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Reduction of (Pyruvato)pentaamminecobalt(III) by Chromium(II) and the Chromium(III) Pyruvate Product

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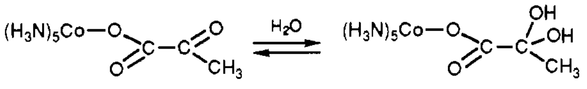
The kinetics of the chromium(II) reduction of the hydrate form of (pyruvato)pentaamminecobalt(III) have been determined in aqueous perchloric acid. The observed pseudo-first-order rate constant is $k_{obsd} = k_1[H^+] + k_2[Cr^{2+}]$, with $k_1 = 2.73 \pm 0.12\ M^{-1}\ s^{-1}$ and $k_2 = 25.5 \pm 1.8\ M^{-1}\ s^{-1}$ at 25 °C. The k_1 path is assigned to dehydration of the ligand to produce the keto form, which has been shown by Price and Taube to be rapidly reduced. The k_2 path gives the rate constant for reduction of the hydrated ligand complex and is about 400 times smaller than that for the keto form. The major chromium product at low acidity (~0.01-0.02 M H^+) is a reddish species identified as the chromium(III)-pyruvate chelate by comparison of its electronic spectrum to those of analogous chelates of other α-hydroxy carboxylate ligands. The kinetics of chelate ring opening in the latter species have been studied, and it is found that the protonated form opens with $k = (1.12 \pm 0.04) \times 10^{-3}\ s^{-1}$ and has an acid dissociation constant of $(8.3 \pm 0.5) \times 10^{-2}$ M. At higher acidities (~0.5 M H^+), the major product is violet with ion-exchange and electronic spectral properties similar to those of $Cr(OH_2)_6^{3+}$ except for a strong UV absorbance. Some pyruvate (<10%) is held back in this fraction, and it is assigned as a mixture of predominantly $Cr(OH_2)_6^{3+}$ plus some monodentate complex with chromium bound to the OH group of the hydrate form of the pyruvate ligand.

Introduction

Previous studies[1-3] have shown that the pyruvate complex of pentaamminecobalt(III) in acidic solution is present as an equilibrium mixture of about 70% as the keto form (I) and 30% as the hydrate (II).



(1)

I II

The reduction of this mixture by chromium(II) was studied by Price and Taube,[1] who showed that the keto form is reduced much more rapidly with $k = 1.1 \times 10^4\ M^{-1}\ s^{-1}$ (25 °C, 1 M $HClO_4$/$NaClO_4$). The rate for the hydrate was not determined. Price and Taube identified the chromium(III) product as the monodentate species $(H_2O)_5CrO_2CC(O)CH_3^{2+}$ based on its electronic spectrum (λ, nm (ϵ, $M^{-1}\ cm^{-1}$): 410 (21.0), 555 (19.9)). However our recent study[4] of the reaction of pyruvate with alkylpentaaquachromium(III) complexes indicates that this product identification may be significantly incomplete. Therefore the present study was undertaken to clarify the nature of the products of the reduction reaction and to characterize fully the chromium(III)-pyruvate complex. In addition, the reduction rate of the hydrate has been determined along with the rate of the hydrate-to-keto reaction in eq 1.

Results

Kinetics of Reduction of (Pyruvato)pentaamminecobalt(III) by Chromium(II). Our preliminary observations confirm those of Price and Taube[1] in that there is a rapid reaction which is complete in a few milliseconds under our concentration conditions, but this does not consume all of the cobalt(III) judging from the absorbance in the 490-nm region. The remaining cobalt(III) is reduced within ~60 s, and the kinetics of this step have been determined here. Therefore, our kinetic observations refer to the behavior of the hydrate form.

