electrochemically oxidized in the OTTLE, $[Co^{III}TrNPc(-2)]_4^{4+}$ is formed directly from Co(I), as in the case of the mononuclear complex.[58] Thus, solutions containing 100% Co(I) or 100% Co(III) are readily obtainable from Co(II) via the hydroxide disproportionation reaction.

The tetranuclear disproportionation reaction is particularly interesting since there is effectively an eight-electron transfer between the Co(I) and Co(III) states. Hence, the possibility exists to utilize this feature in the form of a multielectron redox catalyst. This was investigated by preparing thin films of Co(I)/Co(III), irradiating under vacuum to give Co(I), and reacting with a number of degassed reagents under vacuum. The films reacted with solutions of H_3O^+ (aqueous HCl) and CO_3^{2-} (aqueous Na_2CO_3–NaOH) and slowly with SO_3^{2-} (aqueous Na_2SO_3–NaOH) to give $[Co^{II}TrNPc(-2)]_4$, with no obvious increase in efficiency relative to that of the mononuclear species.[58] Under the conditions used (see the Experimental Section), the quantum yields were obviously very small (<0.1%) and so the products (probably hydrogen, formate ion, and sulfur) were not pursued. Our concern here was to identify a multielectron redox reaction, but the above reactions probably proceed through one-electron pathways, since mononuclear Co^{II}TNPc is equally effective.

However, in addition, a reaction was also seen with NO_2^- (aqueous $NaNO_2$–NaOH), with which the cobalt(I) tetranuclear species was reoxidized to Co(II). No similar reaction was observed in the case of the mononuclear complex. The reduction of biological nitrite to nitrogen, ammonia, or nitric oxide is multielectron in nature. The apparent observation of this reaction with the tetranuclear, but not the mononuclear or binuclear phthalocyanine species, does provide cause to believe that, with the tetranuclear phthalocyanine, some kind of low-yield concerted reaction may be taking place that is not possible with the mononuclear complex, possibly via a nitrosyl intermediate.[60,61] Work is presently in progress to characterize this reaction.

The conversion of Co(III) to Co(I) by irradiation of a film occurred at a much slower rate for the tetranuclear than for the mononuclear complex. This may be the result of a shorter excited-state lifetime of Co(III) in the case of the tetranuclear molecule as a result of intramolecular quenching.

Concluding Comments. The phthalocyanine rings in the tetranuclear cobalt phthalocyanine are in close proximity, and coupling between these rings is evident in all the various oxidation states investigated, but most prominently in the Co^{II}Pc(−2) state. The improvement in oxygen reduction capability over that of model mononuclear and binuclear phthalocyanines is ascribed, in part, to this interaction. The nitrite reduction reaction is indicative of incipient concerted multielectron behavior, but this remains yet to be clearly identified in this system. The very strong aggregation effects seen with the Co(II) tetranuclear species merit further consideration in this respect.

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Registry No. **1**, 31643-49-9; **2**, 115-77-5; **3**, 106799-31-9; **4**, 23277-29-4; **5**, 106799-32-0; **6**, 3468-11-9; **7**, 93673-00-8; **8**, 106799-30-8; **9**, 106782-12-1; **9** (8− ion), 106782-14-3; **9** (4− ion), 106782-13-2; **9** (4+ ion), 106782-15-4; **9** (8+ ion), 106782-16-5; O_2, 7782-44-7; NO_2, 14797-65-0.

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Electron Transfer. 84. Reduction of Carboxylato-Bound Chromium(V) with Iodide[1]

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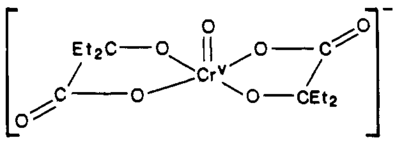
The chromium(V) chelate bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I) is reduced by iodide in aqueous solution buffered by the ligand acid 2-ethyl-2-hydroxybutyric acid and its salt. Very nearly two I^- ions are oxidized per Cr(V) consumed. As in the reductions by HSO_3^- examined previously, the reaction passes through a strongly absorbing Cr(IV) intermediate, which accumulates slowly but disappears suddenly, imparting "clocklike" behavior to the system. The reaction is strongly catalyzed by the Cr(IV) intermediate and is thought also to pass through an iodine atom intermediate ($I^\bullet$), for which Cr(V) and Cr(IV) compete. The proposed reaction sequence (eq 2–7 in the text), in conjunction with rate constants for the component steps obtained by least-squares refinements based on the Runge–Kutta integration procedure, reproduces the observed kinetic profiles. The 1e transactions of I^- with both Cr(V) and Cr(IV) are accelerated by H^+, indicating that both chromium oxidation states are partially converted to a reactive protonated form with $pK^A_{Cr(V)} = 2.9$ and $pK^A_{Cr(IV)} < 2$. The properties of the Cr(III) product correspond to those of a monochelated dicarboxylato derivative of $(H_2O)_3Cr^{III}$, breakage of one chelate ring probably having occurred at the Cr(IV) level. No Cr(III)-bound iodide is detected in the reduction product. Reaction of I^- with Cr(V) is, as expected, markedly slower than with Cr(IV), which is more strongly oxidizing, but the $I^\bullet$ radical reacts with Cr(V) about 50 times as rapidly as with Cr(IV). This apparent inversion of relative rates points to an inner-sphere route for the Cr(V)–$I^\bullet$ reaction. The reaction of HOI with I^- to form I_2 exhibits a bimolecular rate constant of 43 $M^{-1}\ s^{-1}$ (24 °C, pH 2.75, μ = 0.65 M) in the buffer system used, whereas the formation of I_3^- from I_2 and I^- proceeds at a specific rate $>1 \times 10^5\ M^{-1}\ s^{-1}$.

