the non-ionic mechanism than for the ionic mechanism. It is apparent that the evidence for the ionic nature of this and similar reactions needs careful re-examination.

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Summary

The rates of formation of NH_2Cl, CH_3NHCl and $(CH_3)_2NCl$ from HOCl and the appropriate amine have been studied in dilute aqueous solution under a variety of experimental conditions. The reactions are second order with respect to concentrations of the reactants, but the rates show a marked dependence on the pH of the solution.

The observed variations in rates with pH can be quantitatively accounted for by considering that reaction occurs either between HOCl and NH$_3$, CH_3NH_2 or $(CH_3)_2NH$, or between OCl$^-$ and NH$_4$$^+$, $CH_3NH_3$$^+$ or $(CH_3)_2NH_2$$^+$.

It has been shown mathematically that for reactions of this type, between weakly ionized substances, it is impossible to distinguish kinetically between the mechanism which assumes ions to be the reactants and that which assumes molecules to be the reactants. On this basis the validity of the evidence for the ionic nature of the ammonium cyanate reaction has been questioned.

Evidence has been presented which indicates that the molecular mechanism is more probable for the formation of the chloramines. On this basis the rates of the reactions can be expressed by the equations

$$d[NH_2Cl]/dt = 2.5 \times 10^{10} e^{-2500/RT} [NH_3][HOCl]$$
$$d[CH_3NHCl]/dt = 6.0 \times 10^{13} e^{-4500/RT} [CH_3NH_2][HOCl]$$
$$d[(CH_3)_2NCl]/dt = 1.2 \times 10^{11} e^{-800/RT} [(CH_3)_2NH][HOCl]$$

Electric Polarization of Carboxylic Acids. III. A Study of the Association of Some Additional Carboxylic Acids in Benzene Solution[1]

BY ARTHUR A. MARYOTT,[2] MARCUS E. HOBBS AND PAUL M. GROSS

The association of carboxylic acids in hydrocarbon and certain other organic solvents as well as in the vapor phase has been the subject of numerous investigations by a variety of methods. With regard to association in solution, however, relatively few reliable quantitative data are available. Exceptions are the isopiestic measurements of Wall and co-workers[3,4] on benzoic acid and several other non-volatile acids in benzene. Although the more generally applicable methods involving distribution between water and an immiscible organic solvent has been used on occasion, this procedure is open to question because of the effect of the finite solubility of the water on the association equilibrium in the second medium.[5,6]

In earlier papers from this Laboratory,[7,8] it was shown that measurements of the dielectric constants of very dilute solutions of carboxylic acids in the non-polar solvents, benzene and heptane, could be used to study the association of these acids. Assuming that only monomeric and dimeric forms were present at these low concen-

trations, the data permitted evaluation of the dimer–monomer equilibrium constants as well as the polarizations of the monomeric and dimeric forms. The dipole moments obtained for the monomer were in reasonable agreement with values reported in dioxane where the acids do not associate. In all cases the polarization of the dimer was found to be from 17 to 26 cc. greater than would be expected in view of recent electron diffraction studies[9] which indicated a planar symmetrical structure. Evidence was presented, in particular from measurements on the three monofluorobenzoic acids,[8] in support of the planar configuration, and it was concluded that the anomalous polarization of the dimer was due to an exceptionally high atomic polarization rather than to any dipolar contribution.

In the present investigation, the dielectric constants of dilute benzene solutions of seven additional acids have been measured. These include o-toluic, m-toluic, cinnamic (*trans*), crotonic (*trans*), phenylacetic, β-phenylpropionic and stearic acids. These together with acids previously studied afford a sufficient series to determine whether any systematic correlation exists between the structure of the acid and its tendency to associate.

Experimental

Materials.—Reagent grade, thiophene-free benzene was stored over phosphorus pentoxide for several weeks and

(1) The contents of this paper were presented at the St. Louis meeting of the American Chemical Society, March, 1941.

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(3) F. T. Wall and P. E. Rouse, THIS JOURNAL, **63**, 3002 (1941).

