

would activation parameters for the other reactions with an apparent substitution-controlled mechanism.

It is possible that the rapid manganese(III) oxidation of thiocyanate is also substitution controlled, as found in the analogous reaction with cobalt(III).⁵ If the trends observed in complexation reactions of $\text{Fe}^{3+}_{\text{aq}}$ ^{14,15,24} and substitution-controlled redox reactions of $\text{Co}^{3+}_{\text{aq}}$ ^{5,19} are maintained in the manganese(III) series

(24) D. Seewald and N. Sutin, *Inorg. Chem.*, **2**, 643 (1963).

then the rate of the $\text{Mn}^{3+}_{\text{aq}}\text{-SCN}^-$ reaction might be expected to be somewhat higher than those for complexation by Br^- and Cl^- , the rate constants of which are presumably at least $10^6 \text{ M}^{-1} \text{ sec}^{-1}$ at 25° .⁸

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Kinetics and Mechanism of the Reaction between Vanadium(II) and Chromium(VI)

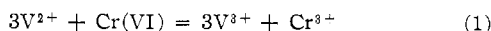
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The rate of oxidation of V(II) with Cr(VI) to form V(III) in perchloric acid solution was studied at 10° , primarily under second-order conditions and with V(II) in excess. The observed rate law for the reaction in 1.00 M NaClO_4 is $-d[\text{Cr(VI)}]/dt = (k_1 + k_2[\text{H}^+] + k_3[\text{V(II)}])[\text{HCrO}_4^-][\text{V(II)}]$ where $k_1 = (1.02 \pm 0.01) \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$, $k_2 = (7.9 \pm 0.26) \times 10^4 \text{ M}^{-2} \text{ sec}^{-1}$, and $k_3 = (1.27 \pm 0.09) \times 10^7 \text{ M}^{-2} \text{ sec}^{-1}$. The first step in the reaction results in the direct formation of V(III) by means of a one-electron redox process. Evidence is presented for the absence of the direct formation of vanadium(IV) under the conditions of these experiments. A mechanism is proposed based on the observed rate law.

Introduction

The net reaction between chromium(VI) and vanadium(II) in acid solution when V(II) is in excess can be represented by the equation



Since it is highly improbable that the mechanism involves a single three-electron transfer step, the reaction must occur in a sequence of steps involving either one-electron processes or a combination of one- and two-electron processes.

The vanadium(II)–chromium(VI) reaction appears to be particularly interesting because V(II) can undergo both one- and two-electron oxidation in aqueous acidic solutions. Previous studies¹ have indicated that whether one- or two-electron transfer occurs may be directly related to oxygen atom transfer. Since V(IV) is an oxo species, there exists the possibility of doing tracer studies² to show the origin of the oxygen in the complex when V(IV) is a product of the overall oxidation reaction.

Although Luther and Rutter³ refer to the oxidation of V(II) by Cr(VI) and have established that the reaction induces the oxidation of iodide ion, no kinetic studies on this very rapid reaction have been published. The objectives of this research were the elucidation of those features of the Cr(VI)–V(II) reaction mechanism that were discernible from the stoichiometry and the form of the rate law and a direct comparison with the corresponding Cr(VI)–V(III) and Cr(VI)–V(IV) reactions.⁴

Experimental Section

Reagents.—Sodium chromate solutions were prepared from Baker's Analyzed reagent grade $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ without further purification. The Cr(VI) concentration was determined with standard Fe(II).

Oxovanadium(IV) perchlorate solutions were prepared by electrolytic reduction of V_2O_5 suspensions at platinum wire electrodes.⁵ Certified reagent grade vanadium pentoxide was purchased from Fischer Scientific Co. Failure to give an iodine test⁶ when V(IV) was shaken with either KIO_3 or KI in CCl_4 was taken as evidence that the concentration of either V(III) or V(V), respectively, was less than 10^{-4} M .⁷ Oxovanadium(IV) solutions were standardized by titration with KMnO_4 . Vanadium(II) perchlorate solutions were prepared by reducing measured aliquots of standard V(IV) in HClO_4 on a Jones reductor. The reduced vanadium solution was delivered into a volumetric flask under a N_2 atmosphere. The N_2 was freed of O_2 by passing tank nitrogen through two columns of Cr(II) solution. Vanadium(II) solutions were prepared just prior to their use. Vanadium(III) perchlorate solutions were prepared by reacting equimolar amounts of V(II) and V(IV) in a volumetric flask. Syringes calibrated⁸ to deliver volumes reproducible to better than $\pm 0.5\%$ were used to make certain that equimolar amounts were used. These solutions were allowed to stand under an atmosphere of deoxygenated N_2 for at least 30 min to ensure complete reaction.⁹

The acid concentration of the vanadium solutions was determined from the acid concentration of the original V(IV) stock solution. An aliquot of V(IV) was placed on a column of the acid form of Dowex 50W-X12 cation-exchange resin and the eluent was titrated with standard base. The difference between the total hydrogen ion concentration and the equivalent concentration of the VO^{2+} species was taken to be the hydrogen ion concentration.

