(CF_2, CF_3CF_2N, CFCl, mult). Anal. Calcd for $C_{12}F_{29}N_4Cl$: C, 18.32; N, 7.12. Found: C, 18.32; N, 7.39.

Properties of $CF_3(C_2F_5)NN(C_2F_5)$ $CFClCFClN(C_2F_5)N(C_2F_5)CF_3$. This compound was found in the reaction vessel as a nonvolatile liquid. It was obtained in ~40% yield. Spectral data were as follows. MS [*m/e* (species) intensity]: 785/783 ($M^+ - F$) 4.6/7.3, 543/541 ($M^+ - C_2F_{10}Cl$) 2.6/8.5, 366 ($C_6F_{14}N_2^+$) 2.6, 297 ($C_5F_{11}N_2^+$) 9.9, 247 ($C_4F_9N_2^+$) 17.6, 164 ($C_3F_6N^+$) 24.9, 119 ($C_2F_5^+$) 100, 69 (CF_3^+) 85.7. IR (liquid): 1223 s, 1134 w, 1087 w, 1071 s, 951 w, 939 w, 887 w, 874 w, 828 w, 812 w, 771 w, 752 s, 738 s, 680 s cm^{-1}. ^{19}F NMR: ϕ −56.6, −57.22 (CF_3N, mult), −80.91, −81.72 (CF_3CF_2, mult), −91.04 to −97.3 (CF_3CF_2, CFCl, mult). Anal. Calcd for $C_{12}F_{28}N_4Cl_2$: C, 17.96; N, 6.98. Found: C, 17.98; N, 6.95.

Properties of $CF_3(C_2F_5)NN(C_2F_5)CF_2CFHN(C_2F_5)N(C_2F_5)CF_3$. This compound was found in the trap cooled at −10 °C as a colorless liquid in ~30% yield. Spectral data were as follows. MS (CI^+) [*m/e* (species) intensity]: 734 [(M^+ + 1) − F] 16.97, 683 ($M^+ - CF_3$) 1.3, 417 ($C_7F_{16}N_2H^+$) 28.4, 385 ($C_6F_{15}N_2^+$) 4.8, 367 ($C_6F_{14}N_2H^+$) 78.2, 297 ($C_5F_{11}N_2^+$) 5.6, 279 ($C_5F_{10}N_2H^+$) 22.0, 229 ($C_4F_8N_2H^+$) 21.1, 119 ($C_2F_5^+$) 74.9, 69 (CF_3^+) 77.4. IR (liquid): 1362 s, 1230 s, 1142 s, 1121 s, 1104 s, 1079 s, 1040 s, 946 s, 931 s, 890 s, 783 w, 739 s, 712 s cm^{-1}. ^{19}F NMR: ϕ −58.9 (CF_3N, mult), −82.7 to −84.38 (CF_3CF_2, mult), −95.79 to −101.87 (CF_2CF_3, CF_2, CFH, mult). ^1H NMR: δ 5.9 (d, mult). Anal. Calcd for $C_{12}F_{29}N_4H$: C, 19.15; N, 7.45. Found: C, 19.18; N, 7.38.

Properties of $CF_3(C_2F_5)NN(C_2F_5)CF_2CH_2N(C_2F_5)N(C_2F_5)CF_3$. This compound was found in the trap cooled at −10 °C. It was a colorless liquid obtained in 30–35% yield. Spectral data were as follows. MS (CI^+) [*m/e* (species) intensity]: 665 ($M^+ - CF_3$) 6.0, 627 ($M^+ - CF_5$) 1.1, 463 ($C_8F_{17}N_3H_2^+$) 6.5, 399 ($C_7F_{15}N_2H_2^+$) 29.7, 385 ($C_6F_{15}N_2^+$) 8.8, 349 ($C_6F_{13}N_2H_2^+$) 100, 311 ($C_6F_{11}N_2H_2^+$) 9.5, 261 ($C_5F_9N_2H_2^+$) 11.4, 119 ($C_2F_5^+$) 14.3, 69 (CF_3^+) 14.6. IR (liquid): 1359 w, 1224 s, 1142 s, 1109 s, 1072 s, 1035 s, 951 s, 938 s, 916 w, 878 w, 751 w, 736 s, 702 w cm^{-1}. ^{19}F NMR: ϕ −58.03 (CF_3N, mult), −81.66 to −85.77 (CF_3CF_2, mult), −94 to −100.72 (CF_3CF_2, CF_2, mult). ^1H NMR: δ 3.63 (CH_2, t), $J_{CH_2-CF_2}$ = 14.9 Hz. Anal. Calcd for $C_{12}F_{28}N_4H_2$: C, 19.62; N, 7.63. Found: C, 19.69; N, 7.65.

Acknowledgment is made for the generous support of fluorine research at the University of Idaho by the National Science Foundation (Grant CHE-8703790) and the Air Force Office of Scientific Research (Grant 87-0067).

Contribution from the Department of Chemistry,
Kent State University, Kent, Ohio 44242

Electron Transfer. 103. Reactions of Aqueous Chromium(IV)[1]

M. C. Ghosh* and E. S. Gould*

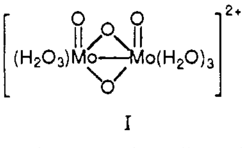
Received March 30, 1990

Reduction of $HCrO_4^-$ with the bridged dimer of Mo^V ($Mo_2O_4^{2+}$) in aqueous solutions buffered by 2-ethyl-2-hydroxybutanoic acid (HLig) and its salt (Lig^-) yields a pink Cr(IV) complex (ϵ_{max}^{510} = 1.3 × 10^3 M^{-1} cm^{-1} when [Lig^-] = 0.05 M). This species is reduced to a bichelate of Cr^{III} with excess $(Mo^V)_2$ but oxidized to a bichelate of Cr^V with excess $Cr_2O_7^{2-}$, indicating that it too is bischelated. The formation of Cr^{IV} from Cr^{VI} and $(Mo^V)_2$ proceeds through two routes, with the activated complex for the second featuring one more H^+ and one more carboxylate group than that for the first. The comproportionation reaction, $Cr^{IV} + Cr^{VI} \rightarrow 2Cr^V$, appears to entail a $Cr^{IV}Cr^{VI}$ complex (K_{assn} = 40 ± 7 M^{-1}), which reacts via both an acid-independent and a [H^+]-proportional path. Data for the reaction of Cr^{IV} with $(Mo^V)_2$ are in accord with the sequence (6)–(9) in which the key step is the reversible, unimolecular conversion to the principal $(Mo^V)_2$ species to an activated form ($k = 5 \times 10^2$ s^{-1} at 25 °C) that reacts rapidly with Cr^{IV}. To form a Cr^{IV} complex of this type stable enough to be examined in conventional mixing experiments, it is necessary that the carboxylate ligand be attached to the Cr^{IV} center prior to reduction and that the usual 1e⁻ reductants, which rapidly reduce Cr^{IV}, be avoided.

