

driving force (expressed as ΔE^0).²¹ On this basis a decrease in k_1 from 2×10^4 to $4 \times 10^3 M^{-1} \text{sec}^{-1}$ may be accounted for in the reaction of $\text{Fe}(\text{EDTA})^{2-}$ with $\text{cyt } c(\text{III})_N$ at pH 9, but this leaves a factor of about 150 in the observed decrease in k_1 to $2.67 \times 10^1 M^{-1} \text{sec}^{-1}$ unexplained. Further rate inhibition may arise from steric factors originating in the limited conformational change known to accompany formation of the high pH derivative.²⁸ The heme pocket presumably is the region in the protein most directly affected by displacement of the Met-80 ligand, but structural perturbations in the vicinity of the heme edge are possible as well. More structural information as well as a better estimate of the E^0 for the high pH $\text{cyt } c(\text{III})$ derivative will be required before a choice can be made among the several possible explanations of the observed rate decrease.

Acknowledgments. We thank Dr. Larry Bennett for helpful comments and suggestions. R. H. acknowledges the National Science Foundation for a Graduate Fellowship (1969–1971). H. B. G. held a John Simon Guggenheim Fellowship during 1972–1973. This research was additionally supported by a grant from the National Science Foundation.

Supplementary Material Available. A listing of k_{obsd} values will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-3132.

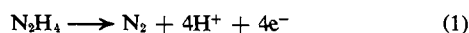
Reaction of Chromium(VI) with Hydrazinium Ion

G. P. Haight, Jr.,*¹ Tracy J. Huang, and Harry Platt

Contribution from the School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801. Received November 16, 1973

Abstract: The study of the stoichiometry and kinetics of oxidation of hydrazinium ion (N_2H_6^+) by chromium(VI) is extended to higher acidities than heretofore. The reaction proceeds through an N-bonded chromate ester *via* two equivalent redox steps. The reaction is catalyzed by acids H^+ , H_3PO_4 , H_2PO_4^- , and HCrO_4^- . Cr(IV) is found to disproportionate, but it is not trapped by Cr(VI) as previously supposed. Revised estimates of Cr(VI)/Cr(V) and Cr(VI)/Cr(IV) potentials are given. The Mn^{2+} effect on Cr(VI) oxidations is critically examined.

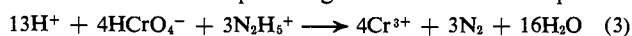
Chromium(VI) oxidations are characterized by pre-equilibria involving chromate(VI) esters² or one-electron reductions to chromium(V)³ and by a variety of steps involving active intermediates Cr(V) and Cr(IV).^{2,3} Hydrazine is of interest as a reducing agent because of the absence of information on N–Cr bonded esters and because of its ability to discriminate between two-equivalent substrates⁴



and one-equivalent substrates⁴



Durham and Beck⁵ have reported on the kinetics of the reaction over the pH range 1–3. We have reported



on the fate of Cr(IV) intermediates as deduced from stoichiometric studies and Mn^{2+} trapping experiments.⁶ We report here the kinetics of the reaction at high acidity, $2.2 M \geq [\text{H}^+] \geq 0.2 M$, and in phosphoric acid buffers of pH 1.6–3.0 and reexamine inferences drawn from the Mn^{2+} trapping experiments.

(1) To whom correspondence should be addressed.

(2) J. K. Beattie and G. P. Haight, Jr., in "Inorganic Reaction Mechanisms Part II," John O. Edwards, Ed., Wiley, New York, N. Y., 1972, pp 93–145.

(3) J. H. Espenson, *Accounts Chem. Res.*, **3**, 347 (1970).

(4) (a) R. E. Kirk and A. W. Browne, *J. Amer. Chem. Soc.*, **50**, 337 (1928); (b) W. C. H. Higginson and J. W. Marshall, *J. Chem. Soc.*, 447 (1957).

(5) M. T. Beck and D. A. Durham, *J. Inorg. Nucl. Chem.*, **32**, 1971 (1970).

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

Experimental Section

Analytical grade reagents were used without further purification. Kinetics were measured by following the disappearance of Cr(VI) at the absorption maximum of 350 nm. Both HCrO_4^- and H_2CrO_4 are present over much of the $[\text{H}_3\text{O}^+]$ range studied, so absolute determination of Cr(VI) was made after making solutions alkaline at 372 nm at the absorbance maximum of CrO_4^{2-} .

