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Acid–Base Studies of Phenols in Benzene. I. The Effects of Added Amine Salts

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Abstract: At 25° in benzene 2,4-dinitrophenol (10^{-5} M) reacts with di-*n*-butylamine to form ion pairs. The formation constant is 830 M^{-1}. In 10^{-4} M phenol the constant is 1047 M^{-1}. The difference is accounted for by quadrupole formation; the constant is 2740 M^{-1}. The addition of di-*n*-butylammonium *p*-toluenesulfonate, bromide, or chloride to a mixture of amine and phenol increases the reaction between them. This is attributed to triple-ion formation. The order of effectiveness is chloride > bromide > tosylate. Benzoate is shown to be much more effective than chloride. At 25° in benzene the phenolic indicator bromphthalein magneta E reacts with di-*n*-butylamine, but the ion-pair formation constant varies systematically. It is shown that Beer's law does not describe these solutions, and that quadrupoles are the main product of the reaction in 2×10^{-5} M indicator solution. The addition of di-*n*-butylammonium tosylate, bromide, or chloride produces marked changes in the absorption spectra. It is postulated that triple ions are formed here too. The order of effectiveness is the same as that for 2,4-dinitrophenol. In benzene phenol markedly increases the extent of reaction between hydrogen chloride and the basic indicator, *p,p'*-dimethylaminoazobenzene. It is shown by infrared studies that there is no direct interaction between phenol and hydrogen chloride in benzene. These effects are ascribed to the high stability of unsymmetrical anionic triple ions which contain phenolate ions as one component.

Benzene as a solvent for acid–base reactions offers the advantage that leveling reactions do not occur, or occur very weakly, so that there is an almost unlimited range of acid–base couples whose interactions can be studied. On the other hand, before full use can be made of this property it will be necessary to unravel quite complex phenomena which accompany proton-transfer reactions in this medium. Because of its low dielectric constant there is ion-pair formation and more extensive aggregation for electrolytes, the extent of polymerization depending upon the particular compound under study.[2] The complications arising from ion-pair and quadrupole formation in acid–base reactions in acetic acid as solvent were elegantly resolved by Kolthoff and Bruckenstein,[3] but their approach failed when applied to even quite dilute solutions of a neutral basic indicator in benzene and similar solvents, suggesting that much more complicated reactions than ion-pair formation were occurring.[4] Part of this complexity may aries from poor hydrogen bonding between solute and solvent, which leads to dimerization of carboxylic acids and of phenols[5] and a possible failure to solvate ions as a consequence. Hammett, in a study of reactions in nitromethane as solvent, pointed out that the inability of the solvent to solvate the anion formed in an acid–base reaction may lead to ion solvation by one or more molecules of the acid.[6] This was confirmed and extended by Kolthoff in studies of acidity in acetonitrile, in which species like $A(HA)_n^-$ (homoconjugate anions) and $A(HX)_n^-$ (heteroconjugate anions, of phenols and carboxylate

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(1) From a thesis submitted by P. M. Lorenz to the Graduate School of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 3614 (1933).

(3) I. M. Kolthoff and S. Bruckenstein, *ibid.*, **78**, 1 (1956); **78**, 10 (1956); **78**, 2974 (1956); **79**, 1 (1957); **79**, 5915 (1957).

(4) L. E. I. Hummelstedt and D. N. Hume, *ibid.*, **83**, 1964 (1961).

(5) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

(6) H. Van Looy and L. P. Hammett, *J. Am. Chem. Soc.*, **81**, 3872 (1959).

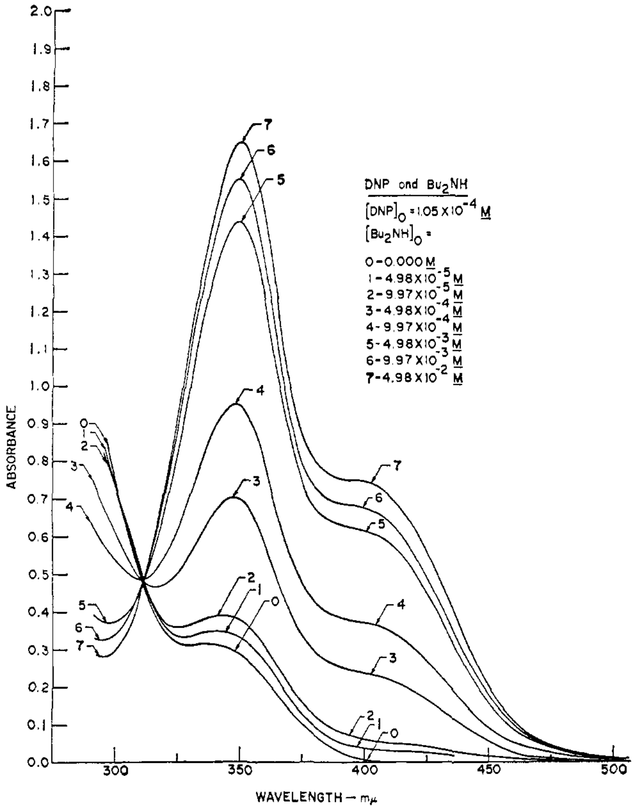

Figure 1. Visible absorption spectra of 2,4-dinitrophenol and di-*n*-butylamine in benzene at 25.0 ± 0.1°.

ions) were detected.[7-9] Similar homoconjugate species have been reported by Barrow to form in carbon tetrachloride,[10] and by Bruckenstein to exist in benzene.[11] In the latter case it was also reported that there was a more extensive reaction between an acid and two different amines than between the acid and either amine. Davis, in the course of her well-known studies with the phenolic indicator bromphthalein magenta E (3′,5′,3′′,5′′-tetrabromophenolphthalein ethyl ester), found that in benzene it gave different spectra with amines of different structure, and that for some substituted guanidines there was a secondary reaction at higher concentrations in which an additional molecule of base added to the ion pair which was originally formed.[12,13]

This research stems from an observation by Pearson and Vogelsang[14] that reactions of the indicator acid 2,4-dinitrophenol with *n*-butylamine or with di-*n*-butylamine went much further to completion on addition of the appropriate amine *p*-toluenesulfonate salt. We report here that this effect exists with bromphthalein magenta E[12] and possibly with phenol itself.[15]

Experimental Section

Spectrophotometry. Infrared spectra were recorded on a Perkin-Elmer Model 21 or Model 521 instrument. Qualitative spectra were run as Nujol mulls between sodium chloride plates. Quantitative spectra were run in a number of demountable cells with sodium chloride windows, or with a variable path length cell. Ultraviolet and visible spectra were recorded on a Cary Model 14 spectrophotometer equipped with a thermostated cell compartment. Cylindrical quartz absorption cells were obtained from the Pyrocell Co. or from the Quaracell Co. They were calibrated by Haupt's method.[16] Solutions were prepared in a bath maintained at 25.0 ± 0.1° and were then transferred to the absorption cell and placed in the spectrophotometer compartment. A period of at least 15 min preceded spectrum recording. Each spectrum was rerun until two successive tracings were identical (to make certain that thermal equilibrium had been reached). Such duplicate absorbance readings were reproducible to ±0.002 absorbance unit (the thickness of the recorded line).

