The Equilibration of Iodobenzene Dichlorides with their Components in Nitromethane

By R. M. Keefer and L. J. Andrews

The equilibration of iodobenzene dichloride and some of its ring substituted derivatives with chlorine and the corresponding iodobenzene in nitromethane solution has been studied from a kinetic viewpoint. The dichloride dissociation constant increases with changes in solvent in the order $CH_3NO_2 < CH_3COOH < CCl_4$. Apparently the dichloride is more polar than its dissociation products. In nitromethane, as in acetic acid, electron withdrawing ring substituents enhance the dissociation constant. There is some evidence that *ortho* substituents produce steric effects which lead to dichloride destabilization. The rates of formation and dissociation of the dichlorides increase with changes in solvent in the order $CCl_4 < CH_3NO_2 < CH_3COOH < CF_3COOH$. Presumably the activated complex is significantly polar in nature. The energies of activation for the forward and reverse processes are much lower in nitromethane than in acetic acid. This should be reflected in the reaction rates were not the entropies of activation much more negative in nitromethane than in acetic acid. The superiority of trifluoroacetic acid as a solvent is attributed to its effectiveness as a hydrogen bonding agent. The dissociation of the dichloride in nitromethane is catalyzed by hydrogen chloride and is tremendously accelerated by small amounts of iodine monochloride. The halogen also functions as a catalyst in acetic acid, but it is much less effective than in nitromethane.

In carbon tetrachloride the equilibration of iodobenzene dichloride with its components does not occur readily in the dark unless a polar catalyst such as iodine monochloride is present.[1] In acetic acid the reaction occurs rapidly at room temperature, and the entropy of activation for dissociation of the dichloride, as well as that for its production from iodobenzene and chlorine, is appreciably negative.[2] It has, therefore, been concluded[1,2] that the activated complex is considerably more polar in character than the dichloride.

To assess more fully the role of the solvent in assisting the formation of the activated complex, a study of the kinetics of formation and dissociation of iodobenzene dichloride and certain of its derivatives in the highly polar medium, nitromethane, has now been conducted. A few qualitative observations concerning the effectiveness of trifluoroacetic acid as solvent also have been made, and the catalytic effects of iodine monochloride on the equilibration process in acetic acid and in nitromethane have been compared.

Experimental

Solvents and Inorganic Reagents.—Eastman Organic Chemicals nitromethane which contained traces of chlorine consuming impurities was used. These were removed by treating the solvent with chlorine and allowing the mixture to stand overnight. The chlorine was removed by distilling the mixture twice through a two foot Vigreux column with the rejection of early fractions. The distillate was then fractionated through a four foot column packed with glass helices. A large constant boiling fraction (102.0°), $n^{20}D$ 1.3824, was collected for use in kinetic work. Iodometric analysis indicated that this material was free from chlorine.

A solution (0.014 M) of chlorine in the purified solvent was allowed to stand overnight in a paraffin sealed absorption cell. The chlorine content of the solution, as determined spectrophotometrically (*vide infra*) dropped by only 3% during that period.

The phosphorus pentoxide method of purifying this solvent[3] was unsatisfactory for the purpose of these experiments. The rate of dichloride equilibration was much more rapid in solvent which had been carefully fractionated after exposure to the pentoxide than in nitromethane which had been purified by chlorination.

Eastman Organic Chemicals trifluoroacetic acid was distilled immediately before use (b.p. 72.0°) or alternately was pre-treated with phosphorus pentoxide before distillation.[4]

The purification of acetic acid and the preparation of iodine monochloride have been described previously.[1,2a] Ohio Chemical Co. chlorine was used without further purification. Matheson Co. gaseous hydrogen chloride was dried by passing it through concentrated sulfuric acid.

All halogen solutions were analyzed iodometrically. Solutions of hydrogen chloride in nitromethane were analyzed by adding an aliquot to a large volume of water containing dextrin and sodium bicarbonate (as a buffer); the resulting aqueous mixtures were titrated with standard silver nitrate to the dichlorofluorescein end-point.