Fast reactions were studied in a Sutin stopped-flow apparatus previously described.⁷ Detection of a chromium(V) intermediate was made by employing a continuous flow of reacting mixtures through the cavity of an esr spectrometer as previously described.⁸

Ionic strength was controlled using NaClO_4 (or LiClO_4) and HClO_4 .

Results

The Rate Law. Figure 1 shows that all runs with excess hydrazine exhibit first-order kinetics in Cr(VI) over several half-lives, giving the pseudo-first-order rate law

$$\frac{-d[\text{Cr(VI)}]}{dt} = k_{\text{obsd}}[\text{Cr(VI)}] \quad (4)$$

Order in NH_3NH_2^+ . The slopes of the lines in Figure 1 are roughly proportional to $[\text{NH}_3\text{NH}_2^+]$. However, the values of k_{obsd} given in Table I show a small but distinct departure from first-order behavior at high $[\text{NH}_3\text{NH}_2^+]$ consistent with the equation

$$k_{\text{obsd}} = k_b[\text{NH}_3\text{NH}_2^+]/(1 + 3.2[\text{NH}_3\text{NH}_2^+]) \quad (5)$$

This result is consistent with the formation of a

(7) S. A. Frennesson, J. K. Beattie, and G. P. Haight, Jr., *J. Amer. Chem. Soc.*, **90**, 6018 (1968).

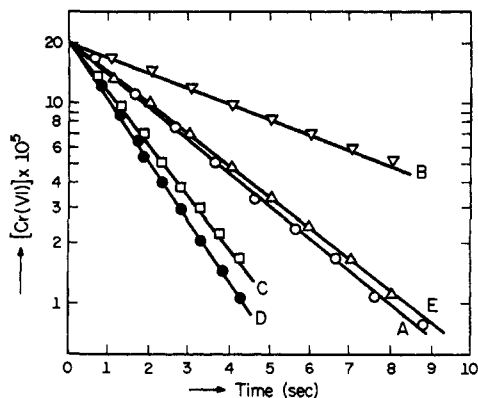


Figure 1. First-order dependence of Cr(VI) on time. All runs in 1.0 M HClO₄. [N₂H₅⁺] = (A) 0.03, (B) 0.01, (C) 0.04, (D) 0.05, (E) 0.02 M.

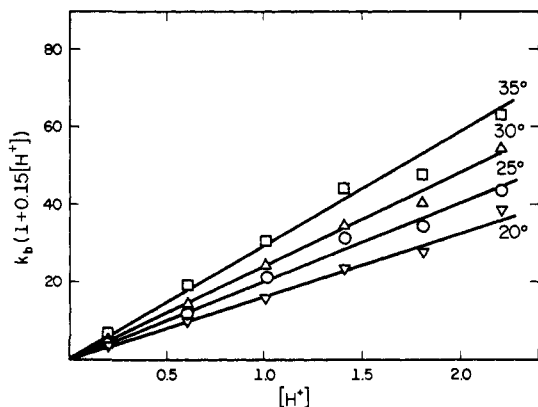


Figure 2. [H⁺] effect: $\mu = 2.2$, [N₂H₅⁺] = 2×10^{-3} M, [HCrO₄⁻]₀ = 2×10^{-4} M.

Table I. Variation of N₂H₅⁺ in 1 M HClO₄^a

$10^3[\text{N}_2\text{H}_5^+]$	$10k_{\text{obsd}}, \text{sec}^{-1}$	$10k_{\text{calcd}}, \text{sec}^{-1}$
0.500	0.96	0.93
0.750	1.38	1.38
1.00	1.87	1.84
2.00	3.51	3.37
3.00	4.95	5.22
4.00	6.73	6.79
5.00	8.57	8.28

^a $K_0 = 3.2$, $\mu = 1.0$ M, $k_1K_0 = 21.7 \text{ M}^{-1} \text{ sec}^{-1}$, [H⁺] = 1.0 M, [Cr(VI)]₀ = 2×10^{-4} M, $T = 25^\circ$.

chromate ester of hydrazinium ion (NH₃⁺NHCrO₃⁻) with $K_f = 3.2 \pm 0.3$.

