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Kinetics and Products of the Anation of $(H_2O)_5CrCH_2CN^{2+}$ by Hypophosphite

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The products and kinetics of the reaction of $H_2PO_2^-$ with $(H_2O)_5CrCH_2CN^{2+}$ have been studied in aqueous acid. The reaction proceeds in two stages. The first stage produces an equilibrium mixture of reactants and $(H_2O)_4(H_2PO_2)CrCH_2CN^+$, and the rate law in excess $H_2PO_2^-$ gives k (M^{-1} s^{-1}) = 0.185 ± 0.021 for $H_2PO_2^-$ and (8.05 ± 2.3) × 10^{-2} for H_3PO_3 with K_1 = 5.45 ± 1.55 M^{-1} (1.0 M $LiClO_4/HClO_4$, 25 °C). The second stage yields $(H_2O)_3(H_2PO_2)_2CrCH_2CN$ with biphasic kinetics which are attributed to rate-controlling isomerization reactions of the hypophosphito complexes. The products have been characterized by low-temperature ion-exchange chromatography and by their reaction with Hg^{2+}. The latter reaction gives $(H_2O)_5CrOPOH_2^{2+}$ plus $(H_2O)_5(H_2PO_2)CrNCCH_2Hg^{3+}$ and $(H_2O)_4Cr(OPOH_2)_2^+$ plus $(H_2O)_3(H_2PO_2)_2CrNCCH_2Hg^{2+}$ as products from $(H_2O)_4(H_2PO_2)CrCH_2CN^+$ and $(H_2O)_3(H_2PO_2)_2CrCH_2CN$, respectively. The $(H_2O)_5CrOPOH_2^{2+}$ product has been characterized by comparison of the electronic spectrum to that of the product of the reaction of $(NH_3)_5CoOPOH_2^{2+}$ and Cr^{2+} and by its reactivity with aqueous $KMnO_4$.

Introduction

There have been several studies of the anation reactions of pentaaquachromium(III) alkyl complexes,[1-4] and the results are summarized in a recent review.[5] These complexes are remarkably labile to substitution compared to most chromium(III) complexes. The substitution lability of the alkyl complexes is of interest kinetically, but it does not seem to have been recognized that it also provides an attractive synthetic route for pentaaquachromium(III) complexes. For example, the following preparative sequence can be carried out in a few minutes at ambient temperature:

$$(H_2O)_5Cr{-}R^{2+} + X \rightleftarrows (H_2O)_4(X)Cr{-}R \xrightarrow{Hg^{2+}} (H_2O)_5CrX + HgR^+ \quad (1)$$

Because the first step is an equilibrium, the products will be a mixture of $(H_2O)_5CrX$ and $Cr(OH_2)_6^{3+}$, but these can generally be separated by ion-exchange chromatography.

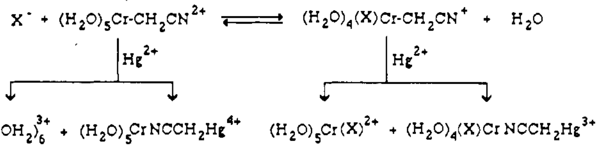
In the present work, the reaction of hypophosphite in aqueous acid with $(H_2O)_5CrCH_2CN^{2+}$ has been studied. The reaction proceeds in two stages, and the kinetics and products of each stage have been characterized. The oxidation state of phosphorus in the products has been established by comparison to the products of the reaction of the phosphite and hypophosphite complexes of $(NH_3)_5Co^{III}$ with chromium(II). This factor was not determined in the earlier study[6] of the chromium(III)–hypophosphite complex, which was prepared under much more vigorous conditions.

The kinetics of the anation reaction have been studied systematically only for NCS^- reacting with various alkyl ligand complexes.[1-3] The mechanism is presumed to be dissociative, but the rate law changes in a way which indicates that the competition of NCS^- and H_2O for the dissociative intermediate is very sensitive to the nature of the alkyl group. Studies with other anions such as hypophosphite may help to clarify the mechanistic details.

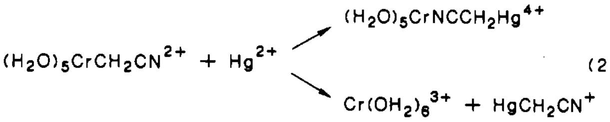
Results and Discussion

When NaH_2PO_2 and $(H_2O)_5CrCH_2CN^{2+}$ react in dilute aqueous acid, the changes in the visible spectrum show that the reaction occurs in two stages. The first stage is complete in less than 1 min while the second stage takes several hours to reach completion. For both processes, the absorbance maxima shift to longer wavelengths while the absorbance decreases in the 409-nm region and increases around 525 nm.

