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Electron Transfer. 125. Intermediate Oxidation States in the Reduction of Chromium(VI) with Hypophosphite[1]

Swapan K. Chandra,* E. Gelerinter, and E. S. Gould*

Department of Chemistry, Kent State University, Kent, Ohio 44242

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When $HCrO_4^-$ is reduced by hypophosphite in solutions buffered by 2-ethyl-2-hydroxybutanoic acid and its anion, chelated complexes of both Cr(V) and Cr(IV), both of them stabilized in the medium used, are formed in parallel reactions. When these reactions are allowed to proceed to completion in the presence of $Cl(NH_3)_5Co^{2+}$, a scavenger for Cr(II), 91−92% of the Cr(VI) taken is found to be converted to Cr(II), indicating that very nearly all of the reacting system proceeds through Cr(IV) and bypasses the more usual state Cr(III). Measured initial rates for formation of the strongly absorbing state Cr(IV) yield a two-term rate law pointing to paths at two different protonation levels, both involving a transition state containing the two redox partners and two ligating carboxyl groups. The formation of Cr(V) proceeds 5.3 times as rapidly as the generation of Cr(IV), a rate ratio essentially independent of reagent and buffer concentrations. Substitution of $D_2PO_2^-$ for $H_2PO_2^-$ retards formation of Cr(IV) 4-fold and generation of Cr(V) by a factor of 2.2. The solvent isotope effect, $(\text{rate})_{D_2O}/(\text{rate})_{H_2O}$, favors the deuterated system, the ratio being 2.2 for formation of Cr(IV) and 1.7 for generation of Cr(V). Our observations favor a sequence initiated by the ligation of $HCrO_4^-$ to a bis chelate of Cr(VI) derived from the buffering carboxylate anion. Conversions of Cr(VI) to Cr(IV) and of Cr(IV) to Cr(II) entail hydride shifts from P(I) to the Cr(=O) function, whereas the formation of Cr(V) and its reduction of the latter to Cr(IV) may involve preliminary coordination of $H_2PO_2^-$ to the chromium center, followed by P−H to O−H tautomerization within the binuclear complex and then single-electron transfer from phosphorus to the chromium center.

It is now clear that reactions between metal-centered oxidants and hydrogen-containing reductants may, in favorable instances, take place in net two-unit transactions entailing hydride-to-metal shifts. Early reports implicated such shifts in reactions of Pt(II) with formate[2] and alkoxide[3] functions and indicated that the reductions of corrin-bound Co(III) by formate and related species may proceed by such a path.[4] A similar shift has been proposed for the reduction of Co(III) by ligated hypophosphite.[5] Scott, Bakac, and Espenson[6] recently described strong evidence that the oxidations of a variety of alcohols by the novel oxidant $[Cr^{IV}O]^{2+}(aq)$ involve hydride transfers within chromium−alcohol complexes. In addition, these authors suggest that analogous shifts may intervene in the corresponding reactions of the more familiar acceptor $HCrO_4^-$.

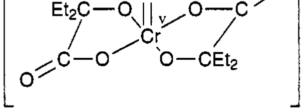
The present report deals with the reduction of chromium(VI) by hypophosphite ($H_2PO_2^-$). These reactions were carried out in solutions buffered by 2-ethyl-2-hydroxybutanoic acid (**I**) and its sodium salt. This medium has been found to stabilize the atypical oxidation states Cr(V) and Cr(IV) markedly,[7] and the intense absorbance of the latter state makes it possible, in favorable cases, to monitor its formation. We here present evidence pointing to competing initial redox acts, one of which entails the generation of Cr(IV) via hydride transfer from phosphorus.

$$(C_2H_5)_2C(OH)COOH$$

I

Experimental Section

Materials. Sodium hypophosphite hydrate, sodium chromate, hypophosphorus acid-d_3 (D_3PO_2), and deuterium oxide (99.9 atom % D) were Aldrich products and were used as received. Lithium perchlorate (used, after two recrystallizations, in kinetic experiments) was prepared as described by Dockal.[8] 2-Ethyl-2-hydroxybutanoic acid (**I**) (Aldrich) was recrystallized (5.0 g in 60 mL of hot hexane) before use.[9] Chloropentaamminecobalt(III) perchlorate, $Cl(NH_3)_5Co(ClO_4)_2$,[10a] and the sodium salt of the Cr(V) chelate, bis(2-ethyl-2-hydroxybutanoato)oxochromate(V) (complex **II**),[10b] were prepared as described.



