Solvent Effect on the Proton-binding Sites in Urocanic Acid
A TAUTOMERIC EQUILIBRIUM STUDY*

(Received for publication, October 11, 1983)

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A 1H NMR study of urocanic acid dissolved in water/dimethyl sulfoxide mixtures together with potentiometric determinations of its two successive acidities in the same solutions reveal that a proton is transferred from the imidazolium ring to the carboxylate group when the amount of dimethyl sulfoxide is increased. An analysis of the potentiometric data by means of the classical Hammett linear relationship allowed the four microscopic acidity constants to be determined. At 20 °C, there are equal fractions of the tautomeric species, i.e. urocanic acid (AH') and its zwitterion (AH++) in the mixture containing 34% dimethyl sulfoxide by weight (≈0.1 in mole fraction), while 50% dimethyl sulfoxide by weight (≈0.2 in mole fraction) is necessary to completely bias the equilibrium: AH++ ↔ AH' toward the molecular form AH'.

Using nuclear magnetic resonance spectroscopy, we have recently shown (1) that addition of dimethyl sulfoxide to an aqueous solution of histidine hydrochloride (AH:+-) induces a proton transfer from the imidazolium ring to the carboxylate group (Scheme 1). In pure Me2SO, the equilibrium AH:+- ↔ AH2 is strongly shifted toward the monocation AH2, which represents 91% of the total histidine hydrochloride.

Previous studies have revealed that addition of a dipolar aprotic solvent such as Me2SO to water solutions decreases the acidity of R-COOH type acids (2-4) while it increases the acidity of the NH+ functionality of pyridium and imidazolium cations (1,5-7). This suggests that the proton shift of Scheme 1 is the reflection of a change in the relative acidities of the COOH and imidazolium moieties of the histidine dication AH:+ on transfer from water to Me2SO. In this regard, one would expect that potentiometric measurements of these acidities on the whole range of H2O/Me2SO mixtures will provide valuable quantitative information on the solvent dependence of the tautomeric equilibrium (Scheme 1). However, the solubility of histidine hydrochloride is too low to allow rigorous pK determinations in the mixtures rich in Me2SO where the proton shift of Scheme 1 occurs.

In our search for a compound which behaves analogously to histidine but is more suitable for a potentiometric analysis, we found that urocanic acid was a good candidate. Of particular interest is the fact that the acidities of the COOH group and the imidazolium ring are much closer in urocanic acid cation (ΔpK = 2.3) than in histidine dication (ΔpK = 4.18) in aqueous solution. Assuming the effect of Me2SO on these functionalities to be similar in the two systems, one could thus expect a complete proton exchange between the AH++ and AH' tautomers of urocanic acid on going from water to Me2SO (Scheme 2).

Since NMR experiments have fully confirmed this expe-
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EXPERIMENTAL PROCEDURES

Materials—Most of the various compounds used in this work were either of analytical grade (Aldrich) or purified according to standard recrystallization or distillation procedures. The inhibited acrylic acid (Aldrich) was distilled on copper chips and the obtained monomer kept in the freezer. The trans conformation of cinnamic and urocanic acids was confirmed by 'H NMR (3, 13). To measure the acidity constants, AH; and AH' were prepared in NMR tubes, and solvent compositions were determined by weight. The spectra were recorded on a Varian XL-100-12 spectrometer using continuous wave modes and a lock (probe temperature, 32 ± 1 °C). The chemical shifts were measured with DSS as the internal reference. In the range of the concentrations of urocanic acid used in the experiment (<0.2 M, cf. Table I), no appreciable effect of dilution was observed on the chemical shifts. Those for AH' (cf. Table I) were obtained by adding directly in the NMR tube the amount of CF3COOH appropriate for a complete protonation.

Acidity Constant Measurements—The acidity constants have been measured by potentiometry at 20 °C, using an electronic pH meter (Tacussel Isis 2000) equipped with a Radiometer G 202 B glass electrode and a Radiometer K 100 calomel electrode. The good reversibility of the glass electrode was controlled in each H2O/Me2SO mixture (denoted SH) by means of buffer solutions previously calibrated with an hydrogen electrode (3, 13). To measure the acidity constants Ks1 and Ks2 of urocanic acid (AH), various buffered solutions with CAH/CAH or CAH/CAH ratios equal to 1/3, 1/1, and 3/1 were prepared so that the molarity of the charged acidic CAH or basic CAH species was equal to 0.01 M, i.e. the ionic strength = 0.01 M.

