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Electron Transfer. 86. Reduction of Carboxylato-Bound Chromium(V) with Nitrite[1]

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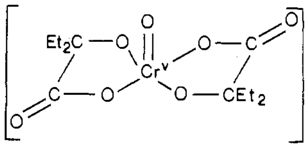
The chromium(V) chelate bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I) is reduced with an equimolar quantity of nitrite in aqueous solutions buffered by the parent acid, 2-ethyl-2-hydroxybutyric acid, and its anion. The reactivity of nitrite contrasts markedly with that of phosphite, which, although a much stronger reductant, reduces Cr(V) immeasurably slowly. Intermediates in the nitrite reaction are one or more Cr(IV) species and, by implication, the $NO_2^{\bullet}$ radical. Properties of the principal Cr(III) product are those of a bis chelate derived from the ligand anion, having, in addition, a coordinated nitrite, which is removed quickly by treatment with strong acid. Except at high pH, the observed kinetic profiles do not satisfactorily fit a biphasic sequence of uncatalyzed steps. Instead, they conform to a series of 1e transactions (reactions 3–6 in the text) in which nitrite is oxidized by both Cr(V) and Cr(IV) to $NO_2^{\bullet}$, for which both oxidation states of chromium then compete. The 1e oxdiations of nitrite by both Cr(V) and Cr(IV) are accelerated by H^+, pointing to partition of both metal ion centers between an active, protonated and a less active, nonprotonated form. Reactions of Cr(V), both with NO_2^- and $NO_2^{\bullet}$, are more rapid than the corresponding reactions of Cr(IV), although the latter has the more strongly positive formal potential, thus indicating that the Cr(V) reactions (but not necessarily those of Cr(IV)) are inner-sphere processes. Sequences analogous to (3)–(6), each involving the intervention of a radical intermediate, have been proposed also for the reductions of Cr(V) by bisulfite, iodide, ascorbate, and hypophosphite. Marked autocatalysis and a clocklike kinetic profile (related to the consumption of Cr^{IV}) are observed only when the ratio $k_{Cr(V)}/k_{Cr(IV)}$ falls well below unity for the anion reductant but greatly exceeds unity for the radical intermediate.

Among over two dozen known chromium(V) compounds,[3] those most conveniently prepared and handled are oxo derivatives featuring a $Cr^{V}O$ unit.[4] The recognized stability of tripositive chromium leads reasonably to the expectation that reactions of such species with 2e reductants may proceed by direct transfer of the oxo oxygen, and this has been shown to be the case for oxidations of olefins,[4b] of substituted phosphines,[4b] and, probably, of Sn(II).[5] With "ambifunctional" reducing agents, which can undergo both 1e and 2e changes, both a 1e oxidation product (generally a radical) and the atypical state Cr(IV) may intervene, thus making possible four different single-electron transfers in addition to a direct two-unit transaction. Suitable interrelationships between specific rates for individual 1e steps can lead to autocatalytic sequences, as have been described for reductions of Cr(V) with bisulfite,[6] iodide,[7] and ascorbic acid.[8]

Reaction of carboxylato-bound Cr(V) with the powerful reductant[9] hypophosphite ($H_2PO_2^-$) has been found to involve a Cr(IV) intermediate and to be moderately autocatalytic,[10] thus implicating the very unusual state P(II), but reduction with phosphite, to which a slightly less negative formal potential may be assigned,[9] is observed to be negligibly slow under comparable conditions.[10] The present report deals with reduction of the bischelated 2-ethyl-2-hydroxybutyrato complex of Cr^{V} (anion I) with nitrous acid. The latter is, on a thermodynamic basis, a much less potent reductant than its P(III) analogue;[9] nevertheless, the reaction proceeds smoothly, exhibiting a small, but perceptible, autocatalytic component. Although the system is quite similar to that involving H_3PO_2,[10] there are instructive differences in detail.



I

Experimental Section

Materials. Sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (the Na salt of I) was prepared[4a] and purified[11] as described. Lithium perchlorate, the "supporting electrolyte" in kinetic measurements, was prepared as described by Dockal[12] and was twice recrystallized before use. The "ligand acid", 2-hydroxy-2-ethylbutanoic acid, and sodium nitrite (Aldrich products) were used as received. Cation-exchange resin (Dowex 50X8, 400 mesh, H^+ form) was pretreated as described[13] and was converted to its Na^+ form by washing with saturated $NaHCO_3$. Anion-exchange resin (Dowex 1X2, 400 mesh, Cl^- form) was washed successively with 0.1 M HCl, distilled water (until acid-free), acetone, and, again, water.

Stoichiometric Studies. The stoichiometry of the reaction between Cr(V) complex I and excess nitrite was determined by mixing the reagents in solutions buffered by the parent carboxylic acid (0.20 M) and its anion (0.10 M). The total volume was 2.5 mL. After 60 min of reaction time, the solution was acidified with 10 mL of cold 0.05 M H_2SO_4, and the unreacted N(III) was titrated with standard $KMnO_4$. Reaction between MnO_4^- and the buffering acid was shown to be negligibly slow under the conditions used. Results are summarized in Table I.

