3620 *Inorg. Chem.* **1988**, *27*, 3620-3623

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Mechanism for Formation and Aquation of Palladium(II) Acetonitrile Complexes in Aqueous Solution. Variable-Temperature and Variable-Pressure Study of Stabilities and Kinetics

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Kinetics and equilibrium for formation and dissociation of the mono and bis complexes between Pd^{2+} and acetonitrile have been studied as a function of temperature (278–298 K) and pressure (1–200 MPa) in aqueous solution. Spectrophotometric equilibrium measurements give stepwise stability constants $K_1^{298} = 15.5 \pm 0.9$ M^{-1} and $K_2^{298} = 2.2 \pm 0.2$ M^{-1}. The pressure dependence of K_1 at 278.2 K gives the reaction volume $\Delta V_1^0 = -2.5 \pm 0.4$ cm^3 mol^{-1}. Stopped-flow spectrophotometry gives $k_1^{298} = 309 \pm 5$ M^{-1} s^{-1} and $k_{-1}^{298} = 16.0 \pm 0.4$ s^{-1}. All values refer to 1.00 M ionic strength. The temperature dependence of the rate constants yields $\Delta H_1^* = 46 \pm 2$ kJ mol^{-1}, $\Delta H_{-1}^* = 59 \pm 1$ kJ mol^{-1}, $\Delta S_1^* = -43 \pm 8$ J K^{-1} mol^{-1} and $\Delta S_{-1}^* = -24 \pm 3$ J K^{-1} mol^{-1}. The experiments indicate that $Pd(MeCN)_2(H_2O)_2^{2+}$ is formed as a mixture of cis and trans isomers, with a ratio [cis]/[trans] ≥ 4 at thermodynamic equilibrium. The kinetics for the second step is interpreted in terms of a rapid formation of the trans isomer and the slower, rate-controlling formation of the cis complex. Variable-pressure stopped-flow measurements at 278.2 K give the activation volumes $\Delta V_1^* = -4.0 \pm 0.8$ cm^3 mol^{-1} and $\Delta V_{-1}^* = -1.5 \pm 0.5$ cm^3 mol^{-1}. The negative values of the entropies and volumes of activation are consistent with an associative mode of activation. Comparison with the ΔV^* values for solvent exchange on other palladium(II) solvates suggests that the mechanism is strongly associative.

Introduction

High-pressure data for complex formation and solvent-exchange reactions on square-planar tetrasolvates are scarce.[2] Only four solvent-exchange reactions of such complexes have been studied so far,[3-7] with activation volumes between −2.2 and −7.1 cm^3 mol^{-1}.[4-7] We have recently reported the first variable-pressure study of a substitution reaction on a square-planar tetrasolvate, the formation and dissociation of $Pd(Me_2SO)(H_2O)_3^{2+}$.[8]

Dimethyl sulfoxide is an ambidentate ligand, which can coordinate either by the oxygen or by the sulfur. This ambiguity leads to difficulties in the interpretation of the kinetic data.[8] Acetonitrile also forms weak complexes with palladium(II), but it can only bind through the nitrogen, and interpretation of volume changes will be unambiguous. In the present paper, we report a study of complex formation between palladium(II) and acetonitrile in aqueous solution. The formation of mono and bis complexes could be observed (eq 1 and 2). The kinetics and

$$Pd(H_2O)_4^{2+} + MeCN \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Pd(MeCN)(H_2O)_3^{2+} + H_2O \quad (1)$$

$$Pd(MeCN)(H_2O)_3^{2+} + MeCN \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Pd(MeCN)_2(H_2O)_2^{2+} + H_2O \quad (2)$$

equilibria for both reactions have been studied as a function of temperature, and reaction 1 has been studied as a function of pressure also.