The acidity constants Ks of the various imidazolium (ImH; and carboxylic acids (BH) studied were similarly measured from buffer solutions made up so as to have ionic strength = 0.01 M = CAH or CBH. Under such experimental conditions, the pKs values associated with the following equilibria where AH represents AH+ + AH-:

\[ AH^+ \xrightleftharpoons{Ks1} AH \xrightarrow{Ks2} SH^+ \]

and

\[ AH \xrightarrow{Ks1} A^- \xrightarrow{Ks2} SH^- \]

are related to the measured activity of the solvated proton in SH, i.e. \( \delta \), by the equations.

\[ pK_s = pS^+ - \log \frac{C_{AH}}{C_{AH}^+} \]

(4)

and

\[ pK_s = pS^- - \log \frac{C_A}{C_A^-} \]

(5)

where pS+, CA, and I denote -log \( \delta_{S^+} \), the molarity of the i species, the coefficient of the simplified Debye-Hückel equation, and the ionic strength, respectively. The coefficient A is known from previous measurements in H2O/Me2SO mixtures (12). In the case of urocanic acid, rigorous calculations of the pKs values have been made in taking account of the contribution of the solvolysis to the AH; = AH equilibrium. Accordingly, the CAH/CAH ratios used in Equation 4 were those calculated after appropriate corrections of the introduced concentrations of AH2 and AH.

RESULTS AND DISCUSSION

NMR Studies—Table I summarizes the chemical shifts measured for the imidazole (H2, H4) and vinylic (H3, H6) protons (cf. Scheme 2) of urocanic acid (AH) in the various D2O/Me2SO-d6 mixtures. As can be seen, there is a progressive but significant high field shift of H2 and H4 for increasing amounts of Me2SO-d6 to an aqueous solution where urocanic acid (AH) is known to exist essentially as the AH- tautomer. This behavior resembles that observed and discussed in detail for the histidine system and is not the result of a simple solvent effect on the parameters for AH-'. Undoubtedly, it is the reflection of the progressive conversion of AH'- which has a protonated imidazole moiety and a carboxylate group into the AH2 tautomer which has a neutral imidazole ring and a COOH functionality. However, and in contrast with histidine (1), the proton transfer between AH- and AH2 is essentially complete in 70% Me2SO by weight, as evidenced by the small variations of the various chemical shifts in going from this medium to pure Me2SO. Also to be noted is the observation that the H2 proton is more affected than the H4 proton on transfer to Me2SO. Since one could reasonably expect that deprotoration of N3 should induce similar shift variations on both H2 and H4 resonances, this suggests that the deprotonation of the imidazole ring of AH'- takes place preferentially at the nitrogen atom H4. Accordingly, AH2 could exist predominantly as the N3-H and not the N1-H tautomer (Equation 6).

\[ \text{AH}^{+} \rightarrow \text{AH}^{2-} \]

(6)

The conversion of AH+- into AH2 is further confirmed by looking at the solvent dependence of the protonation shifts of the H2, H4, and H6 protons of urocanic acid. In each mixture, the protonation shift of a given proton H is measured by the relation:

\[ \Delta \delta_i = \delta^{{AH}^{+}} - \delta^{AH} \]

where \( \delta^{{AH}^{+}} \) and \( \delta^{AH} \) are the chemical shifts of H in the cationic (AH+) and neutral (AH = AH' and/or AH2) forms of uro-
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**TABLE I**

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<tr>
<th>Proton</th>
<th>0</th>
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<th>81.8</th>
<th>100</th>
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<td>AH₂</td>
<td>AH</td>
<td>AH</td>
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<td>8.82</td>
<td>0.23</td>
<td>8.50</td>
<td>8.88</td>
<td>0.38</td>
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<tr>
<td>5</td>
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<td>7.81</td>
<td>0.16</td>
<td>7.73</td>
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<td>0.06</td>
<td>4.55</td>
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<td>6.54</td>
<td>0.00</td>
<td>6.55</td>
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</tr>
</tbody>
</table>

*In parts per million from internal DSS; Δδ = δ₁AH - δ₁AH₂. The solutions with ≤0.8% Me₂SO-d₄ are saturated in urocanic acid (AH), i.e. concentration < 0.1 M, while those with 81.8 and 100% Me₂SO-d₄ contained =0.2 M AH.

**TABLE II**

<table>
<thead>
<tr>
<th>Compound</th>
<th>0</th>
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<th>21.3</th>
<th>31.7</th>
<th>41.4</th>
<th>51.2</th>
<th>61.8</th>
<th>70.5</th>
<th>80.4</th>
<th>91.0</th>
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<td>5.98</td>
<td>5.78</td>
<td>5.70</td>
<td>5.74</td>
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<td>6.99</td>
<td>6.82</td>
<td>6.65</td>
<td>6.42</td>
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<td>5.66</td>
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<td>7.71</td>
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<td>7.16</td>
<td>7.00</td>
<td>7.22</td>
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<tr>
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<td>5.83</td>
<td>5.69</td>
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<td>5.58</td>
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<td>3.65</td>
<td>3.78</td>
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<td>5.61</td>
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<td>5.01</td>
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</tbody>
</table>

*Ref. 27.