Examination of the Cr(III) Reaction Products. Reaction mixtures were 0.052 M in Cr(V) and 0.102 M in $NaNO_2$ and were buffered with equimolar quantities (0.3 M) of the ligand acid and its sodium salt. These were allowed to react for 45 min at room temperature and then subjected to ion-exchange chromatography[14] at 2 °C. The Cr(III) product was not absorbed on the anion-exchange resin and was, in large part, held only weakly on the cation-exchange resin. Elution from the latter (in its Na^+ form) with water rapidly removed 80% of the added chromium as a green species exhibiting maxima at 568 (ϵ = 46) and 446 nm (ϵ = 61 M^{-1} cm^{-1}), values very nearly the same as those for the reaction mixture before ion exchange. A second fraction, eluted with 1.0 M $NaClO_4$, was too small to yield a useful spectrum. The predominant

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[3] See, for example: Mitewa, M.; Bontchev, P. R. *Coord. Chem. Rev.* **1985**, *61*, 241.

[4] (a) Krumpolc, M.; Roček, J. *J. Am. Chem. Soc.* **1979**, *101*, 3206. (b) Samsel, E. G.; Srinivasan, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 7606. (c) Groves, J. T.; Kruper, W. J., Jr. *Isr. J. Chem.* **1985**, *25*, 148.

[5] Ghosh, S. K.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 3357.

[6] Bose, R. N.; Rajasekar, N.; Thompson, D. M.; Gould, E. S., *Inorg. Chem.* **1986**, *25*, 3349.

[7] Ghosh, S. K.; Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1987**, *26*, 899.

[8] Ghosh, S. K.; Bose, R. N.; Gould, E. S. *Inorg. Chem.*, preceding paper in this issue.

[9] Latimer, W. H. *Oxidation Potentials*, 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1952; Chapter 7. This author lists formal potentials for the 2e oxidations of H_3PO_2, H_3PO_3, and HNO_2 as −0.50, −0.28, and +0.94 V at pH 0 (25 °C), and −1.57, −1.12, and +0.01 V for the corresponding anions at pH 14. Potentials appropriate for the medium in which studies involving carboxylato complexes of Cr(V) are carried out (pH near 3) are then approximately −0.7, −0.5, and +0.7 V.

[10] Ghosh, S. K.; Bose, R. N.; Laali, K.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 4737.

[11] Fanchiang, Y.-T.; Bose, R. N.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 4679.

[12] Dockal, E. R.; Everhart, E. T.; Gould, E. S. *J. Am. Chem. Soc.* **1971**, *93*, 5661.

[13] Gould, E. S. *J. Am. Chem. Soc.* **1967**, *89*, 5792.

[14] Separations were carried out by using a 5-cm column, capacity 2.0 mequiv. For estimation of molar absorbances of Cr(III) species, 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., Sect. A* **1952**, *48*, 414.

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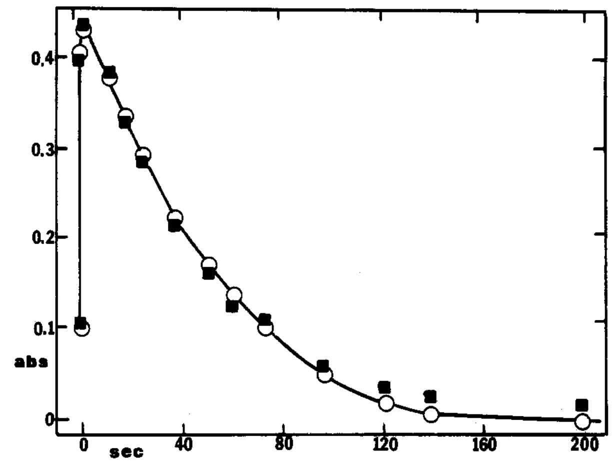

Figure 1. Kinetic profile at 510 nm for the reaction of chromium(V) chelate I (5.0×10^{-4} M) with sodium nitrite (0.0200 M) at 25 °C. The supporting medium was 0.24 M in 2-ethyl-2-hydroxybutyric acid, 0.03 M in its sodium salt, and 0.37 M in $LiClO_4$; the pH was 2.23. The circles represent absorbances calculated from the sequence (2)–(5) in the text, taking k_1 and k_3 as 11.66 and 0.55 $M^{-1}\ s^{-1}$, the ratio k_2/k_4 as 5.88, and $\epsilon_{Cr(IV)}$ as 1166 $M^{-1}\ cm^{-1}$. The squares are absorbances calculated from eq 1 in ref 17, taking k_1 and k_2 as 24.0 and 1.22 $M^{-1}\ s^{-1}$, respectively, and $\epsilon_{Cr(IV)}$ as 1088 $M^{-1}\ cm^{-1}$. The solid line is the experimental curve. Extinction coefficients used ($M^{-1}\ cm^{-1}$): Cr(III), 4.0; Cr(V) 198. Optical path length: 1.00 cm.

product was not stable in strongly acid media, for treatment with 1.0 M $HClO_4$ resulted in the evolution of NO_2, converting the complex to a different species with maxima at 588 ($\epsilon = 48$) and 417 nm ($\epsilon = 58\ M^{-1}\ cm^{-1}$). The latter product was formed also when the original reaction mixture was treated with polysulfonate resin in its H^+ form.