Experimental Section

Chemicals and Solutions. Stock solutions of palladium(II) perchlorate (ca. 45 mM) in 1.00 M perchloric acid were prepared from palladium sponge (Johnson and Matthey, spectrographically standardized), fuming nitric acid (100%, Merck p.a.) and perchloric acid (BDH AnalaR), as described previously.[9] Ligand stock solutions were prepared shortly before use from freshly distilled acetonitrile (MeCN, Merck, p.a.), by dilution with water and perchloric acid to an acid concentration of 1.00 M, and flushed with nitrogen. Water was doubly distilled from quartz. All solutions had an ionic strength of 1.00 M, with perchloric acid as supporting electrolyte. The hydrogen ion concentration of 1.00 M is sufficient to suppress protolysis of $Pd(H_2O)_4^{2+}$.[9]

Equilibrium Measurements. Ambient-pressure UV–visible spectra were recorded with a double-beam Cary-Varian 2200 spectrophotometer with water thermostated cells. Equilibrium measurements were performed at 298.2 K (at 10 wavelengths between 310 and 420 nm) and at 278.2 and 282.2 K (at five wavelengths between 340 and 420 nm). Solutions with $C_{Pd} = 5.03$ and 10.17 mM (298.2 K), $C_{Pd} = 6.28$ and 9.42 mM (278.2 and 288.2 K), and MeCN concentrations between 0 and 800 mM were used.

The pressure dependence of the stability constant K_1 was measured at 278.2 K up to 200 MPa by use of a Perkin-Elmer Lambda 7 spectrophotometer with a high-pressure optical cell described elsewhere.[10] The solutions used had $C_{Pd} = 5.0$ mM and $C_{MeCN} = 35.0$ mM, sufficient to form about 50% of the mono(acetonitrile) complex (cf. Figure 1).

All spectra were recorded quickly after mixing of the solutions, to avoid disturbance from slow subsequent changes. Such changes were observed after a few hours for the highest MeCN concentrations and were probably due to decomposition of the acetonitrile to acetic acid in the acidic palladium solutions.

Kinetic Measurements. The temperature dependence of the kinetics at ambient pressure was studied at 278.2, 288.2, and 298.4 K by use of a Durrum-Gibson stoped-flow instrument operated at the isosbestic points for the reactions not studied. Reaction 1 was thus monitored at 353 nm (eq 1), and reaction 2 at 396 nm (eq 2) (cf. Figure 2). For excess MeCN, both reactions showed pseudo-first-order kinetics. Reaction 1 was studied in a concentration range (6.25 mM < C_{MeCN} < 114 mM) where the influence of the formation of the bis(acetonitrile) complex is negligible (cf. Figure 1). Similarly, reaction 2 was monitored with 0.95 M < C_{MeCN} < 2.5 M, a range where reaction 1 goes to completion and is rapid compared to reaction 2. C_{Pd} was varied between 1.0 and 5.6 mM for reaction 1 and between 0.8 and 11 mM for reaction 2.

The rate of reaction 1 was studied as a function of pressure between 5 and 200 MPa at 278.2 K. Data were collected at 353 nm on a high-pressure stopped-flow instrument that has been described previously.[11] C_{Pd} was 2.50 mM and C_{MeCN} was 8.78, 17.65, 26.35, 40.5 and 54.2 mM. In this range of concentrations, formation of the bis complex $Pd(MeCN)_2(H_2O)_2^{2+}$ is negligible (cf. Figure 1).

Calculations and Results

The spectrophotometric equilibrium measurements at ambient pressure were analyzed by use of a least-squares minimizing program[13] based on the STEPIT procedure.[14] The best fit was

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(1) (a) University of Lund. (b) Université de Lausanne.

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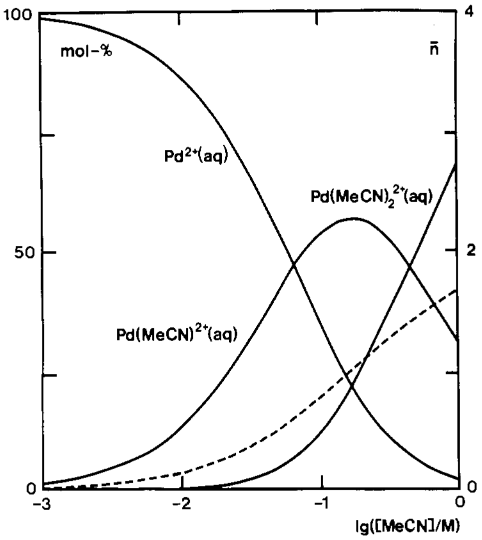

Figure 1. Distribution of palladium and mean ligand number ($\bar{n}$, dashed line) as a function of log ([MeCN]/M) at 298 K, calculated from K_1 = 15.5 M^{-1} and K_2 = 2.2 M^{-1}.

