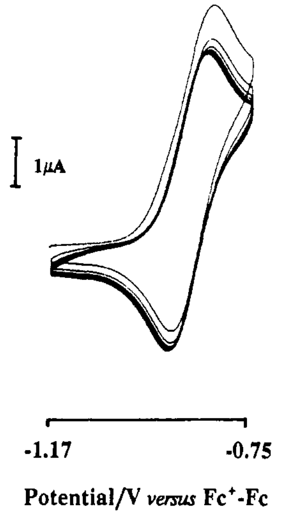

Figure 1. Cyclic voltammogram of a mixture of *trans*- (88%) and *cis*-[$Mo(N_2)_2(PMe_2Ph)_4$] in THF solution at a scan rate of 100 mV s^{-1}.

tungsten secondary electrode, and a silver-wire pseudoreference electrode. The electrolyte was 0.2 M [NBu^n_4][BF_4] in THF solution. Potentials quoted are referenced to the ferrocenium–ferrocene (Fc^+/Fc) couple (=0.00 V; 0.535 V versus the SCE in this electrolyte).

Results and Discussion

During an attempt to prepare *cis*-[$Mo(N_2)_2(PMe_2Ph)_4$] by a published procedure[9,14] (the only obvious difference being that the reaction was run under a modest pressure of N_2 rather than a flow of N_2), an IR spectrum of the oily residue, obtained after removal of solvent following the reduction of $MoCl_3(THF)_3$ in the presence of 90% of the stoichiometric amount of PMe_2Ph, clearly showed the presence of more than one N_2-containing complex. The ^{31}P NMR spectrum of the residue indicated that the cis isomer was present in addition to the previously unreported trans isomer.[15] The isomers were effectively separated by their different solubilities in pentane; the trans isomer is very soluble while the cis is only partially soluble. The cis isomer can be purified by trituration with pentane. Light causes decomposition to occur in solution with the formation of a brown solid. The trans isomer can be purified by trituration with wet deoxygenated methanol. Extended trituration leads to decomposition. As determined by ^{31}P NMR spectroscopy, the highest purity obtained by these methods was 96% for the cis and 92% for the trans isomer. In the ^{31}P NMR spectrum of the trans isomer the six resonances arising from coupling of ^{31}P to $^{95,97}Mo$ ($I = {}^5/_2$, $J \approx 140$ Hz) were observed.[17]

The isomers slowly interconvert. Samples of cis and trans isomers were dissolved in C_6D_6 in separate NMR tubes and their ^{31}P NMR spectra monitored periodically. After 16 days at room temperature in the dark, equilibrium was reached. The equilibrium constant is 2.5 in favor of the cis isomer, corresponding to a difference of 2.2 kJ mol^{-1} in $\Delta G°$ at 23 °C. At the end of 19 days only a small amount of free PMe_2Ph was present in solution in addition to the two isomers.

The cyclic voltammogram of a sample of the trans isomer showed a reversible oxidation wave at $E°' = -0.83$ V versus the Fc^+/Fc couple. The difference in peak potentials was 85 mV. Under the same conditions *trans*-[$Mo(N_2)_2(dppe)_2$], which has been shown to undergo one-electron, electrochemically reversible oxidation, afforded the same peak potential separation.[19] Previously, the cis isomer had been shown to be oxidized irreversibly.[20] On the first anodic scan of the cyclic voltammogram (see Figure 1) of a sample of trans isomer containing 12% cis isomer $i_{pa}/i_{pc} > 1$. In subsequent scans, i_{pa}/i_{pc} decreased rapidly until it became unity. Addition of a sample of the cis isomer to this solution caused an increase in the ratio i_{pa}/i_{pc} upon the next scan but no shift in the value of $E°'$ and no new oxidation waves in the voltammogram. Thus, in the voltammogram the irreversible oxidation of the cis isomer is superimposed upon that of the trans isomer, indicating that the isomers oxidize at similar potentials. This is surprising, considering the significant differences in redox potentials of *cis*- and *trans*-[$Mo(CO)_2(dppe)_2$], for example.[21,22] Oxidation of *cis*-[$Mo(CO)_2(dppe)_2$] produces the cis cation, which rapidly isomerizes to the trans cation. No redox-induced isomerization was observed. Dinitrogen is more labile in *cis*-[$Mo(N_2)_2(PMe_2Ph)_4$] than in trans complexes of molybdenum(0).[23] Loss of N_2 would appear to be even more facile in the cis-Mo(I) cation since even at low temperature oxidation is irreversible. The potential at which the trans isomer is oxidized is precisely that which would have been predicted from the values for *trans*-[$Mo(N_2)_2(Et_2PCH_2CH_2PEt_2)_2$] and *trans*-[$Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2$]: -0.97 and -0.70 V, respectively, versus the Fc^+/Fc couple.[23] In terms of coordinating ability, PMe_2Ph can be considered to be halfway between $Et_2PCH_2CH_2PEt_2$ and $Ph_2PCH_2CH_2PPh_2$ and so the oxidation potential would be expected to occur halfway between the these two potentials, at about -0.83 V, which it does.