Kinetic Measurements and Estimation of Specific Rates. Reactions were monitored by following absorbance changes at 510 nm using a Cary 14 recording spectrophotometer. Total ionic strength was kept near 0.4 M by addition of $LiClO_4$, and pH values were regulated by addition of measured quantities of 2-ethyl-2-hydroxybutyric acid (pK_A 3.32)[15] and its sodium salt. All runs were carried out at 25.0 ± 0.2 °C, generally with nitrite in at least 40-fold excess.

Kinetic profiles taken with NO_2^- in excess featured a rapid rise in absorbance followed by a much more gradual decrease (e.g., Figure 1). The general shapes of the curves resembled that for a reaction in which the first- (or pseudo-first-) order formation of a strongly absorbing transient is followed by its first-order decay. The usual iterative nonlinear least-squares refinement of absorbance data applicable to such a biphasic sequence[16,17] converged for each run, but in some cases, particularly at higher acidities, calculated absorbances during the final stages of reaction fell off significantly less sharply than those observed, suggesting autocatalysis. Fits of all kinetic profiles to an autocatalytic sequence (see Discussion) were obtained by using a combination of the computer program INTEGRAL (to generate curves that were compared to those observed)[6,18,19] and an iterative nonlinear least-squares refinement procedure.[20,21] Parameters resulting from these refinements reproduced the observed curves closely (Figure 1).

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

mmol of Cr^V	mmol of $NaNO_2$	ΔNO_2^-,[b] mmol	$\Delta[Cr^V]/\Delta[NO_2^-]$
0.089	0.367	0.080	1.10
0.096	0.588	0.101	0.95
0.164	0.588	0.155	1.05
0.232	0.784	0.246	0.94

[a] Chromium(V) was added as sodium bis(2–ethyl–2–hydroxybutanoato)oxochromate(V) (Na(I)); reactions were carried out in solutions buffered by the parent hydroxy acid and its sodium salt (see text). [b] Determined by difference by titration with MnO_4^- (see text).

A few runs were carried out with Cr(V) in large excess. The resulting kinetic traces featured the formation of the Cr(V) intermediate, which, under the conditions used, decayed negligibly slowly. The nearly exponential curves obtained were used to confirm the specific rate for the initial step in the redox sequence (see Discussion), and the magnitude of the absorbance increase allowed an independent estimate of the extinction coefficient of the intermediate.

Results and Discussion

Stoichiometric experiments with nitrite in excess (Table I) indicate that the predominant reaction involves equimolar quantities of the two redox partners and is thus represented

$$Cr^VO + NO_2^- \rightarrow Cr^{III} + NO_3^- \qquad (2)$$

Because the pK_A of HNO_2 (2.94)[22] falls within the pH range examined here, partition of the reductant between acidic and basic forms must be considered.

The extinction coefficients of the principal Cr(III) product lie close to those of the complex formed when Cr(V) chelate I is reduced with Fe(II),[16b] VO^{2+},[11] and Sn(II),[5] and may be taken to be characteristic of a bischelated structure derived from the parent carboxylic acid.[23] The primary product here is not the unipositive bis chelate, $[(Lig)_2(H_2O)_2Cr^{III}]^+$, resulting from these metal-center reductants, but is converted rapidly and irreversibly to this diaquo chelate (with liberation of NO_2) on acidification. Moreover, its elution behavior indicates it to be uncharged. Its properties thus correspond to those of a bis chelate in which one of the aquo ligands has been replaced by a nitrite group. The latter is, however, lost on acidification.[24,25]

Kinetic curves taken at 510 nm (λ_{max} for Cr^V) portray the generation and subsequent decay of a strongly absorbing intermediate. Data for runs at lower acidities conform satisfactorily to the superposition of two consecutive first-order processes and may thus be interpreted as the formation of a Cr(IV) intermediate, followed by its reduction by excess nitrite, in apparent analogy

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

(16) See, for example: (a) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; Chapter 4. (b) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2822.

(17) The relationship[16b] describing consecutive first-order reactions with specific rates k and k' is

$$D = A_0\epsilon_A e^{-kt} + \frac{\epsilon_I A_0 k}{k' - k}(e^{-kt} - e^{-k't}) + \frac{D_\infty}{k' - k}(ke^{-k't} - k'e^{-kt}) + D_\infty \qquad (1)$$

where D and D_∞ are the absorbances at time t and at infinite time, ϵ_A and ϵ_I are the extinction coefficients of reagent A and the intermediate, and A_0 is the original concentration of A.

