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

The Kinetics of Dissociation of Derivatives of Iodobenzene Dichloride in Acetic Acid

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In acetic acid solution at 25° an equilibrium is established slowly between iodobenzene dichloride and the parent compounds (iodobenzene and chlorine). Spectrophotometric methods have been used to study the rates of the dissociation and association reactions and to determine the equilibrium constants for a number of *meta* and *para* substituted iodobenzene dichlorides. Both the forward and reverse processes are slowed by electron withdrawing substituents, but the association rate is much more strongly affected than is that of the decomposition reaction. The results of an attempt to correlate the rate and equilibrium constants with the Hammett sigma values are only mildly successful. Energetically the activated complexes are closer to the parent compounds than to the dichlorides. The entropies of activation of both forward and reverse reactions are negative. On the basis of these observations a structure for the activated complex has been proposed.

In acetic acid at 25° iodobenzene dichloride undergoes extensive dissociation to iodobenzene and chlorine (equation 1)

$$\mathrm{ArICl_2} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{ArI} + \mathrm{Cl_2} \qquad K = \frac{k_1}{k_2} = \frac{(\mathrm{ArI})(\mathrm{Cl_2})}{(\mathrm{ArICl_2})} \qquad (1)$$

The equilibration rate is sufficiently slow and the dichloride is intensely enough colored so that kinetic data required for the evaluation of k_1, k_2 and K have been obtained using spectrophotometric methods.[1]

Much information is available concerning the influence of *meta* and *para* substituents on reactivity, as measured by rate or equilibrium constants, at aromatic side chains.[2,3] However, few, if any, other such reactions are known which are experimentally as suitable for the simultaneous assessment of substituent effects on both forward and reverse reaction rates as is the iodobenzene dichloride dissociation. With this point in mind a kinetic study of the dissociation of several *meta* and *para* substituted derivatives of the dichloride has now been made.

Experimental

The Iodobenzenes.—Eastman Organic Chemicals *p*-diiodobenzene was recrystallized twice from ethanol. A sample of 6-iodo-1,2,3,4,5-pentamethylbenzene remaining from an earlier investigation[4] was used without further treatment. *p*-Iodoacetanilide was prepared by iodination of acetanilide[5] and was recrystallized twice from ethanol (m.p. 185–186°). The remaining iodo compounds were prepared by diazotization of the appropriate aniline derivatives followed by treatment of the diazonium salt solutions with potassium iodide. A sample of *p*-nitroiodobenzene, prepared by this method,[6] was furnished by Mr. C. E. Castro. This material was recrystallized from ethanol using decolorizing carbon (m.p. 172–173°). The crude *p*-iodotoluene[7] was recrystallized twice from ethanol, m.p. 32–34°. The *m*-iodotoluene[8] was purified by distillation (b.p. 206°). The crude *p*-iodobenzoic acid was purified through conversion to its dichloride,[9] and the light orange iodide which was regenerated was twice subjected to solution in potassium hydroxide solution followed by reprecipitation with acetic acid. The light tan powder which was recovered was dried at 120° (m.p. 267–270°). *p*-Iodobiphenyl[10] was distilled at 203° (20 mm.), and the solid distillate was recrystallized twice from ethanol using decolorizing carbon (m.p. 110–112°). *m*-Chloroiodobenzene[11] was purified by distillation, b.p. 126–127° (40 mm.).

The iodides thus obtained were sufficiently free of colored impurities to be used directly in the spectrophotometric work.

The Dichlorides.—To prepare the dichlorides, except those of *p*-diiodobenzene and *p*-nitroiodobenzene, solutions of the iodo compound in acetic acid were gassed for a short time with chlorine. The concentration of iodo compound varied from about 0.01–0.08 g. per ml. of acetic acid depending on the solubility of the starting material. With the exception of the derivatives of *p*-iodobenzoic acid and *m*-chloroiodobenzene, precipitation of the dichlorides was complete within a few minutes.

p-Nitroiodobenzene has a low solubility in acetic acid. Its dichloride was prepared by saturating a two phase mixture of 0.3 g. of the nitro compound in 6 ml. of acetic acid with chlorine. After the mixture stood overnight, conversion of the solid phase to dichloride was complete.

