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## Measurement of Acid-Base Equilibrium Constants in Acetonitrile/18-Crown-6 Solutions

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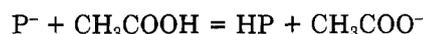
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**Absorbance data were collected at three wavelengths for different mixtures of acetonitrile solutions of acetic acid and substituted phenolates in order to define ionic equilibria. Formation of hydrogen bonded adducts between acid and phenolate in concentration-dependent stoichiometry renders the data, even from very dilute solutions, too complex for an exact algebraic analysis. A quite accurate assessment of the acid-base equilibrium constants is possible, by using only the calculated concentrations of free acids and bases at each ratio of acid/base. Plotting such apparent equilibrium constants vs. the acid/base ratio permits an extrapolation to zero acid concentration in which limit the true value of the acid-base equilibrium constant can be obtained. A similar technique can lead to an estimation of formation constants for conjugate adducts in acetonitrile.**

Measurements of ionic equilibria between various acids and bases in nonaqueous systems have often presented the practitioner of analytical or mechanism chemistry with a difficult task (1-3). Particular complications arise involving anionic bases such as conjugate bases of carboxylic acids and phenols. The technical difficulty of solubilizing small negatively charged anions in solvents such as acetonitrile, dioxane, and benzene has been alleviated by the availability of large polarizable countercations and recently by a variety of com-

plexing agents such as crown ethers and cryptates. However, there remain the intricate ionic equilibria which arise in aprotic solvents. The formation of hydrogen bonded adducts between conjugate acid-base pairs (homoconjugates) and between acids and bases of different structure (heteroconjugates) can often present insurmountable complications to precise determination of simple equilibria between acids and bases.

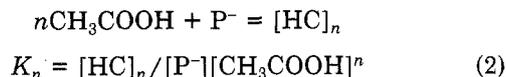
A case in point is the equilibrium between acetic acid and the potassium salts ( $P^-$ ) of substituted phenols (HP) in dry acetonitrile and 18-crown-6 as a solubilizing agent



The acid-base equilibrium ( $K_{eq}$ ) in eq 1 could be observed only in the limit  $[CH_3COOH] \rightarrow 0$ . Note that this and all other equilibrium constants in this paper are expressed in terms of concentrations only, and not activities.

$$K_{eq} = [HP][CH_3COO^-]/[P^-][CH_3COOH] \quad (1)$$

At any finite concentration of  $CH_3COOH$ , where measurements by various analytical techniques are feasible, further equilibria (equilibrium constants as in eq 2) can be encountered



where  $[HC]_n = P^- \cdots [HOOCCH_3]_n$ ,  $n = 1, 2, 3, \dots$ . Since the composition of  $[HC]_n$  would alter as a function of acid added,

Table I. Wavelengths and Molar Absorptivities for the Measurement of Equilibria in CH<sub>3</sub>CN at 20 °C

<i>p</i> -X-phenol X =	$\lambda^a$	$\epsilon_\lambda$		
		P	HP	P... (HP) <sup>b</sup>
-NO <sub>2</sub>	427 <sub>m</sub>	32 110 ± 150	1.68 ± 0.05	7 373
	400 <sub>sh</sub>	16 620 ± 40.6	33.63 ± 0.15	27 550
	380 <sub>sh</sub>	5 334 ± 1.36	221.50 ± 0.89	20 710
-NO	411 <sub>m</sub>	29 242 ± 340		
	400 <sub>sh</sub>	26 458 ± 222		
	380 <sub>sh</sub>	13 254 ± 101		

<sup>a</sup>  $\lambda$  is characterized for P<sup>-</sup>. <sup>b</sup> Estimated error is ±5%.

the adducts formed in a particular solution cannot be characterized.

Even when  $n = 1$ , the number of unknowns in these equilibria (eq 1 and 2) is seven, whereas the number of relationships for mass balance (eq 3–5) together with eq 1 and

$$C_p = [\text{HP}] + [\text{P}^-] + [\text{HC}]_n \quad (3)$$

$$C_t = [\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COO}^-] + n[\text{HC}]_n \quad (4)$$

$$[\text{CH}_3\text{COO}^-] = [\text{HP}] \quad (5)$$

2 is only five. An exact mathematical treatment of this simple case leads to a quartic dependence in one concentration term, [P<sup>-</sup>], in a very awkward algebraic expression. Such an equation would be entirely impractical to use for fitting data for evaluation of parameters.