In 1979 Krumpolc and Roček[3] documented the facile preparation of a series of (bis) chelates of chromium(V), the most robust of which is the 2-ethyl-2-hydroxybutyrato derivative I. These are stable in air and dissolve in nonreducing polar solvents without immediate disproportionation. The availability of these chelates led not only to the mechanistic examinations of the redox reactions of this atypical oxidation state,[4] but also to the generation, via



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[2] Present address: Department of Chemistry, Pittsburg State University, Pittsburg, KS 66762.

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

0020-1669/87/1326-0899$01.50/0

Table I. Stoichiometry of the Reaction of Chromium(V) Chelate I with Sodium Iodide[a]

mmol of Cr^V	mmol of NaI	mmol of I_2 formed[b]	$\Delta I^-/\Delta Cr^V$
0.112	0.570	0.102	1.82
0.169	0.579	0.155	1.83
0.147	0.460	0.150	2.04

[a] Chromium(V) was added as sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I); reactions were carried out in solutions buffered by the parent hydroxy acid and its sodium salt (see text). [b] Determined by titration with $Na_2S_2O_3$.

certain one-electron reductants, to complexes of the still less usual state, Cr(IV), the growth and disappearance of which may, in favorable cases,[5] be monitored.

Considerable kinetic complexity may be associated with the reactions of Cr(V) with reductants that participate in both 1e and 2e changes. In such instances, at least four different 1e transfers are possible, in addition to a direct transaction involving two oxidation units (as is encountered in reductions by Sn(II)[6] and hydrazine.[7]) Depending upon the interrelationships between specific rates for individual steps, autocatalysis may result, as has been reported for reductions of carboxyl-bound chromium(V) with hypophosphorus acid[8] and with bisulfite,[9] the latter leading to marked "clocklike" behavior when the system is examined at a frequency where Cr(IV) absorbs selectively. We here describe analogous action in the Cr(V)–iodide system which, we believe, implicates both I$^\bullet$ and I$^+$ (or equivalent species) as reaction intermediates.

Experimental Section

Materials. Sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (chelate I) was prepared[3] and purified[5b] as described. Lithium perchlorate was prepared by the method of Dockal[10] and was twice recrystallized before use. Sodium iodide (anhydrous) and 2-hydroxy-2-ethylbutanoic acid (the "ligand acid") were Aldrich products and were used as received. Cation-exchange resin (Bio-Rad 50W-X2; 200–400 mesh) was treated before use as described.[11] Sodium perchlorate monohydrate, an Alfa product, was used as received.

Stoichiometric Studies. The stoichiometry of the reaction between the Cr(V) chelate I and excess iodide was determined by carrying out the reaction in 20 cm^3 of buffered solutions that were 0.10 M in the parent carboxylic acid and 0.05 M in its salt. After 2 h of reaction, the solutions were acidified with 8 mL of 1.0 M H_2SO_4 and then titrated immediately with standard $Na_2S_2O_3$ to the starch endpoint. Results are summarized in Table I.

Examination of the Cr(III) Reaction Products. Reaction mixtures, containing 0.016 mmol of Cr(V) in 2.0 mL of solution and buffered with 0.30 M of the parent carboxylic acid and 0.15 M of its sodium salt, were treated with 0.1 mmol of NaI. After 60 min, solutions were extracted repeatedly with CCl_4 to remove iodine. The Cr(III) product in the resulting aqueous phase exhibited absorption maxima at 585 (ϵ = 32 M^{-1} cm^{-1}) and 422 nm (ϵ = 41). When subjected to cation-exchange chromatography at 3 °C,[12] over 70% of the dissolved chromium was eluted with water, leaving behind a minor fraction that was readily removed with 1.0 M $NaClO_4$. The ion-exchange treatment did not alter the extinction coefficients of the Cr(III) species significantly, but slight shifts of the maxima, to 580 and 415 nm, were observed. Over 88% of the chromium taken as Cr(V) was recovered as Cr(III).

