acetoacetate. Reaction took place with the evolution of heat and ended within several minutes. The reaction mixture was fractionated under reduced pressure. The volatile liquid distillates were shown to be alcohols by measurements of the refractive indices and boiling points. The quantity of alcohol was 0.010 mole. An equivalent amount (0.010 mole) of compounds III or IV remained as the residue. When the products were solid (see Table I), they were purified using diethyl ether or petroleum ether as solvent. The liquid products were distilled at 10^{-4} mm. with a pot-still or "falling-film" type molecular still, maintaining the temperature under 70° to prevent heat decomposition. These products are soluble in most organic solvents.

(b) Reaction of Tetraalkoxytitaniums with Acetylacetone and Ethyl Acetoacetate in a Molar Ratio 1:2.—To 0.010 mole of each tetraalkoxytitanium was added 0.020 mole of acetylacetone or ethyl acetoacetate. Reaction took place with the evolution of heat and ended within several minutes. From the reaction mixtures, 0.020 mole of alcohols were removed under reduced pressure. The theoretical amount (0.010 mole) of compounds V or VI remained as the residue. When the products were solid (see Table II), they were purified using diethyl ether or petroleum ether as solvents. The liquid products were distilled with the molecular still. These compounds are soluble in most organic solvents.

Molecular Refraction.—*MR* values for $(PrO)_2Ti(acac)_2$, $(PrO)_2Ti(etac)_2$, $(BuO)_2Ti(acac)_2$ and $(BuO)_2Ti(etac)_2$ were 103.8, 116.6, 113.4 and 125.9, respectively. Since there are no atomic refraction data for hexa-coördinated titanium in the literature, calculation of the molecular refractions was impossible. Instead, the atomic refraction was calculated from observed molecular refractions, and the values of 19.9, 20.1, 20.2 and 20.2, respectively, were obtained for hexa-coördinated titanium from these four *MR* values.

Hydrolyses of the Compounds and Isolation of VIII.—The compounds III, IV and VI were hydrolyzed readily by moisture. Gel-like substances were formed after standing several hours in moist air or instantly by addition of water. In case of dialkoxytitanium-bis-(acetylacetonate)s (V), addition of water gave light-yellow needles. To 1.62 g. of $(BuO)_2Ti(acac)_2$ was added 5 ml. of water. The crystals obtained were filtered and dried to give 0.74 g. of pale-yellow amorphous powder. The powder was recrystallized from chloroform or benzene solution, and again light yellow crystals were obtained. The crystals (plate form) were stable in chloroform or benzene solutions, but they lost their crystalline form and turned to a light yellow amorphous substance, gradually in air and rapidly in a vacuum desiccator. The color gradually turned to brown over 200° and the compound decomposed to a dark-red liquid at 235°.

Anal. Calcd. for $TiC_{10}H_{14}O_5$: Ti, 18.3; C, 45.9; H, 5.38. Found: Ti, 18.2; C, 45.6; H, 5.57.

Hydrolyses of dipropoxy- and diethoxy-titanium-bis-(acetylacetonate) were carried out analogously with the butoxy-compound, and the products obtained were confirmed to be identical with the hydrolysis product of the dibutoxy-compound by chemical analyses.

The aqueous solution of VIII gave transparent gel-like substance after standing several days at room temperature. When heated over 40°, the solution decomposed to an opalescent substance.

Molecular Weight Determinations.—Molecular weights were measured cryoscopically in completely dried benzene. The measurements were carried out in a shielded cryoscopic cell with an electromagnetic stirring device after exclusion of air with a stream of dry nitrogen. Freezing points of benzene solutions of some compounds showed a tendency to decrease with time.

Measurements of Absorption Spectra in the Visible and Ultraviolet Regions.—Ultraviolet absorption measurements were made with a Beckman DU spectrophotometer using 1.0-cm. silica cells. The absorption spectra of III and V measured in appropriate alcohols showed similar curves having a maximum at 325 mμ (log ϵ 3.5). The absorption spectrum of irradiated $(BuO)_2Ti(acac)_2$ in the visible region was measured in *n*-hexane and showed a maximum at 600 mμ and a shoulder near 650 mμ.

The infrared absorption measurements were carried out with a Perkin-Elmer recording spectrophotometer model 112. Liquid samples were measured in thin films and the solid sample was measured using Nujol.

