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Contribution from the Institut de Chimie Minérale et Analytique,
Université de Lausanne, 3 Place du Château, CH-1005 Lausanne, Switzerland

# Variable-Temperature and -Pressure Studies of Solvent Exchange, Complex Formation, and Dissociation of Vanadium(III) in DMSO[1,2]

Ivo Dellavia, Pierre-Yves Sauvageat, Lothar Helm, Yves Ducommun, and André E. Merbach*

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DMSO exchange on hexakis(dimethyl sulfoxide)vanadium(III) has been studied as a function of temperature and pressure by $^1H$ NMR spectroscopy at 200 and 400 MHz, in neat DMSO and in the diluent nitromethane. The following exchange parameters were obtained in neat solvent: $k_{ex}^{298}/s^{-1} = 13.1$; $\Delta H_{ex}^*/kJ\ mol^{-1} = 38.5$; $\Delta S_{ex}^*/J\ K^{-1}\ mol^{-1} = -94.5$; $\Delta V_{ex}^*/cm^3\ mol^{-1} = -10.1$. In the diluent nitromethane a second-order rate law is observed with $k_2^{298}/mol^{-1}\ kg\ s^{-1} = 2.7$. The kinetics of formation and dissociation of $V(DMSO)_5NCS^{2+}$ (NCS = thiocyanate) have been studied in DMSO solution as a function of excess metal ion concentration, temperature, and pressure, by the stopped-flow technique. The thermodynamic stability of the complex was also determined spectrophotometrically. The kinetic and equilibrium data were submitted to a combined analysis. The rate constants and activation parameters for the formation (f) and dissociation (r) of the complex are as follows: $k_f^{298}/M^{-1}\ s^{-1} = 153.8$; $k_r^{298}/s^{-1} = 0.93$; $\Delta H_f^*/kJ\ mol^{-1} = 44.8$; $\Delta H_r^*/kJ\ mol^{-1} = 42.0$; $\Delta S_f^*/J\ K^{-1}\ mol^{-1} = -52.5$; $\Delta S_r^*/J\ K^{-1}\ mol^{-1} = -104.6$; $\Delta V_f^*(313\ K)/cm^3\ mol^{-1} = -0.3$; $\Delta V_r^*(313\ K)/cm^3\ mol^{-1} = -11.8$. The equilibrium constant for the formation of the monoisothiocyanato complex is $K^{298}/M^{-1} = 166.0$, and the enthalpy and entropy of reaction are $\Delta H^\circ/kJ\ mol^{-1} = +2.9$ and $\Delta S^\circ/J\ K^{-1}\ mol^{-1} = +52.1$. The reaction volume is $\Delta V^\circ(318\ K)/cm^3\ mol^{-1} = +11.5$. The results for both processes are discussed and an associative interchange, $I_a$, mechanism is suggested for these substitution reactions on $V(DMSO)_6^{3+}$ as for the analagous reactions in water.

## Introduction

In the field of substitution reactions on solvated transition metal ions, the main effort over the last years has been the assignment of substitution mechanisms on the basis of activation volumes.[3-6] High-pressure NMR techniques have been used to investigate solvent exchange reactions of most high-spin divalent first-row hexasolvated transition metal ions. The measured activation volumes show a gradual changeover in substitution mechanism from $I_a$ to $I_d$ across the series. The change in activation mode occurs after the $d^5$ configuration[5] except for *N,N*-dimethylformamide (DMF) exchange, where the activation volume is already positive for $Mn^{2+}$.[7] This mechanistic singularity, which may be explained by steric effects, was confirmed by a complex formation study between $Mn(DMF)_6^{2+}$ and diethyldithiocarbamate using stopped-flow techniques.[8]

Experimental results in nonaqueous solvents and in water indicate that a similar mechanistic changeover exists also for the trivalent hexasolvated cations,[9] although in nonaqueous solvents results are available only for solvent exchange on chromium,[10,11] iron,[12] and gallium.[13,9] High-pressure studies of dimethyl sulfoxide (DMSO) exchange on these three ions show that the activation volumes change from negative ($Fe^{3+}$ and $Cr^{3+}$) to positive ($Ga^{3+}$) values. To test whether this trend also applies to DMSO exchange on earlier transition elements, we have performed a variable-temperature and -pressure $^1H$ NMR study on the $V(DMSO)_6^{3+}$ ion.[14] Further, we have complemented this work by a variable-temperature and high-pressure stopped-flow study of the thiocyanate complex formation with the same ion.

## Experimental Section

**A. Chemicals and Solutions.** Dimethyl sulfoxide (DMSO, Fluka, pa) was dried over 3-Å molecular sieves for 30 h (water content <25 ppm, measured by Karl Fisher titration) and then filtered and stored in a glovebox. Deuterated nitromethane ($CD_3NO_2$) (Ciba-Geigy, 99.0% D) was dried overnight over 3-Å molecular sieves (Merck), and DMSO-$d_6$ (Ciba-Geigy, 99.8% D) was used without further purification. Trifluoromethanesulfonic acid ($CF_3SO_3H$, Alpha, purum, trivial name triflic acid, HT) was distilled at ambient pressure and degassed under reduced pressure. Syntheses and preparation of solutions for the kinetic studies were performed in a glovebox (water and oxygen content <1 ppm).

$[V(DMSO)_6](CF_3SO_3)_3$ was prepared by dissolving 1.43 g of anhydrous vanadium(III) triflate (prepared as described previously)[15] in 5 mL of triethyl orthoformate (Fluka, purum). A small excess of DMSO was then added dropwise, and a pale green precipitate appeared immediately. The solid was collected by filtration, washed with dry ether (20 mL), and dried under vacuum (40 °C, $5 \times 10^{-4}$ Torr). Anal. Calcd (found): C, 18.63 (18.75); H, 3.76 (3.67); S, 29.84 (29.79); F, 17.68 (17.81); V, 5.27 (5.23); Cl, 0.00 (<0.05).

Sodium thiocyanate (NaSCN, Merck, pa) was recrystallized from water and dried under vacuum. Sodium triflate (NaT), used as an inert electrolyte, was prepared by neutralizing a 1 M triflic acid solution with NaOH (Merck, pa) to pH = 6.2, evaporating the water, recrystallizing the white solid in a water/acetone mixture, and drying the crystals under vacuum.

For the NMR measurements, the solutions were prepared by weighing and the concentrations are given in molality (mol $kg^{-1}$ of solvent). A 1–2% concentration of tetramethylsilane (TMS) was added as a shift and field homogeneity reference.

