exception is a six-coordinate species $[PtI_2(PEt_3)_2(H)(SiH_2I)]$, which has been recovered[12] as a yellow solid after addition of SiH_3I to *trans*-$[PtI_2(PEt_3)_2]$ or alternately by the action of HI on *trans*-$[PtI(PEt_3)_2(SiH_2I)]$; slow decomposition at ambient temperature to the four-coordinate complex *trans*-$[PtI(PEt_3)_2(SiHI_2)]$ has been ascribed[12] to rearrangement accompanied by elimination of H_2. Much more recently, the platinum(IV) congeners $[PtH_2(PMe_3)_2(MPh_3)_2]$ (M = Ge or Sn) have been characterized by Trogler et al.:[19] no evidence was encountered in parallel chemistry for the existence of a silyl analogue (i.e. M = Si), where instead the platinum(II) monosilyl $[PtH(SiPh_3)(PMe_3)_2]$ was recovered in spite of the low steric requirements of the phosphine ligands at Pt.

Identification of platinum(IV) silyls is thus an objective of fundamental interest: a number of key transformations in silyl–platinum(II) chemistry (notably hydrogenolysis of Pt–Si bonds, which is in some circumstances reversible and therefore relevant to catalysis) are believed to occur via oxidative addition, i.e., formation of transient Pt(IV) species;[20] however, the latter have not normally been detectable, even by using in situ NMR spectroscopy on reacting systems.[19,21] In a directly related mechanistic context, the importance of sequential oxidative addition/reductive elimination vs nucleophilic displacement at square Pt(II) as a vehicle for substitution reactions in Pt–Si chemistry has hitherto been difficult to assess, because of departure of the liberated silyl fragment from the Pt center during the elimination step. The synthetic methodology[2,6] described above has recently been adapted to obtain[22] a palladium congener $Pd(chel)_2$ of complex **2**, which is reported to be distinctly more stable than nonchelated bis(silyl) analogues.

Chelation at Pt by the phosphinoethylsilyl ligand chel is accompanied by a diagnostic[23] shift to high frequency (i.e. downfield), to about −80 ppm (Table I) compared with free chelH (−151 ppm) or with the latter coordinated through P only (Table II); this situation is typified by the shifts of −85.5 and −114.1 ppm for the complex $[PtCl(chel)(PPh_2CH_2CH_2SiMe_2Cl)]$ (**7**). Precoordination through P of chelH is evidently an important step in attachment of chel at Pt, as is illustrated by NMR characterization of the intermediates **17–21** although whether or not a similar profile is followed in related chemistry such as regiospecific addition[4] of chelH at Ir(I) remains unknown. Subsequent hydrosilylation at Pt has for the first time been shown to proceed through an octahedral silylplatinum(IV) configuration (**22**), in which the influence of a trans relationship with Si and the oxidized state of the metal combine to reduce $^1J(PtP)$ to an exceptionally low value (1084 Hz). Control of substrate orientation in the vicinity of the metal site that is implicit in selectivity toward a preferred diastereoisomer of complexes **4–6** may be significant in relation to asymmetric catalysis.

Acknowledgment. We thank the NSERC, Canada, and the University of Victoria for financial support.

Registry No. **2**, 80298-94-8; **3**, 80298-95-9; **4**, 134733-12-3; **5**, 134733-13-4; **6**, 134733-14-5; **7**, 134681-59-7; **8**, 134681-60-0; **9**, 134681-61-1; **10**, 134681-62-2; **11**, 134681-63-3; **12**, 134681-64-4; **13**, 80298-99-3; **14**, 134681-65-5; **15**, 134681-66-6; **16**, 134733-15-6; **17**, 134681-58-6; **18**, 134681-69-9; **19**, 134681-70-2; **20**, 134780-97-5; **21**, 134733-16-7; **22**, 134704-96-4; $[PtCl_2(COD)]$, 12080-32-9; $[Pt(COD)_2]$, 12130-66-4; CCl_4, 56-23-5; $PPh_2CH_2CH_2SiMe_2^-$, 134681-67-7; $PPh_2CH_2CH_2SiPh_2^-$, 134681-68-8; $[Pt(COD)Me_2]$, 12266-92-1; [Pt(COD)MeCl], 50978-00-2; $[Pt[PPh_2CH_2CH_2Si^*Me(C^*H(CH_3)(CH_2CH_3)(CH_2))Ph]_2I_2]$ (isomer 1), 134733-17-8; $[Pt[PPh_2CH_2Si^*Me(C^*H(CH_3)(CH_2CH_3)(CH_2))Ph]_2I_2]$ (isomer 2), 134733-18-9; ^{195}Pt, 14191-88-9.

---

(19) Packett, D. L.; Syed, A.; Trogler, W. C. *Organometallics* **1988**, *7*, 159.

(20) Chatt, J.; Eaborn, C.; Ibekwe, S. D.; Kapoor, P. N. *J. Chem. Soc. A* **1970**, 1343.

(21) Glockling, F.; Hooton, H. A. *J. Chem. Soc. A* **1968**, 826.

(22) Schubert, U.; Miller, C. *J. Organomet. Chem.* **1989**, *373*, 165.

(23) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

Contribution from the Department of Chemistry,
Queen's University, Kingston, Ontario, Canada K7L 3N6

Kinetics of the Electron-Exchange Reaction of the Hexacyanoosmate(II/III) Couple in Aqueous Media

Donal H. Macartney

Received September 28, 1990

The kinetics of the electron self-exchange reaction of the $Os(CN)_6^{4-/3-}$ couple have been investigated in aqueous media by using ^{13}C NMR line-broadening techniques. The electron-exchange rate constant for the $Os(CN)_6^{4-/3-}$ couple at 25 °C, $I = 1.0$ M (Na^+), is $(8.9 \pm 0.5) \times 10^4$ M^{-1} s^{-1} with $\Delta H^* = 36 \pm 4$ kJ mol^{-1} and $\Delta S^* = -31 \pm 12$ J K^{-1} mol^{-1}. The rate constants display a first-order dependence on $[Na^+]$ and are dependent on the nature of the cation of the electrolyte, with an observed order of $k_{11}(Li^+) < k_{11}(Na^+) < k_{11}(NH_4^+) < k_{11}(K^+)$. The acid dissociation constants for the $(HNC)_nOs(CN)_{6-n}^{(4-n)-}$ species, $pK_1 = 0.5 \pm 0.3$ and $pK_2 = 2.0 \pm 0.2$ ($I = 1.0$ M (Na^+)), were determined from cyclic voltammetry and ^{13}C NMR chemical shift measurements. The electron-exchange rate constants decrease with increasing acidity owing to the proton equilibria involving the $(HNC)_2Os(CN)_4^{2-}$ ($k_2 = 1.8 \times 10^3$ M^{-1} s^{-1}, $I = 1.0$ M (Na^+)) and $(HNC)Os(CN)_5^{3-}$ ($k_1 = 2.8 \times 10^4$ M^{-1} s^{-1}) species. The exchange rate constants are discussed in terms of the inner-sphere and solvent reorganization barriers and compared with the corresponding parameters for other $M(CN)_n^{4-/3-}$ couples.

