Elution of the chromatographic column with methanol gave a mixture of alcohols (4.0 g.) boiling continuously over the range 80–194°. No attempt was made to identify materials in this fraction due to the large number of isomers potentially present.

ATHENS, OHIO

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

Participation by *ortho* Substituents in the Dissociation of Iodobenzene Dichlorides

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

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The dichlorides of 2-iodoacetanilide, 2-iodobenzanilide, 2-iodobenzyl alcohol and 2′-iodobenzanilide, like those of 2-iodobenzoic acid and its methyl ester, equilibrate with their component iodobenzenes and chlorine in acetic acid much more rapidly than do their *para* isomers. It is suggested that the substituents *ortho* to the iodine atom in these dichlorides promote the reaction through a neighboring group type participation which involves electron release to the iodine atom. The *o*-$OCOCH_3$, *o*-$OCOC_6H_5$ and *o*-COCl groups, which are closely related structurally to those substituents that so strongly enhance the reactivity of iodobenzene dichloride, are ineffective as *ortho* participants in this reaction.

Recently a number of cases have been reported of reactions at an aromatic side chain which are subject to intense acceleration when certain *ortho* substituents are present.[1–4] Presumably these substituents, through participation as neighboring groups, substantially reduce the activation energy required for reaction. This interpretation has been applied in explaining the observation that carboxyl and carbomethoxy groups in *ortho*, but not in *para*, positions very sharply enhance the rate of equilibration of iodobenzene dichloride with its components in acetic acid.[5] It has been suggested, from what is known of the influence of various solvents on the kinetics of the dichloride equilibration process, that the iodine atom is positively polarized in the activated complex.[6] An *o*-carboxyl (or carbomethoxy) substituent apparently is favorably located so that it can facilitate the activation process by donating electrons to the neighboring iodine. For reasons outlined previously it seems unlikely that the bulk of the *o*-substituent can be an important rate-influencing factor in this type of reaction.[7]

If the proposed explanation for the carboxyl and carbomethoxy effects is correct, it may be anticipated that other appropriately located substituents with nucleophilic properties may also increase the reactivity of iodobenzene dichloride. As a result of this investigation, in which the equilibration rates of a number of likely *o*-substituted dichlorides and their *p*-isomers have been studied. four additional participating substituents can be reported.

Experimental

Materials.—The solvents were purified as described previously.[5–7] Except as specified all substituted iodobenzenes which were used were from Eastman Organic Chemicals.

The 2-iodoacetanilide, m.p. 109–111°, was prepared from the free amine and acetic anhydride and recrystallized from water. The 2-iodobenzanilide, m.p. 137–139°, and 4-iodobenzanilide, m.p. 217–219°, were prepared by the Schotten–Baumann method and recrystallized from ethanol. Samples of 2′-iodobenzanilide, m.p. 142–143°, and 4′-iodobenzanilide, m.p. 212–213°, were prepared from 2- and 4-iodobenzoyl chlorides and aniline and were recrystallized from ethanol.[8]

The benzoates of 2- and 4-iodophenol[9] were prepared by standard techniques[10,11] and were recrystallized from methanol. Their respective melting points were 36° and 118–120°. The acetates of 2- and 4-iodophenol were prepared as described previously.[10,12] The latter melted at 29–30°. The former, b.p. 110° (22 mm.), contained a trace of 2-iodophenol as indicated by a faint positive ferric chloride test and by the presence in its infrared spectrum of a band at 2.85 μ (OH stretch) as well as a band at 5.62 μ (which is characteristic of the ester).

The 2- and 4-iodobenzyl alcohols were prepared by lithium aluminum hydride reduction of the iodobenzoic acids by essentially the same procedure which has been used in preparing *o*-chlorobenzyl alcohol.[13] The crude products were recrystallized from water. The melting points[14] of the *o*- and *p*-isomers were, respectively, 87–89° and 72–74°.

Samples of 4-iodobenzoyl chloride,[15] m.p. 71–72°, and of 2-iodobenzamide,[8] m.p. 183–186°, were prepared as described previously.

