Inorganica Chimica Acta, 25 (1977) L91–L92
© Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Mechanistic Information from a High Pressure Nuclear Magnetic Resonance Study of Methanol Exchange between Hexamethanolnickel(II) and Solvent

W. L. EARL, F. K. MEYER and A. E. MERBACH*

Institue de chimie minérale et analytique, Université de Lausanne, 3, Place du Château, CH-1005 Lausanne, Switzerland

Received October 12, 1977

Nuclear magnetic resonance at high pressures has recently proven to be a useful technique to obtain volumes of activation of inter- [1, 2] and intramolecular [3] exchange reactions. Using this technique, we have obtained a volume of activation ΔV^* of +10.9 ± 0.6 cm^3 mol^{-1} for the exchange reaction (1). This value is interpreted as an indication of a

$$Ni(CH_3OH)_6^{2+} + {}^*CH_3OH \rightleftarrows Ni(CH_3OH)_5({}^*CH_3OH)^{2+} + CH_3OH \qquad (1)$$

dissociative interchange I_d mechanism for the solvent exchange reaction.

The determination of inorganic substitution reaction mechanisms in solution has aroused a great deal of interest over the past twenty years. Classically, the separation of these reactions into associative, interchange and dissociative mechanisms has been accomplished by studying their kinetics as a function of temperature, varying chemical composition and concentration. The simplest substitution reactions are those of exchange involving replacement of a solvent molecule bound to a metal ion by another solvent molecule from the bulk. The determination of the mechanisms of solvent exchange reactions is complicated by the fact that the concentration of the free ligand cannot be changed. Furthermore, changing the nature of the ligand implies a serious modification in the solvent and is likely to change the mechanism of the reaction. Consequently, in the case of solvent exchange, the enthalpy ΔH^* and entropy ΔS^* of activation are frequently interpreted to indicate the mechanism of the reaction. Solvent exchange has been studied for slow reactions by isotopic dilution and for rapid reactions by nuclear magnetic resonance. With the latter technique the values reported for the entropy of activation have notoriously low presicion [4]; Funahashi and Jordan [5] have pointed out the embarrassingly large range of activation enthalpies obtained from studies ostensibly on the same system. The accuracy has improved in recent work due to more accurate temperature measurements and by using non-linear least squares curve fitting techniques to fit the experimental spectra with the calculated ones obtained from the NMR relaxation equations including ΔH^* and ΔS^*. Nevertheless, the mechanistic interpretation of these activation parameters for solvent exchange reactions is often ambiguous. As a typical example the reaction given in (1) has been studied by Luz and Meiboom by ^1H NMR as a function of temperature. They obtained a ΔH^* of 10.6 kcal mol^{-1} and ΔS^* of –9.0 cal K^{-1} mol^{-1} [6] from the methyl protons linewidths of the bound methanol, and a ΔH^* of 15.8 kcal mol^{-1} and ΔS^* of + 8.0 cal K^{-1} mol^{-1} [7] from T_1 and T_2 measurements on the OH and CH_3 lines of the bulk methanol.

The volume of activation ΔV^* is an activation parameter available from measurement of the change of the rate constant as a function of pressure. The transition state theory gives equations (2), and it follows that the

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^*}{RT} \qquad (2)$$

effect of pressure on the rate constant depends on the sign and magnitude of the volume of activation. It is clear that in a simple dissociative reaction there is an increase in volume upon going from reactants to the activated complex and that the inverse is true for a simple associative reaction. This simple correlation applies for solvent exchange reactions where no charges are formed or neutralised during the reaction; the electrostrictive contribution to the volume of activation is then negligible [8], and ΔV^* can be directly related to the partial formation, the rupture, or the stretching of a bond during the activation process.

Dry $[Ni(CH_3OH)_6](ClO_4)_2$ was prepared from the hydrated salt and methylorthoformate using van Leeuwen's procedure [9]. The metal content of the crystalline product was obtained by EDTA titration and the composition determined to be the hexamethanolate. Dilute acidic methanol was obtained by adding aqueous $HClO_4$ to methanol and removing the water by reaction with a slight excess of methylorthoformate. NMR solutions were prepared by weighing the crystalline salt and slightly acidic methanol, and adding a small amount of TMS as a shift and linewidth standard. The high pressure NMR probe is the same as described previously [2, 10], with the exception that we have added an external fluorine lock. Rate constants were measured from the linewidth of the methyl protons in the bulk methanol.

The results of five independent determinations of ΔV^* using a linear least-squares fitting of lnk *versus* P are given in the Table. The average of these values obtained between 303 and 310 K is + 10.9 ± 0.6 cm^3

---

*To whom correspondence is to be addressed.

TABLE. Volume of Activation ΔV^* for Methanol Exchange between $Ni(CH_3OH)_6^{2+}$ and Solvent at an Average Temperature of 307 K[a].

Sample	$[Ni(CH_3OH)_6^{2+}]$ (m)	Temperature (K)	P_{max} (bar)	Number of Data	ΔV^* ($cm^3\ mol^{-1}$)
1	0.196	310	1250	6	.+13.5[b]
2	0.490	303	1250	6	+10.0
3	0.289	303	1200	10	+11.8
3	0.289	310	1300	6	+10.7
4	0.167	308	2000	10	+ 9.3
				Average	+10.9 ±0.6[c]

[a]The temperature dependence of ΔV^* is negligible in a small temperature range. [b]Individual values obtained from linear least-squares fittings. [c]Standard deviation of the mean.

mol^{-1}. The data were also fitted to an equation quadratic in pressure. This gives an average volume of activation at zero pressure ΔV_0^* of +12.0 ± 1.7 cm^3 mol^{-1} and an average compressibility coefficient of activation $\Delta\beta^* = -(\partial\Delta V^*/\partial P)_T$ of +1.8 ± 3.0 cm^3 mol^{-1} $kbar^{-1}$. The value of $\Delta\beta^*$ is small or even zero within experimental error; its large standard deviation is due to scatter of the data and to the relatively low pressures used for the measurements.

The positive sign of ΔV^* implies that the solvent exchange (1) has a dissociative D activation mode. For a dissociative D mechanism one would expect a value of the order of the molar volume of methanol which is 40.5 cm^3 mol^{-1} at 307 K. The relatively small observed ΔV^* is a good indication for a dissociative interchange I_d mechanism. Further work with other +2 and +3 ions and with other solvents, for example water using high pressure oxygen-17 NMR, will give more insight into the understanding of fast solvent exchange mechanisms.

Acknowledgement

This work was supported by the Swiss National Science Foundation under grant number 2.575-0.76.

References

1 André E. Merbach and H. Vanni, *Helv. Chim. Acta, 60,* 1124 (1976).
2 H. Vanni, William L. Earl and André E. Merbach, *J. Magn. Res.,* in press.
3 H. D. Lüdemann, R. Rauchschwalbe and E. Lang, *Angew. Chem., 89,* 340 (1977).
4 G. Binsch in, "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackman and F. A. Cotton, eds., Academic Press, New York (1975).
5 S. Funahashi and R. B. Jordan, *Inorg. Chem., 16,* 1301 (1977).
6 Z. Luz and S. Meiboom, *J. Chem. Phys., 40,* 1066 (1964).
7 Z. Luz and S. Meiboom, *J. Chem. Phys., 40,* 2686 (1964).
8 D. R. Stranks, *Pure Appl. Chem., 38,* 303 (1974).
9 P. W. van Leeuwen, *Rec. Trav. Chim., 86,* 247 (1967).
10 William L. Earl, H. Vanni and A. E. Merbach, to be submitted.