The Iodobenzenes and their Dichlorides.—Eastman Organic Chemicals o-iodotoluene (b.p. 92° (17 mm.)), o-chloroiodobenzene (b.p. 109° (17 mm.)) and p-chloroiodobenzene (m.p. 53–54°) were used. The two liquids were freshly distilled before use, and the solid was twice recrystallized from ethanol. All other iodo compounds were prepared and purified as described previously.[2]

The methods of preparation and analysis of most of the dichloride samples also have been described.[2b] Iodobenzene dichloride was also prepared in reasonably good yield by the substitution of nitromethane for acetic acid as the solvent. To prepare p-iodobenzoic acid dichloride a suspension of 0.3 g. of the free iodo compound in 10 ml. of nitromethane saturated with chlorine was allowed to stand in the dark for two days. The light yellow crystalline product was then filtered, washed with carbon tetrachloride and air dried. The equivalent weight (iodometric) of this material was 158 (calcd., 159.5).

p-Chloroiodobenzene dichloride was prepared in acetic acid in the usual[2b] way (equiv. wt. found 151; calcd., 154.7). The dichlorides of o-iodotoluene and o-chloroiodobenzene could not be precipitated from acetic acid solution. They separated rapidly when solutions of about 0.5 g. of the iodo compound in 4 ml. of carbon tetrachloride were gassed with chlorine. The yellow crystalline products were filtered, washed with carbon tetrachloride and air dried. The experimental equivalent weight of the toluene derivative was 146 (calcd., 144.5); that for the o-chlorobenzene derivative was 157 (calcd., 154.7).

The Rate Measurements.—Spectrophotometric procedures were used to investigate reaction rates and to establish the dissociation constants for the various dichlorides. Samples of the reaction mixtures were placed in 1-cm. glass stoppered absorption cells which, except when the reaction rates were very fast, were sealed with paraffin to prevent chlorine loss.

When mixtures of an iodobenzene and chlorine were used as starting materials, the halogen concentration was established by withdrawing a sample from the absorption cell for iodometric analysis after the completion of the reaction. When a dichloride was used as starting material, its concentration was determined by iodometric analysis of the freshly prepared solution from which rate samples were prepared by dilution.

(1) L. J. Andrews and R. M. Keefer, This Journal, **80**, 1723 (1958).

(2) (a) L. J. Andrews and R. M. Keefer, *ibid.*, **79**, 4348 (1957); (b) R. M. Keefer and L. J. Andrews, *ibid.*, **80**, 277 (1958).

(3) (a) A. G. Evans, J. A. G. Jones and G. O. Osborne, *Trans. Faraday Soc.*, **50**, 16 (1954); (b) G. Illuminati and G. Marino, This Journal, **78**, 4975 (1956).

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

TABLE I

EXTINCTION COEFFICIENTS IN NITROMETHANE

ArI	λ, mμ	$\epsilon_{A \cdot I}$	$\epsilon_{A \cdot ICl_2}$	ArI	λ, mμ	$\epsilon_{A \cdot I}$	$\epsilon_{A \cdot ICl}$
C_6H_5I	380	0.05	103	p-$NO_2C_6H_4I$	390	57.6	92
p-$C_6H_5C_6H_4I$	410	.9	184	p-$HOOCC_6H_4I$	380	4.7	106
o-$CH_3C_6H_4I$	390	.00	49.8	m-ClC_6H_4I	380	0.01	89
p-$CH_3C_6H_4I$	390	.16	135	o-ClC_6H_4I	380	.03	66.2
p-$CH_3C_6H_4I$	400	.10	73.6	p-ClC_6H_4I	400	0.2	48.5

The concentrations of added catalysts (ICl and HCl) were also established by volumetric analysis of their stock solutions from which rate samples were prepared. Since slight volatility losses occur in transferring solutions of hydrogen chloride in nitromethane, reported concentrations of the hydrogen halide are only approximate.

In general the optical densities of the various reaction mixtures as a function of time were measured, using the pure solvent as a blank at a wave length in the 380–410 mμ region, until equilibrium was attained. Equation 1 was used to calculate the dichloride concentration at any time during a run from the corresponding optical density d

$$(ArICl_2) = \frac{d - (ArI)_T \, \epsilon_{A \cdot I} - (Cl_4)_T \, \epsilon_{Cl_2}}{\epsilon_{A \cdot ICl_2} - \epsilon_{A \cdot I} - \epsilon_{Cl_2}} \quad (1)$$

The terms $(ArI)_T$ and $(Cl_2)_T$ are related to initial reactant concentrations by equations 2 and 3

$$(ArI)_T = (ArI)_i + (ArICl_2)_i \quad (2)$$

$$(Cl_2)_T = (Cl_2)_i + (ArICl_2)_i \quad (3)$$

In runs with added iodine monochloride the measured optical densities were corrected for the absorption of the catalyst before calculation of the dichloride concentration. At the concentration levels used in the present experiments there was no evidence of the enhancement of iodine monochloride absorption by the aromatic substances, such as was observed when carbon tetrachloride was used as the solvent.[1]

In nitromethane the extinction coefficients of chlorine (ϵ_{Cl_2}) at the wave lengths at which measurements were made are: 12.8 (380 mμ), 8.4(390 mμ), 5.3(400 mμ), 3.7(410 mμ). In acetic acid and in trifluoroacetic acid the ϵ_{Cl_2} values are 13.1 and 12.9, respectively, at 380 mμ. The extinction coefficient of iodine monochloride in acetic acid at 380 mμ is 138, and in nitromethane it varies with wave length as follows: 116(380 mμ), 117(390 mμ), 117(400 mμ).

