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Electron Transfer. 100. Iron-Catalyzed Reduction of Peroxide-Bound Chromium(IV) with Mercapto Acids[1]

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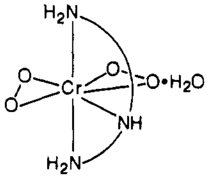
Mercapto carboxylic acids reduce the diperoxochromium(IV) derivative of diethylenetriamine, $Cr^{IV}(dien)(O_2)_2$ (chelate I), slowly in acetate buffers, but the reaction is dramatically catalyzed by dissolved iron. With both mercaptoacetic acid and cysteine, the observed stoichiometry ($RSH:Cr^{IV}$) approaches 5:1. Both Cr(IV) and the peroxo groups are reduced, forming Cr(III) and the dithio acids (R_2S_2). The Cr(III) products contain both acetate and chelating mercapto carboxylate groups, with the ratio of the competing carboxylato ligands dependent on the composition of the reaction medium; Cr(III) spectra indicate predominant O,S-chelation with mercaptoacetate but O,N-chelation with cysteine. Iron exists principally as Fe^{III} in these systems, and its reduction to Fe^{II}, via strongly absorbing Fe^{III}–thiol complexes (in the absence of Cr^{IV}), is too slow to allow a significant catalytic role for Fe^{II} in our reactions. The catalyzed reduction by excess mercaptoacetate is first order in dissolved iron and is accelerated by acetate but exhibits a rate independent of [RSH] at concentrations of the latter greater than 5×10^{-5} M. The rate law accommodates a rapid formation of an Fe^{III}–thiol complex ($K > 10^{5.6}$ M^{-1}), which undergoes electron transfer to Cr(IV) ($k = 1.9 \times 10^3$ M^{-1} s^{-1}), yielding an $RS^{\bullet}$ radical (which dimerizes) and a Cr(III)–peroxo complex (which is quickly reduced). Acceleration by acetate is attributed to partial conversion to an $Fe^{III}(SR)(OAc)$ complex, which is somewhat more active than $Fe^{III}(SR)$. The rate law for reduction by L-cysteine (eq 13) is likewise consistent with a reaction involving an $Fe^{III}(SR)$ species, but the kinetic picture here is complicated by incomplete formation of this complex ($K = 34$ M^{-1}) and by partial dimerization of $FeOH^{2+}$ in our solutions. The incorporation of acetate and mercapto carboxylate groups into the Cr(III) products is believed to arise from the intervention, during the reduction of bound peroxide, of a Cr^{III}–$O^{\bullet}$ transient, which is rapidly protonated to a substitution-labile Cr^{IV}–OH intermediate. Inhibition of redox by 10^{-3} M EDTA suggests that chelation of Fe^{III} by the reductant is necessary for catalytic action and that the reduction of Fe^{III} by unidentate-bound mercapto acid is too slow to sustain a catalytic path entailing recycling between Fe^{II} and Fe^{III}.

Tetrapositive chromium (Cr^{IV}) is generally considered to be an atypical oxidation state, but it may be markedly stabilized through ligation by peroxo anions in conjunction with various nitrogen-containing donors. Among the known diperoxochromium(IV) complexes,[2] the derivative of diethylenetriamine (chelate I)[2bc] is particularly robust and presents minimal problems in its preparation and storage.



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This complex reacts rapidly with a number of metal ion reductants.[3] Of these, VO^{2+} reduces only the Cr(IV) center,[3a] whereas Ti(III), $(Fe^{II})_{aq}$, and $Fe(CN)_6^{4-}$ reduce the peroxo groups as well. Nonmetal-derived reductants (e.g., hydrazine, hydroxylamine, ascorbic acid, and arenediols) tend to react much more slowly,[3b,4] but certain of these reactions are strikingly accelerated by traces of Cu(II), Fe(II), or Fe(III).[4]

The present report describes the reductions of the diperoxochromium(IV) chelate I with the thio acids mercaptoacetic acid (II) and L-cysteine (III) as catalyzed by Fe(II). Although these

$HSCH_2COOH$ $HSCH_2CH(NH_3^+)COO^-$

II III

–SH species are related structurally, the kinetic patterns governing their reactions exhibit instructive differences in detail.

Experimental Section

Materials. Diperoxo(diethylenetriamine)chromium(IV) hydrate, $Cr(dien)(O_2)_2 \cdot H_2O$ (chelate I), was prepared as described by House and Garner.[2b,d] This complex, which precipitated from aqueous solution, was washed with methanol at 0 °C and then dried over P_2O_5 for 12 h.

Table I. Stoichiometries of the Reactions of $(dien)Cr^{IV}(O_2)_2$ with Mercapto Acids[a]

reductant	amt, mmol Cr^{IV}	amt, mmol reductant	$\Delta[red]/\Delta[Cr^{IV}]$
mercaptoacetic acid[b]	0.100	0.703	5.30
	0.151	1.114	5.13
cysteine[c]	0.0070	0.0351	5.0
	0.0035	0.0180	5.1
	0.0100	0.0498	4.98
thiosalicylic acid[b]	0.097	0.542	5.0
thiolactic acid	0.151[b]	0.509	2.54
	0.109[b,d]	0.703	2.59
	0.0035[c]	0.0086	2.4

[a] Reactions, catalyzed by Fe^{2+} (2×10^{-5} M), were carried out in 0.2 M $HOAc–OAc^-$ buffers (pH 4.7); $\mu = 0.25$ M ($LiClO_4$). [b] Excess reductant estimated by titration with I_3^- (see text). [c] Spectrophotometric titration at 382 nm (see text). [d] Mercapto compound was taken as its sodium salt (twice recrystallized).

