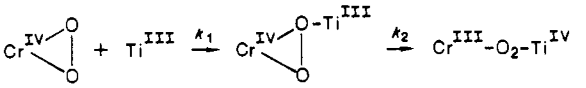
centers should be still more sluggish. Our reaction conditions are somewhat milder than those used by Garner and co-workers,[5] who found that as many as four halide anions can become attached to chromium when decompositions of $Cr^{IV}(O_2)_2$ complexes are carried out at high acidities, and we see no evidence in our systems that more than two carboxylate groups have become bonded to Cr(III).

Our observations appear to be consistent with the sequence (5)–(9), in which the steps (6)–(9) are taken to proceed after the


(5)

$$Cr^{III}–O_2–Ti^{IV} \xrightarrow{H_2O} Cr^{III}–O_2H + Ti^{IV}OH \tag{6}$$

$$Cr^{III}–O_2H + Ti^{III} \rightarrow Cr^{III}–O^{\bullet} + Ti^{IV}OH \tag{7}$$

$$Cr^{III}–O^{\bullet} \xrightarrow{H^+} Cr^{IV}–OH \xrightarrow{Lig} Cr^{IV}–Lig \tag{8}$$

$$Cr^{IV}–Lig + Ti^{III} \rightarrow Cr^{III}–Lig + Ti^{IV} \tag{9}$$

rate-determining steps. The initial act of electron transfer (eq 5) is probably accompanied by breakage of a chromium–peroxy bond as 7-coordinate Cr(IV) is converted to 6-coordinate Cr(III). The proposed Cr(III)–peroxy intermediate brings to mind related complexes described by King and co-workers,[34] who have emphasized the ease with which such species decompose in aqueous media. However, such decompositions are reported to be much slower ($k = 10^{-5}$–10^{-4} s^{-1} at 25 °C) than the redox reactions under consideration. We suspect then that the subsequent attack by Ti(III) on the peroxo complex results in homolysis of the O–O bond (eq 7), that the resulting $Cr^{III}–O^{\bullet}$ fragment is rapidly converted, via internal electron transfer, to a $Cr^{IV}–O$ complex (eq 8), and that rapid ligand exchange involves the latter oxidation state, which is known to be substitution-labile[35] except when bound to strongly chelating groups.[36] Note that reduction by VO^{2+}, during which the O–O bonds remain unbroken, is not accompanied by intrusion of external glycine.

In sum, this work points to considerable versatility of peroxo-bound chromium(IV) species as oxidants. Although only three reductants have been examined, we see that in some cases both oxidizing functions react, whereas in others only the Cr(IV) center is reduced. Evidence has been obtained that both inner- and outer-sphere paths may operate. Moreover, we find that greatly increased substitution lability may be associated with reduction of the peroxo group with 1e reagents. Finally, the marked catalyses of the oxidations of hydroxylamine and ascorbic acid by Fe(II) and Fe(III) are expected to add further detail to an already complicated picture. Examination of these catalyzed reactions is continuing.

Acknowledgment. We are grateful to Dr. James Espenson for valuable discussions and to Arla White for technical assistance.

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(35) (a) Plane, R. A.; Taube, H. *J. Phys. Chem.* **1952**, *56*, 33. (b) Ogard, A. E.; Taube, H. *Ibid.* **1958**, *62*, 357. (c) Rajasekar, N.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 3798.

(36) See, for example: Ghosh, S. K.; Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1987**, *26*, 2684.

Contribution from the Department of Chemistry,
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Electron Transfer. 96. Catalyzed Reduction of Peroxide-Bound Chromium(IV) with Hydroxylamine[1]

