Acid–Base Studies of Phenols in Benzene. II. The Effects of Added Quaternary Ammonium Salts

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Abstract: The phenolic indicators 2,4-dinitrophenol and bromphthalein magenta E in benzene were found to react slowly with glass when tetra-*n*-butylammonium bromide was present, forming the quaternary ammonium salt of the indicator. Various finely divided anhydrous sodium or potassium salts like sodium acetate produced the effect much more quickly. Radiochemical studies showed that sodium did not enter the solution, and one acetate dissolved from sodium acetate for each bromphthalein magenta E molecule initially present. The addition of quaternary ammonium halides and other salts to the quaternary ammonium salt of either phenolic indicator produced a very marked change in their absorption spectra. The effect was approximately the same for a large number of such added salts; only tetra-*n*-butylammonium acetate was inefficient. The addition of quaternary ammonium salts to benzene solutions of 2,4-dinitrophenol and di-*n*-butylamine caused a very marked increase in the extent of the acid–base reaction, presumably because of formation of the quaternary ammonium salt of the indicator and its incorporation into a stable unsymmetrical aggregate. Tetra-*n*-butylammonium salts displaced the acid–base reaction in the order acetate > chloride > bromide > tosylate > iodide > perchlorate. A qualitative study of the reactions of weak bases like aniline with acids like *p*-nitrophenol or 2,4-dinitrophenol showed that tetra-*n*-butylammonium bromide markedly increased the extent of such reactions in benzene, chlorobenzene, carbon tetrachloride, *o*-dichlorobenzene, dioxane, acetone, nitromethane, and *t*-butyl alcohol. There was no perceptible effect in methanol, ethanol, and acetonitrile. This new phenomenon is specific for phenols. Hydrogen chloride, diphenyl phosphate, *p*-toluenesulfonic acid monohydrate, and trichloroacetic acid did not show this effect in benzene.

The first paper of this series described the formation of stable unsymmetrical triple ions on the addition of di-*n*-butylammonium salts to a solution of a phenolic indicator and di-*n*-butylamine in benzene.[2] During the course of that investigation, it was discovered that the addition of tetra-*n*-butylammonium bromide to a benzene solution of the phenolic indicator bromphthalein magenta E (3′,3′′,5′,5′′-tetrabromophenolphthalein ethyl ester) brought about a slow reaction which produced the anionic form of the indicator. The present paper describes the phenomenon, suggests a possible mechanism, and explores some of the consequences of this reaction.

Experimental Section

Spectrophotometry. Measurements were performed on the instruments described in the preceding paper.[2]

Chemicals. Benzene, benzoic acid, di-*n*-butylamine, 2,4-dinitrophenol, and bromphthalein magenta E were purified as before.[2] Chlorobenzene and *o*-dichlorobenzene, Eastman reagent grade solvents, were used as received. Nitromethane was of spectroquality reagent grade (Eastman) and was redistilled. Pyridine, a Brothers Chemical Co. product, was distilled from KOH pellets. Acetonitrile was of spectroquality reagent grade (Matheson Coleman and Bell) and was redistilled. Acetone (Fisher certified grade) was used as received, as was *t*-butyl alcohol (Matheson Coleman and Bell, reagent grade). Dioxane, a Brothers Chemical Co. product, was refluxed over sodium and then distilled. Picric acid (Baker and Adamson reagent grade) was recrystallized from an ethanol–water mixture and dried *in vacuo*. *p*-Nitrophenol, reagent grade (Matheson Coleman and Bell), was purified in the same way. Diphenylguanidine was obtained through the courtesy of the American Cyanamid Corp. It was treated with charcoal in aqueous acid solution, the base was precipitated, dissolved in acetone, refluxed with charcoal, filtered, and again precipitated with water, recrystallized from toluene, and vacuum dried. Tetra-*n*-butylammonium bromide, Eastman Kodak reagent grade, was recrystallized from ethyl acetate and dried by freeze drying a benzene solution. A Nujol mull showed no water. Tetra-*n*-butylammonium iodide (reagent grade, Eastman Kodak) was purified in the same way. Tetra-*n*-butylammonium chloride was prepared from the iodide by allowing it to react in methanol with silver chloride, evaporating the methanol in a rotary evaporator, dissolving the residue in benzene, and freeze drying it. It was recrystallized from a hot benzene–hexane mixture. A Nujol mull showed no water peaks. Tetra-*n*-butylammonium perchlorate was prepared from the iodide by allowing it to react in methanol with silver perchlorate (G. Frederick Smith). It was purified in the same manner as the chloride and recrystallized from ethyl acetate. Tetra-*n*-butylammonium *p*-toluenesulfonate was prepared from the iodide by treating the latter in methanol with silver oxide and titrating the filtrate with a methanol solution of *p*-toluenesulfonic acid. The solvent was removed in a rotary evaporator, and the oily residue was recrystallized from a mixture of ethyl acetate and ether. It was dissolved in benzene, which was then removed by freeze drying. The salt showed a trace of water in its infrared spectrum. Tetra-*n*-butylammonium acetate was prepared from the iodide by reaction in methanol with silver acetate. Removal of the methanol left a yellow oil which was difficult to crystallize. It was dissolved in ethyl acetate, refluxed with charcoal, and precipitated with ether. It was recrystallized from an ethyl acetate–ether mixture and dried by freeze drying a benzene solution. The tetra-*n*-butylammonium salt of bromphthalein magenta E was prepared by Davis' method.[3] Tetra-*n*-butylammonium 2,4-dinitrophenolate was prepared from a methanol solution of the hydroxide by titration with 2,4-dinitrophenol. The addition of water caused the precipitation of the yellow salt. It was recrystallized from benzene. Tetra-*n*-hexylammonium iodide (Eastman Kodak reagent grade) was recrystallized from a benzene–hexane mixture. Tetra-*n*-laurylammonium nitrate was obtained through the courtesy of Mr. J. J. Perez, Department of Plutonium of the French Atomic Energy Commission. It was recrystallized from hexane. Sodium acetate, Mallinckrodt reagent grade, was recrystallized from an ethanol–acetic acid mixture and dried over phosphorus pentoxide in a vacuum oven at 160° for 24 hr. The sodium salt of bromphthalein magenta E was prepared by dissolving the indicator acid in ethanol, slowly adding a little less than 1 equiv of dilute alcoholic NaOH with stirring, removing the ethanol in a rotary evaporator, and refluxing the blue residue with benzene to remove unreacted acid. The sodium salt was dissolved in a small quantity of ethanol. Ben-