II

Kinetic Experiments. Aqueous Cr(VI)−P(I) systems were buffered by mixtures of 2-ethyl-2-hydroxybutanoic acid (HLig) and its sodium salt (Na^+Lig^-). Ionic strength was fixed at 1.0 M by addition of $LiClO_4$.

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[2] Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1962**, 5075.

[3] Foley, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 2732.

[4] (a) Bayston, J. H.; King, N. K.; Looney, F. D.; Winfield, M. E. *J. Am. Chem. Soc.* **1969**, *91*, 2775. (b) Linn, D. E., Jr.; Gould, E. S. *Inorg. Chem.* **1988**, *27*, 1625.

[5] Linn, D. E., Jr.; Gould, E. S. *Inorg. Chem.* **1987**, *26*, 3442; **1988**, *27*, 3140.

[6] Scott, S. L.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1992**, *1114*, 4205.

[7] Ghosh, M. C.; Gould, E. S. *Inorg. Chem.* **1990**, *29*, 4258; **1991**, *30*, 491.

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

[9] Reproducible kinetic results required that this carboxylic acid (used as a buffer component) be especially pure. Traces of colored impurities must be absent. In addition, solutions containing the buffer and Cr(VI) but no added hypophosphite should exhibit no detectable absorbance increase at 510 nm (a Cr(IV) maximum) on standing for 10 min at 25 °C.

[10] (a) Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1318. (b) Krumpolc, M.; Rocek, J. *J. Am. Chem. Soc.* **1979**, *101*, 3206.

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Temperatures were kept at 25.0 ± 0.2 °C. Reactions were generally monitored using a Beckman Model 5260 recording spectrophotometer, and in some cases the growth of Cr(V) (a d^1 center) was followed using ESR spectrometry.[11] To avoid complications due to the reaction of Cr(IV) with unconsumed Cr(VI)[7] and the reaction of Cr(IV) with hypophosphite,[12] kinetic comparisons utilized absorbance changes (reflecting initial rates) which were measured immediately after adding Na_2CrO_4 solutions to buffered hypophosphite.[13]

Initial rates of absorbance increases were calculated using the method of Chandler,[14] in which absorbances (A values) during the first few percent of reaction were related to reaction times (t) by the polynomial expression (1). Least-squares treatment of absorbance data (14 points

$$A = A_0 + a_1t + a_2t^2 + a_3t^3 + ... \qquad (1)$$

per experiment) gave estimates of a_1, the initial rate. Replicate runs generally yielded a_1 values agreeing to better than 3%, but rates for the slow reactions were somewhat less precise.

Absorbance increases stem from parallel generation of Cr(IV) and Cr(V), both from Cr(VI) (eq 2). Here, the ϵ values are molar

$$\mathrm{d(Abs)/d}t = (\mathrm{rate})_{64}(\epsilon_4 - \epsilon_6) + (\mathrm{rate})_{65}(\epsilon_5 - \epsilon_6) \qquad (2)$$

absorbances of the three states, at the wavelength chosen. Although ϵ_5 falls well below ϵ_4 within the range 400–600 nm, the more rapid conversion to Cr(V) (r_{65}) (see Results) gives rise to significant contributions of the latter to the observed changes. Least-squares refinement of absorbance data from replicate runs at three or more wavelengths allowed calculation of rates for the two competing processes. Rates so obtained for formation of Cr(V) were in agreement with those estimated from (the less precise) ESR measurements under the same conditions. At no single wavelength was the absorbance change due to growth of Cr(V) negligible in comparison to that resulting from growth of Cr(IV).

Trapping Experiments with Co(III). A number of reductions by hypophosphite were carried out in the presence of excess $Cl(NH_3)_5Co(ClO_4)_2$ and were allowed to proceed to completion (16 h). The quantity of Co(II) produced in these systems was determined by dilution of the reaction mixture with 9 times its volume of concentrated HCl, allowing any precipitate to settle, and then measuring the absorbance of $CoCl_4^{2-}$ in the supernatant at 692 nm.[10a]

Additional Observations. In separate experiments, the Cr(V) complex **II** was found to be reduced about 30% more rapidly than $HCrO_4^-$ by hypophosphite (under comparable conditions). Phosphorous acid (H_3PO_3) reduces $HCrO_4^-$ about 3 times as rapidly as does hypophosphite but reacts imperceptibly with Cr(V) in our hands. In the absence of chelating hydroxy carboxylic acids, the reaction of $HCrO_4^-$ with hypophosphite within the pH range used in the present study proceeds negligibly slowly.[15]