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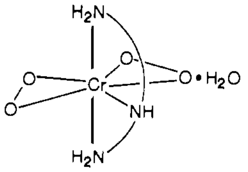
The diperoxochromium(IV) derivative of diethylenetriamine, $Cr^{IV}(dien)(O_2)_2$ (chelate I) reacts very slowly with hydroxylamine in acetate buffers, but the reaction is markedly catalyzed by Fe(II) or Fe(III) and, to a much lesser extent, by Cu(II). With excess NH_3OH^+, products are N_2, Cr(III), and O_2 (the latter arising from the disproportionation of peroxide). The Cr(III) products contain bound acetate groups from the supporting medium and chelating diethylenetriamine. The reaction is half-order in Fe(II) and exhibits kinetic saturation with respect to $[NH_3OH^+]$ (eq 2). The rate law suggests that catalytic iron exists predominantly in an inactive dimeric form with a small active monomeric fraction that forms a 1:1 complex ($K_{assn} = 10^3$ M^{-1}) with NH_3OH^+. The proposed catalytic sequence involves recycling of dissolved iron between the di- and tripositive states, the rapid oxidation of Fe(II) by Cr(IV) ($k = 3 \times 10^3$ M^{-1} s^{-1} at 22 °C), a rate-determining 1e oxidation of Fe(III)-bound hydroxylammonium ion by Cr(IV), and the rapid reaction of $Fe^{III}(OHNH_2^{\bullet})$ with excess NH_3OH^+. Incorporation of external acetate at the Cr(III) center appears to occur during the iron-catalyzed disproportionation of Cr(III)-bound peroxide. The structural requirements for catalytic effectiveness in this reaction are briefly considered.

Although chromium(IV) diperoxo amines have been known since the beginning of the century,[2] interest in their detailed redox chemistry has developed more recently.[3] The most robust of these diperoxo complexes, chelate I (derived from diethylenetriamine),[4] has been found to be an unusually versatile oxidant, for both the Cr(IV) and peroxo functions are reduced rapidly by Ti(III) and by $Fe(CN)_6^{4-}$, whereas VO^{2+} reduces only the Cr(IV) center.[3d] We have reported evidence that both VO^{2+} and Ti(III) utilize inner-sphere paths in these reductions,[3d] whereas the reaction by $Fe(CN)_6^{4-}$ is probably initiated by an outer-sphere transfer. In addition, some (but not all) of these reductions are accompanied by incorporation of anions from the supporting media into the coordination sphere of the Cr(III) product.


I

A number of non-metal-derived reductants, among them hydroxylamine, ascorbic acid, and mercapto-substituted species, have

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[1] Sponsorship of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

[2] (a) Weide, O. F. *Ber. Dtsch. Chem. Ges.* **1897**, *30*, 2178. (b) Hoffman, K. A. *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 3181.

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Table I. Stoichiometry of the Reaction of $(dien)_2Cr^{IV}(O_2)_2$ with NH_3OH^+[a]

mmol of Cr^{IV}	mmol of NH_3OH^+	$10^5[Fe^{II}]$, M	$\Delta[NH_3OH^+]/\Delta[Cr^{IV}]$
0.0044	0.0051	0	1.16
0.0067	0.0077	0	1.15
0.0100	0.0118	0	1.18
0.0040	0.0041	5	1.03
0.0080	0.0082	5	1.03
0.0120	0.0122	5	1.02

[a] Determined by spectrophotometric titration at 382 nm in $HOAc-OAc^-$ buffers. See Experimental Section and footnote 9.

been found to react with chromium(IV) diperoxo complexes only sluggishly in solutions from which transition-metal ions have been excluded, but these reactions may exhibit dramatic and highly specific metal ion catalysis. This report deals with the reduction of the diperoxo complex I with the hydroxylammonium ion, NH_3OH^+, a reaction catalyzed strongly by Fe(II) or Fe(III), marginally by Cu(II), but inappreciably by the remaining usual metal ion centers.

Experimental Section

Materials. Diperoxo(diethylenetriamine)chromium(IV) monohydrate, $Cr(dien)(O_2)_2 \cdot H_2O$ (I) was prepared by the method of House and Garner.[3a,4a] The complex, which precipitated from aqueous solution, was washed with methanol at 0 °C and then dried over P_2O_5 for 10–12 h.

Warning! One sample of this complex exploded violently when touched with a metal spatula on a sintered glass crucible. Subsequent preparations were carried out, without incident, on a small scale (less than 500 mg), and all manipulations were performed with a plastic spatula.

