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HIGH PRESSURE NMR STUDY ON THE KINETICS OF LIGAND EXCHANGE REACTION IN PENTAKIS(DIMETHYL SULFOXIDE)OXOVANADIUM(IV)

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The kinetics of ligand exchange in $[VO(dmso)_5]^{2+}$ (dmso = dimethyl sulfoxide) has been studied by the high pressure NMR method. The volume of activation $\Delta V^{\ddagger}$ for the dmso exchange at the basal positions of $[VO(dmso)_5]^{2+}$ was determined to be (-5.3 ± 0.4) cm^3/mol. This negative value of $\Delta V^{\ddagger}$ is consistent with associative behavior in the ligand substitution processes of oxovanadium(IV) complexes.

Recently, a particular interest has been concerned with respect to high pressure kinetic studies on ligand substitution reactions in metal complexes, since the volume of activation was found to be an effective criterion in determining whether the ligand substitution proceeded via a dissociative or associative pathway. Despite the extensive studies on the kinetics of ligand exchange in VO^{2+} complexes, no data are available for $\Delta V^{\ddagger}$. In this paper we report the value of $\Delta V^{\ddagger}$ for the dmso exchange in $[VO(dmso)_5]^{2+}$, where dmso denotes coordinated dimethyl sulfoxide.

The ^1H NMR measurement was carried out for methyl protons of bulk dimethyl sulfoxide (DMSO) in CD_3NO_2 containing $[VO(dmso)_5](ClO_4)_2$ by using a JEOL FX-100 NMR spectrometer equipped with a high pressure probe which was designed similarly to that described by Merbach et al.[1)] Angerman and Jordan[2)] studied the exchange of dmso in $[VO(dmso)_5]^{2+}$ by NMR and found only a fast exchange region at temperatures above the freezing point of DMSO. However, in our recent study[3)] dealing with the same dmso exchange, a slow exchange region was observed in CD_3NO_2 at temperatures from -15 to 20 °C. In this temperature region, the apparent relaxation time T_2 is controlled by the chemical exchange between DMSO and dmso,[4)] and hence the most reliable value of the rate constant can be obtained. In view of the constancy of the temperature in the high pressure probe, the NMR measurements under elevated pressure was conducted at 13 °C. The preparation of $[VO(dmso)_5](ClO_4)_2$ was performed by adding concentrated $VO(ClO_4)_2$ aqueous solution to distilled DMSO. The resulting blue crystals were filtered, washed with diethyl ether and dried in vacuo. Calcd for $[VO(dmso)_5](ClO_4)_2$: C, 18.3; H, 4.61; S, 24.42%. Found: C, 18.28; H, 4.56; S, 24.38%.

In Fig. 1 the first-order rate constant k is plotted as a function of the applied pressure. This linear plot reveals that the compressibility coefficient of activation is nearly zero. The value of $\Delta V^{\ddagger}$ was determined to be (-5.3 ± 0.4) cm^3/mol directly from the slope.

Merbach et al.[5)] studied the kinetics of water exchange in divalent metal ions (Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+}) under pressure. They determined values of $\Delta V^{\ddagger}$ ranging from -5.0 to 7.2 cm^3/mol and proposed a mechanistic changeover from associative interchange (Ia) to dissociative interchangle (Id). They found a similar trend also for other solvent exchange reactions in CH_3OH, CH_3CN and N,N-dimethylformamide with these divalent ions. On the basis of these facts, we conclude that the dmso exchange in $[VO(dmso)_5]^{2+}$ proceeds associatively. It has been known that the rates of ligand substitutions at the basal positions of VO^{2+} complexes are remarkably affected by the nature of entering ligands, such as basicities and charges.[6,7)] These results were reasonably explained in terms of the Ia mechanism. The negative value of $\Delta V^{\ddagger}$ in the present study is consistent with associative behavior for the ligand substitutions in VO^{2+} complexes.

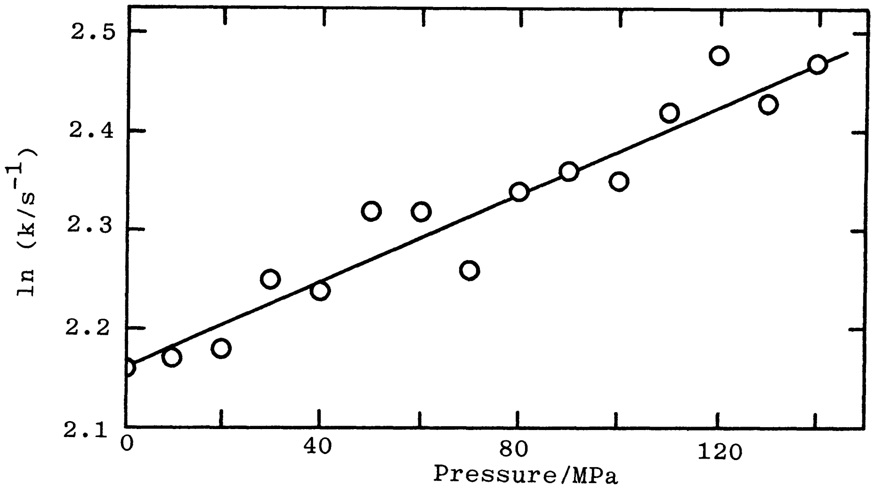

Fig.1. Logarithmic plot of k vs. pressure for the exchange of dmso in $[VO(dmso)_5]^{2+}$ (1.0×10^{-2} mol/dm^3);[dmso]=1.3 mol/dm^3 in CD_3NO_2 at 13 °C.

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References

1) H. Vanni, W. L. Earl, and A. E. Merbach, J. Magn. Reson., 29, 11 (1978).
2) N. S. Angerman and R. B. Jordan, Inorg. Chem., 8, 65 (1969).
3) A. Saito, Y. Ikeda, H. Tomiyasu, and H. Fukutomi, Bull. Res. Lab. Nucl. Reactor (Tokyo Inst. Tech.), 9, 43 (1984).
4) T. J. Swift and R. E. Connick, J. Chem. Phys., 37, 307 (1962).
5) Y. Ducommun, K. E. Newman, and A. E. Merbach, Inorg. Chem., 19, 3696 (1980).
6) O. Yokoyama, H. Tomiyasu, and G. Gordon, Inorg. Chem., 21, 1136 (1982).
7) M. Nishizawa and K. Saito, Inorg. Chem., 17, 3676 (1978).

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