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Mechanisms of Axial and Equatorial Dimethyl Sulfoxide Exchange on $[TiO(DMSO)_5]^{2+}$. A Variable-Temperature and -Pressure ^1H NMR Study[1,2]

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The low-temperature 400-MHz ^1H NMR spectrum of $[TiO(e\text{-}DMSO)_4(a\text{-}DMSO)](CF_3SO_3)_2$ in nitromethane diluent containing excess free dimethyl sulfoxide (DMSO) reveals the signals of equatorial, axial, and free DMSO. Variable-temperature and -pressure line shape measurements were analyzed in terms of two exchange processes, a fast exchange between the a-DMSO (k_{ax}) and the bulk and a slower exchange between the e-DMSO (k_{eq}) and the coalesced a-DMSO and f-DMSO: k_{ax}^{298} (k_{eq}^{298}) = 6100 ± 800 (161 ± 4) s^{-1}, $\Delta H^{\ddagger}$ = 59.8 ± 2 (57.5 ± 1) kJ mol^{-1}, $\Delta S^{\ddagger}$ = +28.3 ± 6 (−9.9 ± 3) J K^{-1} mol^{-1}, and $\Delta V^{\ddagger}$ = +1.6 ± 0.1 (+4.8 ± 0.1) cm^3 mol^{-1}. A D mechanism is suggested for the fast exchange of the loosely bonded a-DMSO with the bulk. It is proposed that the second process, on the other hand, takes place through migration of the a-DMSO molecule to the equatorial plane and concerted loss of an e-DMSO molecule. This leads to an expanded transition state in which the breaking of the Ti(IV)–e-DMSO bond is predominant, as suggested by the positive volume of activation.

Introduction

The ability of many highly oxidized metal ions (e.g. vanadium(IV),[3] chromium(V),[4] molybdenum(V)[5] and molybdenum(VI),[6] etc.) to form oxometal ions is well-known. However, simple monomeric first-row transition metal oxo ions are not very common. The best known and studied is probably the oxovanadium(IV) ion. The evidence of a VO^{2+} moiety in solid complexes and in solution was demonstrated by electronic absorption spectroscopy,[3] electron nuclear double-resonance (ENDOR) spectroscopy,[7] and X-ray studies.[8,9]

In contrast, solid Ti(IV) oxo complexes with a true oxotitanium(IV) core are quite rare.[10,11] Only a few examples are available: TiO(porphyrin),[12] TiO(phthalocyanine),[13,14] $TiOCl_4^{2-}$,[15] and $TiOF_5^{3-}$.[16] On the basis of electron transfer[17,18] and ligand substitution reactions,[19] Sykes and co-workers obtained evidence of the existence of TiO^{2+} in acidic aqueous solutions of titanium(IV). Later, direct evidence for TiO^{2+} from Raman spectroscopy was produced.[20] Semiquantitative and qualitative ^{17}O NMR measurements[21] have shown that monomeric oxotitanium(IV) exists in aqueous acidic solution, but it is in equilibrium with other monomeric species, which most probably include $Ti(OH)_2^{2+}$ and $Ti^{4+}(aq)$. Recently, by the use of EXAFS (extended X-ray absorption fine structure) and XANES (X-ray absorption near-edge structure) techniques, the Ti(IV) ion in a sulfuric acid solution was found to form a –Ti–O–Ti– chain structure,[22] which is known to be present in the $TiOSO_4{\cdot}H_2O$ crystal.[23]

In nonaqueous solution, no information is available and simple monomeric and pentasolvated oxotitanium(IV) compounds have not, to our knowledge, previously been isolated. In this contribution we report the synthesis of $[TiO(DMSO)_5](CF_3SO_3)_2$ and a complete variable-temperature and -pressure study of DMSO exchange on $[TiO(DMSO)_5]^{2+}$ in deuterated nitromethane (CD_3NO_2) diluent.

