Proton Assisted Two-Electron Transfer from Hydroxylammonium Ion to Chromium(VI) through Oxygen Bridges

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Abstract: The reduction of Cr(VI) by NH_3OH^+ has been studied in the pH range 0.0–4.7 and has been found to proceed by two equivalent steps following formation of an O-bonded chromate ester. The ester undergoes internal oxidation and reduction involving acid catalysis. A striking inductive effect due to protonation of $H_2NOCrO_3^-$ is observed. Reactive chromium intermediates include Cr(IV) which disproportionates and Cr(V) which is reduced by NH_3OH^+ to Cr(III). A reactive nitrogen intermediate, HNO, is oxidized primarily to HNO_2. NH_3OH^+ and HNO_2 may react to give N_2O as well. The [Cr(VI)]/[NH_3OH^+] mole consumption ratio is found to vary between 4/3 and 2/3, depending on the ratio of initial reactants and pH. The rate law for the reaction is: $-d[Cr(VI)]/dt = \{[Cr(VI)][NH_3OH^+](k_A[H^+] + k_B[HOAc] + k_C + k_D K_t K_{an}/[H^+] + k_E K_t K_{an}[OAc^-]/K_a)\}/(1 + [H^+]/K_{ac} + K_{ta}\cdot[HOAc] + K_t K_{an}[NH_3OH^+]/[H^+])$. Values for all rate and equilibrium constants have been determined. Replacing –OH on hydroxylamine with –OCH_3 blocks ester formation inhibiting the reaction.

Hydroxylamine (NH_2OH) is a reducing agent potentially capable of one- or two-equivalent oxidation and of formation of N- or O-bonded chromate esters. It was therefore of interest to ascertain how it might fit the developing pattern of pathways available to Cr(VI) substrates.[3]

Both the stoichiometry and the acidity dependence of the kinetics of the reaction between Cr(VI) and NH_3OH^+ are complex. The reaction has been found to involve primary oxidation of NH_3OH^+ to HNO_2 in two equivalent steps with general acid–base catalysis and O-bonded ester formation with Cr(VI).

Experimental Section

Reagent grade $NH_2OH \cdot HCl$ and $Na_2Cr_2O_7 \cdot 2H_2O$ from Mallinckrodt Chemical Works and $CH_3ONH_2 \cdot HCl$ from K&K Laboratories, Inc., were used without further purification. $NH_2OH \cdot HClO_4$ was prepared in solution by adding a stoichiometric amount of $Ba(ClO_4)_2 \cdot 3H_2O$ from G. F. Smith Chemical Co. to $(NH_2OH)_2 \cdot H_2SO_4$ from Eastman Organic Chemicals and filtering out $BaSO_4$ precipitate.

Stoichiometry. In all stoichiometric determinations, Cr(VI) and NH_3OH^+ concentrations of ~0.1 M were used. Excess Cr(VI) was determined as follows. After completion of reaction, the product solution was placed on a cation exchange column containing Dowex 50W-X8 H^+ form 50–100 mesh cation exchange resin. Any excess Cr(VI) was eluted as $HCrO_4^-$ with distilled water and then made basic (pH ≈ 14) with NaOH to make sure all Cr(VI) was in the CrO_4^{2-} form. The absorbance of this solution was then measured at 372 nm, at which CrO_4^{2-} absorbance is a maximum.[4] Excess NH_3OH^+ was determined by oxidation to N_2O by Fe(III). The Fe(II) produced was then determined by titration with permanganate according to the method of Bray, Simpson, and MacKenzie.[5] Gaseous products (N_2O and NO) were detected by mass spectroscopy, HNO_2 was detected by its ultraviolet–visible absorption spectrum,[6,7] and Cr(III) complexes were separated by the chromatographic ion exchange techniques previously discussed.[4] Oxidation of HNO_2 to NO_3^- by Cr(VI)[8] was too slow to be a factor in our kinetic studies.

Kinetics. Cr(VI) concentrations were kept below ~10^{-3} M to avoid interference by the formation of $Cr_2O_7^{2-}$. [NH_3OH^+] was kept between 0.005 and 0.1 M, in order to maintain [NH_3OH^+] constant throughout the course of a given run. [H^+] was varied from 0.01 to 1.0 M using $HClO_4$. $NaClO_4$ was used to maintain constant ionic strength (μ) = 1.0 M. From pH 2.5–5.0, acetic acid–acetate buffers were used along with $NaClO_4$ to maintain a constant μ = 1.0 M. All kinetic studies were performed using a Sutin stopped-flow apparatus which has already been described.[9] The disappearance of Cr(VI) was followed at 350 nm where $HCrO_4^-$ has an absorption maximum. Oscillograms (see Figure 1) were assumed to be approximately absorbance *vs.* time plots since transmittance changes were small. All runs were thermostated to 25.0 ± 0.5° by means of a constant temperature bath. Pseudo-first-order kinetics were observed throughout the study.

Results

Stoichiometry, Products, and Mechanism. The [Cr(VI)]/[NH_3OH^+] mole consumption ratio varied with the ratio of initial reactant concentrations, order of mixing reagents, and with pH, between the limits of 4/3 (corresponding to the formation of HNO_2 and Cr(III)) and 2/3 (corresponding to the formation of N_2O and Cr(III)). Tables I and II summarize these findings. Earlier studies have reported similar limits.[10] Of the gaseous products, only N_2O is observed at pH 0, while a small amount of NO is observed at pH 4.7. Neither gas was measured quantitatively. In an earlier report[11] fortuitous 1/1 stoichiometry at pH 4.7, NO observation, and a brown Cr(III) product resembling $Cr(NO)^{2+}$ suggested that a possible one-step, three-electron process occurred. However, the stoichiometry actually varies from 0.67 ≤ [Cr(VI)]/[NH_3OH^+] ≤ 1.33, the brown product has been resolved into $Cr(OAc)^{2+}$, $Cr(OAc)_2^+$, and Cr^{3+}, and NO has been found to be only a minor product.[12]

With Cr(VI) in excess, HNO_2 is the only nitrogen

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(3) J. K. Beattie and G. P. Haight, Jr., in "Inorganic Reaction Mechanisms, Part II," J. O. Edwards, Ed., Wiley, 1972, pp 93–145.
(4) K. A. Muirhead and G. P. Haight, Jr., *Inorg. Chem.*, **12**, 1117 (1973).
(5) W. C. Bray, M. E. Simpson, and A. A. MacKenzie, *J. Amer. Chem. Soc.*, **41**, 1363 (1919).
(6) K. Singer and P. A. Vamplew, *J. Chem. Soc.*, 3972 (1956).
(7) G. W. King and D. Moule, *Can. J. Chem.*, **40**, 2059 (1962).