Chemicals. Benzene. Eastman Spectroquality reagent grade material was refluxed over calcium hydride for several hours, and then distilled. The purified solvent was kept in a desiccator or in a drybox.

Indicators. 2,4-Dinitrophenol (Matheson Coleman and Bell, reagent grade) was recrystallized from ethanol–water or benzene. The crystals were dried *in vacuo*. Bromphthalein magenta E, as Eastman Kodak reagent grade material, was recrystallized according to the method of Davis,[12] who kindly supplied us with a sample for comparison. Feathery, yellow needles were obtained from benzene. They turned brick red after drying *in vacuo* at 90°. *p,p′*-Dimethylaminoazobenzene (Eastman Kodak) was recrystallized according to Kolthoff and Bruckenstein.[3] Its hydrochloride (Eastman Kodak) was recrystallized from water and dried *in vacuo*.

Phenol. Baker and Adamson reagent grade material was recrystallized from *n*-hexane and dried *in vacuo*.

Bases. *n*-Butylamine (Fisher certified reagent) was stored over KOH pellets and distilled from fresh KOH. A small middle cut was retained. Di-*n*-butylamine (Matheson Coleman and Bell reagent grade) was purified in the same way. Both amines were distilled immediately before use. Stock solutions in benzene were standardized with perchloric acid in glacial acetic acid.

Amine Salts. Di-*n*-butylammonium *p*-toluenesulfonate was prepared by reacting equivalent quantities of the amine and the acid in methanol, precipitating with ether, recrystallizing from a mixture of methanol and ether, and drying *in vacuo*. The chloride and bromide were prepared in water, dehydrated in a rotary evaporator, and purified in the same manner as the tosylate. Tri-*n*-butylammonium salts were prepared in the same way. Infrared spectra of Nujol mulls of these compounds showed no water peaks.

Anhydrous hydrogen chloride was a product of the Air Reduction Corp.

Results and Discussion

I. 2,4-Dinitrophenol. Figure 1 shows the spectrum of 10^{-4} M 2,4-dinitrophenol (DNP) in benzene at 25.0° in the presence of different concentrations of di-*n*-butylamine (Bu_2NH). The acid shows an absorption maximum at 337.5 mμ, with a molar absorptivity of 3070 ± 110 M^{-1} cm^{-1} from 4×10^{-6} to 2×10^{-4} M.[17] The phenolate shows a maximum at 347–353 mμ (depending on concentration) which has a much higher absorptivity than the acid. A secondary maximum appears at 400 mμ. There is a single isosbestic point at 312 mμ for all DNP–amine solutions, either at 10^{-5} or at 10^{-4} M DNP. It was decided to use the anion peak near 350 mμ, correcting for absorption by unreacted DNP, rather than the weaker and more poorly defined band at 400 mμ. It was not possible to obtain a limiting curve for the phenolate in the presence of excess amine, since concentrations of Bu_2NH in excess of 0.2 M were required, and the phenolate spectrum

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[7] I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **83**, 3927 (1961).

[8] I. M. Kolthoff and M. K. Chantooni, Jr., *J. Phys. Chem.*, **66**, 1675 (1962).

[9] I. M. Kolthoff and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **85**, 2195 (1963).

[10] G. M. Barrow and E. A. Yerger, *ibid.*, **76**, 5211 (1954).

[11] S. Bruckenstein and A. Saito, *ibid.*, **87**, 698 (1965).

[12] M. M. Davis and P. J. Schuhmann, *J. Res. Natl. Bur. Std.*, **39**, 221 (1947).

[13] M. M. Davis and H. B. Hetzer, *ibid.*, **46**, 496 (1951).

[14] R. G. Pearson and D. C. Vogelsang, *J. Am. Chem. Soc.*, **80**, 1038 (1958).

[15] P. D. Bartlett and H. J. Dauben, Jr., *ibid.*, **62**, 1339 (1940).

[16] G. W. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).

[17] M. M. Davis, *J. Am. Chem. Soc.*, **84**, 3623 (1962).

Table I. Beer's Law Study of DNP in Bu_2NH Solutions in Benzene at 25.0°

[DNP], M	[Bu_2NH], M	Absorptivity, M^{-1} cm^{-1}	λ peak, mμ
2.6×10^{-6} to 1.1×10^{-4}	0.1	15,900	350
1.1×10^{-5}	0.2	15,960	352
2.0×10^{-6} to 1.0×10^{-4}	1.0	16,100	353
1.1×10^{-4}	5.0	17,050	353

began to change as the nature of the medium changed. This is shown in Table I.

A method of approximations was therefore used to obtain a suitable value for the absorptivity. It was tentatively assumed that only ion pairs were formed in 10^{-5} and in 10^{-4} M DNP solutions.

$$\mathrm{HA} + \mathrm{B} = \mathrm{BH^+A^-} \tag{1}$$

Here HA stands for DNP, B represents the amine, and BH^+A^- is the ion pair. The latter's formation constant, expressed in concentration units, is K_p.

$$K_p = \frac{[\mathrm{BH^+A^-}]}{[\mathrm{B}][\mathrm{HA}]} \tag{2}$$

From Table I it appears that the value of the molar absorptivity of the anion (a_{A^-}) is approximately 16,000 M^{-1} cm^{-1}. Values of K_p were calculated for different values of a_{A^-} ranging from 16,000 to 16,500 in 10^{-4} M DNP solutions. It was assumed that the value of K_p with the smallest standard deviation was associated with the correct value of the molar absorptivity. Nineteen solutions with different concentrations of Bu_2NH were measured at each DNP concentration level. The absorbances in question were at 350 mμ for 10^{-5} M DNP solutions, and at 347.5 mμ for 10^{-4} M DNP. At these wavelengths the molar absorptivities of the acid a_{HA} were 2800 and 2900 M^{-1} cm^{-1}, respectively. The following equations, which are based on Beer's Law and material balance, were used

$$[\mathrm{HA}] = \frac{a_{A^-}b[\mathrm{HA}]_0 - A}{b(a_{A^-} - a_{HA})} \tag{3}$$

in which A is the absorbance of the solution at the peak, $[HA]_0$ is the stoichiometric concentration of DNP, and b is the pathlength (in centimeters)

$$[\mathrm{HA}] = [\mathrm{HA}]_0 - [\mathrm{BH^+A^-}] \tag{4}$$

and

$$[\mathrm{B}] = [\mathrm{B}]_0 - [\mathrm{BH^+A^-}] \tag{5}$$

in which $[B]_0$ is the stoichiometric concentration of amine. A computer program in FORTRAN IV language was drawn up to facilitate the calculations. The results are shown in Table II.

The best value for K_p in 10^{-4} M DNP solutions is 1047 ± 50 M^{-1}, derived from a molar absorptivity of 16,250 M^{-1} cm^{-1}. In 10^{-5} M DNP solutions there is little difference between 830 ± 38 and 810 ± 35. Therefore K_p was chosen as 830, calculated from the same molar absorptivity of 16,250. No trends were found in the chosen values of K_p at higher amine concentrations.