Chromium(III) solutions were prepared from hexaaquochromium(III) perchlorate which had been recrystallized three times from dilute HClO_4 solution. When the ratio of the absorbance at 230 nm to the absorbance at 260 nm reached a minimum

(1) (a) G. Gordon and H. Taube, *Inorg. Chem.*, **1**, 69 (1962); (b) R. C. Thompson and G. Gordon, *ibid.*, **5**, 562 (1966); (c) M. G. Ondrus and G. Gordon, *ibid.*, **10**, 474 (1971).

(2) A. H. Zeltman and L. O. Morgan, *ibid.*, **10**, 2739 (1971); K. L. Bridges, Ph.D. Thesis, University of Iowa, 1972.

(3) R. Luther and T. F. Rutter, *Z. Anorg. Chem.*, **54**, 1 (1907).

(4) K. M. Davies and J. H. Espenson, *J. Amer. Chem. Soc.*, **92**, 1884, 1889 (1970); J. H. Espenson, *Accounts Chem. Res.*, **3**, 347 (1970).

(5) S. C. Furman and C. S. Garner, *J. Amer. Chem. Soc.*, **72**, 1785 (1950).

(6) K. V. Krishnamurty and A. C. Wahi, *ibid.*, **80**, 5921 (1958).

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(9) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **68**, 228 (1964); *Inorg. Chem.*, **3**, 569 (1964).

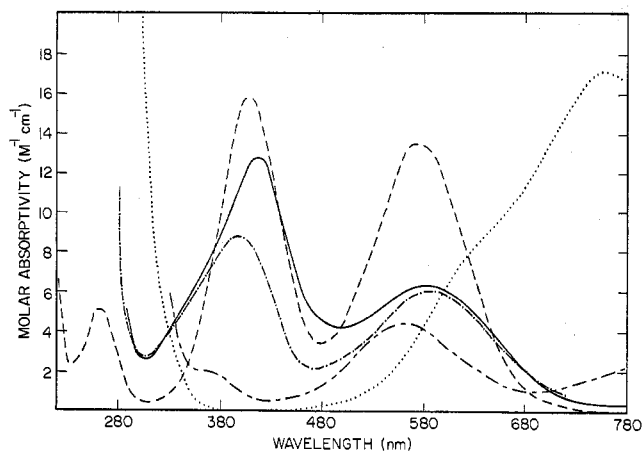


Figure 1.—Various absorption spectra in 0.1 *M* HClO₄ at room temperature. Spectra: V(II) (— — —); V(III) 0.0582 *M* (—) and 0.00522 *M* (— · — ·); V(IV) (· · · · ·); and Cr(III) (· · · · ·).

of 0.25, the solution was judged to be essentially free of polymeric Cr(III) species.¹⁰ The Cr(III) concentration was determined by oxidizing an aliquot with H₂O₂ in basic solution to form Cr(VI) followed by measuring the absorbance at 275 nm.¹¹

Sodium perchlorate, used to maintain constant ionic strength solutions, was prepared and standardized as reported previously.¹² All solutions were prepared from conductivity water obtained by passing distilled water through Barnstead organic and inorganic removal columns.

Stoichiometric and Spectral Studies.—The spectra of the reactant and the product species were determined as a function of both reagent concentration and hydrogen ion concentration. All spectra were recorded at room temperature and at 1.0 *M* ionic strength using a Cary 14 spectrophotometer.

The stoichiometry under conditions of excess V(II) was determined by titrating the excess V(II) with standard Fe(III) after completion of the V(II)-Cr(VI) reactions. The stoichiometry was verified spectrophotometrically. Sodium chromate was rapidly mixed with a perchloric acid solution of V(II) in a 2-cm cuvette and the absorbance was measured at both 760 and 580 nm. Comparison of the measured absorbance with the absorbance calculated from the known molar absorptivities of the various possible products was used to establish the reaction stoichiometry.

Kinetic Studies.—A Durrum-Gibson stopped-flow spectrophotometer with a Kel-F mixing chamber and a 2-cm optical path was used to monitor the V(II)-Cr(VI) reaction. Monochromatic light was obtained with a diffraction grating and a hydrogen lamp. The output voltage from a fast response S20 end-on photomultiplier tube used as a detector was recorded as a function of time on a Tektronix Model 564 storage oscilloscope.

Chromium(VI) and vanadium(II) solutions were transferred from the reservoir syringes to the drive syringes in the stopped-flow instrument and were allowed to come to thermal equilibrium for about 10 min. The temperature around the cuvette, valve block, and drive syringes was held constant to within $\pm 0.05^\circ$ by circulating water from a constant-temperature bath. Both reactant solutions contained the appropriate amounts of HClO₄ and NaClO₄ to maintain 1.0 *M* ionic strength. The progress of the reaction was followed at 350 nm where only Cr(VI) has an appreciable absorbance. The apparent second-order rate constants were calculated from the absorbance data by using a non-linear least-squares program that minimizes the sum of the squared deviations between calculated and observed data points.¹³

Results

Spectra.—The absorption spectra for Cr(VI) and V(III) are acid dependent. The spectrum of V(III) is also concentration dependent. Because of these dependencies and their possible effect on the interpretation of the kinetics of the V(II)-Cr(VI) reaction, all reactant and possible product spectra were evaluated. The spectra of all but Cr(VI) are shown in Figure 1.