(8) D. A. Durham, L. Dozsa, and M. T. Beck, *J. Inorg. Nucl. Chem.*, **33**, 2971 (1971).
(9) S.-Å. Frennesson, J. K. Beattie, and G. P. Haight, Jr., *J. Amer. Chem. Soc.*, **90**, 6018 (1968).
(10) N. Hlasivcová and J. Novák, *Collect. Czech. Chem. Commun.*, **36**, 2027 (1971).
(11) S. Breitbarth and G. P. Haight, Jr., Abstracts of Papers, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., 1967.
(12) G. P. Haight, Jr., and R. Scott, Abstracts of Papers, 165th National Meeting of the American Chemical Society, Dallas, Texas, 1973.

Table I

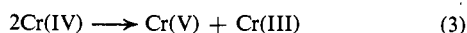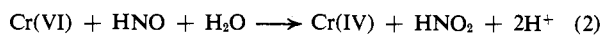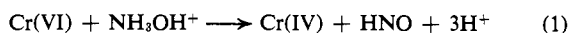| pH	Initial reactant ratio ([Cr(VI)]/ [NH₃OH⁺])	Mole consumption ratio ([Cr(VI)]/ [NH₃OH⁺])
0.5	0.25	0.66
0.5	0.33	0.67
0.5	0.50	0.73
0.5	1.00	0.94
2.1	2.00	1.13
3.4	2.00	1.16
3.8	2.00	1.26
4.3	2.00	1.34[a]

[a] The 1.33 limit must be an inference. $HCrO_4^- + HNO_2 \rightarrow HNO_3$ will slowly increase the ratio beyond 1.34, the higher [Cr(VI)]₀ and the longer the time of the reaction.

Table II

| pH	Reagent in excess	Obsd products	Mole consumption ratio ([Cr(VI)]/ [NH₃OH⁺])
0	NH₃OH⁺	N₂O, Cr³⁺	2/3
0	Cr(VI)	HNO₂, Cr³⁺	~4/3
4.7	NH₃OH⁺	NO, HNO₂, Cr³⁺	1/1 → 4/3
4.7	Cr(VI)	HNO₂, Cr³⁺, CrOAc²⁺	4/3

product (see Table II) and the mole consumption ratio is always ~4/3. (After long periods HNO_3 is produced increasing the ratio toward 2.0.) In excess NH_3OH^+, the nitrogen products and mole consumption ratios vary considerably with changes in pH, order of mixing, and initial reactant ratio.

The stoichiometry suggests the following reaction steps

$$Cr(VI) + NH_3OH^+ \longrightarrow Cr(IV) + HNO + 3H^+ \quad (1)$$

$$Cr(VI) + HNO + H_2O \longrightarrow Cr(IV) + HNO_2 + 2H^+ \quad (2)$$

$$2Cr(IV) \longrightarrow Cr(V) + Cr(III) \quad (3)$$

$$Cr(V) + NH_3OH^+ \longrightarrow Cr(III) + HNO + 3H^+ \quad (4)$$
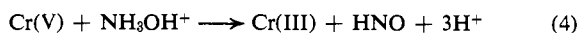
Reaction 3 is selected tentatively as the fate of Cr(IV) by analogy with previous results using hydrazine as the reducing agent[13,14] and for kinetic reasons given below.

We postulate that the variable stoichiometry is the result of the secondary reaction[10,15a,b]

$$HNO_2 + NH_3OH^+ \longrightarrow H_2N_2O_2 \longrightarrow N_2O + H_2O \quad (5)$$
$$+ \quad H_3O^+$$
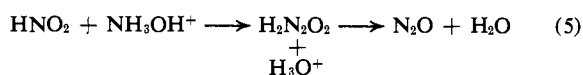
This reaction is too slow to be in evidence except when NH_3OH^+ is in excess. Branching reactions may involve the reactive intermediate HNO which may disappear by any or all of the following pathways: (1) trapping by Cr(VI) (reaction 2), (2) dimerization[10,16–19]

$$2HNO \longrightarrow H_2N_2O_2 \longrightarrow N_2O + H_2O \quad (6)$$
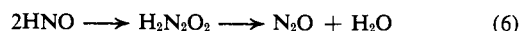
(13) M. T. Beck and D. A. Durham, *J. Inorg. Nucl. Chem.*, **32**, 1971 (1970).

(14) G. P. Haight, Jr., T. J. Huang, and B. Z. Shakhashiri, *J. Inorg. Nucl. Chem.*, **33**, 2169 (1971).

(15) (a) A. Bothner-By and L. Friedman, *J. Chem. Phys.*, **20**, 459 (1962); (b) M. N. Highes and G. Stedman, *J. Chem. Soc.*, 2824 (1963).

(16) F. C. Kohout and F. W. Lampe, *J. Chem. Phys.*, **46**, 4075 (1967).

(17) J. A. Gray and D. W. G. Style, *Trans. Faraday Soc.*, **48**, 1137 (1952).

(18) J. B. Levy, *J. Amer. Chem. Soc.*, **78**, 1780 (1956).

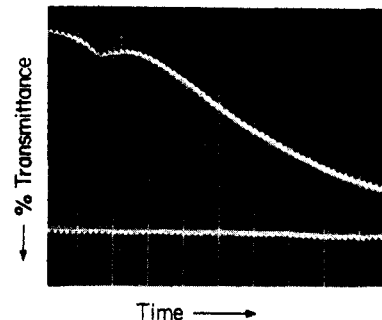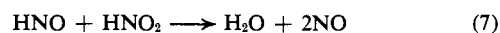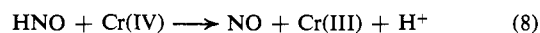(19) A. Serewicz and W. A. Noyes, Jr., *J. Phys. Chem.*, **63**, 843 (1959).

Figure 1. A typical oscillogram showing initial increase in absorbance and first-order decay of [Cr(VI)] at 350 nm: time base 0.1 sec/large division, $[H^+] = 4.4 \times 10^{-5}$ M, $[NH_3OH^+] = 0.02$ M, $[HOAc] = 1.0$ M, $\mu = 1.0$ M.

(3) reaction with HNO_2[20]

$$HNO + HNO_2 \longrightarrow H_2O + 2NO \quad (7)$$

or possibly (4) reaction with Cr(IV)

$$HNO + Cr(IV) \longrightarrow NO + Cr(III) + H^+ \quad (8)$$

The reaction
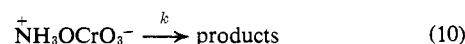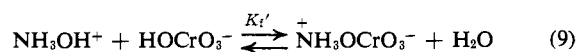
$$H_2N_2O_2 \longrightarrow N_2O + H_2O$$
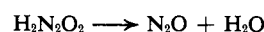
is slow[21] on the time scale of our primary reaction and N_2O is only observed when NH_3OH^+ is in excess and reagent concentrations are quite high (>0.01 M). N_2O is not observed at high pH. Also, the source of NO cannot be determined unambiguously from these results. Reaction 7 seems most likely since (8) requires bimolecular reaction of reactive intermediates which is less likely. This is a weak argument, however, in view of the likely disproportionation of Cr(IV).[14]

Kinetics and Mechanism. NH₃OH⁺ Dependence. In a great majority of runs, a fast (0.2–0.5 sec) initial reaction was observed, marked by a slight increase in absorbance at 350 nm and followed by a smooth first-order decay (see Figure 1). From analysis of the decay, values of k_{obsd} were obtained. The initial reaction could be indicative of complex formation preceding redox as in previous studies with other substrates, such as SCN⁻,[4] or it could be a temporary buildup of Cr(V) as in the reduction of Cr(VI) by oxalic acid.[22] Complex formation is most probable. The effect was too small for quantitative study and the only truly reproducible part of the oscillograms was the first-order decay.

