

Anal. Calcd. for $C_{11}H_{12}F_6O_2N_2$: C, 41.52; H, 3.80; N, 8.80; *MRD*, 56.54. Found: C, 41.39; H, 3.79; N, 8.99; *MRD*, 56.36.

Ethyl 9-Hydroxy-6,6,7,7,8,8-hexafluoro-4-oxanonanoate.—A solution of 19.2 g. (0.073 mole) of 9-hydroxy-6,6,7,7,8,8-hexafluoro-4-oxanonanonitrile in 30 ml. of absolute ethanol was saturated with hydrogen chloride at -20° . After storage in a refrigerator for 20 days, a portion of the excess hydrogen chloride and ethanol was removed by evaporation at 110 mm. and the remaining oil was heated with 100 ml. of water at 65° for 1 hr. The ether extracts of the aqueous suspension were dried with magnesium sulfate and fractionated to yield 17.55 g. (78%) of the product, b.p. $112-113^\circ$ (0.5 mm.), n_D^{20} 1.3916, d_4^{20} 1.386.

Anal. Calcd. for $C_{10}H_{14}F_6O_4$: C, 38.47; H, 4.52; *MRD*, 53.70. Found: C, 38.23; H, 4.69; *MRD*, 53.58.

Diethyl 6,6,7,7,8,8-Hexafluoro-4,10-dioxatridecanedioate.—By the foregoing procedure, 10.0 g. (0.031 mole) of 6,6,7,7,8,8-hexafluoro-4,10-dioxatridecanodinitrile led to 9.00 g. (70%) of the diester-diether, b.p. $131-132^\circ$ (0.07 mm.), n_D^{20} 1.4041, d_4^{20} 1.287.

Anal. Calcd. for $C_{15}H_{22}F_6O_6$: C, 43.70; H, 5.38; *MRD*, 78.84. Found: C, 43.84; H, 5.58; *MRD*, 78.38.

Methyl 9-Hydroxy-6,6,7,7,8,8-hexafluoro-4-oxanonanoate and Dimethyl 6,6,7,7,8,8-Hexafluoro-4,10-dioxatridecanedioate.—Methyl acrylate (20 g., 0.23 mole) was added to a mixture of 21.2 g. (0.1 mole) of 2,2,3,3,4,4-hexafluoropentane-1,2-diol, 1.0 g. (0.004 mole) of the disodium salt of the diol and 200 ml. of anhydrous ether. After stirring at 25° for 8 hr., the reaction mixture was heated under reflux for 5 hr., cooled, washed with water and dried over magnesium sulfate. After evaporation of the ether, the residue was taken up in 250 ml. of hot benzene and cooled to give 6.75 g. (41% recovery) of hexafluoropentane-1,2-diol. Fractional distillation of the filtrate gave 12.25 g. (41% conversion, 54% yield) of methyl 9-hydroxy-6,6,7,7,8,8-hexafluoro-4-oxanonanoate, b.p. 110° (0.4 mm.), n_D^{20} 1.3900, d_4^{20} 1.443.

Anal. Calcd. for $C_9H_{12}F_6O_4$: C, 36.25; H, 4.06; *MRD*, 48.97. Found: C, 36.19; H, 4.29; *MRD*, 48.98.

A higher-boiling fraction from the above preparation consisted of 3.8 g. (19% conversion, 22% yield) of dimethyl 6,6,7,7,8,8-hexafluoro-4,10-dioxatridecanedioate, b.p. 125° (0.06 mm.), n_D^{20} 1.4028, d_4^{20} 1.348.

Anal. Calcd. for $C_{13}H_{18}F_6O_6$: C, 40.63; H, 4.72; *MRD*, 69.58. Found: C, 40.79; H, 4.83; *MRD*, 69.54.

WEST LAFAYETTE, INDIANA

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

The Formation and Dissociation of Iodobenzene Dichloride in Carbon Tetrachloride

BY L. J. ANDREWS AND R. M. KEEFER

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The reaction of iodobenzene with chlorine to form iodobenzene dichloride in carbon tetrachloride is extremely slow in the dark unless a polar catalyst is present. Reaction is induced either by iodine monochloride or by the concomitant action of water and hydrogen chloride. Through the use of iodine monochloride as the catalyst the equilibrium constants for dichloride dissociation in carbon tetrachloride at 25.0° and 45.4° have been evaluated and the kinetics of equilibration have been studied. The degree of dissociation is larger in the non-polar medium than in acetic acid, although the enthalpy of dissociation is insensitive to the change in solvent. The reactions which lead to equilibration are second order with respect to the catalyst. The activation energy for the dissociation step is very small, and that for the reverse process is negative. It is presumed that the catalyst provides a favorable atmosphere for polarization of the reactants in the activated complex.