Warning! A sample of this peroxo compound exploded violently when touched with a metal spatula on a sintered-glass surface. Later preparations were carried out, without incident, on a scale less than 500 mg, and manipulations were performed with a plastic spatula.

Lithium perchlorate (used, after two recrystallizations, in kinetic experiments) was prepared by the method of Dockal.[5] Cation-exchange resin (Dowex 50-X8, 400 mesh, H^+ form) was pretreated as described[6] and was converted to its Na^+ form by washing with saturated $NaHCO_3$. The mercapto acids, mercaptoacetic acid (II) and cysteine (III) (Aldrich products), were used as received; concentrations of these reagents were checked iodometrically. Solutions of $(NH_4)_2Fe(SO_4)_2$ were prepared and stored in the dark; Fe(II) content was confirmed by titration with standard $Cr_2O_7^{2-}$ using diphenylamine as an indicator.[7] Solutions of $Fe(ClO_4)_3$ (Alfa Chemical) were standardized iodometrically. All reactions were carried out in distilled water that had been vigorously boiled and then sparged with O_2-free nitrogen for 4 h before use.

Stoichiometric Studies. Stoichiometries of the reductions of the $Cr^{IV}(O_2)_2$ complex I with excess thio acids were determined by carrying out the reactions in buffered solutions that were 0.1 M each in acetic acid and its anion in the presence of 1.0×10^{-5} M Fe^{2+}. After 30 min, the unreacted thio acid was titrated with standard KI_3. In addition, a number of runs wre carried out with Cr(IV) in excess, using a spectropho-

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(1) Joint sponsorship of this work by the National Science Foundation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

(2) See, for example: (a) Hoffman, K. A. *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 3181. (b) House, D. A.; Garner, C. S. *Nature* **1965**, *208*, 776. (c) Stomberg, R. *Ark. Kemi* **1965**, *24*, 47. (d) House, D. A.; Garner, C. S. *Inorg. Chem.* **1966**, *5*, 840. (e) House, D. A.; Hughes, R. G.; Garner, C. S. *Inorg. Chem.* **1967**, *6*, 1077.

(3) (a) Ghosh, S. K.; Laali, K.; Gould, E. S. *Inorg. Chem.* **1988**, *27*, 4224. (b) Ghosh, S. K.; Gould, E. S. *Inorg. Chem.* **1988**, *27*, 4228.

(4) Ghosh, S. K.; Gould, E. S. *Inorg. Chem.* **1989**, *28*, 1538, 1948.

(5) Dockal, E. R.; Everhart, E. T.; Gould, E. S. *J. Am. Chem. Soc.* **1971**, *93*, 5661.

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

(7) Pierce, W. C.; Haenisch, E. L. *Quantitative Analysis*, 3rd ed.; Wiley: New York, 1948; p 259.

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Table II. Chromium(III) Fractions from Reactions of (dien)$Cr^{IV}(O_2)_2$ with Mercapto Acids[a]

[RSH], M	[OAc^-], M	eluant[b]	ϵ_1[c]	λ_1[c]	ϵ_2	λ_2	RSH/Cr^{III}[d]	% Cr[e]
			A. Mercaptoacetic Acid Reactions					
0.10	0.10	water	64 (60)	526 (519)	52 (43)	391 (393)	[f]	52
		$NaClO_4$	75 (72)	527 (520)	56 (42)	392 (390)	0	49
0.20	0.05	water	109 (76)	528 (515)	95 (59)	396 (388)	[f]	52
		$NaClO_4$	81 (70)	528 (517)	71 (53)	397 (389)	0.48	38
0.50	0.10	water	156 (81)	532 (514)	133 (58)	403 (389)	[f]	77
		$NaClO_4$	88 (90)	529 (518)	155 (88)	395 (391)	1.28	6
			B. Cysteine Reactions					
0.060	0.50	water	75 (60)	535 (532)	61 (50)	397 (397)	[f]	54
		$NaClO_4$	77 (72)	523 (523)	52 (47)	387 (390)	0.13	37
0.50	0.10	water	96 (96)	517 (512)	73 (69)	382 s[g] (382)	[f]	22
		$NaClO_4$	94 (95)	532 (535)	102 (92)	400 s (382)	1.85	69

[a] Reactions were carried out in 1:1 mixtures of HOAc and NaOAc; [Cr^{IV}] = 0.01–0.02 M; [Fe^{II}] = 1 × 10^{-5} M throughout. [b] Fractions eluted from Dowex 50-X8, 400 mesh (Na^+), by using water or 0.5 M $NaClO_4$. [c] Maxima (λ values) are in nm; apparent ϵ values are in M^{-1} cm^{-1}. Parenthetical values refer to spectra recorded just after acidification with 0.1 M $HClO_4$. [d] Bound RS–determined iodometrically (see Experimental Section). [e] Percent of Cr(IV) taken. [f] Ratio could not be determined (see footnote 9). [g] s = shoulder.

tometric titration at 382 nm (λ_{max} for Cr^{IV}). For these determinations successive known quantities of reductant were added to measured quantities of Cr(IV) in the presence of 10^{-5} M Fe^{2+}. Plots of absorbance vs added reductant showed sharp break points near [red]/[Cr^{IV}] = 5.0 for reaction with cysteine but near 2.5 for reaction with thiolactic acid.

Detectable quantities of gas were not liberated in these reactions. Moreover, addition, at the conclusion of the reactions, of the enzyme catalase (0.5 mg/mL of solution), which catalyzes the disproportionation of H_2O_2 and some of its complexes, released no O_2.