For the complex formation study, two stock solutions in DMSO, 0.1 M in $V(DMSO)_6^{3+}$ and $1 \times 10^{-3}$ M in NaSCN were prepared volumetrically. The ionic strength was fixed at 0.5 M with NaT. Concentrations are given in molarity (M = mol $dm^{-3}$ of solution) uncorrected for volume changes due to temperature and/or pressure.[16] Sample solutions were prepared shortly before use by diluting the stock solutions.

**B. Proton NMR Measurements.** Fast-injection experiments were performed on Bruker CXP-200 (4.7 T) and AM-400 (9.4 T) spectrometers using a fast-injection apparatus described elsewhere.[17] Variable-temperature line-broadening spectra were recorded at 400 MHz. The temperature (±0.3 K) was measured by a substitution technique using a 100-Ω Pt resistor.[18] Variable-pressure line-broadening measurements were performed at 400 MHz using a homebuilt high-pressure probe[19] working up to 200 MPa. For the line-broadening experiments either $CD_3NO_2$ or DMSO-$d_6$ was used as an internal field lock. In all cases 5-mm tubes were used.

**C. Equilibrium and Kinetic Spectrophotometric Measurements.** A Perkin-Elmer Lambda 5 spectrophotometer with thermostated cells was used for the equilibrium studies. A high-pressure optical cell[20] was used for variable-pressure equilibrium studies. The experimental setups for

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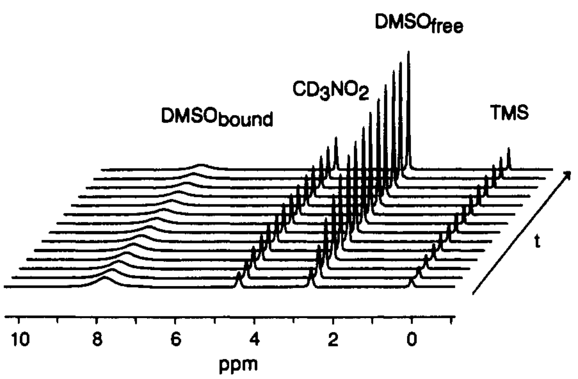

**Figure 1.** Stacked plot of every fourth spectrum after fast-injection of a 0.32-g solution of DMSO-$d_6$ (1.60 mol kg$^{-1}$) in $CD_3NO_2$ into a 0.50-g solution of $[V(DMSO)_6](CF_3SO_3)_3$ (0.10 mol kgl$^{-1}$) in $CD_3NO_2$ at 240.2 K. The time interval between the 200-MHz $^1H$ NMR plotted spectra is 8 s. Each spectrum was recorded over a sweep width of 5 kHz and required 1 scan obtained with a 3-μs pulse. 4K data points were recorded.

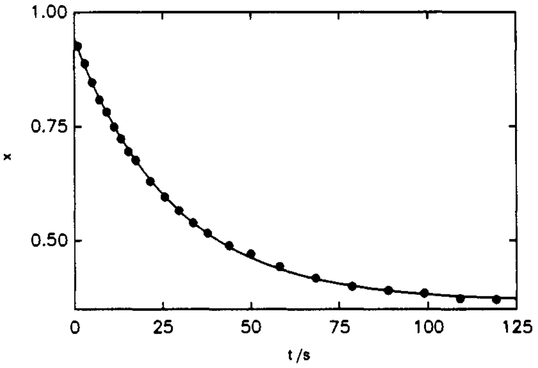

**Figure 2.** Mole fraction $x$ of bound DMSO as a function of time, for the experiment illustrated in Figure 1.

ambient pressure stopped-flow kinetic work were as described previously.[21] For the kinetic pressure dependence studies, a new high-pressure stopped-flow apparatus was used. This apparatus uses the same drive system unit as our first instrument[21] and can support pressures up to 200 MPa in a temperature range 223–373 K with improved temperature stability, a better light throughput, and a response time of 4 ms. Appearance of the complex was monitored at a wavelength of 350 nm, at which neither metal nor ligand absorb significantly.

## Results

**A. Dimethyl Sulfoxide Exchange on $V(DMSO)_6^{3+}$.** DMSO coordinates to the hard $V^{3+}$ cation through the oxygen atom, bonding through the sulfur atom being found only with soft cations from groups 8–10 of the periodic table.[22] This is confirmed by the fact that the S–O stretching frequency decreases from 1053 cm$^{-1}$ in free dimethyl sulfoxide to about 950 cm$^{-1}$ when coordinated to $V^{3+}$.[23]

The $^1H$ NMR spectrum of a DMSO solution containing the $V^{3+}$ metal ion consists of two resonances: a narrow, intense peak due to bulk DMSO and a high-frequency-shifted, smaller, wide peak due to the DMSO bound to the paramagnetic ion (Figure 1). At 308 K, the chemical shift and the full width at half-height of the free (bound) DMSO signal are 2.54 (6.11) ppm and 8.9 (72.3) Hz, respectively. Integration of the two signals at various temperatures gives the expected coordination number of 6.0 ± 0.1.

Because the rate of DMSO exchange with the $V(DMSO)_6^{3+}$ ion is quite slow, paramagnetic line-broadening studies require the use of relatively high temperatures to produce significant exchange-broadening effects. At these high temperatures, our solutions decomposed slowly with time, becoming progressively more blue (probably formation of $VO^{2+}$ ion). Therefore, we used a fresh solution for every variable-temperature measurement and did not extend our study to very high temperatures (370 K in neat solvent and 354 K in $CD_3NO_2$). Low-temperature measurements were limited by the freezing point of DMSO (291 K).

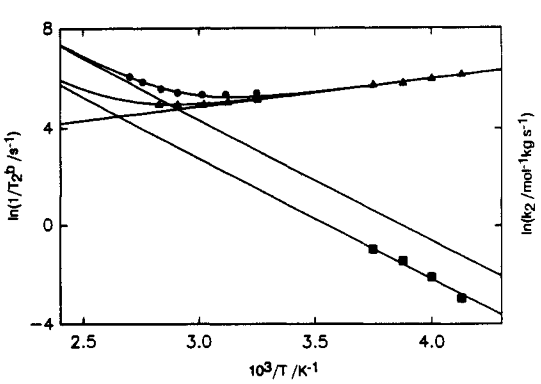

**Figure 3.** Temperature dependence of the transverse relaxation rate, $(1/T_2^b)_{neat}$, from the bound DMSO $^1H$ NMR signal of 0.05 mol kg$^{-1}$ $V(DMSO)_6^{3+}$, in neat DMSO (●) and $(1/T_2^b)_{dil}$ in $CD_3NO_2$ ($[DMSO]_{free}$ = 1.00 mol kg$^{-1}$) (▲), including second-order exchange rates, $k_2$ (■), obtained from fast-injection experiments in $CD_3NO_2$ ($[V(DMSO)_6^{3+}] \approx 0.01$ mol kg$^{-1}$ and $[DMSO]_{free} \approx 0.10$ mol kg$^{-1}$).