Effect of Hydrogen Ion Concentration on k_b . Table II shows that k_b increases linearly with [H⁺] at low

Table II. Variation of [H⁺]^a

[H ⁺]	$10k_{\text{obsd}}, \text{sec}^{-1}$	$10k_{\text{calcd}}, \text{sec}^{-1}$	$k_b, \text{M}^{-1} \text{ sec}^{-1}$
0.2	0.693	0.739	3.47
0.6	2.31	2.10	11.55
1.0	3.46	3.32	17.30
1.0	3.20	3.32	16.00
1.0	3.50	3.32	17.50
1.4	4.95	4.43	24.75
1.8	5.06	5.44	25.30
2.2	6.02	6.37	30.10

^a $\mu = 2.2$ M, $K_0k_1 = 20.2$, [N₂H₅⁺] = 2×10^{-2} M, [HCrO₄⁻]₀ = 2×10^{-4} M. NaClO₄ was added to control μ .

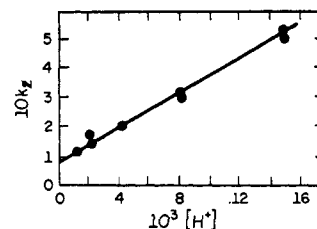
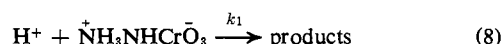
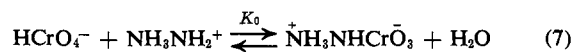
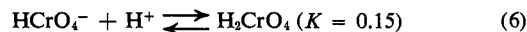


Figure 3. [H⁺] effect in H₃PO₄-H₂PO₄⁻ buffer: [H₃PO₄] + [H₂PO₄⁻] = 0.2 M, [N₂H₅⁺] = 5×10^{-3} M, [Cr(VI)]₀ = 2×10^{-4} M.

[H⁺] but starts to level off at high [H⁺]. The leveling off is consistent with the formation of H₂CrO₄ from HCrO₄⁻.

We postulate the mechanism



$$-\frac{d[\text{Cr(VI)}]}{dt} = k_1K_0[\text{HCrO}_4^-][\text{NH}_3\text{NH}_2^+][\text{H}^+]$$

$$[\text{Cr(VI)}] = [\text{HCrO}_4^-] + [\text{H}_2\text{CrO}_4] + [\overset{+}{\text{N}}\text{H}_3\text{NHCrO}_3^-]$$

$$[\text{Cr(VI)}] = [\text{HCrO}_4^-](1 + 0.15[\text{H}^+] + K_0[\text{N}_2\text{H}_5^+])$$

$$-\frac{d[\text{Cr(VI)}]}{dt} = \frac{k_1K_0[\text{Cr(VI)}][\text{N}_2\text{H}_5^+][\text{H}^+]}{1 + 0.15[\text{H}^+] + K_0[\text{N}_2\text{H}_5^+]} \quad (9)$$

Here

$$\frac{[\text{H}_2\text{CrO}_4]}{[\text{H}^+][\text{HCrO}_4^-]} = 0.15$$

$$\frac{[\overset{+}{\text{N}}\text{H}_3\text{NHCrO}_3^-]}{[\text{N}_2\text{H}_5^+][\text{HCrO}_4^-]} = K_0$$

Since $K_0[\text{N}_2\text{H}_5^+] \ll 1$ for data in Figure 2

$$k_b = \frac{k_1K_0[\text{H}^+]}{1 + 0.15[\text{H}^+]}$$

A plot of $k_b(1 + 0.15[\text{H}^+])$ vs. [H⁺] should yield a straight line with a slope of k_1K_0 if the above mechanism is correct. The linearity obtained from the plots of $k_b(1 + 0.15[\text{H}^+])$ vs. [H⁺] in Figure 2 supports the proposed mechanism.