In acetic acid the values of $\epsilon_{A \cdot I}$ and $\epsilon_{A \cdot ICl_2}$ for iodobenzene at 380 mμ are 0.1 and 97, respectively; in trifluoroacetic acid the corresponding values at 380 mμ are 0.04 and approximately 100. The last value could not be measured accurately for reasons which are given later.

The extinction coefficients of the various iodobenzenes and their dichlorides in nitromethane at wave lengths employed in the rate studies are given in Table I.

Further experimental details, including methods of temperature control are given in earlier publications.[1,2]

The Formation of Iodobenzene Dichloride in Trifluoroacetic Acid.—The optical density at 380 mμ of a freshly prepared solution of iodobenzene (0.001 M) and chlorine (5.6 $\times$ 10^{-3} M) in trifluoroacetic acid was measured in a 1 cm. absorption cell, versus the solvent as a blank, within 45 seconds after its preparation. The reading was 0.528 (as compared to a calculated value of 0.072 for the initial reactants). As was calculated using the extinction coefficient of the dichloride in nitromethane at 380 mμ, this corresponds to a dichloride concentration of 5.1 $\times$ 10^{-3} M. Since the optical density reading diminished rapidly with time, plans for more extensive experiments with this solvent were abandoned. Very likely the drop in optical density results from chlorination[5] of the iodobenzene nucleus. Essentially the same rate picture was obtained for this reaction whether or not phosphorus pentoxide was used in refinement of the solvent.

Results

The Dissociation Constants for the Dichlorides in Nitromethane.

—The equilibrium constants, as as defined in equation 4, which were measured for

(5) L. J. Andrews and R. M. Keefer, THIS JOURNAL, **79**, 5169 (1957).

iodobenzene dichloride and its ring substituted derivatives in nitromethane are summarized in Tables II and III. Some of the constants are based on the equilibrium concentrations of solutions which contained initially only chlorine and the iodoben-

$$ArICl_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ArI + Cl_2 \qquad K = \frac{k_1}{k_2} = \frac{(ArI)(Cl_2)}{(ArICl_2)} \quad (4)$$
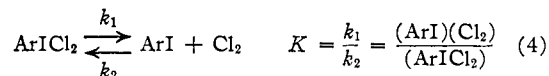
zene. In other cases equilibrium was approached by using the dichloride as starting material. In some instances (Table II), the equilibration process was hastened by the inclusion of iodine monochloride or hydrogen chloride as catalysts in the reaction mixtures. When hydrogen chloride was present, the total halogen content dropped appreciably during the course of reaction. The constants obtained when the hydrogen halide was used are therefore only approximate and are not included in the average value.

The dissociation constants for iodobenzene dichlorine in nitromethane, acetic acid and carbon

TABLE II

THE EQUILIBRIUM CONSTANT FOR THE DISSOCIATION OF IODOBENZENE DICHLORIDE^a IN NITROMETHANE

$10^3(C_6H_5I)_T$, mole/l.	$10^3(Cl_2)_T$, mole/l.	$10^6(ICl)$, mole/l.	10^3K, mole/l.
		$t = 25.0°$	
10.88	10.88		0.47
7.55	7.55		.35
6.10	6.10		.41
6.15	4.87		.50^b
6.10	6.10		.53^c
6.10	6.10		.53^d
5.55	5.55		.44
5.74	5.74	1.45	.33
5.74	5.74	2.91	.46
5.51	5.51	4.5	.43
5.55	5.55	5.81	.42
5.50	5.50	11.4	.39
5.55	5.55	23.36	.41
2.75	2.75		.38
		Av.^{e}	0.42 ± 0.03
		$t = 45.4°$	
11.0	12.5		1.27^b
11.0	6.7		1.21^b
10.95	10.95		1.22
5.58	5.58		1.21
2.73	2.73		1.13
		Av.	1.21 ± 0.03

^{a} Except as indicated by footnote the initial reactant was iodobenzene dichloride. ^{b} The initial reactants were iodobenzene and chlorine. ^{c} 0.058 M HCl was present. The constant was not used in calculating the average. ^{d} 0.018 M HCl was present. The constant was not used in calculating the average. ^{e} The average is based on twenty-one values.