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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] J. Steigman and P. M. Lorenz, *J. Am. Chem. Soc.*, **88**, 2083 (1966).

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

zene was added to it. After several days, shiny green crystals were formed, which were dried *in vacuo*. The sodium salt of 2,4-dinitrophenol was prepared in the same way. The potassium salt of bromphthalein magenta E was of reagent grade (Eastman Kodak). It was recrystallized from a mixture of ethanol and benzene, and dried *in vacuo*. Glass powder was supplied through the courtesy of the Kimble Glass Co. It was Kimble standard flint (R-6) sodalime glass, 100–200 mesh. It was treated in sequence with cleaning mixture, alcoholic KOH, dilute HCl, and large volumes of distilled water, and then dried. Other chemicals were of reagent grade and were used as received.

Radioactive Materials and Measurements. Radioactive measurements of sodium-22 samples were made on a Nuclear-Chicago 1820 B recording spectrometer. Only photons with energies above 0.2 mev were counted. At least 10,000 counts per sample were recorded. Small sample vials were used, each containing 1 ml of solution.

A known weight of powdered glass was shaken with a $Na^{22}Cl$ solution (Squibb and Co. product) of known activity for several days. The slurry containing the radioactive glass was filtered through a very fine porous glass disk. The filtrate was counted, and the specific activity of the glass was determined by difference. A known weight of the active glass was shaken with a benzene solution of bromphthalein magenta E and tetra-*n*-butylammonium bromide in a Teflon bottle until the solution was deep blue. The mixture was then filtered, the filtrate was evaporated to 5 ml, and a 1-ml aliquot was counted. Sodium-22 acetate was prepared from sodium-22 chloride by ion exchange of inactive sodium acetate with a column consisting of 1 g of Dowex 50 W which contained the radioactive sodium. A total volume of 25 ml held the exchanged sodium acetate and column rinsings. One-milliliter aliquots of this solution were counted. The remainder was evaporated to dryness, and the sodium-22 acetate was dried in a vacuum oven at 160°. Its specific activity was identical with those of the solution aliquots. A known weight of this active sodium acetate was shaken with a benzene solution of bromphthalein magenta E and tetra-*n*-butylammonium bromide in a Teflon bottle until the deep blue color of the phenolate anion appeared. The suspension was then filtered, the filtrate was evaporated to dryness, and the residue was taken up in 1 ml of ethanol and counted.

Measurements of C^{14}-containing compounds were made at room temperature in a Model 314-DC Tri-Carb Packard liquid scintillation spectrometer. The instrument was set for coincidence counting, and was adjusted to give a maximum ratio of $(signal)^2$/noise within a 10- to 100-v range. All solutions were counted in small low-potassium-glass vials, and were allowed to remain in the dark for a day before the count was taken.