Results

When the Cr(VI)–hypophosphite reaction is carried out in solutions containing excess $(NH_3)_5CoCl^{2+}$, the latter acts as a scavenger for Cr(II) (eq 3), for none of the other oxidation states of chromium will reduce ammonia-bound cobalt(III), nor will hypophosphite or phosphite.

$$\mathrm{Cr(II) + Co(III) \rightarrow Co(II) + Cr(III)} \qquad (3)$$

Results of these trapping experiments are summarized in Table 1. The high yield of Co(II) tells us that in our medium the Cr(VI) taken in the hypophosphite reductions is converted nearly quantitatively to Cr(II). Although a major portion of the Cr(VI) taken is reduced through Cr(V), the latter state is found also to be reduced almost completely to Cr(II).[16] Apparent departures from quantitative generation of Cr(II) may be attributed partially to its consumption by traces of O_2 and partially to diversion of Cr^{IV} by disproportionation ($2Cr^{IV} \rightarrow Cr^{III} + Cr^{V}$). The latter, a bimolecular process,[17] is seen to become more marked when Cr(IV) is generated at much higher concentration by the very rapid Cr(VI)–As(III) reaction[7] before its reaction with hypophosphite.

Table 1. Hypophosphite Reactions Carried Out with Added $Cl(NH_3)_5Co^{2+}$ (Trapping Experiments)[a]

Cr ([Cr], mM)	$[Co^{III}]$, mM[b]	$[H_2PO_2^-]$, mM	$[As^{III}]$, mM	$[Co^{II}]$, mM[c]	yield of Co^{II}, %[d]
Cr^{VI} (1.00)	15.0	24.0	0	0.92	92
Cr^{VI} (0.50)	15.0	24.0	0	0.46	92
Cr^{VI} (1.00)	15.0	48.0	0	0.91	91
Cr^{VI} (0.60)	9.0	15.0	6.0[e]	0.22	37
Cr^{VI} (0.20)	9.0	6.0	2.0[f]	0.091	46
Cr^{V} (1.00)[g]	15.0	24.0	0	0.91	91
Cr^{III} (1.00)[h]	15.0	20.0	0	0	
none	15.0	24.0	0	0	

[a] Reactions were carried out at 25 °C in buffers which were 0.20 M each in 2-ethyl-2-hydroxybutanoic acid (**I**) and its sodium salt; μ = 1.0 M ($LiClO_4$); waiting period 16 h. [b] $Cl(NH_3)_5Co(ClO_4)_2$. [c] $[Co^{II}]$ estimated in concentrated HCl at 692 nm. [d] $[Co^{II}]_{found}/[Cr]_{taken}$. [e] As^{III} added 5 min before $H_2PO_2^-$. [f] $H_2PO_2^-$ added 5 min before As(III). [g] Cr(V) chelate **II** added as its sodium salt. [h] $(Lig)_2Cr^{III}(H_2O)_2^+$ (ref 7).

Table 2. Kinetic Data at Three Wavelengths for a Representative Run of the $HCrO_4^-$–$H_2PO_2^-$ Reaction in 2-Ethyl-2-hybroxybutanoate (Lig^-) Buffer[a]

	422 nm	510 nm	584 nm
ϵ_6, M^{-1} cm^{-1}	164	17	14
ϵ_5, M^{-1} cm^{-1}	461	160	50
ϵ_4,[b] M^{-1} cm^{-1}	1350	2600	1580
d(Abs)/dt, OD/s × 10^5 [c]	13.0 (12.9)	15.0 (15.2)	8.0 (7.9)

[a] Reactions were run at 25 °C, μ = 1.0 ($LiClO_4$); $[Lig^-]$ = [HLig] = 0.20 M. pH = 2.97. $[Cr^{VI}] = 1.00 \times 10^{-3}$ M; $[H_2PO_2^-] = 24.0 \times 10^{-3}$ M. [b] ϵ_4 obtained from the spectrum of Cr(IV), generated from $HCrO_4^-$ and excess As(III) (see ref 7). [c] Initial rates, obtained by the procedure of Chandler.[14] Parenthetical values were calculated from eq 2 in text, taking r_{64} and r_{65} as 4.52×10^{-8} and 25.8×10^{-8} M s^{-1}.

Representative kinetic data, pertaining to a single system studied at three different wavelengths, appear in Table 2. These lead to three equations of type (2), least-squares refinement of which yields rates $r_{64} = (4.52 \pm 0.08) \times 10^{-8}$ and $r_{65} = (25.8 \pm 0.9) \times 10^{-8}$ M s^{-1} for conversions to Cr(IV) and Cr(V). The value of r_{65} is in agreement with 2.8×10^{-7} M s^{-1} estimated from ESR experiments. Analogous treatment of data taken at various concentrations of reactants and buffer components and within the pH range 2.4–3.9 yielded r_{64} values listed in Table 3. Moreover, the ratio r_{65}/r_{64} was found to be 5.3 ± 0.3 throughout.

