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The Zinc Chloride-catalyzed Reaction of Polymethylbenzenes with Iodine Monochloride in Acetic Acid Solution

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The kinetics of the zinc chloride catalyzed reactions of iodine monochloride with a series of methylbenzenes in acetic acid have been investigated. Under the conditions of these experiments nuclear iodination of the aromatic substances occurs by a process which is first order with respect to each reactant and to the catalyst. In the absence of catalyst the reactions are self-inhibiting since the hydrogen chloride which is produced forms an unreactive complex with iodine monochloride. Zinc chloride also interacts strongly with hydrogen chloride and can be introduced in the reaction media in sufficient quantity to prevent trihalide formation. Evidence has previously been presented that the zinc chloride catalyzed brominations of the more highly alkylated benzenes in acetic acid are subject to steric inhibition. The steric problem is sharply accentuated when iodine, rather than bromine, is the entering halogen. The relative rates of halogenation of pentamethylbenzene and mesitylene, as well as those of certain other pairs of the hydrocarbons, actually reverse when bromine is replaced by iodine monochloride as the halogenating agent. These steric effects are reflected to some extent in the activation energies for the iodination reactions.

As the benzene ring is subjected to increasing methylation it becomes a stronger electron donor[1] and also becomes more susceptible to electrophilic substitution.[2-4] Evidence is accumulating, however, which indicates that in some reactions of highly alkylated benzenes these favorable electronic effects of ring substituents may be counteracted sterically.[4,5] Recently such a steric explanation was used in the interpretation of some of the results of a kinetic study of the rates of the zinc chloride catalyzed bromination of a series of methylbenzenes in acetic acid.[6] This explanation was proposed to account for the fact that the partial rate factors for bromination at positions *ortho*, *meta* and *para* to ring methyl substituents (calculated from the rates of bromination of the isomeric xylenes relative to that of benzene) lead to predicted rates of reaction for the more highly methylated aromatics which are much larger than were observed.[7]

If the suppressed reactivity of the polymethylbenzenes with respect to nuclear halogenation is truly steric in origin, one may anticipate more dramatic indications of a hindrance problem if iodine rather than bromine is employed as the entering halogen atom. This point has now been tested through investigation of the kinetics of the zinc chloride catalyzed iodination of a series of methylbenzenes with iodine monochloride in acetic acid.

Experimental

Materials.—The procedures used in preparing pure acetic acid, the aromatic hydrocarbons and dry zinc chloride have been described previously.[8,9] The iodine monochloride, b.p. 100–103°, was prepared from the elements.[10]

The Rate Runs.—The procedures used in following the rates of the iodination reactions were similar to those used in studying zinc chloride catalyzed brominations of the hydrocarbons.[6] Solutions of known concentrations of the hydrocarbon (0.05–0.200 M), zinc chloride (0.25–1.4 M) and iodine monochloride ($1.9-7.5 \times 10^{-3}$ M) were prepared at the temperature at which rate measurements were conducted. The rate samples prepared from those solutions were placed in 1-cm. glass stoppered absorption cells in the cell housing of the Beckman spectrophotometer, the temperature of which was controlled to ±0.1° during the course of the measurements. In making runs at temperatures in the region of 45° the rate sample was allowed several minutes to equilibrate to housing temperature before the initial readings were made. The rates were followed, generally to better than 80% of completion, by measuring the optical densities of the solutions against acetic acid as the blank at 370 mμ, the wave length of the near-ultraviolet absorption maximum of iodine monochloride in acetic acid. In most runs the readings at completion of reaction at 370 and 520 mμ (a region in which iodine, but not iodine monochloride, absorbs strongly) were recorded, respectively, to determine the correction for the contribution of salt to the measured optical densities and to ascertain whether appreciable quantities of iodine were liberated in the reactions. The production of iodine was observed to a measurable degree only in runs with pentamethylbenzene. Even in these runs (at 25°) the mole ratio of iodine at reaction completion to initial iodine monochloride was estimated not to exceed 1/30. The fact that the 520 mμ readings in runs with pentamethylbenzene increased slowly after iodine monochloride was completely consumed suggested that the iodine was produced by decomposition of the iodinated aromatic hydrocarbon rather than as a direct product of the halogenation reaction. It has been reported previously that in the absence of a catalyst the reaction of pentamethylbenzene with iodine monochloride in acetic acid produces a substantial quantity of chlorinated hydrocarbon and iodine.[11]