Experimental Section

Materials, Syntheses, and Solutions. DMSO (Fluka, purum) was stored over 4-Å molecular sieves (Merck), and deuterated nitromethane (CD_3NO_2) (Ciba-Geigy, 99.0% D) was dried overnight on 3-Å molecular sieves (Merck). The synthesis and the preparation of samples were performed in a glovebox (water and oxygen content <1 ppm).

$[TiO(DMSO)_5](CF_3SO_3)_2$ was prepared by dissolving 1.43 g of anhydrous titanium(III) trifluoromethanesulfonate (triflate) (prepared as described previously)[24] in 5 mL of triethyl orthoformate (Fluka, purum), and the mixture was stirred for 10 min. A small excess of DMSO was then added dropwise to this brown solution, which quickly turned purple ($[Ti(DMSO)_6]^{3+}$, probably); then a white precipitate appeared. Further DMSO (5 mL) was added, followed by 30 mL of dry ether. A white solid slowly crystallized, and it was collected by filtration, washed with dry ether (20 mL), and dried in vacuum. The oxidation of Ti^{3+} to form oxotitanium(IV) is due to the direct abstraction of oxygen from DMSO by Ti^{3+}. Anal. Calcd (found): Ti, 6.36 (6.34); C, 19.15 (19.34); H, 4.02 (3.93); S, 29.82 (30.20); F, 15.14 (15.58); Cl, 0.00 (0.26).

Solutions of $TiO(DMSO)_5^{2+}$ (0.02 mol kg^{-1}) with excess DMSO (0.02 to 0.13 mol kg^{-1}) were prepared by dissolving weighed quantities of triflate salt in suitable amounts of CD_3NO_2 containing 1% tetramethylsilane (TMS) as NMR shift and field homogeneity reference.

NMR Measurements. ^1H NMR spectra were recorded at 400 MHz on a Bruker AM-400 spectrometer. The frequency window was set to 3 kHz. Thirty-two transients obtained with a 3-μs pulse (90° pulse ≈ 9 μs) were accumulated, and 16 384 points were recorded. CD_3NO_2 was used as an internal field lock; the temperature was controlled within ±0.2

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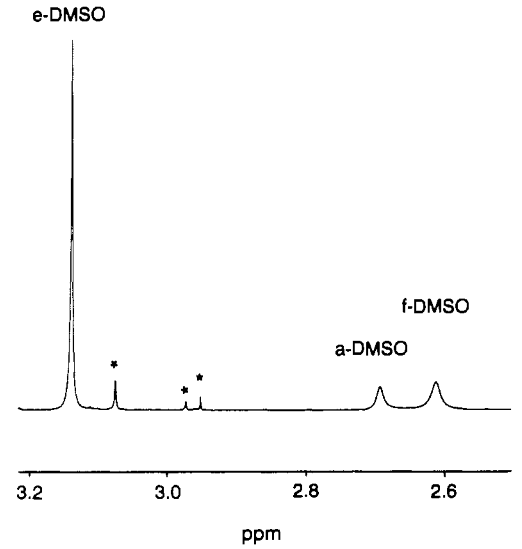

Figure 1. 400-MHz ^{1}H NMR spectrum of a 0.020 mol kg^{-1} $[TiO(DMSO)_5]^{2+}$ (a and e: axially and equatorially bonded DMSO, respectively) solution in CD_3NO_2 diluent at 238.7 K. The concentration in free DMSO (f) is 0.029 mol kg^{-1} (*: impurities).