One way to extend the temperature range (130 K) over which rate data may be obtained is to study the exchange in $CD_3NO_2$ as diluent (fp: 245 K) and to use fast-injection Fourier-transform NMR spectroscopy. In this way the activation parameters, $\Delta H_{ex}^{*}$ and $\Delta S_{ex}^{*}$, can be obtained with higher precision. The good agreement between results from the NMR line-broadening and fast-injection NMR methods (Figure 3) is reassuring. The relaxation effect of the paramagnetic ion (confirmed by $T_1$ measurements of bound and free $^1H$ NMR DMSO signals) prevents saturation of the spin system, even when using short repetition times as often is the case in fast-injection NMR experiments.

A variable-concentration study and a first variable-temperature study were carried out in $CD_3NO_2$ using the fast-injection NMR technique. The isotopic equilibration of reaction 1 as a function

$$V(DMSO)_6^{3+} + 6DMSO\text{-}d_6 \rightleftarrows V(DMSO\text{-}d_6)_6^{3+} + 6DMSO \qquad (1)$$

of concentration of DMSO-$d_6$ and temperature was followed by monitoring the increase in intensity of the proton NMR signal of free DMSO and the decrease of that of bound DMSO after fast injection of a solution of DMSO-$d_6$ in the diluent $CD_3NO_2$ (≈0.5 g) into a similar quantity of a solution of $[V(DMSO)_6](CF_3SO_3)_3$ in deuterated nitromethane. Figure 1 shows a series of fast-injection spectra, and Figure 2, a typical example of a kinetic run. The rate law for the isotopic exchange can be expressed by eq 2,[24] where $k$ represents the rate constant for the

$$-dx/dt = k(x - x_\infty)/(1 - x_\infty) \qquad (2)$$

exchange of a particular dimethyl sulfoxide molecule.[25] $x$ and $x_\infty$ are the mole fractions of bound DMSO at the time of sampling and at exchange equilibrium, respectively. The time dependence of $x$, obtained by integration of the signals ($x = I_{bound}/(I_{bound} + I_{free})$) was fitted to eq 3, resulting from integration of eq 2 with $x = x_0$ at $t = 0$ and $x = x_\infty$ at $t = \infty$. The adjustable parameters were $k$, $x_0$, and $x_\infty$.

$$x = x_\infty + (x_0 - x_\infty)\exp[-kt/(1 - x_\infty)] \qquad (3)$$

The observed rate constants varied linearly (Table I) with the concentration of free dimethyl sulfoxide leading to eq 4, which

$$k_{obs} = k_2[DMSO] \qquad (4)$$

allows one to calculate the second-order rate constant, $k_2$ = (37.4

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**Table I.** Observed and Second-Order Rate Constants for DMSO Exchange on $V(DMSO)_6^{3+}$ as a Function of Free DMSO Concentration Obtained from Fast-Injection NMR Experiments in $CD_3NO_2$

| $T$/K | $[V^{3+}]$/ mol kg$^{-1}$ | [DMSO]/ mol kg$^{-1}$ | $10^3 k_{obs}$/s$^{-1}$ | $10^3 k_2$/mol$^{-1}$ kg s$^{-1}$ |
|---|---|---|---|---|
| 240.7 | 0.0541 | 0.069 | 2.8 ± 0.1 | 40.7 |
| 240.4 | 0.0550 | 0.180 | 7.5 ± 0.2 | 41.7 |
| 240.2 | 0.0510 | 0.391 | 16.1 ± 0.2 | 41.2 |
| 240.2 | 0.0640 | 0.431 | 15.5 ± 0.1 | 35.9 |
| 240.2 | 0.0607 | 0.628 | 22.8 ± 0.2 | 36.3 |

**Table II.** Derived NMR and Kinetic Parameters for the Variable-Temperature and -Pressure Study of DMSO Exchange on Vanadium(III) in Neat Solvent[a]

| | | | |
|---|---|---|---|
| $k_{ex}^{298}$/s$^{-1}$ | 13.1 ± 1.5 | $E_m^b$/kJ mol$^{-1}$ | 9.3 ± 0.5 |
| $\Delta H_{ex}^{*}$/kJ mol$^{-1}$ | 38.5 ± 1.6 | $[DMSO]_M$/mol kg$^{-1}$ [b] | 4.8 ± 1.0 |
| $\Delta S_{ex}^{*}$/J K$^{-1}$ mol$^{-1}$ | −94.5 ± 4.6 | $\Delta V_{ex}^{*}$/cm$^3$ mol$^{-1}$ | −10.1 ± 0.6 |
| $(1/T_{2m}^b)^{298}$/s$^{-1}$ | 193.5 ± 5.8 | $\Delta V_m^{*}$/cm$^3$ mol$^{-1}$ | −2.1 ± 0.4 |

[a] Errors represent one standard deviation. [b] This leads to $k_2^{298}$/mol$^{-1}$ kg s$^{-1}$ = $k_{ex}^{298}/[DMSO]_M$ = 2.7 in $CD_3NO_2$ diluent.

± 1.3) × $10^{-3}$ mol$^{-1}$ kg s$^{-1}$ at 240.3 K. A variable-temperature study was performed in the range 242.2–266.7 K (Figure 3). As discussed below, these results were fitted together with the line-broadening results to obtain the NMR and activation parameters.

A second variable-temperature study using the broadening of the bound DMSO proton signal as a function of temperature (242 < $T$/K < 353) in the diluent $CD_3NO_2$ and neat DMSO was performed (Figure 3).

