N-dealkylation. A small percentage of this pair may produce the perferryl species and free amine and thereby enable oxidation of alternate substrates. However, direct two-electron oxidative cleavage of the [Fe–O–N] complex to generate a formal Fe^V=O species and an amine appears incompatible with the low oxidation potential of amine oxides and with the mechanism proposed for the reverse reaction—amine oxygenation.

Supplementary Material Available: Table of Michaelis–Menten parameters (1 page). Ordering information is given on any current masthead page.

Figure 1. Electronic absorption spectra of the 6+ and 5+ ions in a KCl disk, measured at 270 and 8 K. The sharp line at 4500 cm^{-1} is ascribed to H_2O. The rising background is due to scattering.

Decaammine(μ-dinitrogen-N,N')diosmium(III): Synthesis, Characterization, Reactivity, and Spectral Properties

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The electrochemical oxidation of the decaammine(μ-dinitrogen-N,N')diosmium(5+) ion (I) shows that the 6+ ion (II) has a short half-life in aqueous solution.[1] Disproportionation of II with cleavage of the N≡N bond would result in two nitrido-osmium(VI) species, which makes this ion potentially interesting in relation to dinitrogen fixation. Species II is also interesting because it features rather strong metal–metal interactions, either directly or through the dinitrogen bridging ligand.

We have found that $[(NH_3)_5OsN_2Os(NH_3)_5]Cl_6$ is readily produced by solid-state oxidation of I with chlorine. The oxidation is rapid (∼15 min for completion) and is readily observed as the solid changes color from an emerald green to light blue. The reaction has been shown to go virtually to completion (>95%) by microanalytical data[2] and by IR spectral measurements. Although the complex slowly decomposes in the solid state with the reemergence of the color of the mixed-valence ion, it is moderately stable and may be stored for weeks at 0 °C in the absence of water and light.

The mixed-valence ion I was prepared by the action of a reducing agent on an aqueous mixture of $[Os(NH_3)_5OH_2]^{3+}$ and $[Os(NH_3)_5N_2]Cl_2$,[1] by partial oxidation of $[Os(NH_3)_5N_2]Cl_2$ in deaerated CF_3SO_3H,[3,4] or by the reaction of $[Os(NH_3)_5N_2]^{2+}$ with $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ in nonaqueous solvents.[4] Cyclic voltammetry in 2 M HCl at a carbon paste electrode shows reversible 5+/4+ and 6+/5+ couples respectively at −0.16 and +1.05 V vs. the NHE, leading to a comproportionation constant (K_{com}) of 10^{21}. These values agree well with those reported previously[1] in 0.1 M HCl (−0.16, ∼+1.04 V, K_{com} ∼10^{20}). At scan rates >10 V/s, we find that the 6+/5+ couple is almost reversible, a result that is at variance with that of previous measurements[1] (but,
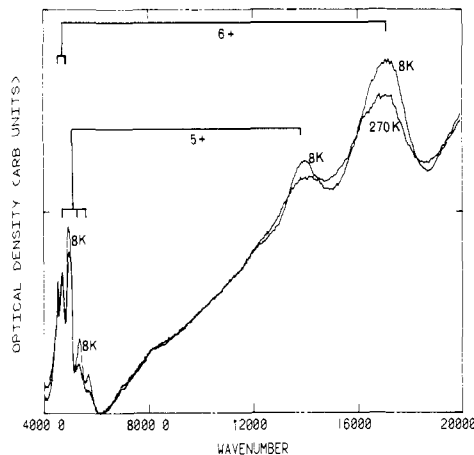
it should be noted that these were made at a different acid concentration). At slower scan rates (<1 V/s) a new wave grows at 0.58 V, which corresponds to the $[Os(NH_3)_5N_2]^{3+/2+}$ couple, with concomitant diminution of the reduction wave of II. The electrochemical experiments provide no evidence for the reduction of dinitrogen. In searching further for dinitrogen reduction, I was oxidized to II in 2 M HCl with a stoichiometric amount of Ce^{4+} at 5 °C, using a hand-operating stopped-flow mixer.[5] The solution immediately changed color from green to the light blue characteristic of II.[6] The concentration of II decayed, following first-order kinetics with a half-life of 40 min at 5 °C, to yield a mixture containing I, $[Os(NH_3)_5N_2]^{2+}$, and unidentified osmium species. Chromatographic and UV–vis measurements indicated that I was the major product (>70%). The qualitative features of the stoichiometry can be accounted for by assuming that the unidentified products are comparised of osmium species in oxidation states above 3+. The possibility that a small amount of N≡N cleavage occurs is not excluded by our observations.

The frequency of the dinitrogen stretch in the IR of II (2200 cm^{-1}) is much greater than that of I (2010 cm^{-1}), but still significantly lower than that of the free dinitrogen (2330 cm^{-1}), and is close to that observed for the mononuclear ions (2212 cm^{-1}).[7] The results indicate that both the mononuclear and binuclear Os(III) complexes are stabilized by π-back-bonding, but less than in I or the mononuclear 2+ ion. These results are in agreement with other chemical, structural, and spectral results on Os(III) complexes, all of which suggest[8-10] that Os(III), unlike Ru(III), is a rather good π-donor.