Under reflux in non-polar media iodobenzene dichloride reacts with acenaphthylene¹ and *p*-dioxene² to give *trans*-dichlorides of the unsaturated starting materials. When the iodo compound is replaced by molecular chlorine and the reactions are carried out at ice temperature, *cis*-dichlorides are produced in substantial amount. Although an unequivocal statement cannot be made on the basis of existing information, it seems unlikely that the *trans* products form through dissociation of iodobenzene dichloride and then reaction of free chlorine with the unsaturates.

The formation of *cis*-dichloride³ in the reaction of cholesteryl benzoate with iodobenzene dichloride in *dry* chloroform is presumed⁴ to result from a direct interaction of the two reactants by a process which leads to a cyclic activated complex.⁵ In moist chloroform the product configuration shifts to *trans* as the water content of the medium is increased. Presumably moisture favors dissociation of the iodobenzene dichloride to free chlorine (or its hydrate), since the product of reaction of

molecular chlorine and cholesteryl benzoate in chloroform is also *trans*.⁶

The reaction of rubber with iodobenzene dichloride in carbon tetrachloride also is believed to occur by a radical^{7,8} or other⁴ process without the liberation of free chlorine.

It has been demonstrated⁹ that, in the polar medium acetic acid, iodobenzene dichloride can function as a halogenating agent through prior dissociation to iodobenzene and chlorine. In this solvent the dichloride equilibrates with its components at a reasonably rapid but easily measurable rate, and the rates of nuclear chlorination of mesitylene and pentamethylbenzene by reaction with the dichloride in acetic acid are identical with the rate of dichloride dissociation.¹⁰ The entropy of activation for the dissociation is negative,¹¹ a fact which

(6) The apparent discrepancy in the stereochemistry of the addition products reported for acenaphthylene and *p*-dioxene as compared to that for the cholesteryl benzoate adduct has not been fully explained (see ref. 2).

(7) G. F. Bloomfield, *J. Chem. Soc.*, 114 (1944).

(8) C. S. Ramakrishnan, D. Raghunath and J. B. Pande, *Trans. Inst. Rubber Ind.*, **30**, 129 (1954); *C. A.*, **49**, 657 (1955).

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

(10) E. Zappi and Sta. J. Cortelezzi, *Bull. soc. chim.*, [5] **1**, 509 (1934), have given cryoscopic evidence that iodobenzene dichloride is also partially dissociated in nitrobenzene and in phosphorus oxychloride.

(11) R. M. Keefer and L. J. Andrews, *THIS JOURNAL*, **80**, 277 (1958).

(1) S. J. Cristol, F. R. Stermitz and P. S. Ramey, *THIS JOURNAL*, **78**, 4939 (1956).

(2) R. K. Summerbell and H. E. Lunk, *ibid.*, **79**, 4802 (1957).

(3) C. J. Berg and E. S. Wallis, *J. Biol. Chem.*, **162**, 683 (1946).

(4) D. H. R. Barton and R. Miller, *THIS JOURNAL*, **72**, 370 (1950).

(5) Cf. M. J. S. Dewar, *Ind. chim. belg.*, **15**, 181 (1950); *C. A.*, **47**, 9118 (1953).

suggests that the solvent is incorporated in an activated complex which has substantial polar character.

In a non-polar medium the activation energy for dissociation of the dichloride may be much larger than in acetic acid. In this sense it seems reasonable that iodobenzene dichloride functions as a chlorine source in addition or substitution reactions in inert media without formation of free halogen. To establish a basis for a better understanding of the influence of solvent polarity on the mechanisms of such reactions, a study of the formation and dissociation of iodobenzene dichloride in carbon tetrachloride has been conducted. Catalysts for the equilibration of the dichloride with its components have been found, and the equilibrium constant has been evaluated. A limited kinetic investigation of the association and dissociation reactions has been made.

Experimental

Materials.—The carbon tetrachloride was Eastman Organic Chemicals sulfur-free grade. For work in which the dried solvent was required samples were withdrawn as needed from a batch which had been stored over ignited (400°) Drierite for at least ten days. Ohio Chemical chlorine was used without further purification. Hydrogen chloride was generated as needed by mixing concentrated hydrochloric and sulfuric acids and was dried with concentrated sulfuric acid. Iodobenzene, b.p. 185.5–186.0°, was freshly distilled before use. Iodobenzene dichloride was prepared in small batches as needed by gassing solutions of iodobenzene in acetic acid with chlorine. Complete details of the method are given elsewhere.¹¹ Iodine monochloride was prepared from the elements.¹²

The Extinction Coefficients of the Reactants.—Spectrophotometric measurements to study the equilibration of iodobenzene dichloride with its components were made at 380 m μ . The molar extinction coefficients at this wave length ($\epsilon = d/lc$ where d is the optical density of a solution of molar concentration c measured in an absorption cell of path length 1 cm.) of the various reactants and catalyst were determined by direct spectrophotometric measurement of stock solutions of the reagents in carbon tetrachloride. The concentrations of the halogen and iodobenzene dichloride solutions were established iodometrically. In the case of solutions which contained chlorine, samples were withdrawn from absorption cells for volumetric analysis after completion of the optical measurements.