Introduction

Kinetic investigations of the electron-exchange and electron-transfer reactions of the $M(CN)_6^{4-/3-}$ couples of the iron triad have been almost exclusively limited to the $Fe(CN)_6^{4-/3-}$ system.[1] The $Fe(CN)_6^{n-}$ species are well-characterized outer-sphere cross-reactants and have been extensively employed in electron-transfer kinetics studies with organic compounds,[2] transition-metal complexes,[3] and metalloproteins.[4] Recently, in this laboratory,

---

(1) (a) Sharpe, A. G. *The Chemistry of Cyano Complexes of the Transition Metals*; Academic Press: London, 1976. (b) Sieklucka, B. *Prog. React. Kinet.* **1989**, *15*, 175.

(2) For recent examples see: (a) Anast, J. M.; Margerum, D. W. *Inorg. Chem.* **1982**, *21*, 3494. (b) Toma, H. E.; Batista, A. A. *J. Inorg. Biochem.* **1984**, *20*, 53. (c) Krack, I.; van Eldik, R. *Inorg. Chem.* **1986**, *25*, 1743.

0020-1669/91/1330-3337$02.50/0

the electron self-exchange for the $Ru(CN)_6^{4-/3-}$ couple, k_{11}(25 °C) = 8.3×10^3 M^{-1} s^{-1} (I = 0.10 M ($NaClO_4$)) was measured directly from ^{13}C NMR line-broadening determinations.[5] A similar value was derived from the application of the Marcus relationship to the rate constants for a series of cross-reactions of the $Ru(CN)_6^{4-/3-}$ couple with metal complexes,[5-7] small inorganic anions,[5] and substituted dihydroxybenzene compounds.[8]

Relatively few electron-transfer kinetic studies have employed the $Os(CN)_6^{3-/4-}$ couple. Hicks[9] observed a pH dependence for the oxidation of $Os(CN)_6^{4-}$ by MnO_4^-, attributed to protonations of the coordinated cyanides, and estimated the electron self-exchange rate constant for the $Os(CN)_6^{4-/3-}$ couple to be about 10^7 M^{-1} s^{-1}. The $Os(CN)_6^{4-}$ ion has also been employed as a reductive quencher for a number of excited state tris(polypyridine)ruthenium species[10] and lanthanide ion cryptand complexes.[11] The $Os(CN)_6^{3-}$ ion ($E°$ = 0.63 V), generated by laser photoionization, has recently been employed, along with the $Fe(CN)_6^{3-}$ ($E°$ = 0.41 V) and $Ru(CN)_6^{3-}$ ($E°$ = 0.92 V) ions, in a kinetic study of the oxidation of ferrocytochrome *c*.[12]

In this paper the results of kinetic and electrochemical investigations of the electron-exchange reactions involving the $Os(CN)_6^{4-/3-}$ couple in aqueous solution are reported. The self-exchange rate constant and activation parameters for this couple have been measured directly, employing ^{13}C NMR line-broadening techniques with ^{13}CN-labeled samples. The dependences of the self-exchange rate constants on pH and the concentration and nature of the electrolyte cation have been investigated. The magnitude of the electron-exchange rate constant is discussed in terms of inner-sphere and solvent reorganizational barriers and is compared with exchange parameters for other $M(CN)_n^{4-/3-}$ couples and Os(II)/Os(III) systems.

Experimental Section

Materials. Potassium hexacyanoosmate(II) trihydrate, $K_4[Os(CN)_6]\cdot 3H_2O$, was prepared from K_2OsCl_6 (Aldrich) by the method of Curtis and Meyer,[13] recrystallizing the potassium salt twice from methanol. The ^{13}CN-labeled salt was synthesized by using $Na^{13}CN$ (90% $^{13}CN^-$, MSD Isotopes) in place of some of the KCN in the preparation. An isotopic enrichment of ≈40% was estimated from ratio of the areas of the CN stretching bands in the infrared spectrum. The $^{13}C{\equiv}N$ stretching bands are found at 2018, 2000 (s), and 1980 (m) cm^{-1} and correspond to the 2066-, 2040-, and 2016-cm^{-1} bands observed in $K_4[Os(CN)_6]\cdot 3H_2O$.[14] Sodium hexachloroiridate(IV) hexahydrate, $Na_2IrCl_6\cdot 6H_2O$, was used as received (Strem). The concentration of the $IrCl_6^{2-}$ ion in solution was determined spectrophotometrically at 488 nm (ϵ = 4030 M^{-1} cm^{-1}).[15]

Physical Measurements. UV-visible spectra were recorded by using a Hewlett-Packard 8452A diode-array spectrophotometer, and infrared spectra were recorded on a Bomem MB-120 FT-IR instrument. Cyclic voltammetric measurements were carried out in aqueous solution with a BAS CV-1B cyclic voltammograph (Bioanalytical Systems) attached to a Houston Instruments 100 X-Y recorder. The working (Pt button) and auxilliary (Pt wire) electrodes in the sample solution were separated from the reference electrode (Ag/AgCl) by a glass frit. The ^{13}C NMR spectra were recorded on a Bruker AM-400 instrument operating at 100.6 MHz. The aqueous samples were run in 5-mm tubes with 30% D_2O serving as an internal lock, and CH_3OH was employed as an external reference. The temperature of the probe was maintained to within 0.5 °C over the temperature range 20–50 °C. Nonlinear least-squares analyses of the pH-dependent electrochemical, kinetic, and NMR chemical shift data were performed by using a Simplex optimization program.

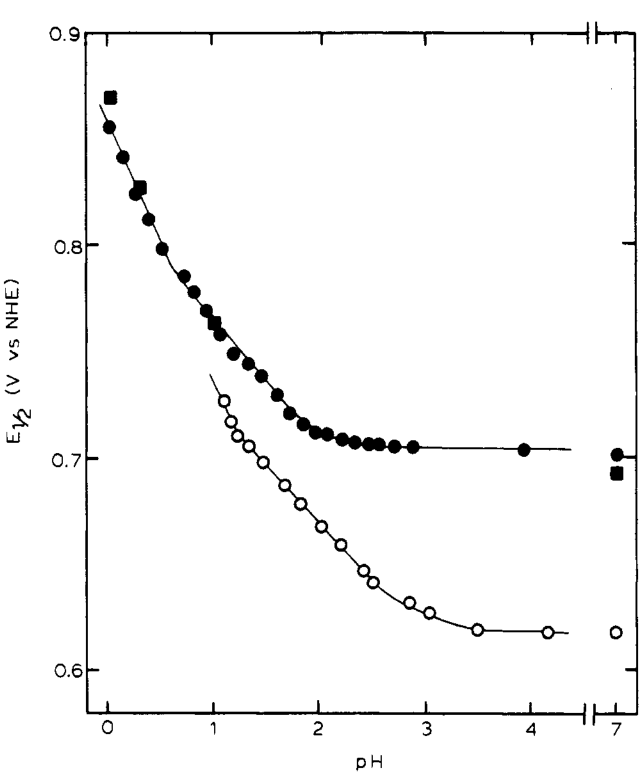
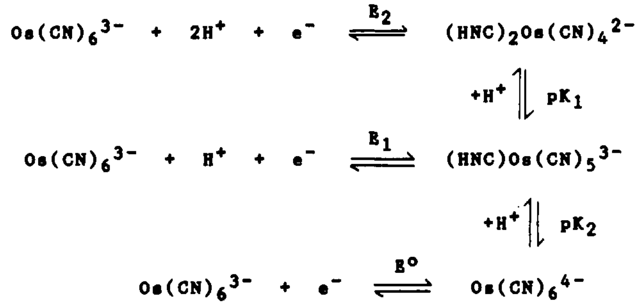


Figure 1. Dependences of $E_{1/2}$ on pH for the reduction of $Os(CN)_6^{3-}$ in aqueous solution at 25 °C and I = 0.10 M (○) and 1.0 M (●) with $HClO_4/NaClO_4$ (this work) and I = 1.0 M (■) with $K^+/HClO_4$ (data from ref 16a). The solid curves represent the fits of the data to eq 1.