Acknowledgment. We are grateful to the National Institutes of Health (Grant GM-38613) for support of this research. Additional funding was received through National Science Foundation U.S.-U.K. Cooperative Research Program Grant INT-8420371. Further support was provided by the University of Nebraska Research Council and NIH Biomedical Research Support Grant RR-07055.

---

(14) George, T. A.; Kovar, R. A. *Inorg. Chem.* **1981**, *20*, 285.

(15) The presence of a second N_2 complex in this reaction has been reported.[9,16]

(16) Anker, M. W.; Chatt, J.; Leigh, G. J.; Wedd, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, 2639.

(17) Values of $^1J_{MoP}$ from 119 to 284 Hz have been reported.[18]

(18) (a) Pregosin, P. S.; Kunz, R. W. *NMR: Basic Princ. Prog.* **1976**, *16*, 16. (b) Alyea, E. C.; Lenkinski, R. E.; Somogyvari, A. *Polyhedron* **1982**, *1*, 130. (c) Masters, A. F.; Bossard, G. E.; George, T. A.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Inorg. Chem.* **1983**, *22*, 908.

(19) Elson, C. M. *Inorg. Chim. Acta* **1976**, *18*, 209.

(20) Chatt, J.; Hussain, W.; Leigh, G. J.; Neukomm, H.; Pickett, C. J.; Rankin, D. A. *J. Chem. Soc., Chem. Commun.* **1980**, 1024.

(21) $E_{1/2}(cis) - E_{1/2}(trans) \approx 0.33$ V: Wimmer, F. L.; Snow, M. R.; Bond, A. M. *Inorg. Chem.* **1974**, *13*, 1617.

(22) George, T. A.; Seibold, C. D. *Inorg. Chem.* **1973**, *12*, 2548.

(23) Hussain, W.; Leigh, G. J.; Ali, H. M.; Pickett, C. J.; Rankin, D. A. *J. Chem. Soc., Dalton Trans.* **1984**, 1703.

Contribution from the Department of Chemistry,
University of Hong Kong, Pokfulam Road, Hong Kong,
and Contribution No. 7799 from the Arthur Amos Noyes
Laboratory, California Institute of Technology,
Pasadena, California 91125

Kinetics of Substitution Reactions of Binuclear Platinum(III) Pyrophosphito- and Sulfato-Bridged Complexes

Chi-Ming Che,*,† Chang-Fan Lo,† Tai-Chu Lau,†
Chung-Kwong Poon,† and Harry B. Gray*,‡

Received February 22, 1988

A great deal of the research on complexes containing metal–metal bonds has been concerned with structural questions, with less attention being paid to chemical reactivity.[1-7] Since binuclear platinum(III) complexes containing the pyrophosphito bridging ligand ($P_2O_5H_2^{2-}$) are well characterized from a structural point of view,[7] we felt that studies of their ligand-substitution reactions would be particularly useful. A specific matter that we have addressed in the [$Pt_2(pop)_4X(OH_2)$]$^{3-}$ (pop = $P_2O_5H_2$; X = Cl,

---

† University of Hong Kong.
‡ California Institute of Technology.