Values of ϵ_{380} for iodobenzene and its dichloride are, respectively, 0.023 and 87.9. The absorption of chlorine is enhanced somewhat by iodobenzene. The ϵ_{380} values for chlorine at 25° in solutions in which the iodobenzene concentrations are 0, 0.12, 0.25 and 0.49 M are, respectively, 23.0, 24.6, 26.7 and 30.3. At 45.4° the ϵ_{380} value for chlorine in 0.48 M iodobenzene is 31.4.

The absorption of iodine monochloride increases in approximately linear fashion with both the iodobenzene and iodobenzene dichloride concentrations of the medium. Over the range of concentrations used in the rate studies the equation

$$\epsilon_{\text{ICI}} = 34.3 + \alpha(\text{C}_6\text{H}_5\text{I}) + \beta(\text{C}_6\text{H}_5\text{ICl}_2) \quad (1)$$

describes these increases, where at 25° $\alpha = 418$ and $\beta = 2070$ and at 45.4° $\alpha = 334$ and $\beta = 2140$.

Since iodine monochloride initiates dissociation of iodobenzene dichloride, optical measurements to determine β values were made rapidly on freshly prepared solutions. The reported β values are based on optical densities at the time of mixing as determined by extrapolation.

Neither iodobenzene dichloride nor hydrogen chloride has any appreciable effect on the absorption of chlorine at 380 m μ .

The Effects of Moisture and of Hydrogen Chloride on the Reaction of Iodobenzene and Chlorine.—Essentially no reaction occurs between chlorine and iodobenzene in either

moist hydrogen chloride-free carbon tetrachloride or in dry carbon tetrachloride containing hydrogen chloride. The optical density of a solution of iodobenzene (0.245 M), chlorine ($7.1 \times 10^{-3} M$) and hydrogen chloride (0.037 M) in Drierite-dried carbon tetrachloride at 380 m μ changed only from 0.187 to 0.198 over a two-hour period. Were the chlorine converted completely to iodobenzene dichloride, the reading should have increased from the initial value to 0.61. Similarly the optical density of a solution of 0.49 M iodobenzene and $7 \times 10^{-3} M$ chlorine in water-equilibrated carbon tetrachloride changed only from 0.210 to 0.219 over a two-hour period; the optical density of a mixture otherwise identical except that it contained hydrogen chloride (0.027 M) increased rapidly with time and reached a maximum value of 0.590 in about four hours. The solution was somewhat murky owing to the separation of water droplets. Therefore the final optical density reading, which corresponds to an iodobenzene dichloride concentration of the order of $6.5 \times 10^{-3} M$, is not a completely reliable criterion of product composition.

The hydrogen chloride concentrations reported above were determined by analysis of samples removed from the cells at the end of the optical measurements. The samples were added to dilute potassium iodide solution and the halogen was destroyed by treatment with a drop of concentrated sodium thiosulfate solution. The solutions were then titrated with standard aqueous sodium hydroxide to the phenolphthalein end-point.

The Iodine Monochloride Catalyzed Equilibration Rate Studies.—Rate samples for runs in which chlorine and iodobenzene were the starting materials were prepared by mixing measured volumes of stock solutions of the reactants and catalyst (at the temperature of the run) directly in the absorption cells. The samples were prepared in a semi-darkened room. The cells were stored in a temperature controlled ($\pm 0.1^\circ$) housing, and optical density readings as a function of time were recorded at 380 m μ , usually until no further increase in optical density occurred. Where they were required, optical densities of the solutions at the time of mixing were estimated by extrapolation procedures. The total halogen content (including dichloride) of the solutions at the ends of the runs was usually determined by iodometric analysis of samples removed from the cells. In most cases this was within a few per cent. of the values at the initiation of reaction. Only in a few runs in which long periods of time were required for equilibration were serious chlorine losses observed. The several absorption cells which were used were checked spectrophotometrically to determine the extent to which they leaked chlorine. In three hours the chlorine content of a $5 \times 10^{-3} M$ solution, contained in the least reliable cell which was used, dropped by less than 2%. All of the rate runs reached high percentages of completion in this time.

The brief periods of exposure of rate samples to light during the optical measurements had no influence on the reaction rates. Two identical rate samples were prepared simultaneously. One was subjected to frequent optical density measurements until it was 80% complete. At this time the second sample, which had been stored in the dark, had the same optical density reading as the illuminated material.

In runs with iodobenzene dichloride as the starting material, procedures similar to those described above were employed. The total halogen content of rate samples at equilibrium was again determined iodometrically, and in general this agreed with the initial value to within a few per cent. In the absence of iodine monochloride, solutions of iodobenzene dichloride in carbon tetrachloride showed no change in optical density for as long as 7-hour periods.