At pH 0 the reaction is, within experimental error, first order in NH₃OH⁺ as well.

O-Methylhydroxylamine (methoxyamine) undergoes oxidation by Cr(VI) at rates which are approximately two orders of magnitude slower than NH₃OH⁺ at pH 4.7 and about one order of magnitude slower at pH 0. Since the methyl group should inhibit the formation of O-bonded esters with $HCrO_4^-$, the mechanism for NH₃OH⁺ oxidation is thought to involve such O-bonded ester formation[3] at all pH's studied.

$$NH_3OH^+ + HOCrO_3^- \underset{}{\overset{K_f'}{\rightleftharpoons}} NH_3OCrO_3^- + H_2O \quad (9)$$

$$NH_3OCrO_3^- \overset{k}{\longrightarrow} products \quad (10)$$

(20) G. P. Haight, Jr., P. Mohilner, and A. Katz, *Acta Chem. Scand.*, **16**, 221 (1962).

(21) J. R. Buchholz and R. E. Powell, *J. Amer. Chem. Soc.*, **85**, 509 (1963).

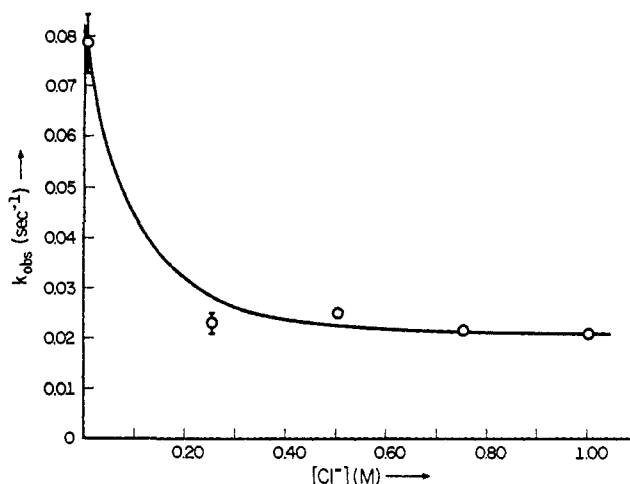(22) F. Hassan and J. Roček, *J. Amer. Chem. Soc.*, **94**, 3181 (1972).

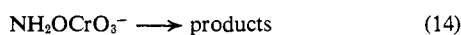**Figure 2.** Variation of k_{obsd} with [Cl⁻]: [H⁺] = 1.0 M, [NH₃OH⁺] = 0.005 M, [HOAc] = [OAc⁻] = 0.0 M.

This leads to the rate expression

$$\text{rate} = \frac{-d[Cr(VI)]}{dt} = \frac{kK_t'[Cr(VI)][NH_3OH^+]}{1 + K_t'[NH_3OH^+]} \quad (11)$$

Figure 5 shows a plot of $1/k_{obsd}$ vs. $1/[NH_3OH^+]$. The intercept is within experimental error of 0.0 indicating that ester formation at pH 0.0 is negligible (i.e., $K_t[NH_3OH^+] \leq 0.1$). Thus at pH 0.0

$$\text{rate} \approx k[Cr(VI)][NH_3OH^+] \quad (12)$$

However, from data at pH 4.7 and [HOAc] = [OAc⁻] = 1.00 (see Table V), it can be seen that $k_{obsd} \neq k[NH_3OH^+]$, so that inclusion of a denominator term first order in [NH₃OH⁺] is necessary, indicating significant formation of an O-bonded ester at pH 4.7. Thus

$$NH_2OH + HCrO_4^- \underset{K_t}{\overset{}{\rightleftharpoons}} NH_2OCrO_3^- + H_2O \quad (13)$$

$$NH_2OCrO_3^- \longrightarrow \text{products} \quad (14)$$

where $K_t = 1.2 \times 10^3$.

Chloride Effect. Inadvertently, a few runs were made in which CrO₃Cl⁻ formed. Figure 2 shows the effect of Cl⁻ on k_{obsd}. Substitution of Cl⁻ for ClO₄⁻ in 1 M H⁺ decreases the rate by a factor of ~6. If CrO₃Cl⁻ forms[23] and is inert to reduction, the rate should decrease by a factor of ~9. Cursory analysis of the rather crude data in Figure 2 indicates a rapid decrease of k_{obsd} to a limiting value. This means that there is a kinetic term in CrO₃Cl⁻, such that in the presence of Cl⁻ the rate law is

$$\frac{-d[Cr(VI)]}{dt} =$$

$$\frac{[NH_3OH^+](k'[HCrO_4^-] + k''[CrO_3Cl^-]) =}{[NH_3OH^+][HCrO_4^-](k' + k''K_{Cl}[H^+][Cl^-])}{1 + K_{Cl}[Cl^-][H^+]} \quad (15)$$

where $K_{Cl} \approx 11$.[24] The decrease in rate indicates that the activated state containing HCrO₄⁻ is more reactive than that containing ClCrO₃⁻.

Deuterium Isotope Effect. ND₃OH⁺ reacts about

(23) (a) G. P. Haight, Jr., D. C. Richardson, and N. H. Coburn, *Inorg. Chem.*, **3**, 1777 (1964); (b) J. Y. Tong and R. L. Johnson, *ibid.*, **5**, 1902 (1966).

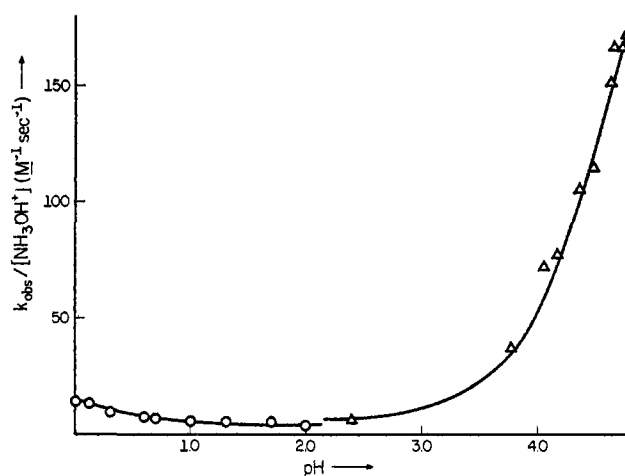(24) J. Y. Tong, *Inorg. Chem.*, **3**, 1804 (1964).