Stoichiometric results are summarized in Table I.

Examination of the Cr(III) Reaction Products. Reaction mixtures were 0.008–0.02 M in Cr(IV) and 10^{-5} M in Fe^{2+}, were buffered with HOAc–OAc^-, and contained a 3–20-fold excess of thio acid. The mixtures were allowed to react for 20 min at room temperature and then subjected to ion-exchange chromatography[8] at 2 °C. In each case, two fractions were obtained. The first was eluted with water alone, and the second with 0.50 M $NaClO_4$. Chromium-bound mercapto acid in the $NaClO_4$ eluate was estimated by acidifying with 0.1 M H_2SO_4, waiting for 20 min, and then titrating the thiol with standard KI_3.[9] The distribution of chromium between the two eluted fractions varied with the ratio of mercapto acid reagent to acetate buffer in the reaction mixture. Spectral characteristics also depended on this ratio, indicating that these fractions, at least in some cases, consisted of mixtures of complexes. Attempts to effect more complete separations were unsuccessful despite several modifications of technique. In the case of the mercaptoacetic acid reductions (but not those with cysteine), acidification of those fractions eluted with water generally shifted absorbance peaks immediately to lower wavelengths with attendant decreases in molar absorbances. Spectra of products from representative reductions by both thio acids are described in Table II. Recovery of total chromium was 83–99%.

Oxidation Products. The principal organic product from oxidation of mercaptoacetic acid was shown to be the dithio acid $(HOOCCH_2S)_2$ by extraction of the acidified reaction mixture with ether, drying the ether extracts with anhydrous Na_2SO_4, and then evaporating the ether. The IR spectrum of the residue (Nujol mull) corresponded to that of the known dithio acid. The oxidation product from cysteine exhibited an absorption maximum at 244 nm, as does a buffered solution of the corresponding dithio acid, cystine. Moreover, acidification of the reaction mixture (pH 2) precipitated the latter acid, the IR spectrum of which was identical with that of an authentic sample.

Kinetic Measurements. Rates were evaluated from changes in absorbance at 382 nm by using a Cary 14 or Beckman Model 5260 recording spectrophotometer. Ionic strength was fixed by addition of $LiClO_4$. Reactions were carried out with the reductant in greater than 10-fold excess. Conversions were followed to at least 98% completion. All reactions were first order in Cr(IV), and rate constants from successive half-lives generally agreed to within 6%. Average values did not differ significantly from those obtained from logarithmic plots of absorbance differences against reaction time. Specific rates from replicate runs agreed to better than 8%. The catalyzed reduction of Cr^{IV}(dien)$(O_2)_2$ by thiolactic (α-mercaptopropionic) acid gave reproducible exponential kinetic curves, but stoichiometric peculiarities were associated with this transformation (Table I). In contrast, reduction by thiosalicylic (2-mercaptobenzoic) acid exhibited straightforward 5:1 stoichiometry, but its reactions yielded traces with at least three kinetic components.

The reductions of Cr^{IV}(dien)$(O_2)_2$, both by mercaptoacetic acid and by cysteine, are catalyzed by Cu^{2+} and by VO^{2+} (although these catalysts are less effective than $Fe^{2+/3+}$); additional study of these catalytic systems is in progress. Additions of Ni^{2+}, Mn^{2+}, MoO_4^{2-}, Co^{2+}, Eu^{3+}, Zn^{2+}, or $Ru(NH_3)_6^{3+}$ (each at the 10^{-4} M level) were without catalytic effect.

The reaction of Fe(III) with excess mercaptoacetate, which is related to the catalytic system of primary interest, was examined briefly by using stop-flow spectrophotometry. This reaction, which was carried out in acetate buffer, featured the formation and decay of a blue species having a broad maximum near 575 nm. The resulting biphasic kinetic traces, taken at this wavelength, were separated into contributing pseudo-first-order processes as described by Bose.[10] Specific rates for both components (Table IV) were proportional to mercaptoacetate concentrations.

Results and Discussion

Our stoichiometric determinations (Table I) indicate that under the reaction conditions employed very nearly five molecules of mercaptoacetic acid or cysteine are consumed by each molecule of the diperoxochromium(IV) complex (I). No detectable O_2 is released. The overall conversion with these reductants may then be represented as (1).[11-13] This stoichiometry is in accord with

$$10RSH + 2Cr^{IV}(dien)(O_2)_2 + 6H^+ \rightarrow 5R_2S_2 + 2(dien)Cr^{III} + 8H_2O \quad (1)$$

the identification of the oxidation product as the corresponding dithio acid, R_2S_2, from both thiols.

The variable spectral properties (Table II) of the Cr(III)-containing fractions from reductions by both mercaptoacetic acid and cysteine indicate that we are dealing, at least in part, with mixtures of Cr(III) products. Values of λ_{max} for all fractions (517–532 and 380–397 nm) are well below those for aquo- and carboxylato-substituted Cr(III) complexes,[14] pointing to coordination by the N-donor functions of diethylenetriamine.[15] As

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(8) Separations were carried out with a 5-cm column, capacity 2 mequiv. For estimation of molar absorbances of Cr(III) products, aliquots were oxidized with basic H_2O_2, and the total chromium content was determined as chromate. (See, for example: Haupt, G. W. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1952**, *48*, 414.)

(9) This determination could not be extended to those fractions eluted with water alone, for these contained unreacted mercapto acid.

(10) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2832.