The molar absorptivity at 350 nm as a function of hydrogen ion concentration was calculated for each substance and is shown in Table I for sodium chromate

TABLE I
MOLAR ABSORPTIVITIES OF 5.26×10^{-3} *M* V(III) AND 1.49×10^{-4} *M* Cr(VI) AT 350 nm IN HClO₄ SOLUTION AT ROOM TEMPERATURE

[H ⁺], <i>M</i>	Molar absorptivity, <i>M</i> ⁻¹ cm ⁻¹	
	V(III)	Cr(VI)
0.01	11.51	1600
0.05	6.31	1599
0.10	6.07	1568
0.50	5.45	1542
0.80	5.41	1498
1.00	5.14	1451

and vanadium(III) perchlorate. The other species each have constant molar absorptivities over the range of conditions used in this study and at 350 nm correspond to: V(II), 2.15 ± 0.03 ; V(IV), 0.84 ± 0.05 ; and Cr(III), 2.51 ± 0.1 *M*⁻¹ cm⁻¹. With the exception of the V(III) solutions, all of the solutions obeyed the Beer-Lambert law. The deviation from linearity for the V(III) solutions at 350 nm was less than 3% at constant hydrogen ion concentrations.

Stoichiometry.—A detailed investigation of the reaction stoichiometry when V(II) is in excess results in an average stoichiometric ratio of 3.07 ± 0.14 which suggests that the stoichiometry is indeed that shown by eq 1. However, in the event that either V(IV) or V(V) were to be produced as initial products of the reaction, they would react to form V(III) as a final product.^{9,14} Therefore, an experiment was designed to detect the initial vanadium product species.

The actual reactive chromium species is not known. The predominant species is HCrO₄⁻ under all conditions with H₂CrO₄ attaining significant concentrations only under conditions of high acid concentrations.¹⁵ All of the results are tabulated in terms of the total Cr(VI) concentration.

Three reaction stoichiometries are possible if only the initial products are considered. The three possibilities include the formation of V(III), V(IV), and V(V).

The direct formation of V(V) can be ruled out as an elementary step because of the unlikely probability of a three-electron transfer. Vanadium(V) could be formed as a result of a sequence of steps if V(III) and/or V(IV) reacted faster with Cr(VI) than does V(II) or if either vanadium species reacted rapidly with one of the potential chromium intermediates. The rates of the V(III)- and V(IV)-Cr(VI) reactions are re-

(10) C. Altman and E. L. King, *J. Amer. Chem. Soc.*, **83**, 2825 (1961).

(11) C. W. Haupt, *J. Res. Nat. Bur. Stand.*, **48**, 414 (1952).

(12) G. Gordon and P. H. Tewari, *J. Phys. Chem.*, **70**, 200 (1966).

(13) The original algorithm by R. H. Moore and R. K. Zeigler is described in publication LASL-2367 and addenda by the Los Alamos laboratories. The present modification of the original program is written in Fortran IV and has been adapted to the IBM 360 mod 65 high-speed computer. A complete listing of the program and the associated subroutines is available upon request.

(14) J. H. Espenson and L. A. Krug, *Inorg. Chem.*, **8**, 2633 (1969).

(15) (a) J. Y. Tong and E. L. King, *J. Amer. Chem. Soc.*, **82**, 3805 (1960); (b) W. Bailey, A. Carrington, C. K. Lott, and M. C. R. Symons, *J. Chem. Soc.*, 290 (1960); (c) G. P. Haight, D. C. Richardson, and N. H. Coburn, *Inorg. Chem.*, **3**, 1777 (1964); (d) D. G. Lee and R. Stewart, *J. Amer. Chem. Soc.*, **86**, 3051 (1964); (e) J. Y. Tong, *Inorg. Chem.*, **3**, 1804 (1964); (f) M. Orhanović and R. G. Wilkins, *J. Amer. Chem. Soc.*, **89**, 278 (1967).

reported^{3,4,16,17} to be slower than the reaction reported here.

The results of mixing experiments indicated that if V(IV) was produced directly in the reaction, the V(IV) would react slowly with the V(II) such that it could be detected. Based upon a detectable concentration limit of 1% of the total vanadium concentration, no V(IV) was observed when the absorbance of the initial product solution was measured during the kinetic runs at 760 nm where V(IV) has a maximum in its absorbance curve.

A further check on the stoichiometry and a determination of the reaction products were obtained from an alternate spectrophotometric analysis of the product solution at 580 nm. In this analysis it was assumed that the initial products were only V(III), V(IV), and Cr(III). Thus, the total absorbance of the solution could be expressed in terms of the initial Cr(VI) and V(II) concentrations and the appropriate molar absorptivities at 580 nm. A plot of absorbance for a series of experiments as a function of the initial V(II) concentration is linear. The molar absorptivity of V(II) calculated from the slope is $4.21 \pm 0.07 M^{-1} \text{ cm}^{-1}$ which is in reasonable agreement with the reported¹² value of $4.10 M^{-1} \text{ cm}^{-1}$. This treatment also results in the conclusion that less than 0.3% V(IV) was formed in the reaction which supports the conclusion that the initial reaction stoichiometry is 3:1 as is shown in eq 1.