For the kinetic results, the initial concentration of cobalt(III) has been reduced to 30% of the cobalt(III) initially added to account for the amount reduced as the keto form in the faster step, and the initial chromium(II) has been corrected accordingly. The absorbance-time curves were well fitted to a first-order exponential decay at both 500 and 310 nm so that $-d[Co(III)]/dt = k_{obsd}[Co(III)]$. This is somewhat surprising because even the corrected initial concentrations have $[Cr(II)] \sim (3-10)[Co(III)]$, and pseudo-first-order conditions really are not satisfied. A full analysis has shown that the apparent first-order behavior results mainly because more than 50% of the reaction is proceeding by a path that is independent of [Cr(II)] for most of the runs. The observed rate constants from the second-order analysis differ by less than 3% from the first-order constants, and the latter are used in the analysis. The variation of k_{obsd} with [Cr(II)] and $[H^+]$ is described by eq 2, where $a = 2.73 \pm 0.12\ M^{-1}\ s^{-1}$ and $b = 25.5 \pm 1.8\ M^{-1}$

$$k_{obsd} = a[H^+] + b[Cr(II)] \qquad (2)$$

s^{-1}, and any concentration independent term must be $<1 \times 10^{-2}\ s^{-1}$ from a least-squares analysis. A plot of $k_{obsd}/[Cr(II)]$ versus $[H^+]/[Cr(II)]$ is shown in Figure 1, and full results are given in the supplementary material.

It is known[5] that Zn^{2+} catalyzes the hydration-dehydration of pyruvate, and our solutions contain Zn^{2+} at half the concentration of Cr^{2+}. In several runs, shown in Figure 1, zinc perchlorate was added at a level equal to the chromium(II) level, and a small increase in rate can be noted but the effect is marginally above the experimental uncertainty. This minimal effect is consistent with the idea that the zinc catalysis of the hydration of pyruvate involves chelate formation. The chelation would be inhibited by the cobalt(III).

Products of Reduction of (Pyruvato)pentaamminecobalt(III) by Chromium(II). As noted above, Price and Taube[1] identified the chromium product as the monodentate carboxylate complex on the basis of its electronic spectrum. This seems unusual because the large reduction rates imply some involvement of the remote carbonyl function. The conditions of the ion-exchange separation[1] were not specified, but it can be inferred that it was done at ambient temperature using perchloric acid as the eluant. Work on the anation of $(H_2O)_5Cr\text{-}CH_2CN^{2+}$ by pyruvate[4] seems to yield different products and indicates that the pyruvate complex is acid sensitive so that the observations of Price and Taube might not represent the true product(s) of the reduction reaction.

Our experiments show that the product of the reduction, separated by ion exchange at 4 °C, is quite sensitive to the acidity of the original reaction solution, to the form of the ion-exchange resin (Na^+ or H^+), and to the acidity of the eluant. If the acidity throughout the reaction and isolation is low (0.01-0.02 M) then the major product is a reddish species that elutes like a 2+ ion. This product was nearly always contaminated with some cobalt(II), but slow elution from Dowex 50W-X8 resin yielded a fraction that appeared to be free of cobalt because it gave no precipitate of cobalt oxide on warming in alkaline hydrogen peroxide. Two such experiments gave the following electronic

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(1) Price, H. J.; Taube, H. *Inorg. Chem.* **1968**, *7*, 1.

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(3) Harrowfield, J. MacB.; Sargeson, A. M. *J. Am. Chem. Soc.* **1979**, *101*, 1514.

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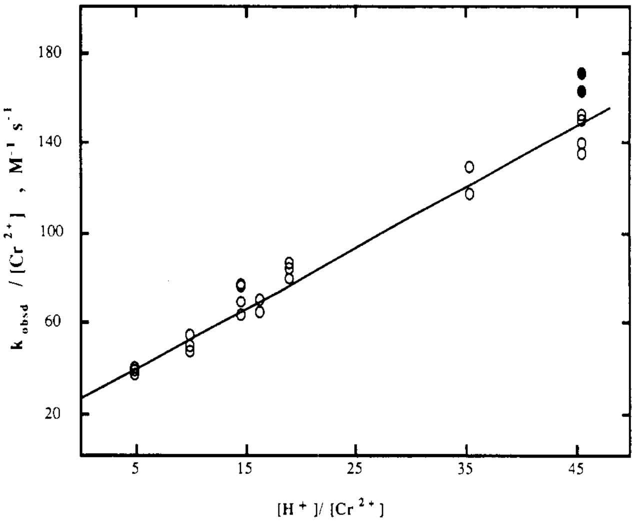


Figure 1. Dependence of the pseudo-first-order rate constant for the reduction of the hydrate form of (pyruvato)pentaamminecobalt(III) by chromium(II) on [H^+] and [Cr^{2+}], for solutions containing [Zn^{2+}] = 0.5[Cr^{2+}] (○) and [Zn^{2+}] = [Cr^{2+}] (●).