General Acid Catalysis. Beck and Durham⁵ observed a second-order term in HCrO₄⁻ in unbuffered solutions at pH 3. If the decomposition of NH₃⁺NHCrO₃⁻ involves general acid catalysis, one should observe increased rates in the presence of other acids. Accordingly, a brief study was made in 0.2 M H₃PO₄-H₂PO₄⁻ buffer over the pH range 1.6-3.0. The results are plotted in Figure 3 from which one may deduce the rate law.

$$-\frac{d[\text{Cr(VI)}]}{dt} = [\text{N}_2\text{H}_5^+][\text{HCrO}_4^-]K_0(k'[\text{H}^+] + k'') \quad (10)$$

with $K_0k' = 27 \pm 3$ and $K_0k'' = 0.09 \pm 0.02$. If K_0k' corresponds to k_1K_0 in eq 8, its value should be $22/(1 + K_p(0.2))$ where K_p is the mean formation constant for chromatophosphate esters. Ester formation should reduce K_0k' to between half and one-third of K_0k_1 . In fact, K_0k' is larger than K_0k_1 by 25%. This indicates

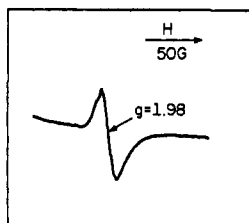


Figure 4. Epr signal due to Cr(V).

acid catalysis by H_3PO_4 and/or H_2PO_4^- . A complete rate law involving general acid catalysis in H_3PO_4 - H_2PO_4^- buffers would be

$$\frac{-d[\text{Cr(VI)}]}{dt} = \frac{K_0[\text{NH}_2\text{NH}_2][\text{Cr(VI)}](k_1[\text{H}^+] + k_2[\text{H}_3\text{PO}_4] + k_3[\text{H}_2\text{PO}_4^-] + k_4[\text{HCrO}_4^-])}{(1 + 0.15[\text{H}^+] + 3.2[\text{NH}_3\text{NH}_2] + 9.4[\text{H}_3\text{PO}_4] + 6[\text{H}_2\text{PO}_4^-])} \quad (11)$$

The values $9.4 = [\text{H}_2\text{PO}_4\text{CrO}_3]/([\text{H}_3\text{PO}_4][\text{HCrO}_4^-])$ and $6 = [\text{HPO}_4\text{CrO}_3^{2-}]/([\text{H}_2\text{PO}_4^-][\text{HCrO}_4^-])$ are obtained from the literature.^{7,8} Values of $k_2 \approx 9$ and $k_3 \approx 0.3$ have been estimated from the data used for Figure 3. This rate law cannot be considered proved. The complexity of the system makes a complete study rather unprofitable. However, the finding of acid catalysis by P(V) species is considered to be well established.

The term $k_4[\text{HCrO}_4^-]$ did not contribute significantly to any of our results.

Effect of Changing Ionic Strength. Table III shows

Table III. Variation of Ionic Strength^a

Variable μ	$k_{\text{obsd}}, \text{sec}^{-1}$	$k_{\text{calcd}}, \text{sec}^{-1}$
1.0	3.51	3.37
1.2 ^c	3.39	3.37
1.4 ^c	3.75	3.37
1.8 ^c	4.08	3.37
2.0 ^c	4.20	3.37
2.2 ^c	4.36	3.37
2.2 ^b	3.20	3.37
2.2 ^b	3.46	3.37
2.2 ^b	3.50	3.37

^a $[\text{N}_2\text{H}_5^+] = 2 \times 10^{-2} \text{ M}$, $[\text{HCrO}_4^-]_0 = 2 \times 10^{-4} \text{ M}$, $[\text{H}^+] = 1.0 \text{ M}$, $K_1k = 20.5$, $T = 25^\circ$. ^b NaClO_4 was added to adjust μ . ^c LiClO_4 was added to adjust μ .

a study made increasing ionic strength from 1.0 to 2.2, using LiClO_4 or NaClO_4 for controlling the ionic strength. Three experiments at $\mu = 1.8, 2.0$, and 2.2 gave rather high results for k_{obsd} . This may arise from the unusual behavior of LiClO_4 in HClO_4 solution. Simple Guggenheim approximation for 1:1 electrolytes indicates γ_{H^+} (activity coefficient) will decrease only slightly on adding NaClO_4 to 1 M HClO_4 but will increase about 40% on adding LiClO_4 to 1 M HClO_4 .⁹ For example

$$\begin{aligned} \gamma_{\text{H}^+}(1 \text{ M HClO}_4) &= 0.823 \\ \gamma_{\text{H}^+}(1 \text{ M HClO}_4 + 1 \text{ M NaClO}_4) &= 0.810 \\ \gamma_{\text{H}^+}(1 \text{ M HClO}_4 + 1 \text{ M LiClO}_4) &= 1.100 \end{aligned}$$

Due to the increase in γ_{H^+} on adding LiClO_4 , the high results for k_{obsd} are expected because of the hydrogen

(8) F. Halloway, *J. Amer. Chem. Soc.*, **74**, 224 (1952).

