detectable decay within the several-millisecond duration of the photomultiplier experiment) and in neutral media it decays at a measurable rate, while in acidic media (pH < 4) the reduction of pertechnetate by H$^•$ rapidly yields polymeric TcO_2. These observations are qualitatively consistent with the known behavior of the manganate congener ($Mn^{VI}O_4^{2-}$), which is stable in alkaline media but rapidly disproportionates to permangante and polymeric MnO_2 in neutral or acidic media.[23]

In unbuffered water the Tc(VI) transient decays by second-order kinetics with $2k/\epsilon l = (1.05 \pm 0.09) \times 10^5$ s^{-1} (average of 14 independent determinations at 360 nm).

$$-d[\mathrm{Tc(VI)}]/dt = 2k[\mathrm{Tc(VI)}]^2 \qquad (1)$$

Independent experiments[24] yield an estimated Tc(VI) extinction coefficient at 360 nm of 1220 M^{-1} cm^{-1}, resulting in a calculated value of $k = 1.3 \times 10^8$ M^{-1} s^{-1}. Lawrance and Sangster[15] have estimated the equivalent rate for Re(VI) to be an order of magnitude larger, i.e. $(1.7 \pm 0.4) \times 10^9$ M^{-1} s^{-1}.

The decay of Tc(VI) by a second-order process is entirely consistent with the expected decomposition of this species via disproportionation to Tc(VII) and, ultimately, Tc(IV). Second-order decay of Tc(VI) means, of course, that the net rate of disappearance of this species is a function of its concentration. Thus, competition between Tc(VI) disproportionation (to yield TcO_2) and various first-order processes (e.g., ligand trapping of Tc(VI) to ultimately yield a Tc complex) will depend directly on the total concentration of Tc in solution.[8] This fact has obvious consequences in ^{99m}Tc radiopharmaceutical syntheses, where TcO_2 is an undesirable product, and in nuclear waste disposal processes, where TcO_2 is the desirable product.

Competition between second-order Tc(VI) disproportionation and first-order scavenging of Tc(VI) is illustrated by experiments in which 0.01 M hydrogen peroxide is added to solutions of pertechnetate before irradiation. In unbuffered water where Tc(VI) is relatively reactive, the added H_2O_2 has no effect on the rate or form of Tc(VI) decay. However, at pH 12 where Tc(VI) is relatively stable, the added H_2O_2 induces a pseudo-first-order decay of Tc(VI) (k_{obs} = ca. 10^3 s^{-1}). From this observation the second-order rate constant governing reaction of Tc(VI) with H_2O_2 at pH 12 is estimated to be 10^5 M^{-1} s^{-1}. The stoichiometry of this reaction is presumed to be

$$\mathrm{Tc^{VI}O_4^{2-} + H_2O_2 \rightarrow Tc^{VII}O_4^- + OH^- + OH^\bullet} \qquad (2)$$

General Chemistry. The reactivity patterns observed for the Tc(VI) and Re(VI) transients can be qualitatively understood on the basis of what is known about the stable Mo(VI) and W(VI) analogues MoO_4^{2-} and WO_4^{2-}. These tetrahedral anions are stable in alkaline media, but in acid they convert into octahedral species, which then rapidly undergo polymerization.[25] In complex formation reactions W(VI) usually reacts somewhat more rapidly than Mo(VI),[26,27] nicely accounting for the fact that the Re(VI) transient is more reactive than the Tc(VI) transient. The greater reactivity of third-row elements, relative to their second-row congeners, is usually ascribed to their slightly greater size, which allows a more facile expansion of the first coordination sphere. This phenomenon presumably also accounts for the fact that perrhenate reacts with OH$^•$, while no such reaction is observed for pertechnetate.

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Registry No. TcO_4^-, 14333-20-1; TcO_4^{2-}, 16050-83-2; ReO_4^{2-}, 15626-53-6; ReO_4, 14333-24-5; $(CH_3)_2CHO$, 3958-66-5; H, 12385-13-6; OH, 3352-57-6; H_2O_2, 7722-84-1; water, 7732-18-5.

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[23] Sutter, J. H.; Colquitt, K.; Sutter, J. R. *Inorg. Chem.* **1974**, *13*, 1444.