The Influence of Hydrogen Chloride on the Spectra of Iodine Monochloride Solutions.—Aromatic halogenation reactions with iodine monochloride in acetic acid are self-inhibiting, since the hydrogen chloride formed as a product binds unreacted halogen as trihalide ion.[11] The present series of kinetic experiments were designed on the assumption that this complication might be avoided if substantial excesses of zinc chloride (relative to the halogen) were present in the reaction mixtures to trap out hydrogen chloride as $HZnCl_3$. It has already been shown that zinc chloride in solutions of hydrogen bromide and bromine in acetic acid prevents tribromide formation.[7]

The validity of the assumption concerning prevention of ICl_2^- (or $HICl_2$) formation was confirmed by measuring the influences of hydrogen chloride, in the presence and absence of zinc chloride, on the spectra of iodine monochloride solutions in acetic acid. The results are summarized in Table I.

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[1] L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954).

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

[3] F. E. Condon, THIS JOURNAL, **70**, 1963 (1948).

[4] H. C. Brown and C. W. McGary, Jr., *ibid.*, **77**, 2310 (1955).

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

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

[7] A similar explanation has been used[4] in the interpretation of the kinetics of mercuration of methylbenzenes.

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

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

[10] A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans Green and Co., London, 1948, p. 846.

[11] L. J. Lambourne and P. W. Robertson, *J. Chem. Soc.*, 1167 (1947).

TABLE I

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

	Soln. I	Soln. II	Soln. III	Soln. IV	Soln. V
$ICl \times 10^3$, *M*	4.88	3.66	3.56	3.56	3.56
$HCl \times 10^3$, *M*	...	186	6.72	6.72	...
$ZnCl_2$, *M*	...	...	...	0.100	0.100
λ, mμ	ε	ε[b]	ε	ε	ε[c]
420	76	36	64	75	76
400	105	53	90	106	108
380	129	100	127	134	133
370	137	149	158	142	141
360	141	208	189	146	141
350	140	264	211	137	132
340	127	287	210	108	115
330	102	250	178	90	86
320	73	173	127	58	58
310	49	125	100	35	35
300	46	169	140	26	23

[a] Reported values of ε, the molecular extinction coefficients, are based on total iodine monochloride (free and complexed) concentrations. [b] This is essentially the spectrum of ICl_2^- (or $HICl_2$). These values for ε do not change appreciably with an increase in the hydrogen chloride concentration. [c] These values do not change markedly as the zinc chloride concentration of the solution is increased up to 0.90 *M*.

Anhydrous hydrogen chloride, for use in these measurements, was generated by mixing concentrated hydrochloric and sulfuric acids. The gas was passed through scrubbers containing sulfuric acid and acetic acid and was collected in purified acetic acid. The resultant stock solution was analyzed gravimetrically.

In Table I (solutions I and II) the spectrum of iodine monochloride in the absence of hydrogen halide and in the presence of a large excess of hydrogen halide are compared. The spectrophotometric data for solution III, which contained a relatively small amount of hydrogen chloride, indicate the presence of a significant amount of trihalide ion or $HICl_2$ (*cf.* solution II). Solution IV, which contains zinc chloride (0.1 *M*) in addition to the components of solution II, displays the spectrum of a hydrogen halide free solution above 350 mμ. The depression in extinction coefficients for this solution below 350 mμ may be traced to the presence of zinc chloride (*cf.* solution V).

An attempt was made to estimate the interaction constant for iodine monochloride and hydrogen chloride at 25.2°. A series of acetic acid solutions of about 3.6×10^{-3} *M* iodine monochloride concentration, which varied in hydrogen chloride from $6.7–16.8 \times 10^{-3}$ *M*, were prepared. The optical densities of these solutions were measured in 1-cm. absorption cells against an acetic acid blank at several wave lengths between 320 and 350 mμ. These values for each solution at each wave length and the known values for the molecular extinction coefficients of iodine monochloride and trihalide (solutions I and II, Table I) were used to calculate values of K_c where

$$K_c = (HICl_2)/(ICl)(HCl) \qquad (1)$$

These varied widely between 200–300. Since the equilibrium constant is large and the extinction coefficients of ICl and $HICl_2$ are not widely different in magnitude, this variation is to be expected.