An aqueous solution was prepared which contained 50 μcuries of sodium acetate-1-C^{14} (Nuclear-Chicago) and 100 mg of recrystallized sodium acetate. It was evaporated to dryness, and the radioactive salt was dried in a vacuum oven at 160°. The specific activity of the salt was determined in dioxane–water solutions containing 0.7 g of PPO, 0.03 g of dimethyl-POPOP, and 10 g of naphthalene per 100 ml of dioxane. Since the reaction with bromphthalein magenta E was run in benzene and measured in toluene, it was necessary to compare activities in benzene–toluene mixtures with those in dioxane–water solutions. Hence the activity of a sample of benzoic acid-C^{14} (Nuclear-Chicago) was measured in both dioxene–water solution and in benzene–toluene solution. In summary, 0.1 ml of the sodium acetate-C^{14} solution in water and 0.1 ml of benzene were added to 5 ml of the dioxane scintillator solution and counted. A similar count was made of the radioactive benzoic acid. For comparison the latter was also counted in benzene–toluene solution. All benzene solutions were counted in a toluene scintillator solution (5 g of PPO and 0.3 g of dimethyl-POPOP in 100 ml of toluene). Ten milliliters of the benzene sample was added to 1 ml of a concentrated scintillator solution. The final concentrations of PPO and of dimethyl-POPOP were the same as those commonly encountered. The benzene solutions of bromphthalein magenta E and quaternary ammonium bromide were shaken with known quantities of sodium acetates-C^{14}, filtered, and measured. Many of these solutions were deep blue in color. However, controls with radioactive benzoic acid in nonradioactive blue indicator solutions showed that there was no perceptible decrease in the measured activity caused by the indicator anion, and hence that there was no serious absorption by the indicator of the fluorescence emitted by the scintillator solution.

Glassware. Early in this research it was observed that the addition of tetra-*n*-butylammonium bromide to benzene solutions of either bromphthalein magenta E or 2,4-dinitrophenol immediately produced the anionic color of either indicator. It was found that this fast reaction was due to a basic residue left on the glass by "Sparkleen," the Fisher Scientific Company's proprietary glass-cleaning detergent. This residue did not react with the indicator acids in benzene solution unless quaternary ammonium salts were also present. All experiments reported in this paper were performed in glassware which had been immersed in a hot solution of nitric acid in sulfuric acid (*Caution*!) or had been quickly washed in 5% aqueous ammonium bifluoride solution. After rinsing with distilled water, the glassware was dried overnight in an oven maintained at 150°.

Results and Discussion

The addition of dilute (millimolar) benzene solutions of tetra-*n*-butylammonium bromide (Bu_4NBr) to benzene solutions of the indicator acids bromphthalein magenta E (BPM-E)[3] or 2,4-dinitrophenol (DNP) resulted in the appearance of their anionic forms after days to weeks of standing. Control experiments showed that oxygen was not the cause of the reaction, and that water had too small an effect to account for the observed change. It was hypothesized that a reaction was occurring which involved the glass wall of the container. A series of qualitative tests showed that either indicator in benzene solutions containing Bu_4NBr reacted quickly with powdered soft glass, powdered Pyrex, anhydrous sodium acetate, anhydrous potassium carbonate, and anhydrous potassium monohydrogen phosphate. It was concluded that the reactions which were originally observed were slow because the surface of the glass vessel was involved, and the rates were probably controlled by diffusion into the silicate network.

There are two independent steps in the over-all reaction. The phenolic indicator first reacts with an available sodium compound, forming its own benzene-insoluble sodium salt, and the latter reacts with tetra-*n*-butylammonium bromide, yielding the quaternary salt of the indicator and (presumably) insoluble sodium bromide. The first step can occur in the absence of quaternary ammonium salt. It is possible to completely decolorize a 10^{-4} M solution of BPM-E in benzene by prolonged shaking with anhydrous sodium acetate, depositing the sodium salt of the indicator on the surface of the solid phase. Similar reactions occurred with all the various anhydrous solids and BPM-E, as well as with the same solids and 2,4-dinitrophenol, *p*-nitrophenol, and a number of sulfonephthalein indicators (but not with phenolphthalein). The second step was effected by shaking the sodium and potassium salts of BPM-E and the sodium salt of DNP with benzene solutions of tetra-*n*-butylammonium bromide, yielding stable solutions whose visible absorption spectra resembled, but were not identical with, those of solutions of the quaternary ammonium salts of the indicators.[3,4]

The application of this sequence of reactions to the glass requires that either indicator reacts with the silicate of the glass, forming its own sodium salt and silicic acid, and the sodium salt then reacts with the quaternary ammonium bromide, forming insoluble sodium bromide and the quaternary salt of the indicator. Tables I and II show the results of exchange experiments with Na^{22}-tagged soft glass and BPM-E in benzene,