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

The Kinetics of Aromatic Hydrocarbon Chlorination in Acetic Acid. The Use of Zinc Chloride as a Catalyst and of Iodobenzene Dichloride as a Halogen Source

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In acetic acid methylbenzenes undergo chlorination by a reaction which is first order in halogen. The reactions are not inhibited by hydrogen chloride and are subject to relatively mild catalysis by zinc chloride. Bromination and iodination reactions in this solvent are of higher order than first in halogen in the absence of catalyst. The reactions are accelerated by zinc chloride and in some cases are complicated by trihalide formation. These differences may be explained in part through consideration of the relative stabilities of trihalide ions in acetic acid and of the role of acetic acid in the substitution reaction. Polymethylbenzenes chlorinate too rapidly in acetic acid for kinetic measurement. To investigate possible steric complications in the reactions of these hydrocarbons, iodobenzene dichloride has been tested as a potentially less reactive chlorinating agent than the free halogens. In this sense it has proved to be unsuitable. It dissociates slowly and comes to equilibrium with its components in dilute solutions in acetic acid. Its rate of reaction with mesitylene and pentamethylbenzene in acetic acid is identical with its rate of dissociation.

The investigation of the relative susceptibilities of a series of polymethylbenzenes to nuclear halogenation with bromine and with iodine monochloride in acetic acid has been simplified by the use of zinc chloride as a catalyst.[1,2] In the presence of this salt the orders of reactions with respect to these halogens reduce to unity and the kinetic complication of trihalide formation[2] is eliminated. In addition, by varying the catalyst concentration, relative halogenation rates for hydrocarbons of widely different reactivities can be established without changing the halogenating agent. With these observations in mind the effects of zinc chloride on the kinetics of chlorination of various methylbenzenes in acetic acid have been studied, and the results are presented in this paper.

One of the original objectives of this investigation was to determine whether the methyl group steric effect, which so markedly influences the susceptibility of polymethylbenzenes to bromination or iodination,[1,2] is less apparent in chlorination reactions. However, the higher molecular weight hydrocarbons, even in the absence of catalyst, react

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[1] L. J. Andrews and R. M. Keefer, THIS JOURNAL, **78**, 4549 (1956).

[2] R. M. Keefer and L. J. Andrews, *ibid.*, **78**, 5623 (1956).

too rapidly with chlorine for kinetic measurement. The possibility, therefore, has been considered that iodobenzene dichloride might serve as a less reactive chlorinating agent for use in a comparative rate study of the more reactive hydrocarbons. Although in this sense iodobenzene dichloride has proved to be an unsuitable reagent in acetic acid, the results of kinetic investigations concerning its function in aromatic chlorination are sufficiently interesting that they are included in this report.

Experimental

Materials.—The procedures used in preparing pure acetic acid, the aromatic hydrocarbons and dry zinc chloride have been described previously.[3,4] Eastman Organic Chemicals cyclohexene and iodobenzene were used without further treatment except for distillation of the latter.

Solutions of chlorine in acetic acid were prepared by passing cylinder gas (Ohio Chemical) directly into the solvent. Halogen analyses of the solutions were made iodometrically. In determining the extinction coefficients of chlorine solutions, the spectrum measurements were made first, and samples for iodometric analysis were then removed by pipet directly from the ground glass stoppered absorption cells to avoid volatility losses. Solutions of hydrogen chloride in acetic acid were prepared and analyzed as described elsewhere.[2]

Iodobenzene dichloride was made in small lots which were used immediately. The standard synthetic method[5] was used with the substitution of carbon tetrachloride for chloroform as the solvent. Iodometric analyses of weighed samples of the fresh product in acetic acid solution were generally within 1% of the theoretical value.

The Spectrum of Chlorine in Acetic Acid and in Solutions Containing Hydrogen Chloride and Zinc Chloride.—Contrary to what was found for solutions of hydrogen bromide and bromine[1] and of hydrogen chloride and iodine monochloride[2] in acetic acid, the ultraviolet spectra (Table I) of solutions of hydrogen chloride and chlorine in acetic acid do not offer positive evidence of the formation of trihalide ion (or HCl_3). The spectrum of a chlorine solution containing zinc chloride, at a concentration typical of that used in the rate runs, and hydrogen chloride is included in Table I.

TABLE I

THE EFFECT OF HYDROGEN CHLORIDE AND ZINC CHLORIDE ON THE SPECTRUM OF CHLORINE IN ACETIC ACID[a]

	Soln. I	Soln. II	Soln. III
$Cl_2 \times 10^3$, M	9.75	9.75	9.75
HCl, M	..	0.112	0.112
$ZnCl_2$, M	..	...	0.200
λ, mμ	ϵ	ϵ	ϵ
300	40.4	42.2	44.0
310	61.6	62.6	64.8
320	74.6	75.6	77.7
330	76.0	76.6	77.9
340	66.5	66.5	68.7
350	50.5	51.0	53.2
360	34.5	35.3	37.2
380	12.9	13.9	15.3

[a] The ϵ values are the molecular extinction coefficients of chlorine.

It is apparent that the salt also has no marked effect on the halogen spectrum.