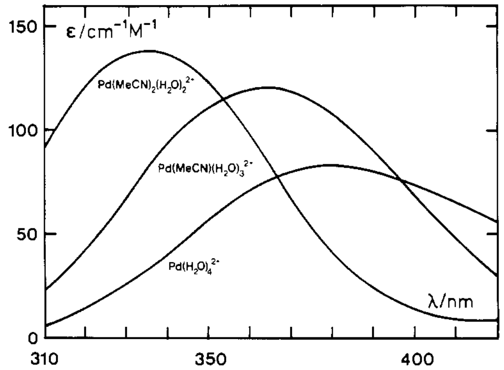

Figure 2. Absorption spectra of the MeCN complexes, calculated from spectra of equilibrated solutions with various distribution of complexes. The spectrum of the bis complex represents an equilibrium mixture with [cis]/[trans] ≥ 4; see text.

Table I. Rate Constants and Stepwise Stability Constants at Ambient Pressure[a]

T/K	k_1	k_{-1}/s^{-1}	$(k_1/k_{-1})/M^{-1}$	K_1/M^{-1}
278.2	71 ± 6	3.13 ± 0.34	22.7 ± 4.4	19.6 ± 0.9
288.2	158 ± 10	8.2 ± 0.3	19.4 ± 1.9	16.7 ± 0.6
298.2			15.5 ± 1.2	15.5 ± 0.9
298.4	294 ± 14	19.0 ± 0.4		

T/K	$k_{2app}/M^{-1}\ s^{-1}$ [b]	k_{-2app}/s^{-1} [b]	$(k_{2app}/k_{-2app})/M^{-1}$	K_2/M^{-1}
278.2	7.4 ± 0.5	6.9 ± 0.7	1.07 ± 0.17	1.94 ± 0.35
288.2	16.0 ± 1.8	19.3 ± 2.6	0.83 ± 0.20	1.67 ± 0.25
298.2	38.7 ± 2.3	33.2 ± 3.0	1.17 ± 0.17	2.20 ± 0.20

[a] Errors quoted are standard deviations. [b] Apparent rate constant yielded by the data treatment. Because of the possibility of formation of cis and trans isomer of the bis complex, they cannot be directly related to k_2 and k_{-2}; cf. Discussion.

Table II. Rate Constants and Activation and Thermodynamic Parameters for Reaction 1 at 298.2 K[a]

const	forward reacn	reverse reacn	equilib
$k^{298}/M^{-1}\ s^{-1}$	309 ± 5	16.0 ± 0.4	
$(k_1^{298}/k_{-1}^{298})/M^{-1}$			15.7 ± 1.2
K_1^{298}/M^{-1} [b]			15.5 ± 0.9
ΔH^{*}/kJ mol^{-1}	46 ± 2	59 ± 1	
ΔH_1^0/kJ mol^{-1} [b]			−8.6 ± 1.6
ΔS^{*}/J K^{-1} mol^{-1}	−54 ± 3	−24 ± 3	
ΔS_1^0/J K^{-1} mol^{-} [b]			−6 ± 5
$\Delta V^{*}/cm^3$ mol^{-1} [c]	−4.0 ± 0.8	−1.5 ± 0.5	
$\Delta V_1^0/cm^3$ mol^{-1} [c]			−2.5 ± 0.4

[a] In 1.00 M perchloric acid medium. Errors quoted are standard deviations. [b] From equilibrium data. [c] Simultaneous fit of all variable-pressure data (kinetics and equilibrium) at 278.2 K.

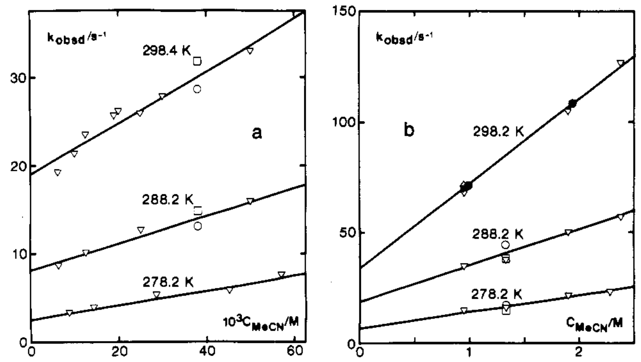

Figure 3. Pseudo-first-order rate constants for (a) reaction 1 and (b) reaction 2 as a function of excess MeCN concentration at ambient pressure. 10^3 C_{Pd}/mM = 0.8 (▼), 1.0 (○), 2.0 (●), 2.5 (▽), 5.6 (□), and 11.2 (△).

