[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C.]

Acid–Base Equilibria in Benzene at Three Temperatures. The Comparative Reactivities of a Phenolic Acid and a Carboxylic Acid with Triethylamine and with 1,3-Diphenylguanidine[1]

BY MARION MACLEAN DAVIS AND MAYA PAABO

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Equilibrium constants for the association of the phenolic indicator, bromophthalein magenta E (3′,5′,3″,5″-tetrabromophenolphthalein ethyl ester), with 1,3-diphenylguanidine and with triethylamine in benzene have been determined spectrophotometrically at 20, 25 and 30°, and the association of benzoic acid with the same two bases also has been determined, using bromophthalein magenta E as the indicator. In all four cases the association has been assumed to conform to the equation

$$\text{B (base)} + \text{HA (acid)} \rightleftharpoons \text{BH}^+\ldots\text{A}^- \text{ (hydrogen-bonded ion-pair)}$$

Values of ΔF_{25}, ΔH and ΔS_{25} have been computed. Benzoic acid is found to be a slightly weaker acid than bromophthalein magenta E in terms of either association with diphenylguanidine in benzene or ionic dissociation in water, but with triethylamine as the reference base, it appears to be much weaker than bromophthalein magenta E. In explanation, it is suggested that both oxygens of the benzoate ion are hydrogen bonded to the diphenylguanidinium ion; the resulting structure should have greater stability than triethylammonium benzoate, in which only one of the benzoate oxygens can be hydrogen bonded to the cation. This explanation is considered to have generality; it points to a reasonable explanation for cases in which changing from water to another solvent brings about a reduction of the strengths of carboxylic acids relative to the strengths of phenols. Differences in spectral absorption curves for several salts of bromophthalein magenta E are noted and discussed.

Introduction

As is well known, benzene is very feebly basic compared to water, and its capacity to promote ionization is extremely small. Therefore, to determine relative strengths of acids in benzene one must add some reference base and determine the equilibrium constants for its association with the various acids. In previous work[2] the relative strengths of benzoic acid and thirty-nine substituted benzoic acids in benzene were determined at 25° in terms of association with 1,3-diphenylguanidine. In the method used, the phenolic acid bromophthalein magenta E (3′,3″,5′,5″-tetrabromophenolphthalein ethyl ester), which is an indicator dye, and the benzoic acid compete for the base. All of the acid–base associations are assumed to conform to the general equation[3]

$$\text{B (base)} + \text{HA (acid)} \rightleftharpoons \text{BH}^+\ldots\text{A}^- \quad (1)$$

Since bases of varying structures may show marked differences in behavior with acids when in aprotic solvents,[3] it was advisable for at least part of the measurements to be repeated with a reference base of a different structural type. Also, it appeared feasible to determine the magnitudes of the changes in entropy and enthalpy accompanying such acid–base associations from measurements at 20, 25 and 30°.

This paper reports and compares the results of studies of the association of both diphenylguanidine (P_2G) and triethylamine (Et_3N) with bromophthalein magenta E (BPM-E) and with benzoic acid (BzOH) in benzene solution at the three temperatures mentioned.

Experimental

Materials.—Bromophthalein magenta E, benzoic acid and 1,3-diphenylguanidine were the highly purified materials used in earlier studies, and the benzene was purified as before.[2] Triethylamine of the best commercial grade was refluxed with acetic anhydride and then fractionally distilled from potassium hydroxide twice. A third distillation from potassium hydroxide was performed immediately before use.

Solutions.—The stoichiometric concentration of bromophthalein magenta E usually was 2.5×10^{-5} *M* or 5×10^{-5} *M*, but in some cases several concentrations in the range 10^{-5} *M* to 10^{-4} *M* were used. For the reaction of bromophthalein magenta E with diphenylguanidine, n (moles of base per mole of the indicator acid) was in the range 0.3 to 1.8; with triethylamine as the base, n varied from 0.5 to 10. In mixtures of bromophthalein magenta E, diphenylguanidine and benzoic acid, n varied from 0.5 to 5, and n' (moles of benzoic acid per mole of indicator acid) varied from 0.5 to 16. In analogous mixtures containing triethylamine as the base, n varied from 2 to 5 and n', from 1 to 8. A few data for the association of triethylamine with benzoic acid, obtained with *2,5-dinitrophenol* as the reference indicator acid, are included in Fig. 3 and related discussion. The concentration of 2,5-dinitrophenol was 2×10^{-4} *M*, n varied from 2 to 20, and n', from 1 to 20.