Scheme I



In order to separate the reaction products, it is convenient to convert them to a kinetically stable form suitable for ion-exchange separation. Reaction with mercury(II) is convenient for this purpose. With $(H_2O)_5CrCH_2CN^{2+}$, the Hg^{2+} reaction proceeds according to eq 2.[7] The $CrNCCH_2Hg^{4+}$ species decomposes to



$$(H_2O)_5CrCH_2CN^{2+} + Hg^{2+} \rightarrow \begin{cases} (H_2O)_5CrNCCH_2Hg^{4+} \\ Cr(OH_2)_6^{3+} + HgCH_2CN^+ \end{cases} \quad (2)$$

$Cr(OH_2)_6^{3+}$ and $HgCH_2CN^+$ with a half-time of about 2 h at ambient temperature.

If $(H_2O)_5CrCH_2CN^{2+}$ reacts with an anion such as $H_2PO_2^-$, then the products of the Hg^{2+} reaction are as shown in Scheme I. Hg^{2+} reacts rapidly with the chromium alkyl complex, but there is a slower reaction between the excess Hg^{2+} and $H_2PO_2^-$ to give a black precipitate. This precipitate was removed by filtration before ion-exchange separation of the chromium(III) products.

The results of the product analysis after 1 min of reaction are summarized in Table I. The products have been identified on the basis of their ion-exchange properties and electronic spectra. The identification of the 2+ species as $(H_2O)_5CrOPOH_2^{2+}$ was confirmed by comparison of its reactivity toward acidic $KMnO_4$ with that of $(H_2O)_5CrOPOH_2^{2+}$ prepared from $(NH_3)_5CoOPOH_2^{2+}$ and Cr^{2+} (see Experimental Section).

Although the spectra of $(H_2O)_5CrOPOH_2^{2+}$ prepared here by two different methods agree well with one another, the peak positions are about 4 nm lower than those reported by Espenson and Binau.[6] It was noted that the spectrum reported by these authors was almost the same as that of the phosphite complex $(H_2O)_5CrOPO_2H_2^{2+}$, given by Brown and Cooper.[8] This observation raised the possibility that Espenson and Binau had actually made the phosphite complex.

Experiments with $(H_2O)_5CrOPO_2H_2^{2+}$ prepared by reaction of Cr(II) with $(NH_3)_5CoOPO_2H_2^{2+}$ confirm that the hypophosphite– and phosphite–chromium(III) complexes have essentially the same spectra. Furthermore, we have qualitatively confirmed the earlier results[6,8] that the hypophosphite complex hydrolyzes much more rapidly than the phosphite one. The difference of ~4 nm in the absorption maxima reported here and elsewhere[6,8] may be due to different methods of establishing the

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Table I. Products of the First Stage of Anation of $(H_2O)_5CrCH_2CN^{2+}$ by $H_2PO_2^-$ [a]

charge	product color	assignment	% Cr[b]	electronic spectra λ, nm (ϵ, M^{-1} cm^{-1})
<2+	...	$Cr(O_2PH_2)_2^+$	3.0 ± 0.3	611 (19), 427 (21)
2+	green	$Cr(O_2PH_2)^{2+}$	18.5 ± 0.5	591 (16.0), 417 (18.0)
3+	violet	$Cr(OH_2)_6^{3+}$	25 ± 1	
3+	green	$(H_2PO_2)CrNCCH_2Hg^{3+}$	23.5 ± 0.5	580 (22), 413 (28)
4+	red-purple	$CrNCCH_2Hg^{4+}$	24.5 ± 0.5	

[a] Products after reaction of 0.16 M $H_2PO_2^-$ and ~6 × 10^{-3} M $(H_2O)_5CrCH_2CN^{2+}$ in 0.012 M $HClO_4$ after 1 min followed by treatment with $Hg(ClO_4)_2$ and ion exchange at 5 °C on Dowex 50W-X2. [b] Determined as chromate; values are the average of two experiments with errors representing the range of values.

Table II. Kinetic Results for First Stage of Anation of $(H_2O)_5CrCH_2CN^{2+}$ by $H_2PO_2^-$ (25 °C, 1.0 M $LiClO_4/HClO_4$)

$10^2[H^+]_{free}$,[a] M	$[NaH_2PO_2]_{tot}$, M	10^2k, s^{-1} obsd[b]	10^2k, s^{-1} calcd[c]	$10^2[H^+]_{free}$,[a] M	$[NaH_2PO_2]_{tot}$, M	10^2k, s^{-1} obsd[b]	10^2k, s^{-1} calcd[c]
0.50	0.165	5.58	6.42	2.00	0.280	8.26	8.31
0.50	0.292	7.82	8.65	2.00	0.280	9.50	8.31
0.50	0.420	10.5	10.9	2.00	0.350	10.9	9.40
0.50	0.420	10.2	10.9	2.00	0.350	9.07	9.40
2.00	0.140	6.12	6.15	2.00	0.420	11.2	10.5
2.00	0.140	5.94	6.15	2.00	0.420	10.5	10.5
2.00	0.210	7.24	7.23	10.0	0.420	10.4	11.2
2.00	0.210	8.03	7.23				

