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The Chlorination of Aromatic Hydrocarbons in Carbon Tetrachloride and in Trifluoroacetic Acid

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In dilute solutions in carbon tetrachloride the chlorination of pentamethylbenzene is subject to catalysis either by hydrogen chloride or by iodine monochloride. The reactions are first order with respect to the hydrocarbon and chlorine and are either 3/2 or mixed first and second order with respect to hydrogen chloride. The reactions are first order with respect to iodine monochloride which is a much more effective catalyst than the hydrogen halide. The formation of chlorobenzene from benzene and chlorine in trifluoroacetic acid occurs rapidly at room temperature by a reaction which is first order in hydrocarbon and in halogen. The activation energy for this reaction is considerably higher than that for halogenations in carbon tetrachloride. All of the results of the *kinetic* studies can be explained in terms of a mechanism in which a polar reagent (a catalyst or the solvent) assists in the ionization of the halogen–halogen bond of a hydrocarbon–halogen complex in the rate-determining step. It should be noted, however, that in the absence of iodine monochloride relatively large amounts of side chain substitution product have been isolated from the pentamethylbenzene–chlorine reaction in carbon tetrachloride.

The rate laws for electrophilic substitution reactions of aromatic hydrocarbons with iodine monochloride and bromine are subject to marked variations in form as the polarity of the solvent is changed.[1-3] This is particularly apparent for the iodine monochloride reactions in which the orders with respect to halogen diminish successively from three to one as the solvent is changed from carbon tetrachloride to acetic acid to trifluoroacetic acid.[1e,g] These differences have been explained on the assumption that in a non-polar medium an aggregate of halogen molecules must play a part in the rate-determining step which is performed by the solvent in a polar medium.

The chlorination of alkylbenzenes in acetic acid has been shown to occur by a reaction which is only first order in halogen.[4,5] It has seemed of interest to extend the rate studies with chlorine to carbon tetrachloride as the medium to determine whether the order with respect to halogen is generally lower for chlorination than for iodination reactions. An extensive study of the kinetics of chlorination of pentamethylbenzene and of the iodine monochloride catalyzed chlorination of mesitylene in this solvent has now been made.

A brief study of the reaction of benzene with chlorine in trifluoroacetic acid also has been conducted to determine whether the observed superiority of the solvent (in terms of rate of reaction) as a medium for iodination[1g] also extends to chlorination processes. The choice of particular hydrocarbons for use in the three series of measurements has been governed entirely by the practical consideration that they react at rates which are conveniently followed.

Experimental

Materials.—The sources and methods of purification of the aromatic hydrocarbons and the solvents have been discussed previously.[1e,g] Resublimed iodine and chlorine taken directly from a cylinder (Ohio Chemical) were used without further purification. Hydrogen chloride, generated from concentrated hydrochloric and sulfuric acids, was dried in a sulfuric acid scrubber. Solutions of the gas in carbon tetrachloride were analyzed by titration with base.

Benzoyl peroxide was recrystallized from chloroform before use, m.p. 101°. Tetrabromocatechol, m.p. 188–190°, was prepared according to the directions of Huntress and Mulliken.[6]

Kinetics of Chlorination of Pentamethylbenzene in Carbon Tetrachloride.—The reaction rates were measured spectrophotometrically. Rate samples, prepared in subdued light from stock solutions of chlorine, pentamethylbenzene and (in most cases) hydrogen chloride in carbon tetrachloride were placed in 1-cm. glass stoppered absorption cells in the housing of the Beckman spectrophotometer. The housing temperature was controlled to $\pm 0.1°$. No errors due to volatility losses of chlorine from absorption cells during the period of rate measurements could be detected. A 2.21×10^{-2} *M* solution of chlorine in carbon tetrachloride gave constant optical density readings at 370 mμ over a 5-hr. period, which substantially exceeded the duration period of even the longest runs in which this solvent was used.

The chlorine content of the reaction mixtures as a function of time was determined by following the changes in optical density of the solutions at 340 mμ or, in some runs, at 370 mμ. The choice of wave length was governed by the initial chlorine content of the solutions. The molecular extinction coefficients of chlorine in pure carbon tetrachloride at these two wave lengths are, respectively, 94.5 and 37.1. Iodometric methods of analysis were used in obtaining the extinction coefficients. Pentamethylbenzene itself, at the concentrations used in the rate runs, does not absorb appreciably at these wave lengths. However, the extinction coefficients of chlorine in the reaction mixtures were found to increase somewhat with increasing aromatic hydrocarbon content of the solutions.

Most runs were followed spectrophotometrically to better than 75% of completion. The measured optical densities were corrected for very small blank readings at infinite reaction time. The hydrogen chloride content of the reaction mixtures at infinite reaction time was measured using samples which were withdrawn directly from the absorption cells. These samples were shaken with a large excess of water, and the resultant mixtures were titrated with base.