In preparing the dichloride of *p*-diiodobenzene in acetic acid solution, mixtures of di- and tetrachloride were isolated unless the initial concentration of chlorine was relatively small. A crystalline precipitate with an equivalent weight corresponding to that of $\mathrm{IC_6H_4ICl_2}$ was obtained from a mixture of 0.60 g. (0.00183 mole) of the diiodide in 63 ml. of 0.0246 *M* chlorine which was allowed to stand for several days at room temperature.

The solid derivatives (which varied from light yellow to yellow-orange) were filtered, washed with carbon tetrachloride and air dried for a short period. The yields varied somewhat because of differences in the solubilities of the products and in the quantities of solvent used. In a typical preparation, that of the *p*-iodobiphenyl derivative, 0.32 g. of product was obtained from a solution of 0.30 g. of the iodide in 10 ml. of acetic acid.

Because of the instability of the solid products,[12] they were freshly prepared just before their use in kinetic work. The derivative of *p*-nitroiodobenzene was uniquely stable. A sample which was kept at room temperature for five days showed no loss in oxidizing power. The product obtained from iodopentamethylbenzene was so unstable that it could not be analyzed or used in kinetic experiments. Almost as soon as it was dry the yellow powder underwent localized decompositions to form a dark brown product. Other samples decomposed as they were introduced into melting point tubes. The decomposition product contained iodine as evidenced by the characteristic violet color of its solution in carbon tetrachloride.

Melting points (or decomposition temperatures) and equivalent weights (by iodometric methods) of the freshly prepared dichlorides are listed in Table I. Procedures similar to those described by Nichol and Sandin[12] were used in determining reported values.

The dichloride obtained from *p*-iodobenzoic acid contained an acetic acid molecule of solvation. This was confirmed by determining its equivalent weight as an acid as well as by iodometric methods. In the former determination a

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[1] R. M. Keefer and L. J. Andrews, THIS JOURNAL, **79**, 4348 (1957).

[2] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 184.

[3] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[4] R. M. Keefer and L. J. Andrews, THIS JOURNAL, **78**, 5623 (1956).

[5] F. D. Chattaway and A. B. Constable, *J. Chem. Soc.*, **105**, 125 (1914).

[6] P. J. Montagne, *Ber.*, **51**, 1489 (1918).

[7] A. J. Vogel, "A Textbook of Practical Organic Chemistry," Longmans Green and Co., New York, N. Y., 1948, p. 575.

[8] F. Beilstein and A. Kuhlberg, *Ann.*, **158**, 347 (1876).

[9] C. Willgerodt, *Ber.*, **27**, 2331 (1894).

[10] F. Ullmann, *Ann.*, **332**, 52 (1904).

[11] A. Klages and C. Lieke, *J. prakt. Chem.*, [2] **61**, 321 (1900).

[12] J. C. Nichol and R. B. Sandin, THIS JOURNAL, **67**, 1307 (1945).

TABLE I

PROPERTIES OF THE IODOBENZENES AND OF THEIR DICHLORIDES

Iodobenzene substituent	Dichloride M.p.,[a] °C.	Dichloride equiv. wt. Found	Calcd.	λ, mμ	Molar extinction coeff. in HOAc $\epsilon_{\text{iodobenzene}}$	$\epsilon_{\text{dichloride}}$
p-I	145–147	200	200.5	390	6.0	132
p-NO_2	172–173	160	160	370	185	286
p-$NHCOCH_3$	114–117	168	167	400	0.1	360
p-CH_3	88–90	148	144.5	400	0.1	54.1
p-COOH[b]	267	187[b]	189.5[b]	390	5.2	55.6
p-C_6H_5	85–87	176.5	175.5	400	1.4	236
m-CH_3	85–87	145	144.5	390	0.06	63.2
m-Cl	92–94	156	154.7	400	0.12	87.5

[a] See ref. 12 and W. Caldwell and E. A. Werner, *J. Chem. Soc.*, **91**, 240, 528 (1907), for comparative melting or decomposition temperatures. These vary somewhat with the rate of heating of samples. Most reported values are temperatures at which gas evolution was observed. In the cases of the dichlorides of *p*-nitroiodobenzene and of *p*-iodobenzoic acid all of the chlorine apparently was expelled when melting occurred; the recorded melting points for these are the same as those of the free iodo compounds. [b] The recorded data apply to *p*-$Cl_2IC_6H_4COOH \cdot CH_3COOH$. The equivalent weight of this material, found by alkalimetric methods, was 191.

weighed sample was shaken with dilute potassium iodide. The solution was then decolorized by dropwise addition of sodium thiosulfate solution, and the mixture was titrated with standard base to the phenolphthalein endpoint.