[a] Calculated from the total $HClO_4$ and NaH_2PO_2 added and K_a = 5.0 × 10^{-2} M for H_3PO_2.[8] $[CrCH_2CN^{2+}]$ = 3 × 10^{-4} M. [b] Values are the average of 10–15 determinations, and errors are 1 standard deviation. [c] Calculated from a least-squares fit of all the data to eq 4.

maxima for the broad and somewhat asymmetric peaks. There seems to be no reason to doubt the nature of the species in the earlier work.

The relative amounts of the $Cr(OH_2)_6^{3+}$ and $CrNCCH_2Hg^{4+}$ products in Table I correspond to those found from the reaction of $(H_2O)_5CrCH_2CN^{2+}$ and Hg^{2+}.[7] The somewhat larger ratio of $CrO_2PH_2^{2+}$ to $(H_2PO_2)CrNCCH_2Hg^{3+}$ indicates that coordinated $H_2PO_2^-$ has some effect on the proportion of these products.

The products of the initial stage of the anation, after reaction with Hg^{2+}, are consistent with Scheme I with the anation reaction

$$H_2PO_2^- + (H_2O)_5CrCH_2CN^{2+} \rightleftarrows (H_2O)_4(H_2PO_2)CrCH_2CN^+ + H_2O \quad (3)$$

The product distribution given in Table I indicates that, in 0.16 M $H_2PO_2^-$, there is 25.0 + 24.5 = 49.5% $(H_2O)_5CrCH_2CN^{2+}$ and 18.5 + 23.5 = 42.0% $(H_2O)_4(H_2PO_2)CrCH_2CN^+$. Therefore, the equilibrium constant for eq 3 is 42/(49.5)(0.16) = 5.3 M^{-1}. This assumes that the reaction of both chromium–alkyl species with Hg^{2+} is fast enough to provide a true sample of the equilibrium system in eq 3. This assumption seems to be justified because the equilibrium constant is in reasonable agreement with that calculated from the kinetic results and the product distribution of the second reaction discussed in the following sections.

Kinetics of the First Stage of Anation. The kinetics of the reaction of $(H_2O)_5CrCH_2CN^{2+}$ and $H_2PO_2^-$ were studied by stopped-flow spectrophotometry at 280 nm, under pseudo-first-order conditions with $[NaH_2PO_2] >> [(H_2O)_5CrCH_2CN^{2+}]$. The results, which are summarized in Table II, conform to the rate law

$$\frac{-d[(H_2O)_5CrCH_2CN^{2+}]}{dt} = (k_3K_a + k_4[H^+])\left(\frac{[NaH_2PO_2]_{tot}}{K_a + [H^+]} + \frac{1}{K_aK_1}\right) \quad (4)$$

This rate law is developed for a system coming to equilibrium to produce $(H_2O)_4(H_2PO_2)CrCH_2CN^+$, in which $H_2PO_2^-$ and H_3PO_3 are reactive species with specific rate constants k_3 and k_4, respectively. The acid dissociation constant for H_3PO_3 is K_a = 5.0 × 10^{-2} M,[8] and K_1 is as defined previously.

A least-squares best fit of the data in Table II to eq 4 gives k_3 = 0.185 ± 0.021 M^{-1} s^{-1}, k_4 = (8.05 ± 2.3) × 10^{-2} M^{-1} s^{-1}, and K_1 = 5.45 ± 1.55 M^{-1}, where the errors are one standard deviation. The value of K_1 is in excellent agreement with that from the product analysis described in the preceding section.

Products of the Second Stage of Anation. Spectrophotometric observations of solutions of $(H_2O)_5CrCH_2CN^{2+}$ and NaH_2PO_2 in dilute acid revealed that changes subsequent to the first reaction occurred over about 4 h. During this period the spectra show isosbestic points at 423, 489, and 524 nm. These observations indicated that the Cr–R bond remained intact, and it seemed most probable that higher hypophosphite complexes were forming. This explanation is consistent with the trace of 1+ species formed after 1 min (Table I). This type of process had not been observed in earlier anation studies with thiocyanate.[1-3]