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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); (c) R. M. Keefer, A. Ottenberg and L. J. Andrews, *ibid.*, **78**, 255 (1956); (d and e) R. M. Keefer and L. J. Andrews, **78**, 3637, 5623 (1956); (f) L. J. Andrews and R. M. Keefer, **78**, 4549 (1956); (g) **79**, 1412 (1957).

[2] T. Tsuruta, K. Sasaki and J. Furukawa, *ibid.*, **74**, 5995 (1952); **76**, 994 (1954).

[3] An extensive series of investigations by P. W. Robertson and co-workers, which have appeared in *J. Chem. Soc.*, have been adequately cited in the papers of ref. 1.

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

[5] R. M. Keefer and L. J. Andrews, THIS JOURNAL, **79**, 4358 (1957).

[6] E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 227.

Kinetics of the Iodine Monochloride Catalyzed Iodination of Mesitylene in Carbon Tetrachloride.—The details concerning preparation of the rate samples and of the kinetic work were essentially the same as were used in studying the chlorination of pentamethylbenzene. Iodine monochloride was generated in the rate samples by adding small aliquots of a stock solution of iodine in carbon tetrachloride to the reaction mixtures.

The rate of reaction of iodine and chlorine to form iodine monochloride in carbon tetrachloride is not, apparently, always rapid.[7] Indeed it was found in the present work that in a carbon tetrachloride solution originally 1.06×10^{-3} *M* in iodine and 1.53×10^{-3} *M* in chlorine approximately 1 hr. was required for complete conversion of iodine to the mixed halogen. This was demonstrated by following the change in optical density of the solution at 518 mμ, the visible absorption maximum of iodine. In solutions which were initially $1\text{–}4 \times 10^{-5}$ *M* in iodine and $1\text{–}5 \times 10^{-3}$ *M* in chlorine (values which approximate the initial halogen concentrations in the rate runs on mesitylene), the conversion of iodine to iodine monochloride proved to be immeasurably fast. In other words the effective catalyst in the mesitylene rate runs was iodine monochloride and not iodine.

All optical densities measured during the runs were corrected for the slight absorption of iodine monochloride at completion of the chlorination reaction. Although this halogen also reacts with mesitylene, the rate is extremely slow[1g] at the concentration levels employed in the present work.

Modifications in the experimental procedure which were required for measurements in the 45° region have been discussed previously.[1g]

Kinetics of Chlorination of Benzene in Trifluoroacetic Acid.—The reactions were again followed spectrophotometrically at 340 mμ. The extinction coefficient of chlorine in trifluoroacetic acid, as determined through a combination of spectrophotometric and iodometric analyses, is 55.8. The experimental methods were essentially those described for the kinetic studies with carbon tetrachloride as the solvent. Over a period of time which exceeded that of the longest run by a factor of two, a solution of 7×10^{-3} *M* chlorine in trifluoroacetic acid contained in an absorption cell dropped about 4% in chlorine content.

The Products of Chlorination of Pentamethylbenzene in Carbon Tetrachloride. (A) In the Absence of Iodine Monochloride.—In a typical experiment 1.00 g. (0.00675 mole) of pentamethylbenzene in 37.5 ml. of carbon tetrachloride was mixed with 12.5 ml. of 0.546 *M* chlorine in a darkened room. The solution was stored in the dark for 1 hr., by which time the solution was decolorized. The bulk of the solvent was removed by distillation, and the concentration process was completed under vacuum. The resulting oil-crystal mixture was dissolved in hot ethanol. When the solution was cooled, 130 mg. of white crystals deposited. These melted over a wide range ending at 110°. This material was recrystallized twice from aqueous acetic acid. From the first recrystallization 70 mg. of product melting over a range ending at 145° was recovered. From the second recrystallization 40 mg. of 6-chloro-1,2,3,-4,5-pentamethylbenzene[8] was obtained. This material, m.p. 153–155° and mixed m.p. 151–154° with an authentic sample prepared by another method,[5] was inert to boiling alcoholic silver nitrate solution.

From the ethanol mother liquor remaining from the original recrystallization of the crude product, an additional 60 mg. of white crystals was obtained by refrigeration. These melted over a wide range ending at 85° and gave a substantial precipitate of silver chloride when treated with alcoholic silver nitrate.

Several attempts were made to increase the yield of the ring chlorinated product by varying the pentamethylbenzene to chlorine ratio of the reaction mixture from less than one to 2/1 and by carrying out the reaction with hydrogen chloride initially present. In all cases the recovery of crystalline material was poor, and the products were obviously mixtures which were rich in reactive halogen (in the alcoholic silver nitrate test).