Under conditions of excess Cr(VI), the net reaction corresponds to the formation of V(V). This conclusion is supported by the fact that both V(III) and V(IV) are oxidized to V(V) in the presence of excess Cr(VI).^{3,4,16,17}

Kinetics.—All of the kinetic data were obtained for reactions in the presence of excess V(II). In a few experiments, the V(II) concentration was greater than ten times the equivalent concentration of Cr(VI). However, the reaction is so rapid under these conditions that the first data points were obtainable only after 30–50% reaction depending upon the concentration of excess V(II). Pseudo-first-order plots of $\log [\text{Cr(VI)}]$ as a function of time were linear from the first observable data points to greater than 90% reaction. This linearity was taken as evidence that the reaction is first order with respect to Cr(VI).

Since the reaction is so fast, all but a few kinetic runs were made under second-order conditions where the excess of V(II) varied from 1.2 to 8.8 times the equivalent concentration of Cr(VI). These conditions permitted earlier portions of the reaction to be followed.

All of the data were treated according to the second-order rate law

$$\frac{1}{3} \frac{d[\text{V(II)}]}{dt} = \frac{d[\text{Cr(VI)}]}{dt} = k_o [\text{Cr(VI)}][\text{V(II)}] \quad (2)$$

Individual kinetic runs showed no apparent deviation from simple second-order behavior from approximately 10% to more than 90% reaction. The deviation of the fitted absorbances from the experimental values was typically less than 1.5%. The observed second-order

rate constants at 10° for various initial Cr(VI) and V(II) concentrations are shown in Table II.

TABLE II
OBSERVED SECOND-ORDER RATE CONSTANTS AT 10°, 0.1 M PERCHLORIC ACID AND 1.0 M IONIC STRENGTH

$10^4[\text{V(II)}]_0$ <i>M</i>	$10^4[\text{Cr(VI)}]_0$ <i>M</i>	$10^4 k_o^a$, $M^{-1} \text{ sec}^{-1}$	$10^4 k_{\text{calcd}}^b$ $M^{-1} \text{ sec}^{-1}$
3.80	8.12	1.146 ± 0.015	1.124
3.80	10.40	1.130 ± 0.023	1.124
3.99	2.01	1.128 ± 0.020^c	1.127
3.99	3.54	1.109 ± 0.006	1.127
3.99	5.20	1.177 ± 0.007	1.127
3.99	6.56	1.132 ± 0.043	1.127
6.55	6.09	1.097 ± 0.002	1.159
6.55	8.12	1.134 ± 0.034	1.159
6.55	10.40	1.173 ± 0.022	1.159
6.88	2.01	1.152 ± 0.021^c	1.163
6.88	3.54	1.167 ± 0.013	1.163
6.88	5.20	1.245 ± 0.009^c	1.163
6.88	6.56	1.187 ± 0.009^c	1.163
13.79	2.01	1.212 ± 0.017^c	1.249
13.79	3.54	1.256 ± 0.049	1.249
20.29	2.01	1.338 ± 0.024^c	1.329
20.29	3.54	1.332 ± 0.008^c	1.329
26.20	17.82	1.400 ± 0.086	1.403
27.76	4.06	1.418 ± 0.031^c	1.422
27.76	8.12	1.422 ± 0.020	1.422
27.76	10.40	1.411 ± 0.026	1.422

^a Average nonlinear least-squares calculated values. The error estimate represents the standard deviation from the mean for from two to four runs. ^b Calculated in terms of the proposed rate law. ^c Represents the standard deviation of the fit for a single run.

The overall trend toward an increase in k_o with increasing initial V(II) concentration suggests that the order of the reaction with respect to vanadium(II) is greater than unity. In general, this type of observation can be represented as

$$-\frac{d[\text{Cr(VI)}]}{dt} = k[\text{Cr(VI)}][\text{V(II)}]^n \quad (3)$$

where n is the order of reaction with respect to V(II). Under pseudo-first-order conditions

$$k_o' = k_a[\text{V(II)}]^n \quad (4)$$

where k_o' is the pseudo-first-order rate constant. The value of n , appropriate to eq 4, was determined from a least-squares analysis to be 1.153 ± 0.016 .

Since a fractional order with respect to vanadium(II) is improbable, it was found that the data are better represented by

$$k_o = k_1 + k_3[\text{V(II)}] \quad (5)$$

That this expression is a good approximation is shown in Figure 2 where k_o , the observed second-order rate constant, is plotted as a function of V(II) concentration.¹⁸ Each of the points in Figure 2 represents the

(18) In order to demonstrate that the contribution from the third-order term in the rate law, while affecting the value of the observed second-order rate constant, does not cause sufficient error in the fit to allow differentiation from experimental noise and error, five sets of absorbance vs. time data containing from 0.01 to 31.0% contribution from a third-order term were generated. The data were synthesized numerically by using a forward integration technique and by using equations based upon eq 5. The synthetic data were analyzed in the same way as the experimental data with the nonlinear least-squares program. The average absorbance errors ranged from 0.0005 to 0.0002, indicating that the fit of the synthetic data to a second-order equation is excellent. The experimental absorbances, on the other hand, show average absorbance errors of about 0.0015. A plot of the second-order rate constant obtained from the synthetic data as a function of the concentrations used reproduced the input rate constants to better than 1.4%. The results obtained from the synthetic data are used as additional support for the conclusion that eq 5 is a reasonable representation of the variation of k_o with V(II) concentration.

