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SHORT COMMUNICATIONS

ACID-BASE EQUILIBRIA IN ACETYLACETONE: DISSOCIATION OF SOME WEAK ACIDS AND THE AUTOPROTOLYSIS CONSTANT OF THE SOLVENT

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The dissociation and homoconjugation constants of 2,5-dichlorobenzenesulfonic, p-toluenesulfonic, methanesulfonic and picric acids have been determined at 25 °C in acetylacetone by conductometry and potentiometry, and compared with those in other solvents. The autoprotolysis constant (K_s) of acetylacetone was estimated potentiometrically with a glass electrode $(pK_s = 19.3)$.

Acetylacetone (2,4-pentanedione) is one of β -diketones which have widely been used as chelating reagents. As a solvent^{1,2)}, it is a protic and less basic solvent with a relatively high dielectric constant (27.20 at 25°C), and most of the 1-1 electrolytes in acetylacetone are fairly well dissociated. In the solvation of acetylacetone towards ions, acetylacetone as well as alcohols such as ethanol and 2,2,2-trifluoroethanol interacts effectively with small anions such as chloride and bromide through hydrogen bonding based on the enol form of the solvent, but cations are not strongly solvated in this solvent like in 2,2,2-trifluoroethanol and acetone.

In this short communication are reported the dissociation equilibria in acetylacetone of 2,5-dichlorobenzenesulfonic, p-toluenesulfonic, methanesulfonic and picric acids, and the calibration of a glass electrode in mixtures of these weak acids with their tetraalkylammonium salts.

Conductometric measurements

The dissociation equilibria of a weak acid, HA, in nonaqueous solvents are generally expressed as follows,

(1)	$HA \iff H^+ +$				A		$K(HA) = [H^{+}][A^{-}]f^{2}/[HA]$		
(2)	A_	+	HA	<u></u>	HA_2^-		$K(HA_2) = [HA_2] / [A] [HA_2]$		
(3)	HA	+	HA	~~>	H ⁺ +	HA2	$K(2HA) = K(HA) \cdot K(HA_2)$		

where K(HA), $K(HA_2^-)$ and K(2HA) are the dissociation, homoconjugation and overall dissociation constants, and other symbols have their usual meanings.

The molar conductivities of p-toluenesulfonic and methanesulfonic acids are

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very small and hardly vary with their concentrations (for example, the molar conductivities of methanesulfonic acid are $(0.70 - 0.58) \text{ S cm}^2 \text{ mol}^{-1}$ in the concentration range of $(10^{-3} - 10^{-2}) \text{ mol dm}^{-3})$, indicating that the dissociation of these acids occurs according to equation (3). The pK(2HA) values were calculated by the conventional method³⁾ and found to be 4.0 and 3.7 for methanesulfonic and p-toluenesulfonic acids, respectively. The conductivity data of 2,5-dichlorobenzenesulfonic acid were treated by the French and Roe method⁴⁾ to yield pK(HA) = 5.1 and K(HA₂⁻) = 8.4 x 10². The application of this method to the solution of picric acid, however, shows that picric acid does not homoconjugate in acetylacetone as well as in propylene carbonate and acetonitrile³⁾.

Potentiometric measurements

Potentiometric measurements were performed with a glass electrode in mixtures of 2,5-dichlorobenzenesulfonic, p-toluenesulfonic, methanesulfonic and picric acids with their tetraalkylammonium salts. From conductometric measurements, these tetraalkylammonium salts are found to be practically completely dissociated in acetylacetone.