The Rates of Chlorinations of the Hydrocarbons.—A single batch of purified acetic acid was used in carrying out the kinetic experiments. Stock solutions of the hydrocarbons and of zinc chloride in acetic acid were prepared from weighed samples of the reagents. Known volumes of these and of stock solutions of chlorine and hydrogen chloride were mixed at the temperature of the rate measurement. Samples of these mixtures, in silica absorption cells (10 cm., 2 cm. or 1 cm., depending on the initial concentration of chlorine), were placed in the housing of the Beckman spectrophotometer. Details concerning temperature control are given elsewhere.[2]

The changes in chlorine concentration were followed, generally to more than 75% of completion, by measuring optical densities of the rate samples (against an acetic acid blank) at a fixed wave length in the 340–370 mμ region. The wave lengths were chosen to provide initial readings, somewhere between 1.0–0.4. The data were, in certain cases, corrected for slight absorption by zinc chloride in the solutions.

The optical densities of dilute solutions of chlorine in acetic acid were observed to change negligibly during the time interval of even the longest rate runs. In other words errors resulting from the volatilization of chlorine were negligible.

The Dissociation of Iodobenzene Dichloride in Acetic Acid.—Qualitative experiments showed that the absorption in the near ultraviolet region of freshly prepared solutions of iodobenzene and chlorine in acetic acid were found to increase slowly with time. These changes were attributed to slow equilibration between iodobenzene dichloride and its components in acetic acid. It was found that the spectrum of an acetic acid solution which was 5.55×10^{-4} M in iodobenzene dichloride and 0.0989 M in iodobenzene did not change with time. The increases in absorption of solutions of chlorine and iodobenzene occurred more rapidly as the iodobenzene concentrations of the media were raised.

The optical density readings at equilibrium for two solutions, initially 2.39×10^{-3} M in chlorine and 0.164 and 0.0164 M in iodobenzene, were (after correction for the absorption of iodobenzene) nearly the same. It was assumed, therefore, that in acetic acid solutions in which the free iodobenzene concentration is of the order of 0.1 M, the conversion of chlorine to dichloride is essentially complete.

Extinction coefficients for iodobenzene dichloride over a short wave length range were calculated from equilibrium optical density readings of two of the solutions described above. These are recorded in Table II. Details of further experiments to determine the forward and reverse rate constants for dissociation of iodobenzene dichloride are included with the results.

TABLE II

THE SPECTRUM OF IODOBENZENE DICHLORIDE IN ACETIC ACID[a]

λ, mμ	350	360	370	380	390
ϵ of soln. I[b]	309	233	147	85.6	...
ϵ of soln. II[c]	312	224	144	86.0	45.6

[a] Based on optical densities after attainment of equilibrium. The optical densities were corrected for iodobenzene absorption. [b] Soln. I was originally 5.55×10^{-4} M in $C_6H_5ICl_2$ and 0.0989 M in C_6H_5I. [c] Soln. II was originally 2.39×10^{-3} M in Cl_2 and 0.164 M in C_6H_5I.

The Kinetics of Reaction of Iodobenzene Dichloride with Mesitylene and Pentamethylbenzene.—All rate measurements were carried out spectrophotometrically using 1-cm. absorption cells and an acetic acid blank. The changes in optical density with time recorded during a run were corrected for any small absorption which was observed at infinite reaction time.

Several hours prior to starting rate runs, a stock acetic acid solution of chlorine containing more than an equivalent amount of iodobenzene was prepared. The rate samples were prepared by mixing known volumes of this solution with known volumes of solutions of the hydrocarbon and, in some cases, of iodobenzene. A single batch of purified acetic acid was used in studying both kinetics of dissociation of iodobenzene dichloride and of chlorinations with iodobenzene dichloride.

The Product of Reaction of Pentamethylbenzene with Iodobenzene Dichloride in Acetic Acid.—To a freshly prepared solution of 0.65 g. (0.0024 mole) of iodobenzene dichloride in 80 ml. of acetic acid was added 0.300 g. (0.00202 mole) of pentamethylbenzene. This solution was allowed to

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[3] N. Ogimachi, L. J. Andrews and R. M. Keefer, THIS JOURNAL, **77**, 4202 (1955).

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

[5] H. J. Lucas and E. R. Kennedy, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 482.

stand in the dark overnight. It was then poured into 250 ml. of water. The slightly gummy precipitated solid, after washing with water and air drying, weighed 0.250 g. This material was recrystallized from ethanol to provide 90 mg. of fine white crystals of m.p. 153–155° (reported[6] m.p. for 6-chloro-1,2,3,4,5-pentamethylbenzene, 155°). The yield, based on crude product, was 67%. The purified product gave no precipitate when it was boiled with alcoholic silver nitrate.