(4) F. T. Wall and F. W. Banes, *ibid.*, **67**, 898 (1945).

(5) R. P. Bell and M. H. M. Arnold, *J. Chem. Soc.*, 1432 (1935).

(6) B. Szyszkowski, *Z. physik. Chem.*, **131**, 175 (1927).

(7) H. A. Pohl, M. E. Hobbs and P. M. Gross, *J. Chem. Phys.*, **9**, 408 (1941).

(8) A. A. Maryott, M. E. Hobbs and P. M. Gross, *ibid.*, **9**, 415 (1941).

(9) L. Pauling and L. O. Brockway, *Proc. Natl. Acad. Sci.*, **20**, 336 (1934); J. Karle and L. O. Brockway, THIS JOURNAL, **66**, 574 (1944).

then distilled over sodium just before use. The distillation was made in an atmosphere of dried nitrogen with a 6-ft. Dufton column.

The carboxylic acids were the "white label" grade from Eastman Kodak Company. Stearic acid was used without further treatment. The remaining acids were recrystallized from benzene or heptane until satisfactory freezing points, observed by the cooling curve method, were obtained. The freezing points were as follows: o-toluic, 103.2°; m-toluic, 110.1–110.4°; cinnamic, 132.4–132.7°; crotonic, 71.4–71.7°; phenylacetic, 76.7–76.9°; β-phenylpropionic, 46.6–46.8°; stearic, 68.3–68.5°.

Equipment and Procedure.—The electrical equipment employing the heterodyne beat principle for the measurement of dielectric constants has been described in a separate publication.[10] The measuring cell, the accessory equipment, and the experimental procedure devised to prevent contamination of the solutions by atmospheric moisture also have been described in detail elsewhere.[11]

Solutions of varying concentrations were made up by the successive additions, directly to the solvent or solution in the cell, of weighed quantities of a concentrated stock solution. Mixing was accomplished by forcing the solution out of the cell and into an attached glass reservoir by means of dried compressed nitrogen. The reservoir was thermostated at the same temperature as the cell to avoid changes in temperature on mixing. This arrangement eliminated the small permanent shift in capacitance, evidently associated with an irreversible effect of temperature on the geometrical capacitance, that accompanied each mixing operation in previous work.

Results

The experimental data are given in Table I. N_2 is the mole fraction of solute based on the monomer molecular weight, $\Delta\epsilon$ is the corresponding difference in dielectric constant between the solution and the solvent and P_2 is the molar polarization calculated for the solute. In each case the data represent two or more independent runs beginning with small additions of solute and making further additions until the highest concentration was reached. In calculating the polarizations, the densities were assumed to be linear functions of the concentration and the proportionality constant, $\Delta d/N_2$, was obtained from one or two of the more concentrated solutions.

The equilibrium constant for the equilibrium, $A_2 = 2A$, and the polarizations of the monomeric and dimeric forms of the acid were obtained from the variation in polarization with concentration. The equilibrium constant, K, is given by

$$K = \frac{2(P_2 - P_d/2)^2 N_2}{(P_s - P_2)(P_s - P_d/2)}$$

where P_s is the polarization of the monomer and P_d the polarization of the dimer. These quantities, evaluated by the method previously described,[7] are listed in the second, third and fourth columns of Table II. The fifth column gives the electronic polarization of the monomer, $P_s(E)$, obtained by summation of the atomic refractivities listed in Landolt–Börnstein "Tabellen," 5th ed. The sixth column gives the sum of atomic and orientation polarizations for the

(10) B. E. Hudson and M. E. Hobbs, *Rev. Sci. Instruments*, **13**, 140 (1942).

(11) H. A. Pohl, M. E. Hobbs and P. M. Gross, *N. Y. Acad. Sci.*, **40**, 389 (1940).