Apparatus and Method.—Absorbance data for specific wave lengths were obtained with a Beckman Model DU quartz photoelectric spectrophotometer, while complete absorption curves were obtained with a Cary recording quartz spectrophotometer (Model 12). Completely independent experiments were performed at 20, 25 and 30°. The laboratory could be automatically maintained at a thermometer reading usually within ±0.5° of the desired values. Absorption cell compartments were thermostated air baths maintained at a thermometer reading constant within ±0.05°. Absorbance readings were made 20 to 30 minutes after the cells were placed in the compartment. Precautions taken to minimize water content of solutions included reboiling the benzene for five to ten minutes, storing stock solutions near anhydrous alumina or silica gel and baking glassware at 110 to 120°. Absorbance measurements were made at 405 and 540 mμ (respectively the approximate absorption maximum of the yellow indicator acid and that of its magenta salt when in benzene solution).[4] The calculated results for the two wave lengths

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[1] Presented at the 135th Meeting of the American Chemical Society at Boston, Massachusetts, April 10, 1959.

[2] M. M. Davis and H. B. Hetzer, *J. Research Natl. Bur. Standards*, **60**, 569 (1958).

[3] See M. M. Davis and P. J. Schuhmann, *ibid.*, **39**, 221 (1947), and following papers. With the low concentrations used in the work, the dimer–monomer equilibrium of the benzoic acid is thought to be the only competing association which may affect accuracy of results, and a correction can be applied for this (see section 4.1 of ref. 2).

were usually in very good agreement (note Figs. 2 and 3 and accompanying captions). Data for 540 mμ (which is thought to be the optimum wave length) were used in final calculations. Values of $K_{\text{assoc.}}$ were calculated as before,[2] except that in associations involving benzoic acid they were corrected, applying dimer-monomer data of Wall and Banes.[5] Throughout the paper association constants are in the units liter mole^{-1}.

Results and Discussion

Absorption Curves.—Figure 1 shows that the main absorption band of the triethylammonium salt of bromophthalein magenta E when in benzene solution is located slightly nearer the infrared than the corresponding band for the diphenylguanidinium salt, while the band characteristic of tetraalkylammonium salts[3] is *much* nearer the infrared. In comparison, the main absorption band for amine oxide salts of bromophthalein magenta in benzene[6] is significantly nearer the ultraviolet region.[7] These variations in absorption indicate that the nature of the cation affects the mobility of anionic electrons, and they furnish one of the strong arguments for making a distinction between salts consisting of ion-pairs and those consisting of *hydrogen-bonded* ion-pairs. In the latter type the cation must be attached to a specific oxygen of the anion and not merely held by coulombic interaction.[3,6,8]

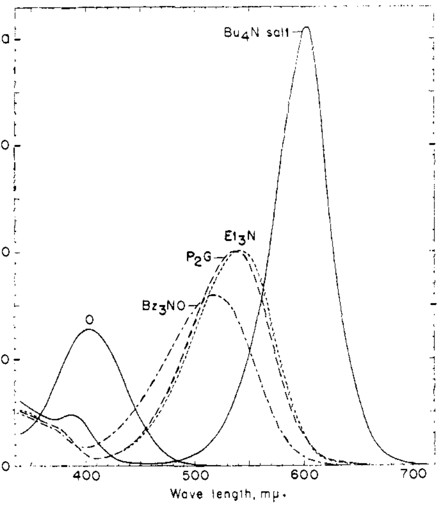

Fig. 1.—Spectral absorption curves for bromophthalein magenta E and several of its salts in benzene solution: O, bromophthalein magenta E without added base; Bz_3NO, P_2G and Et_3N indicate the absorption curves for the salts formed by combination of bromophthalein magenta E with tribenzylamine oxide, 1,3-diphenylguanidine and triethylamine, respectively; Bu_4N salt, curve for the tetra-*n*-butylammonium salt of bromophthalein magenta B (which is the *n*-butyl ester of 3′,5′,3″,5″-tetrabromophenolphthalein).