(11) Also included (for comparison) in Table I are stoichiometries of reductions by thiolactic and thiosalicylic acids. Despite its structural similarity to mercaptoacetic acid, thiolactic acid is seen to react with Cr^{IV}(dien)$(O_2)_2$ in a 5:2 molar ratio, irrespective of the reagent taken in excess, implying oxidation to the sulfenic acid (RSOH) level, even with Cr(IV) in deficiency (eq 2). Although an analogous oxidation by

$$5RSH + 2Cr^{IV}(O_2)_2 + 6H^+ \rightarrow 5RSOH + 2Cr^{III} + 3H_2O \quad (2)$$

a substituted oxaziridine has been reported,[12] this conversion must be considered highly unusual in view of the ease with which sulfenic acids are known to react with substituted thiols.[13] Reduction of the Cr(IV) chelate I by thiosalicylic acid, although stoichiometrically clean, appeared to be kinetically complex. Neither of these reactions was pursued.

(12) Davis, F. A.; Billmers, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 7016.

(13) See, for example: Kice, J. L. *Adv. Phys. Org. Chem.* **1980**, *17*, 65.

(14) Garner, C. S.; House, D. A. *Transition Met. Chem.* (*N.Y.*) **1970**, *7*, 59 (Table 12).

Table III. Kinetic Data for the Reduction of $Cr^{IV}(dien)(O_2)_2$ with Mercaptoacetic Acid (RSH) As Catalyzed by Fe(II)[a]

$10^4[Cr^{IV}]$, M	10^3[RSH], M	$10^6[Fe^{II}]$, M	$[OAc^-]$, M	10^2k,[b] s^{-1}
0.050	0.050	2.5	0.050	0.58 (0.62)
0.20	0.20	2.5	0.050	0.67 (0.62)
0.20	0.80	10.0	0.050	2.3 (2.5)
2.0	2.0	10.0	0.050	2.5 (2.5)
2.0	16.0	10.0	0.050	2.7 (2.5)
2.0	4.0	1.00	0.050	0.28 (0.24)
2.0	4.0	2.5	0.050	0.67 (0.62)
2.0	4.0	5.0	0.050	1.36 (1.24)
2.0	4.0	10.0	0.050	2.7 (2.5)
2.0	4.0	25	0.050	6.4 (6.2)
2.0	4.0	50	0.050	11.0 (12.4)
4.0	8.0	10.0	0.050	2.7 (2.5)
2.0	8.0	10.0	0.100	3.4 (3.0)
2.0	8.0	10.0	0.30	4.8 (5.2)
2.0	8.0	10.0	0.40	6.7 (6.2)
2.0	8.0	10.0	0.10[c]	3.4 (3.0)
2.0	8.0	10.0	0.10[d]	3.2 (3.0)
2.0	4.0	10.0[e]	0.050	2.3 (2.5)
2.0	4.0	10.0	0.050	0.005[f]

[a] Reactions were carried out at 25 °C in $HOAc-OAc^-$ buffers; μ = 0.50 M ($LiClO_4$). The pH was 4.42 ± 0.03 unless otherwise indicated. [b] Pseudo-first-order specific rates, $-d \ln [Cr^{IV}]/dt$; parenthetical values calculated from eq 3 in text, taking a as 1.94×10^3 M^{-1} s^{-1} and b as 1.07×10^5 M^{-2} s^{-1}. [c] pH = 5.01. [d] pH = 3.84. [e] Catalyst added as $Fe(ClO_4)_3$. [f] Na_2H_2EDTA (0.001 M) added.

in earlier studies,[3,4] this ligand, when tridentate, is considered to take the 1,2,6-positions of the octahedron about Cr(III), with the two ligating NH_2's trans to each other, a configuration allied to the preferred structure (I) of the peroxychromium(IV) reactant. The ion-exchange characteristics of the more slowly moving products correspond to those of unipositive ions whereas those fractions eluted with water alone may be reasonably taken as uncharged complexes. The high extinction coefficients of the products formed when the reductant is in greatest excess point to chelation by the thio acids, in addition to ligation by the triamine.

For the reductions with mercaptoacetic acid, maxima associated with the principal product fraction are seen to drift to lower energies as the ratio $[RSH]/[OAc^-]$ in the system increases, suggesting a competition between acetate and the thiol donor (the latter with the weaker ligand field[16]) for the coordination positions on chromium. The rapid shifts, upon acidification, to lesser wavelengths are attributed to aquation of the Cr(III)–S bond and indicate that the lability of this bond in our systems is comparable to those in other carboxylato-substituted species[17] but greater than that in $(en)_2Cr^{III}$ or $(H_2O)_5Cr^{III}$ systems.[16,18] These shifts are accompanied by marked decreases in molar absorbances.

With cysteine reductions, ligand field peaks for Cr(III) migrate instead to higher energies with increased concentration of reductant, despite the perceived increased incorporation of thio units. Here, it is likely that chelation by the thio acid mainly involves the α-NH_2 group, rather than the β-SH function. In accord with this difference, spectral shifts on acidification are somewhat less than those observed for the mercaptoacetate products. The predominant product at very high cysteine concentrations, which appears to contain two sulfur atoms per chromium, is positively charged, reflecting coordination of this thio acid as a uninegative, rather than a dinegative, ligand.

Kinetic data for the iron-catalyzed reduction by mercaptoacetic acid are summarized in Table III. Reactions are first order in Cr(IV) and are seen to be first order in added iron as well. Rates are independent of pH within the (relatively narrow) range 3.8–5.0 and are enhanced modestly by acetate. There is no significant dependence on [reductant] within the range 0.000 05–0.016 M. Reduction rates conform to eq 3. Refinement of the rate data

$$\text{rate} = [Cr^{IV}][Fe]_{\text{added}}(a + b[OAc^-]) \qquad (3)$$

yields the kinetic parameters $a = (1.94 \pm 0.16) \times 10^3$ M^{-1} s^{-1} (pertaining to the acetate-independent term) and $b = (1.07 \pm 0.17) \times 10^5$ M^{-2} s^{-1} (for the acetate-proportional component). Observed rates are compared with those calculated by (3) in the same table.