In 1949 Westheimer presented kinetic evidence that oxidations of alcohols with $HCrO_4^-$ passed through the atypical oxidation state Cr(IV).[2] Further indications accumulated in the 1960s that this state was an intermediate in the reactions of Cr(VI) with 1e⁻ metal-center reductants.[3] A small array of Cr(IV) derivatives have been characterized,[4] but these are generally not stable in aqueous media. Notable exceptions are a group of chromium(IV) diperoxo ammines, which were first prepared near the turn of the century[5] and were eventually examined in detail by Garner and co-workers.[6] Mechanistic studies of complexes of this type[7] are complicated by the presence of three oxidizing functions in a single molecule.

Reports in 1985 mentioned the formation of Cr(IV) complexes devoid of peroxo ligands when α-hydroxy carboxylato chelates of Cr(V) were reduced with Fe^{2+}, VO^{2+}, or U(IV).[8] Although specific rates of a few reactions of such transients could be estimated, study was limited by the competing decay of Cr(IV) in the presence of 1e⁻ reagents.

We here describe the preparation of aqueous Cr(IV) solutions of greatly improved stability by treatment of $HCrO_4^-$ with the dimeric molybdenum(V) cation, I (abbreviated $(Mo^V)_2$), in solutions buffered by excess 2-ethyl-2-hydroxybutanoic acid (II) and its anion. This acid is the most effective member of a group of α-hydroxy carboxylic acids known to stabilize Cr(V) via chelation.[9] We find that it is likewise useful in stabilizing Cr(IV) and, on the basis of earlier evidence,[8a,b] suggest that it is bidentate here as well. In addition to data pertaining to the formation of this unusual state, we include information on its reduction with



I

$(C_2H_5)_2C(OH)COOH$

II

---

[1] Sponsorship of this work by the National Science Foundation (Grant 8619472) is gratefully acknowledged.

[2] See, for example: Watanabe, E.; Westheimer, F. H. *J. Chem. Phys.* **1949**, *17*, 61.

[3] See, for example: (a) Espenson, J. H.; King, E. L. *J. Am. Chem. Soc.* **1963**, *85*, 3328. (b) Sullivan, J. C. *Ibid.* **1965**, *87*, 1495. (c) Espenson, J. H. *Ibid.* **1964**, *86*, 1883. (d) Birk, J. P. *Ibid.* **1969**, *91*, 3189. (e) MacKnight, G. F.; Haight, G. P. *Inorg. Chem.* **1973**, *12*, 1619. (f) For an early critical review, see: Espenson, J. H. *Acc. Chem. Res.* **1970**, *2*, 347.

[4] (a) Clark, H. C.; Sandana, Y. N. *Can. J. Chem.* **1964**, *42*, 50. (b) Wilhelmi, K.; Jonson, O. *Acta Chem. Scand.* **1961**, *15*, 1415. (c) Hagihara, N.; Yamazaki, H. *J. Am. Chem. Soc.* **1959**, *81*, 3160. (d) Alyea, E. C.; Basi, J. S.; Bradley, D. C.; Chisholm, M. H. *J. Chem. Soc. A* **1971**, 772. (e) Dyracz, G.; Roček, J. *J. Am. Chem. Soc.* **1973**, *95*, 4756.

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

[6] (a) House, D. A.; Garner, C. S. *Nature*, **1965**, *208*, 776. (b) House, D. A.; Garner, C. S. *Inorg. Chem.* **1966**, *5*, 840. (c) House, D. A.; Hughes, R. G.; Garner, C. S. *Ibid.* **1967**, *6*, 1077.

[7] Ghosh, S. K.; Laali, K.; Gould, E. S. *Inorg. Chem.* **1988**, *27*, 4224.

[8] (a) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2832. (b) Fanchiang, Y.-T.; Bose, R. N.; Gelerinter, E.; Gould, E. S. *Ibid.* **1985**, *24*, 4679. (c) Bose, R. N.; Gould, E. S. *Ibid.* **1986**, *25*, 94.

[9] Krumpolc, M.; Roček, J. *J. Am. Chem. Soc.* **1979**, *101*, 3206.

0020-1669/90/1329-4258$02.50/0

Table I. Stoichiometry of the $(Mo^V)_2$–Cr^{VI} Reactions[a]

λ, nm	pH	$10^4[Cr^{VI}]$,[c] M	$10^4[(Mo^V)_2]$,[d] M	$10^4\Delta[Cr^{VI}]$, M	$10^4\Delta[(Mo^V)_2]$, M	$\Delta[(Mo^V)_2]/\Delta[Cr^{VI}]$
295	2.8	0.50	2.50		0.80	1.60
		1.00	2.50		1.57	1.57
		1.50	2.50		2.20	1.47
	0.3[b]	1.00	4.50		1.57	1.57
		0.83	2.20		1.29	1.55
510	3.3	50	8.0	16.5		0.49
		50	16.0	34		0.46
		50	24.0	45		0.53
350	0.3[b]	3.0	0.75	0.52		1.44
		3.0	3.0	2.01		1.49

[a] $(Mo^V)_2$ was added as $Mo_2O_4(H_2O)_6(ClO_4)_2$ (salt of cation I). Solutions at pH 2.8 and 3.3 were buffered by the ligating acid (II) and its sodium salt. [b] Reactions in 0.5 M $HClO_4$ (no hydroxy acid or its salt was added). [c] Monomeric Cr^{VI}. [d] $(Mo^V)_2$ dimer.