Scheme I



Results

Reduction Potential of the $Os(CN)_6^{4-/3-}$ Couple. The electrochemical reduction potential of the $Os(CN)_6^{3-/4-}$ couple in neutral solution has been reported to be 0.64 V (0.10 M Na^+)[13] and 0.692 V (1.0 M K^+),[16a] with a strong dependence on the ionic strength (cation concentration) of the medium ($E°$ = 0.634 V, extrapolated to zero ionic strength in K^+ media). In this study cyclic voltammetry measurements on the $Os(CN)_6^{3-/4-}$ reduction potential were carried out in aqueous media (I = 0.10 and 1.0 M ($NaClO_4$))

---

(3) Recent examples are: (a) Powell, M. F.; Wu, J. C.; Bruice, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 3850. (b) Panda, P. K.; Panda, R. K.; Murti, P. S. R. *Int. J. Chem. Kinet.* **1987**, *19*, 155. (c) Doyle, M. P.; Guy, J. K.; Brown, K. C.; Mahapatro, S. N.; Van Zyl, C. M.; Pladziewicz, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 1536.

(4) See for instance: (a) Jackman, M. P.; Sinclair-Day, J. D.; Sisley, M. J.; Sykes, A. G.; Denys, L. A.; Wright, P. E. *J. Am. Chem. Soc.* **1987**, *109*, 6443. (b) Hartshorn, R. T.; Lim, M.-C.; Sykes, A. G. *Inorg. CHem.* **1988**, *27*, 4603. (c) Cheddar, G.; Meyer, T. E.; Cusanovich, M. A.; Stout, C. D.; Tollin, G. *Biochemistry* **1989**, *28*, 6318.

(5) Hoddenbagh, J. M. A.; Macartney, D. H. *Inorg. Chem.* **1990**, *29*, 245.

(6) Hicks, K. W.; Chappelle, G. A. *Inorg. Chem.* **1980**, *19*, 1623.

(7) Juris, A.; Manfrin, M. F.; Maestri, N.; Serpone, N. *Inorg. Chem.* **1978**, *17*, 2258.

(8) Hoddenbagh, J. M. A.; Macartney, D. H. *J. Chem. Soc., Dalton Trans.* **1990**, 615.

(9) Hicks, K. W. *Inorg. Chim. Acta* **1983**, *76*, L115.

(10) Mallouk, T. E.; Krueger, J. S.; Mayer, J. E.; Dymond, C. M. G. *Inorg. Chem.* **1989**, *28*, 3507.

(11) Sabbatini, N.; Perathoner, S.; Lattanzi, G.; Dellonte, S.; Balzani, V. *Inorg. Chem.* **1988**, *27*, 1628.

(12) Cho, K. C.; Chu, W. F.; Choy, C. L.; Che, C. M. *Biochim. Biophys. Acta* **1989**, *973*, 53.

(13) Curtis, J. C.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 1562.

(14) (a) Nakagawa, I.; Shimanouchi, T. *Spectrochim. Acta* **1962**, *18*, 101. (b) Mathieu, J. P.; Poulet, H. *Spectrochim. Acta* **1964**, *19*, 1966. (c) Griffith, W. P.; Turner, G. *J. Chem. Soc. A* **1970**, 858. (d) Hipps, K. W.; Williams, S. D.; Mazur, U. *Inorg. Chem.* **1984**, *23*, 3500.

(15) Bennett, L. E.; Warlop, P. *Inorg. Chem.* **1990**, *29*, 1975.

(16) (a) Opekar, F.; Beran, P. *J. Electroanal. Chem. Interfacial Electrochem.* **1976**, *71*, 120. (b) Oyama, N.; Ohsaka, T.; Yamamoto, N.; Matsui, J.; Hatozaki, O. *J. Electroanal. Chem. Interfacial Electrochem.* **1989**, *265*, 297.

Table I. Electron-Exchange Rate Constants for $M(CN)_n^{4-/3-}$ Couples in Aqueous Media at 25 °C

couple	I, M (M^+)	$10^{-4}k_{11}$, $M^{-1}\ s^{-1}$	ΔH^*, kJ mol^{-1}	ΔS^*, J $K^{-1}\ mol^{-1}$	ref
$Fe(CN)_6^{4-/3-}$	1.0 (K^+)	1.6			*a*
	1.75 (Li^+)[b]	<3			*c*
	1.75 (Na^+)[b]	5.8			*c*
	1.75 (K^+)[b]	8.3			*c*
	1.75 (NH_4^+)[b]	8.4			*c*
$Ru(CN)_6^{4-/3-}$	0.10 (Na^+)	0.83 ± 0.05	40 ± 5	−36 ± 15	*d*
	0.10 (K^+)	2.1 ± 0.4			*d*
	0.50 (K^+)	7.1 ± 0.3			*d*
$Os(CN)_6^{4-/3-}$	0.20 (Na^+)	1.5 ± 0.2			*e*
	0.50 (Na^+)	3.2 ± 0.3			*e*
	1.0 (Li^+)	5.6 ± 0.3	40 ± 2	−20 ± 6	*e*
	1.0 (Na^+)	8.9 ± 0.5	36 ± 4	−31 ± 12	*e*
	1.0 (K^+)	13.5 ± 0.7	37 ± 4	−23 ± 12	*e*
	1.0 (NH_4^+)	10.8 ± 0.4	33 ± 3	−37 ± 9	*e*
$Mo(CN)_8^{4-/3-}$	0.10 (Na^+)	2.5 ± 0.4	31 ± 4	−54 ± 13	*f*
	1.0 (Na^+)	16.4 ± 0.8			*f*
$W(CN)_8^{4-/3-}$	0.10 (Na^+)	1.5 ± 0.3			*f*

[a] Reference 22. [b] At 32 °C, $[M^+]$ = 1.75 M. [c] Reference 23a. [d] Reference 5. [e] This work. [f] Kerr, D.; Macartney, D.H. Manuscript in preparation.

as function of pH in the range 0–7. The increase in $E_{1/2}$ observed upon an increase in the acidity of the solution (Figure 1) is the result of three redox couples, involving the proton equilibria of the $Os(CN)_6^{4-}$ ion, as shown in Scheme I. It is not expected that protonation of $Os(CN)_6^{3-}$ will occur above pH 0, as none was observed for the corresponding $Fe(CN)_6^{3-}$ or $Ru(CN)_6^{3-}$ ions.[1,5] The reduction potential at pH 1.0 (I = 0.10 M), $E_{1/2}$ = 0.733 V, compares favorably with a reported value, $E_{1/2}$ = 0.758 V, measured at pH 1.0 and a slightly higher ionic strength (I = 0.20 M (CF_3COOH/Na^+)).[16b] An increase in $E_{1/2}$ with decreasing pH was also observed by Opekar and Beran[16a] at an ionic strength of 1.0 M in K^+ media, and the values are presented in Figure 1 for comparison. There does not appear to be a significant dependence of the reduction potentials on the nature of the cation (Na^+ or K^+) at the same ionic strength in the pH range measured. This is likely a result of similar relative interactions (Os(II) relative to Os(III)) of the H^+, Na^+, and K^+ cations with the reduced and oxidized anionic complexes.