The dichlorides were precipitated by adding chlorine to 0.1–0.2-g. samples of the substituted iodobenzene in 5 ml. of the appropriate solvent. In most cases acetic acid was used as the solvent, but in a few instances (because the iodobenzene was insoluble or the dichloride was extensively soluble) other media were used. Carbon tetrachloride was employed in preparing the derivatives of 2-iodophenyl benzoate, 2-iodophenyl acetate, and 2- and 4-iodobenzoyl chlorides. An equal volume mixture of chloroform and carbon tetrachloride was used in preparing the dichloride of 2-iodobenzanilide, and the derivative of 2′-iodobenzanilide was precipitated from an equal volume mixture of acetic acid and carbon tetrachloride. Chloroform was used in preparing the iodobenzyl alcohol dichlorides.

The yellow precipitates were filtered, washed with carbon tetrachloride and air-dried for a short time. The iodometric equivalent weights were determined as described previ-

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[8] The general preparative methods and comparative melting points are given by S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1953.

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ously.[5-7] The dichloride of 2-iodophenyl acetate was sufficiently unstable when dry so that it could not be weighed accurately enough to be analyzed. The samples of 2′- and 4′-iodobenzanilide dichlorides had high experimental equivalent weights, probably because of the complication of chlorination of the iodine free rings in drying or preparative processes.

The melting points, equivalent weights and pertinent information on the ultraviolet spectra of the various dichlorides are summarized in Table I.

TABLE I

PROPERTIES OF THE SUBSTITUTED IODOBENZENE DICHLORIDES

Substituent	M.p., °C.	Equiv. wt.[a]	Spectrum[b]		
			λ, mμ	ϵ_{ArI}	ϵ_{ArICl_2}
2-CH_2CH_3	87 d.	149(151.5)	375	0.08	102
2-$NHCOCH_3$	95–97 d.	173(166)	370	.34	305
2-$OCOC_6H_5$	96–99 d.[c]	199(197.5)	380	.17	82
4-$OCOC_6H_5$	130 d.[d]	194(197.5)	380	.01	172
2-$OCOCH_3$	Unstable[e]	....	410	.1	75.7
4-$OCOCH_3$	101–102 d.[f]	173.5(166)	390	.08	82.6
2-$NHCOC_6H_5$	76–77 d.	203(197)	380	.37	294
2-$CONHC_6H_5$	129–145 d.[g]	Impure	380	.2	...
4-$CONHC_6H_5$	139–140 d.	232(197)	370	1.65	...
2-$CONH_2$	130–164 d.[g]	155(159)	..	..	...
2-CH_2OH	77–89[g]	151.5(152.5)	370	.72	130
4-CH_2OH	98–100	157(152.5)	390	.23	87.0
2-COCl	92–93 d.	173(168.7)	380[h]	4.6	89.5
4-COCl	86–88 d.	175(168.7)	390[h]	0.46	58.6
2-$COOCH_3$	[i]	[i]	380[h]	.15	103
4-$COOCH_3$	[i]	[i]	380[h]	.45	95.4

[a] Theoretical values are given in parentheses. [b] Acetic acid was the solvent unless it is otherwise specified. [c] Ref. 10 reports m.p. 98–101°. [d] Ref. 12 reports m.p. 132–133°. [e] Ref. 10 reports the dichloride to be unstable but lists its m.p. as 92–93°. [f] Ref. 12 reports m.p. 116°. [g] The m.p. was not well defined. [h] The solvent was nitromethane. [i] See ref. 5.

The Kinetic Studies.—The spectrophotometric procedures for investigating the rates of equilibration of the dichlorides with their components and for determining the equilibrium constants for the dissociation processes have been described in detail elsewhere.[5-7] The extinction coefficients for the dichlorides which are reported in Table I were in most cases calculated from the optical densities of their freshly prepared solutions. An excess of the appropriate iodobenzene was added to repress dichloride dissociation in those instances in which it occurred rapidly.