Results

Zinc Chloride Catalyzed Chlorination.—The results of earlier investigations indicate that chlorination of methylbenzenes in acetic acid leads to high yields of nuclear substituted products[7] by processes which appear, on the basis of rather limited experimental detail, to be first order in hydrocarbon and in halogen.[8–10]

To assess the effects of zinc chloride on the chlorination rates of several methylbenzenes a more detailed investigation of the kinetics of the uncatalyzed reactions has now been conducted. In agreement with de la Mare and Robertson[9] these new data have been found to conform to the rate law

$$-d(Cl_2)/dt = k(ArH)(Cl_2) \qquad (1)$$

Retardation of the reactions through the accumulation of hydrogen chloride in the medium has not been encountered with any of the hydrocarbons under investigation, and this observation is in accord with the negative spectrophotometric evidence (see Experimental section) for interaction between hydrogen chloride and chlorine in acetic acid solution. Actually for several runs with *p*-xylene in which excesses of hydrogen chloride (as compared to chlorine) were added to the reaction mixtures, a slight enhancement in rates was observed, as was reported previously by de la Mare and Robertson.[9] For those runs in which the initial *p*-xylene to chlorine ratio was large the initial phase of the reaction was abnormally fast, probably because of a trace of *m*-xylene impurity in the hydrocarbon sample.

Table III summarizes the results of the runs, both at 25.2 and 45.3°, on the several hydrocarbons under investigation. Where the variation in hydrocarbon concentration was small, values of k(ArH) were calculated from the slopes of plots of logarithms of the measured optical densities (see Experimental section) *vs.* time. In general the fit of the data to linear plots was excellent except as noted for *p*-xylene. For the few runs in which the hydrocarbon concentration dropped appreciably as reaction occurred, k values were evaluated graphically by the usual procedure for bimolecular reactions.[11]

TABLE III

CHLORINATION RATE CONSTANTS AT 25.2°

$(ArH)_i$, mole/l.	$10^3 \times (Cl_2)_i$, moles/l.	$10^3 \times k$, sec.$^{-1}$ mole^{-1} l.	$(ArH)_i$, mole/l.	$10^3 \times (Cl_2)_i$, moles/l.	$10^3 \times k$, sec.$^{-1}$ mole^{-1} l.
Benzene			Toluene		
0.800	11.6	0.0069	0.400	27.0	0.60
			.400	14.4	.60
o-Xylene			.400	6.8	.61
			.200	6.7–7.1	.74[a]
0.402	7.4	8.3	.196	6.6	3.11[b]
0.201	7.4	7.5	.100	7.1	0.71
p-Xylene			*m*-Xylene		
0.194	30.8	3.56	0.0218	1.65	336
.194	15.4	3.50	.0218	0.85	336
.194	7.7	4.5[d]	.0109	0.85	338[c]
.198	8.6	4.6[e]			
.198	8.6	5.2[f]	Durene		
.097	7.7	4.3	0.00188	1.78	4640
.049	7.7	3.9	0.00188	0.90	3740

[a] Average of two runs of which values of 10^3k were 0.73 and 0.745. [b] Temperature for this run was 45.3°. [c] Average of two runs of which values of 10^3k were 335 and 341. [d] Average of two runs of which values of 10^3k were 4.5 and 4.5. [e] The initial concentration of HCl in the reaction mixture was 0.0112 *M*. [f] The initial concentration of HCl in the reaction mixture was 0.112 *M*.

As zinc chloride is added to the reaction medium, an acceleration of the aromatic hydrocarbon chlorination rate is observed. Equation 2 has been used in interpreting rate runs in the presence of this salt.

$$-d(Cl_2)/dt = k'(ArH)(Cl_2) = [k + k_c(ZnCl_2)][(ArH)(Cl_2)] \qquad (2)$$

Rate constants, k', have been determined for individual runs in the same way as were the constants, k, for the uncatalyzed reaction. These values and the k_c values for the third-order catalytic reactions at 25.2 and 45.3° of the several aromatic hydrocarbons which have been investigated are given in Table IV. Average values of k from Table III have been used in calculating the k_c values.

From the results reported in Tables III and IV it is clear that there are several marked differences in the kinetics of reaction of aromatic hydrocarbons with chlorine and with bromine or iodine monochloride in acetic acid. In discussing these differences the generalized mechanism for aromatic halogenation[1,2,12,13] in solvents of low polarity, which is given in equations 3–5, is useful.

$$ArH + X_2 \rightleftarrows ArH \cdot X_2 \qquad (3)$$

$$ArH \cdot X_2 + E \longrightarrow ArH \cdot X^+ + EX^- \qquad (4)$$

$$ArHX^+ \longrightarrow ArX + H^+ \qquad (5)$$

Equation 4, in which the halogen–halogen bond of an aromatic–halogen π-complex is severed by attack of an electrophilic reagent, E, represents the rate-determining step.