The Kinetic Measurements.—These were carried out in 1-cm. glass-stoppered silica absorption cells which were housed in the cell compartment of a Beckman spectrophotometer. Details of procedures used in controlling temperatures are given elsewhere.[4] All runs were followed by measuring the optical densities of the reaction mixtures at an appropriate wave length as a function of time until equilibrium (*cf.* equation 1) was established. Insofar as was possible a wave length was chosen at which the extinction coefficient of the iodobenzene dichloride was much larger than those of the parent compounds.

The extinction coefficients of chlorine[1] and of the iodo compounds in acetic acid were established by separate measurements of solutions of the pure substances.

The extinction coefficients of those dichlorides which dissociated slowly in acetic acid were obtained by rapid spectrophotometric measurement of freshly prepared solutions of the solids. Small corrections were made to account for slight dissociation, which occurred during the interval between preparation and measurement of the solutions.

To determine the extinction coefficients of the more reactive dichlorides essentially the same procedure as was used in studying iodobenzene dichloride[1] was adopted. Acetic acid solutions of chlorine and the iodo compound were prepared in which the initial concentration of one component was of the order 10^{-2}–10^{-3} *M*. The concentration of the other substance was always at least ten times this value. Two or more such solutions, in which the concentration of the more abundant reactant varied by several fold, were measured spectrophotometrically until dichloride formation ceased. The exact chlorine concentration of the product solution was then determined by iodometric analysis of a sample pipetted directly from the absorption cell. Extinction coefficients for the dichloride were calculated from equilibrium optical density readings on the assumption that the conversion of the more dilute reactant to product was complete. In general the extinction coefficients obtained in this way were independent of the concentration of the reactant which was used in excess. The value reported for *p*-diiodobenzene dichloride was obtained using an excess of the diiodide to prevent formation of the tetrachloride. Representative experimental values of the extinction coefficients of the iodo compounds and of their dichlorides at wave lengths which were employed in the kinetic experiments are given in the right-hand columns of Table I. The extinction coefficients for chlorine which were used are as follows: 22.0 (370 mμ), 13.1 (380 mμ), 8.1 (390 mμ), 5.2 (400 mμ).

As observed earlier[1] errors in the kinetic measurements resulting from volatilization of chlorine during runs are negligible when the reactions are carried out using stoppered absorption cells. In those runs in which free chlorine was present initially, precise determination of the total halogen concentration was postponed until reaction was complete. Then samples removed from the cells were analyzed iodometrically.

Results

The Rate and Equilibrium Constants.—Experimental values of k_1, k_2 and K (see equation 1) for the several iodobenzene derivatives which were investigated are reported in Table II. Equilibrium constants are listed only in those cases in which they could be calculated from spectrophotometric data recorded when reaction mixtures had reached equilibrium. In one case, that of *p*-nitroiodobenzene, the equilibrium concentration of dichloride was sufficiently small so that it could only be determined approximately (accurately enough, however, for later use in evaluating k_2 by equation 5) by the techniques which were employed. In later discussions the equilibrium constant which is used for this compound is the ratio of the average values of measured dissociation and association rate constants.

The calculation of the concentrations of reactants and products either at equilibrium or during the course of the reactions was accomplished using equation 2, which relates the experimentally measured optical density of a reaction mixture to the absorption of its components and the initial reactant concentrations.

$$d = (\text{ArICl}_2)(\epsilon_{\text{ArICl}_2}) + (\text{ArI})(\epsilon_{\text{ArI}}) + (\text{Cl}_2)(\epsilon_{\text{Cl}_2}) \quad (2)$$

As in the experiments with iodobenzene dichloride[1] the kinetic data were in accord with the differential rate law 3.

$$-\text{d}(\text{ArICl}_2)/\text{d}t = k_1(\text{ArICl}_2) - k_2(\text{ArI})(\text{Cl}_2) \quad (3)$$

Some runs were made in which the starting material was the dichloride. Rate constants k_1 (for the dissociation reaction) were then evaluated by graphical procedures based on the equation[13]

$$\ln \frac{A_0^2 - A_eA}{(A - A_e)A_0} = k_1\left(\frac{A_0 + A_e}{A_0 - A_e}\right)t \quad (4)$$

in which A_0, A_e and A are the dichloride concentrations at initiation, at equilibrium and at time, t, respectively. Plots of the left-hand term *versus* time were linear to high percentages of completion.