TABLE III

THE EQUILIBRIUM CONSTANTS FOR THE DISSOCIATION OF SUBSTITUTED IODOBENZENE DICHLORIDES IN NITROMETHANE

10^3(ArI)$_T$, mole/l.	10^3(Cl$_2$)$_T$, mole/l.	Direction[a]	10^3K, mole/l.
p-C$_6$H$_5$C$_6$H$_4$I at 25.0°			
6.30	6.30	D	0.30
4.20	4.20	D	.23
2.10	2.10	D	.36
p-NO$_2$C$_6$H$_4$I at 25.0°			
6.34	6.34	D	14.6
4.22	4.22	D	15.8
p-HOOCC$_6$H$_4$I at 25.0°			
4.16	4.16	D	6.4
2.08	2.08	D	5.5
o-CH$_3$C$_6$H$_4$I at 25.0°			
15.85	15.85	D	0.30
10.58	10.58	D	.39
5.27	5.27	D	.39
p-CH$_3$C$_6$H$_4$I at 25.0°			
10.60	10.60	D[b]	0.16
5.30	5.30	D[b]	.15
5.30	5.30	D	.13
2.65	2.65	D[c]	.20
o-ClC$_6$H$_4$I at 25.0°			
13.25	13.25	D	7.1
8.82	8.82	D	8.2
4.41	4.41	D	8.7
m-ClC$_6$H$_4$I at 25.0°			
72.0	5.93	F	3.1
72.0	2.86	F	3.6
36.0	5.93	F	4.0[d]
4.89	4.89	D	3.8
2.44	2.44	D	3.3
p-ClC$_6$H$_4$I at 25.0°			
33.4	10.59	F	2.3
16.7	12.15	F	2.2
16.7	6.00	F	2.3
9.06	9.06	D	2.1
4.52	4.52	D	1.9
p-ClC$_6$H$_4$I at 45.4°			
33.4	13.61	F	4.2
16.7	13.82	F	5.2
16.7	7.10	F	5.6
14.7	14.7	D	4.3
9.80	9.80	D	4.4
4.90	4.90	D	4.6

[a] D indicates that dichloride was used as starting material; F indicates that the iodobenzene and chlorine were employed as reactants. [b] (ICl) = 6.27 × 10^{-5} M. [c] (ICl) = 3.13 × 10^{-5} M. [d] The average of two determinations.

tetrachloride[1] at 25° are, respectively, 4 × 10^{-4}, 20 × 10^{-4} and 200 × 10^{-4} mole l.$^{-1}$. Since the degree of dissociation increases as the solvent becomes less polar, it might be concluded that the dichloride is more polar than its dissociation products. In general enthalpy changes associated with solvation contribute more to the change in equilibrium constant[6] than do the corresponding entropy changes. From the data of Table II the enthalpy change

(6) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 345.

accompanying the dissociation of iodobenzene dichloride in nitromethane is calculated as 9.8 ± 0.7 kcal. mole^{-1}. The enthalpies of dissociation in the three solvents[1,2] investigated are very similar, and therefore it seems unlikely that the dichloride can be a highly polar entity.

A plot of log K values (25°) for the *meta* and *para* substituted dichlorides against the Hammett σ-values[7] is somewhat better accommodated by a straight line than is the corresponding plot of acetic acid data.[2b] Only the point for the p-carboxy compound is markedly out of line. The same discrepancy was noted for this compound in acetic acid, and the deviation was attributed to a specific solvation of the carboxyl group.[8] The normal electronic effects of this ring substituent may also be modified through solvation effects in nitromethane.

The ρ-value for the dissociation constants in nitromethane is about +2.4 as compared to a value of +1.8 in acetic acid. In other words in both solvents the degree of dichloride dissociation is enhanced by electron withdrawing ring substituents.

Both o-methyl- and o-chloroiodobenzene dichloride have larger dissociation constants than their respective *para* isomers, and the o-chloro derivative is also more dissociated than its *meta* isomer. Undoubtedly the degree of dissociation of the *ortho* isomers is subject to steric enhancement. The increases in K values with the shift of a substituent to the *ortho* position are not, however, dramatically large. Actually the steric influence of *ortho* substituents on dichloride stability should be relatively small since the linear Cl–I–Cl grouping is perpendicular rather than parallel to the plane of the aromatic nucleus.[9]

The Rates of Formation and Dissociation of the Dichlorides.—The rate law for the equilibration of the dichlorides with their components is

$$-d(\text{ArICl}_2)/dt = k_1(\text{ArICl}_2) - k_2(\text{ArI})(\text{Cl}_2) \quad (5)$$

Equation 6, one integrated form[2] of equation 5, was used in evaluating k_2 in the present work.

$$\ln \frac{2A + b - \sqrt{b^2 - 4a}}{2A + b + \sqrt{b^2 - 4a}} = k_2 t \sqrt{b^2 - 4a} + \text{constant}$$
$$(6)$$

When the initial reagents are the free iodobenzene and chlorine, $a = (\text{ArI})_i(\text{Cl}_2)_i$ and $b = -[(\text{ArI})_i + (\text{Cl}_2)_i + K]$. When the dichloride, A, is used as starting material[10] $a = (\text{ArICl}_2)_i^2$ and $b = -[2-(\text{ArICl}_2)_i + K]$.

