the question of whether chloride is bound to the manganese cluster.[19,20] It now seems certain that EXAFS alone will be unable to provide a definite answer, as any Mn-Cl interactions at the extremely long distance of 2.7 Å will be obscured by the strong feature due to the Mn-Mn separation of ~2.7 Å. Indeed, any Mn-Cl distances of ~2.7 Å at the biological site may lead to an erroneous estimate of the number of Mn···Mn separations at ~2.7 Å.

Somewhat to our surprise, the structure of the room-temperature form of $[MnCl_3(bpy)]_n$ is very similar to that of the low-temperature form, with only a few small differences in bond lengths and angles. Comparisons of these are given in Table III. We had wondered whether at higher temperature the bridging Cl^- ions would be found more symmetrically located between the Mn centers. In fact, the opposite was observed; the major difference between the structures is that the low-temperature 2.710 (2) Å Mn-Cl bond is further elongated to 2.762 (2) Å at room temperature.

We believe that the presence of labile Cl^- ligands in $[MnCl_3(bpy)]_n$ and $(NEt_4)_2MnCl_5$ makes these materials extremely useful (and rare) starting materials for Mn^{III} chemistry. Their previous preparations were rather inconvenient, but their facile preparation from readily available complex **1** provides large quantities from simple reagents. We are currently investigating their utility for the synthesis of a variety of Mn complexes of various nuclearities.

Acknowledgment. We thank Sheyi Wang for assistance with figure preparation. This work was supported by NIH Grant GM 39083. G.C. is a Camille and Henry Dreyfus Teacher-Scholar (1987-92).

Supplementary Material Available: Complete listings of atomic coordinates, isotropic and anisotropic thermal parameters, and bond lengths and angles (6 pages); lists of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page. Complete MSC structure reports (No. 89281, low temperature; No. 89481, room temperature) are available on request from the Indiana University Chemistry Library.

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Role of Osmium in the Reaction of the Hydrazinium Cation with Chlorate in Acid Solution[1]

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In their 1944 monograph, Yost and Russell noted in passing the autocatalytic nature of the osmium-catalyzed reaction of the hydrazinium cation with chlorate.[2] This reaction appears to have been discovered some 30 years earlier by Hofmann who found that although the oxidation of the hydrazinium cation by chlorate in acidic solution is imperceptibly slow, it is catalyzed by osmium tetroxide.[3] Bromate[4] and iodate,[5] however, react readily with the hydrazinium cation without requiring a catalyst.

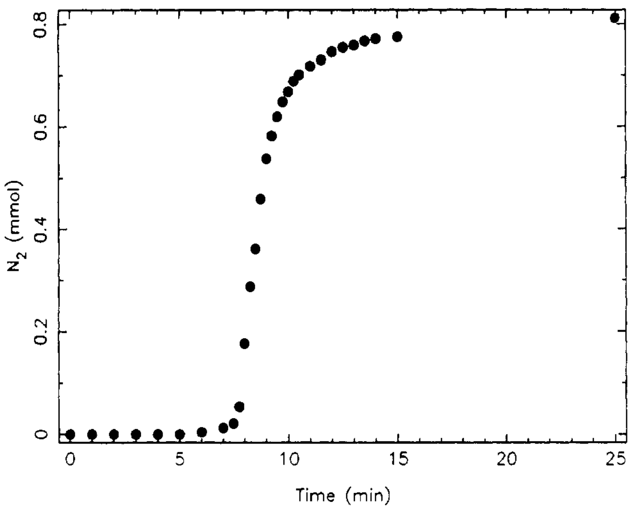

Figure 1. Time course of nitrogen gas evolution for reaction 1. Initial concentrations: $[N_2H_5^+] = 4.4 \times 10^{-2}$ M; $[ClO_3^-] = 4.1 \times 10^{-1}$ M; $[OsO_4] = 1.6 \times 10^{-3}$ M. Total solution volume = 20.0 mL.