In one experiment in which 0.00675 mole of pentamethylbenzene and 0.0137 mole of chlorine were mixed in 50 ml. of carbon tetrachloride, the crude product obtained on boiling off carbon tetrachloride weighed 1.49 g. as compared to a theoretical weight of 1.46 g. for a dichloro derivative of pentamethylbenzene ($C_{11}H_{14}Cl_2$). When 0.00675 mole of pentamethylbenzene and 0.00492 mole of chlorine were used in a similar experiment, the crude product weighed 1.14 g. Were this product composed of the theoretical quantity of monochloropentamethylbenzene ($C_{11}H_{15}Cl$) and unreacted hydrocarbon, it should have weighed 1.17 g. In other words it appears that under the conditions of the reaction, if sufficient halogen is available, substitution does not stop with the formation of the monochloro derivative. Neither does it seem, in terms of the cited weights of crude products, that an addition reaction to form pentamethylbenzene hexachloride occurs to any significant degree.

The crude product from one reaction of equimolar quantities of halogen and hydrocarbon was boiled with alcoholic silver nitrate, and the precipitated silver halide was collected and weighed. On the assumption that the crude product was a mixture of monochloro derivatives of pentamethylbenzene, it was calculated that 82% of the total halogen was recovered as silver chloride.

(B) In the Presence of Iodine Monochloride.—To a solution of 0.96 g. (0.0066 mole) of pentamethylbenzene in 28 ml. of carbon tetrachloride was added a carbon tetrachloride solution composed of 5 ml. of 2×10^{-3} *M* iodine and 17 ml. of 0.381 *M* chlorine (0.0065 mole of chlorine). The reaction was carried out in a semi-dark room. The yellow color of the solution faded almost immediately to the faint brown color of iodine monochloride. The solution was washed with dilute sodium thiosulfate, dried over calcium chloride and concentrated. The crude product, a white solid which was only slightly oily, weighed 1.14 g. and melted over a range ending at 120°. A sample of this material gave only a faint precipitate with alcoholic silver nitrate.

The crude product was recrystallized from ethanol to yield 0.51 g. of crystals of m.p. 145–148°. After a second recrystallization from ethanol 0.364 g. of 6-chloro-1,2,3,4,5-pentamethylbenzene was recovered (m.p. 154–156° and mixed m.p. with an authentic sample 153–155°).

From the mother liquor from the first recrystallization an additional crop of crystals (0.113 g.) of m.p. 120–137° was obtained. These gave only a faintly positive test for reactive chlorine when boiled with alcoholic silver nitrate. The yield of ring chlorinated compound, based on the first and second crops of crystals from the first ethanol recrystallization, was 52%.

The Products of Chlorination of Benzene in Trifluoroacetic Acid.—Because the solubility of chlorine in trifluoroacetic acid is of the order of magnitude of 0.4 *M*, the following scheme was adopted for accumulating a sufficient quantity of reaction products to permit their isolation and characterization.

To a solution of 100 ml. of 0.38 *M* chlorine in trifluoroacetic acid, 3.4 ml. (0.038 mole) of benzene was added. The reaction mixture was kept in semi-darkness. The solution became warm, and a copious evolution of hydrogen chloride occurred. In about 0.5 hr. chlorine was bubbled into the solution rapidly. A small sample was then removed for iodometric analysis for chlorine. Enough benzene was added to make the solution equimolar in halogen and hydrocarbon. This process was repeated several times until a total of 0.123 mole of each reactant had been added.

Trifluoroacetic acid (85 ml.) was removed from the solution of products by distillation through a 10-inch Vigreux column. The distillation temperature did not exceed 72.0°. The boiler residue was dissolved in 20 ml. of carbon disulfide. This solution was washed with water and with dilute potassium hydroxide solution and was dried over calcium chloride.

The carbon disulfide solution was fractionated from a small modified Claisen flask. After removal of the solvent, several fractions were collected with weights, boiling ranges and $n^{26}\text{D}$ values as follows: I, 2.53 g., 130–140°, 1.5271; II, 2.36 g., 140–165°, 1.5303; III, 0.72 g., 165–173°, 1.5395; IV, 0.55 g., 173–176°, 1.5427; V, 0.38 g. (a semisolid which was melted from the condenser). Fraction IV partially solidified on cooling. The refractive index reported for IV was measured using liquid portions of the fraction. The still bottoms weighed 1.28 g.

Crystals collected from fractions IV and V were recrystallized from ethanol. The m.p. and mixed m.p. of the product with *p*-dichlorobenzene was 51–53°.

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[7] J. H. Hildebrand, This Journal, **68**, 915 (1946).

[8] A. Tohl, *Ber.*, **25**, 1524 (1892).

Using an estimated average value of the reported refractive indices of *o*- and *p*-dichlorobenzenes ($n^{26}\text{D}$ 1.5465) and a value of $n^{26}\text{D}$ 1.5225 for chlorobenzene,[9] it was calculated that fractions I–V contained 3.7 g. of chlorobenzene and 2.9 g. of dichlorobenzene (43% yield based on benzene).

It was found by semi-quantitative spectrophotometric methods that the rate constant for the reaction of chlorobenzene with chlorine in trifluoroacetic acid is about one-tenth that for benzene. It is not surprising, therefore, that a substantial amount of dichlorobenzene was formed under the conditions of the product isolation experiment.