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(11) X-band ESR spectra were taken in a flat quartz cell utilizing an IBM 200D-SRC spectrometer. The chelated Cr(V) complex (**II**) derived from the ligand anion exhibits a single peak (g = 1.98, line width 2.5 G).

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

(13) The order of addition appeared to be critical for these measurements. When hypophosphite was added to buffered solutions of Cr(VI), profiles were complicated by small rapid initial decreases in absorbance, possibly reflecting reequilibration of ligands at the Cr(VI) center.

(14) Chandler, W. D.; Lee, E. J.; Lee, D. G. *J. Chem. Educ.* **1987**, *64*, 878. The coefficient a_3 was generally negligible in our experiments, as were those for higher order terms.

(15) See, for example: Haight, G. P., Jr.; Rose, M.; Preer, J. *J. Am. Chem. Soc.* **1968**, *90*, 4809.

(16) An earlier study[12] described the separation and characterization of Cr(III) products obtained from the reductions of Cr(V) and Cr(IV) by hypophosphite in media of the present type, but in the absence of a Co(III) trap. These products were formed, at least in part, from the reaction of Cr(II) with unconsumed oxidant or with atmospheric oxygen (which was not excluded).

(17) Ghosh, M. C.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1992**, *31*, 702.

Table 3. Kinetic Data for the Reaction of $HCrO_4^-$ with $H_2PO_2^-$ in 2-Ethyl-2-hydroxybutanoate Buffers (25 °C, $\mu = 1.0$ M)

$[Cr^{VI}]$, mM	$[P^I]$,[a] mM	$[Lig^-]$,[b] M	[HLig],[c] M	pH	(rate) × 10^8 [d]
1.00	5.1	0.20	0.20	2.93	0.95 ± 0.06 (1.10)
1.00	10.0	0.20	0.20	2.95	1.78 ± 0.07 (1.87)
1.00	15.0	0.20	0.20	2.95	2.77 ± 0.07 (2.82)
1.00	24.0	0.20	0.20	2.97	4.52 ± 0.08 (4.51)
1.00	51.0	0.20	0.20	2.97	9.1 ± 0.2 (9.6)
0.10	24.0	0.20	0.20	2.93	0.54 ± 0.06 (0.52)
0.25	24.0	0.20	0.20	2.95	1.39 ± 0.04 (1.13)
0.50	24.0	0.20	0.20	2.95	2.47 ± 0.04 (2.25)
2.0	24.0	0.20	0.20	2.95	8.6 ± 0.2 (9.0)
4.0	24.0	0.20	0.20	2.97	14.4 ± 0.3 (18.0)
1.0	24.0	0.15	0.15	2.97	2.62 ± 0.07 (2.53)
1.0	24.0	0.10	0.10	2.89	1.28 ± 0.06 (1.48)
1.0	24.0	0.050	0.050	2.87	0.45 ± 0.03 (0.37)
1.0	24.0	0.050	0.15	2.46	2.94 ± 0.04 (2.15)
1.0	24.0	0.10	0.15	2.75	2.91 ± 0.04 (2.59)
1.0	24.0	0.22	0.13	3.11	3.36 ± 0.09 (3.15)
1.0	24.0	0.15	0.020	3.86	< 0.16 (0.15)
1.0	24.0	0.15	0.050	3.43	0.51 ± 0.03 (0.49)
1.0	24.0	0.15	0.10	3.09	1.64 ± 0.06 (1.55)
1.0	24.0	0.15	0.25	2.69	6.9 ± 0.5 (7.3)

[a] NaH_2PO_2. [b] 2-Ethyl-2-hydroxybutanoate. [c] 2-Ethyl-2-hydroxybutanoic acid (**I**). [d] Initial rates (M s^{-1}) of formation of Cr(IV), obtained after adjustment for parallel generation of Cr(V) (see Experimental Section); parenthetical values were calculated using eq 4 in text, taking k_1 as 15.3 M^{-4} s^{-1} and k_2 as 2.5 × 10^4 M^{-5} s^{-1}.