Product Isolation Experiments.—To establish the nature of the reaction products formed under experimental conditions which approximated those of the rate runs, the following experiments on mesitylene and pentamethylbenzene were performed:

A solution of 3.24 g. (0.0270 mole) of mesitylene, 5.44 g. (0.040 mole) of zinc chloride and 1.50 ml. (0.0276 mole) of iodine monochloride in 100 ml. of acetic acid was allowed to stand overnight. The solution, which still showed some halogen color, was then poured into 500 ml. of water. A heavy halogen-contaminated oil, which soon became semisolid, separated. The aqueous phase was decanted, and the crude product was decolorized by warming and shaking with dilute sodium thiosulfate. On cooling this mixture the product separated as a white solid which, after washing with water and air drying, weighed 6.24 g. (94% yield) and melted from 30.5–31.0° (reported[12] for 2-iodomesitylene, m.p. 30.5°). The product gave no perceptible precipitate on boiling with alcoholic silver nitrate solution.

To a solution of 2.00 g. (0.0135 mole) of pentamethylbenzene and 2.72 g. (0.020 mole) of zinc chloride in 50 ml. of acetic acid a total of 0.73 ml. (0.0135 mole) of iodine monochloride was added in small portions over a 15-minute interval. Precipitation of crystalline material began when about three-quarters of the halogen was added. The mixture was allowed to stand overnight, and the light yellow crystalline material was then separated from the deep-brown mother liquor and washed with water. A second crop of crystalline material was obtained by adding 200 ml. of water to the mother liquor. The two batches of crude product, after air drying, weighed 3.70 g. (84% yield) in total. After recrystallization from alcohol, the 6-iodo-1,2,3,4,5-pentamethylbenzene was obtained in the form of shiny white plates, m.p. 138–140° (reported[12] previously, m.p. 127°). Because of the discrepancy in these melting points, combustion and halogen analyses of the product were obtained.

Anal. Calcd. for $C_{11}H_{15}I$: C, 48.18; H, 5.51; I, 46.38. Found: C, 47.91; H, 5.43; I, 46.80.

The product gave no precipitate in boiling alcoholic silver nitrate solution.

Results

The Iodination Rate Constants.—In general the methylbenzenes are much less reactive with respect to zinc chloride catalyzed nuclear halogenation with iodine monochloride than with bromine. For example, the halogenation rate constants $[-d(X_2)/dt/(X_2)(ArH)(ZnCl_2)]$ for the reaction of mesitylene with bromine and with iodine monochloride are, respectively, 15.8 and 0.060 $mole^{-2}\ l.^2\ sec.^{-1}$ in solutions containing similar concentrations of reactants and zinc chloride. It seems probable that at least a part of this difference can be traced to differences in the solvation energies of the two halogens in acetic acid.[13] The same relative order of reactivity of the two halogens has been reported for the uncatalyzed reactions in acetic acid.[11]

To account for the results of kinetic studies of zinc chloride catalyzed bromination of the hydrocarbons in acetic acid the mechanism

$$ArH + Br_2 + ZnCl_2{\cdot}HOAc \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ArHBr^+OAc^- + H^+ZnCl_2Br^- \qquad (2)$$

$$ArHBr^+OAc^- \xrightarrow{k_3} ArBr + HOAc \qquad (3)$$

was postulated.[6] In general the reactions, which were run with the hydrocarbon and catalyst concentrations in large excess of that of the bromine, did not show simple first-order kinetics with respect to halogen. Presumably the back reaction

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[12] See, for example, A. Edinger and P. Goldberg, *Ber.*, **33**, 2875 (1900).

