Inorganica Chimica Acta, 54 (1981) L129–L130
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Dissociative Character of the Solvent Exchange at a Metal Ion

MOTOHARU TANAKA

Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya, 464 Japan

Received May 20, 1981

In a previous paper [1], the activation enthalpy of the solvent exchange at a metal ion has been correlated with the enthalpy of solvent dissociation from the metal ion and the evaporation enthalpy of solvent. In this treatment a simple model based on the dissociative (D) mechanism was proposed (Fig. 1, left). In this model the solvent exchange at a metal ion was considered to involve the following four processes: (1) a solvent molecule dissociates from the metal ion (process AB): (2) this solvent molecule is incorporated in the bulk solvent (process BCD); (3) another solvent molecule leaves the bulk solvent (process DEF); (4) this latter solvent molecule approaches and is accommodated in an available coordination site of the metal ion vacated in process AB (process FG).

The activation enthalpy of the solvent exchange at a metal ion, $\Delta H^{\ddagger}_{ex}$, was expressed as follows:

$$\Delta H^{\ddagger}_{ex} = a\Delta H_d + b\Delta H_v \qquad (1)$$

where ΔH_d is the enthalpy of the solvent dissociation from the metal ion and ΔH_v the evaporation enthalpy of the solvent.

If the solvent exchange at a metal ion proceeds by a dissociative interchange (I_d) mechanism, the potential of the activated complex should be more or less lower than in the purely dissociative mechanism (Fig. 1, right): the energy needed for endothermic processes AB, BC and DE should be more or less compensated by the energy evolved in exothermic processes CD, EF and FG, which occur concurrently with the above endothermic processes. In consequence one may state that the less dissociative the reaction mechanism, the lower the activation enthalpy. In other words the processes in the solvent exchange are all on the way in the activated state of the I_d mechanism. Even in the I_d mechanism $\Delta H^{\ddagger}_{ex}$ was thought to be correlated with ΔH_d and ΔH_v as given by eqn. (1). Therefore according to eqn. (1), the smaller the coefficients *a* and *b*, the less dissociative the reaction mechanism.

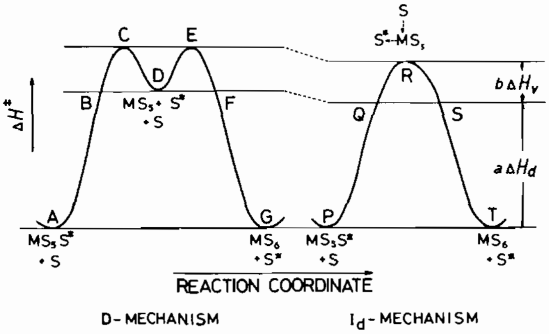

Fig. 1. Reaction profile of solvent exchange at a metal ion. Charges are omitted.

TABLE I. Activation Enthalpy of Solvent Exchange at Some Transition Metal Ions (kJ mol^{-1}).[a]

Solvent	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}
Acetonitrile	30.3	40.6	48.8^{b}	64.3^{c}
Ammonia	33.4		46.8	46.0
N,N-dimethylformamide	37.2^{d}	48.9^{e}	56.8	62.7
Dimethyl sulfoxide	31.0^{f}	47.2^{e}	51.0	54.3
Methanol	28.4^{g}	50.2	57.7	66.0
Water	32.9^{h}	41.4^{h}	46.9^{h}	56.9^{i}

[a] Compilation given in Ref. 1 unless otherwise noted. [b] A. Monnerat, P. Moore, K. E. Newman and A. E. Merbach, *Inorg. Chim. Acta, 47,* 139 (1981). [c] K. E. Newman, F. K. Meyer and A. E. Merbach, *J. Am. Chem. Soc., 101,* 1470 (1979). [d] T. M. Chen and L. O. Morgan, *J. Phys. Chem., 76,* 1973 (1972). [e] Ref. 5. [f] J.-C. Boubel and J.-J. Delpuech, *Adv. Mol. Relax., 7,* 209 (1975). [g] H. Levanon and A. Luz, *J. Chem. Phys., 49,* 2031 (1968). [h] Ref. 2. [i] Y. Ducommun, W. L. Earl and A. E. Merbach, *Inorg. Chem., 18,* 2754 (1979).