The ratio of Fe(III) to Fe(II) in our solutions depends upon the relative rates of two redox transformations. The first is the reaction of $Cr^{IV}(dien)(O_2)_2$ with Fe(II), for which a bimolecular specific rate 4×10^3 M^{-1} s^{-1} (25 °C) has been reported in this medium.[4] The second is the reduction of Fe(III) by mercaptoacetate, which has been found to involve an intermediate (λ_{max} 575 nm).

Kinetic data for the appearance and consumption of this blue transient appear in Table IV. Its loss is taken to reflect the reduction of Fe^{III} to Fe^{II}. The formation of this species (k_1) is, as expected, first order in mercapto acid, as is the case also for its decay (k_2).[19,20] The latter dependence implies that destruction of the complex occurs by bimolecular attack on the Fe(III)–mercaptide adduct by a second unit of reductant, a situation analogous to that observed in the Fe(III)–ascorbate system.[4] This reduction appears to entail an additional act of ligation, for like the formation of the blue complex, it is seen to be inhibited by added acetate.[21] The latter anion presumably competes with mercaptoacetate for coordination positions on Fe(III).[22] The data for this sequence assure us that dissolved iron exists predominantly as Fe(III) after the first few seconds of reaction, since the specific rate of oxidation of Fe(II) greatly exceeds that for reduction of Fe(III). As anticipated, added Fe(III) is found to be catalytically equivalent to Fe(II) (Table III). In the pH range examined, noncomplexed Fe(III) exists predominantly as $FeOH^{2+}$, rather than $(Fe^{3+})_{aq}$ (pK_A 3.0).

The rate of the catalyzed Cr(IV)–mercaptoacetate reaction is found to be independent of [RSH] at concentrations of the latter greater than 5×10^{-5} M. We may thus infer that we are dealing with the region of kinetic saturation. Conversion of over 95% of the catalyst to such a complex in this concentration region implies a formation constant greater than $10^{5.6}$ M^{-1}. However, the catalytically active Fe^{III} intermediate is not the blue species seen in our Cr(IV)-free reactions. The observed blue complex is formed at a rate proportional to [RSH] and is subject to inhibition by acetate. In contrast, the rate of the catalyzed reaction is independent of [RSH] (in the concentration range examined) and is enhanced by acetate.

These experiments thus provide evidence for three mercaptoacetate complexes. The first, formed rapidly and (under our conditions) nearly completely, is catalytically active, whereas the blue complex (the growth of which dominates the stop-flow profiles in the absence of Cr^{IV}) and the thiol-ligated intermediate inter-

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(15) 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*, 4679.

(16) Weschler, C. J.; Deutsch, E. *Inorg. Chem.* **1973**, *12*, 2682.

(17) Ghosh, S. K.; Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1987**, *26*, 3722.

(18) Ardon, M.; Taube, H. *J. Am. Chem. Soc.* **1967**, *89*, 3661.

(19) The assignment of rate constants to components in such biphasic systems is recognized to be ambiguous.[20] In this instance, the larger rate is assigned to the initial step since the alternative choice results in extinction coefficients greatern than 10^4 M^{-1} cm^{-1} for the blue intermediate. This value appears to be exceptionally large for electronic transitions of inorganic complexes of nonaromatic ligands in this spectral region.

(20) See, for example: Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; Chapter 4.

(21) The (limited) array of values for k_1 and k_2 in Table IV conform to eq 4. Refinements in terms of (4) yield limiting specific rates (k_{lim}) of

$$k_{obsd} = \frac{k_{lim}[RSH]}{1 + K_{OAc} - [OAc^-]} \qquad (4)$$

$(2.46 \pm 0.19) \times 10^3$ and $(5.3 \pm 1.7) \times 10^2$ M^{-1} s^{-1} for k_1 and k_2, as well as acetate association constants (K_{OAc^-}) of 11 ± 1 and 35 ± 20 M^{-1} for the two stages of ligation. The high uncertainty in the latter parameter beclouds its significance.

(22) The decrease in the apparent extinction coefficient of the blue intermediate as $[OAc^-]$ in the generating solution is raised (Table IV) also points to a competition between acetate and mercaptoacetate for coordination sites in the Fe(III) center.

Table IV. Reaction of Fe(III) with Mercaptoacetic Acid (RSH): Formation and Decay of the Fe(III)–Mercaptoacetate Complex (λ_{max} 575 nm)[a]

10^3[RSH], M	[HOAc], M	[OAc^-], M	pH	k_1, s^{-1} [b]	k_2, s^{-1} [b]	$10^2\epsilon$ [c]
2.0	0.05	0.05	4.44	3.2	0.35	13.7
8.0	0.05	0.05	4.42	11.8	1.46	14.1
8.0[d]	0.05	0.05	4.43	13.3	1.51	11.5
2.0	0.10	0.10	4.40	2.4	0.27	5.1
2.0	0.20	0.20	4.39	1.51	0.126	3.8
2.0	0.40	0.40	4.42	0.91	0.063	2.7
2.0	0.025	0.10	5.05	2.3	0.29	5.2
2.0	0.050	0.10	4.74	2.7	0.31	4.9