*7.25 at 25 °C from Hofman (28); ~7.0 from Perrin (29); 7.33 at 25 °C from Albert (30).

*7.86 at 25 °C from Albert (30); 7.85 at 25 °C from Perrin (31).

*5.53 at 25 °C from Perrin (31).

*4.25 at 25 °C (32).

*4.44 at 25 °C (32).

*See Footnote 3.

**Fig. 1.** Influence of solvent composition (D₂O/Me₂SO-d₄) on protonation shifts of urocanic acid AH: Δδ = δ₁AH - δ₁AH₂ (T = 32 °C).

Acrylic acid, respectively. As can be seen in Fig. 1, H₂ presents the largest protonation shift in D₂O (ΔδH₂ = 0.34, ΔδH₄ = 0.23, ΔδH₅ = 0.16), i.e. the protonation occurs mainly at the carboxylate group of AH⁻. Increasing the Me₂SO content of the aqueous solution causes, however, a decrease in ΔδH₅ and results concomitantly in a strong increase in the protonation shifts of H₃ and H₅: ΔδH₃ = 0.07, ΔδH₄ = 1.07, ΔδH₅ = 0.35 in 60.8% Me₂SO by weight. Clearly, this observation is again consistent with the protonation occurring at the heterocyclic nitrogens N₁ and/or N₅ of the AH⁺ tautomer in Me₂SO-rich mixtures. That the change in ΔδH₅ is significantly higher than the change in ΔδH₄ also supports the conclusion that the imidazole ring of AH⁺ is preferentially protonated at N₅ rather than at N₁.

**pKₐ Measurements**—Table II summarizes the pKₐ and pK₉ values determined for the two acidities of urocanic acid in the whole range of H₂O/Me₂SO composition. Also given are the pKₐ values for the ionization of the acrylic and trans-cinnamic acids as well as those for the deprotonation of the various substituted imidazolium cations studied in the same media. As previously observed for anilinium and pyridinium cations (4–7), the acidity of imidazolium cations is enhanced in the whole range of H₂O/Me₂SO composition. This acidity is approximately constant until Me₂SO-rich media. However, this situation is consistent with reported changes in pK₉ values for various acetic and benzoic acids and reflects the much lower solvation of a COO⁻ group by Me₂SO than by H₂O (14).

The influence of the Me₂SO content on the two successive deprotonations of urocanic acid cation AH⁺ is easily understood with reference to Fig. 2. As can be seen, the changes in pK₉ and pK₈ of AH⁺ parallel those observed in the pKₐ.
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values of simple carboxylic and imidazolium functionalities, respectively, in H2O/Me2SO mixtures with ≤25% Me2SO by weight. This is in accord with the deprotonation of AH⁺ occurring essentially according to path 1 of Scheme 2 and therefore with the formation of the zwitterion AH⁻⁺ as the major species resulting from the first deprotonation process in these very aqueous media. In contrast, the changes in Kₐ are rather comparable to those observed in Kₐ values of imidazolium cations in H2O/Me2SO mixtures with ≥50% Me2SO. Concomitantly, the variations in Kₐ become closely similar to those observed in the Kₐ values of acrylic and trans-cinnamic acids. Obviously, these results favor path 2 of Scheme 2 as the most reasonable deprotonation process of AH⁺ in these mixtures, thus confirming the NMR observation that AH⁺ is the major neutral form of urocanic acid in media of high Me2SO content.

In mixtures with a Me2SO content in the range 25–50%, the first deprotonation of AH⁺ yields a mixture of both tautomers AH⁻⁻ and AH⁺ whose relative concentrations are governed by the equilibrium constant Kᵥ. In such media, the measured acidity constants Kᵥ and Kₐ are related to the various individual equilibrium constants of Scheme 2 by only three independent equations, i.e. Equations 7–9.

\[
\begin{align*}
Kᵥ + Kₐ &= Kₛ \quad (7) \\
\frac{1}{Kᵥ} + \frac{1}{Kₐ} &= \frac{1}{Kₛ} \quad (8) \\
Kᵥ &= Kₛ \quad (9)
\end{align*}
\]

Therefore, a complete analysis of the system requires an additional relation which has usually been provided by taking advantage of extrathermodynamic assumptions (15–17). There is, however, another method which is especially suitable when the acidity measurements have been carried out in various aquo-organic mixtures. It is based on the observation that the pKₛ values determined in a given solvent S₂ for a series of structurally similar X-substituted acids, obeying the Hammett relationship 10 (18), must be linearly related to the pKₛ values measured for these acids in another solvent S₁.