Table I. Electronic Spectra of Reaction Products and Chromium(III) Complexes

ligand[a]	λ (ϵ)[b]		ref
– acetate 2+	406 (20.7)	568 (21.6)	9
– trifluoroacetate 2+	409 (21.6)	576 (19.7)	*c*
– cyanoacetate 2+	411 (22.4)	570 (22.3)	*d*
– lactate 2+	413 (33.2)[e]	568 (26.8)[e]	10
– lactate 2+	409 (31.2)[e]	563 (25.7)[e]	9
– glycolate 2+	411 (30.5)[e]	568 (24.5)[e]	10
– glycolate 2+	411 (30.9)[e]	569 (24.5)[e]	9
– pyruvate 2+	410 (23)	562 (21)	this work
– pyruvate 2+	410 (21.0)	555 (19.9)	1
= lactate 2+	411 (45.0)	570 (40.1)	10
= glycolate 2+	411 (39.3)	569 (30.3)	10
= lactate +	437 (38.0)	548 (31.0)	10
= glycolate +	436 (38.5)	548 (32.5)	10
= pyruvate +	430 (37.0)	546 (33.0)	this work
– pyruvate 3+[f]	405 (16.3)	568 (14.0)	this work
– ethanol 3+	410 (16.8)	577 (14.6)	*g*
– water 3+	408 (15.6)	574 (13.4)	*h*

[a] The – ligand indicates a monodentate complex of $Cr(OH_2)_5$ with the charge given; = ligand indicates a bidentate chelate of $Cr(OH_2)_4$ with the charge given. [b] λ in nm; ϵ in M^{-1} cm^{-1}. [c] Sisley, M. J.; Jordan, R. B. *Inorg. Chem.* **1987**, *26*, 2833. [d] Kupferschmidt, W. C.; Jordan, R. B. *Inorg. Chem.* **1981**, *20*, 3469. [e] The slightly high ϵ values may be due to some protonated chelate. [f] This refers to the violet 3+ product mixture in Scheme III in a fraction estimated to contain 15–20% Cr(III) bound to pyruvate. [g] Kemp, D. W.; King, E. L. *J. Am. Chem. Soc.* **1967**, *89*, 3433. [h] Laswick, J. A.; Plane, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 3564.

spectra for the product (λ, nm (ϵ, M^{-1} cm^{-1}): 546 (33.4), 431 (37.5); 545 (32.6), 430 (36.5). On the basis of comparisons of the electronic spectrum to previous results, as summarized in Table I, this red species is identified as a pyruvate chelate.

The reddish species transforms to a new species in a period of 1–3 h, depending on the acidity. There is a general decrease in absorbance as the new species forms, with the result that the spectrum of the new product is even more sensitive to the presence of cobalt(II). Our best estimate of the electronic spectral properties with minimal interference give the following peak positions and molar absorptivities: 562 (21), 410 (23). This is as close as we have come to the spectrum reported by Price and Taube[1] with the major difference being their 555-nm peak position. It is possible that their solutions were more contaminated with cobalt(II) and this would tend to cause the observed shift without greatly affecting the peak at 410 nm. We believe that this new product is a monodentate carboxylate complex, as suggested by Price and Taube, consistent with other results in Table I. However it is not the direct product of the reduction reaction but rather is formed from chelate ring opening under the higher acidity conditions of their experiments.

Table II. Kinetic Results for Chelate Ring Opening of (Pyruvato)tetraaquachromium(III) at 25 °C

	10^4k_{obsd}, s^{-1}	
[H^+],[a] M	obsd[b]	calcd[c]
0.020	2.3	2.2
0.020	2.1	2.2
0.051	4.3	4.3
0.25	8.4	8.4
0.50	9.6	9.6

[a] The [H^+] has been corrected for the NH_3 released on reduction of the cobalt(III) complex, which was used to produce the chromium(III) complex. [b] These are the average of values from observations at 420 and 560 nm. The [Cr(III)] is in the range 5 × 10^{-4} to 2 × 10^{-3} M. The ionic strength is 0.041, 0.25, 0.25, 0.25, and 0.55 M, respectively, for the runs in the order tabulated. [c] Values calculated from the least-squares best fit to eq 3.