Table II. Absorbance (at 510 nm) of Intermediate from Reaction of $(Mo^V)_2$ with Cr(VI)[a]

$10^4[(Mo^V)_2]$, M	abs	$10^4[(Mo^V)_2]$, M	abs
0.0	0.02	5.0	0.76
1.50	0.27	5.8	0.72
3.0	0.52	6.7	0.70
4.5	0.72	7.5	0.67

[a] Reactions were carried out in solutions that were 0.13 M in 2-hydroxy-2-ethylbutanoic acid and 0.070 M in its sodium salt (pH 3.05); $[Cr^{VI}] = 5.0 \times 10^{-4}$ M in each case; waiting period after mixing 10 s; path length 1.00 cm.

$(Mo^V)_2$ and its oxidation (to Cr^V) with Cr(VI).

Experimental Section

Materials. Sodium dichromate (MCB, reagent grade) and the "ligand acid" 2-ethyl-2-hydroxybutanoic acid (II) (Aldrich) were used as received. Cation-exchange resin (Dowex 50-X8, 400 mesh, H^+ form) was pretreated as described.[10] Sodium perchlorate solutions were prepared by reaction of $NaHCO_3$ with concentrated $HClO_4$. Preparation of $(Mo^V)_2$ solutions was carried out by aquation of $(NH_4)_2MoOCl_5$ in 0.05 M $HClO_4$.[11] Separation of the desired $Mo_2O_4(H_2O)_6^{2+}$ was accomplished on a deaerated column of Dowex 50-X8 resin under N_2. For studies with excess Cr(VI), elution of $(Mo^V)_2$ was carried out with 2 M $HClO_4$; these solutions were stable for over 1 week in the absence of O_2. For experiments with excess $(Mo^V)_2$, elution was performed with 2 M $NaClO_4$ + 0.1 M $HClO_4$; such solutions were used immediately, for they were found to deteriorate within a few hours. Solutions of $(Mo^V)_2$ were standardized at 295 nm ($\epsilon = 3550\ M^{-1}\ cm^{-1}$).[12]

Stoichiometric Studies. The stoichiometry of the $(Mo^V)_2$–Cr(VI) reaction in buffers of the ligand acid and its anion was determined with both excess $(Mo^V)_2$ and excess Cr(VI). Experiments with excess $(Mo^V)_2$ were carried out by adding measured deficiencies of Cr(VI) to the reductant, waiting 10–15 min for competition of the reaction, and then measuring the decrease in absorbance at 295 nm. These changes were compared to those occurring when Mo(V) was treated with a slight excess of oxidant. Determinations with excess Cr(VI) were made in an analogous manner, monitoring the changes at 510 nm (for conversion of Cr^{VI} to Cr^V) with waiting periods of 45–60 min. Results are summarized in Table I.

In addition, experiments to establish the optimum stoichiometry for formation of the pink intermediate were carried out by mixing known concentrations of Cr(VI) (in ligand buffer) and $(Mo^V)_2$ and then following the appearance of this intermediate at 510 nm. Absorbances observed at various reagent concentrations are listed in Table II.

Examination of Reaction Products. For the reaction with excess $(Mo^V)_2$, mixtures (10 mL) contained 0.150 mmol of Cr(VI), 0.30 mmol of $(Mo^V)_2$, 6.2 mmol of ligand acid, and 2.8 mmol of its sodium salt and exhibited pH 2.96. These were allowed to react for 10 min at 25 °C, were then treated with 7.5 mmol of $NaBrO_3$ to consume unreacted $(Mo^V)_2$,[11b] and were then subjected to cation-exchange chromatography.[13,14] The major fraction (green), comprising 95% of the chromium recovered, was eluted with distilled water. It exhibited maxima at 584 nm ($\epsilon = 49\ M^{-1}\ cm^{-1}$) and 414 nm ($\epsilon = 76\ M^{-1}\ cm^{-1}$). A minor fraction, eluted with 0.5 M $NaClO_4$, showed peaks at 578 nm ($\epsilon = 31\ M^{-1}\ cm^{-1}$) and 411 nm ($\epsilon = 48\ M^{-1}\ cm^{-1}$). The total recovery of chromium was 89%.

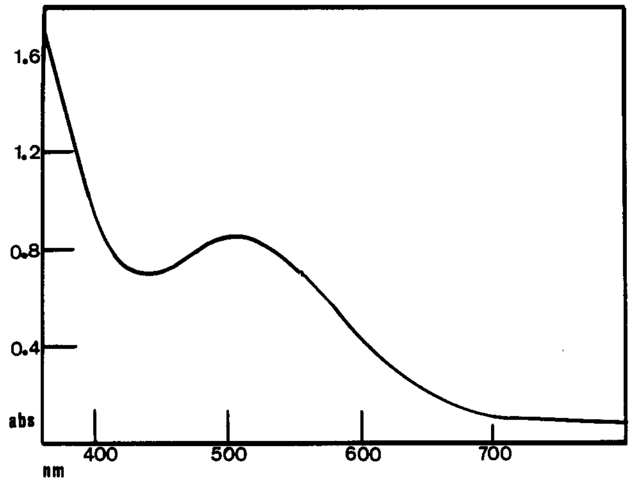


Figure 1. Spectrum of Cr(IV), obtained by mixing equimolar quantities of $Cr_2O_7^{2-}$ and $Mo_2O_4^{2+}$ in a solution 0.050 M each in 2-ethyl-2-hydroxybutanoic acid and its sodium salt. pH = 3.30. The spectrum was recorded 10 s after mixing. The calculated concentration of Cr(IV) is 6.5×10^{-4} M.

For the reaction with excess Cr(VI), mixtures (2.0 mL) were 0.0025 M in $(Mo^V)_2$, 0.0050 M in Cr(VI), and 0.025 M in both the ligand acid and its anion (pH 3.3). After 1 h of reaction time, solutions exhibited a spectrum corresponding to that of the Cr^VO complex of the ligand acid; $\lambda_{max} = 510$ nm ($\epsilon = 176\ M^{-1}\ cm^{-1}$) (reported[8b] $\lambda_{max} = 510$ nm ($\epsilon = 181\ M^{-1}\ cm^{-1}$ in 0.025 M Lig^-)).