(18) Calculations of concentrations of reagents and intermediates during the progress of the reaction utilized a fourth-order Runge–Kutta integration technique[19] and were accomplished by a FORTRAN-77 program on the IBM 3081D computer. 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. Copies of the modified program may be obtained from R.N.B.

(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) 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 $(Abs_{calcd} - Abs_{obsd})^2$, uses the Gaussian method described by McWilliams and co-workers.[21] Trial values of the rate constants were those obtained by treatment of the curves according to (1). Individual experimental points were unweighted.

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

(22) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York, 1976; Vol. 4, p 47. The value given pertains to 25 °C, $\mu = 0.50$.

(23) Visible spectra of a variety of chelated and nonchelated carboxylato complexes of Cr(III) have been compared by Fanchiang.[11]

(24) The spectral shifts accompanying the replacement of bound nitrite by water appear to be uninformative as to the site of attachment (N- vs. O-bound) in the former, for the 568-nm peak is shifted to lower energy (588 nm), whereas the 444-nm peak is shifted to higher energy (417 nm). The ease with which nitrite is removed on acidification suggests that it is O-bound and that the conversion results from H^+-induced breakage of N(III)–O, bonds.[25]

(25) For a brief discussion of "pseudosubstitution" reactions of this type, see: Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1968; p 229.

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

$10^3[Cr^V]$, M	$10^3[NO_2^-]$,[b] M	[LigH],[c] M	$[Lig^-]$,[d] M	pH	k_1,[e] $M^{-1}\ s^{-1}$	k_3,[e] $M^{-1}\ s^{-1}$	k_2/k_4[e]	$10^{-2}\epsilon_{Cr(IV)}$,[e,f] $M^{-1}\ cm^{-1}$
0.50	20.0	0.030	0.12	3.84	1.4	0.075	2.7	6.1
1.00	20.0	0.030	0.12	3.84	1.3	0.078	2.7	6.5
0.50	15.0	0.060	0.060	3.32	4.5	0.078	7.8	6.0
0.50	20.0	0.060	0.060	3.25	3.9	0.11	8.2	6.0
0.50	30.0	0.060	0.060	3.32	4.1	0.078	7.6	6.7
0.50	40.0	0.060	0.060	3.32	4.5	0.073	8.9	6.8
0.50	20.0	0.030	0.060	3.62	2.7	0.079	4.8	6.1
0.50	20.0	0.030	0.030	3.28	4.2	0.078	5.5	5.1
0.50	20.0	0.120	0.120	3.31	3.9	0.13	11	8.8
0.50	20.0	0.060	0.030	3.06	6.6	0.12	4.5	7.0
2.40	0.48	0.060	0.030	3.01	5.4			8.3
0.50	20.0	0.120	0.030	2.74	8.5	0.21	7.4	8.5
2.40	0.48	0.120	0.030	2.71	7.2			7.0
0.50	20.0	0.180	0.030	2.41	9.2	0.40	6.3	9.7
0.50	20.0	0.240	0.030	2.23	11	0.55	5.9	12

[a] 25 °C, μ = 0.40 M ($LiClO_4$); Cr(V) was added as chelate I. [b] Total $NaNO_2$ added. [c] 2-Ethyl-2-hydroxybutyric acid. [d] 2-Ethyl-2-hydroxyutyrate. [e] Parameters from nonlinear least-squares refinement in which absorbances were compared with those obtained by integration of differential equations based on the sequence (3)–(6) (see text and ref 6 and 20). [f] 510 nm.

to the uncatalyzed biphasic reactions of Cr(V) with the 1e reductants Fe(II)[16b] and U(IV).[26] As acidity is increased, however, the observed decline in absorbance during the last 25% reaction becomes progressively more rapid than that calculated[17] for an uncatalyzed sequence, indicating a moderate degree of autocatalysis, (see Figure 1).

The four-step sequence (3)–(6), patterned after that proposed for the Cr(V)–H_3PO_2 system,[10] accommodates data from all runs with nitrite in excess. Intermediates are $NO_2^\bullet$ (N^4) and Cr^{IV}.