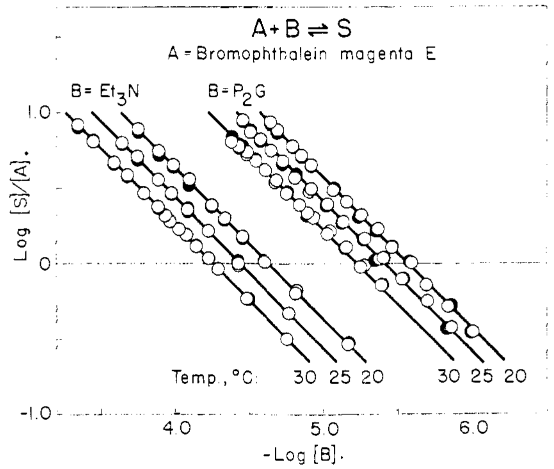

Fig. 2.—Graph constructed from spectral absorbance data and stoichiometric concentrations for mixtures of bromophthalein magenta E with triethylamine or diphenylguanidine in benzene at 30, 25 and 20°. The reaction assumed is addition of acid and base, forming a salt (consisting of hydrogen-bonded ion-pairs). Symbols enclosed in brackets signify equilibrium concentrations of acid, base and salt. The open circles indicate absorbance measurements were made at 540 mμ, and the filled circles indicate supporting data at 405 mμ; in many cases results were the same at both wave lengths.

In the diphenylguanidinium ion, $C_6H_5NHC({=}NH_2)NHC_6H_5^+$, the three nitrogens are not equivalent. Presumably, the 1- and 3-nitrogens are involved in the aniline type of resonance and this opposes the guanidinium type of resonance. The positive charge seems most likely to reside on the $=NH_2$ group. If this assumption is accepted, one may then logically postulate that *both* of the $=NH_2^+$ protons interact with the phenolate oxygen of bromophthalein magenta E,[9] causing enhanced stability of the salt and a slight shift of the spectral absorption toward the ultraviolet.

Association Constants.—The raw data obtained were of the same type as those previously reported.[2] Figs. 2 and 3 show that the results at 405 mμ as well as at 540 mμ are consistent with the 1:1 association postulated, over an extended range of salt to acid ratios. The equilibrium constants obtained are compiled in Table I.[10]

Previously,[2] benzoic acid was found to be *slightly* weaker than bromophthalein magenta in benzene

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[4] The limiting absorption curves were not measurably different at 20, 25 and 30°.

[5] F. T. Wall and F. W. Banes, THIS JOURNAL, **67**, 898 (1945). *For 20, 25 and 30° the* $K_{11}(\times 10^3)$ *values 1.3, 1.6 and 2.0, respectively, were obtained by interpolation. The constant* K_{11} *applies to the reaction* $(C_6H_5COOH)_2 \rightleftharpoons 2C_6H_5COOH$.

[6] M. M. Davis and H. B. Hetzer, *ibid.*, **76**, 4247 (1954).

[7] Using either wave length units or frequency units, values of $\Delta\lambda_{\max}$ for the tetraalkylammonium, triethylammonium and amine oxide salts vary linearly with the reciprocals of the half-band widths. ($\Delta\lambda_{\max.}$ equals $\lambda_{\max.}$ for the salt minus $\lambda_{\max.}$ for the indicator as free acid.)

[8] G. M. Barrow and E. A. Yerger (THIS JOURNAL, **76**, 5211 (1954)) arrived at analogous conclusions about triethylammonium acetate in carbon tetrachloride solution, from infrared spectroscopic data.

[9] E. A. Yerger and G. M. Barrow (*ibid.*, **77**, 4474 (1955)) suggested an analogous structure for diethylammonium acetate in dilute carbon tetrachloride—that is, one with both protons of the diethylammonium ion bonded to one of the carboxylate oxygens.