In the presence of an osmium tetroxide catalyst and excess chlorate, the hydrazinium cation[6] is quantitatively oxidized to nitrogen.[3] The purpose of this work was to ascertain whether, in fact, reaction 1 is autocatalytic and, if so, to identify the autocatalytic species and formulate a satisfactory mechanism.

$$3N_2H_5^+ + 2ClO_3^- \xrightarrow{OsO_4} 3N_2 + 2Cl^- + 6H_2O + 3H^+ \qquad (1)$$

Experimental Section

Hydrazinium sulfate (Eastman Kodak) and sodium chlorate (Fisher) solutions were prepared with reagent grade chemicals and deionized water. Osmium tetroxide crystals (Aldrich) were dissolved in water, and the solution was stored in the dark to retard decomposition.

All experiments were carried out in vigorously stirred solutions at ambient temperatures, approximately 23 °C. The progress of the catalyzed reaction was followed by measuring the amount of nitrogen evolved as a function of time with a gas buret. The potential of a platinum redox electrode versus a reference electrode and a combination pH electrode can also be used to monitor the reaction; the response of a chloride electrode is distorted by the presence of the hydrazinium cation. Light scattering by colloidal osmium dioxide formed during the reaction, as well as gas evolution, interferes with spectroscopic absorbance measurements, particularly in the ultraviolet region.

Results

The Hydrazinium Cation-Chlorate-Osmium Tetroxide System. The catalyzed reaction, carried out in the presence of excess chlorate, was initiated by addition of the osmium tetroxide solution. After an initial phase, during which no gas evolution is detected, nitrogen is produced rapidly until all the hydrazinium cation is consumed; the pH declines simultaneously from 1.82 to 1.45. (The pH is determined by the bisulfate concentration; solutions were unbuffered.) Figure 1 illustrates a typical time course for nitrogen evolution. The induction period is shortened by increasing the concentration of the osmium tetroxide catalyst as well as that of chlorate, while increasing the concentration of the hydrazinium cation has the opposite effect.

To determine whether reaction 1 is autocatalytic, a 2.5-mL aliquot of the chlorate-hydrazinium cation-osmium tetroxide

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(6) Under the acidic conditions of this report, pH 1-2, the dominant form of hydrazine is the hydrazinium cation: $pK_{a1} = 6.07$, $pK_{a2} = 15.05$ at 25 °C.

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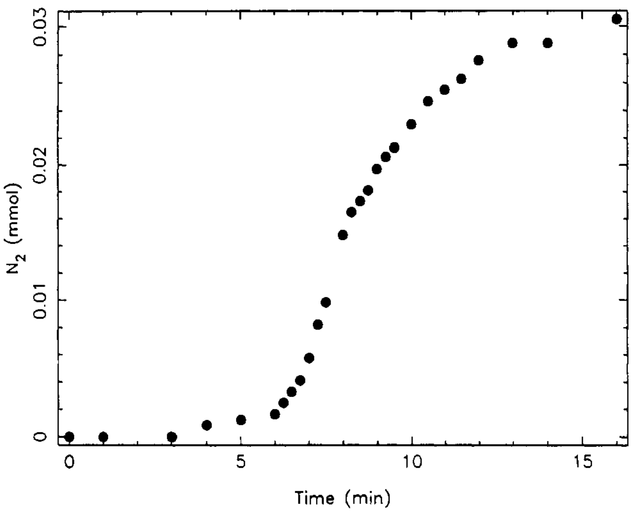

Figure 2. Time course of nitrogen gas evolution for reaction 3. Initial concentrations: $[N_2H_5^+] = 3.0 \times 10^{-2}$ M; $[OsO_4] = 1.6 \times 10^{-3}$ M. Total solution volume = 22.0 mL.

solution (3.0×10^{-1}, 3.0×10^{-2}, and 8.2×10^{-4} M, respectively) in the initial stage of nitrogen production was removed and added to 20 mL of the chlorate–hydrazinium cation solution together with the catalyst. The induction period is reduced from 6.5 to 3.5 min, a greater reduction than could be achieved by adding a comparable amount of OsO_4. A portion of solution removed from a reaction just after nitrogen evolution ceased did not affect the induction period. These observations demonstrate that the reaction is indeed autocatalytic and that the autocatalytic species is an intermediate produced early in the reaction, instead of a product.