In neat DMSO and in the case of slow exchange, the transverse relaxation of the bound DMSO signal, $(1/T_2^b)_{neat}$, can be expressed as the sum of a term due to paramagnetic relaxation, $1/T_{2m}^b$, and a term due to chemical exchange, $1/\tau$ (eq 5). From transition-state theory, the temperature dependence of $\tau$ and its relation to the pseudo-first-order exchange rate constant, $k_{ex}$, is given by eq 6, where $\Delta S_{ex}^{*}$ and $\Delta H_{ex}^{*}$ are the entropy and enthalpy of activation.

$$(1/T_2^b)_{neat} = 1/T_{2m}^b + 1/\tau \tag{5}$$

$$1/\tau = k_{ex} = k_B T/h \exp(\Delta S_{ex}^{*}/R - \Delta H_{ex}^{*}/RT) \tag{6}$$

An Arrhenius temperature dependence for the paramagnetic relaxation rate has been assumed (eq 7), where

$$1/T_{2m}^b = (1/T_{2m}^b)^{298} \exp[E_m^b/R(1/T - 1/298.15)] \tag{7}$$

$(1/T_{2m}^b)^{298}$ is the contribution at 298.15 K and $E_m^b$ is the corresponding activation energy. In $CD_3NO_2$ diluent, eq 5 is replaced by eq 8, and the combination with eq 4 leads to expression 9. We will assume that the observed second-order behavior (eq 4 and Table I) observed in $CD_3NO_2$ is also valid in neat DMSO ($[DMSO]_M$ = 12.8 mol kg$^{-1}$), which leads to eq 10. By introducing $k_2$ from eq 10 in eq 9, we obtain eq 11 for the relaxation of the bound DMSO signal in a inert diluent. [DMSO] is 1 mol kg$^{-1}$ for this study. All the variable-temperature data obtained for $V(DMSO)_6^{3+}$ in neat solvent and in the diluent (line-broadening and fast-injection studies) were fitted simultaneously to eqs 5–7 and 11 using a nonlinear least-squares iteration program with the approximation $1/T_{2m}^b = (1/T_{2m}^b)_{dil}$. The exchange and NMR parameters are listed in Table II, and the experimental data and the calculated curve are illustrated in Figure 3. Note that $[DMSO]_M$ was used as parameter in the iteration procedure and that the found value of 4.8 mol kg$^{-1}$ indicates a leveling effect at very high concentration of DMSO, which is not surprising.[26]

$$(1/T_2^b)_{dil} = (1/T_{2m}^b)_{dil} + k_{obs} \tag{8}$$

$$(1/T_2^b)_{dil} = (1/T_{2m}^b)_{dil} + k_2[DMSO] \tag{9}$$

$$k_{ex} = k_2[DMSO]_M \tag{10}$$

$$(1/T_{2b})_{dil} = (1/T_{2m}^b)_{dil} + k_{ex}[DMSO]/[DMSO]_M \tag{11}$$

**Table III.** Effect of Pressure on the Relaxation Rates of the Proton Signal of the Bound DMSO in Neat Solvent at Several Temperatures[a]

| $P$/MPa | $(1/T_2^b)_{neat}$/s$^{-1}$ | $P$/MPa | $(1/T_2^b)_{neat}$/s$^{-1}$ |
|---|---|---|---|
| 0.1 | 245.9 | 0.1 | 219.2 |
| 0.1 | 245.4 | 0.1 | 219.9 |
| 0.1 | 245.2 | 27 | 230.2 |
| 26 | 251.9 | 50 | 238.6 |
| 50 | 256.7 | 76 | 244.2 |
| 75 | 268.5 | 100 | 257.2 |
| 101 | 284.6 | 125 | 263.5 |
| 126 | 293.2 | 150 | 275.6 |
| 151 | 298.3 | 174 | 289.4 |
| 176 | 305.8 | 198 | 288.3 |
| 0.1 | 226.3 | 0.1 | 274.5 |
| 0.1 | 225.4 | 0.1 | 294.4 |
| 26 | 234.2 | 0.1 | 269.9 |
| 50 | 248.6 | 54 | 325.0 |
| 75 | 254.2 | 74 | 331.9 |
| 100 | 267.7 | 100 | 362.5 |
| 125 | 284.9 | 125 | 368.7 |
| 150 | 289.7 | 150 | 391.9 |
| 176 | 316.4 | 179 | 475.3 |
| 194 | 315.8 | | |

[a] $[V(DMSO)_6^{3+}]$ = 0.05 mol kg$^{-1}$; $T$ = 311.1, 322.7, 332.8, and 349.1 K, respectively.

**Table IV.** Derived NMR and Kinetic Parameters for the Variable-Pressure Study of DMSO Exchange on Vanadium(III) in Neat Solvent

| $T$/K | $(1/T_{2m}^b)_0$/s$^{-1}$ | % $(1/T_{2m}^b)_0$[a] | $(k_{ex})_0$/s$^{-1}$ | % $(k_{ex})_0$[a] |
|---|---|---|---|---|
| 311.1 | 221.0 ± 2.6 | 86 | (26) | 14 |
| 322.7 | 173.4 ± 2.2 | 76 | (46) | 24 |
| 332.8 | 151.6 ± 2.2 | 64 | (74) | 36 |
| 349.1 | (112) | 43 | 168.6 ± 3 | 57 |

[a] Each contribution is expressed as a percentage of the value of $1/T_2^b$. The values in parentheses were fixed during the fitting procedure.

Variable-pressure studies were performed using line-broadening NMR measurements. The pressure dependence of ln $k_{ex}$ can be described by the linear eq 12, if we assume a pressure independent volume of activation, as is often observed for simple solvent-exchange reactions.[27] $k_{ex,0}$ is the exchange rate constant at zero pressure and $\Delta V_{ex}^{*}$ is the solvent exchange activation volume. A similar equation, eq 13, describes the pressure dependence of the paramagnetic relaxation rate, where $\Delta V_m^{*}$ is the paramagnetic relaxation activation volume and $(1/T_{2m}^b)_0$ the contribution at zero pressure. The variable-pressure $1/T_{2b}$ measurements in neat DMSO (Table III) were performed at four different temperatures (311 < $T$/K < 349) in order to separate pressure effects on paramagnetic relaxation and chemical exchange. The four sets of experimental $1/T_2^b$ data were simultaneously nonlinear least-squares fitted to eqs 5, 12, and 13. In theory, $k_{ex,0}$ and $(1/T_{2m}^b)_0$ at each temperature could be fixed at the values obtained from the variable-temperature analysis. In practice, small differences in temperature calibration between the variable-temperature and variable-pressure experiments could cause nonrandom errors in the $1/T_2^b$ measurements. Thus, at each temperature, we fixed only the parameter ($k_{ex,0}$ or $(1/T_{2m}^b)_0$) which contributed least to the magnitude of $1/T_2^b$. The $(1/T_{2m}^b)_0$ and $k_{ex,0}$ values (fixed and fitted) are reported in Table IV, and the corresponding activation volumes are given in Table II.