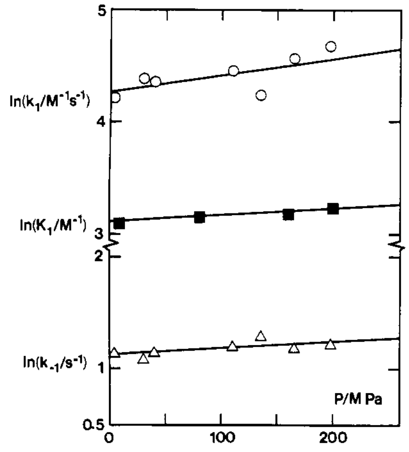

Figure 4. Effect of pressure on the stepwise stability constant K_1 and on the rate constants for reaction 1 at 278.2 K.

obtained for two complexes with stepwise stability constants K_1^{298} = 15.5 ± 0.9 M^{-1} and K_2^{298} = 2.2 ± 0.2 M^{-1} and with molar absorptivities given in Table SIV (supplementary material). The distribution of palladium between the various species calculated from those constants in shown in Figure 1. Figure 2 shows the resolved absorption spectra of the absorbing species calculated from the equilibrium measurements. The temperature dependence of K_1 and K_2 (Table I) gave the enthalpy and entropy changes listed in Table II. The determination of K_2 is not sufficiently precise to enable calculation of ΔH^0 and ΔS^0 (see Table II).

The observed rate constants from the stopped-flow experiments were obtained from least-squares analysis of the first 3 half-lives and represent the average of one to six experiments. Figure 3 shows the concentration dependence of k_{obsd}. The rate constants for forward and reverse reactions were derived by fitting the k_{obsd} values to eq 3, with n = 1, 2. The temperature dependence of

$$k_{obsd} = k_{-n} + k_n[\text{MeCN}] \qquad (3)$$

k_1 and k_{-1} and the apparent rate constants for reaction 2 are contained in Table I. The data for reaction 1 were analyzed by using the Eyring equation with ΔH^{*} and ΔS^{*} (or k^{298}) as parameters. Table II contains all variable-temperature results for reaction 1.

Figure 4 shows the pressure dependence of the equilibrium constant K_1 and of the rate constants for the forward and reverse

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(14) Chandler, P. Quantum Chemistry Program Exchange, Indiana University Chemistry Department, Bloomington, IN.

reaction 1 in a logarithmic scale. Activation and reaction volumes were calculated by a simultaneous fit of those data to eq 4 and 5 (or eq 4 and 6), where K_1^0, ΔV_1^0, k_1^0, and ΔV_1^* (or k_{-1}^0 and

$$\ln K_1 = \ln K_1^0 - \Delta V_1^0 P/RT \qquad (4)$$

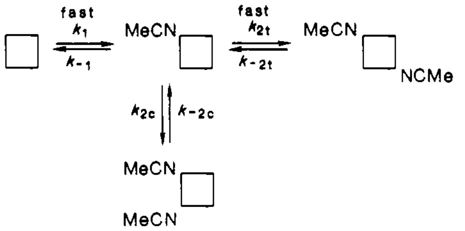
$$\ln k_1 = \ln k_1^0 - \Delta V_1^* P/RT \qquad (5)$$

$$\ln k_{-1} = \ln k_{-1}^0 - \Delta V_{-1}^* P/RT \qquad (6)$$

ΔV_{-1}^*) are adjustable parameters.[15] No significant pressure dependence of the activation volumes could be observed. The so obtained values of ΔV_1^0, ΔV_1^*, and ΔV_{-1}^* are also contained in Table II.