0020-1669/89/1328-3270$01.50/0

Br) series of complexes is the reactivity of a ligand trans to a Pt–Pt bond. For comparison, the substitution behavior of $[Pt_2(SO_4)_4Cl(OH_2)]^{3-}$ also has been investigated.

Experimental Section

Materials. K_2PtCl_4 was obtained from Johnson Matthey Co., Ltd. All chemicals were of analytical grade. $K_4[Pt_2(pop)_4]\cdot 2H_2O$, $K_4[Pt_2(pop)_4XY]$ (XY = Cl_2, ClBr, Br_2), $K_4[Pt_2(SO_4)_4Cl_2]$, and $K_2[Pt_2(SO_4)_4(OH_2)_2]$ were prepared according to standard procedures.[8,9] Solutions containing $[Pt_2(pop)_4Br(OH_2)]^{3-}$ and $[Pt_2(pop)_4Cl(OH_2)]^{3-}$ in water were generated in situ by adding stoichiometric amounts of solid $K_4[Pt_2(pop)_4]\cdot 2H_2O$ to Br_2 and Cl_2 in water, respectively. UV–vis in water, λ_{max}/nm (ϵ_{max}): $[Pt_2(pop)_4Br(OH_2)]^{3-}$, 283 ($29.4 \times 10^3$), 345 (br) ($6.8 \times 10^3$), 405 (br, sh); $[Pt_2(pop)_4Cl(OH_2)]^{3-}$, 263 ($34.5 \times 10^3$), 330 ($5.7 \times 10^3$), 405 (br, sh).

Kinetics. Kinetics measurements were made by using a Unicam SP8000 spectrophotometer. The reaction temperature was maintained to ±0.1 °C by circulating water through the cell holder using either a Lauda WB-20/R or a Forma Scientific 2800 thermostated bath and circulator. The substitution reactions were followed by monitoring the decrease in the $\sigma(X) \rightarrow d\sigma^*$ (Pt) absorption of the reactant complex. Concentrations of the nucleophile Y^- were in at least 30-fold excess (1×10^{-3} to 5×10^{-2} M). The ionic strengths of the reactant solutions were maintained a 0.055 M with $NaClO_4$ and/or $HClO_4$. The pseudo-first-order rate constants k_{obs} were determined from plots of $-\ln (A - A_\infty)$ against time, where A is the absorbance at λ_{max} of the reactant complex and A_∞ is the experimentally determined infinity point. These plots were linear over 3 half-lives. Second-order rate constants k_{XY} were determined from the least-squares slopes of plots of k_{obs} vs $[Y^-]$. Activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were obtained from Eyring plots [$\ln (k/T)$ vs $1/T$] over a temperature range of 10–35 °C.

Results and Discussion

Generation of $[Pt_2(pop)_4X(OH_2)]^{3-}$ (X = Cl, Br). Treatment of $[Pt_2(pop)_4]^{4-}$ with a stoichiometric amount of X_2 in water results in the instantaneous formation of $[Pt_2(pop)_4X(OH_2)]^{3-}$, which reacts with added X^- to give $[Pt_2(pop)_4X_2]^{4-}$. This halogen oxidation reduction is likely to be an atom-transfer process (reaction 1), as in the case of $Pt(CN)_4]^{2-}$.[10]

$$\mathrm{Pt^{II}\cdots Pt^{II}} + \mathrm{X^{\delta+}\text{–}OH^{\delta-}} \xrightarrow{H^+} \mathrm{X\text{–}Pt^{III}\text{–}Pt^{III}\text{–}OH_2} \tag{1}$$

As with other binuclear platinum(III) pyrophosphite complexes, $[Pt_2(pop)_4X(OH_2)]^{3-}$ is characterized by an intense $\sigma(X) \rightarrow d\sigma^*(Pt)$ absorption in the UV–vis region [X = Cl, 263 nm (ϵ_{max} 34.5×10^3); X = Br, 283 nm (ϵ_{max} 29.4×10^3)]. The bands in the monohaloaquo complexes are blue shifted from those of the corresponding $[Pt_2(pop)_4X_2]^{4-}$ species [X = Cl, 282 nm (ϵ_{max} 48.8×10^3), X = Br, 305 nm (ϵ_{max} 55.4×10^3)],[7] in agreement with their formulation as ligand (X) to metal charge-transfer transitions.