Table II. Ion-Pair Formation Constants for DNP and Bu_2NH

Initial [DNP], M	Initial [Bu_2NH], M	a_{A^-}, M^{-1} cm^{-1}	K_p, M^{-1}
10^{-4}	4×10^{-4} to 3×10^{-2}	16,000	1235 ± 375
		16,050	1177 ± 231
		16,100	1135 ± 146
		16,150	1101 ± 92
		16,200	1072 ± 61
		16,250	1047 ± 50
		16,300	1024 ± 56
		16,350	1004 ± 67
		16,400	985 ± 80
		16,450	968 ± 91
		16,500	951 ± 101
10^{-5}	2×10^{-4} to 5×10^{-2}	16,200	846 ± 76
		16,250	830 ± 38
		16,300	810 ± 35
		16,350	789 ± 51

The best value for K_p in 10^{-4} M DNP solutions (1047 M^{-1}) compares fairly well with 950 M^{-1}, obtained by Pearson and Vogelsang[14] for the same stoichiometric concentration of indicator. They measured the absorbance at 400 mμ, and used a different procedure for obtaining a best fit of their data.

The best value for K_p selected for 10^{-5} M DNP solutions is 830 M^{-1}, approximately 25% less than the value for the more concentrated solutions. Some aggregation beyond the ion-pair state is taking place in the 10^{-4} M solutions which is stabilizing the phenolate anion. Four possible causes of this effect were considered: triple-ion formation, the addition of a second molecule of base or of acid to the ion pair, and quadrupole formation.

Triple-ion formation is excluded as the reason for the increase in K_p at higher acid concentration because the fraction of ion pairs which form triple ions is independent of the ion-pair concentration.[18] Consider two ion pairs which react to form a triple ion and another ion

$$2\mathrm{BH^+A^-} \rightleftharpoons \mathrm{A^-BH^+A^-} + \mathrm{BH^+} \tag{6}$$

or

$$\mathrm{BH^+A^-BH^+} + \mathrm{A^-}$$

The formation constant for this reaction is

$$K = \frac{[\mathrm{T}][\mathrm{X}]}{[\mathrm{P}]^2} \tag{7}$$

in which T represents the triple ion, X is the simple ion of opposite charge, and P is the ion pair. Since the concentration of T is equal to that of X

$$K = \frac{[\mathrm{T}]^2}{[\mathrm{P}]^2} \tag{8}$$

Thus the ratio of triple ions to ion pairs is a constant, independent of concentration. Triple ions are probably present in these solutions, and the ion-pair constant K_p contains their contribution, but they cannot be the cause for the increase in K_p at higher DNP concentrations.

The addition of a second molecule of base to the ion pair can be written as

$$\mathrm{BH^+A^-} + \mathrm{B} \rightleftharpoons \mathrm{B_2H^+A^-} \tag{9}$$

The equilibrium constant for this reaction was calculated

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(18) R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 2387 (1933).

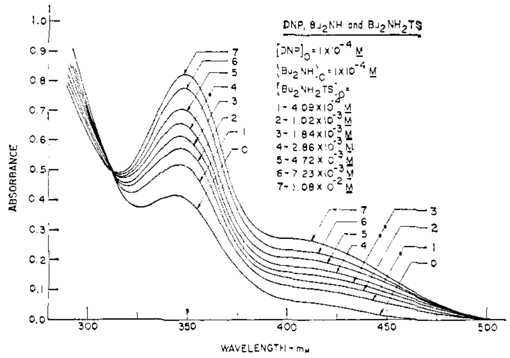

Figure 2. Visible absorption spectra of 2,4-dinitrophenol, di-*n*-butylamine, and di-*n*-butylammonium *p*-toluenesulfonate in benzene at 25.0 ± 0.1 °.

assuming that the true value of K_p was 830 M^{-1}. This secondary constant[13] was found to decrease steadily from 430 M^{-1} to 30 with increasing amine concentration. It was therefore not considered further.

The addition of a second molecule of acid to the ion pair can be written as

$$BH^+A^- + HA \rightleftharpoons BH^+A_2H^- \qquad (10)$$

The corresponding formation constant increased from 1130 to 19,000 with increasing amine concentration.

Quadrupole formation can be formulated in the following way.

$$2BH^+A^- \rightleftharpoons (BH^+A^-)_2 \qquad (11)$$

The formation constant for quadrupoles is

$$K_Q = \frac{[Q]}{[P]^2} \qquad (12)$$

Here Q represents the quadrupole.

The quadrupole formation constant calculated for 10^{-4} M DNP solutions containing Bu$_2$NH is 2740 ± 420 M^{-1}, with no trend evident over the entire concentration region. This was based on the use of 830 M^{-1} for the ion-pair formation constant, and a value of 16,250 M^{-1} cm^{-1} for the molar absorptivity of the phenolate anion in both ion pairs and quadrupoles. It was concluded that this was the cause for the increase in K_p.

There is no direct confirmation of this value from other sources. Maryott[19] measured the dielectric constants of benzene solutions of various amine picrates at different concentrations, but reported no values for dinitrophenolates. He found that di-*n*-butylammonium picrate showed a pronounced decrease in the value of $\Delta E/N_2$ with increasing concentration. The numerator represents the difference between the solution dielectric constant and the solvent dielectric constant at solute mole fraction N_2. He regarded the decrease in the ratio as evidence of a dimerization of the ion pair, with the resulting quadrupole contributing nothing to the dielectric constant of the solution. His quadrupole formation constant recalculated on a molar basis is 200 M^{-1}. This is smaller by an order of magnitude than the quadrupole constant calculated for the dinitrophenolate. The discrepancy may be due to differences between picrates and dinitrophenolates, as well as to some small contribution to the dielectric constant by quadrupoles.

Figure 2 shows, for a solution containing 10^{-4} M Bu$_2$NH and 10^{-4} M DNP, the change in spectrum caused by the addition of increasing quantities of di-*n*-butylammonium *p*-toluenesulfonate. The added salt caused an increase in the yield of anion. There is an isosbestic point at 312 mμ, identical with that observed in Figure 1. Analysis of the data shows that triple ions are formed. The increase in peak absorbance caused by the addition of salt is proportional to the square root of the (unreacted) salt concentration.[3]

The reaction can be written in the following ways.

$$BH^+A^- + BH^+X^- \rightleftharpoons A^-BH^+X^- + BH^+ \qquad (13)$$

or

$$BH^+A^-BH^+ + X^-$$

or

$$BH^+X^-BH^+ + A^-$$

in which BH$^+$X$^-$ refers to the added tosylate salt and BH$^+$A$^-$ is the ion-pair product of the original acid–base reaction. The three triple ions which may be formed are shown above. Two other ions (A$^-$BH$^+$A$^-$ and X$^-$BH$^+$X$^-$) are not considered further since their formation would have required a different stoichiometry. Of the three possible triple ions, the unsymmetrical anion A$^-$BH$^+$X$^-$ is believed to be the principal product, for reasons which are developed later.

The equilibrium constant for this reaction is

$$K_T = \frac{[T]^2}{[BH^+A^-][BH^+X^-]} = \frac{[T]^2}{K_p[HA][B][BH^+X^-]} \qquad (14)$$

In the calculation of K_T it was assumed, as before, that the value of K_p was 830 M^{-1}, and that the molar absorptivity of the dinitrophenolate ion in all forms was 16,250 M^{-1} cm^{-1}. Thirty-two solutions with added di-*n*-butylammonium tosylate in the concentration range 4 × 10^{-4} M to 1.8 × 10^{-2} M were examined. The value of K_T was 0.0372 ± 0.002 at 25.0°.