Solutions of hydroxylammonium perchlorate were prepared by treatment of hydroxylammonium sulfate (Alfa) with an equivalent quantity of $Ba(ClO_4)_2$ and then filtering of the precipitated $BaSO_4$;[5a] their hydroxylamine content was estimated by the method of Bray and co-workers.[5b] Solutions of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ Aldrich, 99.99%) and $Fe(ClO_4)_2 \cdot 6H_2O$ (Alfa) were prepared and stored in the dark; their Fe(II) content was estimated by titration with standard $K_2Cr_2O_7$, using diphenylamine as indicator.[6] Cation exchange resin (Dowex 50-X2, 400 mesh, H^+ form) was pretreated as described.[7] Lithium perchlorate (used in kinetic experiments) was prepared by the method of Dockal[8] and was recrystallized twice. Catalase (Sigma Chemical; bovine liver; 11 000 units/mg) was used as received.

Stoichiometric Studies. The stoichiometry of the reaction of the diperoxochromium(IV) complex I with NH_3OH^+ was determined by spectrophotometric titration at 382 nm. To measured quantities of Cr(IV) (0.004–0.012 mmol) in $HOAc-OAc^-$ buffer were added successive known quantities of NH_3OH^+. Plots of absorbance vs added reductant showed sharp break points at $[NH_3OH^+]/[Cr^{IV}]$ near 1.0 (Table I).[9] When the reaction was carried out in a gas buret, it was found that 1.56 ± 0.06 mol of gas were slowly emitted for each mole of Cr(IV) taken, after which addition of the enzyme catalase (which catalyzes the disproportionation of H_2O_2 and some of its derivatives) released no further gas. Treatment of the diperoxo complex with catalase in the absence of an external reductant released 1.02 mol of O_2/mol of Cr(IV).

Examination of the Cr(III) Reaction Products. Reaction mixtures (volume 2–3 mL) were 0.02 M in Cr(IV) and 10^{-5} M in Fe(II) and were generally buffered with equimolar concentrations (0.05–0.35 M) of HOAc and OAc^-. These were treated with a 10-fold excess of NH_3OH^+ and were then subjected to column chromatography on Dowex 50X-2 at 2 °C.[10] A small fraction (<10%) of the chromium was eluted by water alone,[11] after which the predominant Cr(III) product was slowly eluted with 1.0 M $NaClO_4$. This fraction, after acidification to pH 2, exhibited maxima at 379 ($\epsilon = 55$) and 525 nm ($\epsilon = 49$), values that were not affected by catalysis of the reaction by Fe(II). Recovery of total chromium was 70–90%, with the loss due principally to column-catalyzed polymerization, which, along with column-catalyzed aquation, is known to be troublesome with carboxylato complexes of Cr(III).[12]

Kinetic Measurements. Rates were estimated from absorbance changes at 382 nm, observed by using a Cary 14 or Beckman Model 5260 recording spectrophotometer. Ionic strength was regulated by addition of $LiClO_4$. Reactions were carried out under pseudo-first-order conditions, usually with NH_3OH^+ in greater than 10-fold excess. Conversions were followed for at least 5 half-lives. Rate constants from successive half-life values within a run generally agreed to within 4%, and average values did not differ significantly from those obtained from logarithmic plots of absorbance differences against reaction time. For reactions carried out with measured amounts of added Fe(II), specific rates from replicate runs agreed to better than 7%.

The $Cr(dien)(O_2)_2-NH_3OH^+$ reaction is catalyzed to a modest extent by Cu^{2+}; increasing the concentration of added $CuSO_4$ from 10^{-5} to 10^{-4} M results in a 2-fold acceleration. Additions of Co^{2+}, Ni^{2+}, Mn^{2+}, Ti^{3+}, Zn^{2+}, Ce^{3+}, Ag^+, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, $Co(en)_3^{3+}$, $Ru(NH_3)_6^{3+}$, or $IrCl_6^{3-}$ (each at the 10^{-5}–10^{-4} M level) were without significant effect. Addition of 4×10^{-5} M VO_2^+ raised the reaction rate marginally, but this increase could not be enhanced at higher concentrations. The $Cr^{IV}-NH_3OH^+$ reaction was severely inhibited in the presence of 10^{-3} M EDTA.