Results

Reactions in Carbon Tetrachloride

Hydrogen Chloride Catalyzed Chlorination of Pentamethylbenzene.—To investigate the reaction kinetics of pentamethylbenzene with chlorine in carbon tetrachloride, reaction mixtures were prepared in which the initial halogen concentration was small as compared to that of the hydrocarbon. The disappearance of chlorine from these mixtures was subject to short periods of induction. Once the reactions were started, they accelerated markedly in the initial phases.

On the assumption that the autocatalytic character of the reactions resulted because hydrogen chloride served as a catalyst, a series of rate runs was made in which hydrogen chloride was introduced initially in the reaction mixtures at a concentration which substantially exceeded that of chlorine. For individual runs (followed spectrophotometrically) plots of logarithms of the optical densities of chlorine *versus* time gave straight lines to over 70% of completion of the reactions. Rate constants, *k* (see equation 1), were calculated from the slopes of these lines. The average error in the reported rate constants is estimated to be 5%

$$kt = \ln \frac{1}{d_t} + \text{constant} \qquad (1)$$

Values[10] of $k/(\text{PMB})_{\text{av}}$ for the runs with added hydrogen chloride are summarized in Table I. Although these values increase with increasing hydrogen chloride content of the reaction mixtures, they are independent of wide variations in initial chlorine and pentamethylbenzene concentrations for runs of similar hydrogen chloride concentration. In other words, the reaction is first order in both hydrocarbon and halogen.

The effects of increasing hydrogen chloride on $k/(\text{PMB})_{\text{av}}$ values suggest that the reaction is between first and second order in the hydrogen halide. This is indicated by the solid and dotted lines of Fig. 1 which show, respectively, the conformance of the data to rate laws 2 and 3.

$$\frac{-\text{d}(\text{Cl}_2)}{\text{d}t} = (8.9 \times 10^{-3})(\text{Cl}_2)(\text{PMB})(\text{HCl})^{3/2} \qquad (2)$$

$$\frac{-\text{d}(\text{Cl}_2)}{\text{d}t} = [0.62(\text{HCl}) + 26.9(\text{HCl})^2](\text{Cl}_2)(\text{PMB}) \qquad (3)$$

The value 8.9×10^{-3} sec.$^{-1}$ l.$^{5/2}$ moles$^{-5/2}$ (eq. 2) was obtained from the intercept of the linear plot of log $k/(\text{PMB})_{\text{av}}$ *vs.* 3/2 log HCl_{av}. The values 6.62 sec.$^{-1}$ l.^{2} moles^{-2} and 26.9 sec.$^{-1}$ l.^{3} moles^{-3} (eq. 3) were obtained, respectively, from the intercept and slope of the linear plot of $k/(\text{PMB})_{\text{av}}$ $(\text{HCl})_{\text{av}}$ *vs.* $(\text{HCl})_{\text{av}}$. Either of these curves fits the experimental points, shown by the circles of Fig. 1, reasonably well. Although equation 3 fits the available data somewhat better than equation 2, it is doubtful whether the 3/2 order reaction may be completely disregarded.

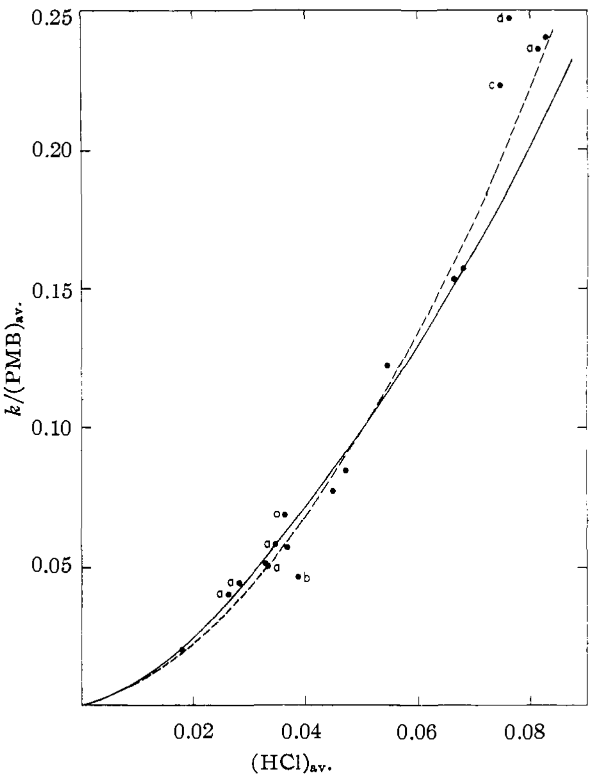

Fig. 1.—The variation in pentamethylbenzene chlorination rate in carbon tetrachloride with hydrogen chloride concentration. The solid line fits equation 2. The dotted line fits equation 3. The letters on the experimental points correspond to runs described in the footnotes of Table I.

