Effect of Water on the Kinetics of Ni^{II}-pyridine 2-azodimethylaniline Complex Formation in Acetonitrile

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Summary The influence of added water on the kinetics of formation of the mono-nickel(II) pyridine 2-azodimethylaniline complex in acetonitrile is reported; complex changes in the activation parameters suggest that the solvent can induce a change of reaction mechanism.

In a stopped-flow study[1] of the reaction of pyridine 2-azodimethylaniline (pada) with the nickel(II) ion in non-aqueous media, we have investigated some novel kinetic effects which have a bearing on reaction mechanisms. In non-aqueous and mixed solvents ligand-substitution reactions have been interpreted in terms of solvent structure[2,3] and the effects of specific solvation.[4]

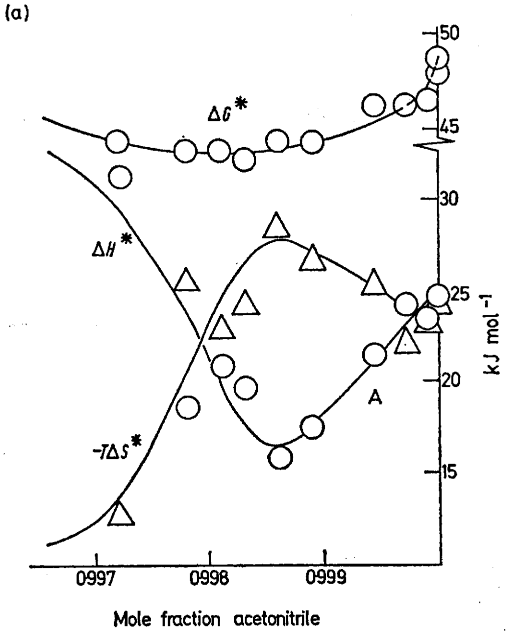
Kinetic behaviour in near-anhydrous acetonitrile is difficult to reproduce,[3] but using anhydrous $Ni(ClO_4)_2$ dissolved in freshly-distilled solvent, and making careful checks on water content,[1] we covered the range 0·900—1·000 mole fraction acetonitrile over the temperature range 273—318 K. Concentrations were in the ranges $10^3[Ni^{2+}] = 0{\cdot}5$—$5{\cdot}0$ mol dm^{-3} and $10^5[\text{pada}] = 2$—3 mol dm^{-3}. Second-order rate constants, k_f, were of $\pm 2\%$ precision, and activation parameters were within $\pm$ 1·5 kJ mol^{-1}. The results are shown in the Figure. The rate constant k_f rises sevenfold in the mole fraction range 1·000—0·995, and then decreases much more gradually. This could arise from a weakening of nickel–MeCN interactions in hydrated complexes such as $[Ni(H_2O)_5{\cdot}MeCN]^{2+}$, as envisaged by Shu and Rorabacher for reactions in the methanol–water system.[4] The initial fall in the ΔH^* values shown in the Figure (a) could be accommodated by this argument.

In the mole fraction range 0·997—0·900 the gradual change in ΔG^* conceals dramatic and largely compensating changes in ΔH^* and ΔS^* which are less easily accounted for. (Two additional points in the Figure (b), obtained from independent runs after an interval of several months, confirmed the extrema). Since the ligand is bidentate a change of mechanism to a sterically-controlled ring-closure[5] is not ruled out, but seems improbable,[1] and we consider it more likely that the solvent is the dominant influence on the reaction.

According to the concerted model[2] the dissociation of a solvent molecule from the solvation shell of an ion is a solvent-modified process. In mixed solvents, where recent results[6] reveal a high degree of ligand specificity, the possibility arises of a change in mechanism from the loss of one co-solvent molecule to the other. Thus the pattern of ΔH^*

and ΔS^* values can be attributed in part to structural contributions arising from entry of a water molecule or an acetonitrile molecule into an acetonitrile-like solvent.

Though there are uncertainties associated with the distribution of the small amount of water, the competition for hydrogen bonds to water provided by the large excess of acetonitrile molecules makes it unlikely that the ligand is selectively hydrated. Recently cited evidence[3] also suggests that the nickel ion in acetonitrile may not be completely hydrated until a concentration of around 0·02 mole fraction of water has been reached, which would coincide with the extreme end of the region (B) in Figure (b). In line with many results for ΔH^* in acetonitrile[1,2,3] the entry of MeCN into bulk solvent is considered to be a condensative process[2] which induces a highly dissociative reaction in region A, where the leaving molecule must be MeCN. In region B however, we propose that there is a change of leaving molecule from MeCN to H_2O. Since water and acetonitrile mix endothermically, the entry of H_2O into the bulk solvent is here not entirely compatible with the liquid structure and so gives a more positive contribution to ΔH^*. The break from B to C is more difficult to account for, unless the 0·03 mole fraction of H_2O is sufficient to significantly modify the liquid structure, and again change the nature of the leaving process. The reaction pathway selected by the reactants is the one of low ΔG^*, but this quantity is a composite one which depends on the relative importance of the bonding and solvent-structural factors, and it is argued that both these factors can give contributions to tilt the balance of ΔH^* and $T\Delta S^*$.



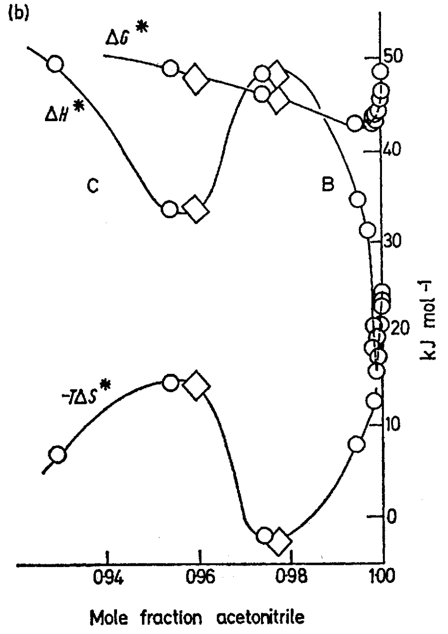


FIGURE. Activation parameters for Ni^{II} pada formation in acetonitrile plus water solvents.

Preliminary results suggest that similar large changes occur in the water-rich regions, and a complete picture for the whole solvent range will be presented later.

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