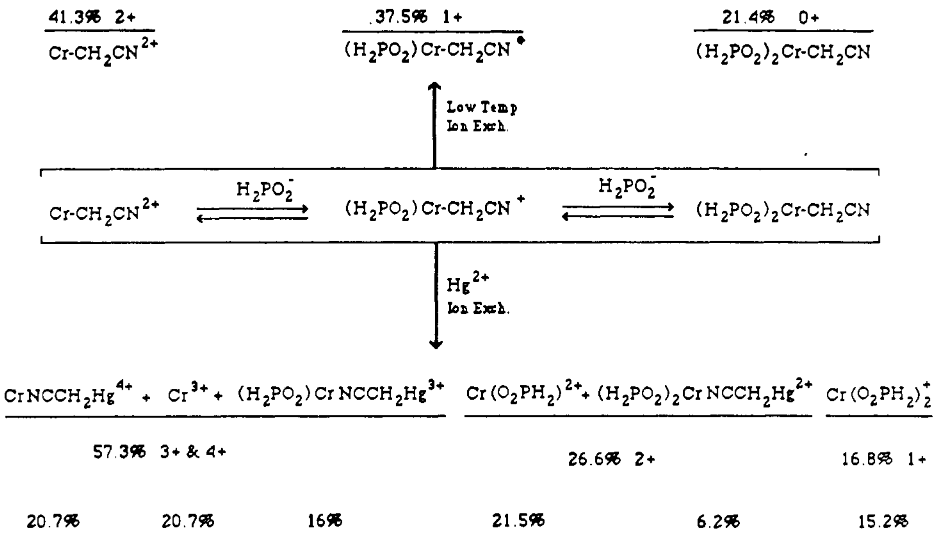
Because of the probable multiplicity of products at the end of the second anation stage, and the kinetic lability of the alkyl complexes, the product analysis was done in two ways. In both cases the initial reaction solution, which contained 0.105 M free $H_2PO_2^-$ (0.14 M total), 0.016 M free H^+ (0.051 M total $HClO_4$), and ~0.006 M $(H_2O)_5CrCH_2CN^{2+}$, was allowed to stand for 3.5 h at ambient temperature (~24 °C) before analysis. In the first method, the solution was treated with excess $Hg(ClO_4)_2$, filtered, and ion-exchanged immediately on Dowex 50W-X8 (H^+) resin by elution with increasing concentrations of $HClO_4$. The 1+ and 2+ products were separated, and the higher charged species were collected together. In the second method the solution was diluted by a factor of 3.3 with ice-cold water and ion-exchanged at 5 °C on Dowex 50W-X12 (H^+). The 0, 1+, and 2+ products were separated by elution with increasing concentrations of $HClO_4$.

The results of the analysis and the species assignments are given in Scheme II. The results of the two methods can be combined to give the complete product distributions from the Hg^{2+} reaction as shown at the bottom of Scheme II. This final assignment can be checked for consistency in two ways. The ratio of $(H_2PO_2)CrNCCH_2Hg^{3+}$ (16% = 57.3 − 41.3) to $(H_2PO_2)Cr^{2+}$ (21.5% = 37.5 − 16) is 0.74, in reasonable agreement with 0.79 obtained from the first reaction (Table I). The calculated amount of $Cr(O_2PH_2)_2^+$ (15.2% = 21.4 − (27.7 − 21.5)) is in good agreement with the 16.8% found.

It can be noted that the ratio of products $CrNCCH_2Hg{:}CrOH_2$ decreases from 1 to 0.75 to 0.41 for $CrCH_2CN^{2+}$, $(H_2PO_2)CrCH_2CN^+$, and $(H_2PO_2)_2CrCH_2CN$, respectively. This may be due to steric inhibition of the added anions or their effect on the nucleophilicity of the chromium center, which makes capture of the leaving group less favorable.

The electronic spectra of the products separated by low-temperature ion exchange were recorded as quickly as possible. The

Scheme II



species assigned as $(H_2O)_4(H_2PO_2)CrCH_2CN^+$ has maxima nm (ϵ, M^{-1} cm^{-1}) at 415 (100.6) and 541 (50.5) while $(H_2O)_3(H_2PO_2)_2CrCH_2CN$ has maxima at 422 (98.6) and 554 (53.2) in 0.1 M $HClO_4$.

The disappearance of $(H_2O)_3(H_2PO_2)_2CrCH_2CN$ was followed at 555 nm. The spectrum of the product of this reaction taken after 4 half-times has maxima in the same positions as those of $(H_2O)_4(H_2PO_2)CrCH_2CN^{2+}$, but the extinction coefficients are about 10% lower at the maxima. The latter factor may be due to subsequent decomposition or to incomplete reaction. Therefore, the reaction is assigned to eq 5. The rate was studied at two

$$(H_2O)_3(H_2PO_2)_2CrCH_2CN \rightarrow (H_2O)_4(H_2PO_2)CrCH_2CN + H_2PO_2^- \quad (5)$$

different acidities, although the actual $[H^+]$ is somewhat uncertain because the product passes directly through the ion-exchange resin and contains H^+ eluted by other products as well as that in the original solution, and is buffered by $H_2PO_2^-$. In any case, at $[H^+] \approx 0.1$ and 0.2 M, the observed rate constants (25 °C) are 6.7×10^{-4} and 4.7×10^{-4} s^{-1}, respectively. The rate constant decreases with increasing $[H^+]$, consistent with an $[H^+]^{-1}$ component to the rate law, but no attempt was made to establish the rate law because of the inevitable uncertainties in $[H^+]$. It is important for the subsequent discussion to note that the magnitude of the rate constant is in the range of $(5-7) \times 10^{-4}$ s^{-1}, however.