Equilibrium constants for dichloride dissociation were evaluated using the equilibrium optical density readings of solutions which contained, at the initiation of reaction, known quantities of the dichloride (and in some cases of iodobenzene and chlorine) and of iodine monochloride. The total halogen concentration at equilibrium, including the dichloride concentration, was checked by iodometric analysis of samples removed from the absorption cells.

The Iodobenzene-Iodine Monochloride Complex.—The near ultraviolet absorption of iodine monochloride in carbon tetrachloride is strongly enhanced in the presence of iodobenzene. On the assumption that this enhancement results because of the formation of a 1:1 aromatic-halogen complex, equilibrium constants for the interaction were determined spectrophotometrically. A series of solutions of

(12) A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 846.

varying iodobenzene (0.08–1 *M*) and iodine monochloride (3×10^{-3} *M* to 6×10^{-3} *M*) concentrations were prepared, and their optical densities *versus* a carbon tetrachloride blank both at 25.1 and 45.4° were recorded at 380 and 390 $m\mu$. Values of K_e , where $K_e = (C_6H_5I \cdot ICl) / (C_6H_5I)(ICl)$, were deduced by graphical interpretation of the data.¹³ The equilibrium constants and extinction coefficients for the com-

TABLE I

THE IODOBENZENE-IODINE MONOCHLORIDE COMPLEX^a

λ , $m\mu$	ϵ c	K_e , l. mole ⁻¹	t , °C.
380	390	1.25	25.1
390	380	1.30	25.1
380	390	0.80	45.4
390	410	0.78	45.4

^a The extinction coefficients of iodine monochloride at 380 and 390 $m\mu$ are 34 and 53, respectively.

plex are summarized in Table I. A value of $\Delta H^0 = 4.4$ kcal./mole was calculated from the constants at 25.1 and 45.4°.

The Preparation of Iodobenzene Dichloride with Iodine Monochloride as a Catalyst.—A freshly prepared solution (10 ml.) of iodobenzene (0.197 *M*), chlorine (0.12 *M*) and iodine monochloride (1.81×10^{-3} *M*) in carbon tetrachloride was stored in the dark. Precipitation of long yellow

$$(\varphi ICl_2) = \frac{d - \epsilon\varphi_1[(\varphi I)_1 + (\varphi ICl_2)_1] - \epsilon_{Cl_2}[(Cl_2)_1 + (\varphi ICl_2)_1] - (ICl)[343 + \alpha(\varphi I)_1 + \alpha(\varphi ICl_2)_1]}{\epsilon\varphi_{ICl_2} - \epsilon\varphi_1 - \epsilon_{Cl_2} + (ICl)(\beta - \alpha)} \quad (2)$$

needles began within 0.5 hour. Two hours after preparation of the original solution, the product was filtered and washed several times with small amounts of carbon tetrachloride. The air-dried material weighed 0.165 g. (50% yield) and had an equivalent weight, as determined iodometrically, of 137; calcd. for $C_6H_5ICl_2$, 137.5. The low yield can be ascribed partly to the solubility (about 0.02 *M*) of iodobenzene dichloride in carbon tetrachloride.

A solution of the same composition, except that it contained no iodine monochloride, yielded no precipitate after three days standing in the dark.

Another such iodine monochloride free solution was exposed to fluorescent room lights. Precipitate formation began within two hours. After four hours of exposure to light, the mixture was filtered, washed with carbon tetrachloride and air-dried. The product weighed 0.140 g. and had an equivalent weight (iodometric) of 147. It is possible, though this point was not further investigated, that the slightly high equivalent weight can be traced to the formation of some ring chlorinated contaminant.

Results

As described in detail in the Experimental section iodobenzene and chlorine react to form their dichloride in carbon tetrachloride provided *both* water and hydrogen chloride are present to serve as catalysts. Analogous cases of cocatalysis by water and a hydrogen halide have been described for the reactions of bromine with ethylene¹⁴ and with mesitylene.¹⁵ Unfortunately it has not proved possible to prepare a series of solutions of water and hydrogen chloride in this solvent in which the solute concentrations are subject to wide variation. The concentration ranges over which such mixtures are homogeneous is apparently very limited. Therefore no quantitative study of dichloride formation in such media has been attempted.

As in the case with non-radical reactions of chlorine in carbon tetrachloride which have too high activation energies to proceed in the absence of

extraneous polar materials,¹⁶ the equilibration of iodobenzene dichloride with its components is subject to catalysis by iodine monochloride. By adopting this substance as a catalyst it has proved feasible to conduct a kinetic investigation of the equilibration of the dichloride with its components in carbon tetrachloride under homogeneous conditions. The reactions have been studied in the dark except for brief periods of exposure to the spectrophotometer light as required in the analytical procedures. Although the reaction rates were not affected by this mild illumination, some evidence is presented in the Experimental section that the dichloride may also be formed from its components in carbon tetrachloride by a photochemical process.

