

Kinetics of Complex Formation of Nickel(II) in Acetic Acid. Evidence for a Dissociative Mode of Activation

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The kinetics of nickel(II) complexation in aqueous solution has been extensively studied [1]. The mechanism generally accepted for the formation of nickel(II) complexes involves rapid formation of an outer-sphere complex between metal ion and ligand, followed by the rate-limiting dissociation of a coordinated water molecule in the inner-coordination sphere of the metal ion [1, 2]. Similar mechanisms have been put forward for the formation of nickel(II) complexes in such non-aqueous solvents as methanol, dimethyl sulfoxide (Me_2SO), *N,N*-dimethylformamide, and acetonitrile [3].

Recently we have studied the kinetics of some reactions in acetic acid [4–7]. The metal ion incorporation into porphyrins has also been investigated in acetic acid [7]. Rates of metalloporphyrin formation are slow when compared to the complexation of metal ions with usual non-cyclic ligands. In order to understand the mechanism of reactions in acetic acid the kinetic studies on simple complexation in acetic acid are required.

In this letter the kinetics of complex formation by nickel(II) acetate with 1-(2-pyridylazo)-2-naphthol (PAN) in acetic acid has been investigated by the stopped-flow spectrophotometric method [8], and compared with data in other solvents. This is the first kinetic study on complex formation in acetic acid between metal ion and the non-cyclic ligand.

By comparing the spectra of PAN in the absence and in the presence of perchloric acid or lithium acetate, it has been found that more than 95% of PAN exist as the base form in acetic acid. Tridentate PAN forms quantitatively the 1:1 Ni(II)–PAN complex in the presence of about ten fold excess Ni(II) over PAN. Under such pseudo first-order conditions, the reverse reaction can be neglected. The reaction was monitored spectrophotometrically at 516 nm and 544 nm. The pseudo-first-order rate law was valid at least up to three half lives. The rate was found proportional to concentrations of nickel(II) acetate

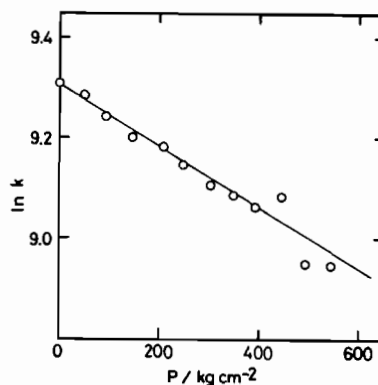


Fig. 1. Pressure dependence of $\ln k$. 25 °C, $[\text{Ni}(\text{OAc})_2] = 1.00 \times 10^{-3} \text{ M}$, $[\text{PAN}] = 4.17 \times 10^{-5} \text{ M}$. Each point is an average of several determinations.

($[\text{Ni}(\text{OAc})_2] = 2.88 \times 10^{-4}, 1.08 \times 10^{-3}, 1.74 \times 10^{-3}, 2.48 \times 10^{-3}, 3.23 \times 10^{-3} \text{ M}$) ($M = \text{mol kg}^{-1}$). Thus the rate equation is expressed as $d[\text{Ni}(\text{II})\text{--PAN}]/dt = k[\text{Ni}(\text{OAc})_2][\text{PAN}]$ where a second-order rate constant k is $1.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C. The amounts of water in the acetic acid solutions were found to be less than $5 \times 10^{-3} \text{ M}$ by the Karl-Fisher titration. Added water (up to 0.058 M) exerted no effect on k .

From the Eyring plot (17, 20, 25, 30, and 35 °C), the enthalpy and entropy of activation were determined: $\Delta H^\ddagger = 49.5 \pm 1 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = 0.1 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1}$. By using a high-pressure stopped-flow apparatus [8], rate constants were obtained at pressures up to 550 kg cm^{-2} . At 25 °C acetic acid freezes at pressures higher than 550 kg cm^{-2} . As apparent from Fig. 1, the rate constant k varies linearly with pressure: the activation volume, ΔV^\ddagger , is independent of pressure. ΔV^\ddagger was determined to be $15.5 \pm 2.6 \text{ cm}^3 \text{ mol}^{-1}$. Because of the low dielectric constant ($\epsilon = 6.18$ at 20 °C) [9, 10] all electrolytes are in the non-dissociated form in acetic acid. Therefore it may be assumed that the volume change due to electrostatic interaction is negligible. Thus the value of ΔV^\ddagger should reflect the intrinsic volume change in the transition state. The considerably large, positive value of ΔV^\ddagger strongly suggests a dissociative mode of activation: the dissociation of an acetic acid molecule in the inner sphere of nickel(II) ion is important in the rate-determining step. Moreover, since the ΔV^\ddagger value is considerably smaller than the partial molar volume of acetic acid ($57.5 \text{ cm}^3 \text{ mol}^{-1}$), the mechanism should be a dissociative interchange.

The kinetics of nickel(II) ion complexation with PAN has also been studied in water ($k = 95 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 25 °C for $\text{Ni}(\text{NO}_3)_2$) [11] and Me_2SO ($k = 56 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, $\Delta H^\ddagger = 54.4 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger =$

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$-29.3 \text{ J mol}^{-1} \text{ K}^{-1}$ at $25 \text{ }^\circ\text{C}$ for $\text{Ni}(\text{ClO}_4)_2$ [12]. The rates in both solvents are abnormally smaller than expected from the Eigen mechanism (solvent exchange rates) [13, 14]: the rates seem to be controlled by the closure of the second chelate ring, because of the internal hydrogen bond in PAN. The rate in acetic acid is two orders of magnitude larger than in water and Me_2SO . According to our preliminary NMR experiments the rate of acetic acid exchange at $\text{Ni}(\text{OAc})_2$ is about the same order as that found for the nickel(II) complexation in acetic acid. Consequently, the rate in the present system is normal and can be taken as a measure of the rates of the normal nickel(II) complexation in acetic acid.

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