Kinetic Investigations of the Cleavage of the Oxo Bridge in the μ-Oxobis[oxo{tris(2-pyridylmethyl)-amine}vanadium(IV)] Ion

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The kinetics of the cleavage of the oxo bridge in the complex $[(tpa)OV(O)VO(tpa)]^{2+}$ [tpa = tris(2-pyridylmethyl)amine] was investigated in 1.0 M $(Na,H)ClO_4$ in the $[H^+]$ range $10^{-3.7}$–$10^{-0.7}$ M. The cleavage was promoted by protonation of the oxo bridge to a hydroxo-bridged dimer which dissociated to monomeric species with a first-order rate constant $k_d = 0.0102(5)$ s^{-1} at 24.0 °C; $\Delta H^{\ddagger} = 66(2)$ kJ mol^{-1} and $\Delta S^{\ddagger} = -60(7)$ J mol^{-1} K^{-1}. The acid dissociation constant, K_a, for the hydroxo bridge was found to be $10^{-2.35(3)}$ M at 24.0 °C; $\Delta H^{\circ} = 7(4)$ kJ mol^{-1} and $\Delta S^{\circ} = -21(11)$ J mol^{-1} K^{-1}. The hydroxo-bridged dimer $[(tpa)OV(OH)VO(tpa)](ClO_4)_3$ was isolated, and magnetic measurements revealed a very weak antiferromagnetic coupling, $J < 1$ cm^{-1}.

Oxo-bridged dinuclear vanadium complexes have attracted attention in recent years and several oxo-bridged dinuclear V^{III},[1-7] mixed valence $V^{IV,V}$[8,9] and V^V[5,10,11] dimers have been prepared. The first example of an oxo-bridged V^{IV} dimer, $[(tpa)OV(O)VO(tpa)]$-$(ClO_4)_2$, was recently[12] isolated and a structure determination of this complex revealed the presence of a linear V–O–V bridge, with the bridging oxo group located *cis* to the terminal oxo group.
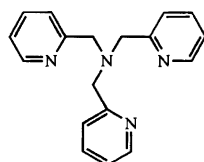
tpa

The complex ion $[(tpa)OV(O)VO(tpa)]^{2+}$ is stable in neutral aqueous solutions.[12] For $[H^+] > 10^{-4}$ M bridge cleavage to monomeric species occur. We report here a study of the kinetics of the bridge cleavage in order to elucidate the mechanism of the reaction. In connection with this work the hydroxo-bridged dimer, $[(tpa)OV(OH)VO(tpa)](ClO_4)_3$, was isolated.

Experimental

Materials. The complex $[(tpa)OV(O)VO(tpa)]$-$(ClO_4)_2 \cdot 2H_2O$ (**I**) was prepared according to the literat-

ure procedure.[12] **CAUTION!** Perchlorates may be shock-sensitive. Scraping with a glass rod against sintered glass and preparations on a larger scale than described should therefore be avoided.

[(tpa)OV(OH)VO(tpa)](ClO₄)₃ (**II**). A solution of **I** (0.024 g) in CH_3CN (0.4 ml) was added to ice-cold 1 M $HClO_4$ (2 ml). The blue solution was quickly filtered, and solid $LiClO_4$ (0.11 g) was added with stirring. The solution was left for crystallization in an ice-bath for ca. 10 min. The resulting violet precipitate was filtered off and washed with two portions of ice-cold ethanol and two portions of diethyl ether and air-dried. Yield: 0.012 g (44%). Calc. for $C_{36}H_{37}Cl_3N_8O_{15}V_2$: C, 41.98; H, 3.62; N, 10.88 Cl, 10.33; Found: C, 41.35; H, 3.71; N, 11.17; Cl, 10.05. UV–VIS (λ_{max}/nm, log(ε/M^{-1} cm^{-1}) in 4 M CF_3SO_3H, $T = 5$ °C): (715, 2.13), (537, 1.91), (357, 3.14)$_{shoulder}$ (255, 4.39). IR (KBr, ν/cm^{-1}) 981 (V=O).