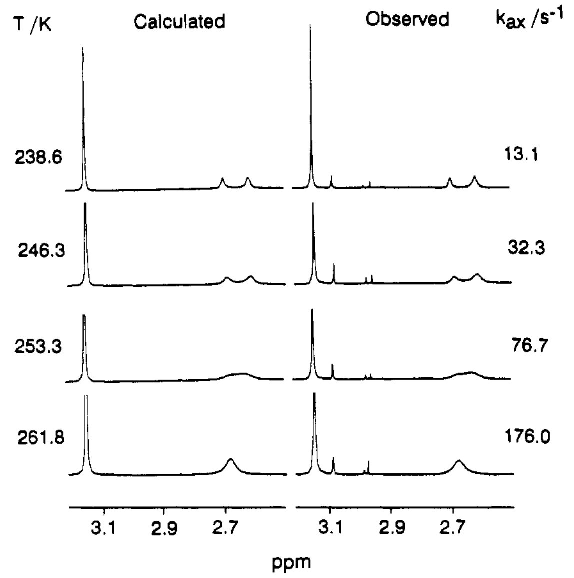

Figure 2. Observed and calculated 400-MHz ^{1}H NMR spectra of a 0.020 mol kg^{-1} $[TiO(DMSO)_5]^{2+}$ solution in CD_3NO_2 diluent ([f-DMSO] = 0.029 mol kg^{-1}) at different temperatures.

°C by gas circulation through the probe and was measured by substitution of the NMR tube for a 100-Ω Pt resistor.[25] Variable-pressure experiments were performed with a homebuilt high-pressure probe working up to 200 MPa, which has been described elsewhere.[26]

Data Treatment and Results

Table I. Effect of Free DMSO Concentration on the Rate Constants k_{ax} for a-DMSO Exchange and k_{eq} for e-DMSO Exchange on $[TiO(DMSO)_5]^{2+}$ in CD_3NO_2 Diluent at Various Temperatures[a]

[f-DMSO]/ mol kg^{-1}	k_{ax}/s^{-1} 238.7 K	k_{ax}/s^{-1} 249.5 K	k_{eq}/s^{-1} 298.7 K
0.018	12.0	46.7	161
0.029	13.1	47.5	162
0.054	12.6	46.4	159
0.092	12.4	47.3	156
0.128	11.9	46.8	161
av	12.4	46.9	160

[a] $[TiO^{2+}]$ = 0.020 mol kg^{-1}.

At low temperature (238.7 K), the 400-MHz ^{1}H NMR spectrum (Figure 1) of $[TiO(DMSO)_5]^{2+}$ in CD_3NO_2 diluent containing excess free DMSO presents three signals at 2.61, 2.69, and 3.14 ppm, corresponding to the free (hereafter simply denoted f-DMSO), axially bonded (a-DMSO), and equatorially bonded (e-DMSO) DMSO, respectively. The integrations of the signals at different temperatures and free DMSO concentrations give the expected ratio of 1:4 between a-DMSO and e-DMSO populations. As the temperature is increased, the f-DMSO and a-DMSO signals start to broaden (Figure 2), showing that chemical exchange occurs between the two environments (intermolecular a-DMSO exchange rate constant $k_{ax} = 1/\tau_{ax}$), according to eq 1, finally leading to coalescence. At higher temperatures, the broadening of the coalesced and e-DMSO signals shows that a second exchange takes place, which can be ascribed to (a) an intermolecular two-site exchange between e-DMSO and bulk DMSO ($k_{eq} = 1/\tau_{eq}$), according to eq 2, and (b) an intramolecular two-site exchange between e-DMSO and a-DMSO ($k_{int} = 1/\tau_{int}$), according to eq 3.

$$[TiO(e\text{-}DMSO)_4(a\text{-}DMSO)]^{2+} + {}^*DMSO \rightleftarrows [TiO(e\text{-}DMSO)_4(a\text{-}{}^*DMSO)]^{2+} + DMSO \quad (1)$$

$$[TiO(e\text{-}DMSO)_4(a\text{-}DMSO)]^{2+} + 4{}^*DMSO \rightleftarrows [TiO(e\text{-}{}^*DMSO)_4(a\text{-}DMSO)]^{2+} + 4DMSO \quad (2)$$

$$[TiO(e\text{-}DMSO)_4(a\text{-}{}^*DMSO)]^{2+} \rightleftarrows [TiO(e\text{-}DMSO)_3(e\text{-}{}^*DMSO)(a\text{-}DMSO)]^{2+} \quad (3)$$