(16) J. H. Espenson, *J. Amer. Chem. Soc.*, **86**, 1883, 5101 (1964).

(17) D. R. Rosseinsky and M. J. Nicol, *J. Chem. Soc. A*, 1196 (1970).

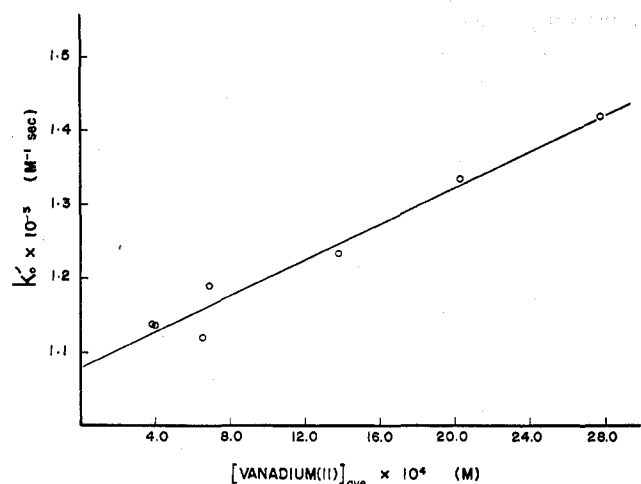


Figure 2.—Plot of the observed second-order rate constant as a function of the initial V(II) concentration. The initial Cr(VI) concentration ranged from 2.01×10^{-5} to 1.78×10^{-4} M at 0.10 M $[H^+]$ and 10° .

average of the second-order rate constants reported in Table II at constant vanadium(II) concentration.

The results of a series of experiments in which the hydrogen ion concentration was varied are summarized in Table III. It is apparent that the observed second-

TABLE III

VARIATION OF THE OBSERVED SECOND-ORDER RATE CONSTANT^a WITH HYDROGEN ION CONCENTRATION AT 10°

$10^4[V(II)]_0$, M	$[H^+]$, M	$10^{-5}k_0$, ^b $M^{-1} \text{sec}^{-1}$	$10^{-5}k_{\text{calcd}}$, ^c $M^{-1} \text{sec}^{-1}$
3.86	0.01	1.035 ± 0.044	1.078
3.86	0.05	1.126 ± 0.060	1.099
3.86	0.50	1.308 ± 0.018	1.311
3.86	0.80	1.436 ± 0.031	1.430
7.54	0.01	1.119 ± 0.072	1.125
7.54	0.05	1.199 ± 0.069	1.145
7.54	0.10	1.171 ± 0.020	1.171
7.54	0.50	1.334 ± 0.001	1.352
7.54	0.80	1.488 ± 0.004^d	1.469
13.14	0.01	1.209 ± 0.021	1.196
13.14	0.50	1.434 ± 0.028	1.469
15.09	0.01	1.210 ± 0.043	1.221
15.09	0.05	1.312 ± 0.053	1.241
15.09	0.10	1.239 ± 0.009	1.265
15.09	0.50	1.477 ± 0.001	1.423
15.09	0.80	1.542 ± 0.010	1.550

^a The $[Cr(VI)]_0$ was varied from 2.03×10^{-5} to 10.40×10^{-5} M while the ionic strength was maintained at 1.0 M with sodium perchlorate. ^b Each rate constant represents the average value obtained over a range of chromium(VI) concentrations for a particular hydrogen ion concentration. The error estimate represents the standard deviation from the mean for from two to five values of k_0 . ^c Calculated directly in terms of the proposed rate law. ^d Represents the standard deviation of the fit for a single run.

order rate constant and consequently the rate of the reaction is increased by an increase in the hydrogen ion concentration.

The apparent order with respect to $[H^+]$ can be obtained from an appropriate plot of $\log k_0$ as a function of $\log [H^+]$ after correction for the effect of vanadium(II) on the overall rate. The resulting value of n was 0.057 ± 0.020 .

The apparent hydrogen ion dependence can be imagined as due to either medium effects or a small contribution from a first-order hydrogen ion dependent path-

way. A fit of the data to a Harned-type equation¹⁹ of the form

$$k_0 = k_2[V(II)]^{0.153} \exp(\beta[H^+]) \quad (6)$$

where β is an adjustable parameter, results in an approximate value of 0.35 for β . This value is considerably larger than that expected from medium effects¹⁹ and suggests that the rate law should contain a first-order term in hydrogen ion concentration.