When di-*n*-butylammonium bromide and chloride were added to Bu$_2$NH and DNP, there was also a marked increase in the phenolate concentration, and analysis showed that triple-ion formation occurred in these solutions as well. However, as the concentration of chloride or of bromide was increased there was a steady decrease in the value of K_T. Thus, for the bromide it decreased from 4.79 × 10^{-2} to 2.51 × 10^{-2}, and for the chloride the decrease was from 8.63 × 10^{-2} to 5.62 × 10^{-2}. It was concluded that some process was occurring at higher halide salt concentrations which decreased the fraction of the salt which was available for reaction with the phenolate ion pair. In the case of the bromide, plots of the (uncorrected) value of K_T against the square root of the (corrected) salt concentration were linear, as were plots against the cube root and the log. Of these the square root plot showed by far the smallest deviation in a least-squares analysis, both for the slope and the intercept. The decrease in K_T was therefore ascribed to quadrupole formation by the bromide.

$$2BH^+Br^- \rightleftharpoons (BH^+Br^-)_2 \qquad (15)$$

It was assumed that the chloride also formed quadrupoles. There were not enough points for an extended analysis because of its limited solubility in benzene.

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(19) A. A. Maryott, *J. Res. Natl. Bur. Std.*, 41, 1 (1948).

A series of successive approximations was used to evaluate the triple-ion formation constant and the quadrupole constant for each halide salt. A best fit of the data was found with a minimum standard deviation for each constant. The final results are shown in Table III.

Table III. Values of K_T and K_Q for Bu_2NH_2Ts, Bu_2NH_2Br, and Bu_2NH_2Cl in Benzene Containing 10^{-4} *M* Bu_2NH and 10^{-4} *M* DNP at 25.0°

Added salt	Concentration range, *M*	K_T	K_Q, M^{-1}
Bu_2NH_2Ts	4×10^{-4} to 1.8×10^{-2}	0.0372 ± 0.002	
Bu_2NH_2Br	4×10^{-4} to 2×10^{-2}	0.050 ± 0.003	56 ± 7
Bu_2NH_2Cl	4×10^{-4} to 3×10^{-3}	0.100 ± 0.005	190 ± 19

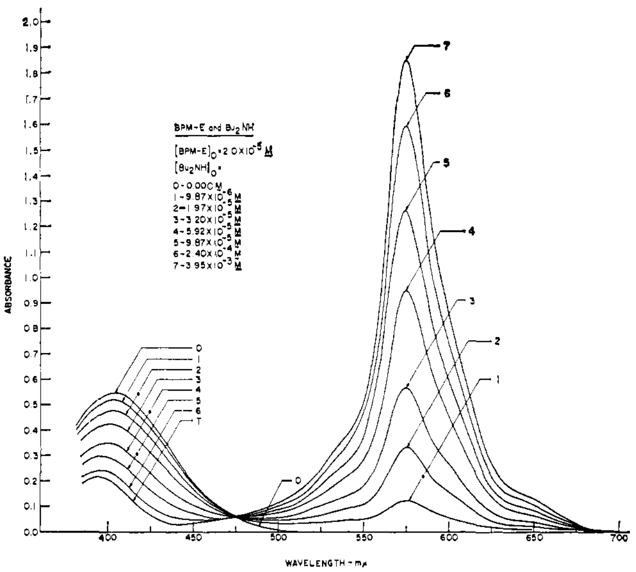

Figure 3. Visible absorption spectra of bromphthalein magenta E and di-*n*-butylamine in benzene at 25.0 ± 0.1°.

The effect of a carboxylate anion on the reaction between Bu_2NH and DNP was examined by adding Bu_2NH to a benzene solution which contained both DNP and benzoic acid (HBz), each at 10^{-4} *M*. It was expected that benzoic acid would compete with the phenol for the amine, and that the phenolate anion would be decreased. Davis observed just such an effect on the addition of various acids to a benzene solution of diphenylguanidine and the phenolic indicator bromphthalein magenta E.[20] In the present case, however, the addition of the benzoic acid was accompanied by a marked increase in the phenolate yield. The increased extent of conversion of DNP is shown by the values calculated for the ion-pair constant, K_p, in the presence of the acid. The average value is about 1700 M^{-1}, whereas in its absence the constant has the value 1047 M^{-1} (see Table II).

At least part of the effect is probably due to triple-ion formation arising from the reaction of di-*n*-butylammonium benzoate with di-*n*-butylammonium 2,4-dinitrophenolate. The ion-pair formation constant for the benzoate salt is not known. A crude estimate of its value was made from data given by Davis.[12] Diphenylguanidine is 14.2 times stronger than Bu_2NH if BPM-E is the reference acid. It was assumed (for lack of information) that it was 14.2 times stronger than Bu_2NH in their reactions with benzoic acid. The ion-pair formation constant for diphenylguanidinium benzoate is 1.83×10^5 M^{-1} at 25°.[20] On this admittedly shaky basis, the corresponding value of K_p for di-*n*-butylammonium benzoate is 1.29×10^4 M^{-1}. With this latter figure, with a value of $K_p = 830$ M^{-1} for the phenolate ion pair, with a molar absorptivity of 16,250 M^{-1} cm^{-1}, and with the increase in absorbance at 347.5 mμ ascribed to triple-ion formation, tentative values of K_T were calculated for the following reaction.

$$BH^+Bz^- + BH^+A^- \rightleftharpoons A^-BH^+Bz^- + BH^+ \qquad (16)$$

The results are shown in Table IV.

The values of K_T first decrease, and then increase. The decrease may be due to quadrupole formation by the amine benzoate, as with the chloride and the bromide. The increase beyond the minimum value may be due to reaction between quadrupoles and ion pairs to form a pair of triple ions, or may be caused by higher unsymmetrical aggregation. The minimum value for the triple-ion constant is five times greater than that found for the chloride salt, pointing to a very strong stabilization of the phenolate anion by the carboxylate group.

Table IV. Triple-Ion Formation Constants for the Reaction of DNP with Bu_2NH in the Presence of HBz in Benzene at 25.0°[a]

Initial [Bu_2NH] $\times 10^4$, *M*	K_T
0.987	1.21
1.97	0.88
3.95	0.65
9.87	0.46
19.7	0.56
39.5	0.73
98.7	0.74
197.4	1.29
394.8	1.84

[a] Initial concentration of DNP and of HBz = 10^{-4} *M*.

II. **Bromphthalein Magenta E.** The acid form of this phenolic indicator was found to obey Beer's law at 405 mμ between 10^{-6} and 4×10^{-5} *M*. A least-squares analysis showed that the molar absorptivity was 26,520 M^{-1} cm^{-1}, which compares fairly well with 26,200, the value recorded by Davis.[12] Comparisons of solutions of the indicator prepared in our laboratory with solutions containing a sample kindly supplied by Dr. Davis showed no significant difference.