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

Table I. Sodium-22-Tagged Glass Exchange at Room Temperature with Benzene Containing BPM-E and Bu_4NBr

Sample	Activity
Background	19,462 counts/hr = 324 counts/min
Powdered soft glass	34,254 counts/min/mg
50 ml of benzene with 10^{-5} M BPM-E, 10^{-3} M Bu_4NBr after shaking with 5 mg of glass	19,551 counts/hr/ml = 326 counts/min/ml
Expected activity for complete exchange	29,722 counts/hr/ml = 495 counts/min/ml

and Na^{22}-tagged sodium acetate and BPM-E in benzene, in the presence of Bu_4NBr.

It was concluded that no sodium entered the benzene solution as a result of the reaction.

Table II. Sodium-22 Acetate Exchange at Room Temperature with Benzene Containing BPM-E and Bu_4NBr

Sample	Activity
Background	17,244 counts/hr = 287 counts/min
Sodium acetate	3080 counts/min/mg
Ethanol solution of evaporated residue from 50 ml of benzene solution, 2×10^{-4} M BPM-E and 5×10^{-3} M Bu_4NBr^-, after shaking with 14.2 mg of sodium acetate	17,386 counts/hr/ml = 290 counts/min/ml
Expected activity for complete exchange	2821 counts/min/ml

It is clear that no sodium enters the benzene solution in this case as well. Table III shows the results of a similar set of experiments with C-14-tagged sodium acetate.

Table III. Results of Sodium Acetate-C^{14} Exchange Experiments at Room Temperature with Benzene Containing BPM-E and Bu_4NBr

Sample	Concn, M
Sodium acetate-C^{14} shaken with benzene for 3 days	1.22×10^{-6}
Sodium acetate-C^{14} shaken with 0.016 M Bu_4NBr for 3 hr	3.50×10^{-6}
Sodium acetate-C^{14} shaken with 0.016 M Bu_4NBr for 3 days	1.24×10^{-5}
Sodium acetate-C^{14} shaken with 0.001M BPM-E for 2 days	1.57×10^{-5}
Sodium acetate-C^{14} shaken with 10^{-4} M BPM-E and 0.015 M Bu_4NBr for 3 hr	0.968×10^{-4}

The main conclusion which is drawn from these results is that one acetate group from solid sodium acetate is released into benzene for each molecule of bromphthalein magenta E initially present, when tetra-*n*-butylammonium bromide is also present. Sodium acetate also shows a small solubility in benzene. The concentration of acetate in benzene after 2 days of shaking with 10^{-3} M BPM-E is probably due to acetic acid released by the formation of the sodium salt of BPM-E.

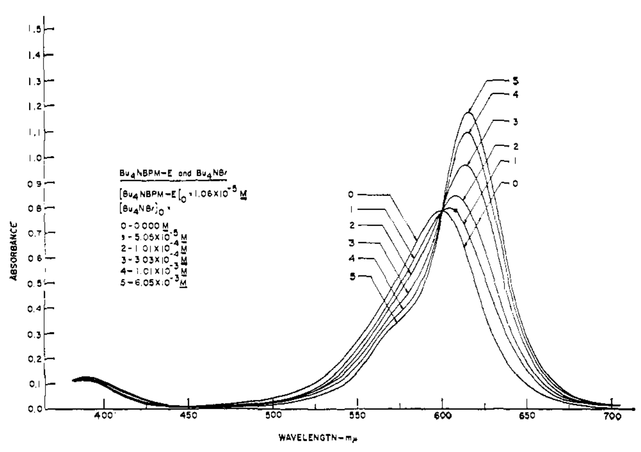

Figure 1. Visible absorption spectra of the tetra-*n*-butylammonium salt of bromphthalein magenta E and tetra-*n*-butylammonium bromide in benzene at 25.0 ± 0.1°.

The driving force for the formation of the sodium salts of the various indicator phenols is not immediately apparent. The sodium or potassium phenolates may be much less soluble in benzene than sodium acetate; but this argument is not universal, since one would expect sodium silicate in a glass network to be less soluble than these phenolates. The acetic acid which is probably released by the reaction is hydrogen bonded more strongly than the phenols,[5] but this is surely not enough to account for the displacement of acetic acid by the very much weaker acid *p*-nitrophenol. Were it not for the release of acetate (presumably as acetic acid) into the solution in the absence of quaternary ammonium salts, one could account for the precipitation by the formation of unsymmetrical anionic hydrogen-bonded double ions on the surface of the sodium acetate or other sodium salt.