(9) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolyte Solutions," 3rd ed, Reinhold, New York, N. Y., 1958, p 605.

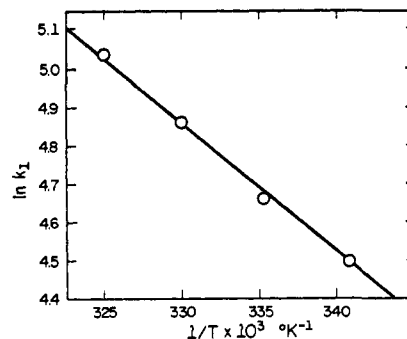


Figure 5. Arrhenius plot, $\ln k_1$ vs. $1/T$.

ion dependence of the reaction rate. Since NaClO_4 behaves similarly to HClO_4 in solution, NaClO_4 was subsequently employed for the study of the effect of changing ionic strength. From the results using NaClO_4 for adjusting the ionic strength, as shown in Table III, we conclude that there is no effect on the rate due to changing ionic strength. This indicates that the rate determining step may involve a neutral species or a neutral and a charged species, although the high ionic strengths used make such a conclusion very tentative.

The denominator in eq 8 approaches 1.0 at high pH and low $[\text{N}_2\text{H}_5^+]$. Values of all constants, estimated from the data and taken from the literature, are given in Table IV.

Table IV. Values of Constants at 25°

$$\begin{aligned} K_0 &= \frac{[\text{NH}_3\text{NHCrO}_3^-]}{[\text{N}_2\text{H}_5^+][\text{HCrO}_4^-]} = 3.2 \text{ M}^{-1} \text{ }^b \\ K_0 &= \frac{[\text{NH}_3\text{OCrO}_3^-]}{[\text{NH}_3\text{OH}^+][\text{HCrO}_4^-]} \leq 0.1 \text{ M}^{-1} \text{ }^{11} \\ K &= \frac{[\text{H}_2\text{CrO}_4]}{[\text{HCrO}_4^-][\text{H}^+]} = 0.15 \text{ M}^{-1}, \text{ }^b 0.2 \text{ M}^{-1}, \text{ }^c 0.15 \text{ M}^{-1} \text{ }^d \\ k_1 &= 6.8 \text{ M}^{-2} \text{ sec}^{-1} (\mu = 1)^b \\ &= 6.5 \text{ M}^{-2} \text{ sec}^{-1} (\mu = 2.2)^b \\ k_2^a &\sim 9 \text{ M}^{-2} \text{ sec}^{-1} \text{ }^b \\ k_3^a &\sim 0.3 \text{ M}^{-2} \text{ sec}^{-1} \text{ }^b \\ k_4 &= 60 \text{ M}^{-2} \text{ sec}^{-1} \text{ }^e, \end{aligned}$$

^a Allowance was made for removal of HCrO_4^- as esters of H_3PO_4 and H_2PO_4^- in estimating k_2 and k_3 .^{7,8} ^b This study. ^c J. Y. Tong, *Inorg. Chem.*, **3**, 1804 (1964). ^d G. P. Haight, Jr., D. C. Richardson, and N. C. Column, *ibid.*, **3**, 1777 (1964). ^e Our calculation.

Chromium(V). Chromium(V) was clearly detected, (Figure 4) although at very low steady-state concentrations, indicating that rate constants for Cr(V) disappearance are large compared to those for Cr(VI). Any mechanism should include Cr(V) as an intermediate.

Activation Parameters. Figure 5 shows a plot of $\log k_1$ vs. $1/T$, giving a straight line from which we calculate $\Delta H^\ddagger = 7.32 \text{ kcal/mol}$ and $\Delta S^\ddagger = -11.8 \text{ eu}$ at 25° . Interpretation is difficult in view of the complexity of the reaction.