For a reversible electrode reaction involving protons the Nernst equation (assuming similar diffusion coefficients of the reductant and oxidant[17] and rapid diffusion of protons) may be written as in eq 1 where $E°$ and $E_{1/2}$ are the formal electrode and half-wave

$$E_{1/2} = E° + \frac{RT}{nF} \ln \left[1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1K_2} \right] \qquad (1)$$

potentials, respectively. The dependence of $E_{1/2}$ on pH for the Os(II)/Os(II) system (Figure 1) is consistent with pH regions for two-proton ($\Delta E_{1/2}$/pH = 118 mV), one-proton ($\Delta E_{1/2}$/pH = 59 mV), and zero-proton couples. From a nonlinear least-squares fit of the cyclic voltammetry data to eq 1 the pK_1 and pK_2 values are estimated to be 1.0 ± 0.2 and 2.8 ± 0.1 at I = 0.10 M and 0.6 ± 0.2 and 1.9 ± 0.1 at I = 1.0 M, respectively.

The analogous acid dissociation constants for the $Fe(CN)_6^{4-}$ and $Ru(CN)_6^{4-}$ systems, measured at I = 0.10 M, are 1.9 and 3.7[18] (extrapolated to pK_1 = 0.8 and pK_2 = 2.5 at I = 1.0 M[19]) and 1.6 and 3.2,[5] respectively. Values of pK_1 = 2.51 and pK_2 = 2.66 for $Os(CN)_6^{4-}$ system at I = 1.0 M ($LiClO_4$) were reported by Hicks[9] from the pH dependence of the rate constants for the oxidation of $Os(CN)_6^{4-}$ by MnO_4^-. A much larger difference between the two pK values, as seen in present study, would be expected on both statistical (ΔpK = 0.48) and electrostatic grounds.

$Os(CN)_6^{4-/3-}$ Electron-Exchange Reaction. Direct measurements of the electron self-exchange rate constants, k_{11}, for the $Os(CN)_6^{4-/3-}$ couple in aqueous solution (30% D_2O) were determined from ^{13}C NMR line-broadening experiments (eq 2).

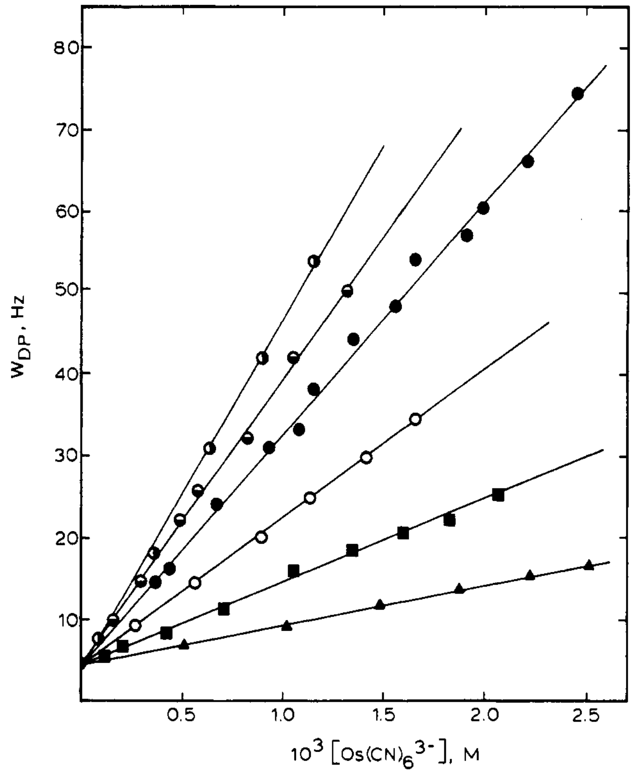


Figure 2. Dependence of the $Os(CN)_6^{4-}$ ^{13}C NMR line width (W_{DP}) on the concentration of $Os(CN)_6^{3-}$ in aqueous solution at 25 °C, I = 0.2 M (▲), 0.5 M (■), and 1.0 M (●) with $NaClO_4$ and I = 1.0 M with $LiClO_4$ (○), KCl (◑), and NH_4Cl (⊖).

$$Os(CN)_6^{4-} + {}^*Os(CN)_6^{3-} \underset{}{\overset{k_{11}}{\rightleftharpoons}} Os(CN)_6^{3-} + {}^*Os(CN)_6^{4-} \quad (2)$$

The diamagnetic $Os(CN)_6^{4-}$ ion has a ^{13}C NMR chemical shift of 142.9 ppm (vs external CH_3OH) at 25 °C, with a half-height line width (W_D) of 4.5 ± 0.5 Hz. The $Os(CN)_6^{3-}$ was generated in solution by the addition of a stoichiometric deficiency of paramagnetic $IrCl_6^{2-}$ ($E°$ = 0.92 V), which rapidly oxidizes the $Os(CN)_6^{4-}$ ion,[20] forming in turn the diamagnetic $IrCl_6^{3-}$ ion. Upon additions of the generated $Os(CN)_6^{3-}$ ion ($[Os(CN)_6^{3-}]$ = (0.3–2.5) × 10^{-3} M) to the $Os(CN)_6^{4-}$ solution (1.0 × 10^{-2} M)

---

[17] The diffusion coefficients for $Os(CN)_6^{4-}$ and $Os(CN)_6^{3-}$ in 0.1 M $HClO_4$ are 5.6 × 10^{-6} and 6.8 × 10^{-6} $cm^2\ s^{-1}$, respectively.[16a]

[18] Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum Press: New York, 1989; Vol. 6, p 433.

[19] Bruhn, H.; Nigam, S.; Holzwarth, J. F. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 129.

[20] (a) The rate constant for the $Os(CN)_6^{4-}/IrCl_6^{2-}$ reaction at 25.0 °C and pH 1.0 (I = 1.0 M (NaCl)) is 9.6 × 10^5 $M^{-1}\ s^{-1}$, with an inverse dependence of the rate on acid concentration.[20b] (b) Imonigie, J. A.; Macartney, D. H. Manuscript in preparation.

the line width (W_{DP}) increased, with no change observed in the chemical shift.

The exchange process is in the slow-exchange domain,[21] with $k_{11}[Os(CN)_6^{3-}] \ll 2\pi(\delta\nu)$, and the electron-exchange rate constant may be determined from the relationship between the extent of line broadening ($W_{DP} - W_D$) and the concentration of the paramagnetic species.

$$\pi(W_{DP} - W_D) = k_{11}[Os(CN)_6^{3-}] \qquad (3)$$

The linear dependences of $W_{DP} - W_D$ on $[Os(CN)_6^{3-}]$ at 25 °C in a variety of electrolyte media are shown in Figure 2. The values of k_{11} determined for the $Os(CN)_6^{4-/3-}$ couple by using eq 3, and the corresponding activation parameters, determined from k_{11} data over the temperature range 20–50 °C, are presented in Table I.