The reduction of Cr(VI) by iron(II)²⁰ and by oxovanadium(IV)¹⁶ shows inhibition by the oxidized product. Such inhibition was given as evidence that the rate-determining step corresponds to the transformation of Cr(V) to Cr(IV). The results shown in Table IV indicate that V(III) does not affect the rate of the

TABLE IV

EFFECT OF VANADIUM(III) ON THE OBSERVED SECOND-ORDER RATE CONSTANT IN THE CHROMIUM(VI)-VANADIUM(II) REACTION AT 10°

$10^4[V(III)]_0$, ^a M	$[H^+]$, M	$10^{-5}k_0$, ^b $M^{-1} \text{sec}^{-1}$
0.0	0.01	1.192 ± 0.009^c
1.49	0.01	1.204 ± 0.026
3.03	0.01	1.154 ± 0.009
7.72	0.01	1.186 ± 0.015^c
0.0	0.10	1.199 ± 0.024
1.49	0.10	1.226 ± 0.016^c
3.03	0.10	1.254 ± 0.008
7.72	0.10	1.267 ± 0.013^c
0.0	0.80	1.488 ± 0.011
1.49	0.80	1.502 ± 0.017^c
3.03	0.80	1.493 ± 0.013
7.72	0.80	1.506 ± 0.014

^a The initial concentrations of Cr(VI) and V(II) were 7.46×10^{-5} and 7.54×10^{-4} M, respectively. ^b The average nonlinear least-squares calculated values. The error estimate represents the standard deviation from the mean for from two to three runs. ^c Represents the standard deviation of the fit for a single run.

Cr(VI)-V(II) reaction.

Vanadium(II) reacts slowly with ClO_4^- to produce chloride ion.²¹ Since the Cr(VI) reacts with chloride ion,^{15c,d} the presence of Cl^- could influence the reaction between Cr(VI) and V(II). The results shown in Table V indicate that chloride ion does not effect the rate.

TABLE V

EFFECT OF CHLORIDE ION ON THE CHROMIUM(VI)-VANADIUM(II) REACTION AT 10°

$[HCl]_0$, M	$10^{-5}k_0$, ^b $M^{-1} \text{sec}^{-1}$
0.01	1.159 ± 0.015
0.05	1.253 ± 0.009
0.10	1.236 ± 0.004

^a The initial concentrations of chromium(VI) and vanadium(II) were 7.46×10^{-5} and 7.54×10^{-4} M, respectively. ^b Average nonlinear least-squares calculated values. The error estimates represent the standard deviation for from two to three runs.

The Rate Law.—The results of experiments in which the concentrations of Cr(VI), V(II), and H^+ were varied require a rate law containing more than one term. Ideally, the final form of the rate law should be expressed in terms of the predominant species, $HCrO_4^-$

(19) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **67**, 1425 (1963); *Inorg. Chem.*, **4**, 1166 (1965).

(20) J. H. Espenson and E. L. King, *J. Amer. Chem. Soc.*, **85**, 3328 (1963); J. H. Espenson, *ibid.*, **92**, 1880 (1970).

(21) W. R. King, Jr. and C. S. Garner, *J. Phys. Chem.*, **58**, 29 (1954).

and V(II), and the analytical Cr(VI) concentration should be replaced by HCrO_4^- . This calculation is carried out in terms of the equilibrium^{15e}



and the approximation that

$$[\text{Cr(VI)}]_{\text{total}} = [\text{H}_2\text{CrO}_4] + [\text{HCrO}_4^-]$$

Thus, the observed rate constants must be multiplied by $[K + [\text{H}^+]]/K$ in order to obtain a rate law in terms of the species²² HCrO_4^- .

A large number of rate laws were tried by using a generalized subroutine of the nonlinear least-squares fitting program.^{13,23} The best fit was determined by comparing the average deviation between fitted and calculated rate constants. The rate law that best fits the experimental data is

$$-\frac{d[\text{Cr(VI)}]}{dt} = (k_1 + k_2[\text{H}^+] + k_3[\text{V(II)}][\text{HCrO}_4^-][\text{V(II)}]) \quad (8)$$

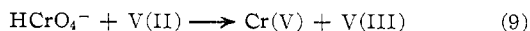
The values calculated for k_1 , k_2 , and k_3 are $(1.02 \pm 0.01) \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$, $(7.9 \pm 0.26) \times 10^4 \text{ M}^{-2} \text{ sec}^{-1}$, and $(1.27 \pm 0.09) \times 10^7 \text{ M}^{-2} \text{ sec}^{-1}$, respectively. The experimental data were reproduced by this rate law with an average per cent deviation of 3.5%. A comparison of the results of the rate constants calculated by means of eq 8 and the experimental values is given in Tables II and III. In this context it should be noted that the rate laws which contained denominator terms such as $(1 + k'[\text{V(II)}])$ and $(1 + k''[\text{H}^+])$ and alternate parallel pathways such as $(k'''[\text{V(II)}][\text{H}^+])$ give considerably poorer fits and average per cent deviations greater than 6.3%. Clearly, the best fit of the data is given by eq 8.