The Equilibrium Constant for Dichloride Formation.—The iodobenzene dichloride concentration of a solution which also contains iodobenzene, chlorine and iodine monochloride is related to the initial concentrations of these several reagents by equation 2.¹⁷ The terms in ϵ are the extinction coeffi-

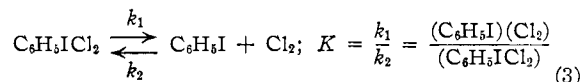
$$d = \epsilon\varphi_{ICl_2}(\varphi ICl_2) + \epsilon\varphi_1(\varphi I) + \epsilon_{Cl_2}(Cl_2) + \epsilon_{ICl}(ICl) \quad (2a)$$

$$(\varphi I) = (\varphi I)_1 + (\varphi ICl_2)_1 - (\varphi ICl_2) \quad (2b)$$

$$(Cl_2) = (Cl_2)_1 + (\varphi ICl_2)_1 - (\varphi ICl_2) \quad (2c)$$

icients of the several absorbing species and α and β are constants which may be used to account for the enhanced absorption of iodine monochloride in the presence of iodobenzene and its dichloride (see Experimental section); d is the optical density of the solution in a 1-cm. absorption cell.

The iodobenzene dichloride concentration at equilibrium of a series of solutions of known initial concentrations of reactants and the catalyst were thus evaluated using the 380 $m\mu$ optical density reading. These values were used to calculate the equilibrium constants (equation 3) which are reported in Table II.



From the constants at 25.0 and 45.4° a value of $\Delta H^0 = 9.8 \pm 0.4$ kcal./mole can be calculated. Although this value of ΔH^0 is close to that determined¹⁰ for the reaction in acetic acid (9.9 kcal./mole), the dissociation constants are over tenfold larger than are found when the polar solvent is used.

The Kinetics of Dichloride Formation.—The kinetics of equilibration of iodobenzene dichloride with its components may be described by equation 4.

$$d(C_6H_5ICl_2/dt) = k_2(C_6H_5I)(Cl_2) - k_1(C_6H_5ICl_2) \quad (4)$$

When the equilibration takes place in carbon tetrachloride solution under the influence of iodine monochloride k_1 and k_2 will vary as shown in equa-

(16) See for example (a) H. D. C. Waters, A. R. Caverhill and P. W. Robertson, *J. Chem. Soc.*, 1168 (1947). (b) L. J. Andrews and R. M. Keefer, *THIS JOURNAL*, **79**, 5169 (1957).

(17) Equation 2 is derived from equations 2a-c and from equation 1, which accounts for the enhanced absorption of iodine monochloride through complex formation with iodobenzene and chlorine.

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

(14) D. M. Williams, *J. Chem. Soc.*, 2911 (1932).

(15) R. M. Keefer, J. H. Blake and L. J. Andrews, *THIS JOURNAL*, **76**, 3062 (1954).

TABLE II

EQUILIBRIUM CONSTANTS FOR THE DISSOCIATION OF IODOBENZENE DICHLORIDE

$10^2(\varphi\text{ICl}_2)_i$, moles/l.	$10^2(X_2)^a$, moles/l.	$10^2(\varphi\text{I})_i$, moles/l.	$10^2(\text{ICl})_i$, moles/l.	$10^2(\varphi\text{ICl}_2)_{\text{eq}}$, moles/l.	10^2K , l. mole ⁻¹
$t = 25.0^\circ$					
4.88	17.33	23.9	5.46	6.02	2.2
4.88	14.90	23.9	5.46	4.88	2.2
4.88	12.63	23.9	5.46	3.86	2.1
9.30	9.55	2.19	2.3
4.65	9.55	0.75	2.0
2.33	9.55	0.23	1.9
..	12.72	53.0	5.83	4.61	2.4
4.35	...	53.0	5.83	3.27	1.8
					Av. 2.1 ± 0.2
$t = 45.4^\circ$					
4.75	16.15	23.3	5.32	3.28	5.7
4.75	14.53	23.3	5.32	2.70	6.2
8.95	4.27	1.17	5.4
4.47	9.55	48.2	5.08	2.21	6.4
4.29	10.33	24.0	5.86	1.41	6.3
..	11.67	48.2	5.86	2.18	6.7
..	11.72	24.0	5.86	1.31	6.1
					Av. 6.1 ± 0.3

^a The term X_2 represents total halogen, including dichloride, as determined by titration after equilibrium is reached.

tions 5 and 6 in which x represents the order of the reaction with respect to the catalyst.