Using Equation 10 where the influence of the solvent is included in the reaction constant ρₓ and eliminating the constituent constant ρₓ between the two solvents S₁ and S₂ leads to Equation 11 which implies plots of pKₛ versus pKₛ to be linear with slopes and intercepts being characteristic of the class of acids studied and depending only on the solvents.

\[
pKₛ - pKₛ = ρₓ
\]

where

\[
pKₛ = \frac{pK蔀}{pK蔀} + pKₓ - \frac{pKₓ}{pKₓ} + pKₓ
\]

A number of experiments have confirmed the validity of Equation 11 for some carboxylic acids, phenols, and anilinium cations in H2O/Me2SO and H2O/N-methylacetamide mixtures (4, 19–22).

Inasmuch as it is attached to a sp² carbon, one could reasonably expect the COOH functionalities of trans-cinnamic acid and the neutral form AH⁺ of urocanic acid to behave as those of 3-substituted acrylic acids. Interestingly, the reactivity of these latter compounds has been successfully related to the ionization of benzoic acids (23). This suggested that the relations (Equation 11) determined for meta- and para-substituted benzoic acids in H2O/Me2SO mixtures should also hold for acrylic-type acids. On this ground, we have used the values of the slopes and intercepts associated with the linear plots pKₛ (path 1) observed for benzoic acids (4) to calculate the pKₛ values of trans-cinnamic and acrylic acids from the pKₛ values measured for these compounds in the various H2O/Me2SO (S₂) mixtures. As can be seen in Table III, there is a remarkable agreement between the calculated and experimental pKₛ values, thus supporting the validity of the treatment. Interestingly, similar calculations for urocanic acid led to consistent pKₛ values for the COOH functionality (pKₛ = 4.67) provided that only the pKₛ measured in H2O/Me2SO mixtures with ≥50% Me2SO be used. This result further emphasizes that the ionization of the COOH group of AH⁺ follows that of the imidazolium moiety in these media, i.e. we have pKₛ = pKᵦ and pKₛ = pKᵦ (path 2 in Scheme 2). The estimation of pKᵦ = pKᵦ = 4.67 in aqueous solution is evidently of great importance since it allows the calculation, via Equation 11, of the pKᵦ values associated with the ionization of the COOH group of AH⁺ in the solvent mixtures with ≤50% Me2SO where paths 1 and 2 are competitive. The knowledge of pKᵦ in these solvents leads in turn to the estimation of the corresponding pKᵦ, pKᵦ, and pKᵦ values from Equations 7–9. The results are given in Table II and illustrated by Fig. 2. Plots of pKᵦ and pKᵦ as well as those for pKᵦ and pKᵦ versus the Me2SO composition intersect in the mixture containing 34% Me2SO by weight for which Kᵦ = 1. Also to be noted is that the results fit very well the relation 12 in this particular mixture.

\[
pKₛ - pKₛ = pKᵦ - pKᵦ = \log₁₀2
\]

The percentage τ of urocanic acid which is present in the molecular form AH⁺ in a given solvent may be calculated through Equation 13.

\[
τ = \frac{100Kᵦ}{1 + Kᵦ}
\]

The τ values thus obtained are included in Table II which shows that the amount of AH⁺ in pure water is 5%, i.e. it is not negligible at all. On addition of Me2SO, τ increases very rapidly to reach 100% in 50% Me2SO by weight, i.e. a mole fraction of ~0.2.

Provided that 1-methylimidazolium cation be excluded from the series, good linear relationships are obtained in plotting the measured pKᵦ for imidazolium cations, showing that Equation 11 also
The slope and intercept values were calculated by linear regression analysis for previously published data (Ref. 4). The mean square deviation analysis is always lower than 0.04 pK unit. Comparison between the calculated pK\text{\footnotesize{\textit{BD}}} values (from Equation 11) and the experimental one for acrylic, trans-cinnamic, and uracilic acids.

<table>
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<tr>
<th>Percentage of MeSO (by weight)</th>
<th>0</th>
<th>10.8</th>
<th>21.3</th>
<th>31.7</th>
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<td>4.29*</td>
<td>4.29*</td>
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<td>5.48*</td>
<td>5.48*</td>
<td>5.47*</td>
<td>5.72*</td>
</tr>
</tbody>
</table>

Equation 11

\[ pK_{\text{\footnotesize{\textit{BD}}}} = 4.67 \pm 0.05 \]

The slope \( \rho_{\text{\footnotesize{\textit{BD}}}} \) of Equation 11 for imidazolium cations is approximately equal to 1 in all solvent mixtures. While this result contrasts with those obtained for carboxylic acids, phenols, indoles, and anilinium ions (4, 19, 20) where the slope \( \rho_{\text{\footnotesize{\textit{BD}}}} \) was found to increase regularly with increasing the MeSO content of the solutions, it is similar to that obtained for pyridinium cations (J. C. Hallé, unpublished results). This similarity was to be expected since both deprotonations of imidazolium and pyridinium cations involve the same type of nitrogen atom.


REFERENCES
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