[a] Reactions were carried out at 24 °C in $HOAc–OAc^-$ buffers; μ = 0.50 M ($LiClO_4$). [Fe^{III}] = 2×10^{-4} M unless otherwise indicated. Conversions were monitored at 575 nm; optical path length = 2.0 cm. [b] Pseudo-first-order specific rates for formation (k_1) and decay (k_2) of blue transient (see text). [c] Extinction coefficient of intermediate (in M^{-1} cm^{-1}). [d] [Fe^{III}] = 4×10^{-4} M.

vening in the subsequent reduction to Fe(II) are both formed too slowly to play a significant catalytic role in the overall conversion. Formulation of these as mono-, di-, and triligated species appears to be consistent with, although not demanded by, our observations. The high formation constant for the catalytically active complex (formulated here as 1:1) suggests chelation. Moreover, the position of the low-energy absorption maximum of the blue complex (575 nm, diagnostic of Fe(III)–S coordination) points to a chelated structure for this species (proposed to be a 2:1 complex), and for the third complex (which features one additional unit of ligand) as well. We are not able to record the spectrum of the catalytically active complex, which is formed and consumed rapidly.

Rate law 3 indicates the operation of two catalytic paths, the first involving the Fe(III)–SR complex as such and the second utilizing a somewhat more active species in which acetate has replaced an Fe(III)-bound water. In analogy with the known $Cr^{IV}(O_2)_2–VO^{2+}$ reaction,[3a] we assume reduction of the Cr^{IV} center to precede reduction of peroxide. Moreover, it is probable that the peroxide function is reduced mainly as a Cr(III)-bound species, rather than being liberated as H_2O_2, for the recognized substitution-inert character of the Cr(III) center (including that in reported Cr(III)–peroxy complexes[23]) implies that the aquation of a peroxychromium(III) intermediate will be much slower than the catalyzed reaction of principal interest. Since kinetic profiles offer no hint that a Cr(III)–peroxide intermediate accumulates, peroxide reduction is taken to proceed in two or more rapid steps following rate-determining electron transfer to chromium.

The sequence we favor is represented schematically by eq 5–12,

$$Fe^{II} + Cr^{IV}(O_2)_2 \rightarrow Fe^{III} + Cr^{III}(O_2)_2^- \quad k = 4 \times 10^3\ M^{-1}\ s^{-1} \qquad (5)$$

$$(Fe^{III})_{aq} \rightleftharpoons FeOH^{2+} + H^+ \qquad pK_A = 3.0 \qquad (6)$$

$$FeOH^{2+} + RSH \rightleftharpoons Fe^{III}(SR^-) + H_2O \qquad K_{RS} > 10^{5.6} \qquad (7)$$

$$Fe^{III}(SR^-) + Cr^{IV}(O_2)_2 \rightarrow Fe^{III} + RS^\bullet + Cr^{III}(O_2)_2^- \quad k = 1.9 \times 10^3\ M^{-1}\ s^{-1} \qquad (8)$$

$$Fe^{III}(SR^-) + OAc^- \xrightleftharpoons{K_{OAc}} Fe^{III}(SR^-)(OAc^-) \qquad (9)$$

$$Fe^{III}(SR^-)(OAc^-) + Cr^{IV}(O_2)_2 \xrightarrow{k'} Fe^{III}(OAc^-) + RS^\bullet + Cr^{III}(O_2)_2^-$$

$$K_{OAc}k' = 1.1 \times 10^5\ M^{-2}\ s^{-1} \qquad (10)$$

$$2RS^\bullet \rightarrow R_2S_2 \quad \text{(rapid)} \qquad (11)$$

$$Cr^{III}(O_2)_2^- + 4RS^- + 8H^+ \rightarrow\rightarrow Cr^{III} + 4H_2O + 2R_2S_2 \quad \text{(rapid)} \qquad (12)$$

with reaction 5 contributing to the Fe(II)-catalyzed reaction only during the first few seconds after mixing. Note that the parameter b in eq 3 (pertaining to the acetate-dependent path) corresponds to the product $K_{OAc}k'$ associated with reactions 9 and 10. Individual values for the contributing constants cannot be obtained from our data. The source for this acetate-related enhancement is uncertain, but it must be, at least in part, electronic, for it may be argued that substitution of basic acetate for bound water on $Fe^{III}(SR^-)$ increases the availability of nonbonding electrons on sulfur, hence facilitating electron transfer to Cr(IV).

The amino group of cysteine (III) interposed between its carboxyl and mercapto functions is converted to $-NH_3^+$ under our reaction conditions. Hence, this reductant would be expected to form less stable complexes with Fe^{III} than does mercaptoacetate. The Fe(III)–cysteine reaction in acidic media has been studied by Jameson and co-workers,[24] who report the formation of a violet complex (λ_{max} 614 nm) and the reduction of Fe(III) by 0.010 M cysteine proceeding at a specific rate of 9.3 s^{-1} (25 °C, pH 4.52), corresponding to a bimolecular rate constant near 900 M^{-1} s^{-1} for this conversion. Since this rate again falls well below that for the $Cr^{IV}(dien)(O_2)_2–Fe(II)$ reaction (4×10^3 M^{-1} s^{-1}), catalytic iron in the cysteine–Cr(IV) system, like that with mercaptoacetate, exists mainly as Fe(III).