[13] The results of R. E. Buckles and J. F. Mills, THIS JOURNAL, **75**, 552 (1953), suggest that there are pronounced differences in the extent to which donor–acceptor type interactions occur in solutions of the two halogens in acetic acid. It seems likely[8] that there are parallel differences in the solvation energies. It is interesting, in this regard, that mesitylene and bromine interact measurably to form 1:1 complexes in both carbon tetrachloride (*K* 0.38) and in acetic acid (*K* 0.11). See J. H. Blake and R. M. Keefer, THIS JOURNAL, **77**, 3707 (1955), and R. M. Keefer, A. Ottenberg and L. J. Andrews, *ibid.*, **78**, 255 (1956). The corresponding equilibrium constant for the interaction of mesitylene and iodine monochloride in carbon tetrachloride is[8] $K = 3.70$. It was found in the present investigation that the extent of this interaction in acetic acid is too small to measure. Apparently solvation by acetic acid markedly reduces both the acidity and the electrophilic character of iodine monochloride.

of equation 2 became appreciable even when relatively small amounts of $H^+ZnCl_2Br^-$ had formed. The reactions were highly sensitive to salt effects. As the zinc chloride concentration was decreased, the apparent reaction order with respect to catalyst dropped off sharply but approached unity only at concentrations below 0.03 *M*.

The kinetic picture for the iodination reaction is much simpler. In the presence of large excesses of hydrocarbon and catalyst, the reactions were found to be first order with respect to each reactant and approximately so with respect to the catalyst when its concentration did not exceed 0.1 *M*. Evidence for the influence of a back reaction (eq. 2) on the over-all rates was completely lacking. At higher zinc chloride concentrations, salt effects again were observed. These points are illustrated in Table II, which lists k_1 values ($k_1 = k/(\text{ArH})\cdot(\text{ZnCl}_2)$) for all of the runs which were made in this investigation. The rate constant k is defined by equation 4

$$kt = \ln (\text{ICl})_i/(\text{ICl})_t = \ln d_i/d_t \qquad (4)$$

in which d represents the measured optical density (see Experimental section).

TABLE II

THE IODINATION RATE CONSTANTS[a]

(ArH)$_i$, mole/l.	10^3 (ICl)$_i$, mole/l.	(ZnCl$_2$)$_i$, mole/l.	$10^3 k_1$, sec.$^{-1}$ mole^{-2} l.^{2}
Mesitylene, $t = 25.2°$			
0.102	7.20	0.056	60.4
.102	7.20	.112	61.6
.050	3.87	.200	72.5
.100	3.87	.200	71.0
.200	3.87	.200	65.5
.200	1.94	.200	67.5
.200	7.74	.200	69.0
.200	3.87	.400	91.5
.100	3.78	.800	146
$t = 45.4°$			
0.100	7.20	0.055	319
.200	7.20	.055	320
.100	7.20	.109	326
Pentamethylbenzene, $t = 25.2°$			
0.205	7.20	0.056	29.1
.103	7.20	.112	30.4
.100	3.77	.206	37.3
.050	3.77	.412	42.0
.100	3.72	.400	42.3
.100	1.86	.400	42.8
.100	7.44	.400	42.2
.050	3.77	.824	61.0
$t = 45.4°$			
0.202	7.20	0.055	167
.101	7.20	.109	173
o-Xylene, $t = 25.2°$			
0.189	3.59	0.800	0.104
.189	7.18	.800	.107
.190	3.60	1.40	.180
$t = 45.4°$			
0.186	3.52	1.37	1.39
m-Xylene, $t = 25.4°$			
0.195	3.68	0.400	1.18
.097	3.68	.800	1.85
.195	7.36	.800	1.85
.097	3.59	1.40	3.33
m-Xylene, $t = 45.5°$			
0.191	3.60	0.392	8.31
.095	3.60	.784	13.1
.191	7.20	.784	12.9
Durene, $t = 25.2°$			
0.074	3.86	.400	1.39
.150	3.86	.800	1.85
.150	7.46	.800	1.89
.074	3.73	1.40	3.14
$t = 45.6°$			
0.147	3.60	0.784	12.5
Isodurene, $t = 25.2°$			
0.079	7.2	0.050	61.3
.081	3.68	.200	76.0
.081	3.68	.400	86.5
.081	7.36	.400	90.0
.081	3.68	.800	129
$t = 45.6°$			
0.078	7.2	0.049	354
Pseudocumene, $t = 25.2°$			
0.100	3.68	0.400	3.97
.100	3.68	.800	6.25
.100	7.36	.800	6.02
.100	3.68	1.40	10.3
p-Xylene, $t = 25.2°$			
0.191	3.68	0.800	0.085
.191	7.36	.800	.079
.191	3.68	1.40	.131
Toluene, $t = 25.2°$			
0.204	3.68	1.40	.018
Benzene, $t = 25.2°$			
0.226	3.68	1.40	<.00016
sym-Triethylbenzene, $t = 25.2°$			
0.102	3.78	0.400	11.3
.102	3.78	.800	18.3

[a] In the cases in which the data of individual runs gave the poorest fit to linearity, the uncertainty in the reported rate constants is estimated not to exceed 5–6%.