$$k_1 = k_d(\text{ICl})^x \quad (5)$$

$$k_2 = k_f(\text{ICl})^x \quad (6)$$

The formation rate constants, k_2 , were evaluated from the results of a series of rate runs in which the initial concentrations of iodobenzene, chlorine and the catalyst were varied widely. The concentration of iodobenzene dichloride during the runs was calculated from optical density readings at 380 $m\mu$ using equation 2. The values of k_2 for individual runs were calculated from the slopes of the lines obtained by plotting the left hand term of equation 7 as a function of time.¹¹

$$\ln \frac{2A + b - \sqrt{b^2 - 4a}}{2A + b + \sqrt{b^2 - 4a}} =$$

$$k_2 t \sqrt{b^2 - 4a} + \text{constant} \quad (7)$$

In this equation $A = \varphi\text{ICl}_2$, $a = (\varphi\text{I})_i(\text{Cl}_2)_i$ and $b = (\varphi\text{I})_i - (\text{Cl}_2)_i - K$; the K values of Table II were used. It was assumed that the iodobenzene concentration did not change significantly from its initial value in making these calculations. On the average the plots of the data according to equation 7 were linear to over two-thirds completion of reaction.

A summary of these runs is presented in Table III. Values of $k_2/(\text{ICl})^2$ for runs in which the iodobenzene concentrations were 0.123 M or greater are relatively constant for a series of runs in which the initial reactant and catalyst concentration varied appreciably. In other words the dichloride formation reaction appears to be second order with respect to the catalyst ($x = 2$ in equations 5 and 6).

At 25.0° the values of $k_2/(\text{ICl})^2$ increase as the iodobenzene concentration falls to low levels, but at 45.4° the reverse effect is observed. The increase at 25.0° might be explained on the assump-

TABLE III

THE RATES RUNS ON THE REACTION TO FORM DICHLORIDE

$(\varphi\text{I})_i$, moles/l.	$10^3(\text{Cl}_2)_i$, moles/l.	$10^3(\text{ICl})_i$, moles/l.	$k_2/(\text{ICl})^2$, sec. ⁻¹ l. ² mole ⁻³
$t = 25.0^\circ$			
0.493	6.49	2.92	164
.493	6.37	2.78	149
.493	6.6	1.51	162
.493	6.30	1.51	168
.493	6.57	0.743	152
.243	6.5	5.87	133
.243	6.47	2.78	156
.243	3.11	2.78	157
.243	1.40	2.78	166
.247	6.30	1.51	173
.123	6.30	3.02	160
.053	6.89	5.83	196
.049	6.87	5.21	181
.243	7.24	2.51	233 ^a
.0247	6.30	5.21	226
$t = 45.4^\circ$			
0.480	5.5	2.94	101
.480	5.65	1.47	127
.0482	6.15	5.86	90
.0240	6.15	5.86	98

^a The solvent in this run was equilibrated with water.

tion that as the iodobenzene concentration is lowered, less iodine monochloride is bound in the form of the molecular complex, $\text{C}_6\text{H}_5\text{I}\cdot\text{ICl}$. If only iodine monochloride, which was not associated with iodobenzene, functioned as a catalyst, the values of $k_2/(\text{ICl})^2$ reported in Table III should vary inversely with the term $[1 + K_c(\varphi\text{I})]^2$ where K_c is the equilibrium constant for the complex formation.¹³ Actually K_c is large enough (see Experimental section) both at 25.0 and 45.4° so that a significant depression in the observed rate constants with increasing iodobenzene concentration might be expected to result. The fact that such a depression does not occur as the iodobenzene concentration is increased beyond 0.12 M at 25° might stem from a compensating enhancement of the rate because of the increase in medium polarity. At 45.4° the medium polarity effect may increase in importance, since K_c values are lower at this temperature than at 25.0°. The reaction rate does appear to be somewhat sensitive to polar additives since the $k_2/(\text{ICl})^2$ value increased appreciably when water-equilibrated carbon tetrachloride was substituted for the dried solvent (see Table III).

No entirely consistent explanation of the iodobenzene effects on reaction rates, as described previously or subsequently, can be offered. In the discussion which follows these effects are treated empirically.

The Kinetics of Dichloride Dissociation.—A series of runs were made in which the decreases in optical density of solutions of varying initial concentrations of iodobenzene dichloride and iodine monochloride were followed spectrophotometrically at 380 $m\mu$. The dichloride concentration during the runs was again calculated using equation 2. Rate constants k_1 were calculated from the slopes of lines obtained by plotting the left-hand term of

(18) A similar case is treated in detail in ref. 16b.

equation 8 (in which A_0 , A_e and A represent, respectively, the dichloride concentration at initiation, at equilibrium and at time t) as a function of time.¹¹ In calculating k_1 values for runs in which

$$\ln \frac{A_0^2 - A_e A}{(A - A_e) A_0} = k_1 \frac{(A_0 + A_e)}{(A_0 - A_e)} t \quad (8)$$

iodobenzene was initially present and remained approximately constant in concentration during the reactions, equation 9 was similarly employed as the integral rate law.¹⁹

$$\ln [(cA_0 - \gamma)/(cA - \gamma)] = ck_1 t \quad (9)$$

In this equation $c = 1 + (\varphi I)/K$ and $\gamma = (\varphi I)(\varphi ICl_2)_i/K$. On the average the data when treated graphically according to equations 8 or 9, using the K values of Table II, conformed to straight lines to better than 80% of completion of the reactions.

