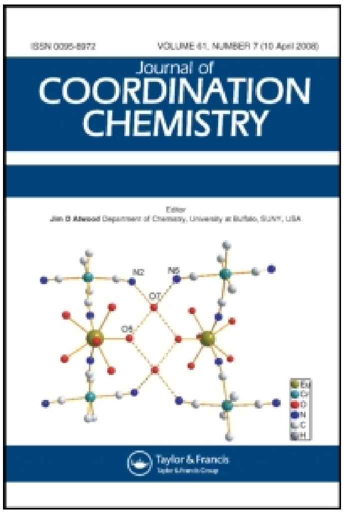

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THE EFFECT OF CHANGES IN WATER STRUCTURE ON THE KINETICS OF PIPERIDINE REPLACEMENT AT THE PENTACYANO (PIPERIDINE) FERRATE (II) COMPLEX IN ACETONITRILE-WATER-SODIUM CHLORIDE MIXTURES

Graciela C. Pedrosa[a]; Julio A. Salas[a]; Miguel Katz[a]; Nestor E. Katz[b]
[a] Cdtedra de Físico-Química, Universidad National de Tucumdn, S.M. de Tucumdn, Argentina [b] Cdtedra de Físico-Química III, Universidad National de Tucumdn, S.M. de Tucumdn, Argentina

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THE EFFECT OF CHANGES IN WATER STRUCTURE ON THE KINETICS OF PIPERIDINE REPLACEMENT AT THE PENTACYANO (PIPERIDINE) FERRATE (II) COMPLEX IN ACETONITRILE-WATER-SODIUM CHLORIDE MIXTURES

GRACIELA C. PEDROSA, JULIO A. SALAS, MIGUEL KATZ
Cátedra de Físico-Química, Universidad Nacional de Tucumán, Avda. Independencia 1800, (4000) S.M. de Tucumán, Argentina.

and NÉSTOR E. KATZ†
Cátedra de Físico-Química III, Universidad Nacional de Tucumán, Ayacucho 491, (4000) S.M. de Tucumán, Argentina.

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The kinetics of piperidine replacement by pyridine at the pentacyano(piperidine) ferrate (II) complex has been investigated under pseudo-first-order conditions in acetonitrile + water mixtures from a mole fraction of acetonitrile $x_2 = 0$ to $x_2 = 0.122$ at constant ionic strength ($I = 1$ mol dm^{-3}, NaCl). The rate constants at 25, 30 and 35° increase on addition of acetonitrile. Transition state solvation predominates over initial state solvation on account of more enhanced releasing ligand-bulk solvent interactions which occur when the mechanism is of a dissociative type. The greater hydrophobic nature of the transition state is indicated by a negative correlation between the difference in activation free energies ($\delta_m \Delta G^{\ddagger}$) and the excess free energy for the solvent mixture (G^E). Thus, when the aqueous mixture becomes richer in acetonitrile, the transition state is stabilized and the rate constant increases. The enthalpies and entropies of activation seem to show inflection points at $x_2 \cong 0.04$, in correspondence with the discontinuity observed in that region for the physical properties of water + acetonitrile mixtures. A correlation between the difference in activation enthalpies ($\delta_m \Delta H^{\ddagger}$) and excess enthalpy of mixing (H^E) points to the fact that solvent structural effects control the kinetics of ligand substitution.

INTRODUCTION

Several reports[1,2] on the kinetics of ligand substitution processes in aqueous binary mixtures have demonstrated that modifications in water structure by added co-solvent are reflected in kinetic parameters. When analysing the influence of solvent dielectric properties on the rates of dissociative solvolysis of metal complexes in water + co-solvent mixtures, structural effects must be included to explain observed deviations from the linear relationship between the logarithm of the rate constant and the reciprocal of the bulk dielectric constant.[3]

Recent studies[4] on the kinetics of ligand replacements at pentacyano (ligand) ferrate (II) complexes have shown the operation of solvation effects in pure water. The reaction of pentacyano (3, 5-dimethylpyridine) ferrate (II) with cyanide ion was investigated in some binary aqueous mixtures,[5] and a low sensitivity of the rate with solvent composition was found. In order to obtain more pertinent information about the influence of solvent structural changes on the kinetics of ligand substitutions, we report in this work

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† To whom correspondence should be addressed.

the kinetic parameters for the dissociation of piperidine from the pentacyano (piperidine) ferrate (II) ion in water + acetonitrile mixtures. The possible swamping out of solvation effects by strong π-backbonding is cancelled here because of the aliphatic nature of the leaving ligand. On the other hand, acetonitrile interacts weakly with water[6] so that solvent-solvent interactions are not expected to prevail over solute-solvent interactions.

