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The Enhancement of Acidity of Very Weak Acids in Tertiary Butyl Alcohol*

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Abstract-The acidity of a solution of acid, HX, and salt, MX, is affected by both the concentration of X^- and M^+ owing to incomplete dissociation of the salt, MX. It was possible to increase the acidity of a solution of 2,6-di-tert-butylphenol - tetrabutylammonium 2,6-di-tert-butylphenolate relative to a dilute solution of tetrabutylammonium hydroxide by increasing the tetrabutylammonium bromide content. This indicates that the dissociation constant of the hydroxide base is sufficiently large that extensive dissociation occurs in dilute solutions. The addition of tetrabutylammonium bromide is therefore recommended as a general method for increasing the acidity and improving the titration characteristics of extermely weak acids.

The dissociation of most tetrabutylammonium salts in tertbutyl alcohol is not extensive owing to the low dielectric constant of the solvent. Of the 1:1 salts that have been investigated, most have constants that range between 10^{-4} to 10^{-6} m/l. Consequently, for a solution of a weak acid and its corresponding salt, the acidity is

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determined by both the equilibria $HX = M^+ + X^-$ and $Bu_4NX = Bu_4N^+ + X^-$. This situation differs from that in aqueous systems where the dissociation of the salt must rarely be taken into account.

It has been shown (2) that it is possible to affect a substantial increase in acidity of an acid solution in equilibrium with its salt by the addition of a second salt (such as Bu_4NClO_4). However, the relative acidity (the acidity relative to that of a dilute solution of tetrabutylammonium hydroxide) is not necessarily increased by the addition of a second salt. If the dissociation constant of the hydroxide is less than that of the salt of the acid, then no change in relative acidity occurs when another tetrabutylammonium salt is added (neglecting changes in activity coefficients). On the other hand, if the dissociation constant of the base is large and that of the salt of the acid small, then the acidity of a dilute base solution is virtually unaffected by an increase in the tetrabutylammonium ion content, while the acidity of the acid solution is increased. Thus, the relative acidity of the acid solution is increased.

Direct comparison of the dissociation constants of tetrabutylammonium hydroxide and tetrabutylammonium salts could not be made, owing to unreliable data on the conductance of hydroxide solutions. The indications were, however, that the dissociation constant of the hydroxide was large, and that the addition of a tetrabutylammonium salt would lead to an increase in relative acidity in many cases. Thus, we chose to study the effect of the addition of Bu_4NBr on the acidity of 2,4-di-tert-butylphenol - tetrabutylammonium 2,4-di-tert-butylphenolate solu-

tions. This was accomplished by performing titrations of 2,4-di-tert-butylphenol in the presence of different amounts of bromide. The size of the potential break at the end point was taken as a measure of the relative acidity.

EXPERIMENTAL

From water-methanol solution 2,4-di-tert-butylphenol (Ethyl Corporation) was recrystallized once. The resulting solid had only a slight yellow tinge. Tetrabutylammonium bromide (Southwestern Analytical Chemicals) was used without further purification. Tetrabutylammonium hydroxide was prepared in water-methanol solution by the silver oxide reaction. The aqueous base solution was treated with benzene to remove amine impurities. Water was pumped off at reduced pressure (10 mm. Hg) and final dilution was made with 10% isopropanol-90% benzene. The final base solution did contain some carbonate impurity, but this has no effect on the titration of such a weak acid as 2,6-di-tert-butylphenol.

The titration assembly using the glass electrode - two phase-SCE electrode system is the same as described previously (1), except that the volume of the sample compartment was reduced to accommodate 15 ml. samples.

The procedure in each case was to add 5.0 ml. 0.0278M 2,6-di-tert-butylphenol to 10 ml. tetrabutylammonium bromide and to titrate with 0.065M tetrabutylammonium hydroxide. Under those conditions, the volume change that occurred with titration did not lead to a large change in the concentration of bromide.

RESULTS

The results of titrations of 2,6-di-tert-butylphenol at initial bromide concentrations of 0.033 to 0.33M are shown in Fig. 1. Comparison of curves D and E shows that even a relatively small amount of bromide has a considerable effect on the shape of the titration curve. This is due primarily to the increased ionic strength of the solution in D, which causes the activity coefficient of the 2,4-di-tert-butylphenolate ion to remain relatively constant throughout the titration. Addition of most any other salt would give the same result.

The relative acidities of 2,6-di-tert-butylphenol in the different bromide solutions are given in Table I. The acidities are given

Table I. Relative Acidities of 2,6-di-tert-butylphenol in
Tetrabutylammonium Bromide Solutions

Conc. bromide	EMF, 10% e.p.
0.00M	41
0.033	52
0.066	57
0.166	63
0.333	74

in terms of millivolts potential change over the interval $\pm 10\%$ end point. Evidently, an increase in the relative acidity does occur when a large amount of bromide is added. Proportionately, this increase is very large, as the potential change at the end point in 0.33M bromide is almost twice as large (and the slope is three times as large) as when

no bromide is added. Absence of complicating factors in the presence of large amounts of bromide is shown by the linearity of the $\log(\text{acid/salt})$ vs. EMF curve, Fig. 2. Moreover, the slope of the line has the theoretical value of 59 mv. / 10-fold change in (acid/salt) ratio.

The slight difference of end points in the presence of bromide and the absence of bromide was accounted for by impurities in the bromide salt. Actual titration of the pure bromide salt alone gave a blank correction of 1.04×10^{-3} meq/mole. When the correction was applied, the end points of all titrations agreed.

The increase in relative acidity of 2,6-di-tert-butylphenol upon addition of tetrabutylammonium bromide leads to the conclusion that the dissociation constant of the hydroxide is greater than that of the 2,6-di-tert-butylphenolate salt. It is logical to expect the dissociation constant of the hydroxide to be larger than those of most salts of very weak acids. Hence, the addition of a large amount of extraneous salt appears to be useful technique for improving the titration of very weak acids.

LITERATURE CITED

- (1) Marple, L. W., Fritz, J. S., Anal. Chem. 34, 796 (1962).
- (2) Marple, L. W., Fritz, J. S., Anal. Chem. (submitted for publication).

FIGURE CAPTIONS

Fig. 1. Ml. Titrant - 0.065M TBAOH in benzene-isopropanol.

Fig. 2. Potential Millivolts vs. S.C.E.

Fig. 1

Fig. 2

END