Some kinetic data have been obtained for the ring-opening process by observing the absorbance decrease at 420 and 560 nm. The results are summarized in Table II. The acid dependence of the pseudo-first-order rate constants is consistent with eq 3,

$$k_{obsd} = \frac{c[H^+]}{d + [H^+]} \tag{3}$$

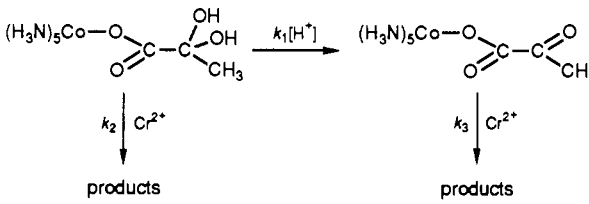
where $c = (1.12 \pm 0.04) \times 10^{-3}$ s^{-1} and $d = (8.3 \pm 0.5) \times 10^{-2}$ M from a nonlinear least-squares analysis. The values predicted by this rate law are compared to the experimental results in Table II.

In addition to the change that has been assigned to ring opening, there is a much slower reaction that occurs over several days in 0.02 M H^+. This reaction has not been studied in any detail, but it results in the appearance of a peak at 325 nm that is typical of free pyruvic acid as well as small decreases in absorbance at 410 and 560 nm. Therefore, the process is assigned to hydrolysis of the monodentate complex to give $Cr(OH_2)_6^{3+}$ and pyruvic acid.

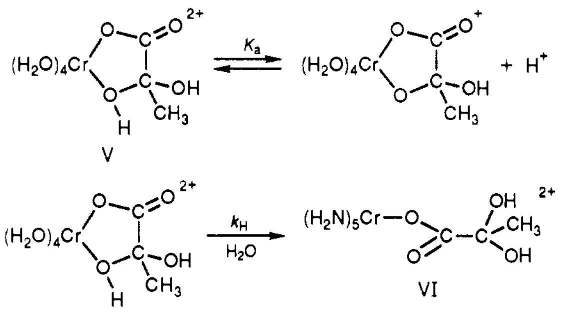
Perhaps the most surprising observation is that the reddish species is not the only pyruvate containing chromium(III) product. In fact, the major product at high acidities (0.5 M $HClO_4$) is a violet fraction that has ion-exchange properties typical of a 3+ ion and a visible electronic spectrum quite similar to that of $Cr(OH_2)_6^{3+}$ (see Table I). The main difference from $Cr(OH_2)_6^{3+}$ is the appearance of a peak at 325 nm, typical of pyruvic acid, and a strong absorbance in the ultraviolet region. The amount of free pyruvic acid was highly variable, judging from the intensity of the 325-nm absorbance (ϵ ~ 10 M^{-1} cm^{-1}), and tended to be larger in initial portions of the 3+ fraction and larger when the elution was done at lower acidity (>0.02 M). The presence of pyruvic acid in the violet fraction can only be ascribed to pyruvate being held back as a chromium complex during the ion-exchange separation, and the free acid is formed by hydrolysis during the separation. The amount of pyruvate in this product is difficult to quantify because of overlap with the 405-nm peak and the ultraviolet absorbance. However, it was possible to determine the amount of free total pyruvate in the fraction that passes directly through the ion-exchange resin, as discussed in the following paragraph. By difference, this indicates that <10% of the pyruvate is held back in the total 3+ fraction.

The product distribution was studied with Cr(II) in 20% excess over Co(III) at several acidities as described in the Experimental Section. When the reduction is done at low acidity (0.01 H^+), the amounts of red chelate and violet 3+ species are 65% and 35% (% based on cobalt(III)). In 0.50 M H^+, the amounts are 19% and 78%, respectively, and 76% of the total pyruvate appears in the fraction not held on the ion-exchange resin. About 5% (100 – 19 – 76) of the pyruvate is not accounted for and is apparently held back in the 3+ fraction. The variation of the product distribution with acidity must be due to reactions after the reduction because the products are primarily the result of the reduction of

Scheme I



Scheme II



the keto form of the cobalt(III) complex whose rate of chromium(II) reduction is independent of [H$^+$].

