At lower cell operating potentials, it seems to be reasonable to assume, with considerably diminished positive potentials at the ethylene electrode, that hydrogen or deuterium ions discharge to give atoms. The reaction system then more nearly resembles a conventional heterogeneous catalytic chemical system.[3,4]

It is difficult to compare the results of other workers in systems similar to ours. In one instance surface adsorption of ethylene was studied in an aqueous sulfuric acid solution[24] where sulfuric acid surface-catalyzed olefin addition reactions might take place and where olefin might exist in a semihydrogenated state at the electrode surface. We also do not find that acetylene and ethylene are equivalent in our cells, as has been observed at bright platinum electrodes at lower ethylene partial pressures[25] than those used here. Actually, acetylene either poisons or reduces electrode performance significantly under our experimental conditions.[1b]

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Electrostatic and Resonance-Energy Effects in Proton Ionization from Pyridinecarboxylic and Anilinesulfonic Acids

L. D. Hansen,*[1a] E. A. Lewis,[1a] J. J. Christensen,[1b] R. M. Izatt,[1b] and D. P. Wrathall[1b]

Contribution from the Department of Chemistry,
University of New Mexico, Albuquerque, New Mexico 87106,
and the Departments of Chemical Engineering and Chemistry and
Contribution No. 8 from the Center for Thermochemical Studies,
Brigham Young University, Provo, Utah 84601. *Received June 15, 1970*

Abstract: For proton-transfer reactions of the type $AH^+ + A\text{–}X^- \rightarrow A + {}^+HA\text{–}X^-$, where A is pyridine or aniline and X^- is carboxylate or sulfonate, respectively, the entropy change is found to result largely from electrostatic effects. The enthalpy change is a result of both electrostatic and resonance effects, and the magnitudes of these effects are calculated.

The pK, $\Delta H°$, and $\Delta S°$ values for proton ionization from the protonated nitrogen in anilinesulfonic and pyridinecarboxylic acids would be expected to differ from the corresponding values for proton ionization from aniline and pyridine, respectively, for three reasons: (a) the charge on the sulfonate or carboxylate group will exert an electrostatic-field effect on the ionizing proton, (b) the presence of a sulfonate or carboxylate group should increase the resonance stabilization of the anion over that of the zwitterion, and (c) the presence of the substituent will affect the specific hydration around the ionizing group. It is the purpose of this paper to evaluate the effects of each of these factors on the $\Delta H°$ and $\Delta S°$ values for proton ionization from the above acids.

The anilinesulfonic and pyridinecarboxylic acids were chosen as a model system for three reasons: (a) accurate pK, $\Delta H°$, and $\Delta S°$ values are available in the literature for the proton ionization reactions,[2–5] (b) the molecules are rigid and of known geometry, and (c) there are three isomers (*i.e.*, ortho, meta, and para) available in each case.

Data

The thermodynamic data used in this study for proton ionization from the 2-, 3-, and 4-pyridinecarboxylic acids, the 2-, 3-, and 4-anilinesulfonic acids, pyridine, and aniline were taken from ref 2a.

The data given in ref 2a for the pyridinecarboxylic acids must be corrected for the presence of microspecies in order to obtain the true values of the thermodynamic quantities for proton ionization from the protonated nitrogen.[6] The microconstants (k_n), microenthalpies (Δh_n), K_z, and the relationships among these quantities are shown in Figure 1. The K_z values used in the

Table I. Microconstant, Microenthalpy Change, and Microentropy Change Values for 2-, 3-, and 4-Pyridinecarboxylic Acids

Acid	$K_z{}^a$	pk_3	Δh_3, kcal/mol	Δs_3, cal/(mol deg)
2-Pyridinecarboxylic acid	0.07	5.29	2.48	−15.9
3-Pyridinecarboxylic acid	0.16	4.75	3.08	−11.4
4-Pyridinecarboxylic acid	0.05	4.84	3.16	−11.5

[a] The K_z values given are the average of independently determined values given in P. O. Lumme, *Suom. Kemistilehti B*, **30**, 168 (1957), and R. W. Greenwood and K. H. Tong, *J. Amer. Chem. Soc.*, **78**, 4896 (1956).