The exchange spectra were least-squares-fitted to the calculated spectra using a program derived from ECHGNC.[27] For axial exchange (eq 1) together with equatorial exchange (case a, eq 2) a Kubo–Sack three-site matrix was constructed and used with the line shape analysis program to obtain the rate constants k_{ax} and k_{eq} for these two exchange processes. The analysis can be repeated with another matrix, corresponding to the axial exchange (eq 1) together with the intramolecular exchange (case b, eq 3). Unfortunately, the line shape analysis of the ^{1}H NMR spectra of $[TiO(DMSO)_5]^{2+}$ in CD_3NO_2 gives the same results whichever of the two matrices is used. It is, therefore, impossible by NMR line shape analysis to distinguish between reaction pathways a and b, or a combination of these two processes. This is because k_{ax} is about 40 times greater than k_{eq} and the a-DMSO and f-DMSO ^{1}H NMR signals are separated by only 30 Hz at low temperature. Once the latter two signals have coalesced, it is impossible to determine whether the e-DMSO exchanges with the a-DMSO or f-DMSO sites. If, on the other hand, k_{ax} and k_{eq} were of the same magnitude, the line shape analysis of the spectra could provide the necessary information to distinguish between the two possible exchange pathways.

Both a-DMSO and e-DMSO exchange rate constants are first order with respect to free DMSO concentration (Table I). The temperature influence on the rate constants was measured between 238.7 and 256.1 K for a-DMSO exchange and between 261.8 and 307.2 K for e-DMSO exchange, with two different free DMSO concentrations (Table II). At low temperatures (up to 260 K), only k_{ax} was fitted, the contribution from k_{eq} being negligible. At intermediate temperatures (260–275 K) the largest contribution was from k_{eq}, which was therefore fitted. In order to take account of the non-negligible contribution from k_{ax}, this was fixed at values extrapolated from the low-temperature data. At high tem-

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Table II. Effect of Temperature on the Rate Constants for a-DMSO (k_{ax}) and e-DMSO (k_{eq}) Exchange on $[TiO(DMSO)_5]^{2+}$ in CD_3NO_2 Diluent[a]

T/K	k_{ax}/s^{-1} [b]	k_{ax}/s^{-1} [c]	T/K	k_{eq}/s^{-1} [b]	k_{eq}/s^{-1} [c]	k_{ax}/s^{-1} [d]
238.7	13.1	11.1	261.8	5.4	5.8	190
243.5	23.0	20.5	268.7	10.7	11.9	400
246.3	32.3	30.0	275.7	20.2	26.7	800
249.5	47.2	46.5	284.1	47.9	50.9	∞
253.3	76.7	76.2	293.4	113	115	∞
256.1	93.7	98.8	298.7	163	169	∞
			301.9		214	∞
			307.2		320	∞

[a] $[TiO^{2+}] = 0.020$ mol kg^{-1}. [b] [f-DMSO] = 0.029 mol kg^{-1}. [c] [f-DMSO] = 0.128 mol kg^{-1}. [d] k_{ax} values used in the fitting procedure (see text).

Table III. Rate Constants and Kinetic Parameters for the Variable-Temperature and Variable-Pressure Study of DMSO Exchange on $[TiO(DMSO)_5]^{2+}$ in CD_3NO_2 Diluent[a]

	a-DMSO exchange	e-DMSO exchange
k^{298}/s^{-1}	6100 ± 800	161 ± 4
$\Delta H^{\ddagger}$/kJ mol^{-1}	59.8 ± 2	57.5 ± 1
$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	+28.3 ± 6	−9.9 ± 3
$\Delta V^{\ddagger}$/cm^3 mol^{-1}	+1.6 ± 0.1	+4.8 ± 0.1

[a] All values refer to the exchange of one particular solvent molecule, and errors represent one standard deviation.

perature (higher than 275 K), only k_{eq} was fitted. The contribution of k_{ax} at these temperatures is negligible, so this exchange rate was taken to be infinite. The values of k_{ax} and k_{eq} were then fitted to the Eyring equation with k^{298} or $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ as adjustable parameters. The rate constants and the activation parameters are listed in Table III.