The rate constants, k, were determined from plots of log d_t *vs.* time. The data, when so treated, conformed well to straight lines except in cases in which the hydrocarbon or zinc chloride (because of $HZnCl_3$ formation) concentrations diminished slightly during the course of the runs. In such cases the data were subjected to slight correction for these concentration changes before the reported rate constants were calculated.

Benzene is highly unreactive to iodine monochloride in acetic acid at 25.2° even when the zinc chloride concentration of the medium is as high as 1.4 *M*. In the one run on benzene at 25.2° (Table II) which was made in this investigation, only 10% of the halogen disappeared in 15 days. Not all of this disappearance represented aromatic halogenation, since the halogen content of a blank run which contained no benzene also diminished measurably during this time. The reported rate constant (although corrected for the blank) is, therefore, only a rough approximation.

The Effect of Alkyl Substituents on Iodination Rates.—Although accurate data for benzene iodination are lacking, partial rate factors[3,4] for the reaction of iodine monochloride at positions *ortho*, *meta* and *para* to methyl substituents on the aromatic nucleus may be calculated from the values of k_1 for toluene and the isomeric xylenes. These partial rate factors (calculated from the rate constants for runs at 25° at 1.4 *M* zinc chloride concentration) lead to predicted iodination rates for the more highly methylated benzenes (*e.g.*, mesitylene and pentamethylbenzene) which are higher than experimental values by several powers of ten. This result may be used to argue that the reaction of iodine monochloride with polymethylbenzenes is subject to some steric inhibition.

The steric problem in the iodination reaction is more conclusively demonstrated by the data of Table III. In this table k_1 values for the zinc chloride catalyzed bromination and iodination reactions, relative to those of *p*-xylene as a reference standard, are compared. The ratios $k_{1(\text{ArH})}/k_{1(p\text{-xylene})}$ for the iodination reactions were calculated from reported rate constants for reactions of the hydrocarbons in 0.8 *M* zinc chloride solution, except for those for toluene and benzene which

TABLE III

THE RELATIVE RATES OF BROMINATION AND IODINATION OF THE METHYLBENZENES AT 25.2 ± 0.2°

Aromatic	$k_{1\text{ArH}}/k_{1(p\text{-xylene})}$ For bromination[a]	For iodination
Benzene	0.002	<0.001
Toluene	.31	.14
o-Xylene	2.3	1.3
m-Xylene	7.1	23
p-Xylene	1	1
Pseudocumene	13.3	75
Mesitylene	625	1800
Durene	65	23
Isodurene	1350	1600
Pentamethylbenzene	2580	740
sym-Triethylbenzene	218	224

[a] These values are from reference 6 and are taken primarily from column I of Table IV of that reference.

are based on data from runs in 1.4 *M* zinc chloride. In the following discussion it is presumed that the rate-determining step in the iodination reaction is mechanistically of the same type as the forward step of eq. 2 for the bromination reaction.

The data of Table III show that the rates of iodination of most of the less highly methylated benzenes, relative to that of *p*-xylene, are more sensitive to the number and location of methyl groups on the hydrocarbon nucleus than are the bromination rates. In the iodination and bromination reactions *p*-xylene is about seven and three times more reactive, respectively, than toluene; the rate of iodination of *m*-xylene is 23 times that of *p*-xylene, but the bromination reactivity ratio of the two hydrocarbons is only seven. The enhancement in the reactivities of mesitylene and pseudocumene over that of *p*-xylene is larger for iodination than for bromination. However, certain of the more highly alkylated hydrocarbons show a reversed reactivity with respect to bromine and iodine monochloride. Relative to *p*-xylene, the rates of iodination of durene and pentamethylbenzene are much less than the bromination rates. In these hydrocarbons the combined bulk of the methyl substituents must constitute a formidable steric barrier to the entering iodine atom. Less convincing evidence for such inhibition in the iodination of pentamethylbenzene has been presented previously.[11]

Since it is probable that the bromination reaction of the polyalkylbenzenes is also to a smaller degree subject to steric repression,[6] no more than the most qualitative interpretation of these halogenation rates is justified. It does appear, however, that even the iodination of *o*-xylene is inhibited sterically. The halogenation reactivities of isodurene and *sym*-triethylbenzene may too, by comparison with those of mesitylene, be used to support the steric argument. It is probable that even the iodination of mesitylene is subject to a methyl group bulk effect which is masked because the orientation of the alkyl substituents is so uniquely favorable electronically[2,3] for electrophilic substitution.