The k_2 values for the compounds on which rate studies were made are reported in Table IV. The k_1 values which are also listed are the products of average values of k_2 and K (see Tables II and III for the latter).

For technical reasons which hinged on limitations in the solubilities of the dichlorides or of the free iodobenzenes and on the variations in the degrees of dissociation of the several dichlorides, kinetic

(7) H. H. Jaffé, Chem. Revs., 53, 191 (1953).

(8) The effects of polar hydroxylic solvents on σ-values have been discussed by B. Gutbezahl and E. Grunwald, THIS JOURNAL, 75, 559 (1953).

(9) E. M. Archer and T. G. D. Van Schalwyk, Acta Cryst., 6, 88 (1953).

(10) The term a has been incorrectly defined in reference 2a.

TABLE IV

THE RATE CONSTANTS FOR EQUILIBRATION OF THE DI-CHLORIDES WITH THEIR COMPONENTS IN NITROMETHANE

$10^3(\text{ArI})_T,^a$ mole/l.	$10^3(\text{Cl}_2)_T,^a$ mole/l.	$10^2k_2,$ mole^{-1} l. sec.$^{-1}$

C_6H_5I at 25.0°

82.0	11.72	3.9
84.8	6.70	4.7
82.0	3.05	5.9
40.6	5.89	3.7
20.5	6.31	3.3
8.46	6.53	4.6

Av. 4.4 ± 0.7 ($k_{1av} = 1.8 \times 10^{-5}$)

39.0	4.73	15.3^b
20.2	6.31	56^c
10.95	10.95	5.7
6.10	6.10	15.6^d
6.10	6.10	8.0^e
5.58	5.58	4.7

$C_{65}HI$ at 45.4°

22.1	6.7	6.7
11.0	6.7	6.3
11.0	12.5	4.7

Av. 5.9 ± 0.8 ($k_{1av} = 7.1 \times 10^{-5}$)

$p\text{-}ClC_6H_4I$ at 25.0°

33.4	11.6	5.0
16.7	12.15	4.8
16.7	6.00	4.1

Av. 4.6 ± 0.4 ($k_{1av} = 1.0 \times 10^{-4}$)

$p\text{-}ClC_6H_4I$ at 45.4°

14.7	14.7	5.0
9.80	9.80	5.3
4.90	4.90	5.2

Av. 5.2 ± 0.1 ($k_{1av} = 2.4 \times 10^{-4}$)

$m\text{-}ClC_6H_4I$ at 25.0°

72.0	5.93	2.6
69.4	6.65	2.4
36.0	5.93	1.6
34.7	6.90	2.0

Av. 2.1 ± 0.4 ($k_{1av} = 7.6 \times 10^{-5}$)

$o\text{-}ClC_6H_4I$ at 25.0°

13.25	13.25	1.56
8.82	8.82	1.50
4.41	4.41	1.46

Av. 1.51 ± 0.04 ($k_{1av} = 1.2 \times 10^{-4}$)

^{a} In those cases in which $(\text{ArI})_T = (\text{Cl}_2)_T$ the initial reactant was the undissociated dichloride; in other instances the rate samples were prepared by mixing stock solutions of chlorine and the iodobenzene. ^{b} In this run the concentration of added water was 0.20 M. ^{c} The solvent used was dried over P_2O_5. ^{d} The concentration of added hydrogen chloride was 0.058 M. ^{e} The concentration of added hydrogen chloride was 0.018 M.

measurements were restricted to only a few of the systems for which equilibrium data are reported.

In general the rate of a reaction in which the activated complex is more polar than the reactants is enhanced as the polarity of the solvent is increased. This fact is often mentioned[11] to explain the ob-

(11) See for example (a) R. Criegee, *Ann.*, **560**, 127 (1948); (b) F. L. J. Sixma, H. Boer, J. P. Wibaut, H. J. Pel and J. de Bruyn, *Rec. trav. chim.*, **70**, 1005 (1951); (c) A. G. Evans, A. Price and J. H. Thomas, *Trans. Faraday Soc.*, **50**, 568 (1954).

servation that the rate of a reaction accelerates when the solvent is changed from a medium such as carbon tetrachloride to one with a high dipole moment such as nitromethane. The rate increase is presumed to result from a more extensive solvation of the activated complex with a resultant decrease in activation energy. The entropy of activation is usually also decreased, but in most cases the activation energy change controls the direction of rate change.[12]