The reaction of bromine with mesitylene in carbon tetrachloride is catalyzed both by hydrogen bromide and by water.[1a] Actually the reaction does not take place in the presence of hydrogen bromide when the solvent has been dehydrated with Drierite (anhydrous calcium sulfate). In the present work it was found that Drierite-dried solvent and carbon tetrachloride taken directly from the container in which it was furnished could be interchanged as reaction media without altering the rate of reaction. Neither was any enhancement of the reaction rate observed when the solvent was composed in part of carbon tetrachloride which had been equilibrated with water (see Table I and Fig. 1 for specific information concerning runs in wet and dry systems). If anything, moisture reduced the reaction rate slightly.

A few attempts were made to influence the rate of pentamethylbenzene chlorination through alteration of the surfaces of absorption cells in which the reactions were run. Methanol-washed cells were alternately air-dried and oven-dried. One cell was coated internally with Desicote (an organosilicon

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[9] E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 774, 794, 1077.

[10] The terms $(\text{PMB})_{\text{av}}$ and $(\text{HCl})_{\text{av}}$ represent concentrations of these two substances at 50% reaction time. They were calculated from known initial concentrations of the reactants and from the final concentrations of hydrogen chloride $(\text{HCl})_f$.

TABLE I

THE HYDROGEN CHLORIDE CATALYZED CHLORINATION OF PENTAMETHYLBENZENE IN CARBON TETRACHLORIDE AT 25.2°

$(PMB)_i$, $10^3 \times$ mole/l.	$(Cl_2)_i$, $10^3 \times$ mole/l.	$(HCl)_f$, $10^3 \times$ mole/l.	$10^2k/(PMB)_{av}$, sec.$^{-1}$ mole^{-1} l.
121.5	8.06	30.2	4.0[a]
121.5	3.76	38.7	5.7
81.0	3.76	49.0	8.8
41.2	3.91	83.4	23.6[a]
40.5	16.12	41.3	5.0[a]
40.5	7.82	36.5	5.1
40.5	3.76	84.7	24.0
40.5	3.60	78.3	24.7[b]
40.5	3.60	76.5	22.3[c]
40.5	3.76	70.0	15.7
40.5	3.76	68.3	15.3
40.5	3.82	56.6	12.2
40.5	3.76	46.8	7.7
40.5	3.76	40.4	4.6[d]
40.5	3.91	38.1	6.8[a]
40.5	3.82	36.5	5.8[a]
40.5	3.91	30.0	4.4[a]
40.5	3.82	19.8	2.0

[a] The solvent was dried with Drierite. [b] The solution contained benzoyl peroxide (10.1×10^{-3} *M*). [c] The solution contained tetrabromocatechol (4.92×10^{-4} *M*). [d] Half of the carbon tetrachloride had been equilibrated with water.

compound). Reactions carried out in these containers conformed to the general rate picture of Fig. 1.

The addition of tetrabromocatechol or benzoyl peroxide to the reaction mixtures did not appreciably alter the rate of reaction. The former compound has been reported to be an effective inhibitor of the bromination of phenanthrene in carbon tetrachloride, a reaction which is presumed to proceed by a radical mechanism.[11] The peroxide is reported to accelerate the rate of side chain chlorination of toluene,[12] although it is apparently ineffective in promoting the bromination of phenanthrene in carbon tetrachloride unless traces of oxygen are eliminated. In the present series of experiments the complete exclusion of oxygen could not readily be accomplished. As has been the general practice in studying halogenations in carbon tetrachloride in this Laboratory,[1a,b,g] no attempt was made to rid the carbon tetrachloride of trace impurities other than water. It is, as a referee has observed, conceivable that the effects of added peroxides might be masked by those of peroxidic impurities already present in the solvent.

The repeated illumination of samples, required for the spectrophotometric rate studies, did not influence the reaction rates. The measured half-life of a frequently illuminated reaction mixture was approximately the same as that of a mixture of the same initial composition which was stored in the dark.

It is reported that chlorination of alkylbenzenes in the dark at low temperature may produce addition or side-chain substitution products and that the reactions are tremendously accelerated by light.[13] It is not clear whether the dark reaction is of a radical type, although the formation of side-chain substitution products is generally considered to occur by a radical rather than by an ionic process.

The results of the kinetic studies on the chlorination of pentamethylbenzene in carbon tetrachloride cannot be rationalized readily in terms of a radical mechanism. It is not likely that hydrogen chloride, an essential catalyst under the conditions of the rate runs, can serve as a source of chain initiating or propagating radicals.[14] The insensitivity of the reactions to intermittent illumination, to a radical reaction inhibitor and to a peroxide serves as a further, though less convincing, negative evidence. It is also, perhaps, pertinent that mesitylene is much less susceptible to hydrogen chloride catalyzed chlorination in carbon tetrachloride than is pentamethylbenzene (see Table II).

