Frost/Kalkwarf

$$A \equiv R^{-1}\{-\Delta a - \Delta a \ln T_0 + \Delta H(p_1{=}0,T_0)T_0^{-1} + R \ln p_0 - R^{-1}a'p_0T_0^{-2}\}$$

$$B \equiv R^{-1}\{\Delta a T_0 - \Delta H(p_1{=}0,T_0)\}$$

$$C \equiv R^{-1}\Delta a$$

$$D \equiv R^{-2}a'$$

Appendix III

Apparently, $C_p(\mathrm{g},p,T)$ for water has not been measured. However, the virial coefficients and the ideal heat capacity $C_p(\mathrm{g},p_1{=}0,T)$ are known. To account for $C_p(\mathrm{g},p_0,T)$ in eq 7 without double differentiation followed by double integration of the very complex virial coefficients, we retained the ideal gas part in the double integral and shifted the rest to the $c_i(\mathrm{g})$ terms (in the following, we omit g for gas).

$$\int_{T_0^{-1}}^{T^{-1}} \mathrm{d}T^{-1} \int_{T_0}^{T} C_p(p_0,T)\,\mathrm{d}T = \int_{T_0^{-1}}^{T^{-1}} \mathrm{d}T^{-1} \int_{T_0}^{T} C_p(p_1{=}0,T)\,\mathrm{d}T - \sum_{i\geqslant 0} (i+1)^{-1}p_0^{i+1} \int_{T_0^{-1}}^{T^{-1}} \mathrm{d}T^{-1} \int_{T_0}^{T} T[\mathrm{d}^2c_i(T)/\mathrm{d}T^2]\,\mathrm{d}T \qquad (15)$$

Applying partial integration with T as the primitive and $\mathrm{d}^2c_i(T)/\mathrm{d}T^2$ as the derivative in the last integrand and adding the result of the integration of the last term of eq 15 to the gas part of the $\sum c_i$ term in eq 7 yields the combined term

$$+T^{-1} \sum_{i\geq 0} (i+1)^{-1}\{c_i(T)p^{i+1} - c_i(T_0)p_0^{i+1} + (T_0 - T) \times [\mathrm{d}c_i(T)/\mathrm{d}T]_{T_0}p_0^{i+1}\}$$

At the same time, this yields yet another type of vapor pressure equation.

Into this term, a substitution is made to account for the fact that Wexler's virial coefficients are $c_i(T)R^{-1}T^{-1}$. (There is a printing error in Wexler's expression for C'. It should read log $(-C')$ instead of $-\log C'$.)

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Aqueous Dissociation of Phenylpropiolic Acid

Lowell M. Schwartz,* Robert I. Gelb, and Daniel A. Laufer

Department of Chemistry, University of Massachusetts, Boston, Massachusetts 02125

The acid dissociation constant of aqueous phenylpropiolic acid (3-phenyl-2-propynoic acid) has been determined between 15 and 45 °C by pH potentiometry. The standard enthalpy and entropy of dissociation are calculated from the temperature variation of the dissociation constant. The ^{13}C NMR resonance displacement of the carboxylate carbon upon acid dissociation was measured, and its correlation with the standard entropy of dissociation implies that the molecular form of aqueous phenylpropiolic acid exists partly as an ion pair in equilibrium with the covalently bonded structure.

The literature seems not to contain reliable values of acid dissociation parameters for aqueous phenylpropiolic acid (3-phenyl-2-propynoic acid). The "Handbook of Biochemistry and Molecular Biology" lists two entries, a value of $\mathrm{p}K_a = 2.269$ at 16.8 °C together with $\Delta H° = -0.792$ kcal mol^{-1} and $\Delta S° = -13$ cal mol^{-1} K^{-1} (*1*) and a value of $\mathrm{p}K_a = 2.23$ at 25 °C (*2*). The entry at 16.8 °C makes reference to a paper by Walde (*3*), but this paper makes further reference to a paper by Harned and Sutherland (*4*) as the primary source. Harned and Sutherland, however, do not mention phenylpropiolic acid so that details of the 16.8 °C experiment are unknown. The 25 °C entry in the handbook is attributed to Mansfield and Whiting (*5*), who, indeed, report a pH potentiometric measurement of $\mathrm{p}K_a$

Table I. Estimates of pK_a for Phenylpropiolic Acid at Various Temperatures

T, °C	pK_a[a]	T, °C	pK_a[a]
15	2.268 ± 0.007	30	2.321 ± 0.007
20	2.277 ± 0.007	35	2.327 ± 0.008
25	2.299 ± 0.008	40	2.344 ± 0.006
25	2.296 ± 0.006	40[b]	2.347 ± 0.006
25[b]	2.294 ± 0.006	45	2.367 ± 0.008

[a] Uncertainties are standard error estimates based on estimated standard deviations of 0.002 pH unit and 0.002 mL in the potentiometric and titrant volume measurements, respectively. [b] Titrations of phenylpropiolic acid with 0.1 M NaOH. All other entries involve titrations with 0.1 M HCl.

in 0.1 M aqueous sodium chloride but only at this fixed temperature. These authors mention a prior literature value (also pK_a = 2.23) of Wilson and Wenzke (*6*), who report this value but offer no experimental information. Several other measurements have been made of pK_a in mixed solvent media. We note that propynoic acid and its derivatives are stronger than most carboxylic acids in aqueous solution. Recent interest in the dissociation process of moderately strong aqueous acids (*7*) has led us to make precise measurements of dissociation parameters of those acids whose literature values are uncertain, and so we report here our results for phenylpropiolic acid.