The dipole moment is not an entirely reliable criterion of relative solvent effectiveness in such processes. A hydroxylic solvent of moderate polarity, such as acetic acid, may serve as a more favorable medium than a highly polar aprotic solvent.[13]

With these points in mind it is interesting to compare the rates of dissociation and formation of the iodobenzene dichlorides in the various solvents for which data are available. In the absence of a catalyst the decomposition or formation of iodobenzene dichloride in carbon tetrachloride is extremely slow. Undoubtedly the activation energies are large in this solvent. In acetic acid and in nitromethane the dichlorides react at measurable rates, and the rate constants are not greatly different for the two media. The k_1 and k_2 values for iodobenzene dichloride are somewhat larger in acetic acid than in nitromethane. The pertinent rate constants and energies and entropies of activation are summarized in Table V.

TABLE V

ENERGIES AND ENTROPIES OF ACTIVATION FOR DICHLORIDE FORMATION

Dichloride	10^4k_1 (25°), sec.$^{-1}$	10^2k_2 (25°), mole^{-1} l. sec.$^{-1}$	$E_1,^a$ kcal./ mole	$\Delta S_1^{\ddagger,b}$ e.u.	$E_2,^a$ kcal./ mole	$\Delta S_2^{\ddagger,b}$ e.u.
		Acetic acid as solvent				
$C_6H_5ICl_2{}^c$	17	9	19.6	−12	12.6	−23
$m\text{-}ClC_6H_4ICl_2{}^d$	15	1.0	19.4	−13	11.8	−30
		Nitromethane as solvent				
$C_6H_5ICl_2$	1.8	4.4	12.5	−40	2.7	−57
$m\text{-}ClC_6H_4ICl_2$	7.6	2.1				
$p\text{-}ClC_3H_4ICl_2$	10	4.6	8.3	−51	1.1	−63

^{a} The estimated error is ± 1 to 1.5 kcal./mole. ^{b} The estimated error is ± 3 to 5 e.u. ^{c} The values listed for iodobenzene dichloride in acetic acid are based on rate and equilibrium constants which are reported in Table VI as determined in the present investigation. The values of E_1 and $\Delta S_1^{\ddagger}$ are in good agreement with the values reported previously.^{2a,b} The values of E_2 and $\Delta S_2^{\ddagger}$ are different due to the use of the new values of ΔH^0 and ΔS_0 reported in Table VI. ^{d} From reference 2b.
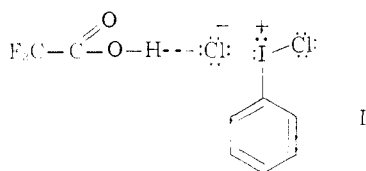
Some caution should be exercised in discussing the theoretical significance of these thermodynamic constants (particularly the values of $\Delta S^{\ddagger}$), since there is a considerable degree of uncertainty in their values. It is evident, however, that the values of E_1 and E_2, the activation energies for the dissociation and formation reactions, are substantially lower (of the order of 7–10 kcal./mole) in nitromethane than in acetic acid. At least for the

(12) E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution," 2nd Ed., Oxford University Press, Amen House, London, England, 1947, Chapter 7.

(13) E. Gelles, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2918 (1954).

reactions in question the highly polar solvent is a considerably more effective solvating agent for the activated complex than is acetic acid. The fact that this superiority is not directly apparent in the observed rate constants must be traced to the very large entropy decreases which accompany the activation processes in nitromethane.

The data of Table V do not lend much support to the conclusion that the hydroxylic character of acetic acid is an important factor in determining its efficiency over nitromethane in promoting reactions in which the activated complex is more polar than the reactants. However qualitative experiments have shown that in trifluoroacetic acid at 25° the formation of iodobenzene dichloride from its components occurs at an immeasurably rapid rate. As indicated by its dielectric constant[14] and dipole moment[15] this solvent is intermediate in polarity between nitromethane and acetic acid. Yet as a medium for fast reaction it is uniquely favorable. A reasonable explanation for this fact is founded on the assumption that the fluorinated acid should be a particularly effective participant in hydrogen bond formation. A substantial lowering of the activation energy for dichloride formation should result from solvation of the type shown in formula I, which is an exaggerated conception of the probable electronic polarization of the activated complex. The entropy changes attendant on this

$$F_3C-C\overset{\displaystyle O}{\underset{\displaystyle }{\diagup}}-O-H\text{-}\text{-}\text{-}:\overset{-}{\ddot{C}}l: \quad :\overset{+}{I}-\ddot{C}l: \qquad \qquad \text{I}$$

mode of solvation apparently do not offset the energetic advantages of trifluoroacetic acid as a reaction medium.