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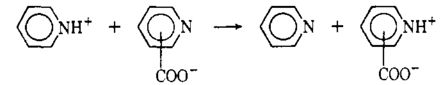
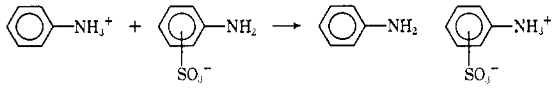
Table II. Electrostatic ΔS and ΔH Values Compared to Experimental $\Delta S°$ and $\Delta H°$ Values for Pyridinecarboxylic and Anilinesulfonic Acids

Substituent position	$\Delta S°$, cal/(deg mol)	ΔS_{elect}, cal/(deg mol)	ΔH_{elect}, kcal/mol	$\Delta H°$, kcal/mol	ϵ_{eff}[a]	$(\partial \ln \epsilon_{eff}/\partial T)_P$[b] $\times 10^4$	r, Å[c]	ζ_0[d]	f_1	f_2
										
2	8.7	10.3	−3.86	2.44	14.8	−14.9	3.23	0.96	0.1283	0.8687
3	4.2	3.7	−0.55	1.84	35.8	−22.2	5.59	0.96	0.0405	0.7922
4	4.3	2.8	−0.31	1.76	44.7	−24.9	6.45	0.96	0.0290	0.7573
										
2	6.2	7.1	−1.50	4.77	25.1	−19.6	3.64	0.79	0.0645	0.9035
3	3.4	2.8	−0.08	2.18	57.4	−30.2	6.30	0.79	0.0167	0.7857
4	3.0	2.2	−0.00	2.74	69.2	−33.4	7.27	0.79	0.0112	0.7488

[a] ϵ_{eff} was calculated using eq 4 and the f_1 and f_2 values. Values of ϵ_i and ϵ_w were taken to be 2.27 and 78.5, respectively. [b] Values of $(\partial \ln \epsilon_i/\partial T)_P$ and $(\partial \ln \epsilon_w/\partial T)_P$ were taken to be -8.8×10^{-4} and -4.6×10^{-3} deg^{-1}, respectively (see eq 5). [c] r is the substituent charge-to-proton distance. The substituent charge was considered to be a point charge at the midpoint of a line joining the carboxylate oxygens or at the center and in the plane of the triangle formed by the sulfonate oxygens. Bond lengths and angles were taken from R. C. Weast, Ed., "Handbook of Chemistry and Physics," 46th ed, Chemical Rubber Co., Cleveland, Ohio, 1965, pp F118–F121. [d] ζ_0 is defined in ref 8, and is a parameter defining the boundary of the oblate ellipsoidal molecular cavity. The molecular cavity volume, τ, was taken to be 260 Å^3 for all molecules.

calculations, together with the calculated values of the microconstants (pk_3), microenthalpy changes (Δh_3), and microentropy changes (Δs_3) for proton ionization from the nitrogen in pyridinecarboxylic acid, are listed in Table I. Since the corrections for microspecies are relatively small, these calculations do not constitute a source of appreciable error.

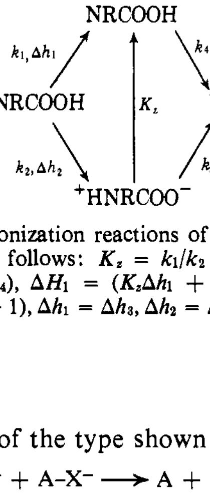


Figure 1. Proton ionization reactions of pyridinecarboxylic acid. Relationships are as follows: $K_z = k_1/k_2 = k_3/k_4$, $K_1 = k_1 + k_2$, $K_2 = k_3k_4/(k_3 + k_4)$, $\Delta H_1 = (K_z\Delta h_1 + \Delta h_2)/(K_z + 1)$, $\Delta H_2 = (K_z\Delta h_4 + \Delta h_3)/(K_z + 1)$, $\Delta h_1 = \Delta h_3$, $\Delta h_2 = \Delta h_4$.