Because of the instability of the dry dichloride of 2-iodophenyl acetate, its solutions in acetic acid (for rate work) were prepared using freshly prepared material which was still slightly wet with the carbon tetrachloride with which it had been washed. The dichloride content of these solutions was determined iodometrically.

The dichlorides of 2- and 4-iodophenol were also found to be extremely unstable in the dry state, as has been observed before.[10,12] An attempt was made to measure the equilibration rate of the *o*-substituted compound in acetic acid using an undried sample of freshly prepared material (as was done with 2-iodophenyl acetate dichloride). However ring chlorination occurred so extensively, as evidenced by the drop in total chlorine content of the reaction mixtures, that the desired equilibrium and rate constants could not be obtained.

Since pure samples of the dichlorides of 2′- and 4′-iodobenzanilides were not obtained, the equilibration process was investigated by following changes with time in the absorption spectra of freshly prepared solutions of the free iodo compounds and chlorine in acetic acid. Twenty-five seconds after its preparation a solution (at 25.0°) which initially was 6.7 × 10^{-3} *M* in chlorine and 6.5 × 10^{-3} *M* in 2′-iodobenzanilide (measured in a 1-cm. absorption cell) had an optical density of 0.500. The absorption attributable to the two initial reactants (in the free state) at this wave length is only 0.082. This reading increased to 0.510 at 65 seconds and then began to diminish with time, undoubtedly because chlorination of the non-iodinated aromatic ring of the anilide was occurring. The very high initial reading must be explained on the assumption that a substantial fraction of the free iodo compound was very rapidly converted to the dichloride. This experiment was repeated. Eighty seconds after preparation of the solution, one-third of it was withdrawn from the absorption cell and replaced by an equal volume of 0.37 *M* durene. Thirty seconds later the optical density reading of the resultant solution was 0.020. It must therefore be concluded that dissociation of 2′-iodobenzanilide dichloride occurs very rapidly in acetic acid, since durene destroys free chlorine rapidly but does not react directly with iodobenzene dichlorides.[5-7]

In a similar experiment it was found that the initial optical density of an acetic acid solution which was 4.8 × 10^{-3} *M* in chlorine and 5.3 × 10^{-3} *M* in 4′-iodobenzanilide was 0.115 (28 seconds after preparation) at 370 mμ. The anticipated reading based on the extinction coefficients of the pure components, assuming that no dichloride was formed, was 0.113. The reading did not increase but actually diminished with time as chlorine was consumed, presumably in a ring halogenation process. In other words, formation of the iodobenzene dichloride appeared to be a much slower process than was the case with 2′-iodobenzanilide.

The dichlorides of 4-iodobenzanilide and of 2-iodobenzamide were prepared but both of them were not soluble enough in acetic acid to permit studies of their equilibration rates.

Results

Equilibrium constants for equilibration of the various substituted iodobenzene dichlorides with their components (equation 1) and rate constants k_1 for the dissociation processes are listed in Table II, which summarizes the kinetic studies. In

$$ArICl_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ArI + Cl_2 \quad K = \frac{k_1}{k_2} = \frac{(ArI)(Cl_2)}{(ArICl_2)} \quad (1)$$

most instances the dissociations occurred at easily measurable rates. However in a few cases, notably in the dissociation of the derivatives of 2-iodoacetanilide, 2-iodobenzyl alcohol and 2-iodobenzanilide in acetic acid and of methyl 2-iodobenzoate dichloride in nitromethane, equilibrium was attained in the short interval between preparation of the solutions of the dichlorides and the initial spectrophotometric measurements. Crude estimates of k_1 for most of these highly reactive dichlorides were obtained by making a rapid series of spectrophotometric measurements of dichloride solutions which contained durene in large excess. Under these conditions free chlorine is removed instantaneously, for practical purposes, by reaction with durene.[5-7] Therefore k_1 may be evaluated, on the basis of changes in the optical density, D, of the reaction mixture, using the rate law

$$-\mathrm{d}D/\mathrm{d}t = -\mathrm{d}(ArICl_2)/\mathrm{d}t = k_1(ArICl_2) \quad (2)$$

Because of the fast rates only the terminal phases of the reactions with durene could be followed.