The coupling of osmium(VI) nitrido complexes is the reverse of that sought for disproportionation of a (μ-dinitrogen)diosmium(III) species to nitridoosmium(VI); it has been observed[11,12] (for compositions somewhat different from ours), and thus the reaction pathway, forward and reverse, has been demonstrated. Our failure to observe disproportionation of II to an amminenitridoosmium(VI) species cannot be taken to mean that the reaction is thermodynamically unfavorable. The principle of microscopic reversibility makes no statement about the rate of the disproportionation relative to others that are possible, and the failure to observe substantial N≡N bond cleavage may simply

(1) Richardson, D. E.; Sen, J. P.; Buhr, J. D.; Taube, H. *Inorg. Chem.* **1982**, *21*, 3136-3140.
(2) Anal. Calcd for $H_{30}N_{12}Cl_6Os_2$: C, 0.00; H, 3.82; N, 21.24; Cl, 26.88. Found: C, 0.00; H, 3.79; N, 19.72; Cl, 26.91. The low nitrogen figure found is a function of the automatic analysis (Lay, P. A.; Sargeson, A. M.; Skelton, R. H.; White, A. H. *J. Am. Chem. Soc.* **1982**, *104*, 6161-6164).
(3) Lay, P. A.; Magnuson, R. H.; Sen, J.; Taube, H. *J. Am. Chem. Soc.* **1982**, *104*, 7658-7659.
(4) Lay, P. A.; Magnuson, R. H.; Taube, H., manuscript in preparation.

(5) Similar in design to that reported by: Inoue, Y.; Perrin, D. D. *J. Phys. Chem.* **1962**, *66*, 1689-1693.
(6) Visible absorption spectrum, 2 M HCl, 5 °C (λ, nm (ε, M^{-1} cm^{-1})): 460 sh (340); 514 (1580); 600 (1760); 660 (1840); 794 sh (360).
(7) Buhr, J. D.; Taube, H. *Inorg. Chem.* **1980**, *19*, 2425-2434.
(8) The structure of $[(NH_3)_5OspzOs(NH_3)_5]Cl_6\cdot2H_2O$[9] indicates back-bonding in Os–N(p_z) bonds; $[Os(NH_3)_5(CH_3CN)]^{3+}$ is remarkably stable to hydrolysis[10] of nitrile in comparison to the Ru(III) analogue.
(9) Bino, A.; Lay, P. A.; Taube, H., manuscript in preparation.
(10) Lay, P. A.; Magnuson, R. H.; Taube, H., unpublished results.
(11) Buhr, J. D.; Taube, H. *Inorg. Chem.* **1979**, *18*, 2208-2212.
(12) Ware, D. C.; Taube, H., manuscripts in preparation.

mean that aquation (with $Os^{III}-N_2$ cleavage) is more rapid.

We have performed temperature-dependent electronic absorption and MCD measurements over the entire spectral region from the UV to the NIR for both I and II. A detailed report and analysis of electronic absorption spectra and MCD of I is given elsewhere.[13] Figure 1 shows the absorption spectrum of II at two temperatures for the near-IR and vis regions in a KCl disk. The bands at 4670, 4950, and 17000 cm^{-1} belong to II[6] and those at 4700, 5400, 5700, and 14000 cm^{-1} are due to I. Careful comparison of MCD signals and absorption spectra of different samples of II confirmed that the observed MCD was due to impurity of I, and no signals from II could be identified. This confirms the diamagnetic nature of the complex and the presence of a strong antiferromagnetic exchange coupling between the osmium ions. The lack of any appreciable temperature dependence in the absorption spectrum of II shows that the exchange coupling is much greater than kT at room temperature, in contrast to the case of the corresponding pyrazine complex.[14]

(13) Dubicki, L.; Krausz, E. R.; Ferguson, J.; Maeder, M.; Magnuson, R. H.; Taube, H. *J. Am. Chem. Soc.*, in press.
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Flow Adsorption Calorimetry with Supercritical Fluids on Silica Gel

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The supercritical state has long held a fascination for chemists as a "fourth state of matter",[1,2] and supercritical fluids are a lively area of current interest for fundamental and industrial chemistry[3] as well as for geochemistry and extraterrestrial chemistry.[4] Of particular significance is the use of supercritical carbon dioxide for tertiary oil recovery, coal extraction, and chromatography in all of which supercritical fluids interact with solid phases.[5–8] The present study evolved from an investigation of the thermodynamics of adsorption on silica gel during supercritical HPLC separations.