Discussion

Intermediate Anhydride. $\text{NH}_2\text{NH}_2+\text{CrO}_3^-$ or $\text{NH}_3^+-\text{NHCrO}_3^-$ constitutes the first chromium(VI) anhydride

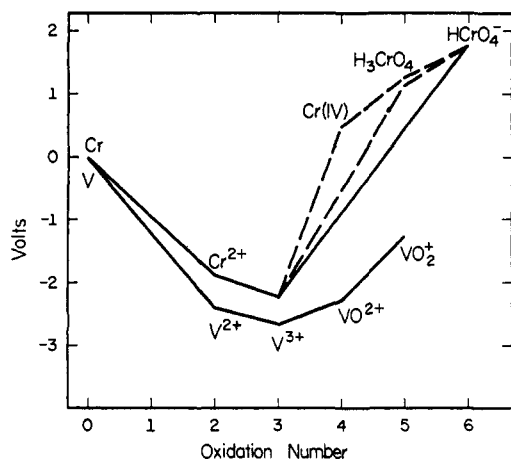
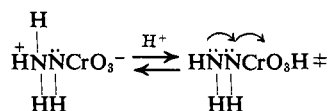
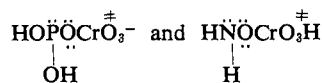


Figure 6. Frost diagram for Cr and V.

having an N–Cr bond for which a formation constant is available. We cannot, on the basis of the data alone, distinguish between $\text{NH}_3^+\text{NHCrO}_3^-$ (I) or $\text{NH}_2\text{NH}_2^+\text{CrO}_3^-$ (II) nor rule out the possibility of $\text{NH}_3^+\text{NH}_2^+\text{CrO}_3^-$ (III) forming and then being activated by solvent. By analogy with studies of Cr(VI) oxidations of H_3PO_3 and NH_3OH^+ , we propose that the ester is I or II and that the rate determining step involves acid or base induced dissociation of H^+ from N to give the activated state

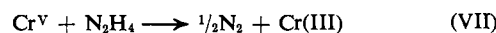
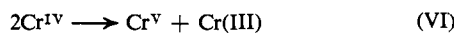
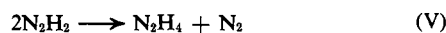
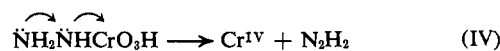
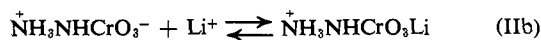


This is similar electronically to the activated states found for P(III)¹⁰ and N(I)¹¹



in which lone pairs of electrons are found on both the bridging atom and the atom to be oxidized. Anhydride III would block all electron pairs and is considered an unlikely precursor to electron transfer. Again, I and II cannot be distinguished.

Detailed Mechanism for Catalysis by a General Acid HB. Presumably the initial nitrogen oxidation product

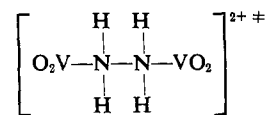


is N_2H_2 . No information on the fate of N_2H_2 is available from this study. Presumably N_2H_2 disproportionates to N_2H_4 and N_2 , making reaction VII a net reaction.

The disproportionation of Cr(IV) is considered proved for this system by the reanalysis of the Mn^{2+} effect⁶ given below. Evidently catalysis by the very small ion, Li^+ , similar to that of H^+ , occurs as well. The absence of any effect due to ionic strength variations suggests a neutral species in the production of the activated state. Whether the zwitterion $\text{NH}_3^+\text{NHCrO}_3^-$ qualifies as neutral is difficult to say. The neutral species could be H_2CrO_4 from the rate law giving



It is interesting to compare the oxidation of N_2H_5^+ by VO_2^+ ¹² with the results reported here. V(V) is only reduced to V(IV) and there is no evidence for intermediate V(III) or V(II) under the conditions of the kinetic study. The activated state requires two VO_2^+ . N_2 is the only oxidation product of N_2H_5^+ characteristic of a two-equivalent primary process. This indicates that N_2H_4 is not oxidized in steps but simultaneously by two VO_2^+ coordinated to each N in N_2H_4 .