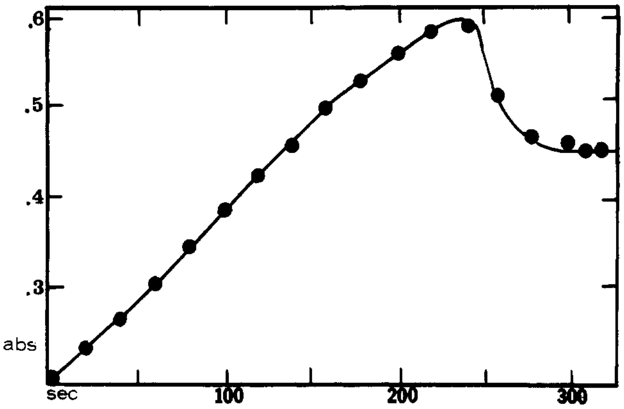

Figure 1. Kinetic profile at 600 nm for reaction of Cr(V) chelate I (5.2 × 10^{-3} M) with iodide (0.254 M) at 25 °C. The supporting medium was 0.150 M in 2-ethyl-2-hydroxybutyric acid, 0.050 M in its sodium salt, and 0.35 M in $LiClO_4$; the pH was 2.86. Note the sharp breakpoint in the curve at 240 s after mixing. The solid line is the experimental curve, whereas the small circles represent absorbances calculated from sequence (2)–(7) in the text, taking k_1 and k_3 as 2.6 × 10^{-3} and 0.116 M^{-1} s^{-1} and the ratio k_2/k_4 as 43. Extinction coefficients used (M^{-1} cm^{-1}): Cr(III), 48; Cr(IV), 240; Cr(V), 38; I_3^-, 39. Optical path length: 1.00 cm.

Kinetic Measurements and Estimation of Specific Rates. Reactions were monitored by following absorbance changes at 600 nm on a Cary 14 recording spectrophotometer. In most instances, total ionic strength was maintained near 0.8 M by addition of $LiClO_4$, and pH values were regulated by addition of measured quantities of 2-ethyl-2-hydroxybutanoic acid (pK_A 3.32)[7] and its sodium salt. All runs were carried out at 25.0 ± 0.2 °C with NaI in excess.

In no case was a simple exponential curve obtained, nor were biphasic patterns characteristic of the reductions of Cr^V (via Cr^{IV}) with metal center reductants[5] seen. Profiles instead indicated the nearly linear growth of a strongly absorbing intermediate and then its much more sudden consumption after a reproducible waiting period (e.g., Figure 1). Fits of our kinetic profiles to a sequence involving autocatalysis by Cr(IV) (see Results and Discussion) were achieved initially by using the program INTEGRAL to generate curves that were compared to those observed.[9,13,14] Specific rates resulting in reasonable agreement between calculated and observed absorbances were further refined by an iterative nonlinear least-squares procedure.[15,16]

Two additional reactions, thought to be rapid steps in the Cr(V)–I$^-$ sequence, were briefly examined by using a Durrum-Gibson stop-flow spectrophotometer. The reaction between HOI (2.5 × 10^{-4} M) and I$^-$ (0.1–0.3 M) in 2-hydroxy-2-ethylbutyrate buffer (pH 2.75) to yield I_3^- was studied at 465 nm and was found to exhibit straightforward exponential curves, corresponding to a bimolecular rate constant of 43 M^{-1} s^{-1} (24 °C, μ = 0.65 M). The formation of I_3^- from I_2 (6.5 × 10^{-5} M)

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(4) (a) Gould, E. S. *Acc. Chem. Res.* **1986**, *19*, 66. (b) For detailed studies of the reactions of this oxidation state with organic species, see, for example: Samsel, E. G.; Srinivasan, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 7606.

(5) (a) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2832. (b) Fanchiang, Y.-T.; Bose, R. N.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 4679.

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(7) Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1981**, *20*, 3176.

(8) Ghosh, S. K.; Bose, R. N.; Laali, K.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 4737.

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

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

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

(12) Separations were carried out with use of Bio-Rad 50W-X2 sulfonate resin, H$^+$ form, 200–300 mesh, column length 5 cm, column capacity 2.0 mequiv. For estimates of extinction coefficients of Cr(III) species, aliquots 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.

(13) Kinetic fits, which utilized a fourth-order Runge–Kutta integration technique,[14] 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. A copy of the modified program may be obtained from R.N.B.

(14) (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.

(15) This program, which was developed by R. Moore and T. W. Newton of Los Alamos National Laboratory, was obtained from Professor Gilbert Gordon. The FORTRAN-IV version was changed, with the help of Dr. J. W. Reed, to FORTRAN-77 in order to adapt to the IBM 3100 system. The program, which minimizes the function $(\mathrm{Abs_{calcd}} - \mathrm{Abs_{obsd}})^2$ uses the Gaussian method described by McWilliams and co-workers.[16] Trial values of the rate constants were those obtained from the INTEGRAL procedure. Individual experimental points were unweighted.