TABLE I

$N_2 \times 10^3$	$\Delta\epsilon \times 10^3$	P_2 (cc.)	$N_2 \times 10^3$	$\Delta\epsilon \times 10^3$	P_{22}(cc.)
Crotonic Acid (*trans*)			1.683	2.482	62.6
0.0962	0.351	80.1	2.165	3.046	61.4
0.2618	0.742	68.1	3.438	4.399	59.6
0.3849	1.026	65.6	4.032	5.050	59.2
1.068	2.242	57.2	6.480	7.448	57.7
1.365	2.752	55.9	9.620	10.45	56.6
3.163	5.464	51.6	$\Delta d/N_2 = 0.349$		
3.388	5.827	51.5	Stearic Acid		
5.953	9.512	49.6	0.0503	0.132	137.4
6.333	9.979	49.3	.0753	.168	132.0
10.55	15.62	47.6	.1706	.306	125.2
15.15	21.73	47.1	.3140	.427	118.9
$\Delta d/N_2 = 0.113$			.5477	.585	114.5
Cinnamic Acid (*trans*)			1.065	.823	110.1
0.0448	0.256	123.1	1.889	1.063	107.0
.0755	.385	114.0	2.395	1.180	105.9
.2230	.917	99.3	3.490	1.370	104.6
.3934	1.444	92.9	4.092	1.450	104.0
.7624	2.497	86.9	8.708	1.777	101.7
1.069	3.297	84.2	$\Delta d/N_2 = -0.044$		
1.084	3.313	83.8	o-Toluic Acid		
2.160	6.043	79.7	0.0788	0.240	81.0
2.444	6.626	78.5	.1199	0.327	76.5
2.486	6.724	78.4	.3408	0.766	69.2
4.420	11.19	76.0	.6620	1.310	65.2
4.569	11.49	75.5	1.862	3.061	60.2
8.620	20.31	73.1	1.905	3.155	60.3
$\Delta d/N_2 = 0.402$			3.257	4.938	58.3
Phenylacetic Acid			4.710	6.726	56.9
0.0851	0.239	77.4	5.639	7.922	56.5
.1533	.392	73.5	6.780	9.264	55.9
.4358	.886	65.8	9.352	12.34	55.2
.6842	1.237	62.4	$\Delta d/N_2 = 0.350$		
1.222	1.944	59.2	m-Toluic Acid		
2.802	3.668	55.0	0.0902	0.357	95.6
3.056	3.938	54.6	.1328	0.500	92.6
5.301	6.197	52.8	.4358	1.225	78.5
6.224	7.015	52.2	.4854	1.354	78.1
.680	10.20	51.0	1.177	2.663	70.3
$\Delta d/N_2 = 0.357$			1.450	3.178	69.3
β-Phenylpropionic Acid			2.711	5.244	65.3
0.0700	0.206	84.5	4.382	7.839	63.2
.1446	.368	78.3	4.958	8.715	62.7
.1855	.457	77.2	6.855	11.49	61.4
.6320	1.163	67.9	9.638	15.45	60.3
.962	1.615	65.6	$\Delta d/N_2 = 0.322$		

dimer, $P_d(A + O) = P_d - 2P_s(E)$, while the dipole moment of the monomer, μ_s, is shown in the last column.

Discussion

The dipole moments of phenylacetic, β-phenylpropionic, and stearic acids are not significantly different from the value of 1.68 reported previously for acetic acid.[7] The moments of the two unsaturated acids, crotonic (2.11) and cinnamic (2.26), are decidedly higher than those of the saturated acids. This increase can be attributed to the induced polarity of the double

TABLE II

CONSTANTS OF ACIDS

Acid	$K \times 10^4$	P_s	P_d	P_s (E)	P_d (A + O)	μ_s
Phenylacetic	2.6	92.6	91.7	37.1	17.5	1.66
β-Phenyl-						
propionic	2.7	96.7	103.1	41.7	19.7	1.65
Crotonic						
(trans)	1.3	113	85.6	21.7	42.2	2.13
Cinnamic						
(trans)	1.5	144	132.8	41.2	50.4	2.26
Stearic	1.7	153	192.9	87.0	18.9	1.80
o-Toluic	2.2	95.1	101.6	37.0	27.6	1.70
	2.70[a]					
m-Toluic	1.8[a]	122	107.5	37.0	33.5	2.05
	1.60					