For other runs in which the initial reactants were chlorine and the iodobenzene, rate constants k_2 (for the formation of the dichloride) were evaluated using equation 5, another integrated form of equation 3

$$\ln \frac{2A + b - \sqrt{b^2 - 4a}}{2A + b + \sqrt{b^2 - 4a}} = k_2t\sqrt{b^2 - 4a} + \text{constant} \quad (5)$$

in which $a = (\text{ArI})_i(\text{Cl}_2)_i$ and $b = -(\text{ArI})_i - (\text{Cl}_2)_i - K$. Again the fit of the data to linearity was good when the left-hand term of this equation was plotted as a function of time.

In cases in which both the rates of formation and dissociation were measured by the procedures described above, the ratios of average k_1 and k_2 values were in reasonably good agreement with the equilibrium constants which were calculated from equilibrium concentrations of reactants and products.

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(13) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 173.

TABLE II

RATE CONSTANTS AND EQUILIBRIUM CONSTANTS FOR THE DECOMPOSITION OF DERIVATIVES OF IODOBENZENE DICHLORIDE IN ACETIC ACID

10^3 (ArI)$_i$, mole/l.	10^3 (Cl$_2$)$_i$, mole/l.	10^3 (ArICl$_2$)$_i$, mole/l.	10^4k_1, sec.$^{-1}$	10^2k_2, sec.$^{-1}$ mole^{-1} l.	10^3K, mole l.$^{-1}$
		p-Diiodobenzene, 25.2°			
1.96	1.75	....	...	6.0	2.5^2
1.96	3.46	....	...	5.6	2.5^4
3.92	1.73	....	...	6.3	2.3^4
3.92	3.61	....	...	7.0	...
7.84	4.14	....	...	5.9	2.4^8
7.84	7.54	....	...	6.8	...
			Av.	6.3 ± 0.4	2.46 ± 0.08
		p-Iodonitrobenzene, 25.2°			
...	....	4.13	0.78	...	[a]
...	....	8.25	.83	...	[a]
...	....	18.2	1.06	...	[a]
22.4	134	....	...	0.6	[a]
		Av.	0.89 ± 0.15		
		p-Iodoacetanilide, 25.2°			
1.26	1.03	....	...	31	0.84
2.52	1.02	....	...	32	0.95
2.53	1.99	....	...	38	1.22
5.06	2.00	....	...	38	1.28
...	....	1.21	3.8^6	...	1.06
...	....	2.42	3.7^5	...	1.04
...	....	4.83	...	...	1.02
		Av.	3.8 ± 0.06	35 ± 3	1.06 ± 0.11
		p-Iodotoluene, 25.2°			
7.63	4.70	....	...	26	1.5
15.26	4.79	....	...	29	1.7
15.26	9.95	....	...	32	1.3
30.6	19.9	....	...	33	0.9
...	....	4.37	2.5	...	1.1
...	....	8.75	2.8	...	1.2
...	....	17.5	3.5	...	1.3
		Av.	2.9 ± 0.4	30 ± 2.5	1.3 ± 0.2
		m-Iodotoluene, 25.2°			
21.9	4.58	....	...	12	1.51
21.9	9.65	....	...	12	1.93
32.8	20.7	....	...	17	1.67
...	....	3.52	2.09	...	1.26
...	....	7.05	2.16	...	1.40
...	....	14.1	1.82	...	1.45
		Av.	2.03 ± 0.13	14 ± 2	1.5 ± 0.2
		p-Iodobiphenyl, 25.2°			
5.90	3.96	....	...	10.6	1.92
11.8	4.18	....	...	10.6	2.10
11.8	8.10	....	...	11.8	2.11
...	....	0.975	2.09	...	1.92
...	....	1.95	2.46	...	2.11
...	....	3.90	2.49	...	2.10
		Av.	2.35 ± 0.17	11.0 ± 0.5	2.04 ± 0.06
		p-Iodobiphenyl, 45.4°			
...	....	1.76	17.0	...	5.2
...	....	3.53	17.1	...	5.4
		p-Iodobenzoic acid, 25.2°			
5.1	22.2	....	...	0.87	...
10.2	23.4	....	...	.98	...
20.4	48.7	....	...	.91	...
28.0	7.50	....	...	...	15.7
...	....	2.14	1.48	...	...
...	....	4.28	1.53	...	...
...	....	8.56	1.50	...	...
		Av.	1.50 ± 0.02	0.92 ± 0.04	
		p-Iodobenzoic acid, 45.4°			
27.9	7.77	....	...	...	44.8[b]
...	....	2.17	10.5	...	...
...	....	4.33	10.5	...	...
...	....	8.67	10.6	...	...
		m-Chloroiodobenzene, 25.2°			
26.3	8.91	....	...	1.18	13.9
52.7	4.39	....	...	1.10	13.9
52.7	9.25	....	...	1.12	13.3
...	....	2.67	1.43	...	...
...	....	5.35	1.51	...	12.5
...	....	10.7	1.51	...	12.6
		Av.	1.48 ± 0.04	1.13 ± 0.03	13.2 ± 0.6
		m-Chloroiodobenzene, 45.2°			
53.3	4.82	....	...	3.9	28.6
53.3	10.3	....	...	3.7	28.3
...	....	2.5	11.5	...	...
...	....	5.25	11.6	...	30.2
...	....	10.5	11.5	...	31.4
		Av.			29.6 ± 1.5