Two uncatalyzed reactions related to the catalytic system at hand were examined briefly. The reaction of the diperoxochromium(IV) complex (1.5×10^{-4} M) with excess Fe(II) (8×10^{-4} to 2×10^{-3} M) in the absence of hydroxylamine was found to be rapid and first order in both components. Stop-flow measurements at 460 nm yielded a bimolecular rate constant of 3.0×10^3 M^{-1} s^{-1} (22 °C, pH 4.4, $\mu = 0.4$ M). In contrast, the reaction of $Fe(ClO_4)_3$ ($(2-4) \times 10^{-4}$ M) with excess NH_3OH^+ ($(2-8) \times 10^3$ M) in the absence of Cr^{IV} was much slower and, at the Fe^{III} concentrations used, poorly reproducible, with pseudo-first-order specific rates (about 0.005 s^{-1}) nearly independent of $[NH_3OH^+]$.

Under analogous conditions, the diperoxochromium(IV) complex was reduced inconveniently, slowly, or not at all, by hydrazine (both in the absence and presence of Fe^{2+}), nitrite, formaldehyde, azide, and *o*-methylhydroxylamine. Reactions with hydroquinone, thiolactic acid, and cysteine in the presence of Fe^{2+} appeared to be kinetically straightforward but yielded Cr(III) species that have not yet been characterized.

Results and Discussion

Spectrophotometric titrations (Table I) indicate that the stoichiometry of the $Cr(dien)(O_2)_2-NH_3OH^+$ reaction closely approaches 1:1, both in the presence and in the absence of Fe(II), allowing us to consider the net reaction as a single-electron transaction, generating Cr(III), N(0), and peroxide. Our manometric measurements (which show slightly more than $^3/_2$ mol of gas to be released/mol of Cr^{IV} taken), although complicated by the disproportionation of peroxide, are consistent with this formulation:

$$2Cr^{IV}(dien)(O_2)_2 + 2NH_3OH^+ + 4H^+ \rightarrow 2Cr^{III}(dien) + N_2 + 2O_2 + 6H_2O \quad (1)$$

Absorption maxima for the principal Cr(III) product (379 and 525 nm) fall well below those for carboxylato- and aquo-substituted species,[13] pointing to ligation by the N-donor sites of diethylenetriamine.[14] When this ligand is tridentate, it is considered to utilize the 1,2,6-positions of the Cr(III) coordination octahedron (with the two end groups trans), being thus closely related to the preferred structure (I) of the $Cr^{IV}(O_2)_2$ chelate taken as a reactant. The elution behavior of the product and the ease with which it undergoes decomposition on polysulfonate resin are not consistent with the known $1,2,6-Cr(dien)(H_2O)_3^{3+}$ cation, but

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(9) Reactions with Fe^{2+} added were carried out in a 1.00-cm cell. The slower reactions with no added Fe^{2+} were run in a 0.20-cm cell.

(10) For estimates of extinction coefficients of Cr(III) complexes, aliquots of the eluates were oxidized with basic H_2O_2, and the chromium content was determined as chromate. See, for example: Haupt, G. W. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1952**, *48*, 414.

(11) When reductions were carried out in 1.0–2.0 M OAc^-, a much greater fraction of the Cr(III) product could be eluted with water alone. This eluate exhibited maxima at 373 ($\epsilon = 80$) and 520 ($\epsilon = 57$) nm at pH 1.5.

(12) See, for example: (a) Gould, E. S. *J. Am. Chem. Soc.* **1968**, *90*, 1740. (b) Hollaway, W. F.; Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1984**, *23*, 2181.

(13) See, for example: (a) Butler, R. D.; Taube, H. *J. Am. Chem. Soc.* **1965**, *87*, 5597. (b) Fanchiang, Y.-T.; Bose, R. N.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2645.

(14) Garner, C. S.; House, D. A. *Transition Met. Chem.* (*N.Y.*) **1970**, *6*, 59. See Table 12 of this review.