Figure 3. Variation of $k_{obsd}/[NH_3OH^+] = kK_t'$ (see eq 11) with pH: O, in HClO₄, [NH₃OH⁺] = 0.1 M, μ = 1.0 M; Δ, in HOAc⁻–OAc⁻ buffers, [NH₃OH⁺] = 0.02 M, [HOAc] = 1.0 M, μ = 1.0 M. Solid line is a plot of the postulated rate law (eq 29) using values for the constants given in Table III.
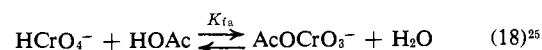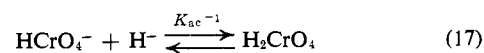
half as fast as NH₃OH⁺ with HCrO₄⁻. In a completely deuterated system the reaction of ND₃OD⁺ with DCrO₄⁻ proceeds at about one-fourth the rate of the reaction of NH₃OH⁺ with HCrO₄⁻. We interpret these results as evidence for protons leaving N in the rate determining step for the redox process. Determination of the exact magnitude of the deuterium isotope effect requires determination of K_t for formation of the deuterated ester.

No isotope effect was observable at pH 4.7. Reactions were quite fast and appeared to proceed at the same rate. If NH₂OH or NH₂OCrO₃⁻ were present in significant concentration, exchange of N–D for N–H in the aqueous medium should be fast compared with the redox reaction. Table VI summarizes these results.

pH Dependence. The variation of $k_{obsd}/[NH_3OH^+]$ = k (from eq 12) with pH is shown in Figure 3. Several features of the curve are notable. First, the reaction is H⁺ and base catalyzed. Secondly, rates in acetic acid are higher than in HClO₄ at the same pH, indicating catalysis by HOAc. Not shown in Figure 3 is the fact that as the pH becomes greater than ~5.5, the reaction slows again as HCrO₄⁻ becomes CrO₄²⁻.[3] The general shape of the curve in Figure 3 suggests, as a first approximation, the following rate law (chloride is absent)

$$\frac{-d[Cr(VI)]}{dt} = [NH_3OH^+][HCrO_4^-](k_1[H^+] +$$

$$k_2[HOAc] + k_3 + k_4/[H^+] + k_5[OAc^-]) \quad (16)$$

It is postulated that [HCrO₄⁻] is diminished by establishment of the following equilibria

$$HCrO_4^- + H^- \underset{K_{ac}^{-1}}{\overset{}{\rightleftharpoons}} H_2CrO_4 \quad (17)$$

$$HCrO_4^- + HOAc \underset{K_{ta}}{\overset{}{\rightleftharpoons}} AcOCrO_3^- + H_2O \quad (18)^{[25]}$$

$$HCrO_4^- + NH_2OH \underset{K_t}{\overset{}{\rightleftharpoons}} NH_2OCrO_3^- + H_2O \quad (13)$$

The ester formed in reaction 13 is merely the deprotonated form of the ester inferred in reaction 9, de-

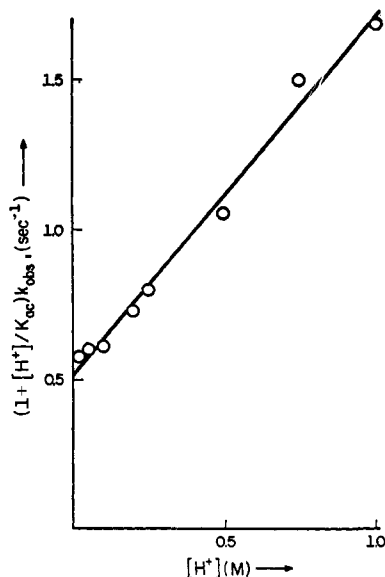(25) U. Kläning and M. C. R. Symons, *J. Chem. Soc.*, 3204 (1961).

Figure 5. Variation of $1/k_{obsd}$ with $1/[NH_3OH^+]$, in $HClO_4$, $[H^+] = 1.0\ M$, and $\mu = 1.0\ M$. The slope gives an estimate for $1/kK_t'$ while an intercept would give $1/k$. (Cf. eq 11.)

Figure 4. Variation of $(1 + ([H^+]/K_{ac}))k_{obsd}$ with $[H^+]$ for $[H^+] = 0.01–1.0\ M$ in $HClO_4$, $[NH_3OH^+] = 0.1\ M$, $\mu = 1.0\ M$, $K_{ac} = 5.0\ M$ (ref 23 and 27). From the intercept, a value for k_C was estimated. The slope gives k_A.

Table III. Values for Measured Constants

Constant[a]	Value[b]	
k_A	13.9 ± 2.6	$M^{-1}\,sec^{-1}$
k_B	9.3 ± 1.6	$M^{-1}\,sec^{-1}$
k_C	4.7 ± 0.8	sec^{-1}
k_D	$(6.7 \pm 1.0) \times 10^{-1}$	sec^{-1}
k_E	10.15 ± 2.0	$M^{-1}\,sec^{-1}$
K_{ac}	5.0 ± 1.3	M
K_t	$(1.2 \pm 0.2) \times 10^3$	M^{-1}
K_t'	≤ 0.1	M^{-1}
K_{ta}	1.5 ± 0.2	M^{-1}

[a] See eq 29. [b] Constants were evaluated using $K_{an} = 10^{-6}\ M$.

scribed above. From these considerations

$$[Cr(VI)] = [HCrO_4^-](1 + [H^+]/K_{ac} +$$
$$K_{ta}[HOAc] + K_tK_{an}[NH_3OH^+]/[H^+]) \quad (19)$$

where reported values of

$$K_{an} = \frac{[NH_2OH][H^+]}{[NH_3OH^+]} \quad (20)$$

vary from 8.7×10^{-7} to $2 \times 10^{-6}\ M$.[26–28]
The rate law then becomes

esters $AcOCrO_3^-$ and $NH_2OCrO_3^-$ given by

$$K_{ta} = \frac{[AcOCrO_3^-]}{[HOAc][HCrO_4^-]}$$

$$K_t = \frac{[NH_2OCrO_3^-]}{[NH_2OH][HCrO_4^-]}$$

are compared in Table IV with formation constants of

$$\frac{-d[Cr(VI)]}{dt} = \frac{[Cr(VI)][NH_3OH^+](k_1[H^+] + k_2[HOAc] + k_3 + k_4/[H^+] + k_5[OAc^-])}{1 + [H^+]/K_{ac} + K_{ta}[HOAc] + K_tK_{an}[NH_3OH^+]/[H^+]} \quad (21)$$

The presence of the $k_5[OAc^-]$ term in the numerator cannot be deduced by cursory inspection of the results given here, but its inclusion fits the results by combining with the much smaller [HOAc] term in studies in which [HOAc] = [OAc^-] alone was varied and also by combining with the inverse $[H^+]$ term at the high pH end of the curve in Figure 3. The inclusion of the $[OAc^-]$ term was necessary to fit the postulated rate law to the observed data (Table V).