Values of activation enthalpy of the solvent exchange at some transition metal ions are summarized in Table I. As predicted previously [1], activation enthalpy of water exchange follows the normal trend $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+}$.

Equation (1) enables us to predict values of activation enthalpy of solvent exchange at manganese(II), iron(II) and cobalt(II) to within 5 kJ mol^{-1}. An exception is the methanol exchange at manganese(II), for which the predicted activation enthalpy is by 7.5 kJ mol^{-1} higher than the experimental. For nickel(II), of which the solvent exchange kinetics has most extensively been studied, the correlation by eqn. (1) is not as good as for these three transition metal ions.

TABLE II. Coefficients *a* and *b* in eqn. (1).

	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}
a	0.448	0.605	0.791	0.917
b	0.592	0.802	0.867	0.978

By means of the least squares method coefficients *a* and *b* are determined for these metal ions and they are tabulated in Table II.

Coefficients *a* and *b* in eqn. (1) are constants characteristic of metal ions and reflect the 'D-character' (or 'Interchange-character') of the reaction. The higher the *a* and *b* values, the larger the 'D-character'. Table II shows that the D-character of the solvent exchange decreases in the order $Ni^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+}$. This is in accord with the recent findings by Merbach and his associates [2, 3] who by a high-pressure NMR study elegantly showed the activation volume ($\Delta V^{\ddagger}_{ex}$) for the exchange of methanol and water at these metal ions decreases in the above order. For manganese(II), $\Delta V^{\ddagger}_{ex}$ is -5.0 cm^3 mol^{-1} for methanol exchange [2] and -5.4 cm^3 mol^{-1} for water exchange [3] pointing to an associative mode of activation (associative interchange (I_a) mechanism) for this metal ion.

Our results summarized in Table II, taken together with these results [2–4], suggest that the change of mechanism of solvent exchange at these transition metal ions is a phenomenon not only for the exchange of methanol and water but also for the other solvents such as acetonitrile, ammonia, *N,N*-dimethylformamide and dimethyl sulfoxide.

Funahashi and Jordan [5] have correlated the activation enthalpy of solvent exchange with Gutmann solvent donicity [6] according to the proposal by Hoffman [7]. The correlation seems satisfactory for most cases. More recently Jordan and his coworkers [8] have presented experimental results on the solvent exchange on an $LNiS^{2+}$ system, where L is a pentadentate Schiff base and S is *N,N*-dimethylformamide or acetonitrile. Their results do not conform to the previous correlation [5] and they propose the following:

$$\Delta H^{\ddagger}_{ex} = c_M Dq_{Ni-S} + b_s \qquad (2)$$

where c_M and b_s are constants for the metal ion and for the solvent, respectively. In view of the fact that Dq_{Ni-S} is a measure of the metal-solvent interaction and that b_s is a solvent parameter, this approach is essentially in line with ours.

Values of c_M coefficient decreases in the order $Ni^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+}$. This order is the same as for the coefficients *a* and *b* in eqn. (1). Thus the same arguments can be made with the coefficient c_M as with coefficients *a* and *b* in eqn. (1).

Acknowledgements

The present work was partially supported by a Grant-in-Aid for Scientific Research (No. 530704) from the Ministry of Education, Science and Culture (Japan).

References

1 M. Tanaka, *Inorg. Chem., 15,* 2325 (1976).

2 Y. Ducommun, K. E. Newman and A. E. Merbach, *Inorg. Chem., 19,* 3696 (1980).

3 F. K. Meyer, K. E. Newman and A. E. Merbach, *J. Am. Chem. Soc., 101,* 5588 (1979).

4 H. Vanni, A. E. Merbach, *Inorg. Chem., 18,* 2758 (1979).

5 S. Funahashi and R. B. Jordan, *Inorg. Chem., 16,* 1301 (1977).

6 V. Gutmann and R. Schmid, *Coord. Chem. Rev., 12,* 263 (1974).

7 H. Hoffmann, *Pure Appl. Chem., 41,* 327 (1975).

8 L. L. Rusnak, E. S. Yang and R. B. Jordan, *Inorg. Chem., 17,* 1810 (1978).