Figure 3 shows the spectra of benzene solutions of BPM-E (2×10^{-5} *M*) containing various concentrations of Bu_2NH. The addition of the amine causes a decrease in the absorbance at 405 mμ, and a shift to shorter wavelengths. A new peak appears at 575 mμ, with shoulders at 525–550 and 600–625 mμ. Solutions of Bu_2NH more concentrated than 2×10^{-3} *M* produced a very small increase in absorbance at 575 mμ. This was accepted tentatively as a limiting curve. Assuming that ion pairs were formed, the molar ab-

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(20) M. M. Davis and H. B. Hetzer, *J. Res. Natl. Bur. Std.*, 60, 2871 (1958).

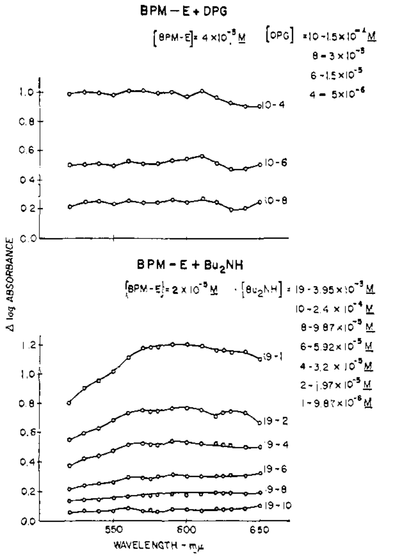

Figure 4. Plots of Δ log absorbance against wavelength for benzene solutions of (a) bromphthalein magenta E and diphenyl guanidine (upper half); (b) bromphthalein magenta E and di-*n*-butylamine (lower half).

sorptivity of the anion at this wavelength was taken as 91,150 M^{-1} cm^{-1}. Values of the ion-pair formation constant were calculated for more dilute amine solutions from the absorbance at 575 mμ.

The values of the ion-pair formation constant steadily increased from 8140 (in 10^{-5} M amine solutions) to 42,150 M^{-1} (in 7.9×10^{-4} M amine). A total of 14 solutions was examined.

When the decrease in absorbance at the acid peak (405 mμ) was used for calculations of K_p, the results were equally poor.

Davis used a logarithmic plot to evaluate the ion-pair constant for this system.[12] She reported a value of 15,500 M^{-1}. When our data were plotted in the same manner, K_p was 20,000 M^{-1}. The explanation for the great variation in K_p obtained by direct calculation is not to be found in any major differences between our data and those of Davis. The logarithmic plot tends to obscure the steady rise in the constant.

If Beer's law is rewritten in logarithmic form[21] one obtains for two solutions of concentrations C_1 and C_2 of the same absorbing substance at any wavelength λ_1

$$\log A_1(\lambda_i) = \log a(\lambda_i) + \log b + \log C_1 \qquad (17)$$

and

$$\log A_2(\lambda_i) = \log a(\lambda_i) + \log b + \log C_2 \qquad (18)$$

in which A is the absorbance, a is the molar absorptivity, and b is the path length. If (18) is subtracted from (17), the result is

$$\log A_1 - \log A_2 = \log C_1 - \log C_2 \qquad (19)$$

Equations 17 and 18 show that plots of log A against wavelength for different concentrations of the same absorbing species will yield a family of curves which are displaced from each other by a constant quantity (log c_1 − log c_2) independent of wavelength. Equation 19 shows that a plot of Δ log A against wavelength should yield a straight line of zero slope.

Figure 4 shows the result of such a plot applied to Davis' data for the reaction between BPM-E and diphenylguanidine, and to our data for the reaction between BPM-E and Bu_2NH. Each open circle represents a calculated point. The behavior of the diphenylguanidine solutions is at least approximately described by the requirement of parallel lines with zero slope. According to Davis' calculation, this system yielded a satisfactory ion-pair constant.[12] On the other hand, it is apparent that Beer's law does not describe the behavior of BPM-E in Bu_2NH solutions, particularly when the amine concentration is low. At higher amine concentrations the curves are almost parallel to each other. This spectral complexity is tentatively ascribed to the formation of ion pairs and quadrupoles in the more dilute solutions, and to quadrupoles and higher aggregates in the concentrated solutions. It is postulated that the ion pair has a different absorption spectrum from the quadrupole and higher aggregates, in the sense that the molar absorptivities are quite different, although the peaks of maximum absorption are about the same (near or at 575 mμ). The limiting spectrum was ascribed to quadrupoles, with resulting molar absorptivity of 182,300 M^{-1} cm^{-1}. Quadrupole formation constants were calculated for the reaction

$$2HA + 2B \rightleftharpoons Q \qquad (20)$$

by means of the equation

$$K'_Q = \frac{[Q]}{[HA]^2[B]^2} \qquad (21)$$

For the 14 solutions which had showed a variation in the ion-pair constant from 8140 to 42,150 M^{-1}, the quadrupole constant was 2.40×10^{13} M^{-3}, with a standard deviation of about 8%, and a small increasing trend in the most concentrated solutions.

Similar calculations were made with absorbance values at the 405-mμ peak (that of the undissociated acid). It was necessary to correct for some absorption by the quadrupole at or near this wavelength. The molar absorptivity of the acid was 26,500, and that for the quadrupole was estimated at 8890 M^{-1} cm^{-1}. The following equation yielded the concentration of unreacted BPM-E

$$[HA] = \frac{A - a_{A^-}b[HA]}{b(a_{HA} - a_{A^-})} \qquad (22)$$

in which A represents the absorbance of a solution at 405 mμ, a_{A^-} is the absorptivity of the anion at 405 mμ, a_{HA} is that of the acid at the same wavelength, b is the path length in centimeters, and $[HA]_0$ is the stoichiometric concentration of the indicator. The average value of K'_Q was 3.30×10^{13}, with a standard deviation of 6%, and a small trend toward higher values in the most concentrated solutions.

Without a more detailed knowledge of the spectra of the different species it is not possible to get the exact values of the equilibrium constants for the various reactions. Nevertheless it can be concluded that symmetrical quadrupole formation is the predominant reaction between bromphthalein magenta E and di-*n*-butylamine when the total indicator concentration is 2×10^{-5} M.

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[21] M. G. Mellon, "Analytical Absorption Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1950, p 102.