The second step in the process—the solubilization of the phenolate anions in the quaternary ammonium bromide solutions—takes place because of a very strong interaction between these anions and the tetra-*n*-butylammonium bromide. In the case of bromphthalein magenta E, the indicator itself in benzene is described by Beer's law over a fairly wide concentration range. Its tetra-*n*-butylammonium salt shows maximum absorption at 600 mμ, where it has a molar absorptivity of 78,700 from 2×10^{-6} to 10^{-4} M. Benzene solutions which contain both the acid and its quaternary ammonium salt show spectra which can be described quantitatively by the simple superposition of the two individual absorption curves. However, if tetra-*n*-butylammonium bromide is added to the tetra-*n*-butylammonium salt of bromphthalein magenta E in benzene there is a very marked increase in absorbance at the maximum, which shifts to longer wavelengths as the bromide concentration is increased. Figure 1 shows these effects for a 1.06×10^{-5} M solution of the indicator salt and different concentrations of quaternary ammonium bromide. There is a clearly defined isosbestic point at 601 mμ, which strongly suggests that two species with different spectra are in equilibrium with each other. The second species shows a peak at or near 615 mμ. There is no indication of a limiting spectrum and hence no equilibrium constant was calculated. In any event, we

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

Table IV. ΔA at 615 mμ of $(Bu_4N)(BPM\text{-}E)$ Caused by Other Quaternary Ammonium Salts in Benzene at 25.0°. Initial Concentration of $(Bu_4N)(BPM\text{-}E) = 10^{-5}$ *M*

Concn, *M*	ΔA for							
	Bu_4NI	$(Hex)_4NI$	Bu_4NBr	Bu_4NClO_4	Bu_4NCl	Bu_4NTs	$(Laur)_4NNO_3$	Bu_4NOAc
5×10^{-5}	0.125	0.090	0.097	0.073	0.060	0.045	0.055	0.030
1×10^{-4}	0.210	0.173	0.202	0.125	0.105	0.095	0.085	0.042
3×10^{-4}	0.365	0.365	0.367	0.277	0.265	0.258	0.167	0.070
1×10^{-3}		0.535	0.495		0.425	0.432	0.312	0.150
2×10^{-3}		0.585	0.532		0.487	0.478	0.407	0.235
6×10^{-3}		0.621	0.572			0.533	0.555	0.378

have no idea of the structure of this new species at the present time. There is no indication from the earlier literature on quaternary ammonium salts that such an interaction should occur. Thus, tetraisoamylammonium picrate in benzene shows virtually the same conductance behavior as the iodide or the thiocyanate[6] as a function of concentration. Presumably the unknown interaction is occurring because two different anions are present in the same solution, and a very stable aggregate—perhaps an unsymmetrical quadrupole involving both anions—is formed. The new species is very stable. This is shown by the fact that acetic acid, which is as strong as bromphthalein magenta E in water, is quantitatively formed from sodium acetate, and BPM-E is quantitatively converted to the anion.

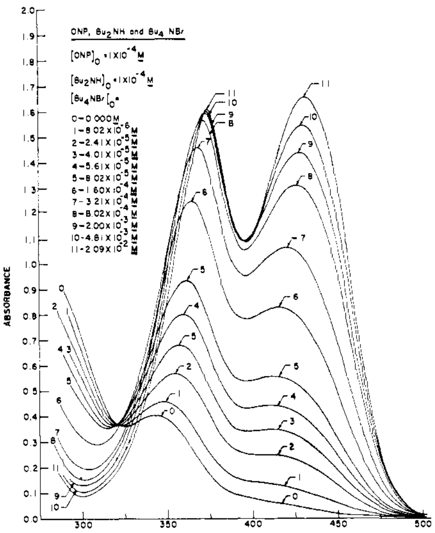

Figure 2. Visible absorption spectra of 2,4-dinitrophenol, di-*n*-butylamine, and tetra-*n*-butylammonium bromide in benzene at 25.0 ± 0.1°.

Eight quaternary ammonium salts were added to solutions of the tetra-*n*-butylammonium salt of BPM-E in benzene. All caused spectral shifts very much like those in Figure 1. All solutions showed an isosbestic point between 601 and 603 mμ and a new peak near 615 mμ at higher concentrations. The relative efficiencies of the various salts in forming the new species were arbitrarily estimated by comparing the increase in absorbance at 615 mμ caused by the addition of the particular salt. These results are shown in Table IV. The following symbols are used: ΔA for the increase in absorbance, $(Hex)_4NI$ for tetra-*n*-hexylammonium iodide, $(Laur)_4NNO_3$ for tetra-*n*-laurylammonium nitrate, Bu_4NTs for tetra-*n*-butylammonium tosylate, and Bu_4NOAc for tetra-*n*-butylammonium acetate.