$$Cr^V + N^3 \xrightarrow{k_1} Cr^{IV} + N^4\ (N^3 = NO_2^-) \tag{3}$$

$$Cr^V + N^4 \xrightarrow{k_2} Cr^{IV} + N^5\ (N^5 = NO_3^-) \tag{4}$$

$$Cr^{IV} + N^3 \xrightarrow{k_3} Cr^{III} + N^4 \tag{5}$$

$$Cr^{IV} + N^4 \xrightarrow{k_4} Cr^{III} + N^5 \tag{6}$$

Generation of differential equations dictated by sequence (3)–(6), application of the steady-state approximation to the radical $NO_2^\bullet$, and employment of the Runge–Kutta integration algorithm were carried out as described for the Cr(V)–HSO_3^- reaction.[6] Values of k_1, k_3, and the ratio k_2/k_4 were allowed to vary independently. Integration then yielded the concentrations of Cr(III), Cr(IV), Cr(V), and nitrite at desired intervals, and incorporation of the molar absorbances of the three chromium states gave calculated absorbance values of the mixture at each point.[27] The sets of parameters giving the closest fit to the observed profiles, resulting from the iterative least-squares refinement,[20] are listed in Table II. Calculated absorbances obtained from one set of parameters pertaining to the proposed catalytic sequence are compared with those based on a straightforward biphasic sequence (without catalysis) and also with the appropriate experimental curve in Figure 1. Early in the reaction, both calculated sets reproduce the observed curve, but during the later stages the catalytic points yield a decidedly superior fit.

For those runs (at lower acidities) conforming satisfactorily to a biphasic sequence without catalysis, the usual ambiguity associated with assignment of rate constants to the kinetic components[16a] is readily resolved by carrying out the corresponding reaction with Cr(V) in excess under conditions where the consumption of the intermediate may be ignored. The specific rate for generation of the intermediate and its extinction coefficient agree with those values resulting when the greater of the two specific rates is assigned to the initial step (k_1).[28] As expected, an analogous ambiguity intrudes when the more complex refinement based on the catalytic sequence is used, for (at least) two sets of parameters are found to fit the experimental curve equally well. Here again, a choice is based on comparison with values of specific rates and $\epsilon_{Cr(IV)}$ obtained from runs with Cr(V) in excess.

Although parameters resulting from such refinements must be considered much less precise than those pertaining to simpler systems that are defined by one or two rate constants, both the Cr(V)–nitrite step (k_1) and the Cr(IV)–nitrite step (k_3) are seen to proceed more rapidly at higher acidities. Values of k_1 are nearly proportional to $[H^+]$ at pH 3.2–3.8 but appear to approach a limiting value somewhat greater than 11 $M^{-1}\ s^{-1}$ at pH below 2.2. This trend is in accord with eq 7, where k_{lim} is the limiting specific

$$(k_1)_{obsd} = \frac{k_{lim}[H^+]}{K_A + [H^+]} \tag{7}$$

rate at high acidities and K_A is the acidity constant of a reagent undergoing partition between a reactive protonated and an unreactive deprotonated form. Refinement of k_1 values according to (7) yields a limiting rate of 12.7 ± 0.8 $M^{-1}\ s^{-1}$ and a K_A value of (9.5 ± 1.9) × 10^{-4} M (pK_A 3.0, 25 °C, μ = 0.40 M). Although the calculated pK_A lies close to values reported both for HNO_2 (2.94)[22] and Cr(V) chelate I (3.26),[11] we prefer to associate it with the latter since in the vast majority of known redox systems protonation of the oxidant increases its reactivity whereas the reverse is true for protonation of the reductant.

Rate constants for the Cr(IV)–nitrite reaction (k_3) do not show kinetic saturation below pH 2.2. The dependency here is described by (8), where k_0, the $[H^+]$-independent component, is calculated

$$(k_3)_{obsd} = k_0 + k_H[H^+] \tag{8}$$

to be (5.1 ± 0.6) × 10^{-2} $M^{-1}\ s^{-1}$ and k_H, associated with an $[H^+]$-proportional component, is 84 ± 2 $M^{-2}\ s^{-1}$. The latter term is presumed to represent a combination of the rate constant for the more active protonated form of Cr(IV) and its K_A value, but neither of these two individual parameters can be evaluated from our data.[29] Similarly, we cannot say whether the apparent increase with acidity in the ratio k_2/k_4 (pertaining to the competition between Cr^V and Cr^{IV} for $NO_2^\bullet$) stems from a decrease in k_4, an

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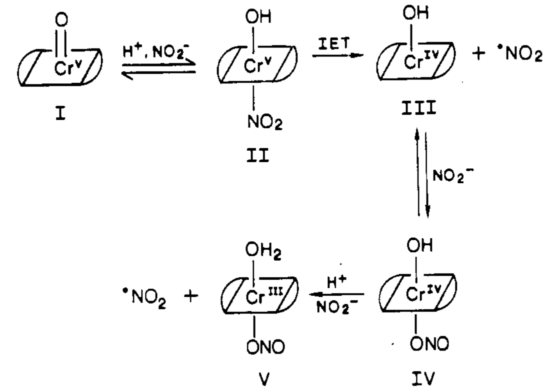
(26) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 165.

(27) Values of $\epsilon_{Cr(III)}$ and $\epsilon_{Cr(V)}$ were taken from the initial and final absorbances. Both of these were kept fixed, but $\epsilon_{Cr(IV)}$ was allowed to vary. Nitrite and nitrate absorb negligibly at the frequencies used.