[10] The attainable precision is better for some K values than for others because: (a) In calculating $K_{\text{assoc.}}$, 1/[B] is deduced from [S]/[A] and the stoichiometry. It is more likely to be in error for K of the order 10^6 than for K of the order 10^4. (b) The less nearly equal the strengths of the two acids competing for a base the lower the attainable precision.

at 25° in terms of association with diphenylguanidine, a conclusion which is in harmony with the relative strengths of the two acids in water in terms of their ionization constants. Similar results were obtained in this work at 20 and 30° (see Table I). However, benzoic acid appears *markedly* weaker than bromophthalein magenta in benzene with triethylamine as the reference base.[11]

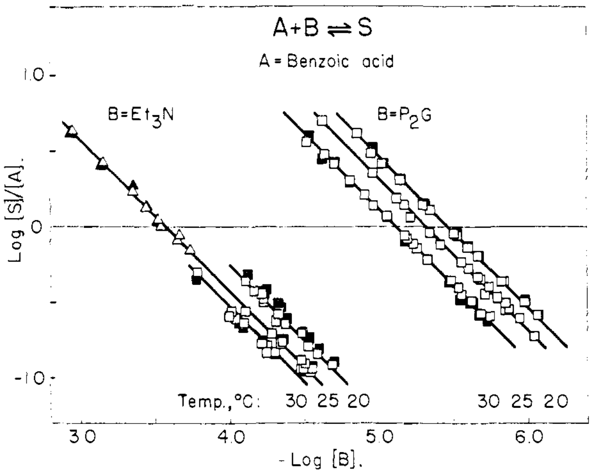


Fig. 3.—Graph constructed from data for the association of benzoic acid with triethylamine or diphenylguanidine in benzene at 30, 25 and 20°. Symbols have the same significance as in Fig. 2. The association was measured indirectly, using an indicator acid; squares indicate experiments in which the indicator acid was bromophthalein magenta E, and triangles, ones in which it was 2,5-dinitrophenol.

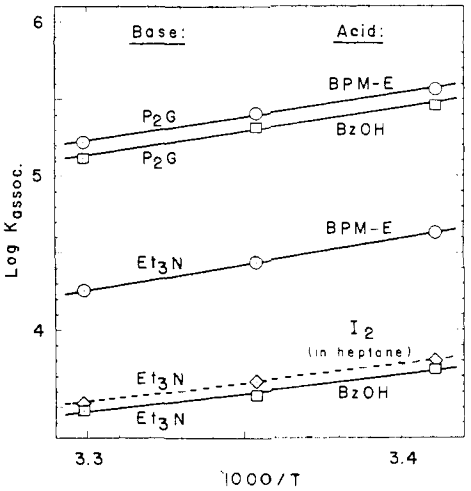
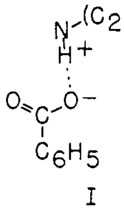


Fig. 4.—Variation of association constants with temperature: P_2G, 1,3-diphenylguanidine; Et_3N, triethylamine; BPM-E, bromophthalein magenta E; BzOH, benzoic acid.



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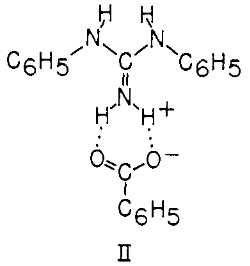

II

In explanation of these observations, it seems possible that in benzene the benzoate ion associates with the triethylammonium ion and with the diphenylguanidinium ion in the differing manners suggested below. Triethylammonium benzoate (I) is considered to consist of hydrogen-bonded ion-pairs in which the cationic proton is attracted to one of the carboxylate oxygens (compare ref. 8). For diphenylguanidine benzoate the symmetrical structure II, stabilized by resonance, is postulated.[12,13] In analogy with hydrated benzoate

TABLE I

EQUILIBRIUM CONSTANTS FOR ACID-BASE ASSOCIATIONS IN BENZENE

Base	Acid	t, °C.	10^{-x} K^a	x	No. expts.	St. dev.	Coeff. var., %
		20	4.26	4	12	0.08	1.9
Et_3N	BPM-E	25	2.74	4	10	.05	1.7
		30	1.80	4	19	.02	1.1
		20	5.58	3	13	.37	6.6
Et_3N	BzOH	25	3.76^b	3	12	.23	6.0
		30	3.00	3	17	.20	6.6
		20	3.68	5	14	.13	3.4
P_2G	BPM-E	25	2.57	5	24	.11	4.3
		30	1.66	5	28	.07	4.3
		20	2.90	5	14	.09	3.0
P_2G	BzOH	25	2.09	5	20	.10	4.6
		30	1.31	5	20	.07	5.1

[a] The values of $10^{-x}K$ were used without rounding off in calculating thermodynamic constants given in Table II. [b] M. M. Davis and M. Paabo (unpublished work) obtained the provisional value 3.72×10^3 using 2,5-dinitrophenol as the reference indicator acid.

