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Activation Enthalpy for the Formation of some Nickel Complexes in Different Solvents

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The solvent dependence of the complex formation kinetics has been the subject of extensive study [1–9]. The rate constant has been correlated with the fluidity (density/viscosity) of the solvent [1]. An attempt to correlate the activation enthalpy for the complex formation with the Gutmann donor number was unsuccessful [8]. In this paper we correlate the activation enthalpy for the formation of some nickel complexes with some solvent parameters.

The formation of a metal complex is postulated to involve the following processes (Fig. 1, left):

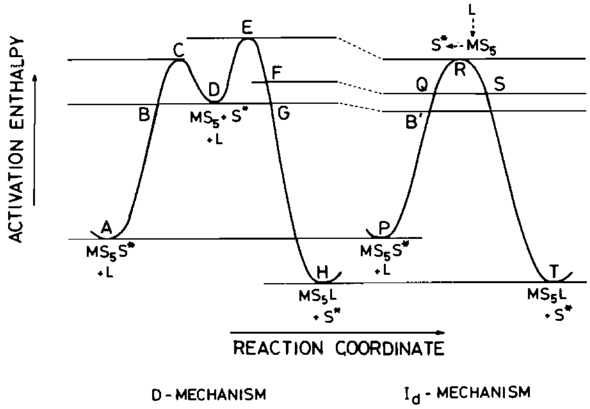

Fig. 1. Reaction profile of the complex formation.

1) A solvent molecule dissociates from the metal ion (AB). This process is assumed to require the enthalpy proportional to the enthalpy for the discharge of the metal ion in the solvent, ΔH_d [10];

2) The dissociated solvent molecule is incorporated in the bulk solvent (BCD). This process is thought to be similar to evaporation-condensation and is assumed to require the enthalpy proportional to the evaporation enthalpy of the solvent, ΔH_v [10];

3) A ligand leaves the bulk solvent (DEF). This process is considered to be similar to the reverse process of dissolution of the ligand in the solvent and is postulated to require the enthalpy proportional to the solubility parameter of solvent;

4) This ligand approaches to and is accommodated in the coordination site vacated in Process (1) (FGH). This process occurs spontaneously.

The reaction profile of the complex formation reaction according to the above model is depicted in Fig. 1.

If the enthalpy needed for Process (2) is higher than the enthalpy for Process (3), the activation enthalpy for the formation of a metal complex $\Delta H_f^\ddagger$ should be expressed as:

$$\Delta H_f^\ddagger = a\Delta H_d + b\Delta H_v \tag{1}$$

where a and b are constants characteristic of the metal ion. This equation conforms to the equation describing the activation enthalpy of solvent exchange at a metal ion in different solvent [10] and it fails to correlate the activation enthalpy for the complex formation (Table I).

On the other hand, if the enthalpy required for Process (2) is lower than the enthalpy for Process (3), $\Delta H_f^\ddagger$ should be correlated with ΔH_d and the solubility parameter δ as follows:

$$\Delta H_f^\ddagger = p\Delta H_d + q\delta \tag{2}$$

where p and q are constants characteristic of the metal ion and the ligand. For the mechanism with less dissociative character (with more interchange charac-

TABLE I. Activation Enthalpy for the Formation ($\Delta H_f^\ddagger$) of some Nickel Complexes in Different Solvents and some Solvent Properties.

Solvent[a]	$\Delta H_f^\ddagger$/kJ mol^{-1}			ΔH_d/kJ mol^{-1} [e]	δ [f]
	NiSCN[b]	Ni-Isoquinoline[b]	Ni-Bipyridine[d]		
MeCN	71.1	49.8	27.6	24.2	12.11
DMF	69.0	51.9	53.1	19.2	11.77
DMSO	32.6	31.8	52.7	9.9	12.93
MeOH	81.5	66.1	71.1	33.3	14.50
H_2O	50.6	49.0[c]	52.7	8.8	16.35

[a] MeCN = Acetonitrile; DMF = Dimethylformamide; DMSO = Dimethyl sulfoxide; MeOH = Methanol. [b] Ref. 8. [c] Ref. 4. [d] Ref. 2. [e] Ref. 10. [f] Ref. 12.

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ter), endothermic processes (AB, BC and DE) occur concurrently with exothermic processes (CD, EF and FH). Then $\Delta H_f^\ddagger$ will be lower (Fig. 1, right): constants *p* and *q* should be more or less lower in the interchange (I_d or I_a) mechanism than in the purely dissociative (D) mechanism [11]. Even in the mechanism with interchange character, eqn. (2) is assumed to apply.

Now the validity of eqn. (2) is tested. Dividing both sides of this equation by ΔH_d, we obtain:

$$\Delta H_f^\ddagger \Delta H_d^{-1} = p + q\delta\Delta H_d^{-1} \qquad (3)$$

Values of ΔH_d and the solubility parameter δ are included in Table I, together with values of $\Delta H_f^\ddagger$. According to Equation (3), $\Delta H_f^\ddagger \Delta H_d^{-1}$ is plotted versus $\delta\Delta H_d^{-1}$ in Fig. 2. The plot lies along a straight line. On the whole the correlation appears good. However $\Delta H_f^\ddagger$ values for 2,2′-bipyridine in acetonitrile and for thiocyanate in dimethyl sulfoxide are too low to be accommodated in the framework of the present model.

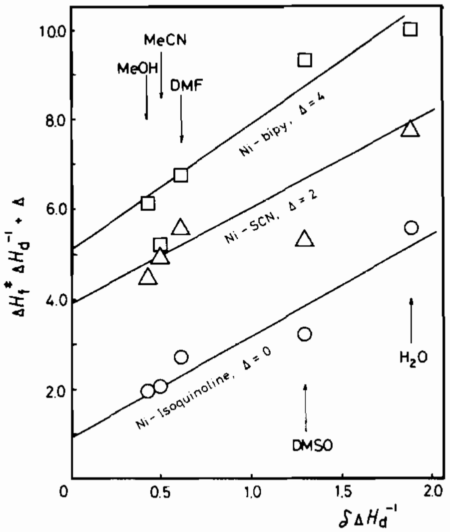

Fig. 2. Activation enthalpy of complex formation correlated with ΔH_d and δ (see eqn. 3). For the abbreviation of solvent names, see Table I.

As stated above, the coefficient *q* is a constant dependent upon the ligand. Since the desolvation of the ligand is involved in the formation of metal complex, the activation enthalpy of this reaction is dependent not only upon the metal ion itself but also on the incoming ligand. Apparent ligand independence of the rate constant of the complex formation [8, 13] has been taken as evidence for the dissociative mode of activation. However this seems to result from the isokinetic relation [1] leading to the decrease in the activation enthalpy, more or less compensated by the decrease in the activation entropy. This should make the rate constant of formation of metal complexes apparently close to the rate constant of solvent exchange and thus independent of the incoming ligand, when the formation of the encounter complex [14] is taken into account.

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