Kinetic data for reductions by cysteine appear in Table V. At low concentrations of iron and cysteine, rates are seen to be very nearly proportional to the concentrations of both. At higher concentrations, both dependencies become less steep than that corresponding to unit order. This "leveling off" in the case of cysteine doubtless reflects an approach to complete conversion to an Fe(III)–mercaptide complex, whereas the departure from linearity with iron may be attributed to partial conversion of this center to an inactive dimeric species, a complication similar to that thought to intrude in the iron-catalyzed $Cr^{IV}(O_2)_2–NH_3OH^+$ reaction.[3b] Partition of the catalyst between the rapidly interconverted forms $FeOH^{2+}$, $Fe_2(OH)_2^{4+}$, and $Fe^{III}(SR^-)$ (of which only the third is active) generates rate law 13 (see Appendix),

$$\text{rate} = k[Cr^{IV}]K_A[RSH] \times \{\sqrt{(K_A[RSH] + 1)^2 + 8K_D[Fe]_T} - K_A[RSH] - 1\}/4K_D \qquad (13)$$

where K_A is the apparent formation constant for the catalyst–reductant complex, K_D is the dimerization constant for Fe^{III}, and $[Fe]_T$ is the total concentration of added iron. Refinement of our kinetic data in terms of (13) yields $k = (2.8 \pm 0.2) \times 10^3$ M^{-1} s^{-1}, $K_A = 34 \pm 7$ M^{-1}, and $K_D = (1.0 \pm 0.4) \times 10^4$ M^{-1}. Rates calculated by (13) are compared to observed values in Table V.

The preferred sequence for oxidation of cysteine, in conjunction with preequilibria 14 and 15, thus corresponds to that for the

$$2FeOH^{2+} \rightleftharpoons Fe_2(OH)_2^{4+} \qquad K_D = 1 \times 10^4\ M^{-1} \qquad (14)$$

$$FeOH^{2+} + RSH \rightleftharpoons Fe^{III}(SR^-) + H_2O \qquad K_A = 34\ M^{-1} \qquad (15)$$

oxidation of mercaptoacetate, save that acceleration by added acetate is not observed. Here, the Fe(III)–thiol complex is less strongly associated, allowing an estimate of its formation constant from the data at hand. Rate-determining bimolecular reaction of $Fe^{III}(SR^-)$ with Cr^{IV} (eq 8), dimerization of the resulting $RS^\bullet$

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(23) See, for example: Adams, A. C.; Crook, J. R.; Bockhoff, F.; King, E. L. *J. Am. Chem. Soc.* **1968**, *90*, 5761.

(24) Jameson, R. F.; Linert, W.; Tschinkowtiz, A.; Gutmann, V. *J. Chem. Soc., Dalton Trans.* **1988**, 943. For earlier studies of this reaction in more basic media, see: Tanaka, N.; Kolthoff, I. M.; Stricks, W. *J. Am. Chem. Soc.* **1955**, *77*, 1996. Leussing, D. L.; Mislan, J. P.; Goll, R. J. *J. Phys. Chem.* **1960**, *64*, 1070.

Table V. Kinetic Data for the Reduction of $Cr^{IV}(dien)(O_2)_2$ with Cysteine (RSH), As Catalyzed by Fe(II)[a]

[RSH], M	$10^5[Fe^{II}]$, M	10^2k, s^{-1} [b]	[RSH], M	$10^5[Fe^{II}]$, M	10^2k, s^{-1} [b]
0.010	0	0.004 (0)	0.030	4.0	5.5 (4.8)
0.010	0.25	0.20 (0.17)	0.040	4.0	5.7 (5.7)
0.010	0.50	0.40 (0.34)	0.080	4.0	6.8 (7.7)
0.010	1.00	0.72 (0.64)	0.160	4.0	8.9 (9.2)
0.010	2.0	1.32 (1.19)	0.320	4.0	10.0 (10.2)
0.010	4.0	2.0 (2.1)	0.010	4.0	3.7[e] (3.7)
0.010	6.0	3.0 (2.9)	0.010	4.0	1.93[f] (2.1)
0.010	8.0	3.5 (3.6)	0.010	4.0	2.3[g] (2.1)
0.010	10.0	4.2 (4.2)	0.010	4.0	2.1[h] (2.1)
0.010	12.0	4.4 (4.8)	0.010	1.00[c]	0.89
0.010	14.0	4.8 (5.3)	0.010	1.00[d]	0.001
0.020	4.0	3.9 (3.7)			

[a] Reactions were carried out at 25 °C in solutions buffered with 0.050 M each of HOAc and OAc^-; $\mu = 0.25$ M ($LiClO_4$); pH = 4.42 ± 0.02; $[Cr^{IV}] = 0.0010$ M (unless otherwise indicated). [b] Pseudo-first-order specific rates, $-d \ln [Cr^{IV}]/dt$; parenthetical values calculated from eq 13 in text in conjunction with the indicated refined values of k, K_D, and K_A. [c] Catalyst added as $Fe(ClO_4)_3$. [d] Na_2EDTA (0.001 M) added. [e] $[Cr^{IV}] = 0.0020$ M. [f] $[HOAc] = [OAc^-] = 0.20$ M. [g] pH 5.12. [h] pH 4.09.

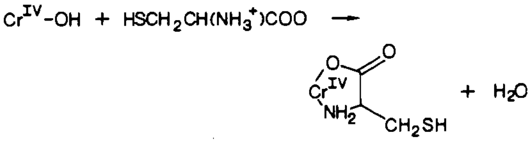
radical (eq 11), and rapid reduction of Cr(III)-bound peroxide (eq 12) are taken to proceed in an analogous manner for the two thiols. Although the specific rate for the initial electron-transfer step (2.8×10^3 M^{-1} s^{-1}) is greater for cysteine, observed rates for this reductant lie below those for mercaptoacetate except at very high thiol concentrations, reflecting incomplete conversion to $Fe^{III}(SR^-)$.