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[11] When triethylamine was used as reference base, benzoic acid was so much weaker than the phenolic acid that the range of salt to acid ratios that could be investigated was restricted and the precision was less (see Fig. 3 and footnote 10b). However, practically the same value of $K_{\text{assoc.}}$ for Et_3N plus BzOH was obtained using the very different indicator acid 2,5-dinitrophenol (Fig. 3 and Table I, footnote *b*). For Et_3N plus 2,5-DNP in benzene at 25° $K_{\text{assoc.}}$ is ~400 (unpublished results of the authors).

[12] The parameters used in constructing II were: (a) Bond angles, HNH, 104°; OCO, 125°; COH, 108°; ONH, 27°. (b) Bond lengths, N–H, 1.00 Å.; C–O, 1.27 Å.; O...N, 2.65 Å.; O...H, 1.81 Å. No determinations of bond angles or bond distances in diphenylguanidinium benzoate or analogous structures have been reported. However, with the assumption of a nearly tetrahedral value for the angle HNH, the other parameters fall well within the ranges of values which have been accepted for amino acids, peptides and like structures. For example, see E. W. Hughes and W. J. Moore, THIS JOURNAL, **71**, 2618 (1949); D. P. Shoemaker, J. Donohue, V. Schomaker and R. B. Corey, *ibid.*, **72**, 2328 (1950); L. Pauling, R. B. Corey and H. R. Branson, *Proc. Natl. Acad. Sci.*, **37**, 205 (1951); C. Robinson and E. J. Ambrose, *Trans. Faraday Soc.*, **48**, 854 (1952); W. J. Orville-Thomas, *Chem. Revs.*, **57**, 1179 (1957). For discussion of bent *versus* linear hydrogen bonds see, for example, A. Elliott, *J. Chem. Phys.*, **20**, 756 (1952); W. G. Moulton and R. A. Kromhout, *ibid.*, **25**, 34 (1956); C. A. Coulson, *Research (London)*, **10**, 149 (1957); L. Hofacker, *Z. Elektrochem.*, **61**, 1048 (1957).

[13] Other conceivable monomeric structures for diphenylguanidinium benzoate include a structure analogous to I but with both protons of $=NH_2^+$ associated with a carboxylate oxygen. Cyclic eight-

Table II

Thermodynamic Constants for Acid–Base Associations in Aprotic Solvents[a]

Solvent	Base	Acid	ΔF_{25}, kcal./mole	ΔH, kcal./mole	ΔS_{25}, cal./mole deg.
Benzene[b]	Triethylamine	Bromophthalein magenta E	−6.1	−15.3	−30.9
Benzene[b]	Triethylamine	Benzoic acid	−4.9	−11.0	−20.7
Benzene[b]	Diphenylguanidine	Bromophthalein magenta E	−7.4	−14.1	−22.6
Benzene[b]	Diphenylguanidine	Benzoic acid	−7.3	−14.1	−22.9
Benzene[c]	Tribenzylamine	Picric acid	−4.4	−11.2	−23.1
Chlorobenzene[d]	*n*-Butylamine	2,4-Dinitrophenol	−3.1	−12.2	−30.5
Chlorobenzene[d]	Di-*n*-butylamine	2,4-Dinitrophenol	−4.6	−11.4	−22.8
Chlorobenzene[d]	Tri-*n*-butylamine	2,4-Dinitrophenol	−5.1	−14.4	−31.3
n-Heptane[e]	Triethylamine	Iodine	−5.0	−12.0	−23.5
Carbon tetrachloride[f]	Benzene	Iodine	+1.1	− 1.1	− 7.4