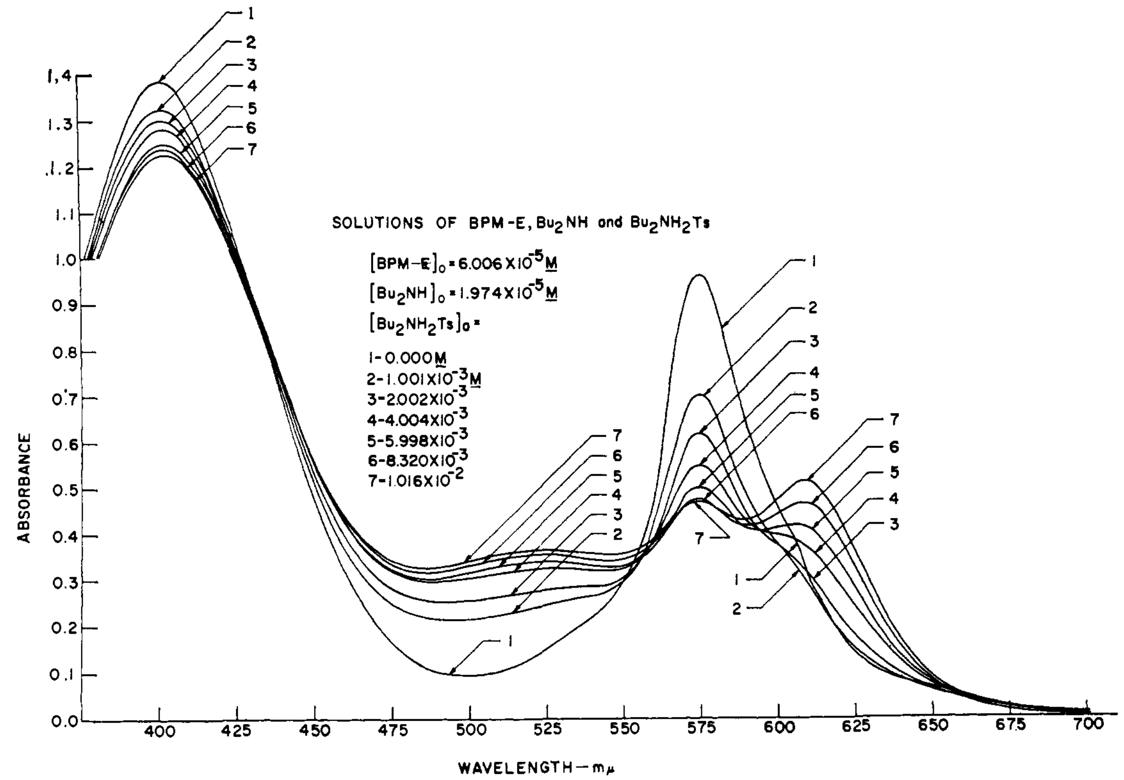

Figure 5. Visible absorption spectra of bromphthalein magenta E, di-*n*-butylamine, and di-*n*-butylammonium *p*-toluenesulfonate in benzene at 25.0 ± 0.1°.

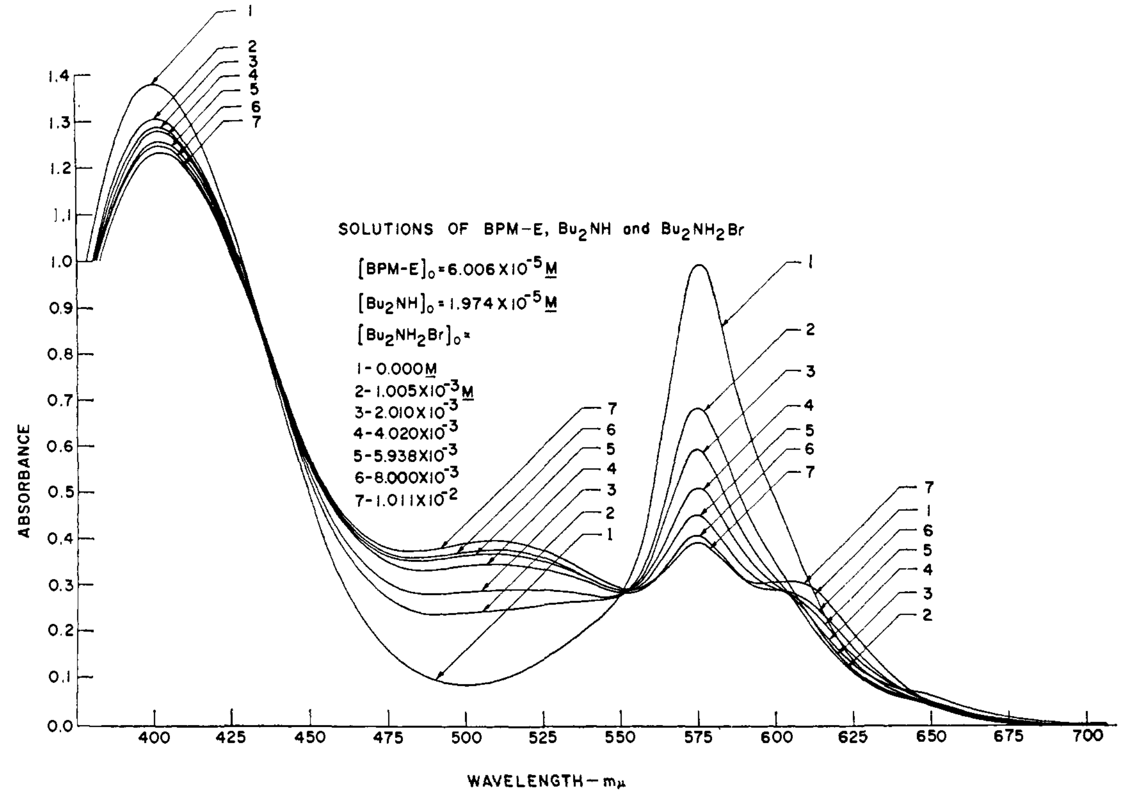

Figure 6. Visible absorption spectra of bromphthalein magenta E, di-*n*-butylamine, and di-*n*-butylammonium bromide in benzene at 25.0 ± 0.1°.

The addition of di-*n*-butylammonium tosylate (Bu_2NH_2Ts), bromide (Bu_2NH_2Br), and chloride (Bu_2NH_2Cl), to benzene solutions containing 6×10^{-5} *M* BPM-E and 2×10^{-5} *M* Bu_2NH, resulted in marked changes in the spectrum of the original solution. These effects are shown in Figures 5, 6, and 7. The added salts cause a decrease in the peak at 575 mμ, as well as a decrease in the acid peak at 405 mμ. Two new peaks