Cation Dependences. The dependence of k_{11} on the concentration of Na^+ in the solution was determined in the range of $[Na^+] = 0.04$–1.0 M by the addition of $NaClO_4$. Figure 3 shows a plot of k_{11} against $[Na^+]$ for the exchange reaction at 25.0 °C. The dependence of the electron-exchange rate constant on the nature of the cation was studied at an ionic strength of 1.0 M by using chloride or perchlorate salts of Li^+, Na^+, K^+, and NH_4^+. The dependences of W_{DP} on $[Os(CN)_6^{3-}]$ for these reactions are shown in Figure 2, and the second-order rate constants are presented in Table I.

pH Dependence. The dependence of k_{11} on pH was investigated at 25 °C at an ionic strength of 1.0 M, using $HClO_4/NaClO_4$ mixtures (30% D_2O). Below pH 4 the electron-exchange rate constant is observed to decrease with an increase in the acid concentration, as shown in Figure 4. The acid dependence may be attributed to three electron-exchange pathways involving the osmium(II) reductant in different states of protonation (eqs 4–6).

$$Os(CN)_6^{4-} + Os(CN)_6^{3-} \overset{k_0}{\rightleftharpoons} Os(CN)_6^{3-} + Os(CN)_6^{4-} \qquad (4)$$

$$(HNC)Os(CN)_5^{3-} + Os(CN)_6^{3-} \overset{k_1}{\rightleftharpoons} Os(CN)_6^{3-} + (HNC)Os(CN)_5^{3-} \qquad (5)$$

$$(HNC)_2Os(CN)_4^{2-} + Os(CN)_6^{3-} \overset{k_2}{\rightleftharpoons} Os(CN)_6^{3-} + (HNC)_2Os(CN)_4^{2-} \qquad (6)$$

An expression for the dependence of the observed electron-exchange rate constant on acid concentration (eq 7) may be written

$$k_{11}(\text{obs}) = \frac{k_2 + k_1K_1/[H^+] + k_0K_1K_2/[H^+]^2}{1 + K_1/[H^+] + K_1K_2/[H^+]^2} \qquad (7)$$

in terms of the specific rate constants k_n, where n is the number of protons on the Os(II) species, and the acid dissociation constants as defined in Scheme I.

A non-linear least-squares fit of the kinetic data to eq 7 (using the pK values determined from the electrochemical experiments as initial estimates) yielded specific rate constants of $k_2 = (1.8 \pm 1.0) \times 10^3$ M^{-1} s^{-1}, $k_1 = (2.8 \pm 0.6) \times 10^4$ M^{-1} s^{-1}, and $k_0 = (8.9 \pm 0.5) \times 10^4$ M^{-1} s^{-1}, with p$K_1 = 0.5 \pm 0.3$ and p$K_2 = 2.3 \pm 0.3$.

The ^{13}C NMR chemical shift of the cyanide carbons on $Os(CN)_6^{4-}$ was observed to move upfield with a decrease in the pH of the solution. The acid dissociation constants K_1 and K_2 were determined in the medium used for the electron-exchange kinetic measurements (30% D_2O, $I = 1.0$ M ($NaClO_4/HClO_4$)) from the pH dependence of the ^{13}C NMR chemical shift in the range of pH = 0–6 (Figure 4). The relationship of the chemical shift (δ_{obs}) to the acid concentration may be expressed as in eq 8, where

$$\delta_{obs} = \frac{\delta_2 + \delta_1K_1/[H^+] + \delta_0K_1K_2/[H^+]^2}{1 + K_1/[H^+] + K_1K_2/[H^+]^2} \qquad (8)$$

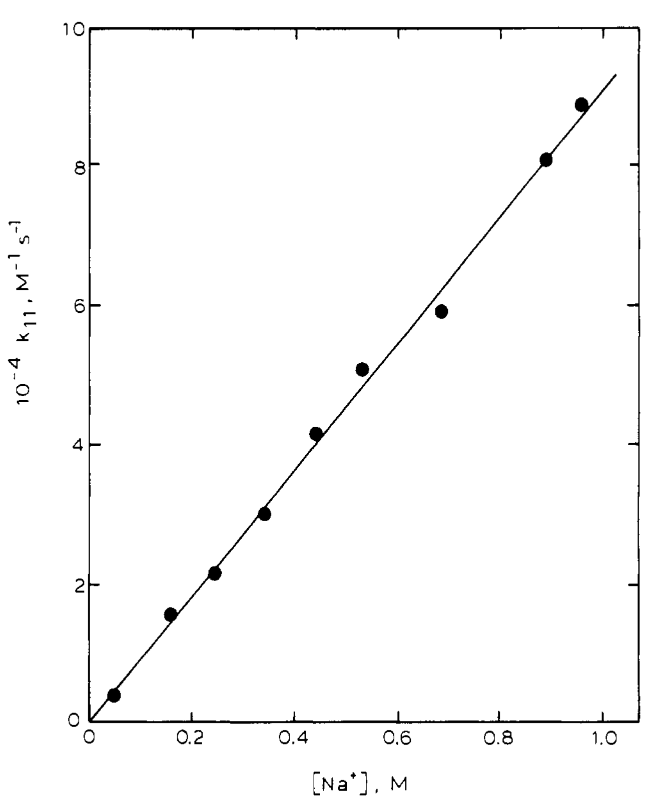


Figure 3. Dependence of k_{11} on $[Na^+]$ for the electron-exchange reaction of the $Os(CN)_6^{4-/3-}$ couple in aqueous media at 25 °C.

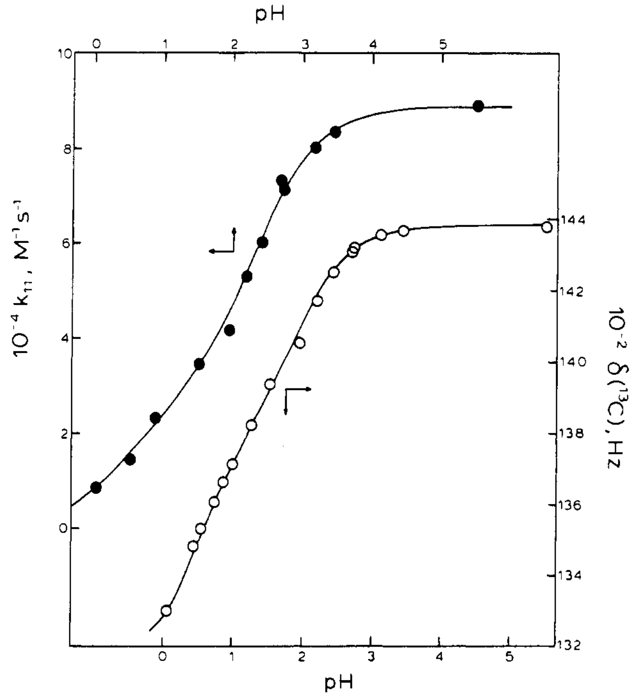


Figure 4. Plots of the pH dependences of k_{11} for the $Os(CN)_6^{4-/3-}$ couple (●) and the ^{13}C chemical shift of $Os(CN)_6^{4-}$ (○) at 25 °C and $I = 1.0$ M ($NaClO_4/HClO_4$). The solid curves represent the fits of the data to eqs 7 and 8, respectively.

