Solvent effects on the reaction of carbanions with Ellman's reagent suggest a transition state in which the solvation of the carbanion is product-like. If proton transfer also occurs through a product-like transition state with respect to solvation, the prediction may be made that in the reverse direction (proton transfer from carbon acid to acetate anion), the solvent effect should be relatively independent of the structure of the carbon acid. Cox and Gibson[34] have measured the rate constants for proton transfer from 2-nitropropane, nitroethane, and 2-methyl ethylacetoacetate to acetate anion as a function of increasing mole fraction Me_2SO. Although the maximum mole fraction of Me_2SO was only 0.4 in their experiments, the observed effects on the rate constants are virtually independent of the structure of the carbon acid. In this direction, the solvent effect (a rate increase of 10^2 at 0.4 mole fraction Me_2SO) would seem to be primarily due to desolvation of acetate anion in the transition state.

The above observations are consistent with a transition-state structure for proton transfer to and from carbon in which the delocalized negative charge on the carbanion and acetate anion is less highly solvated than either the carbanion or acetate anion ground state. In the direction of proton transfer from acetic acid to a carbanion, the solvation of the carbanion would be product-like while the solvation of the acetic acid would be reactant-like. The relative differences in ground-state and transition-state solvations are more than adequate to account for the large increases in rate observed for both proton-transfer and nucleophilic reactions of carbanions on changing the medium from water to Me_2SO.

It has recently been shown that the rate constants for proton transfer from 1-arylnitromethanes to benzoate anion, and the reverse reaction, increase by approximately 10^5 on changing the medium from water to Me_2SO.[35] However, even this large rate acceleration is not enough to increase the rate constants for proton transfer to anywhere near the diffusion-controlled limit. The continued existence of slow proton transfers to and from carbon in Me_2SO could also result from changes in solvation required to reach the transition state. Carbanions are still highly solvated in Me_2SO (compared to the gas phase), the extent of solvation is dependent on carbanion structure, and solvation may be very different between the ground state and transition state.

A large portion of the nitroalkane anomaly in aqueous solution can be accounted for with a transition-state structure in which both the proton donor and acceptor are significantly desolvated in comparison to their anionic ground states. It is possible that the total nitroalkane anomaly could be accounted for by solvation phenomena; however, at the present time it is difficult to assess the contribution of hydrogen bonding between the carbanion and proton donor and the contribution of heavy-atom reorganization to the energy barrier for proton transfer to and from carbon.

Acid–Base Kinetics of Pyridine Studied with a Slow Spectrophotometric Indicator in Methanol

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Abstract: The protonation–deprotonation kinetics of pyridine in methanol has been studied by the electric field jump technique. Kinetic measurements of the electric field insensitive equilibrium $B + H^+ (k_1) \rightleftarrows BH^+ (k_{-1})$, where B denotes pyridine, were obtained by coupling the equilibrium with a field-sensitive, visibly colored indicator equilibrium. Use of the "slow" indicator 2,2′,4,4′,6,6′-hexanitrodiphenylamine allowed observation of the slower of the two relaxation times of the coupled system in a time range where measurements could be made with sufficient precision for a reliable extraction of the rate constants k_1 and k_{-1} from the data. The values obtained are $k_1 = 1.57 \pm 0.32 \times 10^{10}$ dm^3 mol^{-1} s^{-1} and $k_{-1} = 8.43 \pm 1.69 \times 10^4$ s^{-1}. The value for k_1 is within the expected limits for a diffusion-controlled reaction in this solvent. An ionic reaction radius of 3.9 Å is calculated from the protonation rate constant value, which indicates that the neutral species involved is probably a hydrogen-bonded pyridine–methanol complex rather than free pyridine. The value for k_{-1} is 1 order of magnitude greater than the constant for methyl-substituted pyridines, reflecting unsubstituted pyridine's lower basicity in methanol.