Discussion

For reaction 1, the agreement between the stability constant K_1, obtained from the equilibrium measurements, and the value of k_1/k_{-1}, calculated from the kinetics, is good at all temperatures, as shown by Table I. For reaction 2, on the other hand, K_2 is always ca. twice the ratio between the forward and reverse rate constants obtained from the kinetics, indicating that reaction 2 is not an elementary process. At thermodynamic equilibrium, the bis complex is probably a mixture of cis and trans isomers, as has previously been shown in other similar square-planar systems.[18] In the present case, the scheme shown in eq 7 should be valid,



(7)

with c and t denoting cis and trans isomers, respectively. The stepwise stability constant K_2 can then be expressed as eq 8, where

$$K_2 = \frac{[c] + [t]}{[\mathrm{PdMeCN(H_2O)_3}^{2+}][\mathrm{MeCN}]} = K_{2c} + K_{2t} \qquad (8)$$

K_{2c} and K_{2t} are the stability constants of the cis and trans isomers, respectively (eq 9 and 10). Under the experimental conditions

$$K_{2c} = [c]/[\mathrm{PdMeCN(H_2O)_3}^{2+}][\mathrm{MeCN}] \qquad (9)$$

$$K_{2t} = [t]/[\mathrm{PdMeCN(H_2O)_3}^{2+}][\mathrm{MeCN}] \qquad (10)$$

used to study reaction 2, the rate of reaction 1 was always 5 to 6 times greater than that of reaction 2. Formation of the trans complex in eq 7 is expected to be even faster, due to the trans effect of the coordinated MeCN. The reaction scheme can thus be expressed as eq 7. The rate-controlling step is the formation of the cis complex, and the observed pseudo-first-order rate constant cannot be expressed simply as the reversible formation of a single bis complex. The observed rate constants will have a contribution from the fast equilibrium to form the trans complex, as given by eq 11, where α_1 represents the fraction of the preequilibrium

$$k_{\mathrm{obsd}} = k_{-2c} + \alpha_1 k_{2c}[\mathrm{MeCN}] \qquad (11)$$

mixture in the mono complex form (eq 12). The depencence of

$$\alpha_1 = \frac{K_1[\mathrm{MeCN}]}{1 + K_1[\mathrm{MeCN}] + K_1 K_{2t}[\mathrm{MeCN}]^2} \qquad (12)$$

α_1 on free ligand concentration should give rise to some deviation from linearity in eq 11, which could not be observed in Figure 3b, perhaps due to the very limited concentration range covered (0.95 M < [MeCN] < 2.50 M). The value of $k_{-2\mathrm{app}}$ obtained as the intercept in this plot can therefore only be taken as an upper limit for k_{-2c}.

Table III. Rate Constants for Formation (k_1) and Aquation (k_{-1}) of $\mathrm{PdL(H_2O)_3}^{(2-n)+}$ in Aqueous Solution at 298 K[a]

L^{n-}	$k_1/M^{-1}\ s^{-1}$	k_{-1}/s^{-1}	ref
H_2O	41[b]	560[c]	4
Me_2SO	2.45	0.24	7
MeCN	309	16	*d*
Cl^-	1.8×10^4	0.83	16
Br^-	9.2×10^4	0.83	16
I^-	1.1×10^6	0.92	17

[a] All values refer to 1.00 M perchloric acid medium. [b] Water exchange rate $k_{ex} = 560\ s^{-1}$ per coordination site recalculated to second-order units, $4k_{ex}/55$. [c] Water exchange rate k_{ex} for a particular coordination site. [d] This work.

Table IV. Volumes of Activation and Reaction Volumes for the Reaction $\mathrm{Pd(H_2O)_4}^{2+} + L \rightleftarrows \mathrm{PdL(H_2O)_3}^{2+} + H_2O$[a]

L	$\Delta V_1^*/cm^3\ mol^{-1}$	$\Delta V_{-1}^*/$ $cm^3\ mol^{-1}$	$\Delta V^0/cm^3\ mol^{-1}$	ref
H_2O	−2.2 ± 0.2	−2.2 ± 0.2	0	4
Me_2SO	−9.2 ± 0.6	−1.7 ± 0.6	−7.5 ± 0.3	8
MeCN	−4.0 ± 0.8	−1.5 ± 0.5	−2.5 ± 0.4	*b*

[a] In 1.00 M perchloric acid medium. Errors quoted are standard deviations. [b] This work.