(16) McWilliams, P.; Hall, W. S.; Wegner, H. E. *Rev. Sci. Instrum.* **1965**, *33*, 76.

Table II. Kinetic Parameters for the Reduction of Carboxyl-Bound Chromium(V) with Iodide[a]

[Cr(V)], M	[I^-], M	pH	[LigH],[b] M	[Lig^-],[c] M	10^3k_1,[d,e] $M^{-1}\,s^{-1}$	10^2k_3,[d,f] $M^{-1}\,s^{-1}$	k_2/k_4[d]	$10^{-2}\epsilon_{Cr(IV)}$,[d,g] $M^{-1}\,cm^{-1}$
0.0057	0.254	2.98	0.150	0.075	2.8 (2.7)	8.9 (9.2)	46	2.6
0.0057	0.254	3.01	0.200	0.100	2.6 (2.6)	9.6 (8.8)	39	2.7
0.0057	0.254	2.98	0.300	0.150	2.6 (2.7)	9.8 (9.2)	45	2.9
0.0054	0.552	3.21	0.050	0.050	2.5 (1.9)	6.9 (6.6)	55	2.4
0.0054	0.552	3.57	0.050	0.100	1.3 (1.0)	4.6 (4.5)	52	3.1
0.0054	0.552	3.74	0.050	0.150	0.88 (0.74)	3.5 (4.0)	49	3.5
0.0054	0.552	3.92	0.050	0.200	0.54 (0.51)	2.3 (3.6)	46	3.5
0.0054	0.254	2.98	0.100	0.050	2.5 (2.7)	7.5 (9.2)	42	2.4
0.0052	0.254	2.86	0.150	0.050	2.6 (3.1)	11.6 (11.3)	43	2.4
0.0052	0.254	2.74	0.200	0.050	3.0 (3.5)	18 (14)	41	2.5
0.0052	0.254	2.60	0.250	0.050	3.4 (3.9)	22 (18)	51	2.6
0.0052	0.254	2.45	0.300	0.050	4.5 (4.3)	24 (24)	48	2.6
0.0083	0.158	2.45	0.300	0.050	4.2 (4.3)	22 (24)	52	2.7
0.0062	0.234	2.44	0.300	0.050	4.2 (4.3)	22 (25)	57	2.6
0.0052[h]	0.508	2.47	0.300	0.050	4.9 (4.3)	25 (25)	48	2.6
0.0052[i]	0.127	2.46	0.300	0.050	4.5 (4.3)	26 (24)	55	2.8

[a] Reactions were carried out at 25 °C; $\mu = 0.8$ M ($LiClO_4$); chromium(V) was added as sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I). [b] 2-Ethyl-2-hydroxybutyric acid. [c] 2-Ethyl-2-hydroxybutyrate. [d] Parameters obtained from nonlinar least-squares refinement in which observed absorbances were compared with those obtained by integration of differential equations based on sequence (2)–(5) (see text and ref 13 and 15). [e] Values in parentheses calculated by using eq 8, taken k_{lim} as $5.8 \times 10^{-3}\ M^{-1}\,s^{-1}$ and K_A as 1.23×10^{-3} M. [f] Values in parentheses calculated by using eq 9, taking k_0 as 0.029 $M^{-1}\,s^{-1}$ and k_H as 61 $M^{-2}\,s^{-1}$. [g] 600 nm. [h] $\mu = 0.91$ M. [i] $\mu = 0.53$ M.

and NaI (0.0038–0.076 M) in the same buffer, monitored at 350 nm,[17] was observed to be greater than 95% complete in less than 0.001 s, allowing us to estimate a lower limit of $1 \times 10^5\ M^{-1}\,s^{-1}$ (23 °C, $\mu = 0.11$ M) for the specific rate of this conversion.

Results and Discussion

Stoichiometry experiments, carried out with excess iodide (Table I), indicate the oxidation of very nearly 2 mol of iodide to the zerovalent state/mol of Cr(V) taken. The net reaction, shown schematically, is thus

$$Cr^V + 2I^- \rightarrow Cr^{III} + 2I^0 \tag{1}$$

With I^- in excess, nearly complete conversion of I^0 to I_3^- may be assumed.

The spectrum of the predominant Cr(III) product, taken after removal of iodine, resembles that of the complex formed when bis(chelate) I is reduced with the 1e reductants Fe(II), Ti(III), and VO^{2+},[5] a species thought to be a bis-chelated derivative of $(H_2O)_2Cr(III)$ with a net charge of +1. Although the elution behavior of our product points also to a +1 charge, its extinction coefficients ($\epsilon_{585} = 32$, $\epsilon_{422} = 41$) are only about two-thirds of those of the bis(chelate) ($\epsilon_{585} = 48$, $\epsilon_{416} = 61$). We suspect that this is a dicarboxylato product in which just one of the carboxyl ligands is chelated. Observed decay of this product in contact with polysulfonated resin, (due presumably to partial aquation) as reported for related (carboxylato)chromium(III) complexes,[18] is consistent with this assignment. Ligated iodide is absent, for this would shift absorption maxima close to 620 and 475 nm;[19] moreover, the relatively labile Cr^{III}–I linkage would not be expected to survive the reaction periods employed here.[20]