Introduction

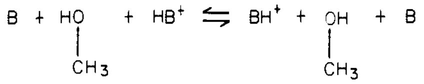
A nuclear magnetic resonance study[1] of proton exchange of ortho and para methyl-substituted pyridinium ions in methanol has revealed that the protonation rates of the bases are very fast with rate constants comparable to the values expected for a diffusion-controlled process in all cases. In this study Cocivera found no appreciable steric effect of ortho methyl substituents on the rates of protonation and deprotonation at the nitrogen atom. It is still in doubt,[2] however, whether the proton transfer involves the free amine B

$$B + CH_3OH_2^+ \rightleftharpoons BH^+ + CH_3OH \tag{1}$$

or a hydrogen-bonded complex

$$B{\cdot}HOCH_3 + CH_3OH_2^+ \rightleftharpoons BH^+{\cdot}O(H)CH_3 + CH_3OH \tag{2}$$

Steric effects are expected to play a significant role in reaction 1 but not in (2). On the other hand the reaction distances of 1.9–3.0 Å calculated from the NMR results are small for reaction 2 where the proton motion in the hydrogen bond is triggered by the more distant protonation of the methanol molecule. The analysis of NMR rate data is complicated by the symmetrical proton exchange[1,3]



$$\mathrm{B} + \underset{\mathrm{CH_3}}{\mathrm{HO}} + \mathrm{HB^+} \rightleftharpoons \mathrm{BH^+} + \underset{\mathrm{CH_3}}{\mathrm{OH}} + \mathrm{B} \tag{3}$$

and by the large salt effects in ionic systems of high concentration.[1,2] Relaxation kinetics is free of these complications because reaction 3 does not contribute to the observed rate and the reactant concentrations are low. We describe here an electric field jump

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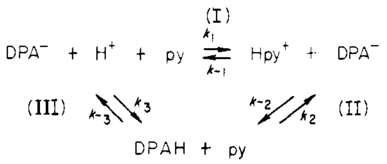
0002-7863/80/1502-7065$01.00/0

Table I

	$10^5 C_0$/mol·dm^{-3}			$10^5 A$/mol·dm^{-3}					
soln no.	DPAH	py	HCl	DPAH	py	DPA$^-$	pyH$^+$	H$^+$	$10^{-5} \times \tau_{\text{exptl}}^{-1}$/s^{-1}
1	5.58	9.39	17.8	3.71	0.448	1.76	8.41	10.1	3.74
2	3.72	6.26	5.55	1.26	1.02	2.365	5.04	2.66	2.42
3	2.60_5	9.39	14.4	1.455	0.684	1.09	8.25	6.47	3.45
4	8.84	3.45		3.07	0.544	5.585	2.81	2.77	3.29
5	8.84	1.725		3.61	0.217	5.07	1.46	3.61	3.40
6	4.42	3.45		0.812	1.06	3.00	2.331	1.18	1.97
7	4.42	1.725		1.16	0.378	3.18	1.314	1.87	2.34

Scheme I



study of the protonation–deprotonation kinetics of the parent compound pyridine. The rate constants obtained are in reasonable agreement with those obtained by NMR for the methyl-substituted pyridines.[1] The protonation reaction was found to be a diffusion-controlled process, while the deprotonation rate is 1 order of magnitude faster than that for the methyl-substituted pyridines, reflecting unsubstituted pyridine's lower basicity in methanol.

Chemical relaxation methods, in general, require the perturbation of a chemical equilibrium by rapidly changing some experimental parameter such as temperature, pressure, or electric field followed by observation of the chemical system as it responds to the new conditions. The size of the chemical response or relaxation effect depends upon the sensitivity of the chemical equilibrium to changes in the experimental parameters. For example, in the temperature-jump (T-jump) technique, the equilibrium to be studied must be temperature dependent ($\Delta H \neq 0$) for a relaxation effect to be observed. However, one may also study equilibria with $\Delta H \approx 0$ by coupling them with equilibria that have a large temperature dependence. This principle is used[4] to study acid–base reactions with ΔH near zero by adding to the system a buffer whose acid–base equilibrium has a large ΔH.