δ_n represents the ^{13}C chemical shift of the corresponding $(HNC)_nOs(CN)_{6-n}^{(4-n)-}$ species. A nonlinear least-squares fit of the chemical shift data to eq 8 yielded δ_2 = 13 100 Hz (130.2 ppm), δ_1 = 13 800 Hz (137.2 ppm), and δ_0 = 14 390 Hz (143.0 ppm), with p$K_1 = 0.5 \pm 0.3$ and p$K_2 = 2.0 \pm 0.1$. The acid dissociation constants are in good agreement with the values determined at the same ionic strength by cyclic voltammetry and from the kinetic measurements. The increase anticipated in the pK values on going from H_2O to 30% D_2O is only about 0.1–0.2 units,[24] within the

---

[21] Swift, T. J.; Connick, R. E. *J. Chem. Phys.* **1962**, *37*, 307.

[22] Kurland, R. J.; Winkler, M. E. *J. Biochem. Biophys. Methods* **1981**, *4*, 215.

[23] (a) Shporer, M.; Ron, G.; Lowewenstein, A.; Navon, G. *Inorg. Chem.* **1965**, *4*, 361. (b) Campion, R. J.; Deck, C. F.; King, P.; Wahl, A. *Inorg. Chem.* **1967**, *6*, 672.

experimental uncertainties in these measurements.

Discussion

The electron self-exchange rate constant for the $Os(CN)_6{}^{4-/3-}$ couple in aqueous solution has been obtained directly from a kinetic study, employing ^{13}C NMR line-broadening techniques. When the effects of the concentration and the nature of the cation in the electrolyte are taken into consideration, the electron-exchange rate constant for $Os(CN)_6{}^{3-/4-}$ is very similar to those for the low-spin d^6/d^5 $M(CN)_6{}^{4-/3-}$ couples of Fe and Ru and the d^2/d^1 $M(CN)_8{}^{4-/3-}$ couples of Mo and W (Table I). The activation parameters obtained for the $Os(CN)_6{}^{4-/3-}$ exchange reaction are also similar to those found for the $Ru(CN)_6{}^{4-/3-}$ and $Mo(CN)_8{}^{4-/3-}$ couples in Na^+ media.

The first-order dependence of the $Os(CN)_6{}^{4-/3-}$ self-exchange rate constant on $[Na^+]$ (Figure 3) indicates that the cation catalyzes the electron-exchange reaction. The effect of changing the nature of the cation of the electrolyte on the electron-exchange rate constant for the $Os(CN)_6{}^{4-/3-}$ couple H^+ (k_1 in eq 5) < Li^+ < Na^+ < $NH_4{}^+$ < K^+, was not unexpected. Similar trends have been reported for the $Fe(CN)_6{}^{4-/3-}$ exchange reaction[23] and for several electron-transfer cross-reactions between $M(CN)_n{}^{4-/3-}$ complexes and anionic reactants.[19,20,25] The cation is regarded as acting as an electrostatic buffer, reducing the repulsion between the two anionic reactants.[26] This role has been supported by the correlations of the electron-transfer rate constants with the crystal radii and the polarizability of the cations.

The electron self-exchange rate constants for a number of transition-metal complex couples, including $Ru(CN)_6{}^{4-/3-}$,[5] have been predicted with reasonable success by using the semiclassical model for outer-sphere bimolecular electron-exchange reactions.[27] The exchange rate constant k_{11} may be expressed (eq 9) as the

$$k_{11} = K_A \nu_n \kappa_{el} \Gamma_n \exp[-(\Delta G^*_{in} + \Delta G^*_{out})/RT] \qquad (9)$$

product of a preequilibrium constant K_A, an effective nuclear frequency ν_n, an electronic factor κ_{el}, an inner-sphere nuclear tunneling factor Γ_n, and a nuclear factor that contains terms for both inner-sphere (ΔG^*_{in}) and solvent (ΔG^*_{out}) reorganization energies.

The inner-sphere term, ΔG^*_{in}, corresponds to the reorganization of bond distances and angles required prior to electron transfer, while the outer-sphere term, ΔG^*_{out}, is the energy needed to change the orientations of the solvent molecules surrounding the reactants. As with other low-spin d^6/d^5 couples,[27] in which electron exchange involves an electron occupying a nonbonding t_{2g} orbital, a small inner-sphere reorganization energy barrier is anticipated and estimated to be about 3 kJ mol^{-1} for the $Os(CN)_6{}^{4-/3-}$ couple.[28] The outer-sphere solvent reorganization barrier, ΔG^*_{out}, may be calculated by using an ellipsoidal cavity dielectric continuum model.[27b,31] For the $Os(CN)_6{}^{4-/3-}$ couple, a value of 28 kJ mol^{-1} is calculated for ΔG^*_{out} by using a metal–metal separation distance of 9.4 Å. The electron-exchange rate constant calculated for the $[Os(CN)_6]^{4-/3-}$ couple from the semiclassical model (eq 9),[32] given the uncertainties in the reorganization parameters, is $(2 \pm 1) \times 10^5$ M^{-1} s^{-1}, a good order of magnitude agreement with the directly measured rate constants determined in this study at $I = 1.0$ M.

The only other osmium(II/III) couples for which an electron self-exchange rate constant has been measured directly are several substituted tris(polypyridine)osmium(II/III) couples. In acetonitrile at 30 °C ($I \approx 0.01$ M) the k_{11} values in the range of $(1-4) \times 10^6$ M^{-1} s^{-1} were determined from ^1H NMR line-broadening experiments.[33] In aqueous media, at higher ionic strengths (0.1–1.0 M), self-exchange rate constants of 10^8–10^9 M^{-1} s^{-1} have been estimated from the application of the Marcus equations[34] to the rate constants for a number of outer-sphere cross-reactions involving these complexes.[35] Estimates for k_{11} of 10^2–10^5 M^{-1} s^{-1} have been reported for a number of osmium amine complex couples,[36] $Os(NH_3)_5X^{(2-n)+/(3-n)+}$ ($X^{n-} = H_2O, NH_3, Cl^-$), from the application of the Marcus relationship to cross-reactions of the Os(III) species with the excited state of a variety of substituted tris(polypyridine)ruthenium(II) complexes.