The products of chlorination of pentamethylbenzene in carbon tetrachloride are, however, much richer in side chain than in nuclear chlorinated material (see Experimental section). The initial chlorine concentrations in the product isolation experiments were of necessity considerably higher than in the kinetic experiments. For the moment it seems most reasonable to assume that this change in reaction conditions was accompanied by a change in mechanism since, structurally speaking, the products are those normally expected from radical processes. However, a non-radical mechanism which accounts for the formation of both side-chain and nuclear chlorinated pentamethylbenzene can be formulated.[15] It is significant that the proposal that low temperature substitution of olefins by chlorine occurs by an ionic mechanism can be successfully defended.[16]

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[11] (a) C. C. Price, THIS JOURNAL, **58**, 1834, 2101 (1936); (b) M. S. Kharasch, P. C. White and F. R. Mayo, *J. Org. Chem.*, **2**, 574 (1938).

[12] M. S. Kharasch, E. Margolis, P. C. White and F. R. Mayo, THIS JOURNAL, **59**, 1405 (1937).

[13] M. S. Kharasch and M. G. Berkman, *J. Org. Chem.*, **6**, 810 (1941).

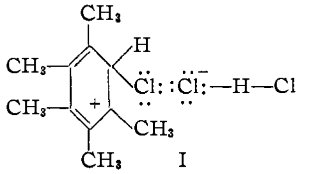
[14] M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, Amen House, London E. C. 4, 1949, p. 145.

[15] The generalized mechanism, which accounts satisfactorily for other[1] low temperature aromatic halogenations in the dark is given in equations 4 and 5. In the rate-determining step the halogen–halogen

$$\mathrm{ArH} + \mathrm{X_2} \overset{K}{\rightleftarrows} \mathrm{ArH{\cdot}X_2} \qquad (4)$$

$$\mathrm{ArH{\cdot}X_2} + \mathrm{E} \xrightarrow{\text{slow}} \mathrm{ArHX^+XE^-} \xrightarrow{\text{fast}} \text{products} + \mathrm{E} \qquad (5)$$

bond of the aromatic halogen complex is broken by the attack of a polar reagent E. Hydrogen chloride, or an aggregate thereof, may serve as the reagent E in pentamethylbenzene chlorination. Formula I is suggested as an approximation of a resonance form which contributes to the structure of the transition state in this reaction. Loss


I

of a proton from the nucleus would lead to ring chlorinated product. Alternately loss of a proton from the methyl substituent on the nucleus followed by allylic rearrangement would lead to side-chain chlorinated product. Side-chain substitution need not cease with the formation of monohalide if sufficient halogen is available.

[16] R. W. Taft, Jr., THIS JOURNAL, **70**, 3364 (1948).

The *kinetics* of chlorination of pentamethylbenzene are of the same general type as those of other aromatic hydrocarbon halogenation reactions in carbon tetrachloride which have been studied in this Laboratory. There is no evidence that in this solvent a simple bimolecular reaction between halogen and hydrocarbon occurs in the dark at room temperature. The additional polar reagent E (footnote 15), which promotes severance of the halogen–halogen bond, seems essential. Unless the halogen molecule itself is sufficiently polar (*e.g.*, ICl),[1g] hydrogen halide or a hydration product of hydrogen halide[1a] can fill this role. A polar halogen may also serve as a catalyst for the reaction of a non-polar halogen. Thus iodine bromide induces reaction between bromine and mesitylene.[1b,2] It has therefore seemed worthwhile to consider the effectiveness of iodine monochloride as an alternate catalyst for chlorinations.

The Iodine Monochloride Catalyzed Reaction.— In the presence of even very small amounts of iodine monochloride the reaction of pentamethylbenzene and chlorine in carbon tetrachloride occurred too rapidly for convenient kinetic measurement. The yield of ring chlorinated product was relatively good as compared to that obtained when hydrogen chloride was used as a catalyst.

The kinetics of the iodine monochloride catalyzed reactions were conveniently followed spectrophotometrically using mesitylene as a hydrocarbon. In most runs the initial concentration of hydrocarbon exceeded that of halogen by a factor of at least ten. The iodine monochloride concentration was kept sufficiently low so that it was not itself consumed by reaction with mesitylene.[1g] On the assumption that the reactions were first order in chlorine, rate constants k (equation 1) were evaluated graphically using the logarithms of optical densities recorded during the course of the runs. The plots were linear until better than 70% of the initial chlorine had reacted except in the runs in which the mesitylene concentration dropped significantly during the course of the reaction.

Rate constants k and values of $k/(\mathrm{ICl})_i(\mathrm{Mes})_{\mathrm{av}}$ are reported in Table II. The term $(\mathrm{Mes})_{\mathrm{av}}$ represents the mesitylene concentration at 50% reaction time. At any given mesitylene concentration values of $k/(\mathrm{ICl})_i(\mathrm{Mes})_{\mathrm{av}}$ are reasonably independent of changes in iodine monochloride and chlorine concentrations. Although the values do show a slight increase with decreasing iodine monochloride concentration and with increasing initial chlorine concentration, the reactions are clearly first order in both halogens.