Table II. Kinetic Data for Reduction of $Cr^{IV}(dien)(O_2)_2$ with NH_3OH^+ (Red) as Catalyzed by Fe(II)[a]

$10^4[Cr^{IV}]$, M	10^3[Red], M	$10^5[Fe^{II}]$, M	10^2k,[b] s^{-1}
2.0	4.0	0.10	0.43 (0.35)
2.0	4.0	0.25	0.51 (0.56)
2.0	4.0	0.50	0.79 (0.79)
2.0	4.0	0.75	0.90 (0.97)
2.0	4.0	1.0	1.14 (1.12)
2.0	4.0	2.5	2.3 (1.8)
2.0	4.0	5.0	2.7 (2.5)
2.0	4.0	7.5	3.0 (3.1)
2.0	4.0	10.0	3.5 (3.5)
2.0	0.50	1.0	0.43 (0.46)
2.0	1.0	1.0	0.57 (0.69)
2.0	2.0	1.0	0.83 (0.93)
2.0	8.0	1.0	1.20 (1.24)
2.0	16.0	1.0	1.10 (1.32)
4.0	4.0	1.0	1.17 (1.12)
8.0	4.0	1.0	0.96 (1.12)
2.0	4.0	1.0	1.06[c] (1.12)
2.0	4.0	1.0	0.96[d] (1.12)
2.0	4.0	0	0.033 (0)
2.0	4.0	0.10	<0.001[e]
2.0	4.0	0	0.086[f]
2.0	4.0	0	0.075[g]
2.0	4.0	0	1.10[h]

[a] Reactions were carried out at 25 °C; μ = 0.40 M ($LiClO_4$). Solutions were buffered with 0.010 M HOAc and 0.010 M OAc^- (pH 4.36) unless otherwise indicated. [b] Values in parentheses calculated from eq 2 in text, taking k_{lim} as 4.4 $M^{-1/2}\ s^{-1}$ and K as 985 M^{-1}. [c] [HOAc] = [OAc^-] = 0.10 M; pH 4.34. [d] [HOAc] = 0.25 M; [OAc^-] = 0.10 M; pH 4.85. [e] 0.001 M EDTA added. [f] 1×10^{-5} M $Fe(CN)_6^{4-}$ added. [g] 1×10^{-5} M $Fe(CN)_6^{3-}$ added. [h] 1.0×10^{-5} M Fe(III) added.

correspond instead to a dipositive species in which an acetate has replaced one of the coordinated waters (two stereoisomers are possible here). The rapidly eluted product, favored at very high acetate concentrations,[11] is almost certainly a diacetato complex.

Kinetic data are assembled in Table II. All reactions are first order in Cr(IV), and catalysis by Fe^{2+} is observed even at the 5×10^{-7} M level. Rates are very nearly proportional to the half-power of [Fe^{II}] added at catalyst concentrations below 1×10^{-4} M and point to kinetic saturation with respect to [NH_3OH^+]. Pseudo-first-order rate constants for disappearance of Cr^{IV} conform to eq 2. Nonlinear least-squares refinement of rate data based

$$k_{obs} = \frac{k[Fe]_{added}^{1/2}K[NH_3OH^+]}{1 + K[NH_3OH^+]} \qquad (2)$$

on this relationship yields a specific rate k, (4.4 ± 0.4) $M^{-1/2}\ s^{-1}$, and an association constant K, $(9.8 \pm 3.9) \times 10^2\ M^{-1}$ (25 °C, μ = 0.4 M). Rates are found to be independent of both acidity and [OAc^-] within the (relatively narrow) range examined. Observed rates are compared to those calculated by (2) in Table II. The rate in the absence of added iron, $3.3 \times 10^{-4}\ s^{-1}$, corresponds to a Fe(II) concentration below 9×10^{-8} M in the distilled water used.