During the induction period, a brown colloid appears (also forming a thin black film on a Teflon-coated stirring bar) and then disappears by the end of the reaction. The dark material, tentatively identified as osmium dioxide (as we discuss later), reacts with chlorate, regenerating osmium tetroxide.

$$3OsO_2 + 2ClO_3^- \rightarrow 3OsO_4 + 2Cl^- \qquad (2)$$

The Hydrazinium Cation–Osmium Tetroxide Subsystem. The identity of the colloidal material was established stoichiometrically. The osmium tetroxide solution was added to an excess of the acidic hydrazinium cation solution. The volume of nitrogen generated corresponded to reduction of Os(VIII) to Os(IV) according to reaction 3. For example, in one experiment employing 22 mL

$$N_2H_5^+ + OsO_4 \rightarrow N_2 + OsO_2 + 2H_2O + H^+ \qquad (3)$$

of a solution containing excess hydrazinium cation and 1.6×10^{-3} M OsO_4, 3.52×10^{-2} mmol of N_2 were expected and, after 10 h had elapsed, 3.5×10^{-2} mmol of N_2 were found.

Subbaraman et al.[7] used two tests to distinguish between osmium(V) oxide, also an insoluble black solid, and osmium dioxide. Osmium(V) oxide is diamagnetic and converts iodide to iodine; on the other hand, osmium dioxide is paramagnetic and does not react with iodide. The dark brown colloidal material did not react with iodide. In a separate experiment this material was precipitated by boiling the suspension and raising its pH to 4.[8] The precipitate was found to be paramagnetic by weighing a sample on a Faraday balance. Furthermore, osmium dioxide has been reported to be the reaction product of "osmic acid" with hydrazinium sulfate.[9]

By following the potential of a platinum electrode in acidic media against a reference electrode, we found that osmium tetroxide and osmium dioxide also undergo a redox reaction.

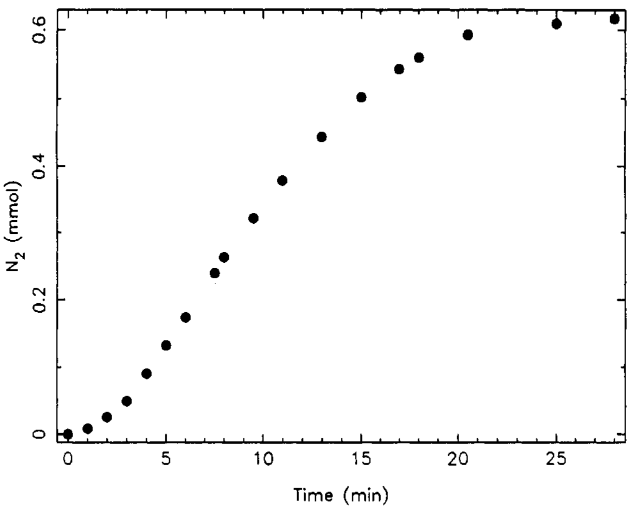

Figure 3. Time course of nitrogen gas evolution for reaction 4. Initial concentrations: $[N_2H_5^+] = 3.0 \times 10^{-2}$ M; $[ClO_2^-] = 3.0 \times 10^{-1}$ M. Total solution volume = 20.0 mL.