To record the spectrum of Cr(IV), reaction mixtures were 1.5×10^{-3} M in Cr(VI), 7.5×10^{-4} M in $(Mo^V)_2$, and 0.5 M each in the ligand acid and its anion. After only 10 s of mixing, the resulting pink solution showed a strong broad peak at 510 nm ($\epsilon = 1.34 \times 10^3\ M^{-1}\ cm^{-1}$) (Figure 1).

Kinetic Measurements and Estimates of Specific Rates. Reactions were monitored by using absorbance changes at 540 nm. Runs with excess $(Mo^V)_2$ were followed by using a Durrum-Gibson stop-flow spectrophotometer. For experiments with excess Cr(VI), the formation of Cr(IV) was studied by using the stop-flow spectrophotometer, but its much slower reaction with Cr(VI) was examined by using a Beckman Model 5260 instrument. In all runs, acidic $(Mo^V)_2$ solutions were added to freshly buffered[15,16] Cr(VI). Ionic strength was maintained at 0.5 M by addition of $NaClO_4$ solution.

Kinetic profiles taken with $(Mo^V)_2$ in excess featured the rapid growth and decay of the Cr(IV) intermediate, but these traces corresponded

---

(10) Gould, E. S. *J. Am. Chem. Soc.* **1967**, *89*, 5792.

(11) (a) Sasaki, Y.; Sykes, A. G. *J. Am. Chem. Soc., Dalton Trans.* **1974**, 1468. (b) Linn, D. E., Jr.; Ghosh, S. K.; Gould, E. S. *Inorg. Chem.* **1989**, *28*, 3225.

(12) (a) Richens, D. T.; Sykes, A. G. *Inorg. Synth.* **1985**, *23*, 137. (b) Ardon, M.; Pernick, A. *Inorg. Chem.* **1973**, *12*, 2484.

(13) Separations were carried out by using a 5-cm column, capacity 2 mequiv. For estimation of extinction coefficients of the Cr(III) products, aliquots were oxidized with basic H_2O, and the total chromium content was determined as chromate.[14]

(14) Haupt, G. W. *J. Res. Natl. Bur. Stand., Sect. A* **1952**, *48*, 41.

(15) Although we observed no immediate spectral changes when dichromate solutions were mixed with 2-ethyl-2-hydroxybutanoate buffers at room temperature, kinetic runs with such buffered solutions, which had been allowed to stand more than 10 min, gave poorly reproducible results, due probably to the slow reduction to Cr(V).[9] Prolonged standing of $(Mo^V)_2$ solutions with these buffers led to comparably serious complications, probably reflecting the several stages of anation (proceeding at very different rates) of this metal center.[16]

(16) Ghosh, M. C. Unpublished results, Kent State University, 1990.

neither to the straightforward superposition of two first-order processes nor to an autocatalytic sequence of the type observed for the $(Mo^V)_2$–Cr^V reaction in similarly buffered media.[16] Such curves were, however, fitted to a reaction sequence in which the intermediate was generated by action of $(Mo^V)_2$ but consumed by a more reactive form of the reductant (see Results and Discussion). This fitting employed the program INTEGRAL to generate curves that were compared to those observed.[17-19]

Additional Observations. An intermediate having the same spectral characteristics as that formed in the $(Mo^V)_2$–Cr^{VI} reaction was observed when $Cr_2O_7^{2-}$ was treated with H_3AsO_3, Sn(II), or U(IV) in solutions buffered with 2-ethyl-2-hydroxybutanoic acid and its salt. Similar transients were observed from reductions of Cr(VI) in buffers derived from the 2-methyl analogue, but other 2-hydroxy acids (lactic, mandelic, and benzilic acids) were much less effective in this respect. Reductions carried out in acetate buffers exhibited no evidence of Cr(IV) formation, nor was this species observed, even momentarily, when Cr(VI) was reduced with salts of Eu(II), Ti(III), Fe(II), or $(NH_3)_6Ru^{II}$, regardless of the medium chosen.

Results and Discussion

The $(Mo^V)_2$–Cr^{VI} reaction, when carried out in unbuffered media at low pH, yields Mo^{VI} and Cr^{III}, irrespective of the ratio of reactants taken. However, the overall stoichiometry in 2-ethyl-2-hydroxybutanoate buffers is seen (Table I) to depend upon the reagent in excess. With excess $(Mo^V)_2$, 2 mol of Cr^{VI} consumes very nearly 3 mol of $(Mo^V)_2$, again yielding Cr^{III}

$$2Cr^{VI} + 3(Mo^V)_2 \rightarrow 2Cr^{III} + 6Mo^{VI} \qquad (1)$$

whereas, with the oxidant in excess, the stoichiometry approaches 2:1, with formation of a bis chelate of Cr^V, the latter also characterized from its spectrum[8b,9]

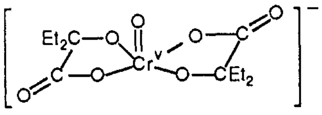
$$2Cr^{VI} + (Mo^V)_2 \rightarrow 2Cr^V + 2Mo^{VI} \qquad (2)$$

Moreover, in solutions buffered by the ligand acid, reactions 1 and 2 are seen to proceed through the same pink intermediate, formed rapidly from equimolar quantities of Cr^{VI} and $(Mo^V)_2$ (Table II)

$$Cr^{VI} + (Mo^V)_2 \rightarrow Cr^{IV} + 2Mo^{VI} \qquad (3)$$

and exhibiting a spectrum[8a] and redox behavior characteristic of a Cr(IV) complex. Differing net stoichiometries then reflect the reduction of this intermediate to Cr(III) by excess $(Mo^V)_2$ or, alternatively, its oxidation to Cr(V) by excess Cr(VI).