Discussion

The rate law for the reduction is consistent with the reaction sequence given in Scheme I, where the dehydration step is written as irreversible because of the rapid reduction of the keto form. If a steady state is assumed for the keto form because of the large reduction rate constant reported by Price and Taube, then Scheme I predicts a k_{obsd} of the same form as eq 2 with $a = k_1 = 2.7$ M^{-1} s^{-1} and $b = k_2 = 25.5$ M^{-1} s^{-1}.

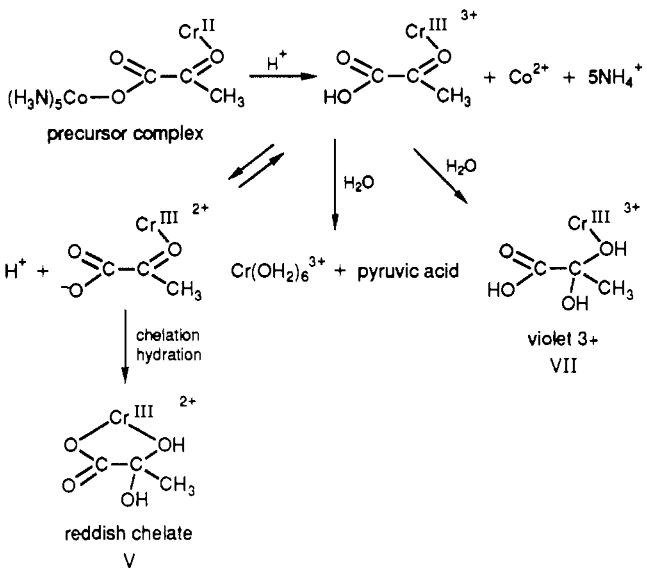
Pocker and Meaney[5] studied the dehydration of the pyruvate anion at 0 °C and found an uncatalyzed path ($k_0 = 9.2 \times 10^{-4}$ s^{-1}) and an acid-catalyzed path ($k_1 = 7 \times 10^2$ M^{-1} s^{-1}). Buschmannn and Knoche[6] reported values for the hydration of pyruvic acid at 25 °C that can be converted to dehydration rate constants from the keto/hydrate ratio (~35/65) to give $k_0 = 0.3$ s^{-1} and $k_1 = 3.4$ M^{-1} s^{-1}. The reactivity of the coordinated pyruvate is closer to that of the acid except that k_0 seems to be proportionately much smaller than k_1.

The rate constant for chromium(II) reduction of the hydrate is about 400 times smaller than that of the keto form[1] but is still ~100 times larger than those for simple carboxylates such as acetate.[7] The simplest rationalization of these observations seems to be that the hydrate proceeds through a bridged intermediate that is stabilized by chelation (III). Butler and Taube[8] also concluded that chelation was important in their study of other α-hydroxy carboxylate complexes such as lactate, methyl lactate and glycolate. The reduction rate constants of 6.65, 11.5, and 3.06 M^{-1} s^{-1} (25 °C), respectively, are also substantially larger than those of their simple carboxylate analogues. It should be noted that the chromium(III) products identified in this study have limited relevance to the hydrate reduction because over 70% of the product must be from the dominant keto form.

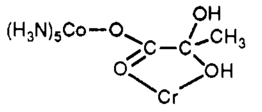
The kinetics of the reaction assigned to chelate ring opening are consistent with the sequence in Scheme II. The predicted rate law has the same form as eq 3, with $c = k_H = 1.12 \times 10^{-3}$ s^{-1} and $d = K_a = 8.3 \times 10^{-2}$ M.

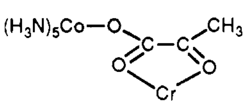
Our results are consistent with the observations of Lane et al.[9] on the analogous lactate and glycolate system, where it is possible to separate the deprotonated chelate at pH ~ 3 and then observe the ring opening by raising the [H$^+$] to 0.05–0.1 M. The process could be reversed by returning to pH ~ 3. The rate constant for ring opening is ~3 × 10^{-2} s^{-1} for both lactate and glycolate complexes, which is about 30 times larger than that with pyruvate.