As with the metal-catalyzed $Cr^{IV}(dien)(O_2)_2$–ascorbate reactions,[4] the reductant acid is found to be incorporated into the ligation sphere of Cr(III) in the reaction product(s). Intercession of carboxylate in this manner, which must occur after initial reduction of Cr(IV), probably reflects the intervention, during reduction of bound peroxide, of a Cr^{III}–$O^\bullet$ radical, which undergoes rapid protonation and internal electron transfer to form a Cr(IV)–OH intermediate (eq 16 and 17). Acetate and unreacted mercapto acid may then compete in anation of this substitution-labile[25] transient (eq 18–20), yielding Cr(IV)–carboxylato species, which are ultimately reduced to Cr^{III} derivatives having spectra listed in Table II. Coordination by cysteine (eq 19) leads mainly to an O,N-bound chelate, whereas ligation by mercaptoacetate (eq 20) forms a S,O-bound complex. The latter act should be accompanied by internal electron transfer, yielding a Cr(III)-bound thiyl radical that, in turn, may be reduced further by another (uncomplexed) thiol (eq 21).[26]

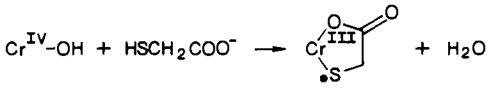
$$Cr^{III}\text{–}OOH + Fe^{II} \rightarrow FeOH^{2+} + Cr^{III}\text{–}O^\bullet \qquad (16)$$

$$Cr^{III}\text{–}O^\bullet + H^+ \rightarrow Cr^{IV}\text{–}OH \qquad (17)$$

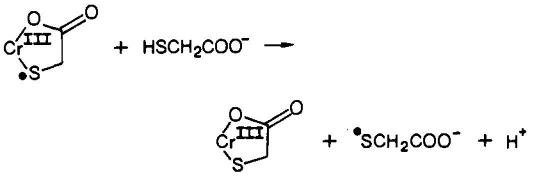
$$Cr^{IV}\text{–}OH + HOAc \rightarrow Cr^{IV}\text{–}OAc + H_2O \qquad (18)$$



(19)



(20)



(21)

Note that the catalytic action of iron in the $Cr^{IV}(O_2)_2$–thiol acid reactions is curtailed by addition of the sequestrant EDTA, whereas in the $Cr^{IV}(O_2)_2$–ascorbate system[4] catalysis survives, although the kinetic patterns are modified. Since recycling between 2+ and 3+ states appears to be catalytically unimportant for both types of reductants in the absence of EDTA, unsequestered Fe(III) may act by polarizing the reductant prior to electron transfer to Cr(IV), a process which probably requires chelation. It is recognized that although EDTA features six donor centers, it occupies, on coordination with the usual transition-metal centers in aqueous solution, only five positions, leaving the sixth bound to water.[27] Thus, donor species can replace Fe(III)-bound water in the Fe(III)–EDTA complex, but additional chelation is no longer favored. Unidentate coordination of Fe(III) to ascorbate allows (inner-sphere) electron transfer, forming the ascorbate radical, for the coordination site lies on the edge of the electronically mobile enolate system of the reductant. With mercapto-subsittuted carboxylates, however, ligation by the negative carboxyl group is preferred, and the latter is insulated from the redox-active thiolate group by the intervening "saturated" fragment. Thus, structural dissimilarities between the two classes of reductants prevent extension of the alternate (slower) Fe(II,III) catalytic mechanism, for which there is evidence in the Fe^{III}(EDTA)-catalyzed ascorbate reaction, to the present mercapto acid systems.

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Appendix. Derivation of Eq 13

The rate-determining step in the Fe(III)-catalyzed reduction of Cr(IV) by RSH is assumed to be the biomolecular reaction of the catalyst–reductant complex, Fe–SR, with the oxidant:

$$\text{rate} = k[FeSR][Cr^{IV}] \qquad (a)$$

Under the conditions used, dissolved iron, $[Fe^{III}]_T$, is taken to be partitioned principally into $FeOH^{2+}$, $(FeOH)_2^{4+}$, and FeSR:

$$[Fe^{III}]_T = [FeSR] + [FeOH^{2+}] + 2[(FeOH)_2^{4+}] \qquad (b)$$

Expression of $[FeOH^{2+}]$ and $[(FeOH)_2^{4+}]$ in terms of the dimerization quotient, K_D (eq 14), the association quotient, K_A (eq 15), and [FeSR], followed by substitution into (b), yields

$$[Fe^{III}]_T = [FeSR] + \frac{[FeSR]}{K_A[RSH]} + \frac{2K_D[FeSR]^2}{K_A{}^2[RSH]^2} \qquad (c)$$

Solving for [FeSR] and substituting into (a) yield (13).

Note that (13) implies a first-order dependence on $[Fe^{III}]_T$ at low concentrations of catalyst, a half-order dependence on $[Fe^{III}]_T$ at high concentrations of catalyst, and a first-order dependence on [RSH] at low concentrations of reductant but implies a rate independent of [RSH] at high concentrations of reductant.

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

(26) Electron transfer constituting step 21 should proceed in the direction indicated, for attachment of a tripositive chromium center to the thiyl radical will make it a more effective oxidant than the unbound radical, $RS^\bullet$.

(27) See, for example: (a) Hoard, J. L.; Kennard, C. H. L.; Smith, G. S. *Inorg. Chem.* **1963**, *2*, 1316. (b) Gerdom, L. E.; Baenziger, N. A.; Goff, H. M. *Inorg. Chem.* **1981**, *20*, 1606.