From this table it appears that there is not very much difference in effectiveness for different chain lengths. For the same cation, the order of decreasing effectiveness is iodide > bromide > perchlorate > chloride > tosylate >> acetate. The differences are rather small among most of the salts, and there is no simple way of accounting for their order. The one striking feature of the data is the effect of the acetate, which is very much smaller than those of the other salts.

2,4-Dinitrophenol behaved very much like BPM-E. At 25° a 1.15×10^{-4} *M* solution in benzene of its tetra-*n*-butylammonium salt had an absorbance of 0.960 at 370 mμ and 1.385 at 422 mμ. In 0.01 *M* tetra-*n*-butylammonium bromide the absorbance at 371 mμ was 1.855, and the absorbance at 430 mμ was 1.850. It served as the indicator acid in an inquiry into the effect of quaternary ammonium salts on an acid–base reaction in benzene. If a new species formed from a quaternary ammonium phenolate and a quaternary ammonium bromide, and if this new species were quite stable, then a given phenol should transfer its proton more readily to a base in the presence of added quaternary ammonium bromide. In fact the reaction in benzene at 25° between di-*n*-butylamine and 2,4-dinitrophenol[2,4] was markedly affected by the addition of tetra-*n*-butylammonium bromide. These effects are shown in Figure 2. The initial concentration of the acid and of the amine was 10^{-4} *M*. The added bromide even in the most dilute solution caused a marked increase in the absorbance at the phenolate peaks, together with a shift to longer wavelengths. There was an isosbestic point at 323 mμ for the more dilute bromide solutions (to 1.6×10^{-4} *M*). In 2×10^{-5} *M* bromide, the wavelengths of the peaks corresponded to to those seen in solutions of tetra-*n*-butylammonium 2,4-dinitrophenolate. In more concentrated bromide solutions, the spectra resembled those of the tetra-*n*-butylammonium salt of the indicator in the presence of tetra-*n*-butylammonium bromide. The interaction of these two compounds must have taken place even in the most dilute bromide solutions. It is apparent that the amine salt is not being formed; the absorption maxima at 337.5 and at 400 mμ in curve 0 were shifted to longer wavelengths in curves 1 to 11. Since there is no apparent reason for the quaternary indicator salt as such to be more stable than the amine salt, and since the interaction of the quaternary ammonium phenolate and the quaternary ammonium bromide is strong, it is reasonable to conclude that the driving force for the increased amine–phenol reaction is the stabilization of the phenolate in some unsymmetrical quaternary am-

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(6) C. A. Kraus, *J. Phys. Chem.*, **60**, 129 (1956).

monium salt aggregate. The amine is simply a convenient repository for the proton of the phenol.

The relative efficiencies of different tetra-*n*-butylammonium salts in influencing the amine–phenol reaction were arbitrarily estimated from the absorption spectra of solutions which contained 10^{-4} *M* phenol, 10^{-4} di-*n*-butylamine, and 10^{-4} *M* quaternary ammonium compound. The absorbance values at the two phenolate peaks for each solution are shown in Table V, together with the wavelengths at which the peaks are found. The latter are shown in parentheses.

Table V. Absorbances of Benzene Solutions of DNP, Bu_2NH, and Quaternary Ammonium Salts, Each 10^{-4} *M*, at 25.0°

Salt	Absorbance (peak), mμ	Absorbance (peak), mμ
None	0.405 (345)	0.072 (400)
Bu_4NClO_4	0.455 (347)	0.130 (400)
Bu_4NI	0.705 (358)	0.372 (413)
Bu_4NTs	0.918 (362)	0.550 (415)
Bu_4NBr	1.055 (363)	0.668 (415)
Bu_4NCl	1.170 (365)	0.755 (415)
Bu_4NOAc	1.455 (366)	0.940 (410)

The various salts have quite different effects on the reaction between the amine and the phenol. The order of decreasing anion efficiency is acetate > chloride > bromide > tosylate > iodide > perchlorate. With the possible exception of the tosylate, this is the order of decreasing basicity in water or (in part) of decreasing ability to form hydrogen bonds.[7,8] From this table and the curves of Figure 2 it can be concluded that there are two reasons for the increased reaction between the acid and the base. First, the anion of the added quaternary ammonium salt hydrogen bonds with the amine cation (the latter bearing the phenolic proton). Secondly, the phenolate anion, as the quaternary ammonium salt, is stabilized in a quaternary ammonium compound structure (whose nature is not yet known). This structure is not a simple ion pair or a symmetrical quadrupole. A different anion (bromide, tosylate, etc.) is obviously necessary for its formation. This suggests that something like an unsymmetrical quadrupole is formed, although it is not clear why such an aggregate should possess a high degree of stability.