(28) When assignment of rate constants to the two components is reversed, agreement between calculated and observed profiles is achieved only if the intermediate is assigned an extinction coefficient exceeding 10^4 M^{-1} cm^{-1} at 510 nm.

(29) The acidity pattern generated by our k_3 values implies a pK_A well below 2 for the Cr(IV) intermediate. As in the case with the analogous intermediate in the Cr(V)–I^- system,[7] this is significantly less than the value (3.42) determined spectrophotometrically[11] for the Cr(V)–VO^{2+} system in which the only inorganic anion present is ClO_4^-. Why this pK_A should decrease in the presence of nucleophilic anions remains a puzzling point.

Scheme I



upward trend in k_2, or a combination of both.

Although both the primary Cr(III) product and the complex obtained from it by loss of nitrite on acidification are taken to be bis(chelates) that are related structurally to the Cr(V) reactant, neither as a "thermodynamically determined" product, for both undergo slow aquation, with breakage of the chelate rings, on standing in the medium employed. Survival of the rings in the redox sequence indicates that chelation persists in all steps involving Cr(V) and Cr(IV). The source of coordinated nitrite in the primary product is less obvious, for although there is evidence that the initial step, (3), in the proposed mechanism involves a Cr(V)-nitrite complex, we believe that the Cr(III)-bound nitrite arises later in the reaction sequence (see below).

Two aspects of this study deserve emphasis. The first is the observed high reactivity of nitrite in comparison to that of its P(III) analogue, phosphite, which is, on a thermodynamic basis,[9] by far the more powerful reductant. This difference is probably due, in part, to the availability of an unshared electron pair on the oxidizable nitrogen but not on the oxidizable phosphorus (which is bound to a nonlabile hydrogen in H_3PO_3 and its anions).[30] The lesser accessibility of monomeric P(IV)[31,32] may also be a contributing factor here.

In addition, this appears to be the first reaction sequence of this type in which the initial 1e reduction of carboxyl-bound Cr(V) is more rapid than that of its Cr(IV) counterpart (which has much the more strongly positive potential),[6,33] although there is evidence that the ratio $k_{Cr(V)}/k_{Cr(IV)}$ exceeds unity for a number of radical intermediates.[6-8,10] This ratio falls below 0.05 for reductions by Ti(III)[34] and U(IV),[26] which are thought to react with both states via outer-sphere routes, and, according to the model of Marcus,[35] should be less than this value for other outer-sphere reductants as well. In the present system, the corresponding ratio (k_1/k_3) lies between 20 and 60 (depending on acidity), indicating the operation of an additional (i.e., an inner-sphere) path for the Cr(V)–NO_2^- step. No conclusion of this sort may be drawn for the Cr(IV)–NO_2^- reaction, (4). By an analogous argument, the k_2/k_4 ratio between 2 and 11 (pertaining to the selectivity of $NO_2^•$ for Cr^V and Cr^{IV}) points to a bridged path for the Cr(V)–$NO_2^•$ reaction.[36]

In applying the steady-state approximation to $NO_2^•$, we are in effect assuming that specific rates k_2 and k_4 pertaining to the reactions of this radical are substantially greater than k_1 and k_3, which refer to its generation. Were it not for the reactions of the radical, the overall sequence would follow 2:1 (rather than 1:1) stoichiometry and would exhibit straightforward biphasic kinetics. The modest degree of autocatalysis that is perceived reflects the increased rate in which the reactive $NO_2^•$ is generated (by reaction 5) as Cr^{IV} is allowed to build up. "Clocklike" behavior, as described for the reactions of Cr(V) with HSO_3^- and I$^-$,[6,7] is not observed here since the consumption of Cr(IV) near the end of the reaction is slow rather than sudden.

Scheme II

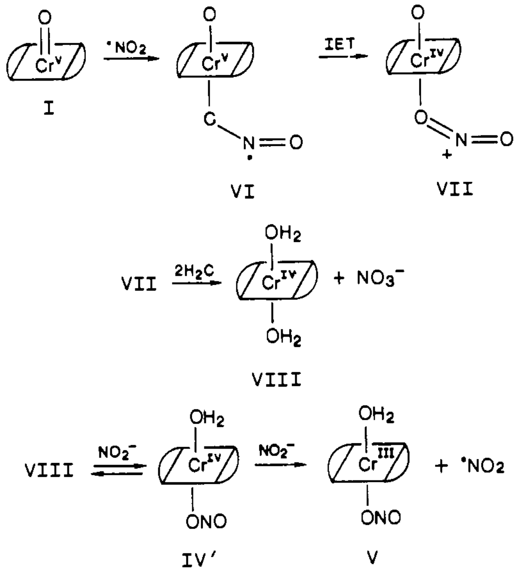


Table III. Reductions of Chelated Chromium(V) with Anionic Reducing Agents[a]

reductant	k_1/k_3[b]	k_2/k_4[c]	autocatalysis	clock reaction?	ref
HSO_3^-	0.005–0.01	20–36	strong	yes	6
$H_2PO_2^-$	0.16–0.3	2–3	slight	no	10
ascorbate	0.005–0.01	7–19	strong	yes	8
I$^-$	0.017–0.03	40–50	strong	yes	7
NO_2^-	20–50	3–10	slight	no	*d*