EXPERIMENTAL

The pentacyano (piperidine) ferrate (II) complex, $[Fe(CN)_5pip]^{3-}$, was prepared in aqueous solution by adding excess piperidine (Fluka *pro analysi*) to $Na_3[Fe(CN)_5NH_3] \cdot 3H_2O$ (prepared as in ref. 7). The values of λ_{max} and ϵ_{max} obtained from visible spectra agree with already published values.[4a]

The kinetics of the reaction

$$[Fe(CN)_5pip]^{3-} + py \longrightarrow [Fe(CN)_5py]^{3-} + pip \qquad (1)$$

were followed under pseudo-first-order conditions by measuring the increase in absorbance at 365 nm (maximum of the $[Fe(CN)_5py]^{3-}$ complex[8]) with a Spekol ZV EK5 visible spectrophotometer provided with thermostatted cells. Temperatures were measured to within 0.1 K. Final concentrations were [complex] = 2×10^{-4} mol dm^{-3}, [pip] = 3×10^{-2} mol dm^{-3}, and [py] = 1 mol dm^{-3}. Ionic strength was maintained at 1 mol dm^{-3} with NaCl. Acetonitrile (Merck *pro analysi*) was added from a mole fraction $x_2 = 0$ to $x_2 = 0.122$. Duplicate or triplicate runs were made at each mole fraction and temperature. Guggenheim's method[9] was applied to evaluate the rate constants, which were reproducible to ±3%. Eyring's equation and a least-squares method were used to calculate the enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation at each mole fraction. Estimated confidence limits in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were ±10 kJ mol^{-1} and ±30 J K^{-1} mol^{-1} respectively (with a 90% probability).

RESULTS

Table I shows the limiting rate constants k_{-L} obtained at different mole fractions of acetonitrile (x_2) and temperatures (T). Reaction (*1*) is known to proceed by a dissociative mechanism (see ref. 4a and references therein), probably I_d (*cf.* ref 10):

$$[Fe(CN)_5L]^{3-} + H_2O \longrightarrow [Fe(CN)_5H_2O]^{3-} + L \qquad (2)$$

$$[Fe(CN)_5H_2O]^{3-} + L' \longrightarrow [Fe(CN)_5L']^{3-} + H_2O \qquad (3)$$

TABLE I

Limiting rate constants k_{-L} for dissociation of piperidine from pentacyano(piperidine) ferrate (II) ion as a function of temperature T and mole fraction of acetonitrile x_2. I = 1 mol dm^{-3} (NaCl).

T = 298.15 K		T = 303.15 K		T = 308.15 K	
x_2	$10^5 k_{-L}(s^{-1})$	x_2	$10^5 k_{-L}(s^{-1})$	x_2	$10^5 k_{-L}(s^{-1})$
0.000	6.2	0.000	12	0.000	20
0.010	7.1	0.010	13	0.010	24
0.055	11	0.055	17	0.055	26
0.122	13	0.122	19	0.122	27

When [L′] $\gg$ [L], the observed rate constant k_{obs} equals k_{-L}, the rate constant for releasing[11] L (piperidine in this study).

The ratio k_x/k_o, where k_x is the rate constant k_{-L} at mole fraction x_2 and k_o is the rate constant k_{-L} in pure water increases on addition of acetonitrile over the whole range of temperatures (see Table I).

In Figure 1, the difference in activation free energies when going from pure water to aqueous acetonitrile, $\delta_m \Delta G^{\ddagger}$ [$= \Delta G^{\ddagger}(x_2) - \Delta G^{\ddagger}(x_2 = 0)$] is plotted against G^E, the excess free energy for the solvent mixture.

Values of $\Delta G^{\ddagger}$ were obtained from the corresponding rate constants (at 298.15 K) while values of G^E were obtained from ref. 2 and interpolated at the mole fractions here considered by a Redlich-Kister form of the type

$$G^E = x_1(1-x_1) \sum_{j=1}^{n} A_j(1-2x_1)^{j-1} \tag{4}$$

A least-squares method was employed for the calculations, which were made on a Radio Shack TRS 80 microcomputer. The optimum number of coefficients A_j was obtained by examining the variation of the standard error of estimate with n (the number of adjustable coefficients).

Figure 2 shows the variation of the activation parameters with x_2. Curve (A) corresponds to the free energies of activation $\Delta G^{\ddagger}$ obtained from the reported rate constants at 298.15 K. Curves (B) and (C) correspond to $\Delta H^{\ddagger}$ and $T\Delta S^{\ddagger}$ respectively.