Substitution Reactions of $[Pt_2(pop)_4X(OH_2)]^{3-}$. Rapid spectral changes were observed when a solution of $[Pt_2(pop)_4X(OH_2)]^{3-}$ was mixed with a solution of excess NaY (X = Cl, Y = Cl; X = Br, Y = Br, Cl, NCS) at pH 1–4. Well-defined isosbestic points were maintained for more than 3 half-lives. (Isosbestic points/nm: X = Br and Cl, 410, 283; X = Br and Y = Br, 420, 292; X = Br and Y = NCS, 302, 255.) The final spectrum was identical with that of an authentic sample of $[Pt_2(pop)_4XY]^{4-}$.[8,11] The observed behavior is fully consistent with the ligand substitution reaction (2).

Table I. Pseudo-First-Order Rate Constants, k_{obs}, for $[Pt_2(pop)_4X(OH_2)]^{3-} + Y^- \rightarrow [Pt_2(pop)_4XY]^{4-}$ (μ = 0.055 M, pH 3.4–4.0, 25 °C)

X	Y	pH	$10^2[Y^-]$, M	10^3k_{obs}, s^{-1}
Cl	Cl	3.8	0.67	0.51
			1.0	0.98
			1.7	1.4
			2.0	1.8
			5.0	3.9
Br	Cl	3.8	0.50	1.4
			1.0	2.6
			1.4	3.2
			2.0	5.7
			3.3	8.9
Br	Br	3.4	0.12	0.35
			0.25	0.85
			0.40	1.7
			0.50	1.8
			1.3	4.4
			2.5	9.5
Br	NCS	4.0	0.10	2.0
			0.23	5.0
			0.50	14.0
			1.0	28.0

Table II. Second-Order Rate Constants at 25 °C and Activation Parameters for $[Pt_2(pop)_4X(OH_2)]^{3-} + Y^- \rightarrow [Pt_2(pop)_4XY]^{4-}$

X	Y	pH	k_{XY}, M^{-1} s^{-1}	$\Delta H^\ddagger$,[a] kJ mol^{-1}	$\Delta S^\ddagger$,[a] J K^{-1} mol^{-1}
Cl	Cl	3.8	0.08 (1)	39 (2)	−135 (10)
Br	Cl	3.8	0.27 (2)	38 (2)	−140 (10)
Br	Br	3.4	0.37 (2)		
Br	Br	[b]	0.34 (2)		
Br	SCN	4.0	2.8 (1)		

[a] Activation parameters were obtained from a plot of $\ln (k_{XY}/T)$ vs $1/T$ over a temperature range of 10–35 °C. [b] In 0.05 M $HClO_4$.

Table III. Effect of Added $[Pt_2(pop)_4]^{4-}$ on the Rate Constants for $[Pt_2(pop)_4X(OH_2)]^{3-} + Y^- \rightarrow [Pt_2(pop)_4(X)Y]^{4-}$ at 25 °C (μ = 0.055 M)

X	Y	pH	k_{XY},[a] M^{-1} s^{-1}	k_{XY},[b] M^{-1} s^{-1}
Cl	Cl	3.8	0.078 (5)	0.08 (1)
Br	Cl	3.8	0.27 (2)	0.28 (2)
Br	Br	3.4	0.37 (2)	0.38 (2)
Br	Br	[c]	0.34 (2)	0.35 (2)
Br	SCN	4.0	2.8 (1)	2.7 (1)

[a] $[Pt_2(pop)_4{}^{4-}] = 3.0 \times 10^{-5}$ M. [b] $[Pt_2(pop)_4{}^{4-}] = 2.0 \times 10^{-4}$ M. [c] In 0.05 M $HClO_4$.