The values of $k_1/(ICl)_i^2$ which were thus obtained are summarized in Table IV. The experimental constants reported for reactions at 25.0° in the absence of iodobenzene vary somewhat with the iodine monochloride concentration. However the general agreement is sufficiently good to support the argument that the equilibration rate shows second-order dependence on the catalyst concentration. Some depression in the rate constants seems to result as iodobenzene is added to the medium. Actually the observed depression is somewhat larger than would be expected if it were due entirely to reduction of the effective catalyst concentration through complex formation with iodobenzene.

TABLE IV

THE RATE RUNS ON DICHLORIDE DISSOCIATION			
$10^3(\varphi ICl_2)_i$, moles/l.	$10^3(ICl)_i$, moles/l.	$10^3(\varphi I)_i$, moles/l.	$k_1/(ICl)_i^2$, sec. ⁻¹ l. ² mole ⁻²
$t = 25.0^\circ$			
9.30	9.55	..	8.0
4.65	9.55	..	9.4
2.33	9.55	..	10.1
8.85	4.52	..	7.7
4.42	4.52	..	6.7
2.21	4.52	..	6.2
4.51	5.92	24.7	5.3 ^a
4.45	5.83	53.0	4.1
$t = 45.4^\circ$			
8.95	8.56	..	8.3
8.95	4.27	..	7.3
4.47	5.86	24.0	7.0
4.47	5.08	53.0	6.5

^a This same value was obtained from a duplicate run.

The Activation Energies.—The heat of dissociation of iodobenzene dichloride is related to the activation energies of the dissociation and association reactions (E_d and E_f) by equation 10.

$$\Delta H^\circ = E_d - E_f \quad (10)$$

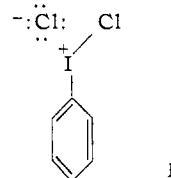
Values of E_d have been calculated from the constants $k_1/(ICl)_i^2$, earlier defined as k_d , at 25.0 and 45.4° for runs of the same iodobenzene concentration (Table IV). The average rate constants for runs with no iodobenzene present initially lead to an E_d value of ca. 0 kcal./mole, while the con-

stants for runs at 0.024 and 0.053 M iodobenzene, respectively, give E_d values of 2 and 4 kcal./mole. Since the rate constants on which these figures are based are rather sensitive to the choice of K values used in their calculation, it is uncertain whether the variations in the calculated E_d values are significant.

The E_f values calculated from the constants, $k_2/(ICl)_i^2$, earlier defined as k_f , at 25.0° and 45.4° are of the order of -3.2 ± 1.0 kcal./mole for runs (Table IV) at 0.49 M iodobenzene. For runs at 0.024 and 0.053 M iodobenzene, respectively, these activation energies are -8 and -7 kcal./mole.

If the values of E_d and E_f for runs at low iodobenzene concentration are used, a value of $\Delta H^\circ = 10$ to 11 kcal./mole can be calculated. This is in good agreement with the figure calculated from the equilibrium constants obtained by direct measurement of equilibrium concentrations of the reactants at low iodobenzene concentrations (Table II).

Very low or negative activation energies are generally observed for high order reactions of halogens in non-polar solvents.²⁰ Certainly the rate-determining steps of these reactions are not high in molecularity. They must be preceded by interactions of the participating substances. The interaction products can be visualized as loose molecular complexes which are thermally unstable, and this instability is reflected in the apparent activation energy which is calculated. In the present case, for example, the rate-determining step in formation of the dichloride might involve a complex of chlorine and iodobenzene and a dimer of iodine monochloride. The activated complex for formation of the dichloride in acetic acid has been described¹¹ by the structure I, which is understood to be solvated. In carbon tetrachloride an iodine monochloride dimer might well fill the role played



by acetic acid. That is it may be incorporated in the activated complex to provide a local polar environment not furnished by the solvent itself.

The Ratios of Forward and Reverse Rate Constants.—Because of the effect of iodobenzene on the rate constants, equilibrium constants K for dichloride dissociation can be calculated from rate constant ratios only in those few cases in which the forward and reverse reactions were measured at the same halobenzene concentrations. The k_d/k_f ratios at 25° for runs at 0.025 and 0.05 M iodobenzene are, respectively, 0.023 and 0.022; at 45° the corresponding k_d/k_f ratios are 0.071 and 0.072. These figures are in good agreement with the K values of Table II. It has been assumed in the calculation of rate constants that the K values (as based on equilibrium concentrations of the reactants) are insensitive to changes in iodobenzene concentration. This assumption seems reasonably

(19) See A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 172.