As already has been mentioned, electron withdrawing ring substituents enhance the degree of dissociation of iodobenzene dichloride both in acetic acid and in nitromethane. With acetic acid as the medium k_1 values are rather insensitive to changes in ring substituents; the increases in K values result primarily from corresponding decreases in k_2 values.[2b] Although data for only three compounds (see Table V) are available, it appears that k_2 values for nitromethane solutions are not much altered by the introduction of electron withdrawing ring substituents (m-Cl and p-Cl). The increases in K values seem to result primarily from increases in k_1 values. It is possible that the changes in substituent effects on k_1 and k_2 with the change in solvent may be traced to differences in the electronic requirements at the reaction site for most effective solvation of the activated complexes in the two media.[16] The thermodynamic data available in

Table V are sufficiently limited in accuracy and in quantity so that they do not serve as useful criteria for testing this supposition.

Catalytic Effects.—The experimental rate constants for certain of the reactions in nitromethane which were investigated could not be reproduced with high precision. This was noticeably evident when the initial reactants were an iodobenzene and chlorine (see Table IV). It was surmised that this behavior might result from trace contamination of the solvent or reactants by substances with catalytic activity. Accordingly experiments were made to determine the effects of small amounts of water, hydrogen chloride and iodine monochloride on the reaction rates.

Added water (0.20 M) was found to increase the rate constant k_2 for the reaction of iodobenzene and chlorine by a factor of three at 25°. On the other hand exposure of the solvent to ignited Drierite for several weeks prior to the making of rate runs had, within experimental error, no effect on k_2 values.[17] When phosphorus pentoxide, rather than Drierite, was used to remove traces of water from the solvent, the reaction rate was enhanced by a factor of over ten times that found using untreated solvent. The phosphorus pentoxide treated nitromethane was fractionated carefully before it was used; apparently traces of strongly catalytic phosphorus compounds were entrained.

The catalytic activity of hydrogen chloride was assessed in terms of runs at 25° with iodobenzene dichloride as starting material. The rate constant k_2 was increased about threefold when the hydrogen halide was introduced at 0.058 M concentration. Quantitative information on runs with added water and hydrogen chloride is given in Table IV.

The catalytic effects of iodine monochloride in nitromethane were astonishingly large (immeasurably so at 25° when (ICl) was much larger than $10^{-4}~M$). It therefore seemed of interest to make a comparative study of the influence of the mixed halogen on the dichloride equilibration process both in nitromethane and in acetic acid. Table VI summarizes the results of a series of runs made to determine the influence of catalyst concentration on the rate of dissociation of iodobenzene dichloride in the two media. Plots of the experimental k_1 values versus the catalyst concentration were found to be linear, as shown in Fig. 1. The slopes of the lines were measured to determine values of k_c (as defined in equation 7 in which k_c and k_u are the rate constants for the catalyzed and uncatalyzed dissociation)

$$k_1 = k_u + k_c(\text{ICl}) \qquad (7)$$

For nitromethane solvent at 25.0° a value of $k_c = 26.1$ mole^{-1} l. sec.$^{-1}$ was calculated; for acetic acid the k_c values at 25.0 and 45.4°, respectively, were 0.95 and 2.60 mole^{-1} l. sec.$^{-1}$. The line (line III, Fig. 1) for nitromethane solutions at 25° extrapolated below the origin. It seems likely that traces of impurities in the medium (of the order of

(14) (a) W. Dannhauser and R. H. Cole, Jr., THIS JOURNAL, **74**, 6105 (1952); (b) F. E. Harris and C. T. O'Konski, ibid., **76**, 4317 (1954).

(15) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p. 304.

(16) The effects of the change in solvent on the influence of ring substituents on the rate constants can be summarized by the statement that the Hammett ρ-values for both the association and dissociation reactions are larger in nitromethane than in acetic acid. Some attention previously has been given to the influence of solvent on the

magnitude of ρ [see ref. 7, p. 219, and L. P. Hammett, THIS JOURNAL, **59**, 96 (1937)], although no universally applicable relationships have been discovered.

