Initial State and Transition State Contributions to Solvent Effects in the Reaction of 2,2′-Bipyridyl with Nickel(II) in Aqueous Methanol

By Michael J. Blandamer, John Burgess, and Robert Sherry
(Department of Chemistry, University of Leicester, Leicester LE1 7RH)

and Robert I. Haines
(Department of Chemistry, University of Rhode Island, Kingston, Rhode Island, 02881)

Summary Kinetic and thermodynamic results show that the variation with solvent composition of the activation enthalpy for reaction of nickel(II) with 2,2′-bipyridyl in aqueous methanol represents the small difference between large destabilisations both of the nickel(II) and of the transition state (intermediate) as the proportion of methanol increases.

Recently we have been able to separate solvent effects on reactivity trends into initial state and transition state components for a variety of substitution and redox reactions of inorganic species.[1] We now report a similar analysis of enthalpy variations for the reaction of nickel(II) with 2,2′-bipyridyl in aqueous methanol, based on previously established kinetic data[2] and on recently obtained calorimetric results.

The reaction of nickel(II) with 2,2′-bipyridyl [equation (1)] takes place by the Eigen–Tamm–Wilkins mechanism,[3] following the rate law of equation (2). In fact the rate

$$\mathrm{Ni^{2+} + bipy \rightarrow Ni(bipy)^{2+}} \qquad (1)$$

$$+\mathrm{d[Ni(bipy)^{2+}]}/\mathrm{d}t = k_\mathrm{f}[\mathrm{Ni^{2+}}][\mathrm{bipy}] \qquad (2)$$

constant k_f is a composite quantity, combining the equilibrium constant for pre-association of the reactants, K_os, and the rate constant for the subsequent interchange step, k_i [equation (3)]. In our present investigation we can only

$$k_\mathrm{f} = K_\mathrm{os}k_\mathrm{i} \qquad (3)$$

deal with k_f ($\Delta H_\mathrm{f}^\ddagger$), and the corresponding 'transition state' thus contains elements of the pre-association equilibrium as well as of the true transition state for the interchange step. Nonetheless our analysis can distinguish between initial state effects and these combined 'other effects,' and thus provides the first step towards a complete and detailed analysis of solvent effects on reactivity in this ubiquitous mechanism for complex formation.

We deal with enthalpies here, rather than with Gibbs free energies and chemical potentials as in our earlier analyses, for two reasons. The first is that solvent effects on $\Delta H^\ddagger$ and $T\Delta S^\ddagger$ are known to be much more marked than those on $\Delta G^\ddagger$ for reactions of this type. The second is that the required single ion parameters for $\mathrm{Ni^{2+}}$ are derivable for partial molar enthalpies (H) but not, at the moment, for chemical potentials (G).

The required kinetic data, our thermochemical results, and our analysis of solvent effects on $\Delta H^\ddagger$ into initial state and 'transition state' contributions, are all included in the Table. Enthalpies of solution of 2,2′-bipyridyl and of anhydrous nickel(II) chloride (prepared by heating the hydrate in a stream of dry hydrogen chloride) were measured using an LKB 8700 calorimeter assembly with ancillary detecting and recording apparatus as described earlier.[4] The difficulty of dissolving the anhydrous nickel(II)chloride sufficiently rapidly or completely is the limiting factor in determining the upper methanol concentration in this analysis; kinetic and 2,2′-bipyridyl solubility data[5] are available over the whole methanol–water composition range. The enthalpies of transfer of nickel(II) chloride were separated into their single ion constituents using the enthalpies of transfer of chloride estimated (by essentially geometric methods) by Krestov and Klopov.[6]

Table. Solvent effects on enthalpies for initial and transition states for the reaction of nickel(II) with 2,2′-bipyridyl in aqueous methanol (at 298·2 K)[a]

x_MeOH	0	0·06	0·10	0·15	0·20
$\delta_\mathrm{m}\Delta H^{\ddagger}$[b]		+0·4	−0·4	−2·1	−2·1
ΔH_soln(bipy)	+6·3	+13·0	+15·7	+16·5	+17·0
∴ $\delta_\mathrm{m}\Delta H$(bipy)		+7	+9	+10	+11
$\Delta H_\mathrm{soln}(\mathrm{NiCl_2})$	−75	−97	−90	−65	(−30)
∴ $\delta_\mathrm{m}\Delta H(\mathrm{NiCl_2})$		−22	−15	+10	(+45)
$\delta_\mathrm{m}\Delta H(\mathrm{Cl^-})$[c]		−0·1	−1·4	−2·0	−2·5
∴ $\delta_\mathrm{m}\Delta H(\mathrm{Ni^{2+}})$		−22	−12	+14	+50
∴ $\delta_\mathrm{m}\Delta H$(is)		−15	−3	+24	(+60)
∴ $\delta_\mathrm{m}\Delta H$(ts)		−15	−3	+22	(+58)