Fig. 1 Potential of a glass electrode vs $log(C_a/C_s)$ plots for some weak acids in acetylacetone

Figure 1 shows the relation between the potential of a glass electrode, E, and $\log(C_a/C_s)$, where C_a and C_s denote the concentrations of these weak acids and their tetraalkylammonium salts, respectively. In the mixture of picric acid with tetraethylammonium picrate, a linear relation with a slope of 59 mV is obtained as shown in Fig. 1, which shows that the glass electrode used responds theoretically to the activity of hydrogen ion, $a(H^+)$, and that the homoconjugation does not occur in this mixture. In the other mixtures, however, the relations between E and $\log(C_a/C_s)$ apparently deviate from the straight line with a slope of 59 mV. From the degrees of this deviation³⁾, values of $K(HA_2^-)$ for 2,5-dichlorobenzenesulfonic, p-toluenesulfonic and methanesulfonic acids were calculated to be 6.0 x 10^2 , 1.0 x 10^3 and 7.8 x 10^3 , respectively. Thus, the pK(HA) values of p-toluenesulfonic and methanesulfonic acids were determined to be 6.7 and 7.9 by using the K(2HA) values obtained conductometrically. The pK(HA) value of picric acid was 7.7 as estimated spectrophotometrically³ in the mixture of methanesulfonic acid with tetrabutylammonium methanesulfonate.

By using the K(HA) and K(HA₂⁻) values thus obtained, the pa(H⁺) values in the above mixtures were calculated³) and plotted vs E in Fig. 2: E = 0.085 + 0.059 log a(H⁺). A good linear relation was also obtained in the solution of tetrabutylammonium acetylacetonate (Bu₄N-AA): E = -1.056 - 0.059 log a(AA⁻). So the autoprotolysis constant (K_s) of acetylacetone was estimated from the following relation, 0.085 + 0.059 log K_s = -1.056, the pK_s value of 19.3 being found.

Solvent effect on dissociation equilibria

The pK(HA) and $K(HA_2^{-})$ values in acetylacetone are presented in Table 1 together with those in propylene carbonate and acetonitrile. The pK(HA) values in acetylacetone are somewhat smaller than those in other two solvents. This is reasonably attributed to the hydrogen bonding ability of acetylacetone towards anions based on the enol form, considering that the dielectric constant of ace-tylacetone (27.20) is much smaller than that of propylene carbonate (64.4) and a little smaller than that of acetonitrile (35.95), and that the solvation ability

 	Acetyla	cetone	Propylene carbonate ³⁾		Acetonitrile ³⁾	
	pK(HA)	K(HA ₂ ⁻)	pK(HA)	K(HA ₂ ⁻)	pK(HA)	$K(HA_2)$
2,5-Dichloro-						
benzenesulfonic	5.1	600	4.9	470	6.2	300
p-Toluenesulfonic	6.7	1000	6.4 ⁵⁾	1700 ⁵⁾	8.0 ⁵⁾	790 ⁵⁾
Picric	7.7	~0	9.2	~0	11.0	2
Methanesulfonic	7.9	7800	8.3	2500	10.1	3000

Table 1 pK(HA) and K(HA₂) values of some weak acids in acetylacetone, propylene carbonate and acetonitrile E51

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of acetylacetone towards cations, that is, the basicity of acetylacetone is rather weaker than that of these two solvents $^{1,2)}$.

The $K(HA_2^{-})$ values in acetylacetone, on the other hand, are also nearly equal to those in other aprotic solvents. This apparently inconsistent solvent property of acetylacetone may be due to the intramolecular hydrogen bonding in the enol form which appreciably reduces the acidity of acetylacetone as well as the basicity. Consequently, the acidity of acetylacetone is not so strong as to stabilize anions by hydrogen bonding to a great extent, and the undissociated weak acids, whose hydrogen bonding ability is rather stronger in a less basic solvent acetylacetone than in propylene carbonate and acetonitrile, homoconjugate their anions excluding the relatively weakly solvated molecules of acetylacetone. Thus, acetylacetone is found to be practically a less basic and less acidic solvent in the dissociation of weak acids, and the pK_s value of 19.3 may be considered to be a reasonable one in this sense.

The solvent properties of acetylacetone in acid-base equilibria will be discussed later in detail.

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