The electron self-exchange rate constant for the $Os(CN)_6{}^{3-/4-}$ couple is observed to decrease upon protonation of the Os(II) species. Hicks observed the same type of pH dependence in the electron-transfer cross-reaction of $Os(CN)_6{}^{4-}$ with $MnO_4{}^-$ in $LiClO_4$ media,[9] and it is also seen in the cross-reaction of $Os(CN)_6{}^{4-}$ with $IrCl_6{}^{2-}$.[20] A very similar pH dependence, with comparable electron-exchange rate parameters, was reported for the $Fe(CN)_6{}^{3-/4-}$ system by Holzwarth.[19] Through the application of the Marcus relationship[34] to the acid-dependent rate constants for the oxidation of $Fe(CN)_6{}^{4-}$ by $IrCl_6{}^{2-}$ (22 °C, $I = 0.93$ M ($NaClO_4$)), electron self-exchange rate constants for the three proton-related couples, $(HNC)_nFe(CN)_{6-n}{}^{(4-n)-}/Fe(CN)_6{}^{3-}$ (analogous to eqs 5–7), were determined to be 8×10^4 M^{-1} s^{-1} for $n = 0$, 1.4×10^4 M^{-1} s^{-1} for $n = 1$, and 3.3×10^3 M^{-1} s^{-1} for $n = 2$. An earlier study[23a] involving a direct measurement of the electron-exchange rate constant (using ^{14}N NMR) for a solution containing 0.25 M each of $H_4Fe(CN)_6$ and $H_3Fe(CN)_6$ at 32 °C indicated a value of $k_{11} < 4 \times 10^3$ M^{-1} s^{-1}.

The $Os(CN)_6{}^{4-/3-}$ electron-exchange processes in eqs 6 and 7 are thus best regarded as occurring through concerted electron- and proton-transfer reactions (no net thermodynamic driving force). This mechanism implies different reorganization barriers for the three electron-exchange couples, with the proton-transfer processes adding to the magnitude of ΔG^*_{in}. Holzwarth[19] attributed the decrease in the $Fe(CN)_6{}^{4-/3-}$ rate constant with an increase in the degree of protonation of the $Fe(CN)_6{}^{4-}$ ion to a superposition of two effects, with an increase in the reorganization energy (increasing ΔG^*_{in}, decreasing k_{11}) upon protonation overcoming the decrease in the electrostatic repulsion between the ions (increasing K_A, increasing k_{11}).

Kinetic studies of electron-transfer reactions of the $Os(CN)_6{}^{4-/3-}$ couple with a variety of inorganic and organic cross-reactants in aqueous media,[20] and the electron-exchange reaction in nonaqueous media, employing tetraalkylammonium salts ($[R_4N]_n$-$[Os(CN)_6]$ (n = 3, 4))[37] are in progress.

---

(24) Saloma, P.; Vesala, A.; Vesala, S. *Acta Chem. Scand.* **1969**, *23*, 2107.

(25) (a) Dennis, C. R.; Basson, S. S.; Leipoldt, J. G. *Polyhedron* **1983**, *2*, 1357. (b) Dennis, C. R.; Leipoldt, J. G.; Basson, S. S.; Van Wyk, A. J. *Inorg. Chem.* **1986**, *25*, 1268.

(26) Spiccia, L.; Swaddle, T. W. *Inorg. Chem.* **1987**, *26*, 2265.

(27) (a) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441. (b) Brunschwig, B. S.; Creutz, C.; Macartney, D. H.; Sham, T.-K.; Sutin, N. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 112.

(28) While the Os(II)–CN bond distance has recently been reported, the average Os–C distance in $Na_4Os(CN)_6 \cdot 10H_2O$ is 2.045 ± 0.028 Å,[29a] an Os(III)–CN distance is not available. In the recently reported structure of an osmium(VI) cyano complex, $Cs_2OsO_2(CN)_4$,[29b] the Os–C bond distance is 2.093 (9) Å. It is therefore assumed that the change in the bond distance upon electron transfer for the osmium couple is less than 0.05 Å and is probably similar to the values for the analogous iron ($\Delta d_0 = -0.026 \pm 0.010$ Å from X-ray diffraction studies[30a] and 0.00 ± 0.01 Å from EXAFS measurements[27]) and ruthenium couples ($\Delta d_0 = \pm 0.035 \pm 0.007$ Å from a postresonance-enhanced Raman scattering technique on the mixed-valence $[(NC)_5Ru-CN-Ru(NH_3)_5]^-$ complex[30b]).

(29) (a) Gentil, L. A.; Navaza, A.; Olabe, J. A.; Rigotti, G. E. *Inorg. Chim. Acta* **1991**, *179*, 89. (b) Purcell, W.; Roodt, A.; Basson, S. S.; Leipoldt, J. G. *Transition Met. Chem.* **1991**, *16*, 60.

(30) (a) Swanson, B. I.; Hamburg, S. I.; Ryan, R. R. *Inorg. Chem.* **1974**, *13*, 1685. (b) Doorn, S. K.; Hupp, J. T. *J. Am. Chem. Soc.* **1989**, *111*, 1142.

(31) (a) Cannon, R. D. *Chem. Phys. Lett.* **1977**, *49*, 299. (b) Brunschwig, B. S.; Ehrenson, S.; Sutin, N. *J. Phys. Chem.* **1986**, *90*, 3657.

(32) The nuclear frequency, $\nu_n = \{[(\nu_{in})^2\Delta G^*_{in} + (\nu_{out})^2\Delta G^*_{out}]/(\Delta G^*_{in} + \Delta G^*_{out})\}^{1/2}$, is calculated to be $(4 \pm 1) \times 10^{12}$ s^{-1} ($\bar{\nu}_{in} = 458$ cm^{-1},[14d] $\bar{\nu}_{out} = 30$ cm^{-1} [27]), while K_A[26] is 6.3×10^{-2} M^{-1} at an ionic strength of 1.0 M. The nuclear tunneling factor Γ_n and the electronic factor κ_{el} are taken to be 1.2 and 0.2 (marginally adiabatic), respectively, the values of employed for the $Ru(CN)_6{}^{4-/3-}$ couple.[5]

(33) (a) Chan, M.-S.; Wahl, A. C. *J. Phys. Chem.* **1978**, *82*, 2542. (b) Triegaardt, D. M.; Wahl, A. C. *J. Phys. Chem.* **1986**, *90*, 1957.

(34) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(35) (a) Nord, G.; Pedersen, B.; Farver, O. *Inorg. Chem.* **1978**, *17*, 2233. (b) Macartney, D. H.; Sutin, N. *Inorg. Chim. Acta* **1983**, *74*, 221. (c) Sarala, R.; Stanbury, D. M. *Inorg. Chem.* **1990**, *29*, 3456.

(36) Creutz, C.; Keller, A. D.; Sutin, N.; Zipp, A. P. *J. Am. Chem. Soc.* **1982**, *104*, 3618.

(37) (a) Alexander, J. J.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 4260. (b) Eller, S.; Fischer, R. D. *Inorg. Chem.* **1990**, *29*, 1289.

Acknowledgment. The financial support of this work by the Natural Sciences and Engineering Research Council of Canada, in the form of operating and equipment grants, is gratefully acknowledged.

Registry No. $Os(CN)_6^{4-}$, 19356-45-7; Na^+, 17341-25-2; Li^+, 17341-24-1; K^+, 24203-36-9; NH_4^+, 14798-03-9.