Scheme III



The greater reactivity and product distribution of the keto form remain to be discussed. The reactivity might be ascribed to stabilization of the precursor complex by chelation, but one would expect the hydrate chelate(III) to be more stable than the keto chelate(IV) because —OH should coordinate more strongly than =O. Therefore, chelation cannot be the major factor affecting the reactivity of the keto form.


III


IV

Gould and co-workers[10,11] have studied several pyridyl-carboxylate complexes that show unusually high rates for Cr(II) attack at the carboxylate group. This effect may be attributed to the pyridyl system providing a moderately low-energy orbital to accept the electron from Cr(II) in a so-called chemical mechanism. For the pyruvate complex, the ketonic oxygen in conjugation with the carboxylate group will produce a lower energy π^* orbital than would be available in the hydrate form. This could explain the high reactivity of the keto form, but adjacent attack does not account for the chelate product or the variation of products with acidity.

The simplest explanation for the reactivity and products seems to be that the reduction proceeds largely by remote attack at the ketonic oxygen. This has precedent from the study of Zanella and Taube[12] on (p-formylbenzoato)pentaamminecobalt(III). On the other hand, Srinivasan et al.[13] have estimated that remote attack contributes <0.2% to reduction of the pyruvato complex. This estimate is based on the reduction rate of the corresponding (μ-carboxylato)dicobalt(III) complex and could be in error if this complex is largely in the hydrate form. The estimate was justified originally by the fact that Price and Taube had not found a carbonyl-bound Cr(III) product, but our results show that such a product is formed.

The proposed mechanism is shown in Scheme III. In order to explain the acid dependence of the product distribution, it is

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(10) Heh, J. C.-K.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 3138.

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proposed that the initial product has Cr(III) bound to the carbonyl oxygen. Then the carboxylate group may ionize and form chelate or the initial product may hydrolyze to give free pyruvate or hydrate to give a monodendate complex (VII), which accounts for the small amount of pyruvate held back in the 3+ fraction. The pyruvate hydrate product (VII) is analogous to that proposed by Zanella and Taube[12] for the *p*-formylbenzoato system. The hydrolytic instability of the initial product is consistent with the generally weak coordination of ketonic oxygen, as observed for the acetone and methyl acetate complexes of pentaamminecobalt(III)[14] and the methyl isonicotinate complex $(NH_3)_5RuNC_5H_4C(OCH_3){=}OCr(OH_2)_5^{5+}$ studied by Gaunder and Taube.[15] The varying amount of chelate with acidity is attributed to the necessity to ionize the carboxylate proton in a fast equilibrium process before chelation can occur. This ionization will be suppressed at higher acidity. The sequence of ionization–hydration–chelation may be as shown in Scheme III, but the stage at which hydration occurs cannot be defined by our observations.

Experimental Section

Materials. (Pyruvato)pentaamminecobalt(III) perchlorate was prepared by published methods[1,3] and characterized by its electronic and proton NMR spectra. Chromium(II) perchlorate solutions were prepared by reduction of solutions of chromium(III) perchlorate at the appropriate acidity with amalgamated zinc.

Product Analysis. Ion-exchange separations of products were done in a cold room at 4 °C on Dowex 50W-X2 resin unless otherwise noted. Chromium was determined spectrophotometrically as chromate after oxidation with alkaline hydrogen peroxide. Free pyruvic acid was determined by the spectrophotometric method of Sokol[16] using a calibration curve based on sodium pyruvate (Sigma).

The variation of the products with acidity was determined with [Cr(II)] = 7×10^{-3} M and [Co(III)] = 5.5×10^{-3} M at ambient temperature. After reaction, the solution was exposed to dioxygen and subjected to ion exchange as described above.