The apparatus shown in Figure 1 may be assembled, for the most part, from readily available components following recent accounts of high-pressure and high-temperature flow calorimeters assembled for heats of mixing.[9–11]

[†]On leave from Indian Institute of Technology, New Delhi, India.
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(2) van der Waals, J. D. *Zittingsv. V. Akad. Wet. (Amsterdam)* **1894**, 133.
(3) See the following recent articles for useful current bibliographies: (a) Crooks, R. M.; Fan, F.-R. F.; Bard, A. J. *J. Am. Chem. Soc.* **1984**, *106*, 6851. (b) Hyatt, J. A. *J. Org. Chem.* **1984**, *49*, 5097.
(4) (a) Street, W. B. *Astrophys. J.* **1973**, *186*, 1107. (b) Street, W. B. *Icarus* **1976**, *29*, 173.
(5) Orr, F. M., Jr.; Taber, J. J. *Science (Washington, D.C.)* **1984**, *224*, 563 and the references cited therein.
(6) Worthy, W. *Chem. Eng. News* **1983**, *61*, 18.
(7) Peader, P. A.; Lee, M. L. *J. Liq. Chromatogr.* **1982**, *5*, 179.
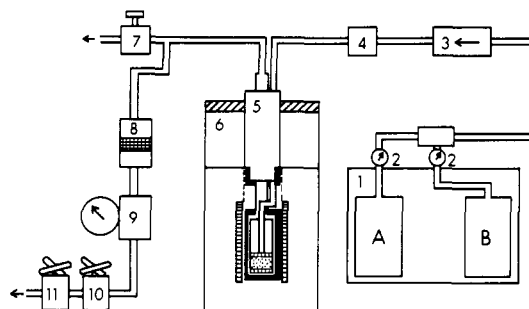(8) Maddocks, R. R. *Chem. Eng. Prog.* **1977**, *73* (6), 59.

Figure 1. Schematic of adsorption flow calorimeter: (1) Perkin-Elmer Model 601 dual piston pumps, (2) Perkin-Elmer Bourden pressure gauges, (3) High Pressure Equipment Co. check valve, (4) High Pressure Equipment Co. safety valve, (5) high-pressure cell, (6) C-80 Setaram calorimeter, (7) Butech Pressure Systems high-temperature valve, (8) Valco filter, (9) Pilgrim Instruments Bourden pressure gauge, (10, 11) Tescom back-pressure regulators, Model 26-1724-24.

Table I. ΔH_{imm} (Batch Mode) of Silica Gel in Some Liquids at 26 °C

liquid	ΔH_{imm}/cal g^{-1}	T_c/°C[a]	P_c/psi[a]
(1) isopentane	−4.83 ± 0.63	187.8	483.5
(2) 10% isopropylamine	−21.66 ± 0.81	190.0[b]	527.0[b]
(3) isopropylamine	−20.33 ± 0.30	209.7	700.0[c]

$(2) - (1) = \Delta H_{ads} = -16.83 \pm 1.02$ cal g^{-1}
ΔH_{ads}(flow mode) at 30 psi $= -17.97 \pm 0.27$ cal g^{-1}

[a]Reference 16. [b]Reference 17. [c]Reference 18.

Table II. Heats of Adsorption, ΔH_{ads} of Isopropylamine on Silica Gel at Different Temperatures and Pressures by Flow Calorimetry

temp, °C	P/psi	ΔH_{ads}/cal/g
26	30	−17.97 ± 0.27
	1000	−17.44 ± 0.84
80	500	−15.79 ± 0.22
	1000	−15.34 ± 0.23
160	500	−12.52 ± 0.80
200	500	−9.86 ± 1.30
	1000	−11.52 ± 0.72
	1500	−13.61 ± 0.16
250	1000	−4.30 ± 0.16

After preliminary calibration of the calorimeter under various batch conditions by heats of solution by KCl and $BaCl_2$ in water[12] and heats of immersion of silica gel in water,[13] the ΔH_{ads} of isopropylamine from an isopentane solution was determined on silica gel using again heats of immersion (batch mode) at ambient temperature (Table I) to establish standards of reference for the more difficult flow studies.

Table II presents ΔH_{ads} values of isopropylamine on the same sample of silica gel (Fisher grade 62) from an isopentane carrier stream over a range of temperatures and pressures from subcritical to supercritical. Results are given in terms of calories *per gram of silica gel*. Since this is a saturation experiment, the observed values at a given temperature and pressure should be (and are) independent of flow rate (7–30 mL/h) or concentration (10–20%) of isopropylamine.

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(11) Wormald, C. J.; Lewis, K. L.; Mosedale, S. *J. Chem. Thermodyn.* **1977**, *9*, 27.
(12) Our ΔH_{soln} values for KCl and $BaCl_2$ of 4.25 ± 0.04 kcal mol^{-1} at 25 °C and −6.65 ± 0.30 kcal mol^{-1} at 75 °C agree well with the literature values of 4.20 and −6.76 kcal mol^{-1}, respectively (Gunn, S. *J. Phys. Chem.* **1965**, *69*, 2902; and Criss, C. M.; Cobble, J. W. *J. Am. Chem. Soc.* **1961**, *83*, 3223).
(13) Our ΔH_{imm} value of −12.55 cal g^{-1} for silica gel in water agrees with the range of values −11.95 to −13.14 cal g^{-1} obtained at Bartlesville Laboratory (Noll, L. A., private communication) by using different samples of silica gel (Fisher, grade 62).