In the absence of a catalyst the solvent alone may function as the reagent E, in which case the reaction should show first-order dependence on halogen. The reactions of toluene and *p*-xylene with iodine monochloride in trifluoroacetic acid behave kineti-

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(6) A. Tohl, *Ber.*, **25**, 1524 (1892).

(7) G. Illuminati and G. Marino, THIS JOURNAL, **78**, 4975 (1956).

(8) K. Lauer and R. Oda, *Ber.*, **69**, 1061 (1936).

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

(10) Chlorinations of phenolic ethers and of anilides in acetic acid have been shown to be second order over-all; see, for example, A. E. Bradfield and B. Jones, *J. Chem. Soc.*, 3073 (1928); B. Jones, *ibid.*, 418, 676 (1942).

(11) The relative values found for k at 25.2° for toluene, *p*-xylene and *o*-xylene are in the ratio 1/6.7/10. These values compare favorably with those (1/6.3/13.4) calculated from the times of 20% reaction at 24° in 99% acetic acid reported by de la Mare and Robertson[9] for reaction mixtures containing equal concentrations of chlorine and hydrocarbon. The rate constants at 25.2° reported in Table III for toluene, and the xylenes are about 1.3 times as large as those which can be estimated from the results reported by de la Mare and Robertson for 24°.

(12) R. M. Keefer, A. Ottenberg and L. J. Andrews, THIS JOURNAL, **78**, 255 (1956).

(13) K. L. Nelson, *J. Org. Chem.*, **21**, 145 (1956).

cally in this way.[14] In acetic acid the uncatalyzed iodination reactions are second order in iodine monochloride,[2] and bromination reactions are second order in halogen, although a small contribution from a first-order process may be detected at low bromine concentrations.[12] Apparently in these cases a second halogen molecule serves as the electrophilic reagent. The superiority of trifluoroacetic acid as compared to acetic acid in promoting halogenation by the first-order process has been ascribed to the importance of proton sharing by the solvent when it participates in the abstraction of halide ion from the complex in the rate determining step.[14]

TABLE IV

RATE CONSTANTS FOR THE ZINC CHLORIDE CATALYZED REACTION AT 25.2°

$(ArH)_i$, mole/l.	$10^3 \times (Cl_2)_i$, moles/l.	$(ZnCl_2)$, mole/l.	$10^3 k'$, sec.$^{-1}$ mole^{-1} l.	$10^3 k_c$, sec.$^{-1}$ mole^{-2} l.^{2}
		Benzene		
0.400	14.0	0.400	0.072	0.16
		Toluene		
0.400	14.4	0.400	8.4	19.5
.400	30.2	.200	3.52	14.6
.400	14.4	.200	3.52	14.6
.400	7.5	.200	3.35	13.7
.400	14.4	.100	1.80	12.0
.200	7.5	.200	3.48	13.9
.100	6.8–7.5	.200	3.57	14.3[a]
.098	6.6	.196	14.9	60.2[b]
		o-Xylene		
0.402	7.4	0.200	33.1	128
0.402	7.4	0.100	19.7	122
		m-Xylene		
0.0109	0.79	0.103	632	2860
0.00109	0.66	0.207	920	2820
		p-Xylene		
0.198	8.0	0.200	24.0	102
.198	8.0	.100	12.7	92
.198	8.0	.050	8.0	91
.198	8.6	.200	34.4	146[c]
		Durene		
0.00188	0.78	0.103	4660	[d]

[a] Average of two runs of which values of $10^3k'$ were 3.52 and 3.61. [b] Temperature for this run was 45.3°. [c] The initial concentration of HCl in the reaction mixture was 0.112 *M*. [d] The k_c value for durene is not reported since the k value required for its calculation is somewhat uncertain (see Table III). The error resulting from this uncertainty might have been minimized were not durene too reactive to permit the determination of k' values at zinc chloride concentrations higher than 0.1 *M*.

In chlorination reactions in acetic acid the solvent again appears to serve satisfactorily as the reagent E. The likelihood that a second molecule of chlorine should fill this role seems minimal since, unlike iodine monochloride, chlorine shows no tendency to coördinate with chloride ion in acetic acid. Actually the rate of first-order bromination of mesitylene in acetic acid is relatively slow,[12] but the hydrocarbon chlorinates virtually instantaneously in this medium even at low (0.01 *M* or less) initial reactant concentrations.