Instrumentation and Kinetic Analysis. Spectrophotometric measurements generally were done on a Cary 219 spectrophotometer. Some measurements, as noted in the text, and the kinetic study of the reduction were done on a Hewlett-Packard 8451 diode-array system. Both spectrophotometers have thermostated cell blocks. The absorbance–time data for kinetic runs were analyzed by nonlinear least-squares and errors quoted are one standard deviation. All kinetic measurements are at 25 °C in 1.0 M $NaClO_4/HClO_4$. In the reduction studies, the $[H^+]$ was varied between 0.020 and 0.040 M and the $[Cr^{2+}]$ between 1.4×10^{-3} and 5.45×10^{-3} M.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support for this work.

Registry No. II, 43227-19-6; V, 121072-63-7; Cr^{2+}, 22541-79-3.

Supplementary Material Available: Table S1, listing the reagent concentrations and observed and calculated rate constants for the reduction of (pyruvato)pentaamminecobalt(III) by chromium(II) (1 page). Ordering information is given on any current masthead page.

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Arsenic(IV). A Pulse-Radiolysis Study

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Four As(IV) species assumed to be $As(OH)_4$ and $HAsO_3^-$ and the corresponding bases $As(OH)_3O^-$ and AsO_3^{2-} (pK_a = 7.38 and 7.81, respectively) were observed by the pulse-radiolysis technique in aqueous arsenious acid, arsenite, and arsenate solutions. $As(OH)_4$ and $As(OH)_3O^-$ were observed in acid and weakly alkaline solution by the reaction of arsenious acid or arsenite with OH. $HAsO_3^-$ and/or AsO_3^{2-} are formed by the reaction of e^-_{aq} with $H_2AsO_4^-$ and $HAsO_4^{2-}$; AsO_3^{2-} is formed by the reaction of arsenite with O^- in strongly alkaline solution and by the reaction of arsenite with the carbonate radical anion CO_3^-. $As(OH)_4$ and $As(OH)_3O^-$ convert into $HAsO_3^-$ and AsO_3^{2-} by general-base-catalyzed reactions. In acid solution an equilibrium between $As(OH)_4$ and $HAsO_3^-$ is observed. The kinetics of dehydration of $As(OH)_4$ suggest a slow dehydration step catalyzed by H^+ followed by protolysis:

$$As(OH)_4 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H_2AsO_3 + H_2O \rightleftarrows HAsO_3^- + H_2O + H^+$$

$k_f/k_r \sim 10^{-3}$–10^{-2}; $k_f = 2.4 \times 10^4 + 3.8 \times 10^8[H^+]\ s^{-1}$. The equilibrium constant for the overall reaction is 1.4×10^{-4}; the standard enthalpy of reaction is 10.4 kJ mol^{-1}. The energy and the entropy of activation for the uncatalyzed and the H^+-catalyzed dehydration of $As(OH)_4$ are 23 kJ mol^{-1} and −93 J $mol^{-1}\ K^{-1}$ and 25 kJ mol^{-1} and −6 J $mol^{-1}\ K^{-1}$, respectively. By comparison with activation parameters of other dehydration–hydration processes, these values are taken to suggest a cyclic transition state containing an extra water molecule. While $As(OH)_4$ and $As(OH)_3O^-$ react with O_2 to yield directly HO_2 and O_2^-, $HAsO_3^-$ and AsO_3^{2-} react with O_2 with formation of a relatively stable complex that subsequently decomposes to HO_2 or O_2^- in reactions catalyzed by H^+ and OH^-. The various As(IV) species disappear in second-order reactions with rate constants ranging from 2×10^7 to $2 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$. As(IV) species are both very strong oxidants and reductants. (Estimates for the standard reduction potentials $As(OH)_4 + e^- + H^+ \rightarrow As(OH)_3 + H_2O$ and $H_3AsO_4 + e^- + H^+ \rightarrow As(OH)_4$ are 2.4 and −1.2 V, respectively.)

Introduction

The present knowledge of the properties of As(IV) in aqueous solution stems from earlier steady-state and pulse-radiolysis experiments on As(III) and As(V) solutions[1-3] and from stoichiometric and kinetic studies of the oxidation of arsenious acid by peroxodisulfate in presence of a ferrous salt as an inductor.[4] The steady-state radiolysis and the study of the induced oxidation of arsenious acid by peroxodisulfate have shown that As(IV) is a powerful reducing agent that is capable of reducing molecular

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