The pressure dependence of k_{ax} and k_{eq} could be studied up to 200 MPa at 257.2 and 294.7 K, respectively. At these temperatures, the contribution of k_{eq} (≈3.5 s^{-1}) and k_{ax} (≈4550 s^{-1}), respectively, can be neglected. Both k_{ax} and k_{eq} values were fitted to eq 4, since we can assume that the corresponding volumes of

$$\ln k = \ln k_0 - P\Delta V^{\ddagger}/RT \qquad (4)$$

activation are pressure independent, as is usual for simple solvent-exchange reactions.[28] k_0 is the exchange rate constant at zero pressure, and $\Delta V^{\ddagger}$ is the solvent exchange activation volume. Figure 3 shows the effect of pressure on the a-DMSO exchange. As the pressure is increased from 0.1 to 199 MPa, the coalesced signal of a-DMSO and f-DMSO broadens due to slowing of the axial exchange and consequent separation of the two peaks. An even greater deceleration can be observed in Figure 4, which shows the effect of pressure on the e-DMSO exchange. This decrease of the exchange rate constants with pressure, illustrated in Figure 5, gives a positive volume of activation for both processes (Table III).

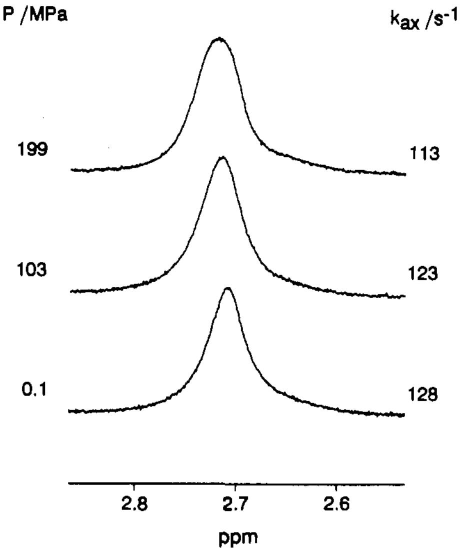

Figure 3. Observed 400-MHz ^{1}H NMR spectra of a 0.020 mol kg^{-1} $[TiO(DMSO)_5]^{2+}$ solution in CD_3NO_2 diluent at 257.2 K as a function of pressure. [f-DMSO] = 0.022 mol kg^{-1}.

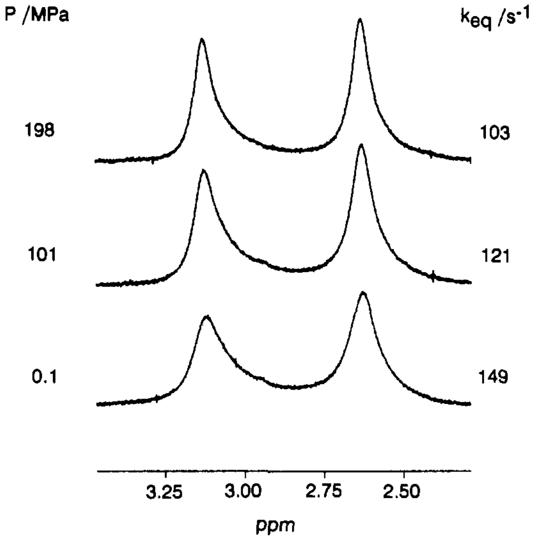

Figure 4. Observed 400-MHz ^{1}H NMR spectra of a 0.020 mol kg^{-1} $[TiO(DMSO)_5]^{2+}$ solution in CD_3NO_2 diluent at 294.7 K as a function of pressure. [f-DMSO] = 0.061 mol kg^{-1}.