The rate superiority of chlorine over bromine and iodine monochloride in the first order (in halogen) substitution reactions may be explained in part by consideration of the solvation energies of the halogens. Acetic acid functions as a donor in interacting with iodine monochloride and with bromine.[15] The extent of this interaction is smaller for bromine than for iodine monochloride and must be even smaller[16] in solutions of chlorine in acetic acid, and the solvation energies for the halogens probably fall off in this same order.[2] In forming a complex with the aromatic hydrocarbon (equation 3) the halogen must undergo some desolvation, and the desolvation energy must make a direct contribution (smaller for chlorine than for the heavier halogens) to the activation energy of the substitution reaction.

It appears, furthermore, that acetic acid is considerably more effective in the transition state of the chlorination reaction as a solvating agent for halide ion which is separating from the aromatic–halogen complex than it is in bromination and iodination reactions. Zinc chloride has a relatively small influence on the kinetics of hydrocarbon chlorination. At concentration levels of zinc chloride at which bromination and iodination reactions are first order with respect to the two reactants and to the catalyst,[1,2] a significant fraction of the chlorination reaction still appears to take place by a catalyst-independent process. Whereas the ratio of k_c/k values for the chlorination reactions studied in this investigation range from 23 for benzene to 8 for *m*-xylene, the corresponding ratio of rate constants[1,4] for mesitylene bromination by reactions which are first order in halogen is of the order of magnitude of 3×10^5.

A comparison of the activation energies for the halogenation reactions also indicates that the influence of zinc chloride is small in chlorinations. For mesitylene bromination the activation energy for the first-order (in bromine) uncatalyzed reaction[4] is 15 kcal./mole and that for the reaction in the presence of zinc chloride[1] is only 7 kcal./mole. Activation energies for the zinc chloride catalyzed iodination reaction of several aromatic hydrocarbons[2] range around 17 kcal./mole, and those for uncatalyzed first-order reactions in iodine monochloride, if measurable, would probably be much higher. The corresponding activation energies for the uncatalyzed and catalyzed chlorination of toluene (calculated from the k and k_c values at 25.2 and 45.3° given in Tables III and IV) are both 13.4 kcal./mole. In view of the identity of these two experimental values, one is inclined to wonder whether the favorable influence of zinc chloride on the chlorination rate might better be classified as a salt effect rather than as true catalysis. It is evident from previous studies of the influences of zinc chloride on the rates of hydrocarbon bromination and iodination reactions that catalytic and environmental effects of this salt cannot be measured separately.

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(14) L. J. Andrews and R. M. Keefer, THIS JOURNAL, **79**, 1412 (1957).

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

(16) L. J. Andrews and R. M. Keefer, *ibid.*, **73**, 462 (1951).

The Relative Halogenation Rates of the Methylbenzenes.—As noted in the introduction, the results of the earlier investigations of the kinetics of zinc chloride catalyzed halogenations indicate that the reactions of highly methylated benzenes are subject to marked steric retardation.[1,2] The steric problem seems to be much more pronounced in iodination than in bromination reactions. Presumably the attack of chlorine on the aromatic nucleus should be less subject to hindrance than that of the larger halogens. The present results provide limited information on this point.

Partial rate factors for halogenation at positions *ortho*, *meta* and *para* to methyl groups relative to that at one position in benzene[17] have been calculated from the chlorination rate constants at 25.2° for benzene, toluene and *o*- and *p*-xylene. For the uncatalyzed reaction they are $o_f = 95$, $m_f = 7.9$ and $p_f = 304$; and for the catalyzed reaction they are $o_f = 130$, $m_f = 6.4$ and $p_f = 235$. These values for the catalyzed reaction may be used to predict a reactivity ratio of 1.3×10^4 for *m*-xylene and benzene as compared with an experimental value of 1.7×10^4. The partial rate factors for the uncatalyzed reaction lead to predicted *m*-xylene/benzene and durene/benzene rate ratios of 1.1×10^4 and 1.9×10^5, respectively. The experimental values are 4.8×10^4 and 5.7×10^5, respectively. In situations in which extreme steric hindrance to halogenation appears to exist, observed polymethylbenzene reactivities are considerably less than those predicted from the partial rate factors.[1,2] In other words, the available data suggest that methylbenzene chlorinations are not unusually sensitive to the methyl group steric effect.

Reactions with Iodobenzene Dichloride.—An attempt has been made to determine the rate constant, *k*, for chlorination of the higher molecular weight methylbenzenes through inclusion of iodobenzene in the reaction mixtures. If an equilibrium were established rapidly and reversibly with respect to formation of iodobenzene dichloride, one might, by adjustment of the iodobenzene concentration, lower the concentration of free chlorine sufficiently to permit rate measurements on the more reactive hydrocarbons.