$$[Pt_2(pop)_4X(OH_2)]^{3-} + Y^- \rightarrow [Pt_2(pop)_4XY]^{4-} \tag{2}$$

This disappearance of $[Pt_2(pop)_4(X)(OH_2)]^{3-}$ follows clean first-order kinetics for more than 3 half-lives. The pseudo-first-order rate constants, k_{obs}, are independent of initial concentration of the diplatinum(III) complex but depend linearly on $[Y^-]$. Thus at pH 1–4 and $[Y^-] \leq 0.05$ M, the experimentally determined rate law is

$$\text{rate} = k_{XY}\{[Pt_2(pop)_4X(OH_2)]^{3-}\}[Y^-] \tag{3}$$

Pseudo-first-order rate conntants, k_{obs}, are collected in Table I. Second-order rate constants, k_{XY}, and activation parameters are given in Table II. The weak dependence of k_{XY} on Y^- together

---

(1) See, for example: Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley-Interscience: New York, 1982; and references therein.

(2) Miskowski, V. M.; Smith, T. P.; Loehr, T. M.; Gray, H. B. *J. Am. Chem. Soc.* **1985**, *107*, 6282.

(3) Drago, R. S.; Tanner, S. P.; Richman, R. M.; Long, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 2897.

(4) Das, K.; Simmons, E. L.; Bear, J. L. *Inorg. Chem.* **1977**, *16*, 1268. Rainen, L.; Howard, R. A.; Kimball, A. P.; Bear, J. L. *Inorg. Chem.* **1975**, *14*, 2752.

(5) Muralidhara, S.; Espenson, J. H.; Ross, S. A. *Inorg. Chem.* **1986**, *25*, 2557. Shimura, M.; Espenson, J. H. *Inorg. Chem.* **1984**, *23*, 4069.

(6) El-Mehdawi, T.; Bryan, S. A.; Roundhill, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 6282.

(7) Roundhill, D. M.; Gray, H. B.; Che, C.-M. *Acc. Chem. Res.* **1989**, *22*, 55.

(8) Che, C.-M.; Butler, L. G.; Grunthaner, P. J.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 4662.

(9) Muraveiskaya, G. S.; Kukina, G. A.; Orlov, V. S.; Evstafeva, O. N.; Paraikoshito, M. A. *Zh. Neorg. Khim.* **1981**, *26*, 1843.

(10) Skinner, C. E.; Jones, M. M. *J. Am. Chem. Soc.* **1969**, *91*, 1984.

(11) The species $[Pt_2(pop)_4Br(NCS)]^{4-}$ was characterized spectroscopically. The $\sigma(X) \rightarrow d\sigma^*$ (Pt) transition occurs at 323 nm, between that of $[Pt_2(pop)_4(NCS)_2]^{4-}$ (337 nm) and $[Pt_2(pop)_4Br_2]^{4-}$ (305 nm).

Table IV. Second-Order Rate Constants, k_{BrBr}, at 25 °C (μ = 0.055 M)

pH	k_{BrBr}, M^{-1} s^{-1}	pH	k_{BrBr}, M^{-1} s^{-1}
2.0	0.31 (2)	5.5	0.90 (3)
2.6	0.32 (2)	5.8	1.07 (5)
3.4	0.37 (2)	6.2	1.20 (5)
3.9	0.40 (2)	6.7	1.52 (5)
4.2	0.46 (2)	7.1	1.86 (10)
4.7	0.47 (2)	7.3	2.10 (10)
5.2	0.67 (3)	7.6	2.84 (10)

Table V. Pseudo-First-Order Rate Constants, k_{obs}, for $[Pt_2(SO_4)_4ClOH_2]^{3-}$ + Cl^- → $[Pt_2(SO_4)_4Cl_2]^{4-}$ at 25 °C (μ = 0.5 M, Adjusted with $HClO_4$)

$[Cl^-]$, M	10^4k_{obs}, s^{-1}	$[Cl^-]$, M	10^4k_{obs}, s^{-1}
0.02	3.5	0.15	24.0
0.05	7.3	0.20	33.0
0.10	15.0		

with the large negative ΔS^* values suggest an interchange mechanism[12] for these anation reactions, and the relatively small activation enthalpies indicate that the axial water molecule is not strongly attached to the Pt-Pt unit for either X = Cl or X = Br.