[a] Data of Wall and Banes[4] converted to mole fraction basis.

bond which should be enhanced by contributions from resonance structure such as

$$\underset{(+)}{\overset{\overset{\displaystyle H}{|}}{R-C}}-\underset{\overset{\displaystyle |}{H}}{C}=C\overset{O^{(-)}}{\underset{O-H}{\diagdown}}$$
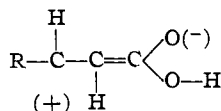
A similar increase in moment has been observed by Wilson and Wenzke[12] for propiolic acid and several other acids having triple bonds.

For phenylacetic, β-phenylpropionic and stearic acids the residual part of the dimer polarization, after elimination of the electronic contribution, is in the range, 16 to 22 cc., previously observed for other acids of the aliphatic series. In these cases $P_d(A + O)$ is apparently attributable entirely to atomic polarization. In o-toluic and m-toluic acids, this term should include, in addition to atomic polarization, a small dipolar contribution from the methyl groups. With free rotation of the phenyl rings about the C_{ar}–C_{al} bond or else equal probability of cis and trans structures for the dimer, one would expect P_d· $(A + O)$ to be about the same for both acids. As this term is about 6 cc. lower for o-toluic acid than for m-toluic acid, it would appear that some definite interaction of the methyl group with the adjacent carboxyl group, probably with the carbonyl oxygen of this group, causes the dimer of o-toluic acid to have a predominately trans structure. The relatively large value of $P_d(A + O)$ for crotonic and cinnamic acids undoubtedly includes, as previously noted, a substantial dipolar contribution associated with the carbon–carbon double bonds. Assuming the atomic polarization to be about 18 cc. in each case, the orientation polarization is 24 cc. for crotonic acid and 32 cc. for cinnamic acid. From these values one calculates 0.95 and 1.10 for the double bond moments in crotonic and cinnamic acids, respectively, provided these moments are directed along the double bonds. By way of comparison, the

(12) C. J. Wilson and H. H. Wenzke, THIS JOURNAL, 57, 1265 (1935).

equivalent double bond moments may also be derived from the moments of the monomers. These latter calculations require assignment of magnitude and direction to the carboxyl group moment. Taking the carboxyl group moment to be the same as the moment of acetic acid and to make an angle of 74° with the C–COOH bond,[13] one calculates 1.04 and 1.27 for these group moments in crotonic and cinnamic acids, respectively, with the negative ends nearest the carboxyl group.[14] In view of the rather tentative nature of the assumptions involved, the agreement between the two sets of data is quite satisfactory and suggests that dipolar resonance structures make a substantial and similar contribution in both the monomer and the dimer.

For two of the acids reported here, namely, o- and m-toluic, independent data on the association constants are available. A comparison of the present values with those obtained by Wall and Banes[4] using the isopiestic method is shown in Table II. In view of the completely unrelated methods of measurement, the agreement between the two sets of data is quite satisfactory.

Including data previously reported, a total of twelve aliphatic and substituted aliphatic acids have been studied. It is of interest to note whether there is any correlation between the structure of the acid and its tendency to associate. Other factors being equal, any substituent which, either by inductive or by resonance effects, tends to draw electrons away from the carboxyl group and thereby makes the effective charge on the oxygens less negative should weaken the hydrogen bonds responsible for the association. Conversely, any structural change tending to make the effective charge on the oxygens more negative should strengthen the association.[15]

The association constants for the various acids listed in Table III do show a systematic variation

TABLE III

DIMER–MONOMER EQUILIBRIUM CONSTANTS AT 30° FOR VARIOUS ALIPHATIC AND SUBSTITUTED ALIPHATIC ACIDS

Acid	$K \times 10^4$
Chloroacetic	8.8
Formic	7.1
Acetic	2.4
Propionic	2.3
Butyric	2.1
Stearic	1.7
Trimethylacetic	1.3
Phenylacetic	2.6
β-Phenylpropionic	2.6
Crotonic (trans)	1.3
Cinnamic (trans)	1.5

(13) M. E. Hobbs and A. J. Weith, THIS JOURNAL, 65, 967 (1943).