In this report, a plain and reasonably accurate empirical approach is described to the problem of measuring acid–base equilibrium constants involving *p*-nitro- and *p*-nitroso-phenolates in equilibrium with acetic acid in acetonitrile.

## EXPERIMENTAL SECTION

**Materials.** Reagents were all reagent grade materials and were dried before use. KOAc was recrystallized from absolute methanol. 18-Crown-6 was recrystallized from toluene followed by complexation to CH<sub>3</sub>CN (1:4) that yielded dry 18-crown-6 upon evacuation in a desiccator. A three-step purification process was adopted (4) to obtain CH<sub>3</sub>CN with water content <10<sup>-3</sup> M. Acetic acid was dried by shaking it with P<sub>2</sub>O<sub>5</sub>.

Potassium salts of the substituted phenols were prepared from the corresponding phenol (purified) and potassium hydroxide in methanol. They were recrystallized from hot methanol and acetone two to three times and then dried over CaSO<sub>4</sub> at 80–100 °C (0.5 mm) for 2–3 days. The salts were characterized by melting point, elemental analysis, and acid titrations. All solvents and substrates were stored over P<sub>2</sub>O<sub>5</sub> under vacuum.

**Solutions.** Potassium salts of the substituted phenols were dissolved in CH<sub>3</sub>CN in the presence of 18-crown-6 40% in excess over the compounds. All solutions were made in predried glassware and stored in desiccators in 0.02–0.08 M concentrations. All transfers were made in airtight syringes. Dilutions were made fresh daily. Equilibria were studied in solutions of (1–30) × 10<sup>-4</sup> M acetic acid and (0.5–2) × 10<sup>-4</sup> M potassium phenolate. Homoconjugates of potassium *p*-nitrophenolate were generated from dilutions of a solution of 10<sup>-4</sup> M potassium salt and 10<sup>-2</sup> M *p*-nitrophenol.

Measurements were made with a Cary 118 spectrophotometer. Temperature control was maintained from a Lauda K4/RD circulating bath connected to the cuvette holder in the cell compartment.

## RESULTS AND DISCUSSION

Spectrophotometric measurements of solutions of potassium phenolates, with low concentrations of acetic acid at the wavelength of absorption maximum of phenolates and at one or two other wavelengths where both the conjugates and the phenolates absorb but the acid forms are transparent, give apparent concentrations of the phenolates [P<sup>-</sup>]<sub>app</sub>. The molar

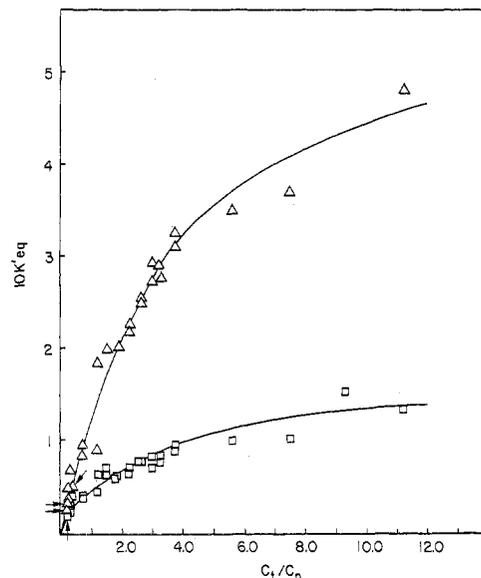


Figure 1. Dependence of  $K'_{eq}$  on the concentration ratio of CH<sub>3</sub>COOH to potassium salt of *p*-nitrophenol in CH<sub>3</sub>CN at 20 °C:  $\Delta$ , 427 nm;  $\square$ , 400 nm. The arrows represent superimposed data points 3 and 6 each, at 427 nm and 400 nm, respectively.