The spectrum (ϵ_{584} = 49 M^{-1} cm^{-1}; ϵ_{414} = 76 M^{-1} cm^{-1}) of the predominant Cr(III) product formed by reduction with $(Mo^V)_2$ in buffered solution corresponds to that of the complex from reduction of the Cr(V) chelate III with ascorbic acid in similarly buffered media.[20] Evidence was presented[20] that this is a bischelated complex derived from the buffering hydroxy acid with one additional monodentate carboxyl group. The elution behavior of this product, indicating the absence of positive charge, is in accord with this assignment, as is its partial decay in contact with polysulfonate resin, which may be attributed to slow aquation, as reported for related (carboxylato)chromium(III) complexes.[21]



III

Table III. Kinetic Data for the $(Mo^V)_2$–Cr^{VI} Reaction with Cr^{VI} in Excess[a]

$10^3[Cr^{VI}]$, M	[LigH],[b] M	[Lig⁻],[c] M	pH	$10^{-3}k_f$,[d] M^{-1} s^{-1}	10^3k_d,[e] s^{-1}
0.50	0.13	0.070	3.04	2.1 (2.3)	1.28 (1.23)
1.00	0.13	0.070	3.05	2.2 (2.3)	2.7 (2.4)
2.0	0.13	0.070	3.04	2.1 (2.3)	4.7 (4.6)
5.0	0.13	0.070	3.06	2.3 (2.3)	10.3 (10.4)
10.0	0.13	0.070	3.04	2.0 (2.3)	17.8 (17.8)
20.0	0.13	0.070	3.02		30 (28)
20.0[f]	0.13	0.070	3.00		30 (28)
20.0[g]	0.13	0.070	3.01		30 (28)
1.30	0.039	0.021	3.06	1.38 (1.53)	
1.30	0.078	0.042	3.05	1.80 (1.85)	
1.30	0.130	0.070	3.03	2.2 (2.2)	
1.30	0.162	0.088	3.04	2.5 (2.6)	
1.30	0.195	0.105	3.06	2.8 (2.8)	
1.30	0.031	0.034	3.35	1.63 (1.46)	
1.30	0.131	0.049	2.89	2.6 (2.3)	
1.30	0.20	0.049	2.71	3.0 (2.8)	
1.30	0.32	0.054	2.55	3.6 (3.8)	
5.0	0.26	0.140	3.01		10.3 (10.4)
5.0	0.065	0.035	3.02		10.3 (10.4)
5.0	0.025	0.025	3.32		8.9 (9.6)
5.0	0.040	0.025	3.15		9.4 (9.9)
5.0	0.100	0.025	2.73		11.2 (11.7)
5.0	0.18	0.025	2.46		13.9 (14.1)
5.0	0.30	0.025	2.27		16.9 (16.9)

[a] Reactions were run at 24.5 ± 0.5 °C; μ = 0.50 M ($NaClO_4$); progress was monitored at 540 nm. Chromium(VI) was added as Na_2CrO_7; $(Mo^V)_2$, added as $Mo_2O_4^{2+}$ (cation I), was 8.0 × 10^{-5} M, unless otherwise indicated. Solutions were buffered with mixtures of the ligand acid, II, and its sodium salt. [b] 2-Ethyl-2-hydroxybutanoic acid (II). [c] 2-Ethyl-2-hydroxybutanoate. [d] Rate constants for generation of Cr(IV) from Cr(VI) and $(Mo^V)_2$, measured by using the stop-flow spectrophotometer. Parenthetical values were calculated from eq 4 in text, with k_0 as 1.20 × 10^3 M^{-1} s^{-1} and k_{LH} as 1.70 × 10^7 M^{-3} s^{-1}. [e] Rate constants for oxidation of Cr(IV) to Cr(V), measured in conventional mixing experiments. Parenthetical values were calculated from eq 5 in text, with K as 40 M^{-1}, $k^0{}_d$ as 0.053 s^{-1}, and k'_d as 8.8 M^{-1} s^{-1}. [f] μ = 0.10 M. [g] $[(Mo^V)_2]$ = 3.4 × 10^{-4} M.

Kinetic data for reactions with Cr(VI) in excess are summarized in Table III. The rapid formation of Cr(IV) and its much slower conversion to Cr(V) are readily separable. The formation is first order in both redox partners and is accelerated both by acidification and by ligation. Bimolecular specific rates for generation of Cr^{IV} (k_f values) are in accord with eq 4, where k_0 =(1.20 ±

$$(k_f)_{obsd} = k_0 + k_{LH}[Lig^-][H^+] \qquad (4)$$

0.095) × 10^3 M^{-1} s^{-1} and k_{LH} = (1.70 ± 0.16) × 10^7 M^{-3} s^{-1}.[22] Two paths thus contribute to the $(Mo^V)_2$–Cr^{VI} reaction, with the transition state for the second featuring an additional proton and one more ligand anion than that for the k_0 component. Although it is reasonable to assign the "extra" H^+ to the oxidant and the anion to the reductant, our data do not direct this choice.

Rates for destruction of Cr(IV) by the Cr^{IV}–Cr^{VI} reaction (k_d values) are likewise enhanced by increased acidity but exhibit kinetic saturation at high values of $[Cr^{VI}]$, indicating the formation of a complex between the two oxidation states. Unimolecular rates are correlated by (5), where K, the association constant for the

$$(k_d)_{obsd} = \frac{K[Cr^{VI}]}{1 + K[Cr^{VI}]}(k^0{}_d + k'_d[H^+]) \qquad (5)$$

$Cr^{IV}Cr^{VI}$ complex, is 40 ± 7 M^{-1}, and $k^0{}_d$ and k'_d, the limiting rates (at high $[Cr^{VI}]$) for the acid-independent and $[H^+]$-proportional paths, are (5.3 ± 0.8) × 10^{-2} s^{-1} and 8.8 ± 1.8 M^{-1} s^{-1} (25 °C, μ = 0.50 M). Table III also compares rates calculated by (4) and (5) with observed values.

---

(17) Bose, R. N.; Rajasekar, N.; Thompson, D. M.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 3349.