$$\ln k_{ex} = \ln k_{ex,0} - P\Delta V_{ex}^{*}/RT \tag{12}$$

$$\ln (1/T_{2m}^b) = \ln [(1/T_{2m}^b)_0] - P\Delta V_m^{*}/RT \tag{13}$$

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(26) By the fixing of $[DMSO]_M$ at 12.8 mol kg$^{-1}$, the quality of the fit is less good: $k_{ex}^{298}$ = 21.1 ± 1.2 s$^{-1}$, $\Delta H_{ex}^{*}$ = 31.6 ± 0.8 kJ mol$^{-1}$, $\Delta S_{ex}^{*}$ = −113.4 ± 2.9 J K$^{-1}$ mol$^{-1}$, $(1/T_{2m}^b)^{298}$ = 196.5 ± 7.8 s$^{-1}$, and $E_m^b$ = 8.9 ± 0.7 kJ mol$^{-1}$.

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**Table V.** Thermodynamic and Kinetic Parameters for Complex Formation and Dissociation of $V(DMSO)_5(NCS)^{2+}$ [a]

| | individual fits | simultaneous fit | | individual fits | simultaneous fit |
|---|---|---|---|---|---|
| $K^{298}/M^{-1}$ | $184.7 \pm 1.9^b$ | $166.0 \pm 7.6^g$ | $\Delta S°/J\ K^{-1}\ mol^{-1}$ | $+48.1 \pm 7.6^d$ | $+52.1 \pm 6.5^g$ |
| $k_f^{298}/M^{-1}\ s^{-1}$ | $140.8 \pm 4.4^c$ | $153.8 \pm 3.0^{g,i}$ | $\Delta S_f^{\ddagger}/J\ K^{-1}\ mol^{-1}$ | $-54.1 \pm 3.8^c$ | $-52.5 \pm 3.0^g$ |
| $k_r^{298}/s^{-1}$ | $1.03 \pm 0.03^c$ | $0.93 \pm 0.01^{g,i}$ | $\Delta S_r^{\ddagger}/J\ K^{-1}\ mol^{-1}$ | $-102.1 \pm 4.1^c$ | $-104.6 \pm 3.9^g$ |
| $\Delta H°/kJ\ mol^{-1}$ | $+2.1 \pm 2.4^d$ | $+2.9 \pm 2.0^g$ | $\Delta V°(318\ K)/cm^3\ mol^{-1}$ | $+10.5 \pm 2.7^e$ | $+11.5 \pm 0.8^h$ |
| $\Delta H_f^{\ddagger}/kJ\ mol^{-1}$ | $44.6 \pm 1.2^c$ | $44.8 \pm 0.9^g$ | $\Delta V_f^{\ddagger}(313\ K)/cm^3\ mol^{-1}$ | $-1.1 \pm 1.1^f$ | $-0.3 \pm 0.4^h$ |
| $\Delta H_r^{\ddagger}/kJ\ mol^{-1}$ | $42.5 \pm 1.2^c$ | $42.0 \pm 1.2^g$ | $\Delta V_r^{\ddagger}(313\ K)/cm^3\ mol^{-1}$ | $-11.6 \pm 1.6^f$ | $-11.8 \pm 0.5^h$ |

[a] At 298 K, $I/M = 0.5$; the errors quoted are standard deviations. [b] Equilibrium data at 298 K. [c] Variable-temperature kinetic data. [d] Variable-temperature equilibrium data: $\log (K^{298}/M^{-1}) = 2.27$. [e] Variable-pressure equilibrium data: $K_0^{318}/M^{-1} = 199.5$. [f] Variable-pressure kinetic data: $k_{f,0}^{313}/M^{-1}\ s^{-1} = 385$, $k_{r,0}^{313}/s^{-1} = 1.6$. [g] Ambient-pressure equilibrium and kinetic data at 298 K. [h] Variable-pressure equilibrium and kinetic data at 318 and 313 K, respectively. [i] Chung and Langford[29] obtained $k_f^{298}/M^{-1}\ s^{-1} = 210$ and $k_r^{298}/s^{-1} = 1.5$ at $I/M = 0.15$ ($NaClO_4$).

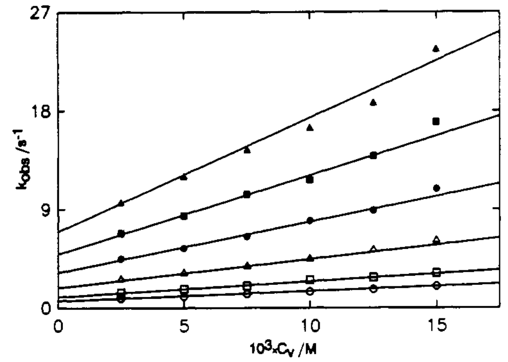

**Figure 4.** Temperature dependence of the observed pseudo-first-order rate constant, $k_{obs}$ ($T/K$ = 291 (○), 298 (□), 308 (△), 318 (●), 326 (■), 333 (▲)), for the formation of $V(DMSO)_5NCS^{2+}$ as a function of $C_V$ ($C_{SCN}/M = 2.5 \times 10^{-4}$ and $I/M = 0.5$).

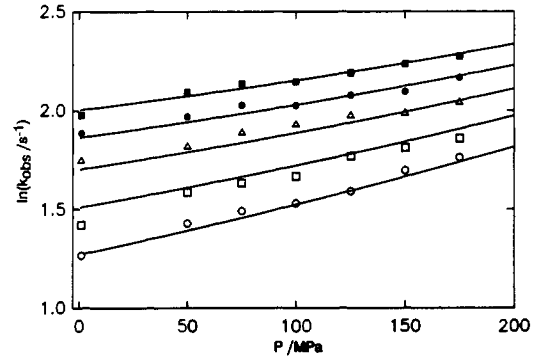

**Figure 5.** Pressure dependence of the observed pseudo-first-order rate constant, $k_{obs}$, for the formation of $V(DMSO)_5NCS^{2+}$ at 313 K and $I/M = 0.5$. $C_{SCN}/M = 2.5 \times 10^{-4}$ and $10^3C_V/M$ = 5.0 (○), 7.5 (□), 10 (△), 12.5 (●), and 15 (■).