The Activation Energies for the Iodination Reactions.—In the absence of marked variations in steric influences of ring substituents one may anticipate that the relative susceptibilities of a series of substituted benzenes to attack by an electrophilic reagent will be governed primarily by the energies of activation of the several reactions.[3,14] The energies of activation for a few of the reactions of the polymethylbenzenes with iodine monochloride in the presence of excess zinc chloride have been calculated from the results of kinetic measurements in the region of 25 and 45° (see Table II) to determine whether the steric factors are sufficiently serious in these cases so that the preceding generalization does not apply. The activation energies and log *A* values are summarized in Table IV. It should be noted that the values of E_a are independent of the concentration of catalyst at which they were evaluated.

TABLE IV

THE ACTIVATION ENERGIES FOR THE IODINATION REACTIONS

Aromatic	($ZnCl_2$), mole/l.	E_a kcal. mole^{-1}	log *A* at 0.8 *M* $ZnCl_2$[a]
o-Xylene	1.4	19.2	10.1
m-Xylene	0.4	18.4	
	.8	18.4	10.7
Mesitylene	.056	15.6	10.6
	.112	15.6	
Durene	.80	17.4	10.0
Isodurene	.05	16.2	11.0
Pentamethylbenzene	.056	16.4	10.7
	.112	16.3	

[a] log A = log k_1 + (E_a/2.3 RT) with k_1 expressed in sec.$^{-1}$ mole^{-2} 1.^{2} All values are for a $ZnCl_2$ concentration of 0.80*M*.

In general the E_a values do diminish as the reactivities of the hydrocarbons increase. The E_a values of mesitylene, isodurene and pentamethylbenzene are, however, closely similar, although the relative susceptibilities of these compounds to electrophilic substitution are markedly different in a reaction[6] in which steric problems do not appear to be overwhelming. In other words there seems to be some evidence that the steric factor which reduces the iodination rate of the highly substituted benzenes is manifested directly in the activation energies. The log *A* values of Table IV are surprisingly unrevealing and do not vary widely for the series of hydrocarbons for which data are reported. Since the individual values are reliable to no more than ±0.2 unit, it seems unwise to use them as the basis for extensive speculation.

The E_a value for the zinc chloride-catalyzed bromination of mesitylene in acetic acid[9] has been reported as 7.1 kcal./mole. The large difference between this value and that for the zinc chloride catalyzed iodination of mesitylene (15.6 kcal./mole) should probably be attributed, at least in part, to differences in the solvation energies of bromine and iodine monochloride in acetic acid and to differences in the enthalpies of formation of $HZnCl_2Br$ and $HZnCl_3$.

The Uncatalyzed Reaction of Mesitylene with Iodine Monochloride.—A reasonable interpretation of the rate-determining process in aromatic halogenation[9] has been made in which the halogen–halogen bond of an aromatic–halogen π-complex[15] is severed by attack of an electrophilic reagent, E (equation 5)

$$ArH{\cdot}X_2 + E \longrightarrow ArHX^+ + EX^- \qquad (5)$$

When acetic acid is the solvent, zinc chloride may serve as the reagent E. In the absence of catalyst the halogen itself apparently can fill this role, since the order of the reaction with respect to

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(14) (a) A. E. Bradfield and B. Jones, *Trans. Faraday Soc.*, **37**, 726 (1941); (b) B. Jones, *J. Chem. Soc.*, 418, 676 (1942); (c) P. B. D. de la Mare, *ibid.*, 4450 (1954); (d) B. Jones and E. Richardson, *ibid.*, 2772 (1955).

(15) See K. L. Nelson, *J. Org. Chem.*, **21**, 145 (1956), for a discussion of the role of the π-complex in aromatic substitution reactions.

halogen increases to second in bromination[9] and probably also in iodination[11] processes.