(18) Kinetic fits, which utilized a fourth-order Runge–Kutta integration technique,[19] were accomplished by a FORTRAN-77 program on an IBM 3081D computer system. The FORTRAN-IV version of the program, for which we thank Professor Gilbert Gordon (Miami University, Oxford, OH) was modified to incorporate the appropriate differential equations and stoichiometric relationships.

(19) (a) Margenau, H.; Murphy, G. M. *The Mathematics of Physics and Chemistry*; Van Nostrand: New York, 1943; p 469. (b) Wiberg, K. In *Techniques of Chemistry*, 3rd ed.; Lewis, E. S., Ed.; Wiley: New York, 1974; Vol. VI, Part I, p 764.

(20) Ghosh, S. K.; Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1987**, *26*, 2684.

(21) See, for example, Hollaway, W. F.; Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1984**, *23*, 2181.

(22) The second term in (4) may be expressed alternatively as k'_{LH}[HLig], where k'_{LH} = (8.2 ± 0.7) × 10^3 M^{-2} s^{-1}.

Table IV. Kinetic Data for the Formation and Destruction of Chromium(IV) in the Reaction of Cr^{VI} with Excess $(Mo^V)_2$[a]

$10^5[Cr^{VI}]$	$10^3[(Mo^V)_2]$	[LigH][b]	[Lig⁻][c]	pH	$10^{-3}k_1$[d]	$10^{-2}k_2$[e]	k_4/k_3[e]	$10^{-3}\epsilon_{Cr(IV)}$[e,f]
3.0	2.0	0.130	0.070	3.06	2.2	5.7	0.26	1.54
6.0	2.0	0.130	0.070	3.06	2.3	5.5	0.25	1.42
12.0	2.0	0.130	0.070	3.06	2.4	4.7	0.20	1.41
8.0	1.00	0.130	0.070	3.08	2.4	5.6	0.23	1.44
8.0	2.0	0.130	0.070	3.05	2.4	5.1	0.21	1.51
8.0	4.0	0.130	0.070	3.06	2.2	5.3	0.22	1.60
8.0	1.00	0.078	0.042	3.06	1.90	5.2	0.22	1.35
8.0	1.00	0.195	0.105	3.07	2.8	5.5	0.23	1.71
8.0	1.00	0.042	0.042	3.33	1.69	4.5	0.21	1.53
8.0	1.00	0.21	0.042	2.63	3.3	5.5	0.24	1.43

[a] Reactions were run at 24.5 ± 0.5 °C; $\mu = 0.50$ M ($NaClO_4$); $\lambda = 540$ nm. Cr(VI) was added as $Na_2Cr_2O_7$; $(Mo^V)_2$ was added as $Mo_2O_4^{2+}$ (cation I). All concentrations are given in molarity. [b] 2-Ethyl-2-hydroxybutanoic acid (II). [c] 2-Ethyl-2-hydroxybutanoate. [d] Specific rates ($M^{-1}\ s^{-1}$) for the $(Mo^V)_2$–Cr^{VI} reaction, obtained from Table III (k_f values) and (4). [e] Parameters obtained from the best fit of integrated forms of (6)–(9) to experimental kinetic curves (see text). Values of k_2 are in s^{-1}; the ratio k_4/k_3 is in M^{-1}. [f] Extinction coefficient of the Cr(IV) complex ($M^{-1}\ cm^{-1}$); 540 nm.

Stop-flow kinetic traces (500–550 nm) of the $(Mo^V)_2$–Cr^{VI} reaction with the reductant in excess show both the growth and destruction of Cr^{IV} (e.g., Figure 2), but here Cr^{IV} is lost via reduction to Cr^{III}. The "downward" portions of such profiles exhibit very little of the exponential character characterizing the late stages of those biphasic curves that result from the combination of first-order processes, and we do not find a more sudden drop often encountered in autocatalytic systems.[20] A large portion of the decay (60–80%) is instead seen to be very nearly linear, indicating that the rate of consumption of Cr(IV) in this region is governed largely by a reaction not involving a chromium species.

We have treated these curves in terms of the sequence (6)–(9) (only oxidation numbers are shown). An essential step, (7), in

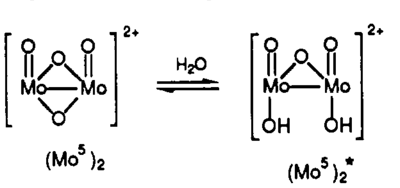
$$Cr^6 + (Mo^5)_2 \xrightarrow{k_1} Cr^4 + 2Mo^6 \qquad (6)$$

$$(Mo^5)_2 \underset{k_3}{\overset{k_2}{\rightleftharpoons}} (Mo^5)_2^* \qquad (7)$$

$$(Mo^5)_2^* + Cr^4 \xrightarrow{k_4} Cr^3 + Mo^5Mo^6 \qquad (8)$$

$$Mo^5Mo^6 + Cr^4 \rightarrow Cr^3 + 2Mo^6 \quad \text{(very rapid)} \qquad (9)$$

the formulated path is the reversible conversion of $(Mo^V)_2$ to an activated form, designated $(Mo^5)_2^*$, a step that appears to intrude also in the redox reactions of $(Mo^V)_2$ with $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$,[23] $IrCl_6^{2-}$,[24] and $Fe(phen)_3^{3+}$,[24] each of which exhibits a prominent oxidant-independent kinetic term. We favor the suggestion by Cayley and co-workers[24] that the active reducing species in such cases is a singly oxo-bridged ion, formed by hydrolytic cleavage of an oxo bridge:



(7′)

A closely related species has recently been proposed as an intermediate in the photochemical decomposition of $(Mo^V)_2$ in aqueous solution.[25]

Expression of eqs 6–9 as differential kinetic equations, application of the steady-state approximation to the active intermediate, $(Mo^5)_2^*$, and utilization of the Runge–Kutta integration procedure were carried out as described.[17] Values of k_1, pertaining to the $(Mo^V)_2$–Cr^{VI} reaction, were taken from reactions with Cr(VI) in excess (Table III), whereas k_2 and the ratio k_4/k_3 were allowed to vary independently. Integration then yielded the concentrations of Cr(VI), Cr(IV), Cr(III), and $(Mo^V)_2$ at 50-ms intervals, and incorporation of the extinction coefficients of the four metal centers gave calculated total absorbances for each point.[26]