From kinetic data pertaining to formation of Cr(IV) (Table 3), these reactions are seen to be very nearly first order each in P(I) and Cr(VI). In addition, rates are proportional to $[Lig^-]^2$ and also increase with acidity, with the $[H^+]$-dependence somewhat more steep than first order. Data conform reasonably to rate law 4. Refinement of values according to (4) yields k_1

$$\text{rate} = \frac{d[Cr^{IV}]}{dt} = [Cr^{VI}][P^I][Lig^-]^2[H^+]\,(k_1 + k_2[H^+] \quad (4)$$

$= 15.3 \pm 0.2$ M^{-4} s^{-1} and $k_2 = (2.5 \pm 0.2) \times 10^4$ M^{-5} s^{-1}. Rates calculated from (4) are compared to experimental values at the right of this table.

Since the relative rates of formation of Cr(V) and Cr(IV) are found not to vary systematically within the ranges of reactants and buffers taken, the rate law for generation of Cr(V), which contributes only minor portions of the total change, may be taken to correspond to, or be closely related to, eq 4.

Results of a limited number of experiments dealing with substrate and solvent deuterium kinetic isotope effects are listed in Table 4. All reactions in this group are carried out using the same concentrations of reagents and buffer components. The substrate isotope effect for generation of Cr(IV), $((rate)_{H_2PO_2}/(rate)_{D_2PO_2} = 3.9)$, is found to be somewhat greater than that for formation of Cr(V) (=2.2) under our conditions. On the other hand, the solvent isotope effect, obtained by substitution of D_2O for solvent water, favors the deuterated system. The ratio $(rate)_{D_2O}/(rate)_{H_2O}$ is found to be 2.2 for conversion to Cr(IV) and 1.7 for conversion to Cr(V).

Discussion

The spectrophotometric studies of the Cr(VI)–hypophosphite reaction in the present ligand environment, taken in combination with ESR examination of this system, make it clear that the reduction is initiated by competing le$^-$ and 2e$^-$ paths, forming chelated Cr(V) and chelated Cr(IV) species. The most notable results arise from those experiments in which $Cl(NH_3)_5Co^{2+}$ was added as a specific trap for Cr(II). Since all but a small portion of Cr(VI) taken is converted to Cr(II) and since Cr(III) cannot be reduced to Cr(II) under our conditions, very nearly every act of reduction must somehow have passed through Cr(IV) and virtually all of the intervening Cr(IV) must have undergone a 2e$^-$ reduction directly to Cr(II). This conclusion must apply as well to the major competing path proceeding through Cr(V). The further implication then is that Cr(V), which is generated by a le$^-$ path, is also consumed by a le$^-$ path which allows it to pass through the obligatory Cr(IV) state.

Table 4. Kinetic Isotope Effects for the $HCrO_4^-$–$H_2PO_2^-$ Reaction in 2-Ethyl-2-hydroxybutanoate Buffers (25 °C, $\mu = 1.0$ M)[a]

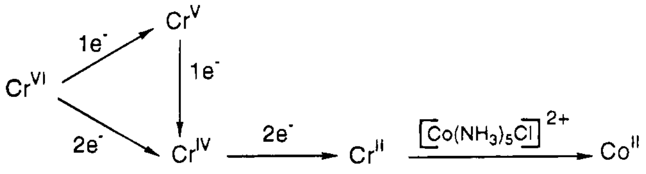
A. Substrate Isotope Effect[b]

reductant	product	rate of formn[c]	method
$H_2PO_2^-$	Cr(IV)	9.3	vis–UV
$D_2PO_2^-$	Cr(IV)	2.41	vis–UV
$H_2PO_2^-$	Cr(V)	49	ESR
$D_2PO_2^-$	Cr(V)	22	ESR

B. Solvent Isotope Effect[d]

% D_2O	product	rate of formn[c]	product	rate of formn[c]
0	Cr(IV)	9.3	Cr(V)	49
25	Cr(IV)	13.6	Cr(V)	59
50	Cr(IV)	14.7	Cr(V)	62
75	Cr(IV)	17.3	Cr(V)	69
100	Cr(IV)	20.2	Cr(V)	82

[a] Reactions were carried out with $[P^I] = 0.051$ M and $[Cr^{VI}] = 0.0010$ M, in buffers which were 0.20 M each in 2-ethyl-2-hydroxybutanoic acid (**I**) and its sodium salt. [b] Reactions in H_2O. [c] Rates (in M s^{-1} × 10^8) are initial values. Measurements in the vis–UV were carried out at three wavelengths (see Experimental Section and Table 2). [d] Experiments evaluating the solvent isotope effect were carried out using NaH_2PO_2 with measurements made in the vis–UV.