Temperature Dependence.—Only a cursory investigation of the dependence of the reaction rate on temperature was attempted. The conditions of the experiment were: $4.02 \times 10^{-5} \text{ M Cr(VI)}$, $6.36 \times 10^{-4} \text{ M V(II)}$, and 1.0 M H^+ . At 10, 20, and 29.9° the observed second-order rate constants were $(1.458 \pm 0.022) \times 10^5$, $(1.715 \pm 0.017) \times 10^5$, and $(1.951 \pm 0.016) \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$, respectively. In view of the general form of the rate law shown in eq 8 and the very small variation in rate with temperature, the activation parameters were not independently evaluated for each of these terms.

Discussion

The mechanistic implications of each of the three parallel reaction pathways suggested by eq 8 will be considered separately.

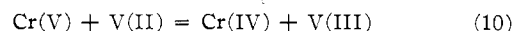
The pathway associated with k_1 is the major one in that it accounts for 95% of the reaction at the lowest acid and lowest V(II) concentrations and accounts for 66% of the reaction at the highest acid and highest V(II) concentrations used. A mechanism consistent with this pathway is



(22) The value of K used in the conversion of $[\text{Cr(VI)}]_{\text{total}}$ to HCrO_4^- was 4.16 ± 0.05 reported by Tong.^{15e} Although his value is reported at 25°, only small temperature variations might be expected¹⁵ and these small changes in K would result in only minor changes in the reported rate constants. Thus, we have used his value directly.

(23) A detailed listing of a variety of different rate laws is given elsewhere: K. Bridges, Ph.D. Thesis, The University of Iowa, 1972, pp 92–93.

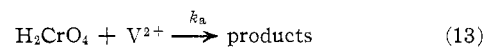
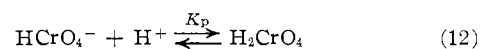
Although there is no direct evidence for the fate of the reduced chromium species produced in the rate-determining step, it is assumed that they are reduced *via* fast one-equivalent steps to Cr(III) as shown below.



Steps analogous to eq 10 and 11 have also been proposed^{16,20,24} to account for the stoichiometry when Cr(VI) is reduced by $\text{V}(\text{H}_2\text{O})_6^{3+}$, $\text{Fe}(\text{phen})_3^{2+}$, $\text{Fe}(\text{bipy})_3^{2+}$, $\text{Fe}(\text{bipy})_2(\text{CN})_2$, $\text{Fe}(\text{CN})_6^{4-}$, $\text{Ta}_6\text{Cl}_{12}^{2+}$, and $\text{Ta}_6\text{Br}_{12}^{2+}$.

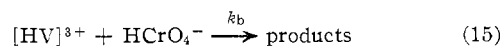
The nature of the proposed Cr(V) intermediate is unknown. In other Cr(VI) reduction reactions, evidence from a study of the hydrogen ion dependence suggests that, in the pH range of 0–3, the Cr(V) intermediate is H_3CrO_4 .²⁵ In the present study, the hydrogen ion dependent pathway accounts for no more than 25% at its maximum contribution. Under these circumstances, the hydrogen ion dependence provides no information about a possible H_3CrO_4 intermediate. The increase in rate with increasing H^+ concentration may be due simply to an increased concentration of protonated Cr(VI) species (*i.e.*, H_2CrO_4). Since the Cr(VI) oxoanion is converted ultimately to a hydrated cation, the net reactions of Cr(VI) consume hydrogen ions and the presence of protonated species should enhance this transformation. Edwards²⁶ has summarized observations on a number of oxoanion reactions and notes that the rates of such reactions are usually accelerated by an increase in the hydrogen ion concentration.

Equations 12 and 13 are consistent with the second



term in eq 8 where k_2 is identified as $K_p k_a$. The value of k_a is calculated to be 3.3×10^5 if K_p is assumed to correspond²² to the protonation constant for HCrO_4^- which has a reported^{15e} value of 0.24.

This mechanism is not unique, however, because the rate law gives only the composition of the activated complex and not the species from which it is generated.²⁷ The k_2 term in the rate law is therefore subject to a classical ambiguity²⁸ in that the mechanism could also be represented as



where k_2 would be identified as $K_v k_b$. If k_b is assumed to be 1×10^9 , which is at the limit of a diffusion control process, K_v is calculated to be 8×10^{-4} . Since transition metal-aquo complexes usually behave as acids in solution,²⁹ K_v is probably less than 10^{-4} . This would necessitate that k_b be greater than the diffusion-con-

(24) J. P. Birk, *J. Amer. Chem. Soc.*, **91**, 3189 (1969); J. H. Espenson and R. J. Kinney, *Inorg. Chem.*, **10**, 378 (1971).

(25) J. K. Beattie and G. P. Haight, Jr., private communication, 1971.

(26) J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin, New York, N. Y., 1965.

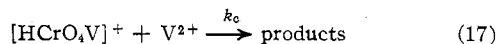
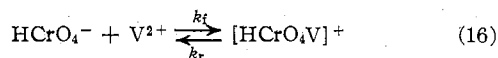
(27) H. Taube, *J. Chem. Educ.*, **36**, 451 (1959).