[a] This dichloride was so highly dissociated at equilibrium that K values could not accurately be obtained using measured equilibrium concentrations. [b] The temperature at which this constant was determined was 45.3°.

Rate constants are only reported in Table II when they were determined by direct kinetic experiments. The few missing values of k_1 or k_2 required for later discussion were calculated from the available rate and equilibrium constants. The k_1 values for *p*-diiodobenzene dichloride could not be obtained directly because the rate of solution of the compound in acetic acid was very low.

The constants, k_1, k_2 and K, were tested for conformance to the Hammett equation 6 which describes variations in rate or equilibrium constants (k), for reactions at aromatic side chains, with changes in ring substituents.

$$\log k = \rho\sigma + \text{constant} \qquad (6)$$

In Fig. 1 plots of values of log k_2 and of log K *versus* corresponding σ values[3] for substituents at positions *meta* or *para* to the iodine atom are shown. The fit of the two sets of data to straight lines is not impressively good, and for the log k_2 values it is difficult to choose the straight line which best accommodates the data. Although it is customary to use the least squares method in drawing such lines there seems little merit in applying this refinement in interpreting the present results. It is possible that the necessary requirement (that the entropy changes are constant or are linearly dependent on free energy changes) for the general application of the Hammett equation may not hold rigorously for all of the reactions under investigation. It also should be observed that the Hammett sigma values are subject to variation with changes in solvent, notably when hydrogen bonding between the ring substituent and the solvent may occur.[14] Actually the dichloride prepared from *p*-iodobenzoic acid contained an acetic acid molecule of solvation, and the points for the *p*-COOH group in Fig. 1 deviate quite markedly from the straight lines which seem best to accommodate the data. It is reasonable to suppose that the forces of solvation of this dichloride result from hydrogen bonding between carboxyl groups of the aromatic and solvent molecule.

A plot of log k_1 values *versus* σ-values is not shown since it does not provide a very stringent test of the Hammett equation. The values are not highly sensitive to changes in ring substituents. The extreme variation in k_1 for the series of compounds investigated is only fourfold, whereas rate con-

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(14) Ref. 3, p. 232.