Kinetic runs. The bridge cleavage in **I** was studied spectrophotometrically on a Perkin-Elmer Lambda 17 spectrophotometer as follows: A solution of **I** in CH_3CN was prepared, and 50 μl of this solution was added to 3.00 ml of aqueous 1.0 M $(Na,H)ClO_4$ in a thermostatted cuvette. The absorbance, A, at 520 nm was then followed for ca. 7 half-lives, the first reading 5 s after mixing. The observed pseudo-first-order rate constants, k_{obs}, were calculated by least-squares refinements of eqn. (1):

$$A(t)_{obs} = (A_{t=0} - A_{t=\infty}) \exp(-k_{obs}t) + A_{t=\infty} \qquad (1)$$

When solid **II** was added directly to the 1.0 M

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(Na,H)ClO$_4$ solution the same value of k_{obs} was obtained. Experiments were carried out in the [H$^+$] range $10^{-3.7}$–$10^{-0.7}$ M at 24.0, 40.0 and 55.0 °C. The change in log([H$^+$]/M) in the 1.0 M (Na,H)ClO$_4$ solution during the reaction was below 0.02 securing pseudo-first-order conditions to be maintained.

Other physical measurements. IR spectra were recorded on a Perkin Elmer 1600 FTIR instrument, and the magnetic susceptibilities were measured by the Faraday method using equipment previously described.[13,14]

Results and discussion

Syntheses. The complex II is to the best of our knowledge the first example of an oxovanadium(IV) dimer containing a [(VO)$_2$(µ-OH)]$^{3+}$ core. Other examples of hydroxo-bridged oxovanadium(IV) dimers have been reported by Wieghardt,[15,16] who isolated dimers containing [(VO)$_2$(µ-OH)$_2$]$^{2+}$ and [(VO)$_2$(µ-OH)(µ-SO$_4$)]$^+$ cores. The half-life for the bridge cleavage in [(tpa)OV(OH)VO(tpa)]$^{3+}$ in 1 M HClO$_4$ is ca. 1 min at room temperature (see below). By cooling the reaction mixture in an ice-bath, however, II in the solid state could be isolated, but unfortunately the crystals of II were not suitable for a crystal structure determination. This compound is unstable in the usual organic solvents such as dimethyl sulfoxide, *N,N*-dimethylformamide and acetonitrile, probably owing to bridge cleavage.

UV–VIS spectroscopy. The complex I displays a very intense absorption in the range 400–600 nm, and this absorption was assigned to a µ-oxo to vanadium charge-transfer transitions.[12] This assignment is supported by the fact that this absorption disappeared upon protonation of the oxo bridge allowing the d–d bands at 537 and 715 nm to be observed (see Experimental). Figure 1 shows the absorption spectra recorded during the bridge cleavage reaction at [H$^+$]=0.01 M. The intense band at 400–600 nm disappears in the course of the reaction. This was found to be the case for all reactions in the entire [H$^+$] range $10^{-3.7}$–$10^{-0.7}$ M and the concentration of the dimer in the equilibriated solutions could be estimated to be below 1%. The shoulder at 335 nm observed in the spectra of equilibriated solutions (Fig. 1) is due to a charge-transfer transition between the tpa and the metal center, indicating that tpa is coordinated to vanadium in the monomeric reaction products.

Kinetics. The reaction scheme associated with the bridge cleavage is depicted in Scheme 1, from which the [H$^+$] dependence of the pseudo-first-order rate constant can be expressed [eqn. (2)]:

$$\log(k_{calc}/s^{-1}) = \log\left(\frac{k_d[H^+]}{[H^+]+K_a}\Big/s^{-1}\right) \tag{2}$$