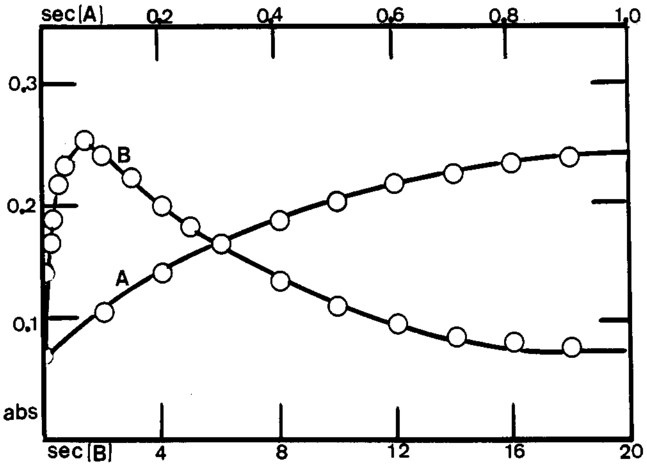


Figure 2. Kinetic profile at 540 nm for the reaction of 8.0×10^{-5} M Cr(VI) with 1.0×10^{-3} M $Mo_2O_4^{2+}$ at 25 °C. The supporting medium was 0.042 M in 2-ethyl-2-hydroxybutanoic acid, 0.042 M in its sodium salt, and 0.46 M in $NaClO_4$; the pH was 3.33. The solid lines are the experimental curves, whereas the circles designate absorbances calculated from integration of the differential kinetic equations (6)–(9) in the text, with k_1 as $1.69 \times 10^3\ M^{-1}\ s^{-1}$, k_2 as $4.5 \times 10^2\ s^{-1}$, and the ratio k_4/k_3 as 0.21 M^{-1}. Extinction coefficients used ($M^{-1}\ cm^{-1}$); Cr^{III}, 42; Cr^{IV}, 1530; Cr^{VI}, 18; $(Mo^V)_2$, 420. Mixing time = 5 ms; optical path length = 2.0 cm.

Values of the parameters k_1, k_2, k_4/k_3, and $\epsilon_{Cr(IV)}$ giving the closest agreement between calculated and observed absorbances appear in Table IV. Calculated absorbances (circles) generated from one set of parameters are compared with the experimental curve in Figure 2. Values of k_2, k_4/k_3, and $\epsilon_{Cr(IV)}$ exhibit no variation with $[H^+]$ or with [Lig⁻] within the (relatively narrow) range examined.

The most novel facet of the present study is the generation of the pink Cr(IV) complex in solutions stable enough to be examined in conventional mixing experiments. There are two keys to this improved stability: (1) The complex must be formed by a 2e⁻ reduction of Cr(VI), rather than by a 1e⁻ reduction of Cr(V), to avoid the rapid 1e⁻ reduction of the Cr(IV) following its generation, and (2) the carboxyl ligand used to stabilize Cr(IV) must be attached to the Cr(VI) reagent prior to the redox process.[27] If, as we propose, the principal Cr(III) product features three coordinating carboxylato groups (two of them partaking in che-

---

(23) Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1939.

(24) Cayley, G. R.; Taylor, R. S.; Wharton, R. K.; Sykes, A. G. *Inorg. Chem.* **1977**, *16*, 1377.

(25) Feliz, M.; Ferraudi, G. *Inorg. Chem.* **1989**, *28*, 4422.

(26) Values of $\epsilon_{Cr(III)}$ and $\epsilon_{Cr(VI)}$ were taken from the final and initial absorbances of the mixture, whereas $\epsilon_{Cr(IV)}$ was allowed to vary during the refinement procedure.

(27) An analogous method has been described for preparation of technetium(V) complexes of α-hydroxy carboxylic acids from TcO_4^-: Columbo, F.; Matarrese, M.; Fazio, F.; Deutsch, E. *Appl. Radiat. Isot.* **1990**, *41*, 221. For a similar conversion of Ru(VII) to a chelated oxoruthenium(V) complex, see: Dengel, A. C.; Griffith, W. P.; O'Mahoney, C. A.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1720.

lation), a similar ligand environment may be inferred for our Cr(IV) complex, for incorporation of these ligands cannot occur after the formation of the (substitution-inert) Cr(III) center.

Note further that the two relatively straightforward bimolecular reactions described here involve complementary redox species. Both participants in the $(Mo^V)_2$–Cr^{VI} reaction undergo $2e^-$ transactions, whereas the partners in the Cr^{IV}–Cr^{VI} reaction change by single units. The $(Mo^V)_2$–Cr^{IV} reaction, featuring a $1e^-$ oxidant and a $2e^-$ reductant, requires preliminary activation of the reductant, leading to the kinetic peculiarities observed for this step.

The ease with which the Cr^{IV}–Cr^{VI} reaction, (10), proceeds is quite unexpected. Formal potentials for Cr^{VI}–Cr^{V} and for

$$Cr^{IV} + Cr^{VI} \rightarrow 2Cr^{V} \qquad (10)$$

Cr^V–Cr^{IV} have been estimated[28] as 0.60 and 1.39 V, respectively, values that have been critically discussed by Linck.[29] Taken in combination, these lead to a highly unfavorable $\Delta E°$ of −0.79 V for (10). Possible variation of these potentials within the pH range 0–3 would be expected to alter the value of $\Delta E°$ but not its sign. The implication here is that chelation with the carboxylate anion employed has stabilized Cr(V) far more effectively than Cr(IV), with the ratio of the association constants of the two complexes exceeding 10^{12}.

Acknowledgment. We are grateful to Dr. R. N. Bose for valuable discussions and to Ms. Arla White for technical assistance.

---

(28) Csanyi, L. J. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1972; Vol. 7, p 510.

(29) Linck, R. G. *Int. Rev. Sci.: Inorg. Chem., Ser. Two* **1974**, *9*, 191.