The reactions studied above are not accelerated by the presence of added $[Pt_2(pop)_4]^{4-}$, as shown by the experimental data set out in Table III. This suggests that a two-electron atom-transfer pathway involving a bridged intermediate, Pt_2-X-Pt_2, is unlikely in the present case. This finding is in contrast with most work on monomeric Pt(II) and Pt(IV) complexes.[13] Presumably, the large Coulombic repulsion between the $[Pt_2(pop)_4X(OH_2)]^{3-}$ and $[Pt_2(pop)_4]^{4-}$ complexes prevents their association in solution even though one-dimensional Pt_2-X-Pt_2 species, $\{K_4[Pt_2(pop)_4X]\}_n$, exist in the solid state.[7] However, studies of the replacement of Cl^- in $[Pt_2(pop)_4Cl_2]^{4-}$ by Br^- have been interpreted[14] in terms of a bridged Pt_2-Cl-Pt_2 intermediate.

The bromide substitution of $[Pt_2(pop)_4Br(OH_2)]^{3-}$ was studied over a wider range of pH. Over the pH range 1-4, the observed rate constant varies only slightly; but as the pH becomes greater than 4.5, it gradually increases with increasing basicity of the solution (Table IV). Roundhill and co-workers found[14] that $[Pt_2(pop)_4]^{4-}$ and $[Pt_2(pop)_4Cl_2]^{4-}$ are dibasic acids with pK_1 of 3.10 and 4.95 and pK_2 of 6.75 and 7.55, respectively. The $[Pt_2(pop)_4Br(OH_2)]^{3-}$ ion would be expected to have smaller pK_a values than $[Pt_2(pop)_4Cl_2]^{4-}$, because of its lower negative charge. Thus at pH >4.5, deprotonation of the bridging pyrophosphite group(s) would occur. The rise in substitution rate therefore suggests that the deprotonated species are somewhat more labile than the parent complex.[14]

Substitution Reactions of $[Pt_2(SO_4)(OH_2)_2]^{2-}$. The reaction of $[Pt_2(SO_4)_4(OH_2)_2]^{2-}$ with Cl^- was studied in an aqueous perchloric acid medium. When a solution of $[Pt_2(SO_4)_4(OH_2)_2]^{2-}$ is treated with Cl^-, it rapidly changes to $[Pt_2(SO_4)_4Cl(OH_2)]^{3-}$,[15] which slowly reacts with Cl^- to give $[Pt_2(SO_4)_4Cl_2]^{4-}$. The final spectrum is identical with that of an authentic sample[13] of $[Pt_2(SO_4)_4Cl_2]^{4-}$. The chloride substitutions can thus be represented by (4) and (5), with reaction 4 much faster than reaction 5.

$$[Pt_2(SO_4)_4(OH_2)_2]^{2-} + Cl^- \rightarrow [Pt_2(SO_4)_4Cl(OH_2)]^{3-} \quad (4)$$

$$[Pt_2(SO_4)_4Cl(OH_2)]^{3-} + Cl^- \rightarrow [Pt_2(SO_4)_4Cl_2]^{4-} \quad (5)$$

The kinetics of reaction 5 were studied at 25 °C. As in the case of $[Pt_2(pop)_4X(OH_2)]^{3-}$, pseudo-first-order rate constants depend linearly on $[Cl^-]$ (Table V); the second-order rate constant k_{ClCl} = 0.016 M^{-1} s^{-1}. The observation that the axially coordinated water molecules in $[Pt_2(pop)_4X(OH_2)]^{3-}$ and $[Pt_2(SO_4)_4Cl(OH_2)]^{3-}$ are labile to substitution is readily interpreted in terms of a strong σ(Pt-Pt) trans effect.[7]

Acknowledgment. Financial support to C.-M.C. and C.-K.P. by the University of Hong Kong and the Croucher Foundation is gratefully acknowledged. Research at the California Institute of Technology was supported by National Science Foundation Grant CHE84-19828.