Figure 2A shows a plot of log(k_{obs}/M^{-1}) vs.
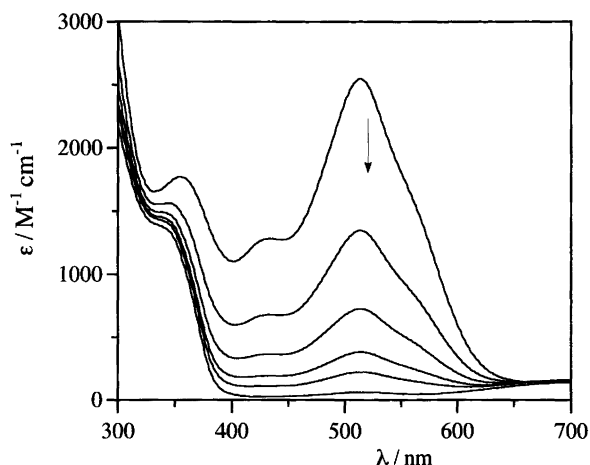
Fig. 1. Absorption spectra of [(tpa)OV(OH)VO(tpa)]-(ClO$_4$)$_2$·2H$_2$O in 0.01 M HClO$_4$/0.99 M NaClO$_4$ at 24.0 °C. The top spectrum was measured 20 s after mixing and the following five spectra after 125, 230, 346, 455 and 1800 s (scanning from 700 nm with a scan rate of 960 nm/min).
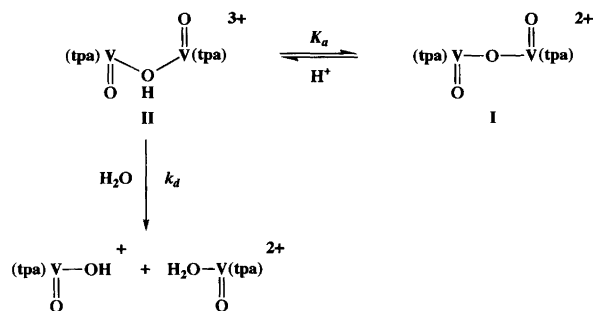
Scheme 1. Reaction scheme for the proposed model for bridge cleavage.

−log([H$^+$]/M). A least-squares fit of eqn. (2) to the data in Fig. 2A gave the values of k_d and K_a listed in Table 1 and the curves shown in Fig. 2A. In Fig. 2B a plot of log($\varepsilon_{t=0(obs)}$/M^{-1} cm^{-1}) vs. −log([H$^+$]/M) at 24.0 °C is shown ($\varepsilon_{t=0(obs)}=A_{t=0}$/[dimer]). From these data an independent determination of K_a could be obtained by a least-squares refinement of the data according to eqn. (3):

$$\log(\varepsilon_{t=0(calc)}/M^{-1} cm^{-1})$$
$$= \log\left(\frac{\varepsilon_1[H^+]+\varepsilon_2 K_a}{[H^+]+K_a}\Big/M^{-1} cm^{-1}\right) \tag{3}$$

ε_1 and ε_2 denote the molar absorption coefficients of the hydroxo-bridged and the oxo-bridged dimers, respectively. This gave the curve in Fig. 2B representing the values 51(27), 8.7(4) × 10^3 M^{-1} cm^{-1} and 10$^{-2.31(4)}$ M for ε_1, ε_2 and K_a, respectively. An excellent agreement beween the two values of K_a, determined by the two independent experiments is observed.

The large negative value of the activation entropy associated with the hydroxo bridge cleavage of II suggests an associative reaction pathway, in accordance with the results from other studies of substitution reactions of

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Table 1. Kinetic and thermodynamic parameters for the bridge cleavage in $[(tpa)OV(O)VO(tpa)]^{2+}$ (Scheme 1) in 1.0 M $(Na,H)ClO_4$.