[a] Enthalpies in kJ mol^{-1}. [b] Calculated from the data of H. P. Bennetto and E. F. Caldin, *J. Chem. Soc. (A)*, 1971, 2207. [c] Estimated from G. A. Krestov and V. J. Klopov, *Zh. Strukt. Khim.*, 1964, **5**, 829.

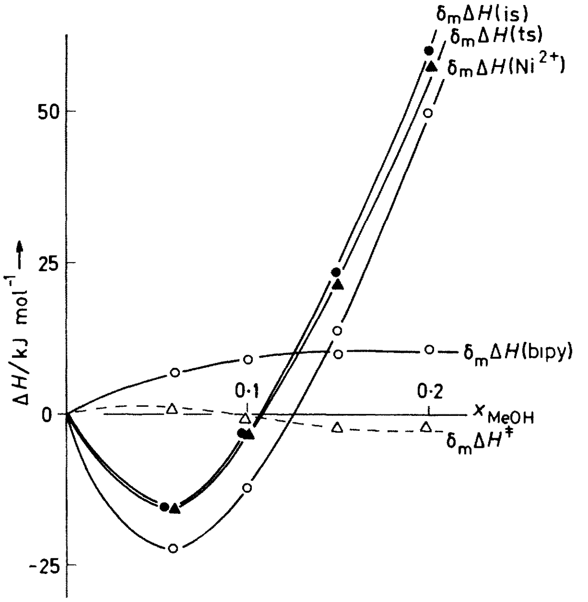

Figure. Separation of solvent effects on enthalpies for the reaction of nickel(II) with 2,2′-bipyridyl in aqueous methanol into initial state and transition state components.

The results in the Table and, more clearly, the graphical presentation in the Figure, show how solvation of the nickel-(II), as Ni^{2+} in the initial state and in the subsequent stages, dominates the solvation effects on enthalpies here. The situation in this reaction, with initial state and transition state trends lying very close together, is very different from, for example, peroxodisulphate oxidation of $Fe(bipy)_2(CN)_2$[7] or such organic substitutions as t-butyl chloride solvolysis[8] or Menschutkin reactions.[9] It is, however, similar to the situation for cyanide attack at the $[Fe(phen)_3]^{2+}$ cation,[10] though for entirely different reasons.

(*Received*, 21*st January* 1980; *Com.* 063.)

---

[1] M. J. Blandamer and J. Burgess, *Pure Appl. Chem.*, 1979, **51**, 2087; and references therein.
[2] H. P. Bennetto and E. F. Caldin, *J. Chem. Soc. (A)*, 1971, 2207.
[3] See, *e.g.*, M. Eigen and K. Tamm, *Z. Elektrochem.*, 1962, **66**, 93, 107; R. G. Wilkins, *Acc. Chem. Res.*, 1970, **3**, 408.
[4] J. Burgess, I. Haigh, and R. D. Peacock, *J. Chem. Soc., Dalton Trans.*, 1974, 1062.
[5] J. Burgess and R. I. Haines, *Chem. Ind. (London)*, in the press.
[6] G. A. Krestov and V. J. Klopov, *Zh. Strukt. Khim.*, 1964, **5**, 829.
[7] M. J. Blandamer, J. Burgess, and R. I. Haines, *J. Chem. Soc., Chem. Commun.*, 1978, 963.
[8] E. M. Arnett, W. G. Bentrude, and P. McC. Duggleby, *J. Am. Chem. Soc.*, 1965, **87**, 2048; and references therein.
[9] M. H. Abraham, *J. Chem. Soc., Chem. Commun.*, 1969, 1307.
[10] M. J. Blandamer, J. Burgess, and A. J. Duffield, *J. Chem. Soc., Dalton Trans.*, 1980, 1.