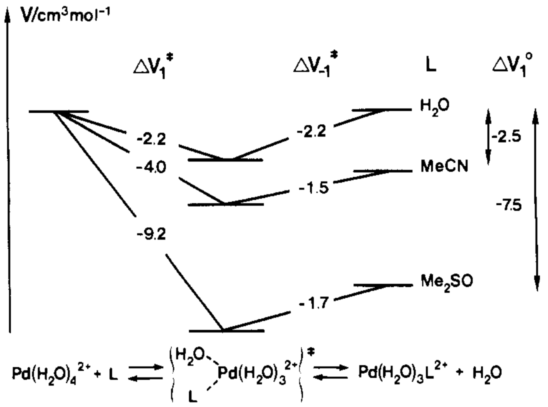


Figure 5. Volume diagram for formation and dissociation of mono complexes between $Pd^{2+}(aq)$ and L.

The present results give some information on the distribution between the cis and the trans isomers at thermodynamic equilibrium. Insertion of the limiting value of k_{-2c} into eq 13, obtained

$$k_{\mathrm{obsd}} - k_{-2c} = \frac{K_1[\mathrm{MeCN}]^2 k_{2c}}{1 + K_1[\mathrm{MeCN}] + K_1(K_2 - k_{2c}/k_{-2c})[\mathrm{MeCN}]^2} \qquad (13)$$

by combination of eq 8, 11, and 12, gives a lower limit for this distribuiton as $K_{2c}/K_{2t} = [c]/[t] \geq 4$ at the three temperatures used. An upper limit of 60 $M^{-1}\ s^{-1}$ at 298 K for k_{2c} is also obtained from this calculation. The rate constant $k_{2\mathrm{app}}$ yielded by the data treatment is by definition equal to $\alpha_1 k_{2c}$. Using α_1 values calculated in the range of free acetonitrile concentrations where reaction 2 was studied also gives values of k_{2c} in agreement with this upper limit.

The rate constants given in Table III for formation and aquation of a series of palladium(II) complexes shows the usual strong dependence of the rate on the nature of the entering ligand and a smaller dependence on the leaving one. There is a big difference in nucleophilicity between the two neutral ligands MeCN and Me_2SO, the N-bonded MeCN being the more efficient of the two. This result makes the low efficiency of Me_2SO as a nucleophile even more noteworthy.[8]

Table IV contains the activation and reaction volumes for the simple palladium(II) reactions studied so far. The values are all negative, which is compatible with associative activation of the

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reactions. There is an overall contraction associated with substitution of water for MeCN and an even larger one when Me_2SO is the entering ligand, as can be seen in Figure 5. It is noteworthy that the three ΔV_{-1}^{*} values are equal within experimental error (-1.9 ± 0.4 cm^3 mol^{-1}). It means that the difference in volume between the transition state and the reactants is independent of the leaving group when water is the incoming ligand. Release of MeCN or Me_2SO into the bulk would produce a large expansion. If an interchange mechanism is operating, the ΔV_{-1}^{*} should be modulated depending on the nature of the outgoing molecule, which is obviously not seen. It suggests that the leaving ligand is still tightly bound to the metal center at the transition state, and it follows that, despite the small values of ΔV_{-1}^{*}, the mechanism of these three reactions is probably very associative, if not limiting (A). As pointed out earlier,[8] it also illustrates the importance of drawing the overall volume diagram of a substitution reaction when activation volumes are used for mechanistic classification.

Acknowledgment. Thanks are due to the Swedish Natural Science Research Council and the Swiss National Science Foundation (Grant No. 2.854-0.85) for financial support.

Supplementary Material Available: Spectrophotometric equilibrium measurements at ambient pressure and 298 (Table SI), 288 (Table SII), or 278 K (Table SIII), molar absorptivities for the various complexes at the wavelengths used (Table SIV), spectrophotometric equilibrium measurements at variable pressure (Table SV), observed rate constants at ambient pressure for reaction 1 (Table SVI) and for reaction 2 (Table SVII), and observed rate constants for reaction 1 as a function of pressure at 278.2 K (Table SVII) (11 pages). Ordering information is given on any current masthead page.