In its similarity to Figure 1, the time course of gas evolution due to the hydrazinium cation–osmium tetroxide reaction (Figure 2) is suggestive of autocatalysis. Therefore, reaction 3 was tested for autocatalysis as described earlier. Aliquots removed at the time when osmium dioxide first appeared did not reduce the induction period as much as portions removed at later times. Autocatalytic activity was retained even 1 day after the hydrazinium cation–osmium tetroxide reaction was over. In addition, the reaction was accelerated by the colloidal material collected above. We therefore believe osmium dioxide has an autocatalytic role.

Hydrazinium Cation–Oxychlorine Reactions. Although the hydrazinium cation does not react with chlorate, the hydrazinium cation is quantitatively oxidized by chlorite to nitrogen. The time course of gas evolution for reaction 4 is shown in Figure 3. At

$$N_2H_5^+ + ClO_2^- \rightarrow N_2 + Cl^- + 2H_2O + H^+ \qquad (4)$$

longer times, chlorine dioxide is produced, as evidenced by its characteristic yellow color, presumably through a side reaction between chlorite and hypochlorite. Reaction between the hydrazinium cation and hypochlorite is altogether more rapid; gas evolution occurs immediately upon mixing. With chlorine dioxide, a very small amount of gas is eventually generated and the yellow color of chlorine dioxide fades, indicating a slow reaction; we judge it irrelevant to the present work. Moreover, spectroscopic evidence does not suggest that chlorine dioxide is at all involved in the osmium-catalyzed hydrazinium cation–chlorate reaction.

Discussion

The stoichiometry of the hydrazinium cation oxidation is a good indicator of the mechanism by which it occurs.[10] One-electron oxidizing agents such as Ce(IV) usually result in the formation of ammonia as well as nitrogen[11]

$$N_2H_5^+ \rightarrow \tfrac{1}{2}N_2 + NH_4^+ + H^+ + e^- \qquad (5)$$

while permanganate, a two-electron oxidant, yields nitrogen alone.[12]

$$N_2H_5^+ \rightarrow N_2 + 5H^+ + 4e^- \qquad (6)$$

The species N_2H_2 is said to be an intermediate in such cases.

Osmium tetroxide, therefore, is a two-electron oxidizing agent, acting in stages:

$$N_2H_5^+ + OsO_4 + 5H^+ \rightarrow Os(VI) + N_2H_2 + 4H_2O \qquad (7)$$

$$N_2H_2 + Os(VI) + 2H_2O \rightarrow OsO_2 + N_2 + 6H^+ \qquad (8)$$

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The net result is reaction 3.

Although an Os(VI) species is the supposed product of Os(VI) ester hydrolysis, H_2OsO_4 (or $OsO_3{\cdot}nH_2O$) has never been positively identified.[13] On the other hand, Os(VI) salts such as potassium osmate, $K_2[OsO_2(OH)_4]$, are well-known. It is with these precautions that we put forward Os(VI) as a key intermediate in the oxidation process.

As mentioned in the Results, we found electrochemical evidence of a reaction between osmium tetroxide and osmium dioxide. This reaction might be a comproportionation to Os(VI).[14] The latter species is invoked as an oxidizing agent for the hydrazinium cation. The sum of reactions 9 and 10 accounts for the autocatalytic activity of osmium dioxide.

$$OsO_4 + OsO_2 + 12H^+ \rightarrow 2Os(VI) + 6H_2O \qquad (9)$$

$$2Os(VI) + N_2H_5^+ + 4H_2O \rightarrow 2OsO_2 + N_2 + 13H^+ \qquad (10)$$

Integration of the autocatalytic rate law $d[N_2]/dt = k[OsO_2][OsO_4]$ requires knowledge of the initial concentration of osmium dioxide, $[OsO_2]_0$,[15] which can only be estimated. For the initial conditions of Figure 2 and with an estimated $[OsO_2]_0 = 1 \times 10^{-5}$ M, we find $k = 6 \pm 1\ M^{-1}\ s^{-1}$.