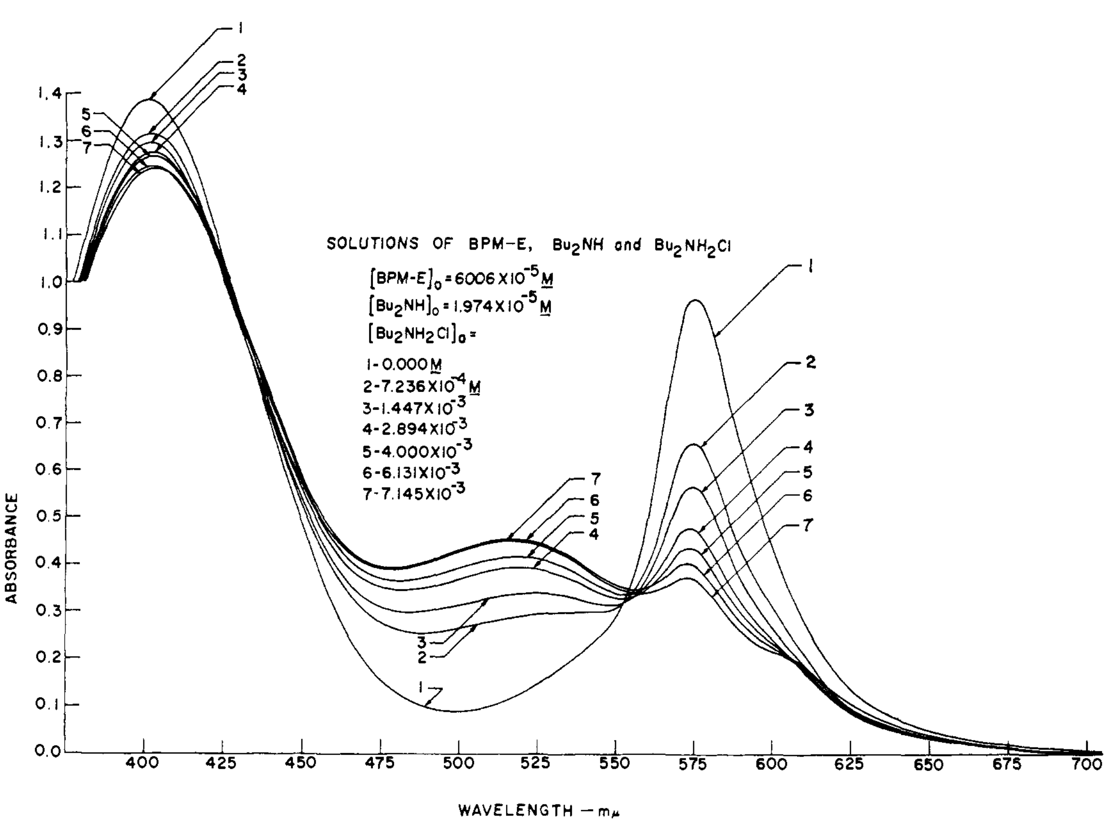

Figure 7. Visible absorption spectra of bromphthalein magenta E, di-*n*-butylamine, and di-*n*-butylammonium chloride in benzene at 25.0 ± 0.1°.

appear; one is between 520 and 540 mμ, and the other lies between 600 and 615 mμ. The three salts give quite different spectra in these two regions.

The decrease in the peak at 575 mμ and in the acid peak at 405 mμ means that the quadrupole concentration is being decreased, and that free acid is being consumed in a new reaction. There is a strong indication from more dilute solutions of BPM-E and Bu_2NH (not shown here) that the new species formed by the added salts absorb not only near 530 and 610 mμ, but also at 575 mμ. The decrease in absorbance at 575 mμ cannot be interpreted solely as a decrease in the symmetrical quadrupole concentration, and quantitative calculations could not be made since true limiting curves for these new species were not obtained. It was not clear whether the new species absorbed in the 405-mμ region. The indication from the more dilute solutions was that they absorbed less than the quadrupole Accordingly a relatively crude analysis of the reactions was carried out by assuming that the decrease in absorbance at 405 mμ directly represented the consumption of free acid. The change in absorbance (ΔA) at this wavelength was examined as a function of the concentration of added salt for the three compounds. The results are shown in Table V.

Three conclusions can be drawn from this table. For each added compound the decrease in absorbance at the acid peak is more closely related to the square root of the salt concentration than to the first power. Secondly, the order of effectiveness in causing the decrease is $Cl^- > Br^- > Ts^-$. Thirdly, there is a decrease in the ratio $\Delta A/(\text{salt})^{1/2}$ with increasing salt concentration which is more marked with the chloride and the bromide, and very much less with the tosylate. The more marked decrease in the ratio for the chloride and the bromide is expected because of the formation of homogeneous quadrupoles by these compounds. It can be concluded that, as with 2,4-dinitrophenol, there is formation of triple ions by these added salts.

Table V. Values of $\Delta A/[Bu_2NH_2{}^+X^-]$ and $\Delta A/([Bu_2NH_2{}^+X^-])^{1/2}$ for 6×10^{-5} *M* BPM-E, 2×10^{-5} *M* Bu_2NH, and Added Salts in Benzene at 25.0°

$[Bu_2NH_2Ts]$, *M*	ΔA (403 mμ)	$\Delta A/[Bu_2NH_2Ts]$	$\Delta A/[Bu_2NH_2Ts]^{1/2}$
1.001×10^{-3}	0.057	56.9	1.79
2.002×10^{-3}	0.080	39.9	1.79
4.004×10^{-3}	0.101	25.2	1.59
5.998×10^{-3}	0.130	21.7	1.68
8.320×10^{-3}	0.145	17.4	1.59
10.16×10^{-3}	0.155	15.3	1.54
$[Bu_2NH_2Br]$, *M*	ΔA (403 mμ)	$\Delta A/[Bu_2NH_2Br]$	$\Delta A/[Bu_2NH_2Br]^{1/2}$
1.005×10^{-3}	0.075	74.6	2.37
2.010×10^{-3}	0.093	46.3	2.08
4.020×10^{-3}	0.105	26.1	1.66
5.938×10^{-3}	0.125	21.1	1.62
8.000×10^{-3}	0.130	16.5	1.48
1.011×10^{-2}	0.146	14.4	1.44
$[Bu_2NH_2Cl]$, *M*	ΔA (403 mμ)	$\Delta A/[Bu_2NH_2Cl]$	$\Delta A/[Bu_2NH_2Cl]^{1/2}$
7.236×10^{-4}	0.078	107.9	2.90
1.447×10^{-3}	0.097	67.0	2.55
2.894×10^{-3}	0.115	39.7	2.14
4.000×10^{-3}	0.126	31.5	1.94
6.131×10^{-3}	0.146	23.8	1.87
7.145×10^{-3}	0.150	21.0	1.78

$$\mathrm{HA + B + BH^+ + X^- \rightleftharpoons A^-BH^+X^- + BH^+} \qquad (23)$$

or

$$\mathrm{BH^+A^-BH^+ + X^-}$$

or

$$\mathrm{BH^+X^-BH^+ + A^-}$$

The consumption of a mole of acid and a mole of base produces a mole of triple ion and a mole of the accompanying simple ion of opposite charge. Hence the change in acid concentration will be proportional to the square root of the added salt concentration. Because of the similarity of these effects with those observed with 2,4-dinitrophenol, it is postulated that anionic unsymmetrical triple ions are also formed with this indicator.

III. **Phenol.** The work of earlier investigators suggested to us that phenol itself may take part in the formation of unsymmetrical triple ions. Hantzsch obtained the relative acidity constants of different acids in various solvents by forming their indicator salts, diluting them until a color change occurred, and comparing the volumes of the diluted solutions.[22,23] Bartlett and Dauben used this technique to show that the reaction of HCl with the basic indicator pentamethoxy red (a substituted triphenylcarbinol) in dioxane as solvent went further toward completion in the presence of phenol and substituted phenols, although phenol alone did not react with the indicator.[15] The effect was attributed by them to hydrogen bonding between the phenol hydroxyl and the chlorine atom of the HCl molecule, rendering the HCl proton more acidic. Swain found a similar enhancement of HCl acidity by phenol in ether, using *p,p'*-dimethylaminoazobenzene as the indicator base.[24]

The hydrochloride of *p,p'*-dimethylaminoazobenzene (methyl yellow) is red. In benzene it is partly dissociated into HCl and the free indicator base, which is yellow. We have found that the addition of phenol to a benzene solution of the hydrochloride strongly increased the red color, an effect similar to those reported by Bartlett and by Swain. Only qualitative observations of this and related effects are reported here. They are shown in Table VI. The following symbols are used: MeY for methyl yellow, MeYHCl for its hydrochloride, PhOH for phenol, HBz for benzoic acid, and DCHBz for 2,6-dichlorobenzoic acid.

Phenol does not visibly react in benzene with the free base. The hydrochloride in benzene is orange because of partial dissociation. Phenol produces a deep red color when added to it. This color is much redder than that produced by the addition of either benzoic acid or 2,6-dichloroacetic acid to the hydrochloride solution.