Figures 4 and 5 are examples of plots used to help estimate values for the constants in the rate expression. A computer program was used to calculate the final values of the constants. The Fortran program used estimated initial values for all constants, then applied a least-square criterion for refining the values. The final results of this analysis are given in Table III. Plots derived from the postulated rate law using these constant values are compared with observed data in Figure 3. The value calculated for K_{ac} is within experimental error of previous determinations of its value.[23,24] The values of the formation constants for the chromate

Table IV. Formation Constants of Chromate Esters

Ester	K_t[a]	pH	Ref	Method[b]
O_3CrONH_3	≤ 0.1	0–4.7	This work	K
$O_3CrONH_2^-$	1.2×10^3	0–4.7	This work	K
O_3CrOAc^-	1.5	0–4.7	This work	K
$O_3CrNHNH_3$	3.2	0	c	K
$\overset{\text{H}}{\underset{\text{\textbar}}{O_3CrOPO_2^{2-}}}$	7	4	31	Sp, Eq
$\overset{\text{H}}{\underset{\text{\textbar}}{O_3CrOP(=O)OH^-}}$	16	0	31	K, P
$\overset{\text{H}}{\underset{\text{\textbar}}{O_3CrOP(=O)^-}}$	11	0	31	K, P
H				
$O_3CrOP(=O)(OH)_2^-$	9.4	1	d	Sp, Eq
$O_3CrOP(=O)_2OH^{2-}$	2.9	5	d	Sp, Eq
$O_3CrOSO_3^{2-}$	4	0	e	Sp, Eq
$O_3CrOSO_2^{2-}$	36	4	e	K, P
$O_3CrS_2O_3^{2-}$	10^4	2	3	Sp
$O_3CrOAsO_2H^{2-}$	22	4.6	f	K, P

[a] $K_t = [O_3CrX^-]/[HX][HCrO_4^-]$. [b] Key: Eq = equilibrium, K = kinetics, P = preequilibrium, Sp = spectrophotometry. [c] G. P. Haight, Jr., and T. J. Huang, to be submitted for publication. [d] F. Holloway, *J. Amer. Chem. Soc.*, **74**, 225 (1952). [e] G. P. Haight, Jr., E. Perchonock, F. Emmenegger, and G. Gordon, *ibid.*, **87**, 3855 (1965). [f] J. G. Mason and A. D. Kowalak, *Inorg. Chem.*, **3**, 1248 (1964).

(26) P. Lumme, P. Lahermo, and J. Tummavuori, *Acta Chem. Scand.*, **19**, 2175 (1965).

(27) H. S. Harned and R. W. Ehlers, *J. Amer. Chem. Soc.*, **55**, 65 (1933).

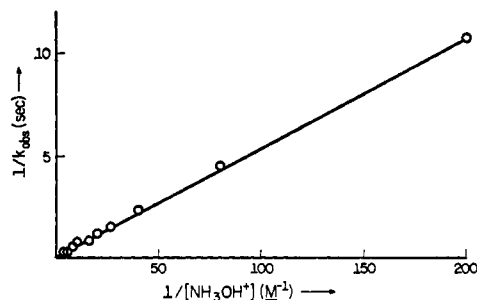(28) A. E. Martell and L. G. Sillen, Ed., *Chem. Soc., Spec. Publ.*, No. 25 (1969).

Table V. Observed and Calculated Constants for Various Runs

[H$^+$] (M)	[HOAc] (M)	[OAc$^-$] (M)	[NH$_3$OH$^+$] (M)	k_{obsd} (sec^{-1})	k_{obsd}(calcd) (sec^{-1})
1.00	0.0	0.0	0.0050	0.093	0.078
1.00	0.0	0.0	0.0125	0.223	0.194
1.00	0.0	0.0	0.0250	0.431	0.388
1.00	0.0	0.0	0.0375	0.671	0.581
1.00	0.0	0.0	0.0500	0.857	0.775
1.00	0.0	0.0	0.0625	1.23	0.969
1.00	0.0	0.0	0.1250	1.98	1.94
1.00	0.0	0.0	0.1875	3.48	2.91
1.00	0.0	0.0	0.2500	3.59	3.87
1.00	0.0	0.0	0.1	1.40	1.55
0.75	0.0	0.0	0.1	1.30	1.32
0.50	0.0	0.0	0.1	0.957	1.06
0.25	0.0	0.0	0.1	0.757	0.779
0.20	0.0	0.0	0.1	0.695	0.719
0.10	0.0	0.0	0.1	0.595	0.597
0.05	0.0	0.0	0.1	0.592	0.534
0.02	0.0	0.0	0.1	0.570	0.497
0.01	0.0	0.0	0.1	0.379	0.485
1.75 $\times$ 10^{-5}	1.00	1.00	0.02	3.45	3.90
1.94 $\times$ 10^{-5}	1.00	0.90	0.02	3.34	3.65
2.19 $\times$ 10^{-5}	1.00	0.80	0.02	3.34	3.38
2.33 $\times$ 10^{-5}	1.00	0.75	0.02	3.06	3.23
3.50 $\times$ 10^{-5}	1.00	0.50	0.02	2.30	2.42
4.38 $\times$ 10^{-5}	1.00	0.40	0.02	2.13	2.04
7.00 $\times$ 10^{-5}	1.00	0.25	0.02	1.54	1.40
8.75 $\times$ 10^{-5}	1.00	0.20	0.02	1.44	1.17
1.75 $\times$ 10^{-4}	1.00	0.10	0.02	0.742	0.669
4.18 $\times$ 10^{-3}	1.00	4.18 $\times$ 10^{-3}	0.02	0.109	0.137
1.75 $\times$ 10^{-5}	0.01	0.01	0.1	0.583	0.730
1.75 $\times$ 10^{-5}	0.05	0.05	0.1	1.22	1.08
1.75 $\times$ 10^{-5}	0.10	0.10	0.1	1.61	1.51
1.75 $\times$ 10^{-5}	0.20	0.20	0.1	2.93	2.35
1.75 $\times$ 10^{-5}	0.30	0.30	0.1	3.29	3.15
1.75 $\times$ 10^{-5}	0.40	0.40	0.1	4.20	3.93
1.75 $\times$ 10^{-5}	0.50	0.50	0.1	4.95	4.68
1.75 $\times$ 10^{-5}	0.60	0.60	0.1	5.78	5.41
1.75 $\times$ 10^{-5}	0.75	0.75	0.1	6.34	6.45
1.75 $\times$ 10^{-5}	0.90	0.90	0.1	7.00	7.44
1.75 $\times$ 10^{-5}	1.00	1.00	0.1	7.04	8.08
1.0 $\times$ 10^{-4}	0.85	0.15	0.0058	0.329	0.309
1.0 $\times$ 10^{-5}	0.36	0.64	0.0058	0.618	(0.823–1.20)^a
1.0 $\times$ 10^{-6}	0.05	0.95	0.0058	0.168	(0.167–0.471)^a

^{a} Corrected for 2 $\times$ 10^{-6} $M > K_a > 1 \times 10^{-6}$ M for both NH$_3$OH$^+$ and HCrO$_4^-$ (ref 29).