Contribution from the Department of Chemistry,
Rensselaer Polytechnic Institute, Troy, New York 12180-3590

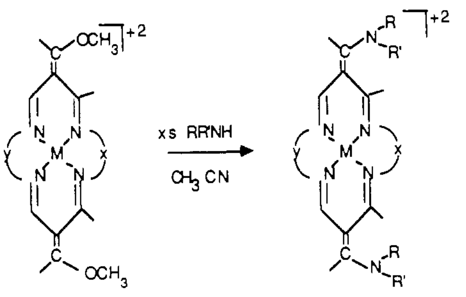
Selective Cleavage of a Vinyl Ether Group from a Nickel(II) Macrocycle Complex and Synthesis of Derivatives

Colin P. Horwitz,* Ralph Navarro, and Gregory C. Dailey

Received November 21, 1989

One of the two vinyl ether moieties is slowly cleaved from the macrocyclic compound $[Ni[(MeOEthi)_2Me_2[14]tetraeneN_4][PF_6]_2$ (**1a**) by dissolving **1a** in methanol to form $[Ni[(MeOEthi)(H)Me_2[14]tetraeneN_4]][PF_6]$ (**3**). The cleavage reaction can be accelerated by addition of aromatic amines, $C_6H_5NH(R)$ (R = H, Me, Et), or sodium alkoxides, NaOR (R = Et, Me), to the methanol solution. Addition of NaOEt to a slurry containing $[Ni[(MeOEthi)_2Me_2[14]tetraeneN_4]][PF_6]_2$ in CH_3OD yields $[Ni[(MeOEthi)(D)Me_2[14]tetraeneN_4]][PF_6]$, as determined by ^1H NMR spectroscopy. Derivative compounds are prepared by the condensation of **3** with either propylamine ($PrNH_2$) or 1-(6-aminohexyl)pyrrole ($PyrHexNH_2$) in CH_3CN to form $[Ni[(PrNHEthi)(H)Me_2[14]tetraeneN_4]][PF_6]$ (**5**) or $[Ni[(PyrHexNHEthi)(H)Me_2[14]tetraeneN_4]][PF_6]$ (**6**), respectively. All compounds were characterized by UV–vis, ^1H NMR, and infrared spectroscopy as well as electrochemistry and elemental analysis.

Reaction of the alkylated Jager macrocycle **1** with a wide variety of primary and secondary amines to form complexes such as **2** (eq 1) has been elegantly demonstrated by Busch and co-workers.[1]



(1)

1 **2**

The excellent reversible dioxygen binding properties exhibited by some of the Fe and Co complexes[2] make them candidates for possible use as O_2 sensors or O_2/N_2 separators if they could be appropriately immobilized.[3] Recently, we have utilized the chemistry shown in eq 1 to append *N*-alkylpyrrole moieties onto the 14-membered Ni(II) macrocycle complex.[4] Polymer films containing the *N*-alkylpyrrole complexes were grown on platinum electrode surfaces through oxidative electropolymerization of the pyrrole groups. Electroactivity was maintained for the Ni center in these films, demonstrating successful immobilization of an intact macrocycle complex.

In order to avoid possible future complications that might arise from chemical and electrochemical properties associated with the polypyrrole backbone, an alternative method was sought for at-

---

(1) (a) Busch, D. H. *Pure Appl. Chem.* **1980**, *52*, 2477. (b) Schammel, W. P.; Zimmer, L. L.; Busch, D. H. *Inorg. Chem.* **1980**, *19*, 3159. (c) Busch, D. H.; Jackels, S. C.; Callahan, R. C.; Grzybowski, J. J.; Zimmer, L. L.; Kojima, M.; Olszanski, D. J.; Schammel, W. P.; Stevens, J. C.; Holter, K. A.; Mocak, J. *Inorg. Chem.* **1981**, *20*, 2834. (d) Busch, D. H.; Olszanski, D. J.; Stevens, J. C.; Schammel, W. P.; Kojima, M.; Herron, N.; Zimmer, L. L.; Holter, K.; Mocak, J. *J. Am. Chem. Soc.* **1981**, *103*, 1472. (e) Korybut-Daszkiewicz, B.; Kojima, M.; Cameron, J. H.; Herron, N.; Chavan, M. Y.; Jircitano, A. J.; Coltrain, B. K.; Neer, G. L.; Alcock, N. W.; Busch, D. H. *Inorg. Chem.* **1984**, *23*, 903. (f) Wolf, V. L.; Jager, E. G. *Z. Anorg. Allg. Chem.* **1966**, *346*, 76.

(2) (a) Stevens, J. C.; Busch, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 3285. (b) Herron, N.; Zimmer, L. L.; Grzybowski, J. J.; Olszanski, D. J.; Jackels, S. C.; Callahan, R. W.; Cameron, J. H.; Christoph, G. G.; Busch, D. H. *J. Am. Chem. Soc.* **1983**, *105*, 6585. (c) Herron, N.; Cameron, J. H.; Neer, C. G.; Busch, D. H. *J. Am. Chem. Soc.* **1983**, *105*, 298. (d) Meade, T. J.; Takeuchi, K. J.; Busch, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 725. (e) Herron, N.; Dickerson, L.; Busch, D. H. *J. Chem. Soc., Chem. Commun.* **1983**, 884. (f) Herron, N.; Chavan, M. Y.; Busch, D. H. *J. Chem. Soc., Dalton Trans.* **1984**, 1491. (g) Goldsby, K. A.; Beato, B. D.; Busch, D. H. *Inorg. Chem.* **1986**, *25*, 2342. (h) Cameron, J. H.; Kojima, M.; Korybut-Daszkiewicz, B.; Coltrain, B. K.; Meade, T. J.; Alcock, N. W.; Busch, D. H. *Inorg. Chem.* **1987**, *26*, 427.

(3) (a) Murray, R. W. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1984; Vol. 13, p 191. (b) Swalen, J. D.; Allara, D. L.; Andrade, J. D.; Chandross, E. A.; Garoff, S.; Israelachvili, J.; McCarthy, T. J.; et al. *Langmuir* **1987**, *3*, 932.

(4) Horwitz, C. P. *Chem. Mater.* **1989**, *1*, 463.

0020-1669/90/1329-4262$02.50/0