The slight increases in values of $k/(\mathrm{ICl})_i(\mathrm{Mes})_{\mathrm{av}}$ with decreasing hydrocarbon concentration probably result from the fact that halogens interact with aromatic hydrocarbons to form 1:1 molecular complexes. It is reasonable to assume that the extent of such complex formation between chlorine and mesitylene is so small[17] that the concentration of free chlorine in the reaction mixtures would not be much affected by changes in the mesitylene concentration. However, iodine monochloride and mesitylene associate extensively in carbon tetrachloride. The equilibrium constant for this interaction at 25° has been measured[18] (K = 3.70 l. mole^{-1}). If it is assumed that iodine monochloride which is bound in a mesitylene complex is ineffective as a catalyst, the rate law for the chlorination reaction should be written[19] as in equation 6.

TABLE II

THE IODINE MONOCHLORIDE CATALYZED CHLORINATION OF MESITYLENE IN CARBON TETRACHLORIDE

$(\mathrm{Mes})_i$, mole/l.	$10^3 \times (\mathrm{Cl_2})_i$, mole/l.	$10^5 \times (\mathrm{ICl})_i$, mole/l.	10^3k, sec.$^{-1}$	$k/(\mathrm{ICl})_i$-$(\mathrm{Mes})_{\mathrm{av}}$, sec.$^{-1}$ mole^{-2} l.^{2}
		t = 25.0°		
0.0250	4.12	2.00	0.79	1720
.0499	4.12	16.00	10.18	1330
.0499	3.72	11.7	7.34	1310
.0499	3.72	11.7	11.5	2050[a]
.0499	3.92	8.00	5.25	1370
.0499	3.84	4.00	2.78[b]	1450
.0499	3.95	2.00	1.59	1660
.0499	3.60	2.00	1.65	1720[c]
.0499	3.60	2.00	1.71	1780[d]
.0507	3.80	2.12	1.82	1760[e]
.0499	4.12	1.00	0.93	1940
.0998	16.5	2.00	3.55	1930
.0998	7.92	2.00	3.28	1710
.0998	3.96	2.00	2.86	1460
.0998	1.98	2.00	2.53	1280
.1996	3.95	2.00	4.91	1240
.399	3.76	2.00	8.13	1020
.0499	3.72	...	0.24	..[f]
		t = 1.2°		
0.0485	3.62	7.77	4.50	1240
.0485	3.64	3.88	2.31	1270
.0485	3.65	1.94	1.31	1440

[a] The solution contained 0.0735 M HCl at the end of the run. [b] Average of two runs of values 2.83 and 2.73. [c] The solution contained tetrabromocatechol (4.92×10^{-4} M). [d] The solution contained benzoyl peroxide (0.0101 M). [e] The solvent was dried with Drierite. [f] The solution contained 0.0373 M HCl at the end of the run.

$$-\mathrm{d}(\mathrm{Cl_2})/\mathrm{d}t = k(\mathrm{Cl_2}) = \frac{k_1(\mathrm{Cl_2})(\mathrm{Mes})(\mathrm{ICl})_\mathrm{T}}{1 + K(\mathrm{Mes})} \qquad (6)$$

If equation 6 correctly explains the experimental data, a plot of values of $1/k$ *versus* $1/(\mathrm{Mes})$ should give a straight line of slope $1/k_1(\mathrm{ICl})_\mathrm{T}$ and intercept $K/k_1(\mathrm{ICl})_\mathrm{T}$. The data for a series of runs at varying mesitylene concentration in which the initial chlorine and the iodine monochloride concentrations were, respectively, 4×10^{-3} M and 2×10^{-5} M conformed to this treatment. A value of K = 1.83 l. mole^{-1} was calculated from the ratio of the intercept and slope of the resultant line. It appears, as is the case in iodine bromide catalyzed bromination of mesitylene in carbon tetrachloride,[1b] that even the complex iodine halide has some catalytic activity.

As can be seen from Table II, hydrogen chloride is much less effective as a catalyst for chlorination of mesitylene than is iodine monochloride. Also the rates of the iodine chloride catalyzed reactions

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(17) L. J. Andrews and R. M. Keefer, THIS JOURNAL, **73**, 462 (1951).

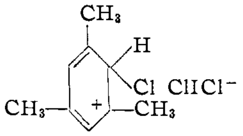
(18) N. Ogimachi, L. J. Andrews and R. M. Keefer, *ibid.*, **77**, 4202 (1955).

(19) The constant k_1 of equation 6 would actually be the product of a rate constant and an equilibrium constant if a chlorine–mesitylene complex (see equations 4 and 5) is a true reaction intermediate.

are insensitive to moisture and to tetrabromocatechol and benzoyl peroxide.