Table VI. Inhibition by Cl$^-$ and D$^+$

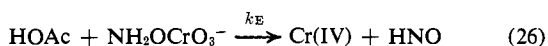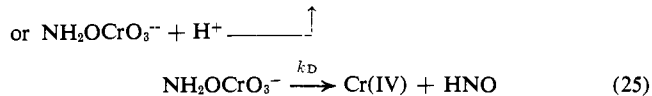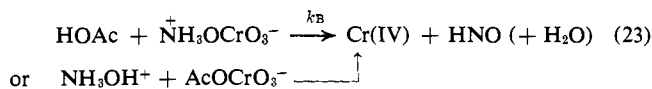| Reactants			pH	k_{obsd} (sec^{-1})	Relative rate
0.005 M NH$_3$OH$^+$Cl$^-$	0.0005 M Na$^+$HCrO$_4^-$	1.0 M HClO$_4$	0.0	0.09	20
0.005 M ND$_3$OH$^+$Cl$^-$	0.0005 M Na$^+$HCrO$_4^-$	1.0 M HClO$_4$	0.0	0.06	13
0.005 M NH$_3$OH$^+$Cl$^-$	0.0005 M Na$^+$HCrO$_4^-$	1.0 M HCl	0.0	0.02	3.7
0.005 M ND$_3$OH$^+$Cl$^-$	0.0005 M Na$^+$HCrO$_4^-$	1.0 M HCl	0.0	0.007	1.6
0.005 M NH$_3$OD$^+$Cl$^-$	0.0005 M Na$^+$DCrO$_4^-$	1.0 M DCl	0.0	0.009	2.0
0.005 M ND$_3$OD$^+$Cl$^-$	0.0005 M Na$^+$DCrO$_4^-$	1.0 M DCl	0.0	0.004	1.0
0.005 M NH$_3$OH$^+$Cl$^-$	0.0001 M Na$^+$HCrO$_4^-$	1.0 M NaAc–1.0 M HAc	4.7	$\geq \sim$2	$\geq \sim$450
0.005 M ND$_3$OH$^+$Cl$^-$	0.0001 M Na$^+$HCrO$_4^-$	1.0 M NaAc–1.0 M HAc	4.7	$\geq \sim$2	$\geq \sim$450

esters previously reported. Table V compares values of k_{obsd} calculated and observed for data covering the entire pH range. Each data point in Table V was derived from four separate runs and 20 separate calculations of k_{obsd}, the average of which appears in the table.

Derivation of the Rate Law from a Proposed Mechanism. It is possible to derive the rate law from mechanisms involving the direct reaction of the acetato-trioxo–chromium(VI) ester with hydroxylamine. However, the chloride inhibition leads us to assume similar inhibition by acetate rather than acceleration. It can

be argued that AcOCrO$_3^-$ would be far less likely to coordinate to NH$_3$OH$^+$ than HCrO$_4^-$ except by expulsion of HOAc to give the same intermediates we have invoked. Thus we prefer the explanation of general acid catalysis to catalysis by acetate coordinated to Cr(VI) as the explanation of our results. There is no decisive experimental evidence for choice between the two explanations.

After ester formation (eq 9 and 13), it is postulated that two-electron internal oxidation and reduction of the ester can occur through any of the following steps

$$H^+ + \overset{+}{N}H_3OCrO_3^- \xrightarrow{k_A} Cr(IV) + HNO \qquad (22)$$

$$\text{HOAc} + \overset{+}{\text{N}}\text{H}_3\text{OCrO}_3^- \xrightarrow{k_B} \text{Cr(IV)} + \text{HNO} (+ \text{H}_2\text{O}) \quad (23)$$

$$\text{or} \quad \text{NH}_3\text{OH}^+ + \text{AcOCrO}_3^- \xrightarrow{\uparrow}$$

$$\overset{+}{\text{N}}\text{H}_3\text{OCrO}_3^- \xrightarrow{k_C} (\text{NH}_2\text{OCrO}_3\text{H}) \longrightarrow \text{Cr(IV)} + \text{HNO} \quad (24)$$

$$\text{or} \quad \text{NH}_2\text{OCrO}_3^{--} + \text{H}^+ \xrightarrow{\uparrow}$$

$$\text{NH}_2\text{OCrO}_3^- \xrightarrow{k_D} \text{Cr(IV)} + \text{HNO} \quad (25)$$

$$\text{HOAc} + \text{NH}_2\text{OCrO}_3^- \xrightarrow{k_E} \text{Cr(IV)} + \text{HNO} \quad (26)$$
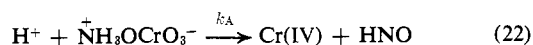
Cr(IV) and HNO then proceed to products through various fast steps. When Mn(II) was added with NH_3OH^+ in large excess at pH 0, the rate of the reaction was unaffected. This suggests (following similar results with hydrazine[14]) that Cr(IV) disproportionates rather than trapping Cr(VI) or forming radicals which trap Cr(VI).[14,29]

The rate expression consistent with steps 22–26 is

$$\frac{-d[\text{HCrO}_4^-]}{dt} = k_A[\text{H}^+][\text{HCrO}_4^-][\text{NH}_3\text{OH}^+] +$$

$$k_B[\text{HOAc}][\text{HCrO}_4^-][\text{NH}_3\text{OH}^+] +$$

$$k_C + k_D[\text{NH}_2\text{OCrO}_3^-] + k_E[\text{HOAc}][\text{NH}_2\text{OCrO}_3^-] \quad (27)$$

Since

$$[\text{NH}_2\text{OCrO}_3^-] = K_t K_{an}[\text{NH}_3\text{OH}^+][\text{HCrO}_4^-]/[\text{H}^+]$$

then

$$\text{rate} = [\text{HCrO}_4^-][\text{NH}_3\text{OH}^+]\left(k_A[\text{H}^+] + k_B[\text{HOAc}] + \right.$$

$$\left. k_C + k_D K_t K_{an}/[\text{H}^+] + \frac{k_E K_t K_{an}}{K_a}[\text{OAc}^-]\right) \quad (28)$$

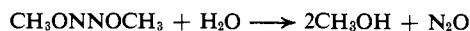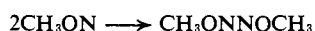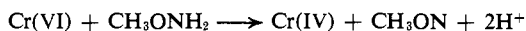where K_a is the dissociation constant of acetic acid

$$K_a = \frac{[\text{H}^+][\text{OAc}^-]}{[\text{HOAc}]} = 1.75 \times 10^{-5} \, M^{28}$$

Considering eq 19

$$\text{rate} = \frac{[\text{Cr(VI)}][\text{NH}_3\text{OH}^+](k_A[\text{H}^+] + k_B[\text{HOAc}] + k_C + k_D K_t K_{an}/[\text{H}^+] + k_E K_t K_{an}[\text{OAc}^-]/K_a)}{1 + [\text{H}^+]/K_{ac} + K_{ta}[\text{HOAc}] + K_t K_{an}[\text{NH}_3\text{OH}^+]/[\text{H}^+]} \quad (29)$$

Equation 29 is the same form as the observed rate law given by eq 21.