The product distribution from the low-temperature ion exchange (Scheme II) gives formation constants of 8.6 M^{-1} for $(H_2O)(H_2PO_2)Cr-CH_2CN^+$ and 5.4 M^{-1} for $(H_2O)_3(H_2PO_2)_2Cr-CH_2CN$.

Kinetics of the Second Stage of Anation. The reaction was studied by standard spectrophotometry at 550 nm, the wavelength of maximum absorbance change, under pseudo-first-order conditions with $[NaH_2PO_2]$ in excess in the range 0.035–0.42 M. The net absorbance change increases from about 0.08 to 0.15 unit as the $[NaH_2PO_2]$ increases for 2.49×10^{-3} M $Cr-CH_2CN^{2+}$ in a 5 cm path length cell. This observation and the product analysis results show that the reaction is not going to completion.

The simplest interpretation for the kinetics and products of the second stage would be in terms of two successive anation reactions as shown by the reactions

$$H_2PO_2^- + Cr-CH_2CN^{2+} \overset{K_1}{\rightleftharpoons} (H_2PO_2)Cr-CH_2CN^+ \quad (6)$$

$$(H_2PO_2)CrCH_2CN^+ + H_2PO_2^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (H_2PO_2)_2Cr-CH_2CN \quad (7)$$

The kinetics of the first stage (eq 6) have been discussed above, and it can be treated as a rapid preequilibrium relative to the second stage (eq 7). Then the observed pseudo-first-order rate constant is given by eq 8.

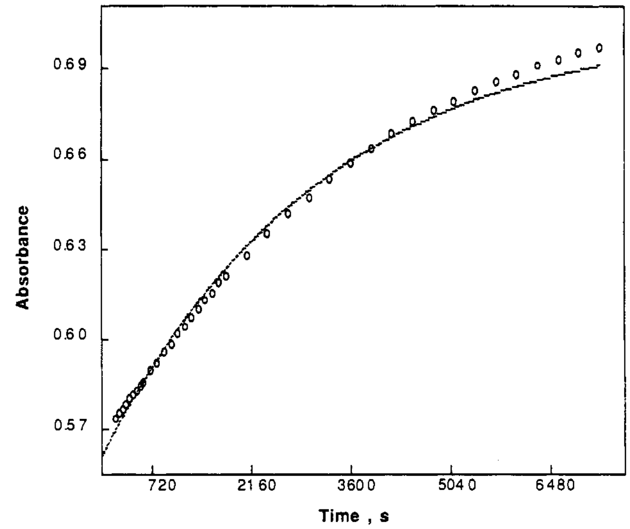


Figure 1. Variation of absorbance with time for the second stage of the reaction of $(H_2O)_5CrCH_2CN^{2+}$ (2.49×10^{-3} M) and NaH_2PO_2 (0.28 M) in 0.020 M H^+ at 550 nm. Circles are experimental points. The line is the best fit to a single-exponential equation: absorbance = 0.701 − 0.1353 exp((-3.15×10^{-4})t).

$$k_{obsd} = \frac{k_2K_1[H_2PO_2^-]^2}{K_1[H_2PO_2^-] + 1} + k_{-2} \quad (8)$$

However, least-squares fits of the absorbance–time data to a first-order rate law show a persistent pattern of deviations between the observed and predicted values, especially for $[NaH_2PO_2] \geq 0.14$ M, as shown at 0.28 M in Figure 1.

Even if these deviations are ignored, two problems arise. The apparent rate constants change from 1.2×10^{-4} to 3.5×10^{-4} s^{-1} as $[NaH_2PO_2]$ changes from 0.035 to 0.42. This change is much less than predicted from eq 8 with $K_1 \approx 5.5$ M^{-1} as indicated from the study of the first reaction. An even more serious difficulty is that the reverse rate (k_{-2}) of eq 7 has been measured, as noted above, and will be $\gtrsim 7 \times 10^{-4}$ under the acidity conditions of the study of the second anation step. Since, in general, the observed rate constant is the sum of the forward and reverse rate constants, the second stage must have $k_{obsd} > 7 \times 10^{-4}$ s^{-1} if it is due to eq 7. This is substantially greater than any of the experimental rate constants for the second stage.