(17) In nitromethane the rates of SN1 reactions of t-butyl bromide also are not markedly enhanced by water unless its concentration becomes very appreciable.[14]

TABLE VI

THE IODINE MONOCHLORIDE CATALYZED DISSOCIATION OF IODOBENZENE DICHLORIDE

HOAc as solvent			CH₃NO₂ as solvent		
$10^3(\varphi ICl_2)_i$, mole/l.	$10^4(ICl)$, mole/l.	10^4k_1, sec.$^{-1}$	$10^3(\varphi ICl_2)_i$, mole/l.	$10^4(ICl)$, mole/l.	10^4k_1, sec.$^{-1}$
$t = 25.0°$			$t = 25.0°$		
5.65^a	...	1.7^b	5.45	1.12	25.8
5.61	5.67	6.1	5.51	0.63	11.2
5.65	11.4	12.7	5.74	.58	9.5
5.65	22.7	23.1	5.51	.47	6.4
$t = 45.4°$			5.45	.42	7.5
5.85^a	...	14.1^b	5.51	.31	3.6
6.27	1.39	17.2	5.74	.29	3.2
5.85	2.78	21.4	5.45	.28	3.8
5.81	5.57	28.3	5.74	.15	0.4

^{a} Average values of K determined from equilibrium readings were 1.9×10^{-3} and 4.2×10^{-3} mole/l., respectively, at 25.0 and 45.4°; the values reported previously[2a] were 1.5×10^{-3} at 25.0° and 4.3×10^{-3} at 45.6°. From the new equilibrium constants, values of $\Delta H^0 = 7.0$ kcal./mole and $\Delta S^0 = 11$ e.u. have been calculated. ^{b} Previously reported values[2a] for k_1 were 1.5×10^{-4} (sec.$^{-1}$) at 25.0° and 12.7×10^{-4} at 45.6°.

1.5×10^{-5} M), which destroyed small amounts of iodine monochloride, were the cause of the discrepancy. Because of this difficulty plans to study the reaction rate in nitromethane at 45° were abandoned. Runs with measurable rates could have been made at this temperature only if the catalyst were present over a very limited range of low concentration. In view of these results liquid iodobenzenes which were used in rate work were stored over mercury to prevent iodine contamination.

From the k_c values at 25.0 and 45.4° an activation energy of 9.3 kcal./mole and an activation entropy of -29 e.u. can be calculated for the iodine monochloride catalyzed dissociation of iodobenzene dichloride in acetic acid. The activation energy is about 10 kcal./mole less than that for the uncatalyzed reaction in this solvent (see Table V).

It has previously been proposed that iodine monochloride (probably as a dimer) promotes the equilibration of iodobenzene dichloride with its components in carbon tetrachloride in much the same way as do the solvent molecules of a polar medium. Through its incorporation in the activated complex a suitable local environment for polarization of the reacting substances is provided. It is surprising that the mixed halogen displays marked catalytic action at very low concentrations
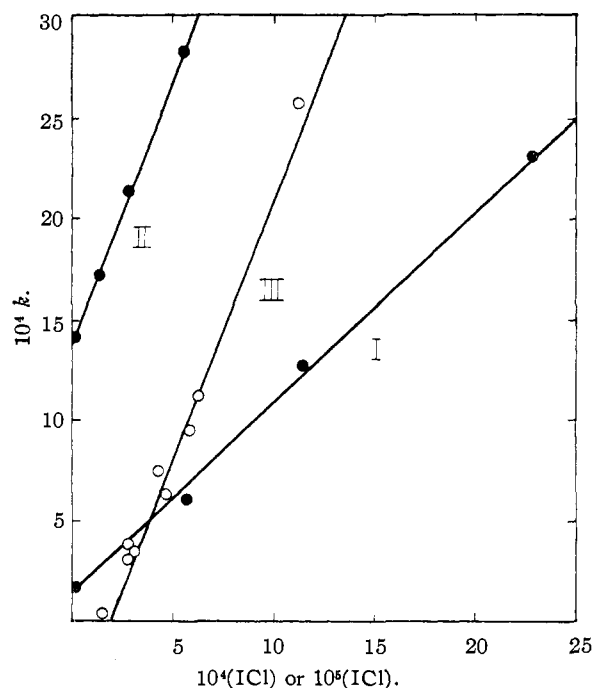

Fig. 1.—The rate constants for the iodine monochloride catalyzed dissociation of iodobenzene dichloride. Lines I and II are for reactions in acetic acid at 25.0 and 45.4°, respectively, with abscissa values corresponding to $10^4(ICl)$. Line III is for reaction in nitromethane at 25.0° with abscissa values corresponding to $10^5(ICl)$.

in ionizing solvents such as acetic acid and nitromethane.

In terms of the k_c values iodine monochloride is over twenty-five times more effective in catalyzing the reaction in nitromethane than in acetic acid. There is, however, good evidence[4] that acetic acid has strong donor properties and can interact extensively with iodine monochloride. Nitromethane, like iodine monochloride, is an acceptor molecule. The energy requirements for the desolvation of the catalyst, which must accompany its inclusion in the activated complex, are probably much lower in nitromethane than in acetic acid. This difference would be reflected in the activation energies for the catalyzed reactions in the two solvents.

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