The reduction path initiated by generation of Cr(IV) brings to mind the sequence proposed by Scott and co-workers[6] for the oxidations of alcohols by $HCrO_4^-$ in the absence of ligands which stabilize the intervening states. The operation of the alternate path in the present system reminds us that with hypophosphite we have yet another nominally "2e$^-$ reductant" which, like Sn(II) and $Mo_2O_4^{2+}$, may enter into single-electron transactions if the driving force be sufficient.[18,19] One-electron oxidations of $H_2PO_2^-$ necessarily generate a derivative of P(II). The latter is a highly atypical state which is supported by considerable spectroscopic evidence[20] and which appears to intervene also in the Ce(IV) oxidation of Co(III)-bound hypophosphite.[5,21]

The two-term rate law (eq 4) for formation of Cr(IV) indicates contributions from two paths. Both transition states feature a

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[18] Ghosh, M. C.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1991**, *30*, 1039.

[19] Although the disproportionation of Cr^{IV} $(2Cr^{IV} \rightarrow Cr^V + Cr^{III})^{17}$ and the Cr^{VI}–Cr^{II} reaction $(Cr^{VI} + Cr^{II} \rightarrow Cr^V + Cr^{III})^6$ may account, in part, for the slight departure from quantitative conversion to Cr^{II} (Table 1), neither can contribute a significant fraction of the total $[Cr^V]$ in the reacting system since diversion to Cr^{III}, a nonreducible coproduct in each case, is found to be minimal. Note that the known[7] oxidation of Cr^{IV} by Cr^{VI} can generate no more than a minor portion of Cr^V present since the latter is seen to be formed much more rapidly than Cr^{IV} (Table 2).

[20] See, for example: Andrews, L.; Withnal, R. *J. Am. Chem. Soc.* **1988**, *110*, 5605.

unit each of the redox partners and two units of the ligand, but the two routes differ in protonation levels. In view of evidence that the Cr(IV) product is a bis chelate,[7] it is reasonable to assume the operation of a preliminary equilibrium, $Cr^{VI} + 2\ Lig^- \rightleftharpoons Cr^{VI}(Lig)_2$. No hint of kinetic saturation is evident at ligand concentrations as great as 0.22 M, pointing to relatively small association constants ($<4\ M^{-1}$) for both stages of ligation. Such low values, pertaining to the interactions between negative ions, are not unexpected.

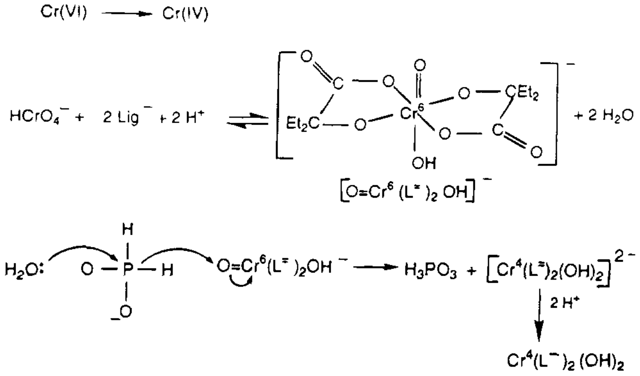
Since redox transformations are generally favored by protonation of the oxidant rather than the reductant, both stages of protonation may be taken to involve the Cr(VI) center. Although pK_A values cannot be evaluated from the present data, they must lie well below 2.5.

When $D_2PO_2^-$ is substituted for $H_2PO_2^-$, the generation of Cr(IV) is inhibited nearly 4-fold and that of Cr(V) about 2-fold. These substantial retardations indicate that the activation processes for both conversions entail stretching of the phosphorus–hydrogen bond. For the formation of Cr(IV) (a $2e^-$ process) a hydride shift to Cr(VI), analogous to that proposed for oxidations of alcohols by Cr(VI)[6] and by Ru(IV)[22] and for the $(corrin)Co^{III}$–formate reaction,[4b] comes to mind. The magnitude of the observed effect lies closes to that reported (3.5) for the oxidation of methanol by $[Cr^{IV}O]^{2+}$ [6] but falls below the recorded value (near 9) for its oxidation by $[(bipy)_2(py)RuO]^{2+}$.[22] To the extent that this effect may be thought to reflect the approach to linearity of the participating centers (P–H•·O=Cr) in the activated complex,[23] the transition state for formation of Cr(IV) in the present system may be taken to resemble that in the $[Cr^{IV}O]^{2+}$–methanol reaction[6] rather than that in the $(corrin)Co^{III}$–formate reaction ($k_{HCOO^-}/k_{DCOO^-} = 1.8$),[4b] for which a cyclic activated complex is favored.