There is some indication that phenol also aids the reactions of the two carboxylic acids with the free base. Thus, 0.1 *M* benzoic acid in benzene does not visibly react with the indicator base, but does so to a small extent when phenol is added. The stronger acid, 2,6-dichlorobenzoic acid, reacts to some extent with methyl yellow; the addition of phenol definitely increases the yield of the indicator conjugate acid.

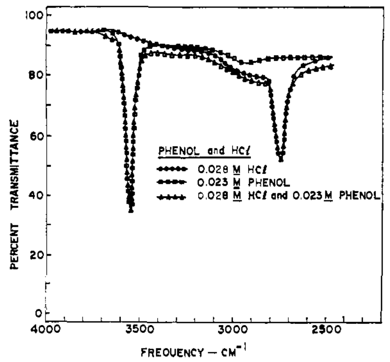

Figure 8. Infrared absorption spectra of phenol and hydrogen chloride in benzene.

The hypothesis of hydrogen bonding between phenol and HCl advanced by Bartlett and Dauben was found to be inapplicable to solutions in benzene. It is quite possible that it applies to solutions in dioxane, which is quite basic relative to benzene.[15] Figure 8 shows the infrared absorption curves in benzene of 0.028 *M* HCl, of 0.023 *M* phenol, and of a mixture of 0.028 *M* HCl and 0.023 *M* phenol each run against benzene in the reference cell. It can be seen that the HCl stretching frequency at 2750 cm^{-1} is unaffected by phenol, and that the phenolic OH stretching frequency at 3560 cm^{-1} is not altered by HCl. It can be concluded that there is no interaction between them in this solvent.

Table VI. Reactions of Phenol, Benzoic Acid, and 2,6-Dichlorobenzoic Acid with Methyl Yellow and Its Hydrochloride in Benzene at Room Temperature

Indicator	Acid	Color
10^{-4} *M* MeY		Yellow
	0.1 *M* PhOH	Yellow
	0.1 *M* HBz	Yellow
	0.1 *M* HBz + 0.1 *M*PhOH	Pale orange
	0.01 *M* DCHBz	Yellow
	0.01 *M* DCHBz + 0.1 *M* PhOH	Orange
	0.1 *M* DCHBz	Orange
	0.1 *M* DCHBz + 0.1 *M* PhOH	Red-orange
10^{-4} *M* MeYHCl		Orange
	0.01 *M* PhOH	Red-orange
	0.1 *M* PhOH	Deep red
	0.1 *M* HBz	Red-orange
	0.1 *M* DCHBz	Red

We believe that these effects arise because of the formation of stable unsymmetrical anionic triple ions

$$\mathrm{MeYH^+Cl^- \rightleftharpoons MeY + HCl} \qquad (24)$$

$$\mathrm{MeY + PhOH + MeYH^+Cl^- \rightleftharpoons Cl^-MeYH^+OPh^- + MeYH^+} \qquad (25)$$

in which $\mathrm{Cl^-MeYH^+OPh^-}$ is the unsymmetrical triple anion, and $\mathrm{MeYH^+}$ is the indicator cation. In the same way, stable unsymmetrical triple ions may be formed from phenolate and carboxylate anions and the methyl yellow conjugate acid. It is possible that a heteroconjugate anion of chloride and phenol ($\mathrm{Cl^-}$-PhOH) is formed, as in acetonitrile,[7–9] and there is no direct proof to the contrary at the present time. The indicator stoichiometry would be different in the two

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(22) A. Hantzsch, *Z. Elektrochem.*, **29**, 226 (1923).
(23) A. Hantzsch, *Ber.*, **58**, 627, 631 (1925).
(24) C. G. Swain, *J. Am. Chem. Soc.*, 70, 1119 (1948).

suggested reactions, and this should settle the question. However, since their spectra show that anionic forms of the two phenolic indicators DNP and BPM-E are clearly generated in triple-ion formation with added salts, and there is both a chemical and a formal resemblance between their reactions and that of phenol with methyl yellow hydrochloride, it is postulated that the phenol exists as the phenolate, and that the reaction products are the unsymmetrical anionic triple ion and the indicator cation.

The three possible triple ions which can form with the two phenolic indicators (and by analogy with phenol) were represented in eq 13. Of these, the formation of the cationic triple ion $BH^+A^-BH^+$ (in which A^- represents a phenolate anion) would require that the ion pair BH^+X^- of the added salt be broken to yield an X^- simple ion. Such a break should occur most readily with a salt which is weakly hydrogen bonded, *e.g.*, bromide, and most reluctantly with a salt which is strongly hydrogen bonded, like chloride. There is no direct demonstration that this is the case, but Bufalini and Stern[25] found that hydrogen bonding between methanol and quaternary ammonium salts in benzene was stronger for a chloride than for a bromide. From the point of view of charge distribution, the tosylate should hydrogen bond even more poorly than the bromide. Since the opposite order of effectiveness is seen with both indicator phenols, the cationic triple ion $BH^+A^-BH^+$ is therefore excluded. The cationic triple ion $BH^+X^-BH^+$ (accompanied by a phenolate anion) is not a major factor in these reactions for two reasons. In the first place, in this cation the hydrogen-bonding ability of the central anion X^- should be more important than those of the two cations; conversely in the unsymmetrical anion $A^-BH^+X^-$ the hydrogen-bonding ability of the central ammonium ion should be more important than that of either anion. Pearson and Vogelsang[14] found that with the primary amine *n*-hexylamine the addition of *n*-hexylammonium tosylate increased the extent of reaction with 2,4-dinitrophenol by a factor of 50, whereas the addition of a little less dibutylammonium tosylate to a mixture of Bu_2NH and DNP increased the extent of reaction threefold. In the present study, with one base and three anions, added chloride was only three times more effective than added tosylate in the reaction of DNP with Bu_2NH.

Secondly, the spectra in Figures 5, 6, and 7 are markedly different from each other. Triple ions are probably formed in these solutions. If they consisted of $BH^+X^-BH^+$ (with free phenolate anions) it would be expected that the phenolate anions would show the same spectra at 600–615 and at 520–540 mμ, regardless of the nature of X^- (tosylate, bromide, or chloride). However, the tosylate solutions show a marked peak at 600–615 mμ, the bromide solutions a smaller one, and the chloride solutions virtually none at all. At the same time the broad peak at 520–540 mμ is much more marked for chloride than for tosylate. This suggests an anionic unsymmetrical triple ion.

The reason for the very high stability of this unsymmetrical structure is not apparent. Bruckenstein[11] found that two different amines in benzene reacted more extensively with a carboxylic acid than either one alone. He suggested therefore that there was some stability deriving from unsymmetrical structures. Whether the two cases are treating similar processes is not yet clear. It is clear in the present work that phenols form these structures quite readily, much more so than carboxylic acids, and it is improbable that simple electrostatic forces are involved. The order of efficiency toward phenolates is carboxylate $>>$ chloride $>$bromide $>$ tosylate. If the effect were primarily electrostatic, chloride should be more effective than carboxylate because of its higher charge density.

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[25] J. Bufalini and K. H. Stern, *J. Am. Chem. Soc.*, 83, 4362 (1961).