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

justified since the effects of iodobenzene on the reaction rates probably are reflected to the same degree in the rate constant for the forward and reverse reactions.

The Effects of Medium Polarity on Dichloride Dissociation.—If photochemical processes are omitted from consideration, it now seems clear that the dissociation of iodobenzene dichloride in a non-polar medium requires a polar catalyst. The arguments outlined in the introduction which suggest that the dichloride does not liberate free chlorine as an intermediate when it reacts with unsaturates to form their dihalides are thus strongly supported. It is particularly significant that not only Barton and Miller⁴ but also Cristol, Stermitz and Ramey¹ found that when moisture was in-

cluded in the medium in such reactions, the geometric configuration of the addition product shifted toward that obtained when free chlorine rather than the dichloride was used as the halogen source. Although the results of the present investigation indicate that water alone will not promote dichloride dissociation, it is entirely conceivable that traces of hydrogen chloride were present in the chloroform solvent used in these reactions. It is also possible that water functions without a co-catalyst in chloroform.

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DAVIS, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Proton Magnetic Shieldings in the Haloalkanes

BY AKSEL A. BOTHNER-BY AND C. NAAR-COLIN

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The failure of the classical theory to account quantitatively for the dependence of proton magnetic resonance line position on sample bulk susceptibility is explained in terms of induced molecular magnetic anisotropy in the medium. Methods for obtaining relative intramolecular shielding constants are discussed. Relative shielding constants for protons in a number of haloalkanes are presented. Some of the factors contributing to shielding in the haloalkanes are discussed, and a correlation with molecular electric dipole moment is noted.

Introduction.—Nuclear magnetic resonance (hereinafter n.m.r.) spectroscopy has shown itself to be a powerful tool in the solution of qualitative analytical problems in organic chemistry, as in diverse other fields. One of the pressing problems in the application of this technique is the elaboration of a method for dissecting the intramolecular chemical shielding (as it would be measured in a single molecule) from the other influences affecting n.m.r. line position, such as volume susceptibility, sample shape and orientation, solvent magnetic anisotropy and chemical association. A theory permitting the complete separation of these effects would be of great value in the application of n.m.r. as an analytical tool. It would also facilitate further development of the theory of proton shielding in organic molecules.¹⁻³

Previous measurements on haloalkanes have indicated the existence of important correlations between structure and line position. The pioneering work of Meyer and Gutowsky⁴ established a trend toward less proton shielding as the number of halogens on the carbon bearing the proton is increased. Measurements made by Shoolery and Dailey⁵ indicate that the protons of methyl halides as well as the protons in the α -position of the ethyl halides are progressively less shielded in the series iodide-bromide-chloride. These findings suggested a close connection between electronegativity and proton

shielding,⁵ which if preserved throughout the range of organic compounds would greatly simplify the interpretation of proton magnetic resonance spectra.

Binary mixtures of alkyl halides and/or saturated hydrocarbons show quite "regular" solution behavior with respect to solvent susceptibility corrections.⁶ This "regular" behavior makes possible a reasonably accurate estimation of true intramolecular shielding constants. Even in this case solvent interaction is not negligible; however, the uncertainties in the shieldings are small compared to the shielding differences themselves so that a true order of shieldings may be obtained.

Interaction in Solution and Standardization of Spectra.—In the absence of chemical association, binary mixtures of simple aliphatic compounds exhibit proton magnetic resonance lines, the positions of which are predictable on the basis of the expression⁷

$$\mathcal{H} = (1 - \sigma_i)\mathcal{H}_i^0(1 - \alpha\kappa) \quad (1)$$

where \mathcal{H} is the resonant field for protons at the frequency employed, σ_i is the intramolecular shielding factor for the i th proton, \mathcal{H}_i^0 is the field which must be applied externally to the sample in order to excite resonance in the i th proton, α is a constant dependent on the sample shape, and κ is the volume susceptibility of the liquid. The constant α has values ranging from 2.3 to 3.0 for a variety of binary mixtures of non-polar liquids in cylindrical sample tubes oriented transversely to the field.⁶ The classically calculated value of α for this geometry is

(6) A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **26**, 1647 (1957), and unpublished work.

(7) E. R. Andrew, "Nuclear Magnetic Resonance," Cambridge University Press, 1956, p. 78.

(1) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950); **86**, 243 (1956).
 (2) J. A. Pople, *J. Chem. Phys.*, **26**, 1111 (1956); *Proc. Roy. Soc. (London)*, **A236**, 515 (1956); **A239**, 541, 550 (1957).
 (3) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).
 (4) L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953).
 (5) J. N. Shoolery and B. P. Dailey, *THIS JOURNAL*, **77**, 3977 (1953).