Theory

For reactions of the type shown in eq 1, the electrostatic contribution to $\Delta S°$ (ΔS_{elect}) and $\Delta H°$ (ΔH_{elect}) can be calculated from molecular parameters and physical constants as shown in eq 2 and 3,[7] where

$$\mathrm{AH^+ + A\text{-}X^- \longrightarrow A + {}^+HA\text{-}X^-} \qquad (1)$$

$$\Delta S_{elect} = \frac{-Ne^2}{r\epsilon_{eff}}\left(\frac{\partial \ln \epsilon_{eff}}{\partial T}\right)_P \qquad (2)$$

$$\Delta H_{elect} = \frac{-Ne^2}{r\epsilon_{eff}}\left[1 + T\left(\frac{\partial \ln \epsilon_{eff}}{\partial T}\right)_P\right] \qquad (3)$$

N is Avogadro's number, e is the charge on an electron, r is the substituent charge-to-proton distance, ϵ_{eff} is the effective dielectric constant, T is temperature, and P is pressure.

The values of ϵ_{eff} for charge–charge interactions in an oblate ellipsoidal cavity which is appropriate for benzenoid-type compounds can be calculated from eq 4,[8] where f_1 and f_2 are functions of the size (τ) and shape of the molecular cavity as defined in ref 8, ϵ_i is the internal dielectric constant of the cavity, and ϵ_w is the dielectric constant of the solvent water. The $(\partial \ln \epsilon_{eff}/\partial T)_P$ term can be evaluated from eq 5, which was derived from eq 4.

$$1/\epsilon_{eff} = f_1/\epsilon_i + f_2/\epsilon_w \qquad (4)$$

$$\left(\frac{\partial \ln \epsilon_{eff}}{\partial T}\right)_P = \frac{f_1\epsilon_{eff}}{\epsilon_i}\left(\frac{\partial \ln \epsilon_i}{\partial T}\right)_P + \frac{f_2\epsilon_{eff}}{\epsilon_w}\left(\frac{\partial \ln \epsilon_w}{\partial T}\right)_P \qquad (5)$$

Calculations

For the specific cases of proton exchange between the nitrogen atoms in pyridinecarboxylic acid and pyridine and between anilinesulfonic acid and aniline (eq 1), the proper selection of values for ϵ, r, and τ allows the calculation of the parameters in eq 2–5 and therefore the calculation of values of ΔS_{elect} and ΔH_{elect}. The ϵ_i and $(\partial \ln \epsilon_i/\partial T)_P$ values were set equal to the corresponding values for liquid benzene at 25°, and the values of τ and r can be established from various measurements.[8]

Calculated values of ΔS_{elect} and ΔH_{elect}, together with the values of the parameters used in the calculations, are given in Table II.

The calculated values are more sensitive to the choice of the value for r than for any of the other variables. The relative error in ΔS_{elect} is approximately twice the relative error in r for the 2 isomers, approximately 1.5 times for the 3 isomers, and approximately the same for the 4 isomers. The other relative errors in ΔS_{elect} are about one-half the relative error in the value of τ and equal to the relative error in the reciprocal of ϵ. The uncertainty in the ΔS_{elect} values from all sources is estimated to be less than 1 cal/(mol deg). The calculated values of ΔH_{elect} are much more sensitive to

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(7) E. J. King, "Acid-Base Equilibria," Macmillan, New York, N. Y., 1965, pp 204 ff.

(8) J. N. Sarmousakis, *J. Chem. Phys.*, **12**, 277 (1944).

errors in the values of the parameters used primarily because of the $[1 + T(\partial \ln \epsilon_{eff}/\partial T)]$ term in eq 3. The total uncertainty in the ΔH_{elect} values is estimated to be less than 1 kcal/mol for the 2 isomers and less than 0.5 kcal/mol for the 3 and 4 isomers.

It should be pointed out that errors in the calculated values of ΔS_{elect} and ΔH_{elect} resulting from errors in the parameters used in the calculations are most likely systematic within a given series of compounds. Thus the trends in the calculated values with substituent position are more certain than are the absolute values.