We have employed the electric field analogue of this principle to study the protonation–deprotonation kinetics of pyridine, which according to 1 or 2 may be represented as in eq 4. The electric

$$CH_3OH_2^+ + py \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Hpy^+ + CH_3OH \qquad (4)$$

moments of $CH_3OH_2^+$ (hereinafter abbreviated as H$^+$) and pyH$^+$ are assumed to be roughly similar; therefore direct measurement of the dynamics of equilibrium 3 via the E-jump technique would be expected to be difficult, if not impossible.[5] However, coupling (3) to field-dependent equilibria results in a coupled system with a measurable relaxation amplitude. The resulting system is shown in Scheme I, where DPAH refers to the indicator 2,2′,4,4′,6,6′-hexanitrodiphenylamine (dipicrylamine).

Another experimental difficulty with spectrophotometric[6] E-jump is the decreasing signal to noise ratio at faster oscilloscope scan rates.[7] However, the indicator dipicrylamine is a "slow" indicator in methanol due to steric hindrance of the proton in the protonation reaction of the indicator anion.[8] Use of this indicator allows observation of the second, slower relaxation time of the coupled system, in a time range that is easily and accurately accessible by our equipment. The relaxation time of (III) is still close enough to that of (I), however, that k_1 and k_{-1} enter explicitly into the expression for the second relaxation time. (If (I) equilibrated much faster than (III), the second relaxation time would measure only the equilibrium constant of (I).[9])

The relaxation amplitude was further enhanced for some of the solutions by increasing the proton concentration via addition of HCl.

Experimental Section

2,2′,4,4′,6,6′-Hexanitrodiphenylamine (dipicrylamine) (Eastman Kodak) decomposes at ~245 °C as reported in the literature. Solutions in Baker absolute methanol (confirmed to have a water content less than 0.05% by weight by a Karl Fischer titration) were prepared by dilution of stock solutions made up by weight.

Pyridine (Amachem Reagent Grade) was stored over neutral alumina before use. Solutions were prepared by dilution of stock solutions prepared by volume not more than 1 week before use. The concentrations of the stock solutions were checked spectrophotometrically ($\lambda_{\max} = 256.5$ nm, $\epsilon_{256.5} = 2398$ dm^3·mol^{-1}·cm^{-1}).

Hydrochloric acid solutions were prepared by dilution of stock solutions made up approximately by volume; the exact equilibrium hydrogen ion concentration was determined by calculation from the dipicrylamine anion absorbance for each kinetic solution. All solutions were kinetically monitored at the anion wavelength of 450 nm ($\epsilon_{450} = 25\,000$ dm^3·mol^{-1}·cm^{-1}).[8]

Kinetic Measurements

The electric field jump apparatus with spectrophotometric detection has been described previously.[6] All signals were stored with a Tektronix R7912 transient digitizer. Three to six signals of about 250 data points each were averaged and the resulting data analyzed with a nonlinear least-squares computer program. Four to six such averaged data sets were collected for each experimental solution; the reproducibility of the calculated relaxation time was ±5 to ±10%.

Results and Discussion

The two relaxation times which describe the coupled system are given by

$$\tau_{\text{I}}^{-1} = \tfrac{1}{2}(a_{11} + a_{22}) + \{[\tfrac{1}{2}(a_{11} - a_{22})]^2 + a_{12}a_{21}\}^{1/2} \qquad (5)$$

$$\tau_{\text{II}}^{-1} = \tfrac{1}{2}(a_{11} + a_{22}) - \{[\tfrac{1}{2}(a_{11} - a_{22})]^2 + a_{12}a_{21}\}^{1/2} \qquad (6)$$

where

$$a_{11} = k_{-2}([\text{DPAH}] + [\text{py}]) + k_2([\text{DPAH}^-] + [\text{pyH}^+]) + k_3 + k_{-3}[\text{H}^+]$$