The activation energy for the iodine chloride catalyzed reaction was calculated from data obtained in runs at 25.0 and 1.2° in which the initial mesitylene and chlorine concentrations were, respectively, 0.049 M and 4×10^{-3} M. The third-order rate constants, $k/(\mathrm{ICl})(\mathrm{Mes})_{\mathrm{av}}$, at the two temperatures were obtained from the slopes of the straight lines obtained by plotting values of $k/(\mathrm{Mes})_{\mathrm{av}}$ *versus* $(\mathrm{ICl})_{\mathrm{T}}$. Instead of passing through the origin these lines had a small positive ordinate intercept. From these third-order constants a value of E_a = 0.41 kcal./mole was calculated. This low value is of the same general order of magnitude as that observed for other halogenations in carbon tetrachloride.[1b,20]

The transition state for the chlorination reaction must be composed of a molecule each of aromatic hydrocarbon, chlorine and iodine monochloride. The structure of the product of the rate-determining step is presumed to be similar to that for other substitution reactions which have higher over-all orders in halogen.[1b,g] This structure, represented as the ion pair II, resembles that (I) suggested as an intermediate in the hydrogen chloride catalyzed chlorination of pentamethylbenzene.



II

Trifluoroacetic Acid as a Solvent

Chlorination of Benzene.—In trifluoroacetic acid the chlorination of benzene occurs rapidly at room temperature. Chlorobenzene also reacts rapidly enough with chlorine in this solvent, so that significant amounts of dichlorobenzenes are obtained from the reaction of equimolar quantities of chlorine and benzene.

In the solutions prepared for the spectrophotometric rate studies, the benzene concentration was in large excess of that of halogen. Rate constants k (equation 1) were again evaluated graphically for individual runs on the assumption that the reactions were first order in halogen. The data are summarized in Table III. The constancy of values of $k/(\mathrm{C_6H_6})$ over wide ranges of initial reactant concentrations establishes the over-all order of the reaction as two. The activation energy of the reaction, calculated from the rate constants at 25.0 and 45.4°, is 11.4 kcal./mole.

The reactions of toluene and p-xylene with iodine monochloride in trifluoroacetic acid[1g] are also first order in each of the reactants, and the activation energy for the toluene reaction is 12.7 kcal./mole. Furthermore, like chlorobenzene, the monoiodo derivatives are readily susceptible to further halogenation in trifluoroacetic acid.

TABLE III

THE CHLORINATION OF BENZENE IN TRIFLUOROACETIC ACID AT 25.0°

$(\mathrm{C_6H_6})$, mole/l.	$10^3 \times (\mathrm{Cl_2})_i$, mole/l.	$10^3\ k/(\mathrm{C_6H_6})$, sec.$^{-1}$ mole^{-1}/l.
0.696	6.77	6.26
.348	13.54	6.52
.348	6.77	6.55
.336	2.88	7.44
.168	5.76	7.09
.164	5.6	24.2[a]

[a] The temperature in this run was 45.4°.

The Influence of Solvent on the Course of Aromatic Chlorination

The results of this investigation seem to fit within the broad scope of the mechanism[1,3] (eq. 4 and 5) which has been used in explaining the kinetics of reaction of aromatic hydrocarbons in a wide variety of solvents with other halogens than chlorine. The low activation energies for the reactions in carbon tetrachloride can be explained in part on the assumption that aromatic–halogen complexes, which are thermally unstable, are reaction intermediates. The overall halogen orders for iodination,[1g] iodine bromide catalyzed bromination[1b] and iodine monochloride catalyzed chlorination in this solvent are, respectively, 3, 3 and 2. These results are in accord with the observation that in acetic acid the halogen order is less for chlorination than for bromination[1c] or iodination.[1e]

The activation energies for halogenations increase as the polarity of the medium is increased. Presumably the increased activation energy results from an increase in the desolvation energies of the reactants. Polar solvents favor the ionization reaction of the rate-determining step and minimize or eliminate the participation of additional halogen molecules or of added catalysts in that step. Certainly the effects of changing the chlorination medium from carbon tetrachloride to trifluoroacetic acid are in accord with these generalizations.[21]

The present results along with those of the investigation of aromatic iodination[1g] indicate clearly the effectiveness of trifluoroacetic acid as a solvent for carrying out rapid halogenations at low temperatures. Presumably, as a relatively strong acid, this solvent itself functions, through proton sharing with the departing halide ion, as the reagent E (equation 5) in the rate determining step.

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(20) L. M. Yeddanapalli and N. S. Gnanapragasam, *J. Chem. Soc.*, 4394 (1956). These authors report that Ea values for the uncatalyzed or iodine bromide catalyzed bromination of phenol vary with temperature, a fact which suggests that the mechanism of the reaction must be altered by temperature change.

(21) Halogenations are sometimes of mixed order in halogen, and the over-all halogen order may change with changing concentration of aromatic substance (see ref. 1c and P. W. Robertson, P. B. D. de la Mare and W. T. G. Johnston, *J. Chem. Soc.*, 276 (1943), for pertinent results on brominations in acetic acid). In other words the aromatic substance itself may influence, either by complexing the halogens or by changing the nature of the solvent, the kinetic form of the reaction. The reaction temperature is also reported to influence over-all halogen order (see the preceding reference). This is reasonable since activation energies for processes which differ in molecularity in halogen are not necessarily the same.