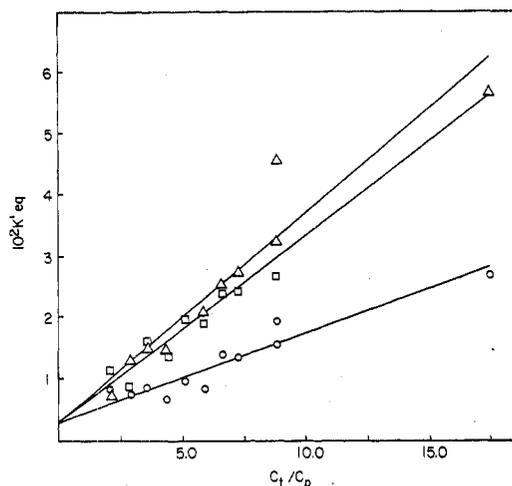


Figure 2. Dependence of  $K'_{eq}$  on the concentration ratio of CH<sub>3</sub>COOH to potassium salt of *p*-nitrosophenol in CH<sub>3</sub>CN, at 20 °C:  $\Delta$ , 411 nm;  $\square$ , 400 nm;  $\circ$ , 380 nm.

absorptivities that were determined to be used for calculation of concentrations of species in the solutions are given in Table I. If the apparent concentrations of the phenols [HP]<sub>app</sub> are calculated from the difference between  $C_p$  and [P<sup>-</sup>]<sub>app</sub>, they are generally overestimated in proportion to the formation of hydrogen bonded adducts. Apparent equilibrium constants ( $K'_{eq}$ ) calculated from these apparent concentrations, therefore, are higher, in proportion to the ratio  $C_t/C_p$ , than the true thermodynamic constants. The deviation of  $K'_{eq}$  from  $K_{eq}$  is the largest when measured at  $\lambda_{max}$  of the phenolate and exhibits nonlinear dependence on  $C_t/C_p$  as the composition of the adduct formed changes. The curves for *p*-nitrophenolate are given in Figure 1. There is a more linear relationship for *p*-nitrosophenolate (Figure 2) in the concentration range studied. But, whatever shape the deviation from  $K_{eq}$  may assume at higher  $C_t/C_p$ , initially it is linear and all lines converge distinctly into a common intercept on the y axis of both Figures 1 and 2. The value of  $K_{eq}$  is given by these intercepts at CH<sub>3</sub>COOH → 0. A value of  $K_{eq} = 0.021 \pm 0.005$  is calculated as the average of intercepts obtained from regression analysis of data sets fitted to a hyperbolic function for the *p*-nitrophenolate–acetic acid system. This compares well with 0.025 calculated from the ionization constants in

Table II.  $pK_a$  Values of Acetic Acid and Substituted Phenols in  $CH_3CN$  and in  $H_2O$  at  $20^\circ C$ 

compound	$pK_a$	
	$CH_3CN$	$H_2O^b$
$CH_3COOH$	22.30 <sup>a</sup>	4.70
<i>p</i> -nitrophenol	20.60	7.20
	20.70 <sup>a</sup>	
<i>p</i> -nitrosophenol	19.84	6.70

<sup>a</sup> From ref 6,  $25^\circ C$ . <sup>b</sup> From ref 7,  $25^\circ C$ .

$CH_3CN$ , of acetic acid  $10^{-22.3}$  and *p*-nitrophenol  $10^{-20.7}$  reported by Kolthoff et al. (5). Similarly, the intercept given by linear least-squares fit of the data in Figure 2 yields  $K_{eq} = (3.5 \pm 0.4) \times 10^{-3}$  for the *p*-nitrosophenolate-acetic acid system. This value allows the calculation of  $K_a = 10^{-19.84}$  for *p*-nitrosophenol in  $CH_3CN$  taking  $K_a = 10^{-22.3}$  for acetic acid ( $K_{CH_3CN} = 10^{-28.5}$ ) (5).

The order of basicities of the two substituted phenols parallels their aqueous basicities, whereas acetic acid, as reported earlier (6), is a weaker acid than either of the phenols in acetonitrile contrary to water (Table II).

Scans of solutions of *p*-nitrophenolate and acetic acid also showed a maximum near 380 nm owing to an apparent production of hydrogen bonded adducts between  $P^-$  and  $CH_3COOH$ . These spectra were similar to those produced from scans of acetonitrile solutions of potassium *p*-nitrophenolate and *p*-nitrophenol. In the latter system, the formation of the homoconjugates  $P^- \cdots [HP]$  (2) and  $P^- \cdots [HP]_2$  (1) has been characterized and a formation constant for the latter,  $K_2 = 10^{4.9}$ , has been reported (1).