[a] All thermodynamic constants given in the table are based on association constants expressed in l./mole units (that is, K_c values). [b] This work. [c] See A. A. Maryott, *J. Research Natl. Bur. Standards*, **41**, 7 (1948); M. M. Davis and E. A. McDonald, *ibid.*, **42**, 595 (1949). [d] J. W. Bayles and A. Chetwyn, *J. Chem. Soc.* (*London*), 2328 (1958). The thermodynamic constants given in this table were estimated using data in Tables I and II, *ref. cit.*, and converting K_x values (association constants expressed in mole fraction units of concentration) to the corresponding K_c values. [e] S. Nagakura, THIS JOURNAL, **80**, 520 (1958). [f] Thermodynamic constants are based on data of L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 4500 (1952), and of R. M. Keefer and L. J. Andrews, *ibid.*, **77**, 2164 (1955); however, the constants have been recomputed, using association constants expressed in l./mole units (instead of l./mole fraction units).

ions, *both* carboxylate oxygens of II are associated with protons.[14] The marked disparity in the strengths of benzoic acid and the phenolic acid in terms of association with triethylamine in benzene is paralleled by the "enhancement of acidity. . . relative to carboxylic acids" which phenols are said to exhibit when the solvent is changed from water to pyridine.[15] Such disparities seem to arise largely from the variable behavior of carboxylic acids, which appear to be more strongly acidic when both carboxylate oxygens can undergo hydrogen bonding with molecules of solvent or with whatever substance happens to be functioning as the reference base.[16]

Thermodynamic Data.—The relationship between values of log $K_{\text{assoc.}}$ for the four reactions and the reciprocal of the absolute temperature is shown in Fig. 4. The values for the slopes of the lines, which were obtained by the method of least squares, were used in the customary way to determine the magnitudes of ΔH and ΔS.

Table II is a compilation of the thermodynamic constants, ΔF_{25}, ΔH and ΔS_{25}, for the four reactions studied, and contains additional values from the literature for purposes of comparison. Only four hydrogen acids, three of which are phenolic, are represented in Table II. The thermodynamic constants obtained for the association of triethylamine with benzoic acid in benzene are similar in magnitude to corresponding constants reported in the literature for the interaction of triethylamine with the Lewis acid iodine in the solvent *n*-heptane. However, this should not be taken as an indication that benzoic acid and iodine are about equally strong as acids, as the extent of acid–base association depends among other things on the nature of the solvent.[17] The thermodynamic constants for associations involving aliphatic amines or diphenylguanidine are much greater in magnitude than the constants which have been reported for the interaction of benzene with iodine in carbon tetrachloride.

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member structures with possibly *linear* hydrogen bonds are also conceivable; *e.g.*, structures with (a) both benzoate oxygens bonded to the protons of the two C_6H_5NH- groups of diphenylguanidinium, or (b) one oxygen of benzoate bonded to a C_6H_5NH- proton and the other bonded to an $-NH_2$ proton of diphenylguanidinium (suggested by D. H. McDaniel and E. A. Yerger Dickens, respectively).

(14) See M. L. Huggins, *J. Org. Chem.*, **1**, 407 (1936). A monohydrated benzoate ion closely analogous to II can be constructed with the following parameters: (a) Bond angles, HOH, 108°; OCO, 125°; COH, 106°; O. . .OH, 27°. (b) Bond lengths, O–H, 0.96 Å.; C–O, 1.27 Å.; O. . .O, 2.55 Å.; O. . .H, 1.76 Å. More extensive hydration than this is, of course, expected in aqueous solutions.

(15) C. A. Streuli and R. R. Miron, *Anal. Chem.*, **30**, 1978 (1958).

(16) For other cases where this generalization may apply see F. H. Verhoek, THIS JOURNAL, **58**, 2577 (1936); R. N. Evans and J. E. Davenport, *ibid.*, **59**, 1920 (1937); J. D. S. Goulden, *Spectrochim. Acta*, **6**, 129 (1954); M. Mandel, *Ind. chim. belge*, **23**, 721 (1958). Also see N. A. Izmaĭlov. *Zhur. Fiz. Khim.*, **24**, 321 (1950).

(17) *E.g.*, equilibrium constants found for the association of tri-*n*-butylamine with 2,4-dinitrophenol in the three aprotic solvents heptane, benzene and chlorobenzene were 100, 614 and 3800, respectively; R. G. Pearson and D. C. Vogelsong, THIS JOURNAL, **80**, 1038 (1958). More extensive association of triethylamine with iodine in benzene than in heptane is indicated by some unpublished data of the authors.