Inorganica Chimica Acta, 146 (1988) 7–8

High Pressure Oxygen-17 NMR Study on the Kinetics of Water Exchange Reaction in Pentaquaoxovanadium(IV)

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(Received December 29, 1987)

Merbach and coworkers have studied extensively the effect of pressure on the rate of water exchange in divalent metal ions by use of high pressure NMR [1]. They reported the values of $\Delta V^{\ddagger}$ for V^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} to be −4.1, −5.4, 3.8, 6.1 and 7.2 cm^3 mol^{-1}, respectively explaining that the mechanism changed over from I_a to I_d as the $\Delta V^{\ddagger}$ values increased. With respect to oxovanadium(IV) complexes, only exchange reactions with organic solvents have been studied under high pressure [2, 3]. This paper presents the results of high pressure ^{17}O NMR experiments on the kinetics of water exchange in $[VO(H_2O)_5]^{2+}$.

Experimental

A JEOL FX-100 NMR spectrometer equipped with a high pressure probe, which was designed similarly to a high pressure probe for ^1H NMR [2]. In order to gain the better sensitivity of NMR signals, ^{17}O enriched water (Merck, $^{17}O = 23\%$) was used. The $[VO(H_2O)_5]^{2+}$ stock solution was prepared by mixing oxovanadium(IV) sulfate with barium perchlorate in D_2O and precipitating barium sulfate. The ionic strength of the NMR sample solutions was adjusted to 3.0 mol dm^{-3} by sodium perchlorate and the solution was slightly acidified by perchloric acid.

Results and Discussion

The water exchange in $[VO(H_2O)_5]^{2+}$ under normal pressure was studied by Wüthrich and Connick using ^{17}O NMR [4]. The transverse relaxation time T_2 for bulk water was found to be controlled by water exchange at the basal positions at temperatures above 40 °C. Based on these results, we measured the ^{17}O NMR spectra for bulk water in the presence of $[VO(H_2O)_5]^{2+}$ at 65 °C, where the slow exchange region [5] should be applied.

The observed first-order rate constant k_{obs} for the water exchange at the basal positions can be obtained by the following equation under the present conditions

$$k_{obs} = (1/T_2 - 1/T_{20})/P_M$$

where T_2 and T_{20} denote the transverse relaxation time in the presence and the absence of the complex, respectively, and P_M refers to the probability factor. Figure 1 represents a plot of $\ln(T_{20}^0/T_{20})$ *versus* applied pressure P, where T_{20}^0 denotes T_{20} at $P = 0$. As seen in Fig. 1, the plot decreases linearly with increasing P. This agrees well with the results by Merbach *et al.* [6]. In Fig. 2, $\ln k_{obs}$ is plotted as a function of P. The linear relationship in Fig. 2 indicates that the compressibility coefficient is negligibly small and that the value of $\Delta V^{\ddagger}$ can be determined directly from the slope to be 1.9 ± 0.2 dm^3 mol^{-1}. This slightly positive value of $\Delta V^{\ddagger}$ may favor the I_d mechanism for the direct water exchange at the basal positions. However, a pathway involving an intramolecular water exchange between the axial and basal positions can not be ruled out, since the water molecule at the axial position is extremely labile [4], and hence the intramolecular water exchange, where a small volume change is expected, coincides with the observed water exchange. It is interesting to compare the

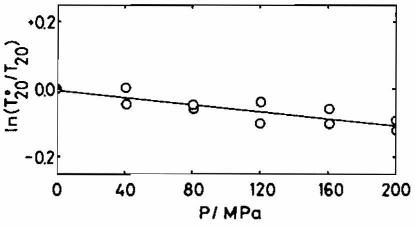

Fig. 1. Plot of $\ln(T_{20}^0/T_{20})$ *vs.* P.

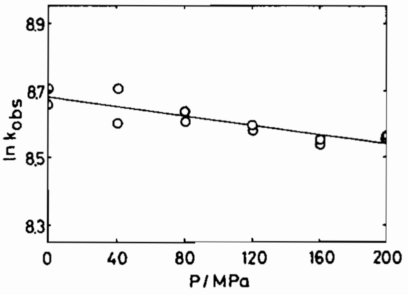

Fig. 2. Plot of $\ln k_{obs}$ *vs.* P. $[VO(H_2O)_5]^{2+} = 0.6$ mol dm^{-3} at 65 °C.

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value of $\Delta V^{\ddagger}$ with that of $\Delta S^{\ddagger}$ in the same reaction. According to Wüthrich and Connick [4], $\Delta S^{\ddagger}$ was reported to be -2.5 J K^{-1} mol^{-1}. The nearly zero value of $\Delta S^{\ddagger}$ consists with the results of the present study.

Acknowledgements

The authors wish to express their thanks to Professor Gilbert Gordon of Miami University for helpful discussion. The present work is supported by a Grant-in-Aid for Scientific Research No. 60470045 from the Ministry of Education, Science and Culture.

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