Investigation has shown, however, that while an equilibrium is indeed established between iodobenzene dichloride and its components in acetic acid solution, the equilibration process is relatively slow. When mesitylene or pentamethylbenzene are chlorinated in solutions containing iodobenzene, the chlorination rate is independent of the aromatic hydrocarbon and iodobenzene concentrations and is controlled by the rate of decomposition of iodobenzene dichloride into its components (see equations 6 and 7).

$$C_6H_5ICl_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} C_6H_5I + Cl_2$$

$$k_1/k_2 = K = \frac{(C_6H_5I)(Cl_2)}{(C_6H_5ICl_2)} \qquad (6)$$

$$ArH + Cl_2 \xrightarrow{k_3} ArCl + HCl \qquad (7)$$

In other words, for the reactions of pentamethylbenzene and mesitylene the condition that $k_3(ArH) >> k_2(C_6H_5I)$ must hold.

In Table V rate constants k_1 for the reactions of these two hydrocarbons with iodobenzene in acetic acid are summarized. These were calculated on the assumption that the rate law for chlorination is

$$-d(ArH)/dt = -d(C_6H_5ICl_2)/dt = k_1(C_6H_5ICl_2) \qquad (8)$$

TABLE V

RATE CONSTANTS AT 25.2° FOR CHLORINATION BY $C_6H_5ICl_2$

$(ArH)_i$, mole/l.	$10^3 \times (Cl_2)_i$, moles/l.	$10^3 \times (\varphi I)_i$, moles/l.	$10^3 k_1$, sec.$^{-1}$	$(ArH)_i$, mole/l.	$10^3 \times (Cl_2)_i$, moles/l.	$10^3 \times (\varphi I)_i$, moles/l.	$10^3 k_1$, sec.$^{-1}$
Mesitylene				Pentamethylbenzene			
0.400	4.6	25.7	0.145	0.100	5.4	25.7	0.177
.100	18.8	18.8	.246[a]	.0100	11.1	11.9	.226
.100	9.2	31.6	.234	.0102	9.9	11.9	.277
.100	4.6	45.5	.184	.0100	9.7	11.6	2.38[b]
.100	4.6	25.7	.184	.0100	5.4	25.7	0.207
.100	2.3	22.8	.184	.0100	5.4	5.9	.212
.010	5.5	25.7	.199	.0102	4.9	5.9	.227
				.0100	4.8	5.8	2.02[b]
Cyclohexene				.0100	2.77	2.97	0.206
0.102	18.8	18.8	0.232[a]				

[a] Crystalline $C_6H_5ICl_2$ was used in preparing rate samples. [b] Temperature for these two runs was 45.6°. Rate constants for these two runs and for the runs just above them in the table were used in calculating the reported activation energy. These runs were all made on the same day using the same batches of stock solutions.

As the disappearance of iodobenzene dichloride was followed spectrophotometrically (see Experimental section), k_1 values for each run were actually determined from the slopes of linear plots of the logarithms of measured optical densities *versus* time. The reactions were in general followed to at least 74% completion.

In most cases the initial iodobenzene dichloride concentrations of the reaction mixtures were established through dilution of relatively concentrated solutions of iodobenzene and chlorine in acetic acid, which had been prepared sufficiently well in advance so that the chlorine was largely converted to the dichloride. When solid iodobenzene dichloride itself was used as the dihalide source, the rate samples were made up using freshly prepared solutions of the solid in acetic acid. In all reported runs, therefore, the initial iodobenzene dichloride concentrations are approximated by the values of $(Cl_2)_i$ given in Table V. It may be assumed that any free chlorine initially present in the reaction mixtures disappeared immediately by reaction with the aromatic hydrocarbon.

The rate constants for runs of widely varying concentrations of the various reactants are all of the order of magnitude of 0.2×10^{-3} sec.$^{-1}$ at 25.2° for both pentamethylbenzene and mesitylene and are in close agreement with the rate constant measured for one run in which the aromatic hydrocarbon was replaced by cyclohexene, a substance which consumes free chlorine rapidly.

The constant k_1 was evaluated independently by studying the rate of equilibration of iodobenzene dichloride with its components in acetic acid. Solutions of the solid dichloride in acetic acid were prepared and standardized iodometrically. The changes in optical density of these solutions at an

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(17) J. E. Condon, THIS JOURNAL, **70**, 1963 (1948).

appropriate wave length in the 340–380 mμ region were followed to the time of equilibration. The concentrations of free chlorine and of iodobenzene dichloride throughout the runs were calculated from measured optical densities using the extinction coefficients given in Tables I and II.