Indeed, at 380 nm, absorbance readings in the presence of  $CH_3COOH$  were higher than that for pure *p*-nitrophenolate at the same concentration ( $5.8 \times 10^{-5} M$ ).

If one assumes that the predominant form of conjugation of acid to base is 1:1 at low ratios of  $C_t/C_p$ , then the absorbance at 380 nm can be accounted for by two terms as in eq 6, where

$$A = [HC]\epsilon_{HC} + [P^-]\epsilon_{P^-} \quad (6)$$

$\epsilon_{HC}$  and  $\epsilon_{P^-}$  are the molar absorptivities of the adduct and phenolate, respectively. Neglecting the acid-base equilibrium this time,  $C_p = [HC] + [P^-]$  and the absorbance of the *p*-nitrophenolate alone at the same concentration is  $A_0 = C_p\epsilon_{P^-}$ , which gives eq 7 when substituted into eq 6.

$$A - A_0 = \Delta A = [HC](\epsilon_{HC} - \epsilon_{P^-}) = [HC]\Delta\epsilon \quad (7)$$

An apparent constant  $K'_1$  can be calculated from apparent concentrations  $[P^-]'$  and  $[CH_3COOH]'$  (calculated from absorbances at 427 nm) according to eq 8 in which  $[HC]$  is expressed as  $\Delta A/\Delta\epsilon$  from eq 7

$$\Delta\epsilon K'_1 = \frac{\Delta A}{[P^-]'[CH_3COOH]'} \quad (8)$$

The deviation of  $\Delta\epsilon K'_1$  from the thermodynamic constant times  $\Delta\epsilon$ ,  $\Delta\epsilon K_1$ , is a function of acid concentration. A plot of  $\Delta\epsilon K'_1$  as a function of  $C_p/C_t$  (Figure 3) shows a leveling off

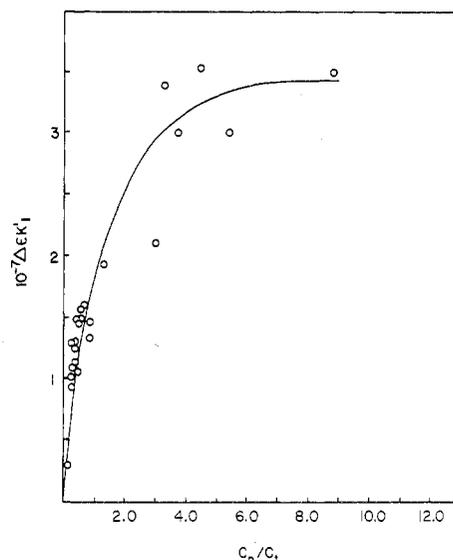


Figure 3. Apparent formation constant  $K'_1$  for a hydrogen bonded adduct of *p*-nitrophenolate and  $CH_3COOH$  times  $\Delta\epsilon$  vs. the concentration ratio of phenolate to acid in  $CH_3CN$ ,  $20^\circ C$ .

at a maximum of  $3.5 \times 10^7$  in the limit  $C_p \gg C_t$ . A reasonable estimate of  $\Delta\epsilon$  might be made from the data in Table I. Taking into account that  $\epsilon_{HC}$  for the homoconjugate of *p*-nitrophenol is calculated for an adduct of two chromophores, one estimate for the heteroconjugate would be  $\epsilon_{HC}/2 = 10350$  (380 nm). Since acetic acid is a weaker acid than *p*-nitrophenol in acetonitrile, the proton is expected to reside farther from  $P^-$  in the heteroconjugate than in the homoconjugate. Therefore,  $10350 > \epsilon_{HC} > 5330$  and taking a medium value of  $\sim 8000$  for  $\epsilon_{HC}$  gives  $\Delta\epsilon \sim 2500$ . With this estimate  $K_1 \sim 1.4 \times 10^4 M^{-1}$  is calculated, which falls in the range of formation constants of other adducts in acetonitrile.

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**Registry No.** Potassium *p*-nitrophenolate, 1124-31-8; potassium *p*-nitrosophenolate, 81409-00-9;  $CH_3COOH$ , 64-19-7.

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