These results point to a specificity for phenols in this unknown aggregate, and suggest that carboxylic acids do not take part in its formation. The question of specificity was investigated further by preparing a benzene solution of DNP, Bu_2NH, and benzoic acid (HBz), each at 10^{-4} *M*, adding various quantities of Bu_4NBr and recording the phenolate absorbances at the two peaks. The results are shown in Table VI. The wavelengths at the two peaks are expressed in millimicrons and are shown in parentheses.

Table VI. Peak Absorbances for Solutions of DNP, Bu_2NH, and HBz, Each Initially at 10^{-4} *M*, with Added Bu_4NBr at 25.0°

$[Bu_4NBr]_0$,	No added HBz		10^{-4} *M* HBz	
M	*A* (peak)	*A* (peak)	*A* (peak)	*A* (peak)
0.000	0.405 (345)	0.072 (400)	0.497 (340)	0.102 (400)
4×10^{-4}	1.492 (368)	1.132 (422)	1.430 (368)	0.940 (415)
8×10^{-4}	1.565 (372)	1.300 (426)	1.488 (369)	1.110 (423)
1×10^{-3}	1.570 (372)	1.352 (427)	1.515 (370)	1.175 (423)
2×10^{-3}	1 590 (373)	1.435 (428)	1.550 (373)	1.340 (428)
4×10^{-3}	1.590 (373)	1.518 (430)	1.585 (374)	1.480 (429)
6×10^{-3}	1.595 (374)	1.560 (430)	1.600 (374)	1.545 (429)
8×10^{-3}	1.598 (373)	1.580 (430)	1.605 (374)	1.575 (430)
1×10^{-2}	1.602 (374)	1.620 (430)	1.610 (374)	1.598 (430)

There is an initial increase in phenolate concentration resulting from the addition of benzoic acid (in the absence of quaternary ammonium bromide). This is probably due to the formation of an anionic unsymmetrical triple ion.[2] The addition of as little as 4×10^{-4} mole/l. of Bu_4NBr causes a marked increase in the phenolate absorbance, but the benzoic acid in turn produces a small reduction in the anion yield, probably by competition with the quaternary ammonium salt for the amine. As the concentration of Bu_4NBr is increased, the benzoic acid exerts progressively less effect on the reaction. There is very little difference in absorbance between solutions with and without benzoic acid from 4×10^{-3} *M* quaternary ammonium bromide to 10^{-2} *M* bromide. A similar effect is seen in the wavelengths of the absorption maxima. It was concluded that carboxylates do not take part in the formation of this new structure to any significant extent.

This specificity for phenols was also examined by observing the effects of added Bu_4NBr on the reactions of the basic indicator *p,p'*-dimethylaminoazobenzene with a number of acids in benzene. The basic form of this indicator is yellow. Its conjugate acid is red. A dilute solution of the dye (about 10^{-4} *M*) was divided into equal parts, and to each was added enough of the following acids to produce an orange color: hydrogen chloride, diphenyl phosphate, *p*-toluenesulfonic acid monohydrate, trichloroacetic acid, and picric acid. Some tetra-*n*-butylammonium bromide was then added to each solution. There was a color change toward yellow for the solutions containing hydrogen chloride, diphenyl phosphate, *p*-toluenesulfonic acid monohydrate, and trichloroacetic acid. The solution containing picric acid turned deep red. The added bromide simply serves as a hydrogen-bonding base in competition with the indicator base for the acid in the case of the first four solutions.[8] The new structure, on the other hand, stabilizes picrate, and the proton is transferred to the indicator base.

A number of qualitative observations were carried out to determine the extent to which tetra-*n*-butylammonium bromide could influence the reaction between a number of phenols and a number of nitrogenous bases in different solvents. The phenols were *p*-nitrophenol, 2,4-dinitrophenol, and 2,4,6-trinitrophenol (picric acid). All are virtually colorless in benzene, and form yellow anions. Their acidity constants in water cover a span of approximately 9 p*K* units.[9] The bases included triphenylamine, diphenylamine, aniline, pyridine, di-*n*-butylamine, and diphenylguanidine. They also cover a range of approximately 9 p*K* units from diphenylamine to diphenylguanidine.[10,11] Each phenol was initially 10^{-4} *M*, each base was 10^{-4} *M*, and the quaternary

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(9) G. Kortum, W. Vogel, and K. Andrussow, "Dissociation Constants of Organic Acids in Aqueous Solutions," Butterworth and Co. (Publishers) Ltd., London, 1961.

(10) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1962.

(11) "Handbook of Chemistry and Physics," 44th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1962.

ammonium bromide was 10^{-3} M in concentration. Each solution containing the quaternary ammonium salt was compared with a control composed of the phenol and the salt alone. This was made necessary by the reaction of picric acid with the bromide in the benzenoid solvents. The results are shown in Tables VII and VIII.