Kinetic profiles, at 600 nm, point to the generation and subsequent loss of an intermediate that absorbs strongly in the region characteristic of complexes of Cr(IV).[8,9] We are not, however, dealing with straightforward biphasic patterns obtained from the superposition of consecutive first-order processes, for in such instances the rising portion of the curve is invariably steeper than the falling portion, whereas the reverse is true in the present study (Figure 1). The observed steep descents call to mind the traces encountered in the $Cr(V)–HSO_3^-$ reaction, which has been shown to be strongly autocatalytic.[9] Such autocatalysis reflects the participation of three oxidation states, differing by one unit, derived from both reaction partners, i.e., chromium(V), chromium(IV), and chromium(III) and I^-, $I^\bullet$, and I(I).

Reaction series (2)–(7) accommodates the observed kinetic curve for each run. The first four steps are single-electron transactions, and the final two steps are considered to be rapid in comparison to the others.[21] Near the beginning of each run,

$$Cr^V + I^- \xrightarrow{k_1} Cr^{IV} + I^\bullet \tag{2}$$

$$Cr^V + I^\bullet \xrightarrow{k_2} Cr^{IV} + I^I \tag{3}$$

$$Cr^{IV} + I^- \xrightarrow{k_3} Cr^{III} + I^\bullet \tag{4}$$

$$Cr^{IV} + I^\bullet \xrightarrow{k_4} Cr^{III} + I^I \tag{5}$$

$$I^I + I^- \rightarrow I_2 \text{ (rapid)} \tag{6}$$

$$I_2 + I^- \rightarrow I_3^- \text{ (rapid)} \tag{7}$$

only (2) and (3) occur, but as Cr^{IV} accumulates, reaction 4 becomes important, increasing the concentration of the $I^\bullet$ radical. Autocatalysis occurs because $I^\bullet$ reacts more rapidly with Cr^V than with Cr^{IV} and reaction with Cr^V regenerates Cr^{IV}. When Cr^V is consumed, reactions 4 and 5 predominate, resulting in the relatively sudden reduction of Cr^{IV} to Cr^{III}.

Derivation of differential equations dictated by sequence (2)–(5), application of the steady-state approximation to $I^\bullet$, and utilization of the Runge–Kutta integration procedure[14] (in conjunction with the overall reaction stoichiometry) were carried out in a manner analogous to that described for the $Cr(V)–HSO_3^-$ reaction.[9] In accord with our kinetic data for the rapid reactions 6 ($k = 43\ M^{-1}\,s^{-1}$) and 7 ($k > 1 \times 10^5\ M^{-1}\,s^{-1}$), "I(I)" formed (HOI) is considered to be rapidly converted to I_2, and thence to I_3^-, in the medium employed. Values of k_1, k_3, and the ratio k_2/k_4 were varied independently. Integration then gave the concentrations of Cr(V), Cr(IV), Cr(III), I^-, and I_3^- at 20-s intervals. Incorporation of extinction coefficients of the three chromium oxidation states and that of I_3^- yielded calculated values for the

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(17) At 353 nm the reported extinction coefficient for I_3^- is $2.64 \times 10^4\ M^{-1}\,cm^{-1}$, whereas that for I_2 in water is only 18 $M^{-1}\,cm^{-1}$; see, for example: Awtrey, A. D.; Connick, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 1842. At the concentrations of iodide taken, 73–98% of the dissolved iodine is converted to I_3^- at equilibrium.

(18) See, for example: (a) Hollaway, W. F.; Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1984**, *23*, 2181. (b) Gould, E. S. *J. Am. Chem. Soc.* **1968**, *90*, 1740 (footnote 10).

(19) Taube, H.; Myers, H. *J. Am. Chem. Soc.* **1954**, *76*, 2103.

(20) Espenson, J. H. *Inorg. Chem.* **1964**, *3*, 968.

(21) Of the many authors who have reported evidence supporting the intervention of the $I^\bullet$ radical in reacting systems, the following may be considered representative: (a) Nord, G.; Pedersen, B.; Farver, O. *Inorg. Chem.* **1978**, *17*, 2233. (b) Piemont, E.; Leibenguth, J. L.; Schwing, J. P. *Bull. Soc. Chim. Fr.* **1979**, 254. (c) Adedinsewu, C. O.; Adegite, A. *Inorg. Chem.* **1979**, *18*, 4597. (d) Stanbury, D. M.; Wilmarth, W. K.; Khalaf, S.; Po, H. N. *Inorg. Chem.* **1980**, *19*, 2715. (e) Raycheba, J. M.; Margerum, D. W. *Inorg. Chem.* **1981**, *20*, 45.

absorbance of the reaction mixture at each point,[22] and the group of parameters resulting in the closest approximation to the observed curves was used as the set of trial values for a final iterative nonlinear least-squares refinement.[15]

Values of the parameters k_1, k_3, k_2/k_4, and $\epsilon_{Cr(IV)}$ resulting from these refinements appear in Table II. Calculated absorbances (solid circles) obtained from one set of these parameters are compared with the corresponding experimental (continuous) curve in Figure 1. As with the Cr(V)–HSO_3^- system,[9] the "clocklike" behavior of the reaction at 600 nm mirrors the slow growth and rapid decay of Cr(IV).