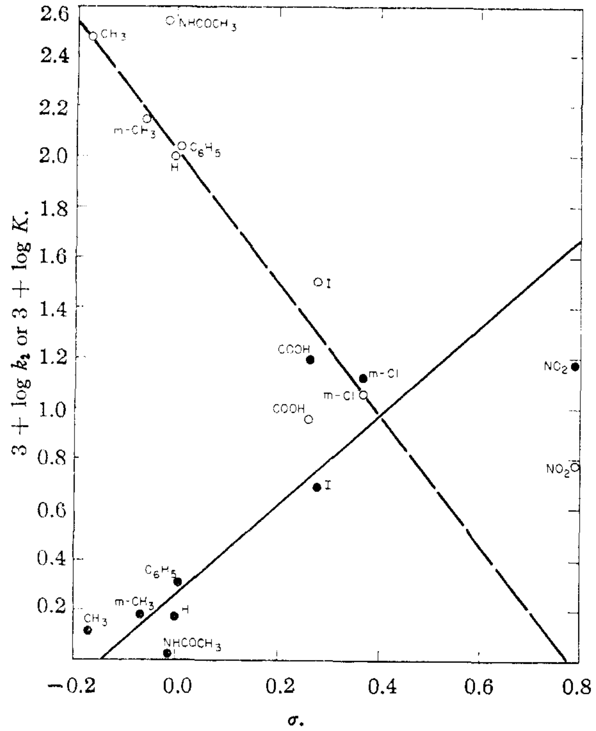

Fig. 1.—Plots of log k_2 and log K *versus* Hammett sigma values. Except as noted all substituents are *para*. Open circles and filled circles represent, respectively, log k_2 and log K values. The data for iodobenzene are taken from ref. 1. Experimental values of k_2 and K for *p*-diiodobenzene were respectively halved and doubled to make a statistical correction for the presence of two iodine atoms on the aromatic nucleus before this plot was made.

stants (k_2) for dichloride formation show a 60-fold variation.

Thermodynamic Constants.—Unfortunately in only a limited number of cases could rate and equilibrium constants be obtained at temperatures far enough above 25° so that a complete set of thermodynamic constants for the dissociation and association processes could be calculated. Some of the equilibria (equation 1) shifted far enough to the right with temperature increases so that equilibrium concentrations of the reactants could not be ascertained accurately. In some cases the rates of reaction became too rapid to measure.

Table III summarizes the values of ΔH_d^0 and ΔS_d^0 for the dissociation of the dichloride which were calculated from available equilibrium constants (Table II) measured at 25.2 and 45.4°; corresponding values for the energies and entropies of activation (E_1 and $\Delta S_1^{\pm}$), calculated (see ref. 13, pages 96 and 97) from rate constants at these two temperatures, are also listed. Except for *m*-chloroiodobenzene the reported values of $\Delta S_2^{\pm}$, the entropy of activation of the reaction to form dichloride, are the differences in the experimental values of $\Delta S_1^{\pm}$ and ΔS_d^0.

TABLE III

THERMODYNAMIC CONSTANTS FOR THE DISSOCIATION OF THE DICHLORIDES AND FOR THE FORWARD AND REVERSE REACTIONS

Iodobenzene dichloride derivative	ΔH_d^0, kcal.	ΔS_d^0, e.u.	E_1, kcal.	$-\Delta S_1^{\pm}$, e.u.	$-\Delta S_2^{\pm} = \Delta S_d^0 - \Delta S_1^{\pm}$, e.u.
Unsubstituted[a]	9.9	20.4	20.2	10.4	30.8
4-COOH	9.8	24.4	18.3	16.8	41.2
4-C_6H_5	9.0	17.7	18.6	14.8	32.5
3-Cl	7.6	16.9	19.4	13.1	30.1[b]

[a] Data taken from ref. 1. [b] Calculated from the experimental rate constants for the formation of the dichloride (Table II).

The values of $\Delta S_1^{\pm}$ and $\Delta S_2^{\pm}$ for the *p*-iodobenzoic acid reactions are somewhat more negative than those tabulated for the other reactions, a fact which may account in part for the poor fit of data for this compound to the lines of Fig. 1. Because a molecule of solvation is actually incorporated in the dichloride of the acid derivative, it is not surprising that such abnormalities are observed.

Other values of $\Delta S_2^{\pm}$ are relatively independent of structural changes, although $\Delta S_1^{\pm}$ values are subject to some variation and these variations are reflected to a degree in ΔS_d^0. This fact may account for the poor fit of log K values in Fig. 1 to a straight line.

The values of E_1, the activation energy for dichloride dissociation, are all of the order of 18–20 kcal./mole whereas the corresponding values of E_2, ($E_1 - \Delta H_d^0$), are of the order 9–12 kcal./mole. Since k_1 values are much less sensitive to changes in ring substituents than are k_2 values, one might expect that the magnitude of E_1 would be less influenced by substituent effects than that of E_2. This would be the case if the stabilities of the free iodo compounds were subject to more variation with changes in structure than were the stabilities of the dichlorides and of their activated complexes. A more extensive set of thermodynamic data (including more information on entropy changes) than is available in Table III is required for a satisfactory justification of this interpretation.