In the absence of participating *ortho* groups k_1 values for typical ring-substituted iodobenzene dichlorides are not markedly influenced by the nature or position of the substituents and range[6,7] from about 1 × 10^{-4} to 5 × 10^{-4} sec.$^{-1}$ at 25° in acetic acid. However the k_1 value for 2-iodoacetanilide dichloride is approximately one hundred times that for 4-iodoacetanilide dichloride, which is normal in its reactivity.

The dissociation rate constant for the dichloride of 2-iodobenzyl alcohol is about sixty times that for the 4-iodobenzyl alcohol derivative. The high reactivity of the *o*-isomer can scarcely be ascribed to steric influences of the hydroxymethyl group since its dimensions are similar to those of an ethyl

TABLE II

EQUILIBRIUM AND RATE CONSTANTS FOR THE DISSOCIATION OF SUBSTITUTED IODOBENZENE DICHLORIDES IN ACETIC ACID AND NITROMETHANE[a]

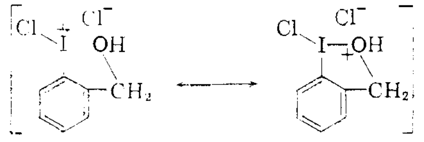
$10^3(\text{ArICl}_2)$, moles/l.	10^3K, mole/l.	10^4k_1, sec.$^{-1}$	$10^3(\text{ArICl}_2)$, moles/l.	10^3K, moles/l.	10^4k_1, sec.$^{-1}$
Acetic acid solvent					
	2-CH$_2$CH$_3$, 25.0°			2-NHCOCH$_3$, 25.0°	
10.38	1.4	1.60	3.83	16.8	
6.84	1.2	1.50	2.18	17.1	
3.38	1.0	1.51	1.22	16.2	
Av.	1.2 ± 0.1	1.54 ± 0.04	0.68	15.7	
			.35	17.3	390
			6.28[b]		320
	4-NHCOCH$_3$, 25.2°		2.09[b]		
	1.06 ± 0.11	3.8 ± 0.06[d]	Av.	16.8 ± 0.8[c]	
	4-CH$_2$OH, 25.0°			2-CH$_2$OH, 25.0°	
11.37	1.59	2.52	13.58	3.50	
7.54	1.55	2.24	7.25	3.27	
3.80	1.45	2.36	3.57	3.25	
Av.	1.53 ± 0.05	2.34 ± 0.10	10.06[b]	...	130
			Av.	3.29 ± 0.13[e]	
	4-OCOCH$_3$, 25.0°			2-OCOCH$_3$	
9.77	3.0	1.95	15.86	4.6	5.9[f]
6.45	2.9	1.91	10.58	4.2	6.1[f]
3.18	2.5	1.96	5.29	4.0	6.1[f]
Av.	2.8 ± 0.2	1.94 ± 0.2	Av.	4.3 ± 0.2	6.0
	4-OCOC$_6$H, 25.0°			2-OCOC$_6$H$_5$, 25.0°	
6.70	2.88	1.85	8.54	22.2	2.26
4.54	2.98	1.84	5.71	15.3	2.30
2.24	2.82	1.79	2.83	16.9	2.14
Av.	2.89 ± 0.06	1.83 ± 0.02	Av.	18.1 ± 2.7	2.23 ± 0.06
	2-NHCOC$_6$H$_5$, 25.0°			2-NHCOCH$_3$, 45.2°	
8.59	13.6		1.94	41.1	
5.86	14.2		1.01	38.8	
3.14[g]	13.7		Av.	40 ± 2[h]	
6.28[b]		370			
Av.	13.8 ± 0.2			2-CH$_2$OH, 45.2°	
	4-OCOC$_6$H$_5$, 45.2°				
8.18	7.2	13.0	13.30	7.8	
5.46	7.4	13.9	8.82	7.8	
2.73	7.6	13.9	4.34	7.4	
Av.	7.4 ± 0.1	13.6 ± 0.4	Av.	7.7 ± 0.2	
				2-OCOC$_6$H$_5$, 45.2°	
			14.23	49.8	15.8
			9.40	48.0	15.6
			4.69	...	16.8
			Av.	49	16.1 ± 0.5
Nitromethane solvent					
	4-COOCH$_3$, 25.0°			2-COOCH$_3$, 25.0°	
10.32	3.9	5.9	10.30	1.6	High
6.82	3.5	6.4	6.81	1.2	
3.35	3.3	6.7	3.38	1.1	
Av.	3.6 ± 0.2	6.3 ± 0.3	Av.	1.3 ± 0.2	
	4-COCl, 25.0°			2-COCl, 25.0°	
12.2	14.9	16.8	11.50	8.5	14.5
8.06	14.6	18.1	7.71	8.7	14.6
			3.80	8.9	16.6
			Av.	8.7 ± 0.1	15.2 ± 0.9