Discussion

The agreement between the $\Delta S°$ and ΔS_{elect} values for the anilinesulfonic and pyridinecarboxylic acids indicates that the $\Delta S°$ values for the reactions in Table II result largely from electrostatic interactions and also that the parameters used to calculate ΔS_{elect} were good approximations. Hence, ΔH_{elect} values for the pyridinecarboxylic and anilinesulfonic acids calculated using the same parameters would be expected to closely approximate the electrostatic part of $\Delta H°$.

It is apparent from the difference between the $\Delta H°$ and ΔH_{elect} values in Table II that $\Delta H°$ also contains a large nonelectrostatic contribution. This nonelectrostatic term probably results from the greater resonance stabilization of the anion than of the zwitterion, and in the case of the 2-substituted molecules also from intramolecular hydrogen bonding (specific hydration). These conclusions could possibly be tested by making molecular orbital calculations of the relative resonance energies of the anion and zwitterion forms of the pyridinecarboxylic and anilinesulfonic acids. Such calculations are beyond the scope of the present work. It was impossible from the calculations done here to determine the relative effects of resonance stabilization and specific hydration.

The results of this study may be compared with those of a similar, earlier study by Hepler.[9] In that study, $\Delta H°$ values for reactions of the type shown in eq 1 (except that X was uncharged and hence the reactions were isoionic), where A was phenolate and X was nitro or chloro, were divided into two components, ΔH_{int}, which results from resonance and inductive effects, and ΔH_{ext}, which results from solute–solvent interactions. If the ΔH_{elect} values were subtracted from the $\Delta H°$ values reported in this paper, a quantity $(\Delta H° - \Delta H_{elect})$ very similar in meaning to ΔH_{int} would be obtained. Further, Hepler concluded that $\Delta S°$ values for this type of reaction (eq 1) result solely from external effects. This conclusion agrees with the results of this study if external effects on $\Delta S°$ are equated to electrostatic effects on $\Delta S°$ (*i.e.*, $\Delta S_{elect} = \Delta S_{ext}$).

Hepler's[9] analysis is based on Pitzer's[10] observation that the internal entropy for an acid and its conjugate base is nearly constant for isoionic reactions. However, for the reactions considered in this paper the internal electrostatic interaction in the zwitterion would be expected to have some effect on the vibrational and rotational states of the X^- group, *i.e.*, through both resonance effects and charge–charge interactions. A 2-kcal/mol barrier height at room temperature would decrease the entropy of a free rotor by about 1 cal/(mol deg).[11] Although this effect is probably within the uncertainty in the calculation of ΔS_{elect}, it may account for the trend in the $\Delta S° - \Delta S_{elect}$ values since the effect would probably decrease in going through the series from the 2 to the 4 isomer.

Although the compounds included in this study and those studied by Hepler are not the same, the similarities are strong enough to allow a general comparison to be made between the $\Delta H° - \Delta H_{elect}$ and ΔH_{int} values. There is general agreement between ΔH_{int} values calculated by Hepler[9] and $\Delta H° - \Delta H_{elect}$ values in this study as to sign, magnitude, and trend with substituent position.

The major difference between the model used in this study and the model used by Hepler[9] is the relation between ΔH_{ext} (or ΔH_{elect} as defined in this study) and $\Delta S°$ (eq 6). Hepler chose a linear relation with $\beta = 280°$ (valid only for isoionic reactions), while in this

$$\Delta H_{elect} = \Delta H_{ext} = \beta \Delta S° \qquad (6)$$

study a nonlinear relation with $\beta = [1 + T(\partial \ln \epsilon_{eff}/\partial T)]/(\partial \ln \epsilon_{eff}/\partial T)$ was chosen. Further work is now being done in order to determine the suitability of these different models.

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[9] L. G. Hepler, *J. Amer. Chem. Soc.*, **85**, 3089 (1963).

[10] K. S. Pitzer, *ibid.*, **59**, 2365 (1937).

[11] G. N. Lewis and M. Randall, "Thermodynamics," 2nd ed, McGraw-Hill, New York, N. Y., 1961, Table 27–13, p 446.