The absorbance–time data are well fitted by a model for two first-order reactions. The results for $[NaH_2PO_2]$ between 0.14

Scheme III

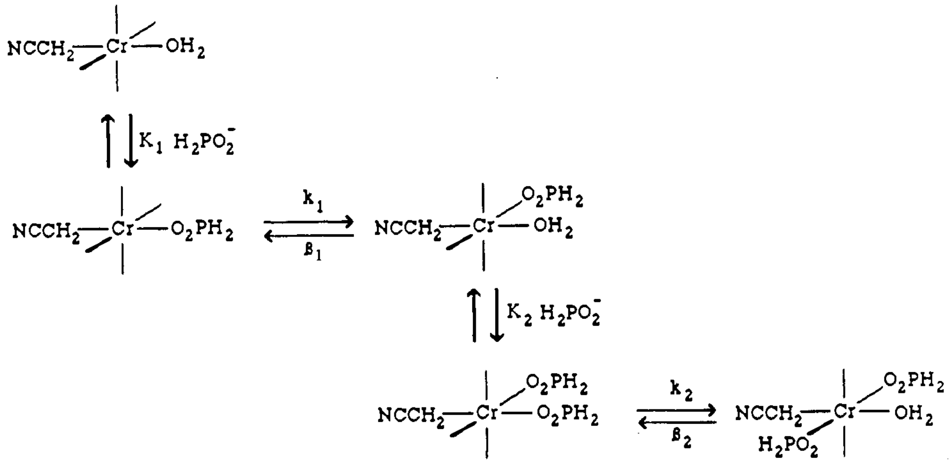


Table III. Kinetic Parameters for the Second Stage of Anation (25 °C, 1.0 M $LiClO_4/HClO_4$, (2–3) × 10^{-3} M $CrCH_2CN^{2+}$)

$[NaH_2PO_2]_{tot}$, M	$10^2[H^+]_{free}$, M	10^4b, s^{-1} obsd	10^4b, s^{-1} calcd[a]	10^8c, s^{-2} obsd	10^8c, s^{-2} calcd[b]	$10^4\gamma_1$, s^{-1} obsd[c]	$10^4\gamma_1$, s^{-1} calcd[d]
0.035	2.00	1.46	1.49	0.487	0.497	0.908	0.974
0.070	0.60	1.99	1.94	0.851	0.815	1.37	1.31
0.070	2.00	1.77	1.80	0.699	0.710	1.09	1.21
0.070	10.0	1.49	1.46	0.502	0.483	0.972	0.955
0.140	2.00	2.04	2.27	0.950	1.11	1.25	1.54
0.140	2.00	2.22	2.27	1.08	1.11	1.48	1.54
0.210	0.60	2.95	2.79	1.82	1.67	2.18	1.89
0.210	2.00	2.59	2.60	1.44	1.45	1.81	1.72
0.210	10.0	2.17	2.01	0.981	0.876	1.49	1.36
0.280	2.00	2.68	2.84	1.60	1.73	1.77	1.92
0.280	2.00	2.84	2.84	1.74	1.73	1.97	1.92
0.420	0.60	3.80	3.35	2.92	2.41	2.52	2.25
0.420	2.00	3.04	3.17	2.05	2.17	2.10	2.14
0.420	2.00	2.95	3.17	1.97	2.17	2.02	2.14
0.420	10.0	2.90	2.54	1.68	1.39	2.06	1.72

[a] Calculated from a least-squares fit by assuming $k_2 = 9.2 \times 10^{-5}$ and $\beta_2 = 5.7 \times 10^{-5}$ and the best-fit parameters $k_1 = 2.96 \times 10^{-4}$ and $\beta_1 = 5.12 \times 10^{-5}$. [b] Calculated with $k_1\beta_2$ and $\beta_1\beta_2$ fixed at values indicated in footnote *a* and the best-fit value of $k_1k_2 = 2.72 \times 10^{-8}$. [c] Least-squares best-fit values from fits with γ_2 fixed at values calculated from the parameters in footnote *a*. [d] Values calculated from the parameters in footnote *a*.

and 0.42 M indicate that one rate constant is ~0.9 × 10^{-4} s^{-1} and the second varies from ~1 × 10^{-4} to 2 × 10^{-4} s^{-1} as $[NaH_2PO_2]$ increases. However, this does not remove the problem that eq 7 is too fast to be a rate-controlling step for the second stage.