To check the order of the uncatalyzed reaction of iodine monochloride and to compare the efficiencies of zinc chloride and iodine monochloride in functioning as the reagent E, a few rate runs on the iodination of mesitylene, without catalyst, were made. In analyzing the data from these runs it was assumed that, compared to free iodine monochloride, ICl_2^- (or $HICl_2$) is ineffective as a halogenating agent. Since the runs were self-inhibiting, because of the conversion of free halogen to ICl_2^- as hydrogen chloride was formed, none of the runs was followed to more than 45% of total halogen consumption. The rate law

$$-\mathrm{d}(ICl)/\mathrm{d}t = k_b(ArH)(ICl)^2 = k_b(ArH)(ICl)_T^2/[1 + K_c(Cl^-)]^2 \quad (6)$$

in which $(ICl)_T = (ICl) + (ICl_2^-)$, was assumed. Values of $(ICl)_T$ during the course of the runs were calculated from the optical densities of the solutions at 370 mμ using the approximation (see Table I) that the trihalide ion has the same extinction coefficient as free iodine monochloride at this wave length. Values of free chloride ion concentrations were estimated from the relationship

$$(Cl^-) = (ICl)_i - (ICl)_T - K_c(Cl^-)(ICl)_T/[1 + K_c(Cl^-)] \quad (7)$$

on the assumption that $K_c = 250$ (see eq. 1, Experimental section).[16] The k_b values were calculated from the measured values of $(ICl)_T$ during the course of the runs by use of eq. 8.

$$[1/(ICl)_T - 1/(ICl)_i]\,[1 + K_c(Cl^-)]^2 = k_b(ArH)_t \quad (8)$$

Average values of k_b for each of the runs are reported in Table V.

TABLE V

THE UNCATALYZED IODINATION OF MESITYLENE (25.2°)

$(ArH)_i$, mole/l.	$(ICl)_i$, 10^3 mole/l.	k_b, mole^{-2} l.^{2} sec.$^{-1}$
0.200	1.84	0.11
.200	3.68	.10
.200	7.36	.09

Since at low zinc chloride concentrations, the k_1 value for mesitylene iodination is approximately 0.06 mole^{-2} l.^{2} sec.$^{-1}$, on a mole for mole basis iodine monochloride is actually a somewhat more effective reagent E than is zinc chloride. The data of previous publications[6,9] indicate, however, that in the bromination of mesitylene in acetic acid zinc chloride is (on a mole for mole basis) about five times more effective as the reagent E than is bromine.

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(16) R. E. Buckles and J. F. Mills, THIS JOURNAL, **76**, 4845 (1954), report much higher values for the association constant of iodine monochloride with quaternary ammonium chlorides in acetic acid.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

A Novel Stereospecific Synthesis of Hydrophenanthrones[1]

BY ERNEST WENKERT AND TRAVIS E. STEVENS[2]

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A new synthetic scheme, leading stereospecifically in only four steps from the Reimer–Tiemann product of 4-methyl-1-naphthol to a hydrophenanthrone, is presented. The stereochemistry of all intermediates is discussed.

The hydrophenanthrene skeleton I is the basic ring structure common to all aromatic tricyclic diterpenes and could serve potentially as a synthetic precursor for the hydroaromatic tricyclic diterpenes as well as possibly for the steroids. Three *formally* different routes have been followed in the past for the synthesis of compounds of general structure I. One procedure has involved the prior coupling of rings A and C by various means and a subsequent formation of ring B by acid-catalyzed cyclization.[3] This scheme has led recently to the non-specific total synthesis of *d,l*-ferruginol[3o] and *d,l*-podocarpic acid.[3s] A second route has consisted of varied syntheses of 1-methyl-2-tetralones for rings B and C and a subsequent incorporation of ring A by the Robinson cyclohexenone synthesis.[4] The utility of this method has been portrayed excellently by the total syntheses of the steroid nucleus[4a] and *d,l*-dehydroabietic acid.[4d] Finally, a third synthetic pathway to the tricyclic ring system I has been accomplished

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(1) Part of this work was presented at the Symposium on the Chemistry of Natural Products, Technion, Haifa, Israel, June 28–29, 1955, and at the 14th International Congress of Pure and Applied Chemistry, Zurich, Switzerland, July 21–27, 1955.

(2) National Science Foundation predoctoral fellow, 1953–1955.

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