$$a_{12} = k_{-3}[\text{DPA}^-] - k_{-2}[\text{DPAH}] - k_2[\text{DPA}^-]$$

$$a_{21} = k_3 - k_{-1} + k_{-3}[\text{H}^+] - k_1[\text{H}^+]$$

$$a_{22} = k_{-1} + k_1([\text{py}] + [\text{H}^+]) + k_{-3}[\text{DPA}^-]$$

Values of k_3 and k_{-3} for the protonation–deprotonation kinetics of dipicrylamine in methanol at 25 °C are 2.28×10^9 dm^3·mol^{-1}·s^{-1} and 1.31×10^5 s^{-1}, respectively.[8] With $k_{-1} = k_1 K^{\text{pyH}^+}{}_{\text{A}}$ and $k_{-2} = k_2 K^{\text{pyH}}{}_{\text{A}}/K^{\text{pyH}^+}{}_{\text{A}}$ and with use of the thermodynamic acid dis-

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(4) Bernasconi, C. F. "Relaxation Kinetics"; Academic Press: New York, 1976, p 102.

(5) Metal ion hydrolyses in aqueous solution, $M^{n+}(aq) = MOH^{(n-1)+}(aq) + H^+(aq)$, are, for example, much easier to investigate by the E-jump technique, even though there is also no change in net formal charge as reaction proceeds, because two product ions replace one reactant ion and one of the two product ions, hydronium, has a uniquely high mobility.

(6) Olsen, S. L.; Holmes, L. P.; Eyring, E. M. *Rev. Sci. Instrum.* **1974**, *45*, 859–861.

(7) Reference 4, p 192.

(8) Strohbusch, F.; Marshall, D. B.; Vazquez, F. A.; Cummings, A. L.; Erying, E. M. *J. Chem. Soc., Faraday Trans.* 1 **1979**, *75*, 2137–2142.

(9) Reference 4, p 61.

sociation constant values of $K^{\mathrm{DPAH}}{}_{\mathrm{A}} = 5.42 \times 10^{-5}$[5] and $K^{\mathrm{pyH^+}}{}_{\mathrm{A}} = 5.37 \times 10^{-6}\ \mathrm{dm^3 \cdot mol^{-1}}$,[10] the two unknowns are k_1 and k_2.

Activity coefficients, f, calculated from the Debye–Hückel limiting law were used in the equilibrium calculations for the ionic species. Changes in ionic strength due to relaxation were negligibly small[11] so $k_{-3} = k_{-3}{}^{\circ}f^2$ and k_2 was calculated as $k_2 = k_2{}^{\circ}f^2$, but higher order activity corrections were neglected. The experimental activities and relaxation times are summarized in Table I.

It has been shown recently that small amounts (0.1–0.3%) of water can significantly alter conductivities and stability constants of acids in alcohol solutions.[12] However, no systematic deviations of decay times from those reported in Table I are detectable when a sample solution is deliberately made 0.1% and then 1.0% by weight water. This chemical system should be comparatively insensitive to perturbations by water since the rate of protonation of the dipicrylamine anion is limited not by rotation of protonated solvent molecules but rather by steric interference of nitro groups on the anion.[8,13]

The equations for τ_{I}^{-1} and τ_{II}^{-1} were programmed on an LSI-11 computer. The values for k_1 and k_2 were iteratively incremented, calculating $\tau_{\mathrm{theory}} - \tau_{\mathrm{exptl}}$ for each solution. Final values of k_1 and k_2 were obtained at the minimum in the standard deviation. Solution no. 6 was discarded in the final calculations for reasons discussed below.