[a] Reactions of the Cr(V) chelate I in aqueous media, pH 2–4. Solutions were buffered with 2-ethyl-2-hydroxybutyric acid and its anion. [b] Relative rates at which the reductant reacts, via 1e transfer, with Cr(V) reactant and Cr(IV) intermediate. [c] Relative rates at which the radical intermediate from the reductant reacts with Cr(V) and Cr(IV) (see, for example, the sequence (2)–(5) in text). [d] This work.

Our results are consistent with a sequence initiated by formation of precursor complex II (Scheme I), which undergoes internal electron transfer (IET), yielding the $NO_2^•$ radical and the coordinatively unsaturated Cr(IV) intermediate III. The latter then captures NO_2^- (which is in excess in most of our runs), yielding the Cr(IV)–ONO complex IV, which then suffers further reduction (here represented as an outer-sphere process) by external nitrite. An analogous sequence (Scheme II) may be envisaged for that portion of the reaction involving reduction by the $NO_2^•$ radical. Here, internal electron transfer within precursor VI forms the Cr(IV)–N(V) intermediate VII, which features an electron-deficient nitrogen atom. Complex VII then undergoes rapid hydration (at nitrogen) and aquation (at Cr^{IV}) to yield the Cr^{IV}(H_2O)$_2$ complex VIII, which, like the related intermediate III, is converted to a nitrito complex (IV′) and then reduced to Cr^{III}.

Although the observed pattern of individual specific rates indicates that reduction of Cr(V) by NO_2^- or by $NO_2^•$ entails preliminary invasion of the metal coordination sphere by the reductant, we suggest that the nitrite in the Cr(III) product (V) arises from ligation at the Cr(IV) level. Electron transfer to Cr(V) from bound nitrite would be expected make it a much less effective ligand. Moreover, the proposed catalytic sequence requires that $NO_2^•$ be released into solution, for Cr^V and Cr^{IV} compete for it, the former more successfully.

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(30) See, for example: Gutowski, H. S.; McCall, D. W.; Slichter, C. P. *J. Chem. Phys.* **1953**, *21*, 279.

(31) Hypophosphoric acid, $H_4P_2O_6$, which may be considered a dimeric derivative of P(IV), has long been known.[32] However, we find no report of its preparation by oxidation of a P(III) species.

(32) See, for example: Yost, D. M.; Russell, H., Jr. *Systematic Inorganic Chemistry of the Fifth-and-Sixth Group Nonmetallic Elements*; Prentice Hall: Englewood Cliffs, NJ, 1944; p 205.

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Sequences analogous to (3)–(6) have now been proposed for the reductions of carboxylate-bound chromium(V) by five anionic reducing agents (Table III). In comparing the selectivities toward Cr(V) and Cr(IV) (k_1/k_3) for these five reductants and for the radical intermediates derived from them (k_2/k_4), we see that marked autocatalysis and clocklike kinetic profiles related to the consumption of Cr(IV) are associated with dramatic turnarounds (10^3-fold) in $k_{\mathrm{Cr(V)}}/k_{\mathrm{Cr(IV)}}$ ratios in a given system. With hypophosphite (for which reversal in these selectivites is less striking) and with nitrite (for which both rate ratios exceed unity), autocatalytic behavior is subdued, and no clocklike pattern is evident. Despite elaborate arguments to the contrary,[6] such a reversal is not a requirement for autocatalysis, but without it a preponderant portion of the overall reaction proceeds along a noncatalytic path.

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Ruthenium(II)-Assisted Borohydride Reduction of Acetonitrile

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The sodium borohydride reduction of $[\mathrm{Ru(MeCN)_3(triars)}](\mathrm{CF_3SO_3})_2$ (triars = $\mathrm{MeC(CH_2AsPh_2)_3}$) in methanol yields the bis(amine) hydride $[\mathrm{RuH(NH_2CH_2Me)_2(triars)}](\mathrm{CF_3SO_3})$. The amine and methylene protons are inequivalent on the NMR time scale up to +80 °C. Deuterium substitution studies support the intermediacy of a metal–imine complex in the reduction. By contrast, reaction of $\mathrm{NaBH_4}$ and $[\mathrm{Ru(MeCN)_3(triphos)}](\mathrm{CF_3SO_3})_2$ (triphos = $\mathrm{MeC(CH_2PPh_2)_3}$) gives the hydride borohydride complex $[\mathrm{RuH(BH_4)(triphos)}]$. NMR and GC measurements prove that MeCN is not reduced to amine in this case. The difference in reactivity is attributed to the difference in trans effects of the phosphorus and arsenic donors.