[24] Experimental conditions were adjusted so that the concentration of pertechnetate was greater than 10^{-3} M and the concentration of e_{aq}^- was less than 10^{-6} M. Under these conditions radical recombinations are negligible and the dose absorbed by the solution[16] can be directly related to the concentration of Tc(VI) produced by the dose. The photomultiplier experiment monitors the difference between solution absorbance before and after the pulse, and thus under these conditions directly yields the absorpton resulting from the Tc(VI) product.

[25] Honig, D. S.; Kustin, K. *Inorg. Chem.* **1972**, *11*, 65.

[26] Diebler, H.; Timms, R. E. *J. Chem. Soc. A* **1971**, 273.

[27] Von Felten, H.; Wernli, B.; Gamsjager, H.; Baertschi, P. *J. Chem. Soc., Dalton Trans.* **1978**, 496.

[28] Schwochau, K. In *Technetium in Chemistry and Nuclear Medicine*; Nicolini, M., Bandoli, G., Mazzi, U., Eds.; Raven Press: New York, 1985; p 14.

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^{1}H NMR Kinetic Study of Dimethyl Sulfoxide Exchange on Tetrakis(dimethyl sulfoxide)platinum(II) at Variable Temperature and Pressure[1,2]

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Determination of activation volumes from the pressure dependence of exchange rates for solvated metal ions is a useful method for the diagnosis of mechanisms.[4] For octahedrally coordinated solvated cations, there are now sufficient data to correlate both the sign and the magnitude of ΔV^* with the intimate mechanism.[5]

For square-planar solvates, the interpretation of activation volumes in molecular terms is expected to be more complex, since these solvates are subject to large changes in coordination geometry when passing from the ground state to the transition state. Few square-planar solvent-exchange reactions have been studied,[6-9] and only three values of ΔV^* have been reported so far.[7-9] The activation volumes for the water exchanges on the tetraaqua cations of palladium(II) and platinum(II) have small negative values.[8,9] Attribution of the stoichiometric mechanism (interchange, I_a, or limiting associative, A) is however still an open question, and more data are needed before ΔV^* can be used for detailed mechanistic assignments in square-planar solvates.

The present report is a ^{1}H NMR investigation of the dimethyl sulfoxide exchange on $Pt(Me_2SO)_4^{2+}$ as a function of temperature and pressure in CD_3NO_2. Dimethyl sulfoxide is an ambidentate ligand, and the complex contains two O-bonded and two S-bonded ligands that are exchanging with the free ligand at different rates. It is favorable to follow these exchanges in a noncoordinating diluent like nitromethane, since it allows variation of the ligand concentration, thus giving an opportunity to establish the rate law. The use of a diluent of high dielectric constant and of uncharged ligands minimizes the electrostriction changes along the reaction path, so that the measured volumes of activation will reflect primarily the intrinsic changes of molecular volumes on going to the transition state.[7]

Experimental Section

Chemicals and Solutions. Dimethyl sulfoxide, Me_2SO (Merck, spectral grade), was distilled and dried overnight over 4-Å molecular sieves

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[1] High-Pressure NMR Kinetics. 36.

[2] Part 35: Stebler-Röthlisberger, M.; Hummel, W.; Pittet, P.-A.; Bürgi, H.-B.; Ludi, A.; Merbach, A. E. *Inorg. Chem.* **1988**, *27*, 1358.

[3] (a) University of Lausanne. (b) University of Lund.

[4] *Inorganic High Pressure Chemistry: Kinetics and Mechanism*; van Eldik, R., Ed.; Elsevier: Amsterdam, 1986.

[5] Ducommun, Y.; Merbach, A. E. In *Inorganic High Pressure Chemistry: Kinetics and Mechanism*; van Eldik, R., Ed.; Elsevier: Amsterdam, 1986; Chapter 2.

[6] Gröning, Ö.; Drakenberg, T.; Elding, L. I. *Inorg. Chem.* **1982**, *21*, 1820.

[7] Tubino, M.; Merbach, A. E. *Inorg. Chim. Acta* **1983**, *71*, 149.

[8] Helm, L.; Elding, L. I.; Merbach, A. E. *Helv. Chim. Acta* **1984**, *67*, 1453.