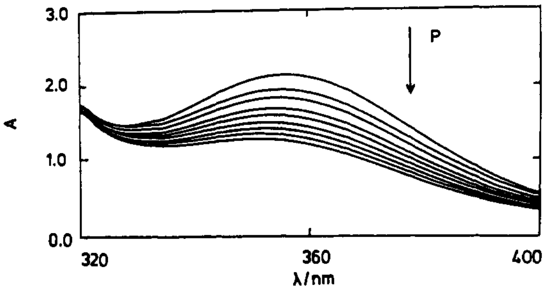

**Figure 6.** Absorption spectra of an aqueous solution $4 \times 10^{-3}$ M in $V^{3+}$ and $3 \times 10^{-3}$ M in $NCS^-$ at variable pressure ($3 < P/MPa < 200$, $I/M = 0.5$, $T/K = 318$).

**B. Equilibrium and Kinetic Studies of Formation and Dissociation of $V(DMSO)_5NCS^{2+}$.** The kinetics of monocomplex formation and dissociation of $V(DMSO)_5NCS^{2+}$ (reaction 14)

$$V(DMSO)_6^{3+} + NCS^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} V(DMSO)_5NCS^{2+} + DMSO \quad (14)$$

were studied as a function of metal ion concentration, temperature, and pressure. Here too, the hard $V^{3+}$ cation binds to the hard nitrogen end of the ambidentate $NCS^-$ anion. This is confirmed by the structure of $K_3[V(NCS)_6]\cdot 12H_2O$ determined by X-ray diffraction, in which the mean V–N distance is 2.044 (2) Å.[28] Under the pseudo-first-order conditions (eq 15) of at least 10-fold

$$k_{obs} = k_fC_V + k_r \quad (15)$$

excess metal, the reaction was found to follow first-order kinetics over more than 4 half-lives. Plots of the observed first-order rate constant, $k_{obs}$, against the vanadium concentration, $C_V$, measured at constant ionic strength ($I/M$ = 0.5 NaT) were linear with nonzero intercepts indicating a reversible reaction (Figure 4). The $k_{obs}$ values obtained at various temperatures between 291.2 and 333.2 K were analyzed using eq 15 and the Eyring equation for the temperature dependence of $k_f$ and $k_r$. A four-parameter simultaneous analysis of the data yielded the $k_f^{298}$ (or $\Delta S_f^{\ddagger}$), $k_r^{298}$ (or $\Delta S_r^{\ddagger}$), $\Delta H_f^{\ddagger}$, and $\Delta H_r^{\ddagger}$ values listed in Table V. The variation of $k_{obs}$ as a function of pressure (Figure 5) was measured at 313 K with five solutions of increasing vanadium concentrations ($5.0 \leq 10^3C_V/M \leq 15$, $C_{NCS}/M = 2.5 \times 10^{-4}$). The data were analyzed using eq 16 and assuming pressure independent volumes

$$\ln k_{obs} = \ln \{k_{f,0}C_V \exp[-(\Delta V_f^{\ddagger}P/RT)] + k_{r,0} \exp[-(\Delta V_r^{\ddagger}P/RT)]\} \quad (16)$$

of activation $\Delta V_f^{\ddagger}$ and $\Delta V_r^{\ddagger}$. The results are listed in Table V. A spectrophotometric determination of the stability constant $K^{298}$ of the $V(DMSO)_5NCS^{2+}$ complex was also made. The equilibrium constant was determined from the least-squares analysis of the absorbance measurements ($I/M$ = 0.5 NaT) at various wavelengths between 348 and 380 nm and at different concentrations ($0.25 \leq 10^2C_V/M \leq 1.5$, $1 \leq 10^4C_{NCS}/M \leq 2.5$), with the equilibrium constant and molar extinction coefficients as parameters of the minimizing program SPECFIT.[30] With excess metal conditions, the best fit was obtained for a 1:1 complex, with stability constant $\log (K^{298}/M^{-1}) = 2.27 \pm 0.01$ and molar absorptivity $\epsilon/M^{-1}\ cm^{-1} = 931$ at 352 nm, in reasonable agreement with the log $K$ value calculated from the kinetics ($\log ((k_f/k_r)/M^{-1}) = 2.13$). The variable-temperature (290.8–324.1 K), and pressure (up to 200 MPa at 350 nm and 318 K; Figure 6) studies were carried out with solutions of $C_V/M = 3.0 \times 10^{-3}$ to $10.0 \times 10^{-3}$ and $C_{NCS}/M = 2.0 \times 10^{-3}$ to $3.0 \times 10^{-3}$. The analysis of the variable-temperature data gives the $K^{298}$, $\Delta S^0$, and $\Delta H^0$ values reported in Table V. The variable-pressure data were analyzed with eq 17, giving $K_0^{318}$ and $\Delta V^0$. Finally, the varia-

$$\ln K = \ln (k_{f,0}/k_{r,0}) - (\Delta V_f^{\ddagger} - \Delta V_r^{\ddagger})P/RT \quad (17)$$

ble-pressure kinetic and equilibrium data were fitted simultaneously using eqs 16 and 17, with $k_{f,0}^{313}$, $k_{r,0}^{313}$, $K_0^{298}$, $\Delta V_f^{\ddagger}$, and $\Delta V_r^{\ddagger}$ as adjustable parameters and $\Delta V^0 = \Delta V_f^{\ddagger} - \Delta V_r^{\ddagger}$. Similarly

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**Table VI.** Activation and Reaction Volumes ($cm^3\ mol^{-1}$) for Solvent Exchange and Complex Formation Reactions on Trivalent Octahedral Metal Cations in $H_2O$ and in DMSO

| | in $H_2O$ | | | | | in DMSO | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $Ti^{3+}$ | $V^{3+}$ | $Cr^{3+}$ | $Fe^{3+}$ | $Ga^{3+}$ | $V^{3+\,a}$ | $Cr^{3+}$ | $Fe^{3+}$ | $Ga^{3+}$ | ref |
| solvent exchange $\Delta V_{ex}^{*}$ | −12.1 | −8.9 | −9.6 | −5.4 | +5.0 | −10.1 | −11.3 | −3.1 | +13.1 | 5 |
| Hahx$^b \Delta V_f^{*}$ | | | | −10.0 | | | | +3.0 | | 31, 32 |
| Hipt$^c \Delta V_f^{*}$ | | | | −8.7 | +4.0 | | | +10.9 | | 33, 34, 32 |
| $SCN^- \Delta V_f^{*}$ | | −9.4 | | −6.1 | | −0.3 | | +3.3 | | 35, 31, 32 |
| $SCN^- \Delta V_f^{*}$ | | −17.9 | | −15.0$^d$ | | −11.8 | | −8.5 | | 35, 32 |
| $SCN^- \Delta V^\circ$ | | +8.5 | | +8.9 | | +11.5 | | +12.4 | | 35, 36, 36 |

[a] This work. [b] Hahx = acetohydroxamic acid. [c] Hipt = 4-isopropyltropolone. [d] Calculated from $\Delta V_r^{*} = \Delta V_f^{*} - \Delta V^\circ$.