Introduction

The efficacy of sodium borohydride as a reducing agent in organic synthesis is apparent in the extant chemical literature. Substrates such as aldehydes and ketones are smoothly reduced by $\mathrm{NaBH_4}$.[1] However, nitriles are more difficult to reduce, usually requiring a much more powerful reductant (e.g., $\mathrm{LiAlH_4}$) or conversion to alkylnitrilium salts before addition of borohydride.[2] Alternatively, the transformation of nitriles to amines can be affected by $\mathrm{NaBH_4}$ in the presence of $\mathrm{CoCl_2}$[3] or of Raney nickel[4] in alcohols.

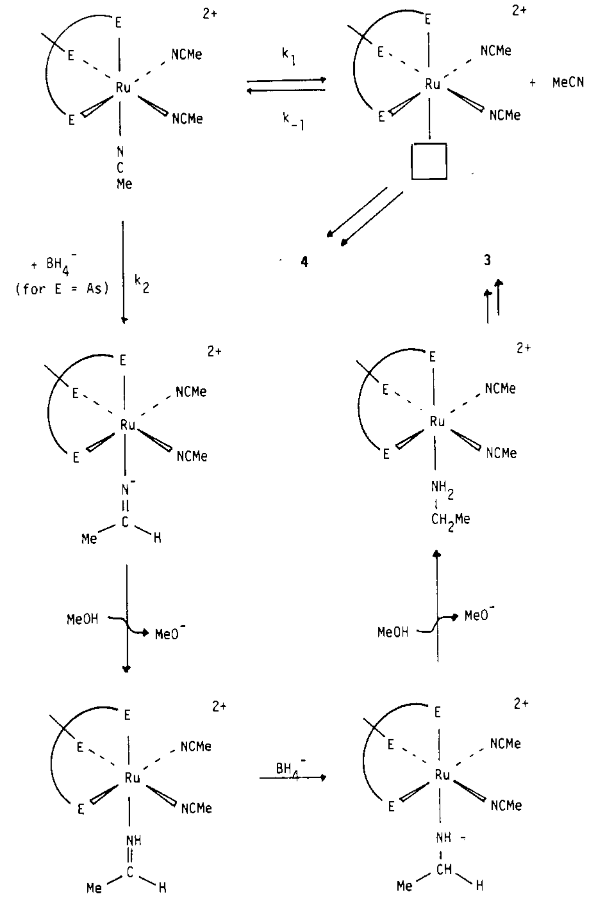
During the process of exploring new ruthenium solvento complexes with the facially coordinating coligand tripod $\mathrm{MeC(CH_2EPh_2)_3}$ [tripod, E = P (triphos) or As (triars); see Scheme I], it became apparent that the newly synthesized tris(acetonitrile) complexes $[\mathrm{Ru(MeCN)_3(tripod)}](\mathrm{CF_3SO_3})_2$ (tripod = triars (**1**) and triphos (**2**))[5] could potentially assist in the borohydride reduction of the coordinated nitrile. Thus, Crabtree and Pearman[6] report that the reaction of *fac*-$[\mathrm{Ru(MeCN)_3(PMePh_2)_3}]^{2+}$ with $\mathrm{NaBH_4}$ gives *mer*-$[\mathrm{RuH(BH_4)(PMePh_2)_3}]$ with formation of 1 equiv of ethylamine. The results of this study are reported herein.

Results and Discussion

Reaction of 1 with Borohydride. On the basis of earlier work by Crabtree and Pearman,[6] treatment of **1** with $\mathrm{NaBH_4}$ was expected to yield a hydride borohydride complex with concomitant reduction of nitrile. Although the addition of an 8–10 molar excess of $\mathrm{NaBH_4}$ to a MeOH solution of **1** resulted in reduction of the coordinated acetonitrile, instead of a complex analogous to that of Crabtree and Pearman[6] the bis(amine) hydride $[\mathrm{RuH(NH_2CH_2Me)_2(triars)}](\mathrm{CF_3SO_3})$ (**3**) was produced (eq 1). It has not proved possible to give a balanced equation for this reaction because the formation of **3** is always accompanied by 20–30% amounts of another as yet unidentified product, X. Further, it has been independently established that **3** reacts with $\mathrm{BH_4^-}$ with release of ethylamine and formation of X.

$$\underset{\mathbf{1}}{[\mathrm{Ru(MeCN)_3(triars)}](\mathrm{CF_3SO_3})_2} \xrightarrow[\mathrm{MeOH}]{\mathrm{NaBH_4}} \underset{\mathbf{3}}{[\mathrm{RuH(NH_2CH_2Me)_2(triars)}](\mathrm{CF_3SO_3})} \quad (1)$$

Scheme I[a]



[a] The tripod ligands represented are $\mathrm{MeC(CH_2EPh_2)_3}$ (E = P (triphos), As (triars)).

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