[9] Helm, L.; Elding, L. I.; Merbach, A. E. *Inorg. Chem.* **1985**, *24*, 1719.

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Table I. Effect of Free $\mathrm{Me_2SO}$ Concentration on the Second-Order Rate Constant k_O for $\mathrm{Me_2S}\mathit{O}$ Exchange and k_S for $\mathrm{Me_2}\mathit{S}\mathrm{O}$ Exchange on $\mathrm{Pt(Me_2S}\mathit{O}\mathrm{)_2(Me_2}\mathit{S}\mathrm{O)_2^{2+}}$ in $\mathrm{CD_3NO_2}$ Diluent at Various Temperatures[a]

	k_O/kg mol^{-1} s^{-1}			k_S/kg mol^{-1} s^{-1}
$[\mathrm{Me_2SO}]$/mol kg^{-1}	238.0 K	258.6 K	284.3 K	366.4 K
0.084	205	651	3220	248
0.146	204		2970	189
0.157	187	715	3370	197
0.202	191	743	3200	179
0.538	185	688	3320	135
average	194	699	3200	~2 × 10^2

[a] $C_\mathrm{Pt} = 0.096$ mol kg^{-1}.

before use. Benzene (Fluka, p.a.) and deuteriated nitromethane, $\mathrm{CD_3NO_2}$ (Ciba-Geigy), were dried overnight on 3-Å molecular sieves. $\mathrm{Pt(Me_2SO)_4(CF_3SO_3)_2}$ was prepared from $\mathrm{Pt(H_2O)_4(ClO_4)_2}$ via $\mathrm{Pt(OH)_2}\cdot x\mathrm{H_2O}$ as described elsewhere.[10,11] The salt was collected on a Millipore filter and dried under reduced pressure. Solutions of $\mathrm{Pt(Me_2SO)_4^{2+}}$ with excess $\mathrm{Me_2SO}$ were prepared by weighing the triflate salt in the diluent $\mathrm{CD_3NO_2}$ containing 1–2% benzene as NMR reference. The absence of water in the solutions was checked by NMR spectroscopy.

NMR Measurements. ^{1}H NMR spectra were recorded at 200 MHz on a Bruker CXP-200 spectrometer. The sweep width was set to 1.6 kHz. Transients (4–32) obtained with a 2-μs pulse (90° pulse, ~6 μs) were accumulated. $\mathrm{CD_3NO_2}$ was used as an internal field lock. The temperature was controlled within ±0.2 °C by gas circulation through the probe and was measured by substitution of the NMR tube for a platinum resistor.[12] Variable-pressure measurements were performed with a high-pressure probe described elsewhere.[13]

Results and Discussion

In the solid state, the complex has two O- and two S-bonded ligands, in a cis configuration.[11] IR[14] and EXAFS[15] data show that this conformation is kept in solution. At low temperature, the ^{1}H NMR spectrum of $\mathrm{Pt(Me_2SO)_4^{2+}}$ in $\mathrm{Me_2SO}$ diluted with the noncoordinating $\mathrm{CD_3NO_2}$ shows three signals. The signal at 2.52 ppm corresponds to free $\mathrm{Me_2SO}$ (hereafter simply denoted $\mathrm{Me_2SO}$). The methyl protons of the O-bonded $\mathrm{Me_2SO}$ ligands (denoted $\mathrm{Me_2S}\mathit{O}$) are too far from the platinum center to produce an observable coupling (^4J) and give rise to a singlet at 3.00 ppm. For S-bonded $\mathrm{Me_2SO}$ ($\mathrm{Me_2}\mathit{S}\mathrm{O}$), a single signal is observed at 3.60 ppm, resolved into a triplet at higher temperatures due to the ^{1}H–^{195}Pt scalar coupling ($^3J = 14$ Hz). Integrations of the two signals give an equal amount of $\mathrm{Me_2S}\mathit{O}$ and $\mathrm{Me_2}\mathit{S}\mathrm{O}$ in the complex, in accordance with the available structural information.[14,15] Because of the large trans effect of $\mathrm{Me_2}\mathit{S}\mathrm{O}$,[16] the two $\mathrm{Me_2S}\mathit{O}$ groups are expected to exchange more rapidly with $\mathrm{Me_2SO}$ than the $\mathrm{Me_2}\mathit{S}\mathrm{O}$ groups. As the temperature is increased, the $\mathrm{Me_2SO}$ and $\mathrm{Me_2S}\mathit{O}$ signals start to broaden, showing that chemical exchange occurs between the two environments, according to eq 1,