The Activated Complex.—In the iodobenzene dichloride molecule, as established by X-ray diffraction measurements,[15] the ICl_2 grouping is linear and symmetrical and lies at approximately right angles to the plane of the benzene ring. Alternately this molecule has been described in terms of a trigonal bipyramid about iodine with the chlorine atoms at apical positions and the phenyl group and two unshared electron pairs at equatorial positions.[16] This structure has been likened to those of organic derivatives of group 5 and 6 elements of the Periodic Table. In this regard it is interesting to observe that the effects of ring substituents on the dissociation constant of iodobenzene dichloride are directionally similar to those reported for the dissociation of diphenylselenium dihalides (to halogen and the diphenylselenium) in carbon tetrachloride.[17] The dipole moment of iodobenzene dichloride in benzene is substantially higher than that of iodobenzene, and it has been suggested that

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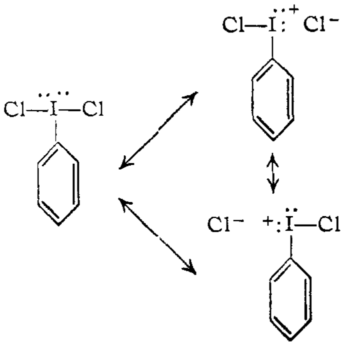
(15) E. M. Archer and T. G. D. Van Schalkwyk, *Acta Cryst.*, **6**, 88 (1953).

(16) J. D. McCullough, *ibid.*, **6**, 746 (1953).

(17) (a) J. D. McCullough and B. A. Eckerson, THIS JOURNAL, **67**, 707 (1945); **73**, 2954 (1951); (b) J. D. McCullough and M. K. Barsh, *ibid.*, **71**, 3029 (1949).

the dichloride molecule has some ionic character[18] (*cf.* formula I).



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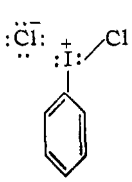
In forming the dichloride, chlorine must accept electrons from the iodine atom of the iodobenzene molecule. Thus the rate of formation of dichloride is accelerated by electron releasing ring substituents and is retarded by electron withdrawing substituents (see Fig. 1). Directionally speaking ring substituents have this same general influence on the rates of dichloride dissociation, although in magnitude the effects are much less pronounced than in the reaction to form dichloride. Therefore in forming the activated complex the dichloride must to some degree release electrons to departing chlorine.

The fact that an entropy loss occurs on activation of an iodobenzene dichloride (Table III) may be explained on the assumption that molecules of acetic acid are incorporated as the activated complex is formed. Inherent in this suggestion is the implication that the complex is more ionic in character than the dichloride. However the increase in polarization which accompanies the activation process is probably small since the dissociation rate is not highly sensitive to the introduction of ring substituents at positions *meta* and *para* to the iodine atom. It therefore seems questionable whether the entire entropy change (*ca.* −10 e.u.) can be traced to the trapping of solvent molecules in the complex.

It has been pointed out to the authors that formation of the activated complex from the dichloride may take place with the sacrifice of vibrational degrees of freedom in I–Cl bonds.[19] It is conceivable that this would be reflected to some degree in the activation entropy.

A structure for the activated complex which is reasonable in terms of the preceding observations is represented by formula II (molecules of solvation are not included).



II

One cannot, on the basis of available information, make unambiguous comment on the geometry of II. The structure as written pictures the activated complex as a more polar entity than the dichloride or its dissociation products. The degree of polarization of the complex is probably overemphasized, although the indicated charge distribution is in accord with the effects of substituents on assocation and dissociation rates. Chlorine with a complete octet of electrons is shown as displaced sufficiently far from its normal position in the dichloride so that, as observed experimentally, a considerable energy input should be required for its formation from the dichloride. Also the two chlorine atoms are placed close enough to each other so that collapse of the complex to form the free iodo compound and chlorine is readily permitted.

To test these conclusions further experiments with non-polar substances as solvents are planned.

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[18] E. N. Guryanova and Y. A. Syrkin, *Acta Physicochim. U.R.S.S.*, **11**, 657 (1939).

[19] Professor Melvin Calvin has suggested that wagging vibrations may disappear in the activation process.