Table VII. Reactions of Phenolic Acids with Nitrogen Bases in Benzene in the Presence of Bu_4NBr at Room Temperature

Acid (10^{-4} M)	Base (10^{-4} M)	Reaction	Greater reaction caused by 10^{-3} M Bu_4NBr
Picric acid	Diphenylguanidine	Yes	Yes
	Di-*n*-butylamine	Yes	Yes
	Pyridine	Yes	Yes
	Aniline	Slight	Yes
	Diphenylamine	No	Yes
	Triphenylamine	No	No
2,4-Dinitrophenol	Diphenylguanidine	Yes	Yes
	Di-*n*-butylamine	Yes	Yes
	Pyridine	Yes	Yes
	Aniline	No	Yes
	Diphenylamine	No	No
p-Nitrophenol	Diphenylguanidine	No	Yes
	Di-*n*-butylamine	No	Yes
	Pyridine	No	No
	Aniline	No	No
	Diphenylamine	No	No

It was evident that aniline, which reacts only slightly with picric acid or DNP in benzene, reacts much more strongly with either in the presence of the quaternary ammonium salt. Diphenylamine, which is much weaker than aniline in water, reacts to some extent with picric acid in the presence of the added salt. *p*-Nitrophenol, which is quite weak in water, does not react with the two strongest bases in benzene, but does so if Bu_4NBr is present.

Reactions in eleven solvents were studied in the same qualitative fashion. *p*-Nitrophenol was the acid, and di-*n*-butylamine, aniline, and pyridine were the bases. Each was 10^{-4} M in concentration. The bromide was 10^{-3} M. Diphenylamine was found to be inert toward *p*-nitrophenol even in the presence of added Bu_4NBr; it is not included in Table VIII. The various solvents are arranged in the order of increasing dielectric constant. The value of the latter is shown in parentheses after the name of the solvent in the first part of the table.

From Table VII it can be concluded that weak bases can be protonated by a suitable phenol in the presence of a quaternary ammonium salt. Thus, diphenylamine reacts with picric acid, and aniline reacts with 2,4-dinitrophenol under these conditions. From Table VIII it is evident that there are two groups of solvents. Ethanol, methanol, and acetonitrile form one group in which the quaternary ammonium bromide does not affect the acid–base reaction. The remaining solvents resemble benzene. There is no obvious effect of dielectric constant, since nitromethane and acetonitrile, with relatively high dielectric constants, differ from each other. The lack of effect of the added salt in the lower alcohols may be due to strong solvation. The positive results found in *t*-butyl alcohol recall the reports of Marple and Fritz[12,13] that quaternary ammonium salts improve the end points in potentiometric titrations of hindered phenols in that solvent. This effect may also be due to the formation of stable unsymmetrical aggregates of quaternary ammonium ions and two different anions, of which one is a phenolate.

Table VIII. Reactions of *p*-Nitrophenol with Various Bases in Different Solvents at Room Temperature. Effect of Added Bu_4NBr

Base	Solvent	Reaction	Greater reaction caused by Bu_4NBr
Di-*n*-butylamine	Dioxane (D = 2.2)	No	Yes
	Carbon tetrachloride (D = 2.2)	No	Yes
	Benzene (D = 2.3)	No	Yes
	Chlorobenzene (D = 5.6)	Slight	Yes
	o-Dichlorobenzene	Yes	Yes
	(D = 9.9)	Yes	Yes
	t-Butyl alcohol (D = 11.5)	Yes	Yes
	Acetone (D = 20.7)	Yes	Yes
	Ethanol (D = 24.3)	Yes	No
	Methanol (D = 32.6)	Yes	No
	Nitromethane (D = 38)	Yes	Yes
	Acetonitrile (D = 39)	Yes	No
Pyridine	Dioxane	No	No
	Carbon tetrachloride	No	Yes
	Benzene	No	No
	Chlorobenzene	No	Slight
	o-Dichlorobenzene	Slight	Slight
	t-Butyl alcohol	Slight	Yes
	Pyridine (D = 12.3)	Yes	Yes
	Acetone	No	Slight
	Ethanol	Slight	No
	Methanol	Yes	No
	Nitromethane	Slight	Yes
	Acetonitrile	Slight	No
Aniline	Dioxane	No	No
	Carbon tetrachloride	No	Slight
	Benzene	No	No
	Chlorobenzene	No	No
	o-Dichlorobenzene	No	No
	t-Butyl alcohol	No	No
	Acetone	No	No
	Ethanol	Slight	No
	Methanol	Yes	No
	Nitromethane	No	No
	Acetonitrile	Slight	No

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