$$\mathrm{Pt(Me_2S}\mathit{O}\mathrm{)_2(Me_2}\mathit{S}\mathrm{O)_2^{2+} + {}^*Me_2SO} \overset{2k_\mathrm{O}}{\rightleftharpoons} \mathrm{Pt({}^*Me_2S}\mathit{O}\mathrm{)(Me_2S}\mathit{O}\mathrm{)(Me_2}\mathit{S}\mathrm{O)_2^{2+} + Me_2SO} \tag{1}$$

finally leading to coalescence. At higher temperatures, the broadening of the coalesced and $\mathrm{Me_2}\mathit{S}\mathrm{O}$ signals shows that a second exchange takes place, which can be ascribed either to a mutual intramolecular exchange between $\mathrm{Me_2S}\mathit{O}$ and $\mathrm{Me_2}\mathit{S}\mathrm{O}$ or to an exchange of $\mathrm{Me_2}\mathit{S}\mathrm{O}$ with the bulk $\mathrm{Me_2SO}$ (eq 2). The

$$\mathrm{Pt(Me_2S}\mathit{O}\mathrm{)_2(Me_2}\mathit{S}\mathrm{O)_2^{2+} + {}^*Me_2SO} \overset{2k_\mathrm{S}}{\rightleftharpoons} \mathrm{Pt(Me_2S}\mathit{O}\mathrm{)_2({}^*Me_2}\mathit{S}\mathrm{O)(Me_2}\mathit{S}\mathrm{O)^{2+} + Me_2SO} \tag{2}$$

Table II. Effect of Temperature on the Second-Order Rate Constants for $\mathrm{Me_2S}\mathit{O}$ (k_O) and $\mathrm{Me_2}\mathit{S}\mathrm{O}$ (k_S) Exchange on $\mathrm{Pt(Me_2S}\mathit{O}\mathrm{)_2(Me_2}\mathit{S}\mathrm{O)_2^{2+}}$ in $\mathrm{CD_3NO_2}$ Diluent[a]

T/K	k_O/kg mol^{-1} s^{-1}	T/K	k_O/kg mol^{-1} s^{-1}	k_S/kg mol^{-1} s^{-1}
238.0	191	304.8	8530	
243.1	274	315.4	13500	
248.3	358	325.8	22500	20
253.4	515	336.1	31600	49
258.6	743	346.2	49400	70
263.7	1000	353.2		111
269.2	1370	360.5		136
274.5	1810	366.4		159
284.3	3200	373.2		253
292.2	4850			

[a] $[\mathrm{Me_2SO}] = 0.264$ mol kg^{-1}, $C_\mathrm{Pt} = 0.096$ mol kg^{-1}.

$\mathrm{Me_2S}\mathit{O}$ exchange is first order with respect to $\mathrm{Me_2SO}$ concentration (see Table I), as expected for substitution on square-planar complexes. Some decomposition was observed at the higher temperatures where the second exchange occurs. There is a nonzero intercept in the plot of observed rate constants vs $\mathrm{Me_2SO}$ concentration. This nonreproducible intercept is most probably due to formation of decomposition products rather than to an intramolecular isomerization. The main reaction follows second-order kinetics. The rate laws can thus be expressed by eq 3 for $\mathrm{Me_2S}\mathit{O}$ and eq 4 for $\mathrm{Me_2}\mathit{S}\mathrm{O}$ exchanges, where k_O and k_S

$$-\frac{\mathrm{d[Pt(Me_2S}\mathit{O}\mathrm{)_2(Me_2}\mathit{S}\mathrm{O)_2^{2+}]}}{\mathrm{d}t} = 2k_\mathrm{O}\mathrm{[Pt(Me_2S}\mathit{O}\mathrm{)_2(Me_2}\mathit{S}\mathrm{O)_2^{2+}][Me_2SO]} \tag{3}$$