Two adverse conditions can arise in a chemical system of this kind. First, one may have observed τ_{I}^{-1} instead of τ_{II}^{-1} in all or some of the solutions. However, the standard deviation obtained when the data are fitted to eq 5 is in all cases much higher than that obtained for eq 6 for individual solutions and combinations of solutions. Furthermore, the rate constants obtained are physically meaningless, k_1 being several orders of magnitude above the theoretically highest possible value for a diffusion-controlled reaction. Second, one may have observed a mixture of τ_{I} and τ_{II}, if τ_{I} is close to τ_{II} in value. Two independent facts rule out this possibility as well: the decay time in each case was calculated repeatedly from each set of data, shifting the data window by two points each time. No systematic deviation was observed in the calculated τ value.[14] In addition, reaction capacity factors (which are proportional to the amplitudes) and amplitude ratios of the two normal modes were calculated by using the formalism described by Purdie et al.[15] In all cases except no. 6, the ratio of amplitude II to amplitude I was greater than 8. The reaction capacity factor of the first normal mode was also largest for no. 6. Solution no. 6 was therefore not used in the final calculation of the rate constants. The values obtained for k_1 and k_2 were as follows: $k_1 = (1.57 \pm 0.32) \times 10^{10}\ \mathrm{dm^3 \cdot mol^{-1} \cdot s^{-1}}$ and $k_2 = (1.71 \pm 0.34) \times 10^8\ \mathrm{s^{-1}}$, giving $k_{-1} = k_1 K^{\mathrm{pyH^+}}{}_{\mathrm{A}} = (8.43 \pm 1.69) \times 10^4\ \mathrm{dm^3 \cdot mol^{-1} \cdot s^{-1}}$ and $k_{-2} = k_2 K^{\mathrm{DPAH}}{}_{\mathrm{A}}/K^{\mathrm{pyH^+}}{}_{\mathrm{A}} = (1.72 \pm 0.34) \times 10^9\ \mathrm{dm^3 \cdot mol^{-1} \cdot s^{-1}}$. From the rate constant k_1 of the diffusion-controlled protonation of pyridine a reaction distance of 3.9 Å is calculated. This is larger than those of the methyl-substituted pyridines. If the requirement for proper orientation of the reactants[9] is taken into account, the agreement is in this case better with the mechanism of 5 than with that of eq 6. The deprotonation rate constant is 1 order of magnitude higher than those determined by Cocivera for methyl-substituted pyridines,[1] reflecting the lower basicity of unsubstituted pyridine in methanol.

Acknowledgment. F.S. gratefully acknowledges financial support by the Duetsche Forschungsgemeinschaft. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This work was also funded by a grant from the University of Utah Research Committee.

Supplementary Material Available: Details of the reaction capacity factor and amplitude ratio calculation (9 pages) are available. Ordering information is given on any current masthead page.

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Photoreduction of Hemin in Alcohol-Containing Mixed Solvents

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Received October 29, 1979

Abstract: The photochemical behavior of chlorohemin, iron(III) protoporphyrin IX chloride, in deaerated aqueous solutions containing 18% v/v pyridine and varying types and concentrations of alcohols has been investigated. When the alcoholic component of the solvent was methanol, ethanol, or 2-propanol, ultraviolet irradiation caused the reduction of the Fe(III) complex to bis(pyridine)(protoporphyrin IX)iron(II). When the alcohol was *tert*-butyl alcohol, no photoreduction was observed upon continuous irradiation. The study of the dependence of quantum yields on irradiation wavelength, pH, and alcohol concentration, as well as flash photolysis experiments, led to formulation of a photoreduction mechanism involving photochemical electron transfer from the alcohol to the Fe(III) center (with or without intervening ·OH radicals), followed by secondary reactions of the alcohol-derived radicals.

Introduction

Owing to their biological importance metalloporphyrin complexes have been widely studied.[1,2] In particular, considerable attention has been given to their redox activity because of the role played by these compounds in biological systems as electron carriers. As far as the photochemical behavior of metalloporphyrins is concerned, the greatest interest has been devoted to the magnesium porphyrins in connection with the photosyntetic processes,[3] however, in recent years some metalloporphyrin com-

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