Figure 3 shows the correlation existing between the difference in activation enthalpies when going from pure water to aqueous acetonitrile, $\delta_m \Delta H^{\ddagger}$ [$= \Delta H^{\ddagger}(x_2) - \Delta H^{\ddagger}(x_2 = 0)$] and H^E, the excess enthalpy of mixing of water + acetonitrile at 298.15 K. These latter values were obtained from ref. 12 and interpolated by an equation similar to (*4*).

DISCUSSION

Due to the dissociative nature of the activation process for reaction (*1*) in aqueous solution, considerable rearrangements of water molecules are expected to take place during the expansion of the releasing species. Previous workers[4] have shown that interactions between leaving ligands and bulk solvent seem to determine the energetics of the activation process in pure water. Therefore, it can be predicted that addition of inert salts or organic co-solvents that modify the structure of water would bring about changes of the

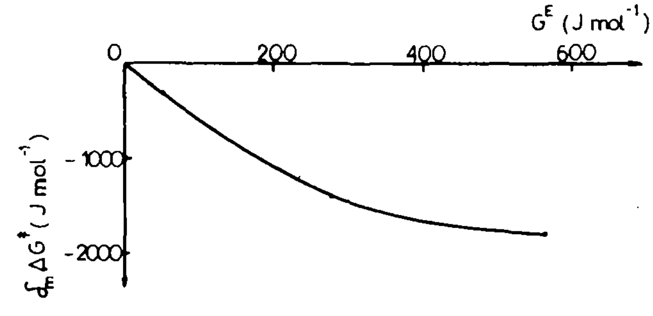

FIGURE 1 Dependence of $\delta_m \Delta G^{\ddagger}$ for the reaction of $[Fe(CN)_5pip]^{3-}$ with py under limiting conditions on G^E, at 298.15 K.

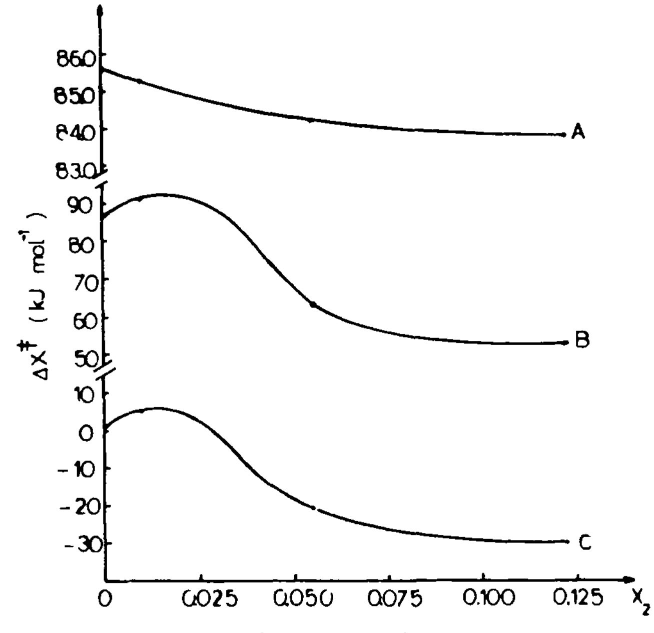

FIGURE 2 Variations in $\Delta G^\ddagger$ (A), $\Delta H^\ddagger$ (B) and $T\Delta S^\ddagger$ (C) for the dissociation of piperidine (from its complex with $[Fe(CN)_5]^{3-}$) with mole fraction of acetonitrile.

activation parameters. Recently,[13] we detected significant variations in the rate constants at 298.15 K for the release of pyrrolidine from pentacyano (pyrrolidine) ferrate (II) when inorganic and alkylammonium salts were added to its aqueous solutions, a result which was adscribed to modifications in water structure.