The association constant for VO_2^+ and N_2H_4 was not determined. The second-order term in Cr(VI) observed by Beck and Durham could be attributed to a pathway leading to Cr(V) similar to that for VO_2^+ to VO^{2+} . However, we prefer to include HCrO_4^- in the collection of acid catalysts for the $\text{Cr}^{\text{VI}}-\text{N}_2\text{H}_5^+$ reaction. No second-order term in HCrO_4^- appeared in our data.

Since the $\text{VO}_2^+/\text{VO}^{2+}$ potential of 1.00 V is sufficient to oxidize hydrazine by a two-equivalent process and $\text{VO}_2^+/\text{V}^{3+} = 0.65$ V is not so, this would indicate that the Cr(VI)/Cr(IV) potential is greater than 0.65 V, while Cr(VI)/Cr(V) is less than 1.00 V and also less than Cr(VI)/Cr(IV). This conclusion is consistent with the suggestion of Roček¹³ that Cr(V) can disproportionate to Cr(VI) and Cr(IV). It also argues further against the capture of Cr(IV) by Cr(VI), which is potentially unfavorable if this analysis is correct. Limits for chromium potentials thus deduced are shown in the Frost diagram, Figure 6. Cr(VI) oxidizes $\text{Mn}(\text{C}_2\text{O}_4)_2^{2-}$ to $\text{Mn}(\text{C}_2\text{O}_4)_3^{3-}$,¹⁴ but may not oxidize N_2H_5^+ by a path involving $2\text{Cr}(\text{VI}) \rightarrow 2\text{Cr}(\text{V})$ corresponding to the V(V) reaction. Thus $0.5 \text{ V} < \text{Cr}(\text{VI})/\text{Cr}(\text{V}) < 0.65 \text{ V}$. Similarly, $\text{Cr}(\text{VI})/\text{Cr}(\text{IV}) > 0.65 \text{ V}$ and $\text{Cr}(\text{IV})/\text{Cr}(\text{III}) > 1.70$,¹³ leaving a large uncertainty as to Cr(IV) potentials. Even so, one can conclude that Cr(IV) and Cr(V) both disproportionate readily while none of the vanadium species from V(II) to V(IV) disproportionate. This raises a serious question concerning our previous interpretation of the effect of Mn^{2+} on the rate of the $\text{Cr}^{\text{VI}}-\text{N}_2\text{H}_5^+$ reaction.⁶

Effect of Manganese(II). It has been previously reported (see Figure 2, ref 6) that the rate of reduction of Cr(VI) by N_2H_5^+ is halved by Mn(II) in the presence of excess Cr(VI). Mn(II) has no effect on the rate in the presence of excess N_2H_5^+ . These two results led us to conclude that when Mn(II) traps Cr(IV) to give

(10) G. P. Haight, F. Smentowski, M. Rose, and C. Heller, *J. Amer. Chem. Soc.*, **90**, 6325 (1968).

(11) R. Scott, G. P. Haight, and J. Cooper to be submitted for publication.

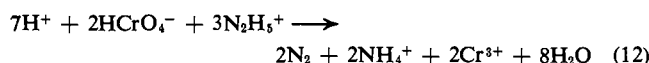
(12) G. Bengtsson, *Acta Chem. Scand.*, **25**, 2989 (1971).

(13) J. Roček and M. Rahman, *J. Amer. Chem. Soc.*, **93**, 5455, 5462 (1971).

(14) C. Huber and G. P. Haight, Jr., unpublished results.

Mn(III) and Cr(III) it interrupts a pathway involving $\text{Cr(VI)} + \text{Cr(IV)} \rightarrow 2\text{Cr(V)}$, thus halving the rate of disappearance of Cr(VI) when Cr(VI) is present in excess. In excess N_2H_5^+ , Mn(II) interrupted a path involving $2\text{Cr(IV)} \rightarrow \text{Cr(V)} + \text{Cr(III)}$ which would not affect the rate of Cr(VI) disappearance.