	24.0 °C	40.0 °C	55.0 °C	$\Delta H^a/kJ\ mol^{-1}$	$\Delta S^a/J\ mol^{-1}\ K^{-1}$
k_d/s^{-1}	0.0102(5)	0.0438(16)	0.137(11)	66(2)	−60(7)
−log(K_a/M)	2.35(3)	2.26(3)	2.26(6)	7(4)	−21(11)

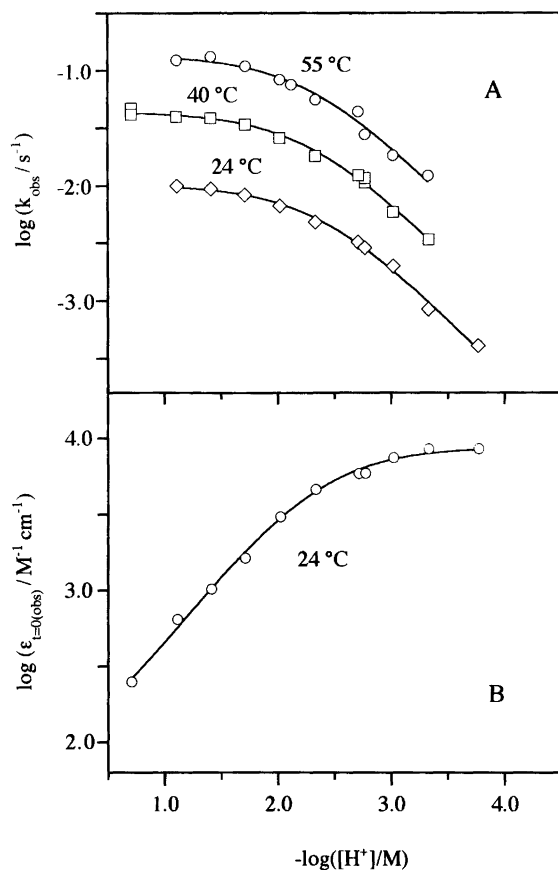$^a\Delta H°$ or $\Delta H^{\ddagger}$, and analogously for ΔS, depending on the parameter.

Fig. 2. (A) log(k_{obs}/s^{-1}) vs. $-$log$([H^+]/M)$ for the bridge cleavage in $[(tpa)OV(O)V(tpa)]^{2+}$ in 1.0 M $(Na,H)ClO_4$; the markers ◇, □ and ○ represent experimental values at 24.0, 40.0 and 55.0 °C, respectively. The curves are based on eqn. (2) using the constants in Table 1. (B) log$(\varepsilon_{t=0(obs)}/M^{-1}cm^{-1})$ vs. $-$log$([H^+]/M)$ for $[(tpa)OV(O)V(tpa)]^{2+}$ in 1.0 M $(Na,H)ClO_4$ at $\lambda = 520$ nm. The circles represent experimental values and the curve is based on eqn. (3) using the constants given in the text.

may be due to several factors. It is well known that the presence of heteroaromatic N-donors in the first coordination sphere of a metal increases the acidity of terminal water ligands as well as hydroxo bridges as compared to complexes containing aliphatic N-donors.[21] Furthermore, the deprotonated form, the oxo-bridged, is stabilized by the donation of electrons from the p-orbitals on the bridging oxygen to the d-orbitals on the metal centers. Finally, from the known structures of I^{12} and $[(tpa)(SCN)Cr(O)Cr(NCS)(tpa)]^{2+}$ [20] we note that the linear bridging geometry results in stacking of adjacent pyridine groups. The energetically favorable ring-stacking interactions between the pyridine groups may thus contribute to the high acidity. The aspect of ring-stacking interactions has also been included in a discussion of the structures of this type of complexes.[22]

Magnetic measurements. In complex I a very strong antiferromagnetic coupling $(J > 600\ cm^{-1})$ was observed.[12] This strong interaction was explained in terms of π overlap via the p-orbitals on the bridging oxygen, an overlap being facilitated by the linear bridge geometry. The magnetic susceptibility of a powdered sample of II measured in the temperature range 4–300 K showed only a very weak, if any, antiferromagnetic coupling $(J < 1\ cm^{-1})$. One possible explanation for this very weak coupling may have its origin in the lengthening of the vanadium-(bridging)oxygen bond by protonation of the oxo bridge in I, from 1.804 Å[12] to about 1.98 Å. However, this alone can hardly explain the dramatic decrease of the exchange coupling. A more likely explanation may have its background in the V–O–V angle in II being significantly smaller than 180°. A decrease of this bond angle will effectively reduce the π overlap and thus reduce the exchange coupling.

oxovanadium(IV) complexes.[17,18] The first-order rate constant at room temperature for the exchange of water ligands *cis* to the oxo group in the aqua ion $[VO(OH_2)_5]^{2+}$ has been estimated to be ca. $0.1\ M^{-1}\ s^{-1}$,[19] one order of magnitude larger than k_d. Consistent with the suggested associative pathway this may be explained by the steric hindrance to the incoming water molecule caused by the bulky tpa ligand in II.