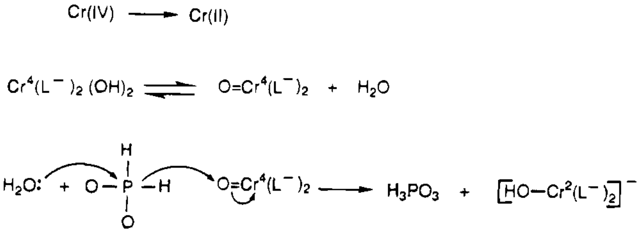
The deuterium isotope effect for the conversion of Cr(VI) to Cr(V), a net $1e^-$ transformation, is too large to correspond to a straightforward electron transfer process.[24] Two mechanistic possibilities may be considered. The first is a direct transfer of a P-bound hydrogen atom to the oxochromium(VI) function. Alternatively (and more credibly), tautomerization (P–H to O–H) within a $Cr(VI)-H_2PO_2^-$ complex may trigger transfer of an electron from phosphorus to Cr(VI). Although, in the absence of complicating features, deuterium isotope effects associated with transfers of protons and hydrogen atoms are expected[23] to be greater than those for hydride transfers, reported ranges for the three types of processes are known to overlap broadly.

When the reacting system is transferred from H_2O to D_2O, the formation of Cr(IV) is accelerated approximately 2-fold, whereas the rate of generation of Cr(V) is increased by a factor of 1.7. These solvent isotope effects are in accord with the picture of Bunton and Shiner,[23,25] who point out that protonation of a reaction intermediate (which is reflected in the rate law) is more pronounced in the deuterated solvent. The magnitude of the effect is close to that predicted by these authors ($k_{H_2O}/k_{D_2O} = 0.5-0.7$).[26]

Scheme 1



Scheme 2



Sequences for the predominant route in conversion of Cr(VI) to Cr(IV) and for Cr(IV) to Cr(II), given as Schemes 1 and 2, appear to be consistent with our data and with earlier observations concerning the various chromium species in the present medium. It is assumed that bis-chelation of Cr(VI) precedes reduction to lower states and that the chelated intermediate features the dinegative form of the ligand (L^{2-}) known to be present in anion **II**, the related complex of Cr(V),[10b,27] a less acidic center than Cr(VI). The proposed chelate is taken to be 6-coordinate in analogy with a number of reported $Cr^{VI}(=O)$ complexes[28] in which the coordination sphere of Cr(VI) is expanded beyond the more usual tetrahedral unit. It is likely that the hydride shift from hypophosphite to the $Cr^{VI}(=O)$ function is initiated by nucleophilic attack by water, thus avoiding the formation of the electron-deficient fragment HPO_2^+. Subsequent protonation of the bidentate ligand converts it to its uninegative form (L^-) thought to be typical of chelates of the lower oxidation states.

A closely related route is indicated for reduction of Cr(IV) (Scheme 2). Although recent evidence[29] favors a 6-coordinate dihydroxy structure, $Cr^4(L^-)_2(OH)_2$, for the predominant Cr(IV) complex in this medium, it does not rule out a minor contribution of an oxo-substituted form, $O{=}Cr^4(L^-)_2$, analogous to that favored[6] for the aqua-substituted Cr(IV) cation. Such a coordinatively unsaturated complex would be expected to be particularly susceptible to external attack by hydride.

The suggested path for formation of Cr(V) (Scheme 3) features an oxygen-bridged intermediate which serves to hold the Cr(VI) and P(I) centers in proximity. Jenkins[30] has stressed the importance of intramolecular proton transfer (P–H to O–H) in hypophosphite in determining the rates of its oxidation by several diverse reagents. Such transfers proceed with half-life

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(21) For recent reports of complexes featuring P(II), see: (a) Scherer, O. J.; Braun, J.; Walther, P.; Heckmann, G.; Wolmershauser, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 852. (b) Corrigan, J. F.; Doherty, S.; Taylor, N. J.; Carty, A. J. *J. Am. Chem. Soc.* **1994**, *116*, 9799.

(22) Roecker, L.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 746.

(23) See, for example: Saunders, W. H., Jr. *Tech. Chem. (N.Y.)* **1974**, *6*, 222, 241.

(24) See, for example: Itzkowitz, M. M.; Nordmeyer, F. R. *Inorg. Chem.* **1975**, *14*, 2124.

(25) Bunton, C. A.; Shiner, V. J. *J. Am. Chem. Soc.* **1961**, *83*, 42, 3207.

(26) In view of the lesser precision associated with the rates of generation of Cr(V) (which contributes only minor portions of the total absorbance changes), we are reluctant to comment on the apparent slight difference in solvent isotope effects for the two conversions.