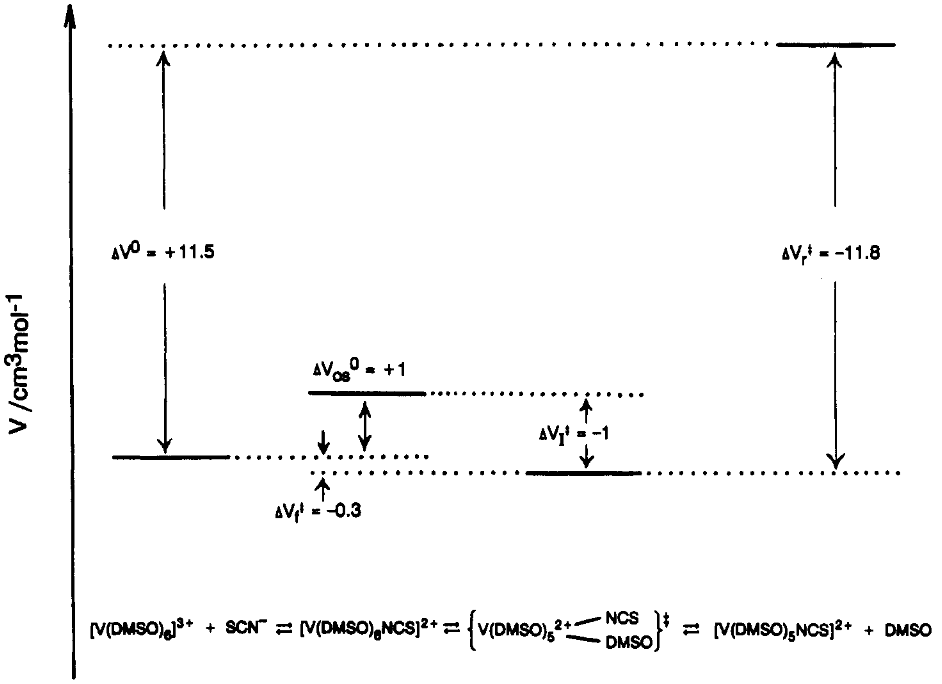

**Figure 7.** Volume diagram for the reaction between $V(DMSO)_6^{3+}$ and $NCS^-$.

all variable-temperature data were fitted simultaneously and show, like the variable-pressure data, excellent consistency between the kinetic and equilibrium data (Table V).

## Discussion

Table VI gives the available volumes of activation for solvent exchange on trivalent hexasolvated first-row transition metal ions in water and in DMSO. It is clear that for these ions there is a gradual change of mechanism on going from left to right across the series. From these data an associative activation mode can be ascribed for DMSO exchange on $V^{3+}$, as already observed for water exchange on this ion. Considering the decrease of ionic radii ($r_i$/pm)[37] and the filling of $t_{2g}$ orbitals, we would expect a decrease in associative character from $Ti^{3+}$ (67, $t_{2g}^1$), through $V^{3+}$ (64, $t_{2g}^2$) to $Cr^{3+}$ (61, $t_{2g}^3$). In water the observed activation volumes were respectively −12.1, −8.9, and −9.6 $cm^3\ mol^{-1}$. The apparently anomalous trend for $V^{3+}$ and $Cr^{3+}$, attributed to possible experimental errors,[15] is found again in DMSO with values of −10.1 and −11.3 $cm^3\ mol^{-1}$ for these two ions. For very associative interchange, $I_a$, processes, approaching a limiting A mechanism, we would expect more negative activation volumes for a DMSO exchange, than for a water exchange process, due to the larger size of the former solvent molecule: this is precisely what is found for both $V^{3+}$ and $Cr^{3+}$. The $Fe^{3+}$ ion is already a borderline case, with a non-negligible dissociative component; the steric factors are becoming very important, and for that reason the $I_a$ interchange is less associative in the bulkier solvent DMSO than in water. The strongly negative value of $\Delta S_{ex}^{*}$ for DMSO exchange on $V^{3+}$ is also consistent with an associative activation mode, although one should recall that the activation entropy, as determined in NMR studies of solvent exchange on paramagnetic metal ions, is not always a conclusive criterion for the assignment of the activation mode.[38] Further, the second-order rate law observed in the diluent $CD_3NO_2$ is consistent with an interchange or an associative mechanism. Therefore, in the light of the above arguments we conclude that DMSO exchange on $V(DMSO)_6^{3+}$ occurs via an $I_a$ mechanism with a strong associative character, as observed previously in water.[15]

The substitution of a solvent molecule on a hexasolvated transition metal ion by a ligand can be described by the Eigen–Wilkins mechanism.[39] Formation of an outer-sphere (or encounter) complex occurs first, in a fast pre-equilibrium. This pre-association is followed by the slow interchange of the bound solvent molecule with the ligand, as shown in eq 18. For an I

$$[MS_6]^{3+} + L^{n-} \overset{K_{os}}{\rightleftharpoons} [MS_6,L]^{(3-n)+} \underset{k_{-I}}{\overset{k_I}{\rightleftharpoons}} [MS_5L]^{(3-n)+} + S \tag{18}$$

mechanism, the observed first-order rate constant, $k_{obs}$, is given by the product of the formation constant of the outer-sphere