$$-\frac{\mathrm{d[Pt(Me_2S}\mathit{O}\mathrm{)_2(Me_2}\mathit{S}\mathrm{O)_2^{2+}]}}{\mathrm{d}t} = 2k_\mathrm{S}\mathrm{[Pt(Me_2S}\mathit{O}\mathrm{)_2(Me_2}\mathit{S}\mathrm{O)_2^{2+}][Me_2SO]} \tag{4}$$

denote the second-order rate constants per coordination site for $\mathrm{Me_2S}\mathit{O}$ and $\mathrm{Me_2}\mathit{S}\mathrm{O}$ exchange, respectively. The second-order rate constants in eq 3 and 4 are related by eq 5 and 6 to the corresponding observed first-order rate constants $k_{\mathrm{obsd,O}}$ and $k_{\mathrm{obsd,}S}$, obtained by a line shape analysis based on the Kubo–Sack theory.[17]

$$k_{\mathrm{obsd,O}} = -\frac{\mathrm{d[Pt(Me_2S}\mathit{O}\mathrm{)_2(Me_2}\mathit{S}\mathrm{O)_2^{2+}]}}{\mathrm{2[Pt(Me_2S}\mathit{O}\mathrm{)_2(Me_2}\mathit{S}\mathrm{O)_2^{2+}]d}t} = k_\mathrm{O}\mathrm{[Me_2SO]} \tag{5}$$

$$k_{\mathrm{obsd,S}} = -\frac{\mathrm{d[Pt(Me_2S}\mathit{O}\mathrm{)_2(Me_2}\mathit{S}\mathrm{O)_2^{2+}]}}{\mathrm{2[Pt(Me_2S}\mathit{O}\mathrm{)_2(Me_2}\mathit{S}\mathrm{O)_2^{2+}]d}t} = k_\mathrm{S}\mathrm{[Me_2SO]} \tag{6}$$

The temperature influence on the rate constants was measured between 238.0 and 346.2 K for $\mathrm{Me_2S}\mathit{O}$ exchange and between 325.8 and 373.2 K for $\mathrm{Me_2}\mathit{S}\mathrm{O}$ exchange (Table II). The data were fitted to the Eyring equation with k^{298} or $\Delta S^\ddagger$ and $\Delta H^\ddagger$ as adjustable parameters. The second-order exchange rate constant per coordination site obtained with this treatment for the $\mathrm{Me_2S}\mathit{O}$ exchange is $k_\mathrm{O}^{298} = 3.2 \times 10^3$ kg mol^{-1} s^{-1}. For $\mathrm{Me_2}\mathit{S}\mathrm{O}$ exchange, extrapolation of k_S to 298 K is delicate and leads to a value of $k_\mathrm{S}^{298} \simeq 2$ kg mol^{-1} s^{-1} per coordination site.

In Table III are listed the rate constants and activation parameters for the solvent-exchange reactions of square-planar solvates that have been studied so far. Although quantitative comparisons of rate constants are invalidated by the different media used, it can be seen that the exchange of $\mathrm{Me_2S}\mathit{O}$ is fast, as expected for a ligand leaving trans to a sulfur. The reaction is ca. 10^8 times faster than the water exchange on $\mathrm{Pt(H_2O)_4^{2+}}$ (where the leaving oxygen is trans to another oxygen), in quantitative agreement with previous estimation of the magnitude of the trans- effect of $\mathrm{Me_2}\mathit{S}\mathrm{O}$ compared to that of water (3×10^6, evaluated from comparisons of rate constants in aqueous solution).[16] The $\mathrm{Me_2}\mathit{S}\mathrm{O}$ exchange is only ca. 10^3 times slower than the $\mathrm{Me_2S}\mathit{O}$ exchange, which might be due to a lower efficiency

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(10) Elding, L. I. *Inorg. Chim. Acta* **1976**, *20*, 65.

(11) Elding, L. I.; Oskarsson, Å. *Inorg. Chim. Acta* **1987**, *130*, 203.

(12) Ammann, C.; Meier, P.; Merbach, A. E. *J. Magn. Reson.* **1982**, *46*, 319.

(13) Pisaniello, D. L.; Helm, L.; Meier, P.; Merbach, A. E. *J. Am. Chem. Soc.* **1983**, *105*, 4528.

