental rate constants are then defined by equation 15

$$k'_{obs} = [k_3K_2(\mathrm{ArH}) + k_4(\mathrm{ArI})]/(\mathrm{ArH})_i[1 + K_2(\mathrm{ArH})] \qquad (15)$$

The conformance of the data for individual rate runs to equation 10 can be explained on the assumption that k_4 (for the follow reaction of monoiodide to form diiodide) is similar in magnitude[19] to k_3K_2. To estimate k_4, rate runs on the reaction of 2-iodo-1,4-dimethylbenzene with iodine monochloride in trifluoroacetic acid were made. The data were interpreted by equation 10. The result-

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(17) See P. B. D. de la Mare, R. A. Scott and P. W. Robertson, *J. Chem. Soc.*, 509 (1945), for an example based on olefin addition.

(18) An additional equation might be added here to account for the formation of very small amounts of iodine during the reactions (*cf.* footnote 14).

(19) H. C. Brown and M. Grayson, THIS JOURNAL, **75**, 6285 (1953), have reached similar conclusions concerning the relative rates of consecutive reactions in interpreting the kinetics of a Friedel–Crafts reaction of benzene.

TABLE II

RATE CONSTANTS FOR IODINATION IN TRIFLUOROACETIC ACID

$10^3(\mathrm{ArH})_i$, mole/l.	$10^3(\mathrm{ICl})_i$, mole/l.	$10^3k'_{\mathrm{obs}}(\mathrm{ArH})_i$, sec.$^{-1}$	k'_{obs}, mole^{-1} l. sec.$^{-1}$
	Toluene, t = 25.2°		
225.6	3.82	1.94	0.0086
228	3.82	2.11	.0092[a]
112.8	3.82	1.36	.0120
56.4	3.82	0.844	.0149
56.4	7.64	.800	.0142
56.4	15.3	.790	.0140
235	4.00	1.62	.0070[b]
224	4.00	1.72	.0075[b]
	t = 1.6°		
241	4.10	0.276	.00114[b]
	p-Xylene, t = 25.2°		
51.5	4.27	4.00	.078
25.8	4.27	2.48	.096
25.8	8.55	2.08	.081
25.7	7.96	2.10	.082
12.9	4.27	1.36	.105
	2-Iodo-1,4-dimethylbenzene, t = 25.2°		
46.8	4.06	1.50	.032
23.4	4.06	0.865	.037

[a] Initial HCl concentration of 0.0565 M. [b] A separately purified batch of solvent was used for these runs on which the reported activation energy is based.

ant rate constants, k'_{obs}, are reported in Table II. These values are a little less than one-half those obtained for p-xylene. Qualitatively, then, the mechanism of equations 11–13 appears to be satisfactory. Since k'_{obs} values for the aromatic hydrocarbons vary somewhat with the hydrocarbon concentration, a more quantitative test of the above mechanism would require a more elaborate series of rate measurements than has been made. Plans for such measurements were abandoned when the extent of corrosive action of the solvent fumes on the spectrophotometer, and also on the experimenters, became overwhelmingly objectionable.

The k'_{obs} values obtained for toluene were tested to see whether their variation with changing values of $(\mathrm{ArH})_i$ could be explained on the assumption that the equilibrium constant K_2 was large. Values of K_2 calculated from the rate constants, as explained elsewhere,[3] were found to be at least ten times as large as the measured equilibrium constant for the benzene–iodine monochloride complex in trifluoroacetic acid (see the Experimental section). It seems improbable that the equilibrium constants for the benzene and toluene complexes should differ by such a large factor. It seems preferable to ascribe the major share of the diminution in k'_{obs} with increasing aromatic hydrocarbon concentration to a solvent effect similar to that noted for the bromination of mesitylene in acetic acid solution.[4b]

The activation energy for the reaction of toluene with iodine monochloride was calculated from k'_{obs} values for runs at 25.2 and 1.6° as 12.7 kcal. This figure is several kilocalories less than that observed for zinc chloride catalyzed iodinations in acetic acid.[1c]

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Stereospecificity in Brominations of Bibenzyl and Acenaphthene with N-Bromosuccinimide

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Reaction of N-bromosuccinimide and bibenzyl or α-bromobibenzyl in carbon tetrachloride under peroxide initiation affords chiefly *meso*-α,α'-dibromobibenzyl in which the minimum ratio of *meso*- to *dl*-dibromide is 11 to 1. Reaction of N-bromosuccinimide and *erythro*-2-deutero-1,2-diphenylethyl bromide (IIa) affords chiefly *meso*-α,α'-dibromobibenzyl with a 60% loss of deuterium, corresponding to a preference for abstraction of Hb over Ha in IIc of 5 to 1. Reaction of N-bromosuccinimide and acenaphthene affords chiefly 1,2-dibromoacenaphthene for which the *trans*-structure has been established by partial resolution. The results are discussed in terms of the Bloomfield chain mechanism; the stereospecificity of the chain propagating steps is attributed to steric effects and to dipole interactions in the transition state.

The use of N-bromosuccinimide to effect the introduction of bromine at a carbon atom adjacent to an aromatic ring or to a double bond (the Wohl–Ziegler reaction) has been the subject of many investigations.[1] The generally accepted mechanism for this reaction is that proposed by Bloomfield,[2] involving a free radical chain mechanism.

$$\text{N-bromosuccinimide} \xrightarrow{\text{peroxide}} \text{succinimide radical} \quad (1)$$

$$\text{RH} + \text{succinimide radical} \longrightarrow \text{R}\cdot + \text{succinimide} \quad (2)$$

$$\text{R}\cdot + \text{N-bromosuccinimide} \longrightarrow \text{R–Br} + \text{succinimide radical} \quad (3)$$

Information on the initiating steps has been provided by Ford and Waters.[3] The influence of electrical effects on the side chain bromination[4a] and chlorination[4b] of m- and p-substituted toluenes[4] and the influence of steric effects on hydrogen

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[1] For reviews of this work up to 1951, see C. Djerassi, *Chem. Revs.*, **43**, 271 (1948); T. D. Waugh, "N-Bromosuccinimide, Its Reactions and Uses," Arapahoe Chemicals, Inc., Boulder, Colorado, May, 1951.

[2] G. F. Bloomfield, *J. Chem. Soc.*, 114 (1944).

[3] M. C. Ford and W. A. Waters, *J. Chem. Soc.*, 2240 (1952); M. C. Ford, *ibid.*, 2529 (1955).

[4] (a) E. C. Kooyman, R. Van Helden and A. F. Bickel, *Koninkl. Ned. Akad. Wetenschap. Proc.*, **56B**, 75 (1953); (b) R. Van Helden and E. C. Kooyman, *Rec. trav. chim.*, **73**, 269 (1954).