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complex, $K_{os}$, and the first-order rate constant, $k_I$ (eq 19), assuming

$$k_f = K_{os}k_I \tag{19}$$

$$\Delta V_f^{\ddagger} = \Delta V_{os}^0 + \Delta V_I^{\ddagger} \tag{20}$$

$K_{os}[MS_6]^{3+} \ll 1$. The derivative of eq 19 as a function of pressure gives eq 20, relating the activation volume for the forward reaction, $\Delta V_f^{\ddagger}$, to the volume change during outer-sphere complex formation, $\Delta V_{os}^0$, and to the activation volume for the interchange step, $\Delta V_I^{\ddagger}$. $\Delta V_{os}^0$ can be estimated using eq 21,[40] where $k_B$ is the

$$\Delta V_{os}^0 = -RT\{\{[z_1z_2e^2(\zeta + 0.5a\kappa(\zeta + \beta))]/[(1 + a\kappa)^2\epsilon k_BTa]\} + \beta\} \tag{21}$$

$$\kappa = (8 \times 10^{-3}\pi Ne^2I/\epsilon k_BT)^{0.5}$$

Boltzmann constant, $\epsilon$ the dielectric constant, and $I$ the ionic strength. In DMSO, the value of $\zeta$, the pressure coefficient of the dielectric constant, $\partial(\ln \epsilon)/\partial P$, is unknown. One can however replace $\zeta$ by the isothermal compressibility $\beta$, because the dielectric constant and the density of the solution have similar pressure dependences (±10%).[8] Using a distance of closest approach $a$/cm $= 7 \times 10^{-8}$ and $\beta/\text{MPa}^{-1} = \zeta/\text{MPa}^{-1} = 4.34 \times 10^{-4}$,[41] we calculated the following $\Delta V_{os}^0/\text{cm}^3\ \text{mol}^{-1}$ values as a function of ionic strength ($I$/M): +4.4 (0) and +0.7 (0.5). However, $\Delta V_{os}^0$ cannot be estimated with high accuracy due to deviation from the Debye–Hückel model at high ionic strength. Using an estimated value of +1 cm$^3$ mol$^{-1}$ for the formation of the outer-sphere complex $[V(DMSO)_6SCN]^{2+}$, a value of $\Delta V_I^{\ddagger}$ of the order of −1 cm$^3$ mol$^{-1}$ can be estimated for the volume of activation of the interchange step (Figure 7). It should now be recalled that $\Delta V_I^{\ddagger}$ can be considered as the sum of an intrinsic and a solvational contribution (eq 22). The solvational contribution, $\Delta V_{I,solv}^{\ddagger}$, due

$$\Delta V_I^{\ddagger} = \Delta V_{I,int}^{\ddagger} + \Delta V_{I,solv}^{\ddagger} \tag{22}$$

to the dipole rearrangement of the outer-sphere complex is difficult to estimate. However, for an associative activation mode of substitution it is expected that the incoming ligand $SCN^-$ is close to the $V^{3+}$ ion at the transition state. By use of eq 21 and a distance of closest approach of $3 \times 10^{-8}$ cm, one obtains a value of +5 cm$^3$ mol$^{-1}$ for the solvational rearrangement ($\Delta V_{os}^0 + \Delta V_{I,solv}^{\ddagger}$), due to the penetration of $SCN^-$ in the first coordination sphere (notice that this would not be the case for an $I_d$ process, where a $V^{3+}$/DMSO bond breaking would be rate determining). Consequently, the $\Delta V_{I,int}^{\ddagger}$ term is of the order of −5 cm$^3$ mol$^{-1}$, as expected for an associative activation mode.

The use of activation parameters for the assignment of complex formation reactions needs a careful evaluation, as performed above, of the contributions due to charge neutralization (or dipole rearrangement) as well as solvation changes. A further complication is due to the asymmetry of the reaction pathway (eq 18). If both the $\Delta V_I^{\ddagger}$ and $\Delta V_{-I}^{\ddagger}$ values are of the same sign the assignment is clear, otherwise great care has to be taken into account. For this reason it is very important to have a knowledge of the full reaction profile ($\Delta V_f^{\ddagger}$, $\Delta V_r^{\ddagger}$, or $\Delta V^0$) to make a safe mechanistic interpretation. Fortunately, for the reverse reaction, which mainly includes bond formation with a neutral solvent molecule (in terms of an $I_a$ mechanism), the outer-sphere and $\Delta V_{-I,solv}^{\ddagger}$ contributions to $\Delta V_r^{\ddagger}$ can be neglected. This confirms the assignment of an $I_a$ mechanism ($\Delta V_{-I,int}^{\ddagger} \approx -12$ cm$^3$ mol$^{-1}$) for the complex formation reaction of $V^{3+}$ with $SCN^-$ in DMSO.

Table VI shows that the reaction volumes $\Delta V^0$ for the complex formation reactions of $V^{3+}$ and $Fe^{3+}$ with $SCN^-$ are positive and slightly larger in DMSO (≈+12 cm$^3$ mol$^{-1}$) than in water (≈+9 cm$^3$ mol$^{-1}$). It should be emphasized that part of this large positive term is due to the fact that complex formation is accompanied by charge neutralization. Further, the comparison of the $\Delta V_f^{\ddagger}$ and $\Delta V_r^{\ddagger}$ values clearly indicates that the behavior is more associative for $V^{3+}$ than $Fe^{3+}$, both in water and DMSO; this behavior parallels that observed for the solvent exchange reactions around these ions. On the change of solvent from water to DMSO, the minimum in the reaction profile diminishes for $V^{3+}$, indicating a less associative character for the complex formation in this latter solvent, which is still clearly of an $I_a$ type. This trend is reflected for $Fe^{3+}$, but no minimum in the reaction profile is observed in DMSO, the transition state having a volume intermediate between those of the reactants and products. One is therefore tempted, in this case, to assign an interchange mechanism, without specification of the activation mode.

A mechanistic substitution changeover, from $I_a$ to $I_d$, along the first-row trivalent high-spin transition metal ions has been observed in water. With this study we confirm this trend in DMSO: both solvent exchange and complex formation in this bulkier solvent occur through associative interchange $I_a$ mechanisms for $V^{3+}$.

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**Registry No.** $V(DMSO)_6^{3+}$, 45284-59-1; DMSO, 67-68-5; SCN, 302-04-5.

**Supplementary Material Available:** Second-order rate constants and transverse relaxation rates for the DMSO exchange on $V^{3+}$ as a function of temperature (Tables SI and SII), absorbance values of the solutions as a function of vanadium and thiocyanate concentrations (Table SIII), stability constants of $[V(DMSO)_5NCS]^{2+}$ as a function of temperature and pressure (Tables SIV and SV), and Figure S1, presenting the pressure dependence of the transverse relaxation rate of the bound solvent $^1$H NMR signal at various temperatures (5 pages). Ordering information is given on any current masthead page.

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(41) $\zeta/\text{MPa}^{-1} = 4.14 \times 10^{-4}$ at 298 K,[42] but the isothermal compressibility increases by about 5% between 298 and 313 K for a series of nonaqueous solvents.[43]

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