(14) (a) Wayland, B. B.; Schramm, R. F. *Chem. Commun.* **1968**, 1465. (b) Wayland, B. B.; Schramm, R. F. *Inorg. Chem.* **1969**, *8*, 971. (c) Price, J. H.; Williamson, A. N.; Schramm, R. F.; Wayland, B. B. *Inorg. Chem.* **1972**, *11*, 1250.

(15) Persson, I.; Hedman, B.; Elding, L. I. to be submitted for publication.

(16) Elding, L. I.; Gröning, Ö. *Inorg. Chem.* **1978**, *17*, 1872.

(17) Using a computer program derived from EXCNG (Delpuech, J.-J.; Ducom, J.; Michon, V. *Bull. Soc. Chim. Fr.* **1971**, 1848). The exchange matrix used in this calculation is given as supplementary material.

Table III. Rate Constants and Activation Parameters for Solvent Exchange on Pt and Pd Solvates[a]

solvate	k_{ex}^{298}/kg mol^{-1} s^{-1}	ΔH^*/kJ mol^{-1}	ΔS^*/J K^{-1} mol^{-1}	ΔV^*/cm^3 mol^{-1} (T/K)	ref
$Pt(Me_2SO)_4^{2+}$[b,c]	(3.2 ± 0.1) × 10^3	32.8 ± 0.2	−62.0 ± 0.7	−2.5 ± 0.3 (264.5)	this work
$Pt(Me_2SO)_4^{2+}$[b,d]	2 ± 1[e]	47 ± 4	−74 ± 10	−5 ± 3 (360)[f]	this work
$Pt(H_2O)_4^{2+}$	(7.1 ± 0.5) × 10^{-6}	89.7 ± 2.4	−43 ± 30	−4.6 ± 0.2 (297)	9
$Pd(H_2O)_4^{2+}$	41 ± 1	49.5 ± 1.5	−48 ± 6	−2.2 ± 0.2 (324)	8
trans-$Pd(Me_2S)_2Cl_2$	197 ± 7[g]	38.1 ± 1.0[g]	−73.2 ± 3.7[g]	−5.9 ± 1.6 (300)[h]	7

[a] All values refer to the exchange of one particular solvent molecule. [b] With CD_3NO_2 as diluent. [c] O-bonded exchange. [d] S-bonded exchange. [e] Calculated from ΔS^* and ΔH^*; see text. [f] Estimated; see text. [g] With C_6H_5CN as diluent. [h] Intrinsic ΔV^* in an hypothetical nonsolvating solvent.[7]

Table IV. Effect of Pressure on the Rate Constant for $Me_2S\mathit{O}$ Exchange on $Pt(Me_2S\mathit{O})_2(Me_2\mathit{S}O)_2^{2+}$ in CD_3NO_2 Diluent at 264.5 K[a]

P/MPa	k_O/kg mol^{-1} s^{-1}	P/MPa	k_O/kg mol^{-1} s^{-1}
0.1	1009	100.0	1212
1.0	1072	126.0	1189
25.0	1069	152.0	1272
50.0	1101	169.0	1251
81.0	1139	180.0	1260

[a] $[Me_2SO]$ = 0.264 mol kg^{-1}, C_{Pt} = 0.100 mol kg^{-1}.

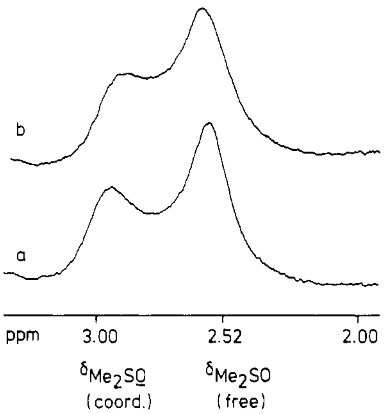

Figure 1. ^1H NMR spectra of a 0.100 mol kg^{-1} $Pt(Me_2S\mathit{O})_2(Me_2\mathit{S}O)_2^{2+}$ solution in CD_3NO_2 diluent at 264.5 K and 0.1 MPa (a) and 180 MPa (b). The concentration in free Me_2SO is 0.264 mol kg^{-1}.

of S-bonded ligands as leaving groups when compared to O-bonded ones.