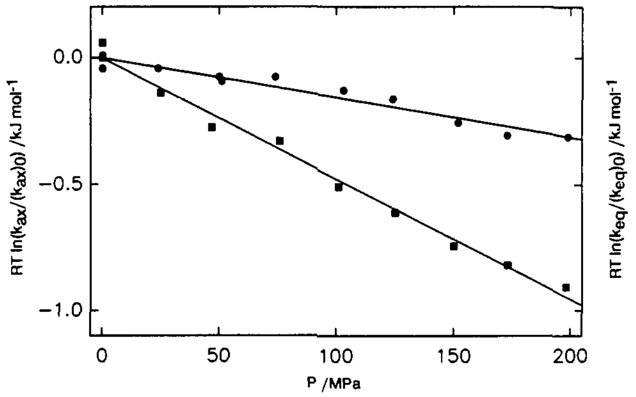

Figure 5. Plot of $RT \ln (k/k_0)$ vs pressure for a-DMSO and e-DMSO exchange on $[TiO(DMSO)_5]^{2+}$ (0.020 mol kg^{-1}) in CD_3NO_2 diluent: (●) k_{ax}, $T = 257.2$ K and [f-DMSO] = 0.022 mol kg^{-1}; (■) k_{eq}, $T = 294.7$ K and [f-DMSO] = 0.061 mol kg^{-1}.

Discussion

Table IV gives the available rate constants and activation parameters for solvent exchange on VO^{2+} and TiO^{2+} ions. The DMSO exchange on $[TiO(DMSO)_5]^{2+}$ is the only published quantitative study of solvent exchange on an oxotitanium(IV) ion. However the oxotitanium(IV) ion, as well the oxovanadium(IV) ion, is very interesting from a mechanistic point of view. It contains three coordinated oxygen types which are structurally and kinetically distinct, and therefore four exchanges are possible:

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Table IV. Rate Constants and Activation Parameters for Solvent Exchange on $[VO(solvent)_5]^{2+}$ and $[TiO(solvent)_5]^{2+}$

solvent	k^{298}/s^{-1}	$\Delta H^*/$ kJ mol^{-1}	$\Delta S^*/$ J K^{-1} mol^{-1}	$\Delta V^*/$ cm^3 mol^{-1}	ref
		$[VO(solvent)_5]^{2+}$			
H_2O	500 (eq)	57.3	−2.4	+1.9[a]	29
	$\approx 10^9$ (ax)				29
DMSO	1760 (eq)	60.1	+18.5	−5.3[b]	30
DMF	575 (eq)	30.3	−87.7		31
	200 (eq)	54.8	−17.2		32
	46 000 (ax)	64.0	+58.0		32
CH_3CN	2850 (eq)	29.5	−83.7		33
CH_3OH	565 (eq)	39.6	−59.4		34
DMA	4700 (eq)	42.3	−33.1		32
		$[TiO(solvent)_5]^{2+}$			
DMSO	161 (eq)	57.5	−9.9	+4.8	this work
	6100 (ax)	59.8	+28.3	+1.6	this work

[a] Reference 35. [b] Reference 36.

the oxo oxygen exchange, k_o, the intermolecular solvent axial exchange, k_{ax}, the intermolecular solvent equatorial exchange, k_{eq}, and the intramolecular rearrangement of solvent from axial to equatorial sites, k_{int}.