[a] The various iodobenzene dichlorides are identified by the substituents *ortho* or *para* to the ICl$_2$ group. [b] Durene (0.124 *M*) was present in these runs. The reported k_1-values are of very limited accuracy because of the rapidity of the reactions. [c] Based on twelve values. [d] From ref. 6*a*. [e] Based on six values. [f] Approximate values based on the initial rate for dichloride dissociation neglecting the reverse reaction. This procedure was used since some chlorine was lost, through aromatic substitution, in the later stages of the reaction. [g] Excess free iodo compound (0.025 *M*) was present. [h] Based on four values.

group, and 2-ethyliodobenzene dichloride dissociates relatively slowly in acetic acid at 25°. The dichloride of 2-iodobenzanilide also has an exceptionally high dissociation rate constant in acetic acid at 25°. Comparable data for its *p*-isomer could not be obtained because of technical difficulties which are described in the Experimental section. It seems likely, however, that its k_1-value would be similar to that for 4-iodoacetanilide dichloride. Qualitative but convincing evidence is also given in the Experimental section that the dichloride of 2′-iodobenzanilide dissociates much more rapidly than does that of its *p*-isomer.

Actually the dichlorides bearing *o*-$COOCH_3$ and *o*-$CONHC_6H_5$ substituents, unlike the other fast reacting *o*-substituted compounds, are even too reactive to permit the determination of their k_1-values by the method of adding durene to the reaction mixtures. An attempt was made to obtain a semi-quantitative estimate of the dissociation rate of methyl 2-iodobenzoate dichloride by following its formation in a solution (acetic acid, 25.0°) originally 6.52×10^{-3} *M* in the free iodo compound and $6.29 \times 10^{-3}M$ in chlorine. The reaction was, however, immeasurably fast. The *K*-value, 2.92×10^{-3} mole/l., calculated from equilibrium concentrations was in good agreement with that, 2.68×10^{-3} mole/l., previously obtained by using the dichloride as starting material.

In addition to the *o*-$COOCH_3$ and *o*-COOH groups,[5] the *o*-CH_2OH, *o*-$NHCOCH_3$, *o*-$NHCOC_6H_5$ and *o*-$CONHC_6H_5$ groups can now be included as substituents which very likely participate as neighboring groups in promoting the equilibration rate for iodobenzene dichloride in acetic acid. Structures I–III, similar to those proposed[5] to account for the *o*-$COOCH_3$ effect, can be written to describe in part the contribution of these substituents to the activated complex for the equilibration reaction.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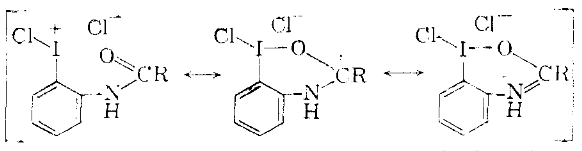
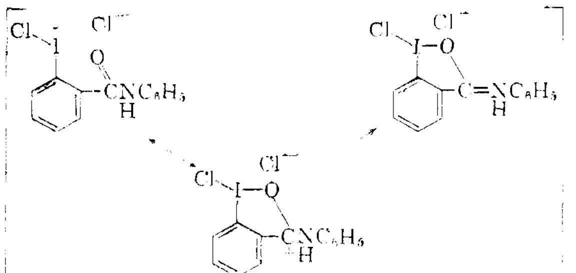