(14) The alternative solution leading to values of 1.57 and 1.80 for crotonic and cinnamic acids, respectively, is in poor agreement with the values derived from the dimer and seems unreasonable in that it requires the positive end of the dipole to be nearest the carboxyl group.

(15) M. L. Huggins, J. Org. Chem., 1, 407 (1936).

with structure. In going through the aliphatic series from formic to stearic acid, there is a progressive decrease in the equilibrium constant, or increase in the tendency to associate. Replacement of a hydrogen atom by the more electropositive methyl group produces by far the greatest effect in passing from formic to acetic acid. As expected, trimethylacetic acid, with the three α-methyl groups, shows a greater tendency to associate than do any of the straight chain acids. Electronegative substituents such as the chlorine atom and the phenyl group decrease the tendency to associate. On the other hand, the two unsaturated acids, crotonic and cinnamic, show greater association than the corresponding saturated acids, propionic and β-phenylpropionic. As already mentioned with regard to the dipole moments of these acids, there appears to be substantial bond moment attributable to resonance. This resonance makes the charge on the carbonyl oxygen more negative and thus strengthens the association.
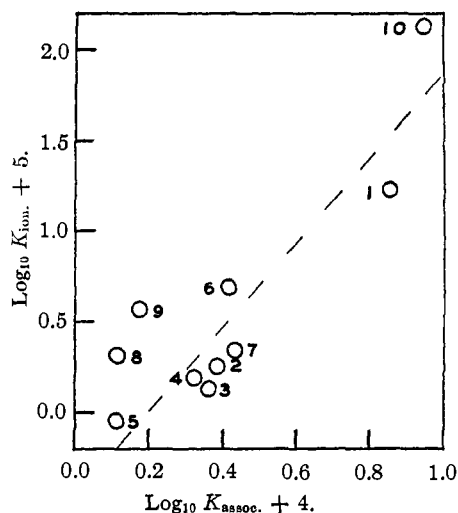

Fig. 1.—Comparison of the ionization and association constants of some acids: 1, formic; 2, acetic; 3, propionic, 4, n-butyric; 5, trimethylacetic; 6, phenylacetic; 7, β-phenylpropionic; 8, trans-crotonic; 9, trans-cinnamic; 10, chloroacetic.

It might be added that there is some correlation between the dimer–monomer equilibrium constants in benzene and the ionization constants of these acids in water. A graphical comparison is shown in Fig. 1 where the logarithm of the ionization constant[16] is plotted as ordinate and the logarithm of the association constant as abscissa. In general, the stronger the acid the less is its tendency to associate. Such a correlation is to be expected insofar as the inductive effect of the substituent is the determining factor. The relationship appears to be roughly linear in some cases with a given structural change having about twice as large an effect on the free energy of ionization as on the free energy of association. On the other hand, chloroacetic acid, although much stronger than formic acid, is only slightly less associated than the latter. Exceptions to the rule are the two unsaturated acids where the situation is complicated by resonance. Both crotonic acid and cinnamic acid are decidedly stronger than the corresponding saturated acids and also more highly associated in benzene.

Summary

The dimer–monomer equilibrium constants and the molar polarization of the monomeric and dimeric forms of o-toluic, m-toluic, phenylacetic, β-phenylpropionic, crotonic, cinnamic and stearic acids in benzene at 30° have been determined from measurements of the dielectric constants of very dilute solutions. In cases where a comparison could be made, the equilibrium constants are in satisfactory agreement with data obtained by a thermodynamic method.

The dipole moments of the two unsaturated acids, crotonic and cinnamic, are enhanced by resonance.

In the aliphatic series including acids previously studied, there appears to be a correlation between the structure of the acid and its tendency to associate, electronegative substituents diminishing and electropositive substituents increasing the extent of association.

(16) J. F. J. Dippy, Chem. Rev., 25, 151 (1939).