A model that is consistent with the biphasic nature of the second stage and treats eq 7 as a fast equilibrium is shown in Scheme III. It is proposed that the rate-limiting steps are isomerizations that move the $H_2PO_2^-$ ligand from trans to cis positions relative to the $-CH_2CN$ ligand. This proposal is based on the idea that facile anation occurs by displacement of a labile water molecule trans to $-CH_2CN$.[1]

Under pseudo-first-order conditions ($[NaH_2PO_2] >> [CrCH_2CN^{2+}]$) the time dependence of the absorbance predicted from Scheme III has the general form

$$A_t = A_\infty + \chi_1 e^{-\gamma_1 t} + \chi_2 e^{-\gamma_2 t} \tag{9}$$

where

$$\gamma_{1,2} = (b \pm (b^2 - 4c)^{1/2})/2$$
$$b = k_1' + k_2' + \beta_1' + \beta_2' \tag{10}$$
$$c = k_1'k_2' + k_1'\beta_2' + \beta_1'\beta_2'$$

and

$$k_1' = \frac{k_1K_1[H_2PO_2^-]}{K_1[H_2PO_2^-] + 1} \qquad \beta_1' = \frac{\beta_1}{K_2[H_2PO_2^-] + 1}$$

$$k_2' = \frac{k_2K_2[H_2PO_2^-]}{K_2[H_2PO_2^-] + 1} \qquad \beta_2' = \beta_2 \tag{11}$$

In order to evaluate the contributions of k_1, k_2, β_1, and β_2 to γ_1 and γ_2, it proved more convenient to work with *b* and *c* as given by eq 12.

$$b = \gamma_1 + \gamma_2 \qquad c = \gamma_1\gamma_2 \tag{12}$$

A value of $K_1 = 5.45$ M^{-1} was taken from the kinetic results, and $K_2 = 5.4$ M^{-1} was determined from the product analysis. An iterative procedure was used in which k_2 and β_2 were assumed, and the dependence of *b* on $[H_2PO_2^-]$ was used to evaluate k_1 and β_1 by a least-squares fit. Then $k_1\beta_2$ and $\beta_1\beta_2$ were fixed and the variation of *c* with $[H_2PO_2^-]$ was used to determine k_1k_2. The process was continued until the latter value of k_1k_2 agreed with the originally assumed k_2 and the k_1 from the fit of the *b* values. The self-consistent values are $k_1 = 2.96 \times 10^{-4}$ s^{-1}, $\beta_1 = 5.1 \times 10^{-5}$ s^{-1}, $k_2 = 9.2 \times 10^{-5}$ s^{-1}, and $\beta_2 = 5.7 \times 10^{-5}$ s^{-1}. The observed and calculated values of *b* and *c* are compared in Table III.

The absorbance–time data were refitted with the restriction that γ_2 was fixed at the value calculated from the above parameters. The best-fit values of γ_1 are compared to those calculated from k_1, k_2, β_1, and β_2 in Table III.

Conclusions

It has been shown that anation of $(H_2O)_5CrCH_2CN^{2+}$ by NaH_2PO_2 proceeds in two stages to give $(H_2O)_4(H_2PO_2)CrCH_2CN^+$ and $(H_2O)_3(H_2PO_2)_2Cr{-}CH_2CN$. The rate of production of the latter species seems to be controlled by isomerization of the former followed by relatively fast anation of the isomer with an H_2O trans to $-CH_2CN$.

All of these complexes undergo electrophilic attack by Hg^{2+} to form respectively $CrOH_2$ and $CrNCCH_2Hg$ complexes. The amount of the latter product decreases with increasing substitution of $H_2PO_2^-$ on the chromium–alkyl reactant. The product studies illustrate the preparative utility of these reactions as described by eq 1. This aspect could be improved by using an alkyl group that would not form an analogue of $CrNCCH_2Hg$.

The mechanism for the first anation reaction remains uncertain. For the two anions that have been studied with $(H_2O)_5Cr-CH_2CN^{2+}$, the rate laws are as follows for SCN^-

$$k_{obsd} = (9.05 \times 10^{-2})[NCS^-] + (2.73 \times 10^{-2})$$

and for $H_2PO_2^-$

$$k_{obsd} = (18.5 \times 10^{-2})[H_2PO_2^-] + (3.39 \times 10^{-2})$$

Although the forward rate constant is 2 times larger for $H_2PO_2^-$, this could be due to more favorable competition with water for a dissociative intermediate in a D mechanism. Even if this competition ratio were increased by a factor of 2 above the upper limit given for NCS^- ($\leq$0.067),[3] a saturation effect on k_{obsd} would not have been detected over the concentration range of $H_2PO_2^-$ studied here. However, it remains unclear why the competition ratio for NCS^- seems to vary so widely (<0.067 to 4.7)[3] with the alkyl ligand in no obvious systematic way, if a D mechanism is operating.

Experimental Section

Materials. Solutions of $(H_2O)_5CrCH_2CN^{2+}$ were prepared from ICH_2CN and Cr^{2+} as described elsewhere.[9] $LiClO_4 \cdot 3H_2O$ was synthesized from Li_2CO_3 and $HClO_4$. Stock solutions of this salt were standardized by passing aliquots through a column of Dowex 50W-X2 (H^+ form) and titrating the liberated H^+ with standard base.