Regeneration of osmium tetroxide can be brought about by reduction of chlorate to hypochlorite. No doubt chlorite is an intermediate in reaction 11; however, the much faster reaction

$$OsO_2 + ClO_3^- + H^+ \rightarrow OsO_4 + HClO \qquad (11)$$

of hypochlorite with the hydrazinium cation compared with reaction 4 suggests the following step is more significant:

$$2HClO + N_2H_5^+ \rightarrow 2Cl^- + N_2 + 2H_2O + 3H^+ \qquad (12)$$

The sum (3) + (9) + (10) + 2(11) + (12) equals the stoichiometry of overall reaction 1.

Reactions 3 and 9-12 comprise our mechanism for the osmium tetroxide catalyzed hydrazinium cation-chlorate reaction. Rate constants for these steps are not reported in the literature. Some of the reactions might be amenable to study via spectroscopic and stopped-flow techniques, provided interference from colloidal osmium dioxide and nitrogen gas can be minimized. The overall reaction with chlorate could produce exotic nonlinear dynamics in an open (flow) reactor, and we expect to continue its study under these conditions.

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Reinvestigation of the Vanadium-Oxygen Stretch in the IR Spectrum of Bis[*N*-(4-chlorophenyl)salicylideneaminato]oxovanadium(IV)

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Introduction

Oxovanadium(IV) complexes have been extensively studied.[1-3] Most of these complexes exhibit a strong band in the IR region near 1000 cm^{-1}, which has been assigned to the V=O stretching frequency.[1,2] In contrast, several complexes have been reported[4-12] in which this stretch appears at lower energy—below 900 cm^{-1}. This shift has been explained in terms of polymerization, which occurs by interaction of the vanadyl oxygen in one molecule with the open axial site of vanadium in another molecule,[6-10] and Mathew et al. suggested that a low-frequency V-O stretch may be a diagnostic test for oxygen bridging in vanadyl complexes.[8] However, in 1977 Pasquali, Marchetti, and Floriani reported an oxovanadium(IV) compound with a V-O stretch of 885 cm^{-1} whose crystal structure revealed monomeric units.[11] They explained the shift in the V-O stretch of this compound in terms of electron withdrawal by chlorine on the ligand and cautioned against using the frequency of the V-O stretch to infer whether or not polymerization of the type described above is present. Reported here is a reinvestigation of the infrared spectrum of the vanadyl complex reported by Pasquali et al.[11] It is shown that two forms of this compound exist, the monomeric form, reported by Pasquali et al., and a form which is apparently polymeric.

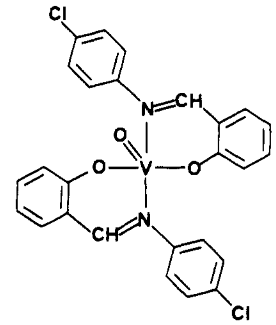

Figure 1. $V(O)L_2$.

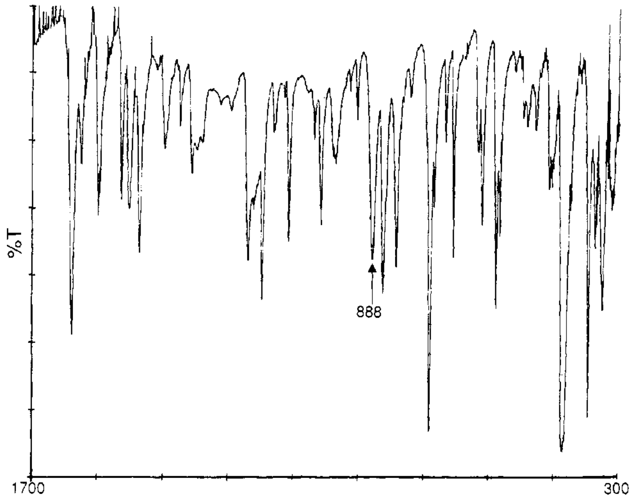

Figure 2. IR spectrum for the needle form of $V(O)L_2$.

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