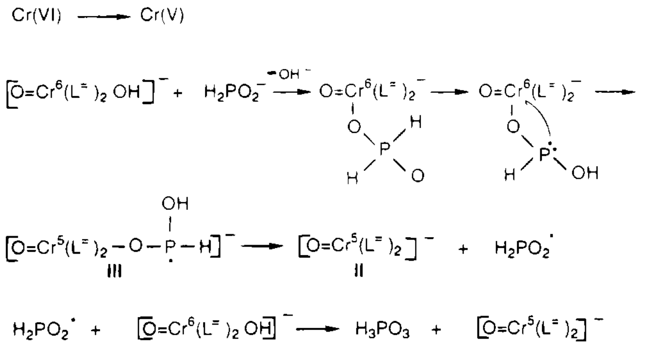
(27) See, for example: (a) Krumpolc, M.; DeBoer, B. B.; Rocek, J. *J. Am. Chem. Soc.* **1978**, *100*, 145.

(28) See, for example: (a) Edwards, A. J.; Falconer, W. E.; Sunder, W. A. *J. Chem. Soc., Dalton Trans.* **1974**, 541. (b) Gerlach, J. N.; Gard, G. L. *Inorg. Chem.* **1971**, *10*, 1541. (c) Brown, S. D.; Emme, L. M.; Gard, G. L. *J. Inorg. Nucl. Chem.* **1985**, *37*, 2557. (d) Stomberg, R.; Ainalem, I.-B. *Acta Chem. Scand.* **1968**, *21*, 897.

(29) Ghosh, M. C.; Gould, E. S. *J. Am. Chem. Soc.* **1993**, *115*, 3167.

(30) Jenkins, W. A.; Yost, D. M. *J. Inorg. Nucl. Chem.* **1959**, *11*, 297.

Scheme 3



periods greater than 50 h in chromium-free systems, but it is likely that preliminary coordination to a strongly electrophilic Cr(VI) center will substantially mobilize P-bound protons, leaving an exposed electron pair on phosphorus and facilitating the ensuing electron transfer to Cr(VI). Although it is perhaps conceivable that the resulting Cr(V)−P(II) intermediate (complex **III**) might undergo a second act of transfer, yielding Cr(IV)-bound phosphorus(III), the low rate at which Cr(IV) is generated from Cr(V) in our systems appears to rule out such a path as a major contributor. It is more reasonable that the principal fate of complex **III** is heterolysis to the $H_2PO_2^{\bullet}$ radical, which may then be consumed by unreduced Cr(VI) in a rapid follow-up reaction.[31] An analogous sequence (not shown here), upon which Scheme 3 is patterned, has been espoused by Ghosh[12] for the net 1e$^-$ reduction of Cr(V) to Cr(IV), again using hypophosphite.

In sum, the present study emphasizes the redox versatility of hypophosphite, the anion of the sole stable mononuclear oxyacid derived from the unipositive state of a nitrogen group element, but serves to remind us that selectivity between paths may be strongly dependent on the coreagent, even when we are dealing with consecutive oxidation states of the same element.

In the medium at hand, $H_2PO_2^-$ is seen to react with Cr(IV) preponderantly by hydride transfer but reduces Cr(V) by a net 1e$^-$ process (the nature of which is less certain) and uses a combination of the two routes in its reaction with Cr(VI).[32,33] Why a hydride transfer path for the Cr(V)-hypophosphite reaction (leading directly to the stable state Cr^{III}) appears to be mechanistically disfavored remains a puzzling point.

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(31) A reviewer asks whether a portion of the Co^{2+} formed in the sequence proceeding through Cr(V) may arise from reaction of $H_2PO_2^{\bullet}$ with the Co(III) trap taken. We have examined, in the presence of $Cl(NH_3)_5Co^{2+}$, two chromium-free systems most likely to generate this P(II) species—the oxidation of hypophosphite by the 1e$^-$ reagents Cl_2 and $Ce(IV)_{aq}$ (25 °C, waiting period 2 h). Despite complications due to precipitation in the Ce(IV) system, we find no evidence of the generation of Co^{2+} in either case.

(32) The redox behavior of hypophosphite stands in contrast to that of $As(OH)_3$, which, despite scattered reports to the contrary,[33] appears to enter only into two-unit transactions under ordinary conditions.[18]

(33) See, for example: Woods, R.; Kolthoff, I. M.; Meehan, E. J. *J. Am. Chem. Soc.* **1963**, *85*, 2385, 3324.