The pressure dependence of k_O could be studied up to 180 MPa at 264.5 K (Table IV). Figure 1 shows the effect of pressure on the $Me_2S\mathit{O}$ exchange. As the pressure is increased from 0.1 to 180 MPa, the signals merge together toward coalescence. This acceleration of the exchange rate with pressure gives a negative volume of activation, $\Delta V^* = -2.5$ cm^3 mol^{-1} (Table III), characteristic of a process controlled by bond making. An approximate ΔV^* value has also been estimated for $Me_2\mathit{S}O$ exchange, but it is unfortunately rather uncertain, because of the decomposition occurring at the high temperature of this measurement. There is no significant difference between the activation volumes for the O- and S-bonded exchanges, if the experimental errors are taken into account. Together with the large negative activation entropies and the second-order rate laws, the negative activation volumes support the assignment of associative modes of activation for both reactions. The additional information on the rate law that can be collected with inert diluents is a valuable complement to the variable-pressure studies. Information is not available in pure solvent, where mechanistic conclusions can solely be based on the activation parameters. The volumes of activation for square-planar solvent-exchange reactions listed in Table III are all negative and relatively small. It can be concluded that these exchanges proceed through a common associatively activated mechanism. However, more data for solvent exchange as well as for simple complex formation reactions with neutral ligands[18,19] have to be collected and compared before a classification in terms of interchange (I_a) or limiting associative (A) mechanism can be made.

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Registry No. *cis*-$Pt(Me_2S\mathit{O})_2(Me_2\mathit{S}O)_2^{2+}$, 45188-20-3; Me_2SO, 67-68-5.

Supplementary Material Available: The five-sites exchange matrix used for the calculation of the exchange rates (1 page). Ordering information is given on any current masthead page.

(18) Ducommun, Y.; Merbach, A. E.; Hellquist, B.; Elding, L. I. *Inorg. Chem.* **1987**, *26*, 1759.
(19) Hellquist, B.; Elding, L. I.; Ducommun, Y. *Inorg. Chem.* **1988**, *27*, 3620.

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The Nature of Iridium(III) in Aqueous Alkaline Medium. An ^{18}O-Tracer Study

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Since the pioneering work of Hunt and Taube,[1] it has been known that the hexaaquachromium(III) ion is slow to exchange its bound water with solvent. Subsequently, the hexaaqua ions of rhodium(III)[2] and iridium(III)[3,4] were shown to be even more inert. While solvent-exchange mechanisms for acidic chromium(III) and rhodium(III) have been proposed,[5-7] nothing is known about exchange mechanisms for aqueous iridium(III). This study provides the first definitive evidence for existence of the monomeric hexahydroxoiridate(III) ion in solution as well as the first measurements of oxygen-exchange rates at the iridium(III) center.

Iridium(III) forms a mixture of microcrystalline and amorphous hydroxide precipitates in the near-neutral pH region (6 ≤ pH ≤ 8). The X-ray powder pattern of the iridium(III) hydroxide shows a major component of the mixture to be isomorphous with $Cr(OH_2)_3(OH)_3$.[8] The solid hydroxides readily dissolve in aqueous acid or base to give a mixture of $Ir(OH_2)_6^{3+}$ or $Ir(OH)_6^{3-}$ and some oligomers of unknown composition. In solutions of $[OH^-]$ > 0.5 M, the monomer–oligomer equilibria strongly favor the monomeric iridium(III) ion. Evidence for the hydrolysis of oligomers that are formed as $Ir(OH_2)_3(OH)_3$ dissolves in basic solution is provided by the observation of a λ_{max} = 310 nm absorption band at $[OH^-]$ > 0.5 M (λ_{max} = 265 and 310 nm for $Ir(OH_2)_6^{3+}$ [3]). This band increased in intensity with increasing $[OH^-]$. The hydrolysis is further supported by results of ^{18}O-tracer experiments that are discussed below. These results indicate that the primary solution species in 1 M OH^- contains six equivalent oxygen atoms in its first coordination sphere.

We found that the iridium(III) hydroxide containing some polymer could be rapidly precipitated from a basic solution free from solvent water and without inducing exchange (±0.1%) of coordinated oxygen. Thus, despite the presence of polymeric

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