Specific rates obtained from our procedure are necessarily less precise than those pertaining to simpler kinetic systems involving just one or two adjustable parameters. Nevertheless, it is evident that both the Cr(V)–I^- reaction (k_1) and the Cr(IV)–I^- reaction (k_3) are accelerated by H^+ but are very nearly unaffected by addition of excess ligand anion (Lig^-). Values of k_1 are very nearly proportional to $[H^+]$ in the pH range 3.5–4 but approach a limiting value very near 0.005 M^{-1} s^{-1} below pH 2.5. Such a pattern indicates partition of one of the reagents, in this case a Cr(V) species, into an unreactive deprotonated and a reactive protonated form, the latter having an acidity constant near that of the buffering acid employed. This partition is described by eq 8, where

$$(k_1)_{obsd} = \frac{k_{lim}[H^+]}{K_A + [H^+]} \tag{8}$$

k_{lim} is the limiting specific rate pertaining to reaction of the protonated oxidant. Refinement of observed k_1 values according to (8) leads to a limiting rate of $(5.8 \pm 0.4) \times 10^{-3}$ M^{-1} s^{-1} and a K_A value of $(1.2 \pm 0.2) \times 10^{-3}$ M (25 °C, $\mu = 0.8$).

Specific rates for the Cr(IV)–I^- reaction (k_3) exhibit no evidence of kinetic saturation within the pH range examined. Rates for this step conform to (9), where k_0, the $[H^+]$-independent com-

$$(k_3)_{obsd} = k_0 + k_H[H^+] \tag{9}$$

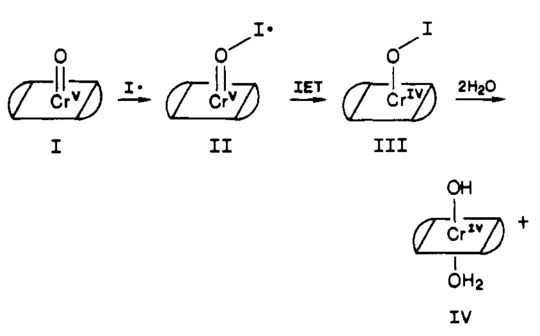
ponent, is calculated to be $(2.9 \pm 0.9) \times 10^{-2}$ M^{-1} s^{-1}, and k_H, pertaining to the $[H^+]$-proportional contribution, is 61 ± 4 M^{-2} s^{-1}. The latter term contains the specific rate of the active form and its K_A value, but neither of these individual parameters can be evaluated from the data at hand. Differences in the algebraic forms of (8) and (9) arise from the higher pK_A value for the active protonated form of Cr(V) and from the circumstance that the deprotonated form of Cr(IV), although less active than the protonated form, makes a detectable kinetic contribution. Values (in parentheses) of $(k_1)_{obsd}$ and $(k_3)_{obsd}$, calculated from (8) and (9), are compared with experimental rate constants in Table II. Note also that neither k_1 nor k_3 exhibits a significant kinetic salt effect within the range $\mu = 0.53$–0.91 M.[23,24]

Neither our Cr(III) product, which has been assigned a structure with two carboxylato groups (one chelated), nor the bis(chelate) obtained by reaction of the same Cr(V) oxidant with rapidly acting metal center reductants[5,6,25] is thermodynamically favored, for both undergo aquation to $Cr(H_2O)_6^{3+}$ on long standing in the medium at hand. Our product almost certainly arises from breakage of one of the chelate rings (at the "alkoxide" oxygens) and attendant aquation, and this ligand substitution process may be presumed to occur at the Cr(IV) level, for such reorganizations of the ligand sphere about Cr(V) and Cr(III) centers are observed to be slow in comparison to the redox reaction being considered. This difference in reduction products gives no direct information concerning the mechanism(s) of electron transfer, for the bis(chelate) has been found to be formed in outer-sphere reductions by Ti(III)[26] $IrCl_6^{3-}$,[6] as well as in reductions by Fe(II) and VO^{2+}, which are thought to proceed through bridged transition states.[5] The ligand environment in the product instead reflects the competition between ligand substitution involving the initial Cr(IV) intermediate and its further reduction to Cr(III). Slow reduction of Cr(IV) or the presence of strongly nucleophilic ligands, or a combination of both, favors disruption of the bis(chelate), as has been observed for the Ce(III)-catalyzed disproportionation of Cr(V) complex I[27] and for its reduction with H_3PO_2.[8]