Since oxidation of Fe(II) by the Cr(IV) complex has been found to be much more rapid ($k = 3 \times 10^3\ M^{-1}\ s^{-1}$ at 22 °C) than reduction of Fe(III) by hydroxylamine in our media, the added iron may be taken to exist preponderantly in the tripositive state after the first few seconds of reaction; moreover, added Fe(III) is seen to be catalytically equivalent to Fe(II) at the 10^{-5} M level (Table II). The observed half-order dependence on added iron suggests that Fe(III) exists predominantly as an inactive dimer with a small active fraction in the monomeric form. This distribution brings to mind that reported for Fe(III) in perchlorate media (with acetate absent) (eq 3) but is dissimilar to the monomer-trimer equilibrium (eq 4) described for acetate media (with hydroxylamine absent). However, neither of these equilibria is applicable as such to the system at hand, for both imply rates proportional to $[H^+]^2$ and (4) suggests a steep inverse acetate dependence as well. Neither of these effects is perceived, indicating the participation of another ligating species.

$$Fe_2(OH)_2^{4+} + 2H^+ \rightleftharpoons 2Fe(III) + 2H_2O \qquad (3)^{15}$$

$$Fe_3(OH)_2(OAc)_6^+ + 2H^+ \rightleftharpoons 3Fe(III) + 2H_2O + 6OAc^- \qquad (4)^{16}$$

The observed kinetic saturation with respect to hydroxylamine is consistent with the formation of a complex of this reductant and Fe(III).[17] Since this donor is converted almost completely to its conjugate acid (pK = 6.0)[18] in our experiments, coordination must be taken to involve its hydroxyl function.[19] Our observations appear to be consistent with sequence in (5)–(9), in which iron

$$Cr^{IV} + Fe^{II} \rightarrow Fe^{III} + Cr^{III} \quad \text{(rapid)} \qquad (5)$$

$$2Fe^{III} \overset{K_6}{\rightleftharpoons} (Fe^{III})_2 \qquad (6)$$

$$Fe^{III} + NH_3OH^+ \overset{K_7}{\rightleftharpoons} (H_3NOH)Fe^{III} \qquad (7)$$

$$(H_3NOH)Fe^{III} + Cr^{IV} \xrightarrow{k_8} Fe^{III}(OHNH_2^\bullet) + H^+ + Cr^{III} \quad \text{(slow)} \qquad (8)$$

$$Fe^{III}(OHNH_2^\bullet) + NH_3OH^+ \rightarrow Fe^{II} + N_2 + 3H^+ + 2H_2O \quad \text{(rapid)} \qquad (9)$$

is recycled between the di- and tripositive states, as is thought to occur in the Fe(II)-catalyzed reductions of $S_2O_8^{2-}$ with $N_2H_5^+$ and with As(III).[20,21] This sequence generates a rate law algebraically equivalent to eq 2 with $K = K_7$ and $k = k_8(2K_6)^{-1/2}$. Step 9, the reaction of the Fe^{III}-bound hydroxylamine radical[22] with excess NH_3OH^+, accommodates the observed stoichiometry. It is related to that proposed by Bridgart[23] for the Cu(II)-catalyzed NH_2OH–$Fe(CN)_6^{3-}$ reaction. As the relative concentration of oxidant is increased, it competes more effectively with NH_3OH^+ for this radical cation, and further oxidation of nitrogen to positive states, e.g. N(I),[24] N(III),[25] and N(V),[26] assumes importance.

The properties of the principal Cr(III) products indicate that acetate groups from the supporting media have become bound to the Cr(III) center during, or shortly after, redox. Earlier work[3d] suggests that such ligation is associated with homolysis of the O–O bond in bound peroxide, for it is not observed during reduction of chelate I with VO^{2+}, a reaction which preserves the peroxide linkage. Since the primary redox reaction does not involve peroxide directly, incorporation of acetate must occur in a follow-up step, i.e., during metal-catalyzed disproportionation of peroxide. We suspect the initial formation of a Cr(III)-peroxy species, closely related to those found by King and co-workers[27] to be unstable in aqueous media. The proposed sequence for its decomposition, (10)–(13), is patterned after the accepted route for Fe(II)-cata-