K_a for the hydroxo bridge in the chromium(III) complex $[(tpa)(SCN)Cr(OH)Cr(NCS)(tpa)]^{3+}$, prepared by Holwerda[20] is $10^{-2.05}$ M, close to the value for II. The high acidity of the hydroxo bridge in these two complexes

References

1. Chandrasekhar, P. and Bird, P. H. *Inorg. Chem. 23* (1984) 3677.
2. Christou, G., Heinrich, D., Money, J. K., Rambo, J. R., Huffman, J. and Folting, K. *Polyhedron 8* (1989) 1723.
3. Kanamori, K., Kameda, E., Kabetani, T., Suemoto, T., Okamoto, K. and Kaizaki, S. *Bull. Chem. Soc. Jpn. 68* (1995) 2581.

4. Money, J. K., Folting, K., Huffman, J. C. and Christou, G. *Inorg. Chem. 26* (1987) 944.
5. Knopp, P., Wieghardt, K., Nuber, B., Weiss, J. and Sheldrick, W. S. *Inorg. Chem. 29* (1990) 363.
6. Brand, S. G., Edelstein, N., Hawkins, C. J., Shalimoff, G., Snow, M. R. and Tiekink, E. R. T. *Inorg. Chem. 29* (1990) 434.
7. Zhang, Y. and Holm, R. H. *Inorg. Chem. 29* (1990) 911.
8. Nishizawa, M., Hirotsu, K., Ooi, S. and Saito, K. *J. Chem. Soc., Chem. Commun.* (1979) 707.
9. Kojima, A., Okazaki, K., Ooi, S. and Saito, K. *Inorg. Chem. 22* (1983) 1168.
10. Nakajima, K., Kojima, M., Toriumi, K., Saito, K. and Fujita, J. *Bull. Chem. Soc. Jpn. 62* (1989) 760.
11. Ludwig, E., Schilde, U., Uhlemann, E., Weller, F. and Dehnicke, K. *Z. Anorg. Allg. Chem. 619* (1993) 669.
12. Toftlund, H., Larsen, S. and Murray, K. S. *Inorg. Chem. 30* (1991) 3964.
13. Josephsen, J. and Pedersen, E. *Inorg. Chem. 16* (1977) 2534.
14. Pedersen, E. *Acta Chem. Scand. 26* (1972) 333.
15. Wieghardt, K., Bossek, U., Volckmar, K., Swiridoff, W. and Weiss, J. *Inorg. Chem. 23* (1984) 1387.
16. Neves, A., Wieghardt, K., Nuber, B. and Weiss, J. *Inorg. Chim. Acta 150* (1988) 183.
17. Nishizawa, M. and Saito, K. *Inorg. Chem. 17* (1978) 3676.
18. Nishizawa, M. and Saito, K. *Inorg. Chem. 19* (1980) 2284.
19. Lincoln S. F. and Merbach, A. E. *Advances in Inorganic Chemistry*, Vol. 42. Academic Press, New York 1995, p. 49 and references therein.
20. Gafford, B. G., Holwerda, R. A., Schugar, H. J. and Potenza, J. A. *Inorg. Chem. 27* (1988) 1126.
21. Springborg, J. *Advances in Inorganic Chemistry*, Vol. 32. Academic Press, New York 1988, p. 109 and references therein.
22. Hazell, A., Jensen, K. B., McKenzie, C. J. and Toftlund, H. *Inorg. Chem. 33* (1994) 3127.