II, R = CH_3 or C_6H_5


III

It has been concluded earlier[7] that in the activated state a perpendicular orientation of the aromatic ring and the plane described by the three halogen atoms of the iodobenzene dichloride molecule is an energetically acceptable or preferred arrangement, and this conclusion may be assumed to apply to structures I–III.

It is interesting to note that in other types of reaction, the oxygen of a hydroxymethyl substituent on the aromatic nucleus (*cf.* structure I) is sufficiently nucleophilic in nature to interact effectively with an electron-deficient substituent at a neighboring position. Thus under the influence of acid, 1,8-bis-(phenylhydroxymethyl)-naphthalene undergoes preferential dehydration to a cyclic ether, presumably through the generation of a carbonium ion in which the positive center coordinates with the oxygen atom rather than with the phenyl group of the neighboring *peri* substituent.[16]

In view of the demonstrated capacity of *o*-acetamido and *o*-benzamido substituents to participate in the iodobenzene dichloride reaction, it is surprising that the dichlorides of 2-iodophenyl acetate and 2-iodophenyl benzoate are comparable in reactivity to their *p*-isomers in acetic acid. A consideration of molecular models reveals no abnormalities in the structures of the dichlorides of the *o*-acetoxy and benzoxy derivatives which would prevent, for geometric reasons, the formation of cyclic activated complexes similar to those shown in structure II.

Two possible explanations can be suggested for the fact that although *o*-NHCOR functions as a neighboring group *o*-OCOR does not. Either the aryl bound oxygen of the acetoxy and benzoxy groups is sufficiently electronegative to reduce the nucleophilic character of the substituents to ineffective levels, or the hydrogen atom bound to nitrogen in the amido substituents is in some way involved in the participation process. In the second explanation it is implied that the hydrogen atoms in question promote the polarization of the I–Cl bond through hydrogen bonding to chlorine. This seems rather improbable since on activation the two chlorine atoms of the dichloride must begin to approach each other and, in so doing, move out of the sphere of influence of the amido hydrogen atoms.

The first suggested explanation is also of dubious acceptability. There is, however, some further indication that *o*-substituents which at first glance appear to be potential "internal nucleophilic catalysts"[3] may be ineffective because they contain a highly electronegative atom. For this reason presumably, the dichloride of 2-iodobenzoyl chloride dissociates at about the same rate as that of 4-iodobenzoyl chloride in nitromethane at 25°. This solvent was chosen, rather than acetic acid, for investigation of *o*- and *p*-COCl effects to avoid the complication of interchange of halogen between the ring substituents and the solvent. To ensure that this change in solvent did not alter significantly the capacity of an *o*-substituent to serve as a neighboring group, the equilibration rates of the

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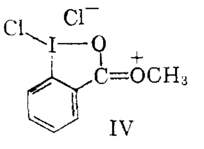
(16) R. T. Letsinger and P. T. Lansbury, This Journal, **81**, 935 (1959).

dichlorides of methyl 2- and 4-iodobenzoate were determined in nitromethane. As in acetic acid the *p*-substituted dichloride dissociated at an easily measurable rate, but its *o*-isomer reached equilibrium with its components too rapidly for kinetic measurements to be made. The methoxyl, like the chlorine of the *o*-COCl group, should have an unfavorable inductive effect on the nucleophilic character of the *o*-$COOCH_3$ group. However this inductive influence may be over-shadowed by the contribution of methoxyl to resonance stabilization of the activated complex (*cf.* structure IV). It is, of course, possible that the methoxyl oxygen itself


IV

may be the nucleophilic center for coördination of *o*-$COOCH_3$ with the iodine atom.