Consideration of the relative rates at which Cr(IV) and Cr(V) oxidize I^- to $I^•$ (k_1 vs. k_3) is complicated by the different acid dependencies governing the two processes. Within the pH range examined, reaction with the much more strongly oxidizing Cr(IV)[9,28] is 30–65 times as rapid as with Cr(V). This ratio exceeds only slightly the estimated lower limit (20) for the analogous ratio for outer-sphere reductions by $Ti(OH)^{2+}$ [26] and is consistent with (but does not require) an outer-sphere route for both I^- oxidations. The inversion in relative rates (k_2/k_4) for oxidation of $I^•$, which reacts with Cr(V) 50 times as rapidly as with Cr(IV), implies an inner-sphere path for the Cr(V)–$I^•$ reaction but permits no direct conclusion about Cr(IV)–$I^•$ (reaction 5).[29]

Our kinetic results effectively eliminate two mechanisms for the overall conversion that, on initial thought, might seem attractive. Direct oxygen atom transfer, as has been demonstrated for oxidations of olefins and phosphines in nonaqueous media,[4b] would convert iodide to hypoiodite, which, under our conditions, would react rapidly with excess I^- to yield I_2 (reaction 6). However, this route is in accord neither with the complexity of the kinetic pattern nor with the observed intervention of Cr(IV). A second possibility, involving the intermediacy of a Cr(V)–I^- complex that may undergo internal electron transfer to yield Cr(IV)–$I^•$ and, thence, Cr(III) + I^I, permits the appearance of a Cr(IV) species but does not accommodate the prominent autocatalysis. We cannot rule out coordination of iodide to Cr(V) or Cr(IV). However, the autocatalytic process requires that $I^•$ be noncomplexed, for Cr(IV) and Cr(V) compete for it, the latter more successfully.

A less obvious path for the Cr(V)–$I^•$ reaction (which, however, appears to be free from major inconsistencies) involves interaction of the radical with the "oxo" oxygen of the Cr(V) chelate, forming an O–I precursor, II, having an expanded octet about iodine. Precursor II then undergoes internal electron transfer (IET) to "successor complex" III, which is then cleaved hydrolytically (either at the Cr–O or I–O bond) to yield hypoiodite:



Substitution of I^- for H_2O in the proposed Cr(IV) intermediate IV may occur, but it cannot be demonstrated to be a significant

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[22] The value of $\epsilon_{Cr(V)}$ was taken from the initial absorbance of the reaction mixture, that of $\epsilon_{Cr(III)}$ was taken from the final absorbance (after removal of iodine), and that for $\epsilon_{I_3^-}$ was independently determined as 39 M^{-1} cm^{-1} at 600 nm. Each of these was kept fixed, but $\epsilon_{Cr(IV)}$ was allowed to "float".

[23] Since the activation process for k_1 involves bringing together two negatively charged redox partners and one unit of H^+, it should, in principle, be subject to a negative kinetic salt effect. This may be observable at considerably lower ionic strengths.

[24] The principal protonation positions for the Cr(V) reactant and the Cr(IV) intermediate are probably different. For Cr(V), the most basic sites are almost certainly the "alkoxy" oxygens, from which H^+ is removed during ligation to the pentapositive center. Complexes of Cr(IV), like those of its isoelectronic counterpart V(III), are probably hexacovalent, and in bis(chelates) of the type under consideration, the alkoxy oxygens are protonated. Protonation equilibria for this state may involve axially coordinated water molecules.

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step in the primary redox path. It would, however, be expected to facilitate cleavage of the chelate ring(s), for incorporation of ligated halide is known markedly to enhance substitution lability at metal ion centers.[30] A sequence analogous to (10) may be envisaged for the Cr(IV)–I$^\bullet$ reaction 5, but this almost certainly occurs after disruption of the bis-chelated structure. As in the proposed route pertaining to the Cr(V)–HSO_3^- system,[9] the Cr(V)–I$^\bullet$ reaction, the most rapid among the electron-transfer steps, appears to be the only one involving interaction of a radical with an oxo-bound metal ion center.

It has been emphasized that autocatalysis of the type observed here and in the related Cr(V)-HSO_3^- reaction[9] reflects the capacity of both the reductant and the oxidant to undergo both one- and two-electron changes in the same medium. Analogous, but less striking, behavior in the Cr(V)–H_3PO_2 system[8] lends support to the proposed intervention of the unusual oxidation state P(II), and similar autocatalysis has been noted in the reductions of carboxylato-bound Cr(V) with SCN^- and with $S_2O_3^{2-}$,[31] although in the latter two instances competing scissions of the respective radical intermediates lead to a still more complicated kinetic picture. Among possible organic reductants, ascorbic acid reacts rapidly, generating an analogous profile, which, however, appears to be modified by strong association to the oxidant.[31]

Finally, it would be anticipated that other electron acceptors derived from transition metals in their higher oxidation states might exhibit related reduction patterns when treated with suitably versatile donors. Preliminary examinations[31] of the reductions of VO^{2+} and MoO_2^{2+} by vitamin B_{12s} (cob(I)alamin) indicates that this is the case.