In this case, NaCl was added to allow comparisons of k_{-L} with similar reactions.[4] Besides, the influence of halide salts on the kinetics is rather slight.[13] Let us consider the

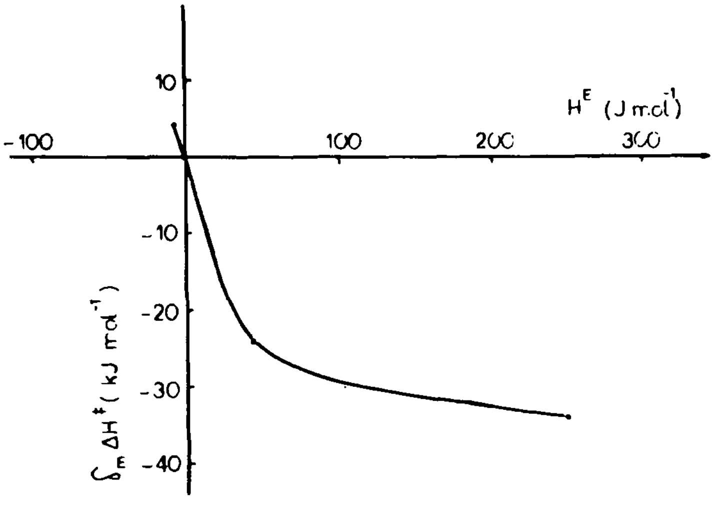

FIGURE 3 Correlation between $\delta_m \Delta H^\ddagger$ for ligand replacement at the $[Fe(CN)_5pip]^{3-}$ complex and H^E (at 298.15 K).

of added co-solvent. The ratio of the rate constants k_x/k_o increases with increasing raction of acetonitrile in the range 25-35°, as shown by Table I. Low sensitivity to composition is observed at 25°: the rate constant increases by a factor of 2 when rom $x_2 = 0$ to $x_2 = 0.122$, in contrast to the high sensitivity observed for solvolysis tyl chloride, as expected because of charge separation on passing to the transition

rate enhancement observed here is small but significant and can be explained if we r first the correlation between $\delta_m \Delta G^\ddagger$ and G^E (see Fig. 1). As already pointed Burgess *et al.*,[2] points falling in the negative $\delta_m \Delta G^\ddagger$ -positive G^E quadrant es that the transition state is more hydrophobic than the initial state. It can be ed that piperidine will expose its hydrophobic methylene groups to bulk solvent Fe-N bond is stretched on activation. We then suggest that the transition state will ilized with increasing mole fraction of acetonitrile because of the decrease in free resulting when small amounts of a "good" solvent to a molecule is added to a solvating medium,[6] and the rate constant will increase consequently. This conclu- rees with the fact that transition state solvation seems to dominate over initial olvation for aquation reactions of anionic complexes in water + co-solvent es.[3]

range of temperatures employed to calculate $\Delta H^\ddagger$ and $\Delta S^\ddagger$ is small enough to ize the effect of variations of solvent structure with temperature (*cf.* ref. 14) but y is not large enough to obtain positive values of $\Delta S^\ddagger$ at every value of x_2, as ed for a dissociative mechanism. We shall therefore discuss trends in activation ters rather than absolute values. It is well known that $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are much ensitive to the environment than $\Delta G^\ddagger$. Figure 2 shows that curves for $\Delta H^\ddagger$ and *vs.* x_2 seem to have inflection points at $x_2 \cong 0.04$ and largely compensate each o give a slowly varying $\Delta G^\ddagger$. The mole fraction $x_2 = 0.04$ corresponds to a discon- in physical properties with solvent composition for aqueous acetonitrile.[15] Some + ligand recombination reactions also show extrema in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ in the same sition range where the physical properties of the solvent mixture exhibit extrema.[1] therefore be deduced that, for the reaction under study, solvent structural effects l the activation parameters in water-rich regions, a phenomenon which is also ed by the correlation existing between $\delta_m \Delta H^\ddagger$ and H^E (see Figure 3). This corre- is the first to be reported, to our knowledge, for substitutions in transition metal xes. In the region $x_2 < 0.04$, $\Delta H^\ddagger$ increases as the solvent becomes "stiffer" 0); *i.e.*, as there are more H-bonds to break. $\Delta H^\ddagger$ decreases at $x_2 > 0.04$ with the ion of water structure[12] ($H^E > 0$). Concomitant variations in $\Delta S^\ddagger$ are observed, a compensation generally associated with solvation effects.[1] The lack of correlation n $\delta_m T\Delta S^\ddagger\ [= T\Delta S^\ddagger(x_2) - T\Delta S^\ddagger(x_2 = 0)]$ and TS^E (S^E being the excess entropy solvent mixture) can be attributed to the fact that H^E and TS^E do not compensate ther. Nonetheless, trends in both H^E and TS^E are reflected in variations in $\Delta H^\ddagger$ $S^\ddagger$ for the dissociation of *N, N*-dimethyl ethylenediamine from its complex with yanoferrate (II) in aqueous methanol.[16] We therefore conclude that solvent proper- responsible for the kinetic effects observed in the release of piperidine from the yano (piperidine) ferrate (II) complex when small fractions of acetonitrile are o solvent water.

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