Supplementary Material Available: Tables of observed ^{13}C NMR line widths as a function of $[Os(CN)_6^{3-}]$, temperature, pH, cation concentration, and ionic strength (3 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, University of New Brunswick,
Bag Service Number 45222, Fredericton, NB, Canada E3B 6E2

Quantitative Preparations of 1,3,2-Dithiazolium, 1,3,2,4-Dithiadiazolium, and 1-Halo-1,2,4,3,5-trithiadiazolium Cations by the General, Symmetry-Allowed Cycloadditions of $SNSAsF_6$ with Alkynes, Nitriles, and Thiazyl Halides. Kinetics of Cycloadditions of the 1,3-Dipolar-like SNS^+ with Aliphatic and Aromatic Nitriles and Alkynes

Simon Parsons, Jack Passmore,* Melbourne J. Schriver, and Xiaoping Sun

Received December 4, 1990

The dithionitronium cation (SNS^+) undergoes general, quantitative, thermally allowed cycloaddition reactions with alkynes (giving 1,3,2-dithiazolium salts), nitriles (giving 1,3,2,4-dithiadiazolium salts), and thiazyl halides (generated in situ, to give 1-halo-1,2,4,3,5-trithiadiazolium salts). When carried out in SO_2 solvent with SNS^+ as the AsF_6^- salt, these cycloadditions give analytically and spectroscopically pure products in one step, which have been characterized by chemical analysis, NMR (^1H, ^{19}F, ^{13}C, ^{14}N) and vibrational spectroscopy, melting point, and X-ray crystallography (published previously). The wide generality of these reactions is unusual in the context of sulfur–nitrogen chemistry. The rates of cycloadditions of SNS^+ to various alkynes and nitriles were systematically investigated, and lg (relative rate) was shown to be approximately porportional to –IP(triple bond). This is consistent with the results of MO calculations, which predict that the dominant orbital interaction during these cycloadditions is between the LUMO(SNS^+) and the HOMO(triple bond), even for electrophilic alkynes and nitriles. Our rate/IP correlation for nitrile cycloaddition rates is quantitative, but for alkynes it is only qualitative. This is interpreted in terms of an asynchronous transition state in which steric effects are significant for alkynes but not nitriles. Surprisingly long ^1H longitudinal NMR relaxation times (T_1) were also determined for $H\overline{CSNSC}H^+$ (47 ± 7 s) and $CF_3\overline{CSNSC}H^+$ (63 ± 3 s) in SO_2 solvent.

Introduction

Despite significant recent progress,[1] much of the chemistry of sulfur–nitrogen compounds is nonquantitative and poorly understood.[2] In contrast, we have shown that the SNS^+ (cf. ONO^+) cation (as the AsF_6^- salt) undergoes quantitative, symmetry-allowed cycloaddition reactions with some alkynes (CF_3CCCF_3, HCCH, MeCCH),[3,4] nitriles (RCN, R = Me, tBu, CF_3, I),[3,5] alkenes (*E*-MeCHCHMe, H_2CCH_2),[6] and SN^+.[1f,g] We now show that quantitative cycloaddition reactions in fact occur with a very wide range of alkynes, nitriles, and thiazyl halides to give analytically and spectroscopically (IR, multinuclear NMR) pure materials (see Table I and II).[7] Cycloaddition of SNS^+ to alkynes and nitriles thus appears to be completely general and potentially extendable to other triply bonded systems (e.g. phosphaalkynes[8]). This is in contrast to other cycloadditions involving sulfur–nitrogen compounds, which usually possess less generality. For example, cycloadditions of S_4N_4 are restricted to strained alkenes[9] (e.g. norbornene) and $ClSNSCl^+$ [10] and $RR'\overline{CSNSC}RR'^+$ (R,R' = H,H and H,Me)[6] will cycloadd to some alkynes (HCCH, MeCCH), but there is no reaction with CF_3CCCF_3 or nitriles.[11]

We show that the reactions of RCN (R = Me, $2,5\text{-}Me_2C_6H_3$, C_6H_5, $3,5\text{-}(O_2N)_2C_6H_3$, $p\text{-}O_2NC_6H_4$) and CF_3CCCF_3 with SNS^+ are first order in both reactants, consistent with the proposed cycloadditions. In addition, we show that the logarithm of the second-order rate constants for a wide variety of alkynes and nitriles is approximately proportional to –IP of the triple bond. Within the context of Sustmann's classification of 1,3-dipolar cycloadditions[12] the reactions of SNS^+ are of "type III", in which

---

(1) (a) Banister, A. J. *Nature* **1972**, *237*, 92. (b) Chivers, T. *Chem. Rev.* **1985**, *85*, 341. (c) Bestari, K. T.; Boere, R. T.; Oakley, R. T. *J. Am. Chem. Soc.* **1989**, *111*, 1579. (d) Cordes, A. W.; Goddard, J. D.; Oakley, R. T.; Westwood, N. P. C. *J. Am. Chem. Soc.* **1989**, *111*, 6147. (e) Oakley, R. T. *Prog. Inorg. Chem.* **1988**, *36*, 299. (f) Passmore, J.; Schriver, M. J. *Inorg. Chem.* **1988**, *27*, 2749. (g) Brooks, W. V. F.; Cameron, T. S.; Grein, F.; Parsons, S.; Passmore, J.; Schriver, M. J. *J. Chem. Soc., Chem. Commun.*, in press.

(2) Heal, H. G. *The Inorganic Chemistry of Sulphur, Nitrogen and Phosphorus*; Academic Press: London, 1980.

(3) Maclean, G. K.; Passmore, J.; Rao, M. N. S.; Schriver, M. J.; White, P. S.; Bethall, D.; Pilkington, R. S.; Sutcliffe, L. H. *J. Chem. Soc., Dalton Trans.* **1985**, 1405.

(4) Awere, E. G.; Burford, N.; Mailer, C.; Passmore, J.; White, P. S.; Banister, A. J.; Oberhammer, H.; Sutcliffe, L. H. *J. Chem. Soc., Chem. Commun.* **1987**, 66.

(5) Burford, N.; Passmore, J.; Schriver, M. J. *J. Chem. Soc., Chem. Commun.* **1986**, 140.

(6) Burford, N.; Johnson, J. P.; Passmore, J.; Schriver, M. J.; White, P. S. *J. Chem. Soc., Chem. Commun.* **1986**, 966.

(7) While certain reactions of SNS^+ (notably with some phenyl-substituted derivatives) appear from their color changes (typically to brown or black) to involve some side reactions, no products other than the expected 1,3,2-dithiazolium or 1,3,2,4-dithiadiazolium cations are detectable by NMR spectroscopy. The reactions involving phenyl derivatives will form the subject of a future paper: Parsons, S.; Passmore, J.; Sun, X. P. Manuscript in preparation.

(8) Regitz, M. *Chem. Rev.* **1990**, *90*, 191.

(9) (a) Brinkman, M. R.; Allen, C. W. *J. Am. Chem. Soc.* **1972**, *94*, 2550. (b) Mock, W. L.; Mehrotu, L. *J. Chem. Soc., Chem. Commun.* **1976**, 123. (c) Ertl, V. G.; Weiss, J. *Z. Anorg. Allg. Chem.* **1976**, *420*, 155.

(10) Parsons, S.; Passmore, J.; Schriver, M. J.; White, P. S. *Can. J. Chem.* **1990**, *68*, 852.

(11) The cycloadditions of SNS^+ with alkenes appear to be more limited and will be the subject of another publication. Schriver, M. J. Ph.D. Thesis, University of New Brunswick, 1989.

0020-1669/91/1330-3342$02.50/0 © 1991 American Chemical Society