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$$\mathrm{Cr^{III}{-}OOH + Fe^{II} \rightarrow Fe^{III}{-}OH + Cr^{III}{-}O^{\bullet}} \qquad (10)$$

$$\mathrm{Cr^{III}{-}O^{\bullet} \xrightarrow{H^+} Cr^{IV}{-}OH \xrightarrow{OAc^-} Cr^{IV}{-}OAc} \qquad (11)$$

$$\mathrm{Cr^{IV}{-}OAc + Cr^{III}{-}OOH \rightarrow Cr^{III}{-}OAc + Cr^{III}{-}O_2^{\bullet} + H^+} \qquad (12)$$

$$\mathrm{Cr^{III}{-}O_2^{\bullet} + Fe^{III}{-}OH \rightarrow Cr^{III} + O_2 + Fe^{II} + OH^-} \qquad (13)$$

lyzed decomposition of H_2O_2.[28] Here the Fe(II)-induced homolysis of Cr(III)-bound peroxide (eq 10) is taken to yield a $\mathrm{Cr^{III}{-}O^{\bullet}}$ fragment, which is rapidly converted (eq 11) via internal electron transfer and protonation to a $\mathrm{Cr^{IV}{-}OH}$ complex, derived from an oxidation state known to be substitution-labile.[29] Ligand substitution at this center should yield an acetato derivative of Cr(IV), which would undergo reduction by bound peroxide in the subsequent step (eq 12). At high acetate concentrations, partial conversion to diacetato species would be expected.

Finally, it may be asked why iron and (to a much lesser extent) copper are active catalysts for the Cr(IV)–NH_3OH^+ reaction whereas other transition metal ions fail. The suggested sequence (5)–(9) implies that the catalytic metal must exist in two accessible oxidation state differing by a single unit and that the higher must coordinate effectively with the hydroxylammonium cation. Moreover, the reduction potential of the upper state should be sufficiently positive to allow the electron transfer in step 9 to proceed, a requirement that excludes the poorly oxidizing Ti(IV).[30] Catalysis by the Co(II,III) pair is probably disfavored by the multiplicity gap separating high-spin Co(II) from low-spin Co(III) (the predominant states in the more usual ligand environments). Beyond this, it is desirable that ligand substitution at the upper of the two catalytic metal states be rapid. Thus, the catalytic action of Fe(III) is eliminated in the presence of excess EDTA, and the systems $\mathrm{Fe(CN)_6^{3-/4-}}$, $\mathrm{Ru(NH_3)_6^{3+/2+}}$, and $\mathrm{IrCl_6^{2-/3-}}$ are found to be inactive, although each features a formal potential that should allow recycling between states in the system at hand.[31]

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(28) See, for example: Kochi, J. K. *Free Radicals*; Wiley: New York, 1973; Vol. I, p 628.

(29) (a) Ogard, A. E.; Taube, H. *J. Phys. Chem.* **1958**, *62*, 357. (b) Rajasekar, N.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 3798.

(30) The formal potential for Ti(III,IV) is recorded as +0.056 V at 1 M H^+. This value drops sharply as pH is increased. See, for example: Latimer, W. M. *Oxidation Potentials*; 2nd ed.; Prentice-Hall, Englewood Cliffs, NJ, 1952; p 368.

(31) A reviewer suggests an alternate sequence, (14)–(17), in which Fe(II) attacks a peroxide ligand, forming a Cr(IV) bound hydroxyl species, II,

$$\mathrm{\underset{I}{Cr^{IV}(O_2)_2} + Fe^{II} \xrightarrow{H_2O} \underset{II}{(O_2)Cr^{IV}(OH^{\bullet})} + FeOH^{2+}} \qquad (14)$$

$$\mathrm{\underset{II}{(O_2)Cr^{IV}(OH^{\bullet})} \rightarrow \underset{III}{(O_2^-)Cr^{IV}(OH)}} \qquad (15)$$

$$\mathrm{\underset{III}{(O_2^-)Cr^{IV}(OH)} \rightarrow O_2 + \underset{IV}{Cr^{III}(OH)}} \qquad (16)$$

$$\mathrm{Cr^{III}(OH) + OAc^- \rightarrow Cr^{III}(OH)(OAc)} \qquad (17)$$

followed by internal conversion to a superoxo complex, III, which, in turn, yields O_2 and a coordinatively unsaturated Cr(III) intermediate, IV. Acetate then enters the coordination sphere of the latter. This scheme, in which the role of NH_3OH^+ is to maintain an adequate concentration of catalytic Fe(II), accommodates the observed stoichiometry and the intrusion of carboxylate from the medium. It does not appear, however, to be consistent with rate law 2, because the Fe(III)–NH_3OH^+ redox reaction is known to be slow. The Cr(IV) complex would function as a scavenger for Fe(II), and the kinetic dependence on [$\mathrm{Cr^{IV}}$] would disappear. In addition, this scheme suggests that the incorporation of acetate is dependent on the extrusion of O_2, whereas our earlier experiments with the Cr(IV)–Ti(III) system[3d] show that acetate intrudes even when all bound peroxide is reduced to water.