Experimental Section

Phenylpropiolic acid was obtained from Aldrich Chemical Co. Samples were analyzed by titration with standardized NaOH. Aliquots (50 mL) were titrated in a thermostated cell (±0.1 °C) with standard 0.1 M HCl or 0.1 M NaOH. Typically 20 pH vs. volume data points were recorded. pH measurements employed a Model 801 Orion pH meter fitted with conventional separate glass and reference electrodes. The meter was not standardized because the computer program (*8*) was capable of compensating for the standardization automatically. Special care was taken to equilibrate the electrodes at each temperature by waiting until the meter stabilized to 0.001 pH unit for 0.5 h before beginning the titration.

^{13}C NMR measurements employed a Bruker HX-270 spectrometer operating at 67.89 MHz. Sample solutions contained partially neutralized phenylpropiolic acid between 0.02 and 0.05 M in 5% v/v D_2O and were maintained at 30 ± 1 °C. Only seven resonance lines were observed corresponding to the same number of nonequivalent carbons in the molecule. No spurious resonances were detected. The calculational method by which intrinsic chemical shifts of the undissociated acid and anion were extracted from the observed resonances has been described previously (*7*).

Results and Discussion

We have previously described (*8*) an elaborate procedure for treatment of titration data which yields highly accurate and precise pK_a values. The calculational method is based on an iterative nonlinear regression solution to the model equations which incorporate equilibria, conservation equations, and activity coefficient correlations. Statistical uncertainties in both the pH and titrant volume measurements are propagated into standard error estimates of the resulting pK_a values.

Results of our experiments and calculations are shown in Table I. We notice that replicate titrations with HCl at 25 °C yield pK_a values which agree well within statistical uncertainty and that corroborating titrations done with NaOH at 25 and 40 °C also yield pK_a values which agree with the corresponding HCl titrations. These results lend a degree of confidence to the accuracy of the determinations. Our value at 25 °C is reasonably consistent with that reported in ref *5*. That is a conditional equilibrium constant in 0.1 M NaCl while ours is a thermodynamic value.

Standard enthalpy and entropy of dissociation were calculated from the slopes of pK_a vs. T^{-1} and $T(pK_a)$ vs. T plots fitted to the 10 entries in Table I. We found $\Delta H^\circ = -1.39 \pm 0.06$ kcal mol^{-1} and $\Delta S^\circ = -15.2 \pm 0.2$ cal mol^{-1} K^{-1}, where the uncertainties quoted are standard error estimates based on the scatter of the 10 points from the straight lines fitted by least squares. The high precision of these thermodynamic values attests both to the high precision of the 10 pK_a values and to the lack of curvature of the van't Hoff plots. We note that these values are in serious disagreement with those reported in ref *1*, but lacking the original source of those data, we cannot speculate on the reasons for the disagreement.

In a previous paper (*7*) we presented evidence based on complexometric, thermodynamic, and ^{13}C NMR measurements that the undissociated forms of moderately strong acids exist in aqueous solution as ion-pair complexes in equilibrium with covalently bonded structures. Part of the rationale for this hypothesis was an observed linear correlation between standard entropy of acid dissociation ΔS° and the displacement $\Delta\delta_1$ (ppm) of the ^{13}C NMR resonance line of the carboxylic carbon upon acid dissociation. That correlation is based on data for 19 carboxylic and aminocarboxylic acids and is represented by the equation $-\Delta S^\circ = 6.0\Delta\delta_1 - 7.1$. The scatter of data points from this line has a standard deviation of 1.8 cal mol^{-1} K^{-1}. We have measured the ^{13}C NMR spectral displacements of phenylpropiolic acid and anion and have found that the carboxylate carbon resonance is displaced by 3.85 ± 0.10 ppm as the acid is neutralized. If this value is substituted for $\Delta\delta_1$ in the correlation equation, a value of ΔS° of -16.0 cal mol^{-1} K^{-1} is predicted which we note deviates by 0.8 cal mol^{-1} K^{-1} from the experimental value reported above. Since this deviation is well within the uncertainty of the correlation, we conclude that the dissociation process for phenylpropiolic acid is the same as that of the other acids embodied in the correlation. Following the reasoning described in ref *7*, the observed value of $\Delta S^\circ = -15.2$ cal mol^{-1} K^{-1} leads to an approximate ratio of ion pair to covalently bonded structures of 0.64, which implies that approximately 40% of undissociated phenylpropiolic acid exists as an ion pair.

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