In the presence of Mn(II) the stoichiometry is altered to



Evidently Cr(IV) cannot oxidize N_2H_5^+ before Cr(IV) reacts with other species or disproportionates. A re-analysis of Figure 2, ref 6, leads us now to propose that Cr(IV) disproportionates in the absence of Mn^{2+} when either Cr(VI) or N_2H_5^+ is in excess. The halving of the rate in excess Cr(VI) can be shown to be an artifact of the change in stoichiometry shown by eq 12. Thus trapping of Cr(IV) by Cr(VI) in the absence of Mn(II) is no longer necessary to explain the results. In the presence of excess Cr(VI), it is $[\text{N}_2\text{H}_5^+]$ which changes significantly during a run. Figure 2, ref 6, shows that $t_{1/2}$ is halved when Mn^{2+} is present. Therefore, when no Mn^{2+} is present (using eq 3)

$$\frac{d[\text{N}_2\text{H}_5^+]}{dt} = k_1[\text{Cr(VI)}][\text{N}_2\text{H}_5^+] = \frac{3}{4} \frac{d[\text{Cr(VI)}]}{dt}$$

When Mn^{2+} is present (using eq 12)

$$\frac{d[\text{N}_2\text{H}_5^+]}{dt} = 2k_1[\text{Cr(VI)}][\text{N}_2\text{H}_5^+] = \frac{3}{2} \frac{d[\text{Cr(VI)}]}{dt}$$

$$\frac{d[\text{Cr(VI)}]}{dt} = \frac{4k_1}{3} [\text{Cr(VI)}][\text{N}_2\text{H}_5^+]$$

in both cases. Thus the "slower" rate in presence of Mn^{2+} is an artifact of the change in stoichiometry and faster consumption of N_2H_5^+ .

The oxidations of NH_3OH^+ and NH_3NH_2^+ are notable in that each requires two equivalent oxidation involving electron pair transfer to Cr(VI) involving a bridging atom. Neither appears to trap Cr(IV). While NH_3OH^+ forms a bridge to Cr(VI) exclusively through the oxygen atom,¹¹ it forms a weaker complex than NH_3NH_2^+ consistent with the generally greater donor ability of >N: over >O: . However, most possible N complexes with Cr(VI) cannot be studied due to saturation of N atoms with protons as in NH_4^+ and RNH_3^+ , whereas oxygen in potential ligands virtually always has a pair of electrons free to form dative bonds.

Acknowledgment. The authors wish to thank the National Institutes of Health and the National Science Foundation for support of this research.

Application of the Principle of Least Motion to Organic Reactions. III.^{1,2} Eliminations, Enolizations, and Homo-enolizations

Oswald S. Tee,*^{3a} Julianna A. Altmann,^{3b} and Keith Yates^{3b}

Contribution from the Departments of Chemistry, Sir George Williams University, Montreal 107, Quebec, Canada, and the University of Toronto, Toronto, Ontario, Canada M5S 1A1. Received August 18, 1973

Abstract: Using the PLM approach developed previously calculations of the stereochemical paths involving the least motion of atoms have been carried out for 15 further reactant-product systems. These include: 1,2-, 1,3-, and 1,4-eliminations, acetylene formation, allene formation, enolizations, homo-enolizations, a concerted 1,2-hydride shift, and epoxidation. Again there is remarkable agreement with available experimental observations. The only major discrepancy with experiment is in the 1,3-elimination of 2-norbornyl tosylates for which a truly concerted process may not apply.

The system chosen by Hine⁴ to illustrate the principle of least motion (PLM) as applied to atoms was a prototypical 1,2-elimination, namely, the transformation of ethyl chloride into ethylene. Calculation of the minimum sum of the squares of the atomic displacements⁴ (E_{min})¹ for the syn and anti modes of this elimination gave results favoring the latter.^{1,4} Subsequently, a more general method of calculation was

devised¹ and applied^{1,2} to a variety of reactions which could have, in principle, more than one stereochemical pathway. The results obtained agreed remarkably well with experimental observations and with more sophisticated theoretical models.^{1,2}

In the present paper we explore further the applicability of the method to the stereochemistry of various types of elimination, enolization, homo-enolization, a concerted 1,2-hydride shift, and epoxidation. The method of calculation has been described previously^{1,2} and does not need further elaboration. Molecular geometries were calculated either from published

(1) Part I: O. S. Tee, *J. Amer. Chem. Soc.*, **91**, 7144 (1969).

(2) Part II: O. S. Tee and K. Yates, *J. Amer. Chem. Soc.*, **94**, 3074 (1972).

(3) (a) Sir George Williams University; (b) University of Toronto.

(4) J. Hine, *J. Amer. Chem. Soc.*, **88**, 5525 (1966).