O-Methylhydroxylammonium Ion. The oxidation by Cr(VI) of *O*-methylhydroxylammonium ion was studied briefly in order to provide evidence whether NH_3OH^+ was O- or N-bonded to Cr in the activated complex. Reaction rates were slower by approximately two orders of magnitude, but reaction did occur. Changes in pH had only a small effect on the rate, the reaction proceeding faster at pH 0 than at pH 4.7. At pH 0, significant oxidation of CH_3OH (a product of initial oxidation of CH_3ONH_2) by Cr(VI)[30] occurred while at pH 4.7, N_2O and CH_3OH (as well as Cr(III)) were the chief products. Evidently, the reaction proceeds by

$$\text{Cr(VI)} + \text{CH}_3\text{ONH}_2 \longrightarrow \text{Cr(IV)} + \text{CH}_3\text{ON} + 2\text{H}^+$$

$$2\text{CH}_3\text{ON} \longrightarrow \text{CH}_3\text{ONNOCH}_3$$

$$\text{CH}_3\text{ONNOCH}_3 + \text{H}_2\text{O} \longrightarrow 2\text{CH}_3\text{OH} + \text{N}_2\text{O}$$

(29) J. O. Edwards, Ed., "Inorganic Reaction Mechanisms, Part 1," W. A. Benjamin, 1964, p 150.

(30) J. Lal, S. N. Shukla, and A. C. Chatterji, *Z. Phys. Chem. (Leipzig)*, **228**, 173 (1965).

followed again by Cr(IV) disproportionation and two-electron reduction of Cr(V) by CH_3ONH_2 giving an overall $[\text{Cr(VI)}]/[\text{CH}_3\text{ONH}_2]$ mole consumption ratio of 2/3. This ratio was observed at pH 4.7. At pH 0, however, higher mole consumption ratios (~ 2.5) were observed and are attributed to CH_3OH oxidation. No evidence of HNO_2 or NO_2^- was found at either pH extreme indicating that the methyl group also blocks oxidation of CH_3ON by Cr(VI).

Discussion

The ester $^+\text{H}_3\text{NOCrO}_3^- \rightleftarrows \text{H}_2\text{NOCrO}_3\text{H}$ undergoes acid and base assisted internal oxidation and reduction. For electron transfer to occur, it appears necessary to protonate an oxide ligand on Cr and to deprotonate H_3N^+- to allow migration of an electron pair to Cr through the π-system of the bridging O.

$$\text{products} \quad (30)$$
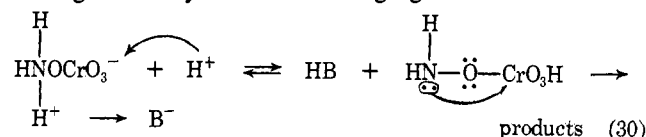
B^- may be either H_2O or OAc^-

In the oxidation of H_3PO_2 and H_3PO_3 by Cr(VI),[31] ester formation also occurs, and acid assisted deprotonation of P was necessary for electron transfer to occur.

$$\text{products} \quad (31)$$
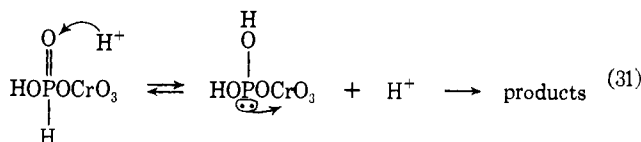
It appears that neutral hydroxylamine is similar in needing coordination to Cr(VI) and using general acid-base assistance to deprotonate an electron pair.

$$\text{products} \quad (32)$$
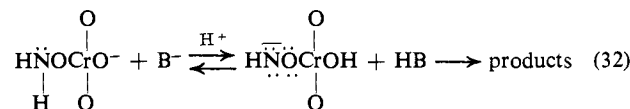
Thus, N– is deprotonated. N–H protons are also labilized by CrO_3 coordination to $\text{H}_3\text{NO}-$ and by protonation of an oxygen bonded to chromium producing an inductive effect, drawing negative charge away from N. Acetic acid catalysis probably functions through protonation of an oxide ligand coupled with OAc^- assisted deprotonation of N, since rate $= k_2[\text{HOAc}]$ is equivalent to rate $= k[\text{H}^+][\text{OAc}^-]/K_a$.

It might be expected that deprotonation of $\text{H}_3\text{N}^+\text{-OCrO}_3^-$ would be the dominant effect. However, the inductive effect is of unexpectedly great importance. $\text{H}_2\text{NOCrO}_3^-$ (which is detectable) decays at a slower rate than $^+\text{H}_3\text{NOCrO}_3^-$ which presumably reacts through the tautomer $\text{H}_2\text{NOCrO}_3\text{H}$. The k_C term could also describe a pathway involving
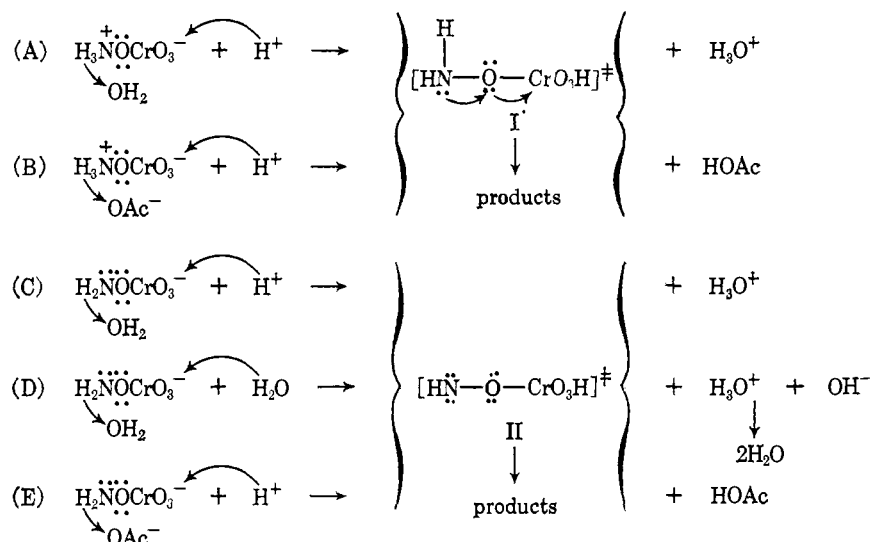
$$\text{H}_2\text{NOCrO}_3^- + \text{H}^+ \rightleftarrows \text{H}_2\text{NOCrO}_3\text{H}$$
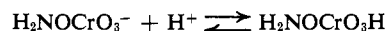
giving a term

$$k_C'[\text{H}_2\text{NOCrO}_3^-][\text{H}^+] = k_C' K_{ae}[\text{H}_3\overset{+}{\text{N}}\text{OCrO}_3^-]$$

(31) G. P. Haight, Jr., M. Rose, and J. Preer, *J. Amer. Chem. Soc.*, **90**, 4812 (1968).