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Ligand-Substitutional Nature of Technetium(III). Rate and Mechanism of Ligand Exchange of Tris(acetylacetonato)technetium(III) in Acetylacetone

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Tris(acetylacetonato)technetium(III), $^{99}Tc(acac)_3$, undergoes ligand exchange in acetylacetone (Hacac) at 125–141 °C. The rate observed by the ^{14}C-labeling method is expressed by rate = k_1[complex] at [complex] = 0.003–0.007 M, [Hacac] = 9.7 M, and [H_2O] = 0.04–0.1 M; $k_1 = (2.1 \pm 0.1) \times 10^{-4}$ s^{-1} at 141 °C. No water catalysis was observed. ΔH^{*} and ΔS^{*} are 119 ± 7 kJ mol^{-1} and -27 ± 18 J K^{-1} mol^{-1}, respectively. The dilution with acetonitrile reduced the rate linearly with [Hacac]. The deuterium isotope effect $k_1(\mathrm{H})/k_1(\mathrm{D})$ was modest (2.3 ± 0.3). The I_a mechanism is assigned to the rate-determining formation of the intermediate containing a one-ended acac$^-$ and a unidentate Hacac. The lability and the mechanism are regarded as reflecting straightforwardly the kinetic nature of Tc^{III} on the basis of the previously reported linear free energy relationship between the present exchange system and the ligand-substitution processes of aqua complexes for various tervalent metal ions (Kido, H.; Saito, K. *J. Am. Chem. Soc.*, **1988**, *110*, 3187–3190). The lability of Tc^{III} with the low-spin d^4 configuration was found to be very close to that of Cr^{III}, much lower than that of Mo^{III}, and slightly higher than that of Ru^{III} and Rh^{III}; $Mo^{III} \gg Tc^{III} > Ru^{III} > Rh^{III}$. The mechanism is consistent with that previously proposed for $M^{III}(acac)_3$ complexes, on the basis of an estimated ionic radius of Tc^{III}.

Technetium chemistry has been greatly developing in the last decade[1] despite experimental difficulties, in response to radiopharmaceutical demands for ^{99m}Tc compounds[1-3] and in recognition of the key location of the element in the periodic table, a central position of the d block, particularly for understanding the chemistry of 4d and 5d transition series. However, there has been no systematic information on kinetics and mechanisms of simple ligand-substitution reactions of basic complexes despite their basic importance, although some scattered data are available (vide infra). Tris(acetylacetonato)technetium(III), $^{99}Tc(acac)_3$, can afford a basic understanding of the ligand-substitutional nature of Tc^{III} on the basis of a systematization of the ligand-exchange kinetics of [$M^{III}(acac)_3$] (M = Al, Sc, V, Cr, Mn, Fe, Co, Ga, Mo, Ru, Rh, In).[4]

$Tc(acac)_3$ is known to have the low spin (LS) d^4 configuration.[5] Metal ions with this configuration are classified as substitution inert,[6,7] but a systematic and mechanistic understanding of their ligand-substitution reactions is insufficient.

Table I. Observed First-Order Rate Constants for Ligand Exchange of $^{99}Tc(acac)_3$ in Acetylacetone

T/°C	[Tc^{III}]/M	[H_2O]/M	$k_1{}^d/10^{-5}$ s^{-1}
125	0.0029	0.04	5.3 ± 0.3
	0.0026	0.09	5.1 ± 0.3
133	0.0029	0.04	10.2 ± 0.4
	0.0026	0.09	9.0 ± 0.2
141	0.0023	0.02	22.4 ± 0.5
	0.0030	0.08	21.4 ± 0.8
	0.0071	0.03	21.1 ± 0.6
	0.0027	0.11	14.5 ± 0.4^a
	0.0029	0.05	9.9 ± 0.9^b
	0.0029	0.03	4.2 ± 0.2^c

[a] Hacac[3-$^2H_2$] (deuterium content: 63%). [b] Diluted with CH_3CN; [Hacac] = 4.9 M. [c] Diluted with CH_3CN; [Hacac] = 1.9 M. [d] Errors are calculated at the 70% confidence level.

This paper elucidates the unknown kinetic nature of Tc^{III} with the LS d^4 configuration.

Experimental Section

$^{99}Tc(acac[2\text{-}^{14}C])_3$ (100 mg) was prepared by heating a degassed solution of $^{99}Tc(acac)_3$[5] (200 mg) and Hacac[2-^{14}C][8] (1.5 g) in aceto-

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