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Redox Reactions of Superoxotitanium(IV) in Acidic Perchlorate Solution

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The ultraviolet absorption spectrum of superoxotitanium(IV), prepared by the rapid reaction of cerium(IV) and excess peroxotitanium(IV), TiO_2^{2+}, was determined. On the basis of extensive stopped-flow studies of the decay of superoxotitanium(IV), two forms of the complex formulated as TiO_2^{3+} and $TiO_2(OH)^{2+}$ are proposed. A value of 1.6 M^{-1} at an ionic strength of 1.0 M ($LiClO_4$) was determined for the hydrolysis constant of TiO_2^{3+}. The decay constant for TiO_2^{3+} (k_{d1}) is larger than that for $TiO_2(OH)^{2+}$ (k_{d2}); at 25 °C, the ratio $k_{d1}/k_{d2} \approx 13$. The redox reactions of superoxotitanium(IV) with a number of substrates were investigated by means of the multimixing, stopped-flow technique. On the basis of the variation of the second-order rate constants with [H^+], it is concluded that TiO_2^{3+} is the more reactive form of superoxotitanium(IV) toward the anionic or neutral reductants sulfur(IV), hexachloroiridate(III), iodide ion, and bromide ion. The hydrolyzed form $TiO_2(OH)^{2+}$ shows increased reactivity toward the cationic reductants iron(II), titanium(III), and oxovanadium(IV). It is proposed that reduction of superoxotitanium(IV) proceeds by a 1-equiv mechanism and is a facile process; the rate constants are only slightly less than that observed for protonated superoxide, HO_2. The rate constants for oxidation of superoxotitanium(IV), however, are orders of magnitude smaller than for HO_2. Rate constants ($M^{-1}\ s^{-1}$) determined in 1 M perchloric acid at 25 °C are as follows: 1.1×10^6 (I^-); 3.5×10^5 ($IrCl_6^{3-}$); 1.8×10^5 (Fe^{2+}); 1.3×10^4 (Ti(III)); 4.5×10^3 (S(IV)); 3.1×10^2 (VO^{2+}); ~13 (Cl_2); ~2 (Br^-).

Introduction

We have proposed that superoxotitanium(IV), tentatively formulated as TiO_2^{3+}, is formed by the rapid oxidation of peroxotitanium(IV), TiO_2^{2+}, by cerium(IV) in acidic perchlorate solution.[1] The strictly first-order decay of superoxotitanium(IV) produces half as much peroxotitanium(IV). We have interpreted these observations by the reaction scheme shown in eq 1 and 2.

$$TiO_2^{3+} = O_2 + Ti^{3+} \quad k_d \qquad (1)$$

$$Ti^{3+} + TiO_2^{3+} + H_2O = TiO^{2+} + TiO_2^{2+} + 2H^+ \quad \text{fast} \qquad (2)$$

The decay rate is relatively slow on the stopped-flow time scale ($k_d = 0.12\ s^{-1}$ in 1 M perchloric acid at 25 °C).[1] We therefore have been able to study the kinetics of reactions of superoxotitanium(IV) with selected reductants and oxidants by means of multimixing, stopped-flow procedures. In several cases the rate constants for the corresponding reactions of protonated superoxide, $HO_2^\bullet$, have been determined by other investigators by pulse radiolysis techniques.[2–4] A comparison of these results enables us to assess the effect of metal ion coordination on the redox chemistry of superoxide.

In this paper we report the results of kinetic studies on the redox reactions of superoxotitanium(IV) with sulfur(IV), oxovanadium(IV), iron(II), titanium(III), hexachloroiridate(III), bromide ion, iodide ion, and chlorine. In addition, we have extended our earlier studies on the decay of superoxotitanium(IV) and have measured its absorption spectrum.

Experimental Section

Reagents. Solutions of H_2O_2, $TiO(ClO_4)_2$, $TiO(CF_3SO_3)_2$, $Ti(CF_3SO_3)_3$, $Fe(ClO_4)_2$, $VO(ClO_4)_2$, VO_2ClO_4, Na_2SO_3, and Ce(IV) were prepared by methods described previously.[1,5,6] Chlorine solutions were prepared by dissolution of the reagent-grade gas in perchloric acid. Sodium hexachloroiridate(III) was made by the hydrazine reduction of Johnson-Matthey $Na_2IrCl_6{\cdot}6H_2O$ or $(NH_4)_2IrCl_6$, followed by two recrystallizations from ethanol.[7]

All other chemicals were of reagent grade and were used without further purification. Deionized water was distilled twice before use; the last distillation was from alkaline permanganate.

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