---

(12) Langford, C. H.; Gray, H. B. *Ligand Substitution Processes*; Benjamin: New York, 1965.

(13) Mason, W. R. *Coord. Chem. Rev.* **1972**, *7*, 241.

(14) Bryan, S. A.; Dickson, M. K.; Roundhill, D. M. *Inorg. Chem.* **1987**, *26*, 3878.

(15) Orlova, V. S.; Muraveiskaya, G. C.; Evstafeva, O. N. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1975**, *20*, 753.

Contribution No. 7915 from the Arthur Amos Noyes Laboratory, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

Electrochemical Oxidation of the $Ru(sar)^{2+}$ (sar = Sarcophagine) Ion and Its Relation to the Disproportionation of $Ru(sar)^{3+}$ in Aqueous Solution

Paul Bernhard[†] and Fred C. Anson*

Received January 30, 1989

Recently a kinetic study of the disproportionation of the $Ru(sar)^{3+}$ ion (sar (Figure 1): 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane) was presented.[1] The spectroscopic characterization of Ru(IV) intermediates[2] confirmed earlier indications[3] that the initial stage of the disproportionation of ruthenium amine complexes, which leads eventually to ligand oxidation, involves metal-centered electron-transfer chemistry accompanied by rapid deprotonation of the coordinated amines (eq 1-4). Chemical or electrochemical oxidation of $Ru(sar)^{2+}$ in D_2O was not accompanied by rapid H-D exchange on any of the methylene groups in the complex.[1] For this reason, the site of the deprotonation involved in equilibrium 3 is believed to be one of the coordinated nitrogen atoms in the complex. Experimental estimates of the rate and equilibrium constants for reactions 1-4 have been obtained:[1] $K_{III}k_d$ = 37 s^{-1}, k_{-d} = 6.2 × 10^3 M^{-1} s^{-1}, and k_e = 6 × 10^{-4} to 12 s^{-1}.[4] Furthermore, the kinetics of the reaction of $Ru(sar)^{2+}$ with dioxygen, which follows a complex pathway, provided an approximate value for pK_{III} of 6.2-6.4, from which a value of (6-9) × 10^7 M^{-1} s^{-1} was calculated for k_d.

$$Ru(sar)^{3+} = Ru^{III}(sar(-H^+))^{2+} + H^+ \quad K_{III} \quad (1)$$

$$Ru(sar)^{3+} + Ru^{III}(sar(-H^+))^{2+} = Ru(sar)^{2+} + Ru^{IV}(sar(-H^+))^{3+} \quad k_d, k_{-d} \quad (2)$$

$$Ru^{IV}(sar(-H^+))^{3+} = Ru^{IV}(sar(-2H^+))^{2+} + H^+ \quad K_{IV} \quad (3)$$

$$\{Ru(IV)\} \rightarrow Ru(imine{-}sar)^{2+} \quad k_e \quad (4)$$

(The notation follows that utilized in ref 2.)

In order to probe the consistency of these results and to clarify a remaining uncertainty about pK_{IV}, we carried out an electrochemical investigation of the oxidation of $Ru(sar)^{2+}$ in aqueous solution. Earlier attempts to study the pH dependence with stationary platinum or glassy-carbon electrodes were thwarted by poor reproducibility above pH 4, where the results depended strongly upon the pretreatment of the electrode surfaces. Fortunately, the potentials of interest turned out to be accessible to measurement with mercury electrodes without serious interference from the limit set by the anodic oxidation of mercury. Hanging mercury drop electrodes provided the necessary surface reproducibility. The results of this study, presented in this paper, include a Pourbaix (E^f vs pH) diagram for the $Ru^{IV/III/II}$sar system and a comparison with some related complexes.

---

* Corresponding author.

[†] Present address: Ciba-Geigy AG, Ch-1701 Fribourg, Switzerland.

0020-1669/89/1328-3272$01.50/0