In aqueous solution, the exchange rates of the oxo oxygen in TiO^{2+} [21] and VO^{2+} [37,38] are 1.6×10^4 and 2.4×10^{-5} s^{-1}, respectively. This enormous difference was explained by a relatively easily protonated oxo oxygen in the case of oxotitanium(IV).[21]

Early line-broadening studies[29,39,40] show that the water molecule in the axial position of $[VO(H_2O)_5]^{2+}$ exchanges very rapidly, $k_{ax} \approx 10^9$–10^{11} s^{-1}, and the axial *N,N*-dimethylformamide exchange rate on $[VO(DMF)_5]^{2+}$ is equal to 4.6×10^4 s^{-1}.[32] Due to the paramagnetism of the VO^{2+} entity, the kinetic information was obtained indirectly using the Swift and Connick approach, that is by studying the line width behavior of the bulk solvent. In contrast, for diamagnetic TiO^{2+}, the lower axial DMSO exchange rate on $[TiO(DMSO)_5]^{2+}$ allowed us to observe the a-DMSO ^1H NMR signal: this constitutes the first direct evidence of an axial solvent exchange on an oxotitanium(IV) or oxovanadium(IV) ion. It is known[8,9] that the structure of oxovanadium(IV) complexes is significantly distorted so that the V(IV) center is situated 0.1–0.3 Å above the plane defined by the four equatorial coordination sites. The molecule in the axial position is at a long distance compared to the equatorial molecules. No crystal structure determination of pentasolvated oxotitanium(IV) complexes has been published to date. However, the structure of $[TiO(DMSO)_5]^{2+}$ should be similar to that of the oxovanadium(IV) analog. Thus we expect the axial titanium–DMSO bond to be weaker than the equatorial bonds. We therefore suggest a D mechanism, supported by the first-order rate law and the high a-DMSO exchange rate. In general, we would expect this to be reflected by a large positive activation volume. In this case, however, since the axial titanium–DMSO bond is long, only a small change in volume is necessary to reach the transition state. The small positive activation volume (+1.6 cm^3 mol^{-1}) obtained for the a-DMSO exchange is, therefore, not surprising.

Rate constants for equatorial complex formation of $[VO(H_2O)_5]^{2+}$ and $[TiO(H_2O)_5]^{2+}$ summarized by Saito and Sasaki[41] and for solvent exchange on VO^{2+} reported in Table IV are mostly in the range from 10^2 to 10^3 s^{-1}. On the other hand, the anation reactions of [VO(*N*-(2-pyridylmethyl)iminodiacetato)(H_2O)][42] and [VO(nitrilotriacetato)$(H_2O)]^{-}$ [43] in which the axial site is blocked by the tertiary amino nitrogen group are much slower (rate constants are 1–10^{-1} M^{-1} s^{-1} at room temperature). The above authors consider that the values for the latter reactions probably represent the real rate of equatorial substitution and, therefore, that the other "equatorial substitution rates" are determined by an intramolecular process in which the ligand at the very labile axial site migrates to the equatorial site. A mechanism of substitution at the equatorial site involving axial–equatorial migration of the substituting ligand seems also to operate in the Mo_2^{4+} aqua dimer.[44]

A similar reaction pathway is suggested for e-DMSO exchange on $[TiO(DMSO)_5]^{2+}$, with migration of the a-DMSO molecule to the equatorial plane and concerted loss of an e-DMSO molecule. This mechanism is compatible with the observed first-order rate law and an expanded transition state in which the breaking of the Ti(IV)–e-DMSO bond is predominant, as suggested by the positive activation volume (+4.8 cm^3 mol^{-1}).[45] However, direct exchange between e-DMSO and the bulk cannot be ruled out.

In conclusion, the $[TiO(DMSO)_5]^{2+}$ complex exhibits two distinct DMSO-exchange processes. For the first time on an oxotitanium(IV) or oxovanadium(IV) ion, we observe directly the axial intermolecular solvent exchange. For this fast reaction, a D mechanism is proposed. In addition, we observe a slower equatorial exchange process for which we propose a concerted mechanism involving axial–equatorial migration with an expanded transition state.

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Supplementary Material Available: Rate constants for a-DMSO and e-DMSO exchange on $[TiO(DMSO)_5]^{2+}$ as a function of pressure (Table SI) (1 page). Ordering information is given on any current masthead page.

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