No clear definition of the structural requirements of *o*-substituents for nucleophilic participation in the iodobenzene dichloride equilibration process can as yet be made.[17] Certainly the activation energy required for dissociation must be substantially lowered by those substituents which are effective participants. The activation energy for dichloride formation, in these cases, should also be reduced. As may be expected the k_2-values (equation 1), as well as the k_1-values, for equilibration processes in which the *ortho* effect is observed are (in cases where data are available) substantially larger than those for reactions of the corresponding *p*-isomers. However the *ortho* effects are more noticeably manifested in k_1 than k_2-values. Unfortunately the reactions which are markedly influenced by neighboring groups are sufficiently fast so that it is experimentally impracticable to obtain thermodynamic data for activation processes by the methods of this investigation. A comparison of energies and entropies of activation for the highly reactive *o*-substituted dichlorides and their *p*-isomers would be of considerable value in interpreting the nature of the *o*-substituent effect.

The equilibrium constants at 25.0 and 45.2°, reported in Table II, for the dichlorides of 2-iodoacetanilide and 2-iodobenzyl alcohol were used to calculate the heats and entropies of dissociation. These constants and those for the dichlorides of 2- and 4-iodophenyl benzoates, as well as the entropies and energies of activation for dissociation of the benzoate derivatives, are listed in Table III.

TABLE III

THERMODYNAMIC CONSTANTS FOR DISSOCIATION OF SUBSTITUTED IODOBENZENE DICHLORIDES IN ACETIC ACID

Substituent	$\Delta H°$, kcal./mole	$\Delta S°$, e.u.	E_1, kcal./mole	$-\Delta S_1^{\ddagger}$, e.u.
$\text{2-NH}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{CH}_3$	8.2 ± 0.7	19.4 ± 2.3	....	....
$\text{2-CH}_2\text{OH}$	8.0 ± 0.4	15.4 ± 1.3	....	....
$\text{4-O}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{C}_6\text{H}_5$	8.8 ± 0.2	17.9 ± 0.7	18.8 ± 0.3	14.8 ± 1.0
$\text{2-O}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{C}_6\text{H}_5$	9.3 ± 1.3	23.1 ± 4.4	18.5 ± 0.4	13.2 ± 1.3

In general the thermodynamic constants resemble those found for reactions of other dichlorides in acetic acid, and they are unrevealing so far as the present discussion is concerned.

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[17] From an inspection of molecular models it appears that the *o*-$COOCH_3$ and *o*-$CONHC_6H_5$ groups are ideally constituted structurally for effective participation (see structures III and IV). It is noteworthy that of all the *o*-substituted dichlorides which have been investigated so far those of methyl 2-iodobenzoate and 2′-iodobenzanilide are the most reactive.

[CONTRIBUTION FROM MONSANTO CHEMICAL CO., PLASTICS DIVISION RESEARCH DEPARTMENT]

The Catalytic Effect of Water on the Cyanoethylation of *t*-Carbinamines

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Water and other compounds possessing a labile hydrogen attached to an atom having a pair of electrons available for complex formation are active catalysts for the cyanoethylation of *t*-carbinamines. A mechanism is proposed which involves proton transfer by the "catalyst" as the step terminating the reaction. Steric factors of reactants and "catalysts" as well as solubility characteristics are considered.

Introduction

The cyanoethylation reaction (Michael addition of active hydrogen compounds to the double bond of acrylonitrile) has been widely studied and mechanisms for the reaction with alcohols, amines and ketones have been postulated.[1-8]

Recent work has described yield improvements in cyanoethylation of *t*-carbinamines of highly branched structure by using dilute aqueous acidic catalysts.[8] In this fashion, the yield of the cyanoethylated derivative of *t*-butylamine was increased from about 5 to 89% and the yield, using 1,1,3,3-tetramethylbutylamine, was raised from 0 to 83%. It has now been found that these other supposed

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