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Reactions of Disubstituted Alkanes with a Nickel(I) Macrocycle

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The reactions of disubstituted alkanes, $X(CH_2)_nY$ (X, Y = Cl, Br, I, OH, OTs), with the cationic macrocyclic ion (1*R*,4*S*,8*R*,11*S*)-(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)nickel(I), abbreviated $\mathrm{Ni(tmc)^+}$, are characterized by kinetic accelerations compared to the rates for the monohalides, most noticeably for the smaller molecules, n = 2, 3. No transient organonickel species is detected for any vicinal disubstituted alkane, and the alkene is formed quantitatively. This is attributed to a "reductive elimination" reaction between $\mathrm{Ni(tmc)^+}$ and the radical $\mathrm{^{\bullet}CH_2CH_2OH}$, known to result from the very rapid unimolecular solvolysis of the initially formed $\mathrm{^{\bullet}CH_2CH_2Y}$. Although $\mathrm{Br(CH_2)_3OH}$ yields 1-propanol from the hydrolysis of the observed species $\mathrm{(tmc)Ni(CH_2)_3OH^+}$, 1,3-disubstituted propanes (X, Y = Br, Cl, OTs) form cyclopropane exclusively. A rapid, unimolecular reaction of $\mathrm{(tmc)Ni(CH_2)_3Y^+}$ appears responsible. The 1,4-disubstituted alkanes yield $\mathrm{(tmc)Ni(CH_2)_4Y^+}$ with deficient $\mathrm{Ni(tmc)^+}$, but ethylene is formed rapidly and quantitatively in the presence of even a catalytic concentration of $\mathrm{Ni(tmc)^+}$ (with Y = Br, I and to some extent Y = Cl). Similarly, $\mathrm{(tmc)NiCH(CH_3)(CH_2)_3Y^+}$ forms a 1:1 mixture of ethylene and propene (Y = Br, I) when $\mathrm{Ni(tmc)^+}$ is present and otherwise hydrolyzes to 1-Y-pentane. Alkene formation from 1,4-disubstituted alkanes is attributed to the reaction of $\mathrm{(tmc)Ni(CH_2)_4Y^+}$ with $\mathrm{Ni(tmc)^+}$, producing a species $\mathrm{(tmc)Ni(CH_2)_4^{\bullet +}}$ that yields ethylene and regenerates $\mathrm{Ni(tmc)^+}$. The formation of cyclopentane as the exclusive product from the reaction of 1,5-dibromopentane with excess $\mathrm{Ni(tmc)^+}$ is attributed to a unimolecular reaction of $\mathrm{(tmc)Ni(CH_2)_5^{\bullet +}}$.

Introduction

Some results concerning the nickel alkyls of the tetraaza macrocycle known as tmc[1] have already been reported.[2-5] These include the characterization of the mechanism by which nickel–carbon bonds are formed[3,4] and some of the reactions they undergo.[6,7]

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(1) The complex depicted is (1*R*,4*S*,8*R*,11*S*)-(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)nickel(I), which we abbreviate as (*R*,*S*,*R*,*S*)-$\mathrm{Ni(tmc)^+}$ or, when it is not confusing, simply as $\mathrm{Ni(tmc)^+}$. Convenient electrochemical, photochemical, and chemical methods have been reported[2-4] for the preparation of the highly unstable and air-sensitive solutions of the nickel(I) reagent from the nickel(II) salt, which is very stable and is readily prepared.[5]

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(6) Ram, M. S.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1986**, *25*, 4115.

(7) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 5353.

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