$NaH_2PO_2 \cdot H_2O$ (Fisher) was used as received. A spectrophotometric analysis involving the oxidation of $H_2PO_2^-$ by IO_3^- [10] was used to check the purity of this reagent. $H_2PO_3^-$ was found not to react with IO_3^- in the time taken to do the analysis. The molar absorptivity of I_2 at 460 nm as calculated from the results was 727 M^{-1} cm^{-1}, which is in satisfactory agreement with the literature value of 746 M^{-1} cm^{-1} determined by more direct methods.[11]

$Co(NH_3)_5OPOH_2^{2+}$ and $Co(NH_3)_5OPO_2H_2^{2+}$. (Hypophosphito)- and (phosphito)pentaamminecobalt(III) were prepared by warming a solution 1.5×10^{-3} M in $(Co(NH_3)_5OH_2)(CF_3SO_3)_3$ and 10 M in the appropriate ligand at 45 °C for about 1.5 h. Before it was warmed, the solution was adjusted to pH 3–4 by using aqueous $HClO_4$ in the case of NaH_2PO_2 and NaOH pellets in the case of H_3PO_3. The rose red product was eluted from Dowex 50W-X2 (Na^+ by using of 0.5 M $HClO_4$, leaving the unreacted $Co(NH_3)_5OH_2^{3+}$ on the resin. The electronic spectra of the hypophosphito and phosphito complexes in 0.5 M $HClO_4$ were very similar to one another and to that of the corresponding phosphato species (λ, nm (ϵ, M^{-1} cm^{-1})): $Co(NH_3)_5OH_2^{2+}$ 518 (61.7), 354 (49.5); $Co(NH_3)_5OPO_2H_2^{2+}$, 516 (62.9), 353 (48.5); $Co(NH_3)_5OPO_3H_2^{2+}$ 517.5 (63.7), 356 (48.3).[12] $Co(NH_3)_5OPOH_2^{2+}$ was found to decolorize acidic $KMnO_4$ readily at room temperature, while the reaction only occurred at 50–60 °C for $Co(NH_3)_5OPO_2H_2^{2+}$.

$(H_2O)_5CrOPOH_2^{2+}$ and $(H_2O)_5CrOPO_2H_2^{2+}$. These complexes were prepared by the reaction of the appropriate $Co(NH_3)_5X^{2+}$ complex with Cr^{2+} in acidic aqueous solution. In both cases the reaction was complete within a few minutes, judging from the color change of the solution (lilac to green). After ion-exchange purification $(H_2O)_5CrOPOH_2^{2+}$ was found to have absorption maxima at 592 and 416.5 nm with molar absorptivities of 15.5 and 17.2 M^{-1} cm^{-1}, respectively, in 0.5 M $HClO_4$. $(H_2O)_5CrOPO_2H_2^{2+}$ had a very similar spectrum with peaks (λ, nm (ϵ, M^{-1} cm^{-1})) at 592 nm (15.9) and 417 (17.3). As for the Co(III) complexes, the hypophosphito species decolorized acidic $KMnO_4$ at room temperature, while phosphito–Cr(III) did so only at elevated temperatures.

Instrumentation. The rapid reactions were studied by means of the Aminco-Morrow stopped-flow device described previously.[13,14] Slower runs were conducted in the thermostated cell block of a Cary 219 spectrophotometer, and electronic spectra were recorded at room temperature on the same instrument. The wavelength accuracy of the spectrophotometer used here is correct within 0.2 nm, based on comparison to the H_2 emission spectrum. In most cases, the use of 5 cm path length optical cells was necessary because of the very small absorbance changes involved.

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Registry No. NaH_2PO_2, 7681-53-0; $(H_2O)_5CrCH_2CN^{2+}$, 76068-68-3; $[Co(NH_3)_5OPOH_2]^{2+}$, 44820-03-3; $[Co(NH_3)_5OPO_2H_2]^{2+}$, 105253-44-9; $[Co(NH_3)_5OH_2](CF_3SO_3)_3$, 69897-22-9; H_3PO_3, 13598-36-2; $[(H_2O)_5CrOPOH_2]^{2+}$, 104185-22-0; $[(H_2O)_5CrOPO_2H_2]^{2+}$, 36537-26-5; $Cr(OH_2)_6^{3+}$, 14873-01-9; $[(H_2O)_3CrCH_2CN(O_2PH_2)_2]^+$, 105253-45-0; $[(H_2O)_4CrCH_2CN(O_2PH_2)]^{2+}$, 105253-46-1; $[(H_2O)_4(H_2PO_2)CrNCCH_2Hg]^{3+}$, 105253-47-2; $[(H_2O)_5CrNCCH_2Hg]^{4+}$, 103905-29-9; Cr^{2+}, 22541-79-3.

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