(A) $H_3\overset{+..}{N}\overset{..}{O}CrO_3^- + H^+ \longrightarrow$
$\overset{\diagdown}{O}H_2$

(B) $H_3\overset{+..}{N}\overset{..}{O}CrO_3^- + H^+ \longrightarrow$
$\overset{\diagdown}{O}Ac^-$

(C) $H_2\overset{..}{N}\overset{..}{O}CrO_3^- + H^+ \longrightarrow$
$\overset{\diagdown}{O}H_2$

(D) $H_2\overset{..}{N}\overset{..}{O}CrO_3^- + H_2O \longrightarrow$
$\overset{\diagdown}{O}H_2$

(E) $H_2\overset{..}{N}\overset{..}{O}CrO_3^- + H^+ \longrightarrow$
$\overset{\diagdown}{O}Ac^-$

$[H\overset{|}{\underset{..}{N}}—\overset{..}{O}—CrO_3H]^‡$

I'

$\downarrow$

products

$+ H_3O^+$

$+ HOAc$

$+ H_3O^+$

$[H\overset{..}{N}—\overset{..}{O}—CrO_3H]^‡$

II

$\downarrow$

products

$+ H_3O^+ + OH^-$

$\downarrow$

$2H_2O$

$+ HOAc$
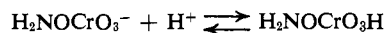
K_{ae} is the acid dissociation constant for $^+H_3NOCrO_3^-$ with a limiting value of 10^{-2} or less. k_C' is thus 2.8×10^3 M^{-1} sec^{-1} (cf. Table III). If it is assumed that $[^+H_3NOCrO_3^-] \gg [H_2NOCrO_3H]$ and that the ratio of the two species equals the product of the ratios of the two protonation constants for $HCrO_4^-$ and NH_2OH or 2×10^5, then the k_C term is $k_C''[H_2NOCrO_3H]$ with $k_C'' = 5.6 \times 10^5$, implying great reactivity for species containing a lone pair on –N– and a protonated terminal oxygen.

The inductive effect observed here suggests that the activated state for the Cr(VI)–P(III) reaction (eq 31)[31] may be $HOP(O)OCrO_3H$ rather than $HOP(OH)OCrO_3$. Protonation of CrO_3 coordinated to $H_2PO_3^-$ should certainly labilize the –P–H bond and induce transfer of the resulting lone pair of electrons to Cr.

The term $k_5[OAc^-]$ posed an interesting problem of interpretation. It is mathematically consistent with a step involving direct deprotonation of $^+H_3NOCrO_3^-$ by OAc^-. However, this term becomes important at high pH where $^+H_3NOCrO_3^-$ is already over 90% converted to $H_2NOCrO_3^-$. Therefore, the physical argument can be advanced that a reaction to produce this species is not likely to produce catalysis in the pH range in question. It is intriguing to note that the $k_5[OAc^-]$ term is equivalent to $k_5K_a[HOAc]/[H^+]$. This latter term could arise in the event of acid catalysis of the internal redox reaction of $H_2NOCrO_3^-$. This suggests that the decomposition of both $^+H_3NOCrO_3^-$ and $H_2NOCrO_3^-$ enjoy the benefits of acid catalysis. The scheme

$$H_2NOCrO_3^- + H^+ \rightleftarrows H_2NOCrO_3H$$

$$H_2NOCrO_3H + B^- \rightleftarrows H\overset{..}{N}\overset{..}{O}CrO_2H + HB \longrightarrow products$$

should be a very favorable one, setting up the formation of HNO and providing protons needed for the oxide ions in reduced Cr(IV). The term $k_5[OAc^-]$ could also be interpreted as a reaction of $AcOCrO_3^- + NH_2OH$. Significant $H_2NOCrO_3^-$ formation argues against this possibility.

Our interpretation of the five observed pathways for reaction involves only two reactive intermediates, $H_2\overset{..}{N}\overset{..}{O}CrO_3H$ (I) and $H\overset{..}{N}\overset{..}{O}CrO_3H$ (II), formed as indicated in Chart I.
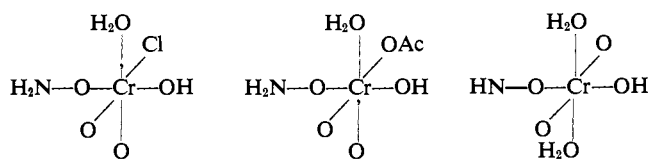
We have no basis for speculation on whether the N–O

bond or the Cr–O bond for the bridging oxygen is broken. All primary products, Cr(IV) and HNO$_2$, are labile to ^{18}O exchange with water in the pH range used.

Previous studies[3] interpret Cr(VI) activation as requiring expansion of the coordination sphere to a coordination number of six to facilitate conversion to six-coordinate chromium(IV). If two water molecules coordinate to $H_2NOCrO_3^-$ to produce the activated state, one can reasonably postulate that protonation of oxygen will reduce Cr–O bond order and facilitate coordination of water to produce

$$H_2N—O—\underset{\underset{H_2O}{O}}{\overset{\overset{H_2O}{|}}{\underset{|}{Cr}}}—OH$$
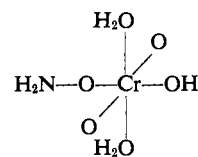
as an activated state. Other possible activated states include

$$H_2N—O—\underset{\underset{O}{O}}{\overset{\overset{H_2O}{|}}{\underset{|}{Cr}}}—Cl \qquad H_2N—O—\underset{\underset{O}{O}}{\overset{\overset{H_2O}{|}}{\underset{|}{Cr}}}—OAc \qquad HN—O—\underset{\underset{H_2O}{O}}{\overset{\overset{H_2O}{|}}{\underset{|}{Cr}}}—OH$$

Summary of Inductive Effects. (a) Substitution of CrO_3 for H^+ on NH_3OH^+ increases the acidity constant of NH_3OH^+ from 10^{-6} to 10^{-3} labilizing protons on N. (b) Protonation of $H_2NOCrO_3^-$ decreases K_f from 10^3 to <0.1 M^{-1} by weakening the –O– bridge bond. (c) Protonation of $–CrO_3$ labilizes protons on N, induces electron pair transfer to take place, and perhaps weakens the oxygen bridge bond between Cr and N. (d) Protonation of $–CrO_3$ enhances Lewis acidity of Cr facilitating expansion of coordination number of Cr to six as required by Cr(IV) product.