The equilibrium constants, $K = k_1/k_2$, for each run were calculated from equilibrium readings. The individual rate constants for the forward and reverse reaction are also related by differential equation 9.

$$-\mathrm{d}(C_6H_5ICl_2)/\mathrm{d}t = k_1(C_6H_5ICl_2) - k_2(C_6H_5I)(Cl_2) \quad (9)$$

A useful integrated form of equation 9 is given in equation 10, in which $a = (C_6H_5ICl_2)_i$, $b = -2(C_6H_5ICl_2)_i - K$ and $A = (C_6H_5ICl_2)$. The

$$\ln \frac{2A + b - \sqrt{b^2 - 4a}}{2A + b + \sqrt{b^2 - 4a}} - \ln \frac{2a + b - \sqrt{b^2 - 4a}}{2a + b + \sqrt{b^2 - 4a}} = k_2t\sqrt{b^2 - 4a} \quad (10)$$

constants k_2 were determined from the slopes of the linear plots of the left-hand term of equation 10 *vs.* time. The results of these runs are summarized in Table VI, in which the values of k_1 and K for the several runs at 25.2 and 45.6° are listed along with equilibrium values of the optical densities of the reaction mixtures.

TABLE VI

RATE CONSTANTS AND EQUILIBRIUM CONSTANTS FOR THE DECOMPOSITION OF IODOBENZENE DICHLORIDE

$10^3 \times$ $(C_6H_5ICl_2)$, moles/l.	λ,[a] mμ	d_{eq}	10^3k_1, sec.$^{-1}$	10^3K,[b] moles/l.	t, °C.
13.7	380	0.900	...	1.47	25.2
2.73	340	.340	0.139	1.54	25.2
1.37	360	.134	0.148	1.44	25.2
2.75	360	.254	1.24	4.3	45.6
1.37	360	.100	1.30	4.3	45.6

[a] Wave length at which runs were made; 1-cm. absorption cells and an acetic blank were used. [b] Value of $\Delta H^0 = 9.9$ kcal./mole is calculated from average K values at the two temperatures.

One run also was made at 25.2° in which the change in optical density at 380 mμ of an acetic acid solution originally 2.97×10^{-3} M in iodobenzene and 3.23×10^{-3} M in chlorine was followed to the equilibrium point. An equilibrium constant ($K = 2.0 \times 10^{-3}$ mole/l.), calculated from the equilibrium data for this run, compares favorably with an average value of 1.5×10^{-3} mole/l. for the runs reported in Table VI. Rate constants for this run were evaluated graphically according to equation 10 with, in this case, $a = (C_6H_5I)_i(Cl_2)_i$ and $b = -(C_6H_5I)_i - (Cl_2)_i - K$. The resultant k_1 value, 0.16×10^{-3} sec.$^{-1}$, was also in good agreement with the values listed in Table VI.

Although the values of k_1 reported in Table V are on the average somewhat higher than those in Table VI, the agreement is sufficiently good to support the proposed mechanism for the aromatic chlorinations by iodobenzene dichloride. It is particularly gratifying that the activation energy calculated from rate constants k_1 for the reaction of pentamethylbenzene with iodobenzene at 25.2 and 45.6° ($E_a = 20.1$ kcal./mole) is almost identical with that calculated from the averages of rate constants for the dissociation of iodobenzene dichloride which are given in Table VI ($E_a = 20.2$ kcal./mole.)

A few qualitative tests were made to determine the behavior of iodobenzene dichloride in non-polar solvents. Dilute solutions of the dihalide in benzene and in carbon tetrachloride showed no changes in spectra over a several-hour period, an indication that dissociation to form the component materials did not occur. Similarly the ultraviolet spectrum of a benzene solution of the dichloride which contained an excess of cyclohexene remained invariant for several hours, and then the dichloride suddenly disappeared completely from the solution.

The reaction which occurred may well have been radical induced. Certainly, further work on the function of the dihalide as a halogen source in nonpolar media is required to rationalize the results of earlier investigators.[18–20]

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Nature of Aliphatic C-Nitroso Compounds. I. Study of the Rate of Dissociation of the Aliphatic C-Nitroso Dimer in Various Solvents

BY JOSEPH R. SCHWARTZ

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The rate of dissociation of two aliphatic nitroso dimers, $(CH_3)_2C(NO)CH_2R$, with R = CH_3 and R = OAc in a series of solvents at several temperatures is reported. From the activation parameters, it is concluded that the inductive effect is mainly responsible for rate trends and solvent effects observed.

Introduction

It has been known for some time that many aliphatic C-nitroso compounds exist in the solid state as dimers and, when dissolved in various solvents, dissociate into blue monomers at a measurably slow rate.[1,2] Crystal studies on the dimer show that the N–N distance is between the single- and

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(2) N. V. Sidgwick, "Organic Chemistry of Nitrogen Compounds," Oxford University Press, London, 1942, p. 204.