(28) E. L. King, "How Chemical Reactions Occur," W. A. Benjamin, New York, N. Y., 1963, p 78.

(29) M. M. Jones, "Elementary Coordination Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1964, Chapter 6.

trolled limit. Thus the mechanism suggested by eq 14 and 15 can probably be eliminated.

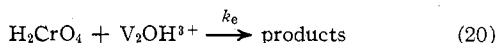
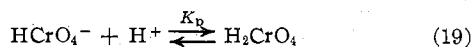
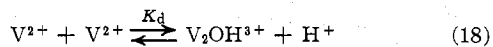
A mechanism consistent with the third term in eq 8 is



By assuming a steady-state concentration for the $[\text{HCrO}_4\text{V}]^+$ intermediate and that $k_e[\text{V(II)}] \ll k_r$, it can be seen that k_3 is identified as $k_e k_f / k_r$.

The ratio k_f/k_r represents the formation constant for the $[\text{HCrO}_4\text{V}]^+$ complex. Chromium(VI) complexes with other transition metal ions have been reported,^{20,24,30-33} although they are quite unstable in acidic solution. Espenson and Helzer³³ report a formation constant of 0.43 for an Fe(III)-Cr(VI) complex in which an additional proton is lost. If the value of k_e is $\leq 1.2 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$, the complex between V(II) and HCrO_4^- must have a stability constant ≥ 0.01 . Under these conditions the mechanism shown in eq 16 and 17 satisfies eq 8. As is usual, however, the rate law does not lead to a single unique mechanism.

The k_3 term in the rate law is also subject to an ambiguity in that an alternate mechanism could also be written



where k_3 would be identified as $K_d K_p k_e$. Support for this mechanism comes from the fact that a vanadium(II) dimer³⁴ has been postulated to exist in perchloric acid solutions as concentrated as 0.1 M. However,

(30) J. C. Sullivan and J. E. French, *Inorg. Chem.*, **3**, 832 (1964).

(31) E. L. King and J. A. Neptune, *J. Amer. Chem. Soc.*, **77**, 3186 (1955).

(32) J. Y. Tong and E. L. King, *ibid.*, **76**, 2132 (1954).

(33) J. H. Espenson and S. R. Helzer, *Inorg. Chem.*, **8**, 1051 (1969).

(34) W. J. Biermann and W. K. Wong, *Can. J. Chem.*, **41**, 2510 (1963).

a comparison can be made with the dimerization constant³⁵ for vanadium(III) which is given by the equation

$$[(\text{VOH})_2^{4+}][\text{H}^+]^2/[\text{V}^{3+}]^2 = 1.26 \times 10^{-4}$$

It should be expected that K_d would be less than 1.26×10^{-4} because of the lower charge on vanadium(II) and because of stabilization of the dimer due to the extra hydrogen ion. Since K_p is reported to have a value of 0.24, the calculated value of k_e would have to be greater than $4 \times 10^{11} \text{ M}^{-1} \text{ sec}^{-1}$. On this basis, the mechanism represented by eq 18-20 need not be considered.

Although eq 16 and 17 might represent an inner-sphere process, this pathway corresponds to a minor contribution to the overall reaction and the bulk of the reaction is most probably outer-sphere. Davies and Espenson⁴ have argued in terms of an outer-sphere mechanism for the vanadium(III) reduction of HCrO_4^- because the reaction proceeds somewhat faster than loss of water from the primary coordination sphere of $\text{V}(\text{H}_2\text{O})_6^{3+}$. A similar argument can be applied in this study since the rate of the reaction of vanadium(II) with HCrO_4^- is approximately three orders of magnitude greater than the rate of water exchange on vanadium(II).³⁶ This argument does, however, neglect the possibility of substitution on HCrO_4^- .

Recent studies by Lin and Beattie³⁷ have indicated that substitution on HCrO_4^- is hydrogen ion catalyzed and proceeds at a rate sufficiently rapid such as to allow an inner-sphere mechanism under the conditions employed for all of the experiments involving one-equivalent reducing agents.²⁵

Acknowledgments.—The authors wish to acknowledge the Atomic Energy Commission and the University of Iowa for financial support of this research.

(35) L. Pajdowski, *J. Inorg. Nucl. Chem.*, **28**, 433 (1966).

(36) M. V. Olson, Y. Kanazawa, and H. Taube, *J. Chem. Phys.*, **51**, 289 (1969).

(37) C. T. Lin and J. K. Beattie, *J. Amer. Chem. Soc.*, **94**, 3011 (1972).

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Lead Orthophosphates. I. Solubility and Hydrolysis of Secondary Lead Orthophosphate

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The solubility of secondary lead orthophosphate $[\text{PbHPO}_4]_{(s)}$ has been measured in dilute phosphoric acid solutions. Interpretation of the data in terms of the formation of the soluble species $\text{PbH}_2\text{PO}_4^+$ and PbHPO_4^0 resulted in ΔG_f° for $\text{PbHPO}_4]_{(s)}$ of $-281.8 \text{ kcal mol}^{-1}$. The association constants obtained were $10^{3.1 \pm 0.5}$ and $10^{1.5 \pm 0.5}$, respectively for PbHPO_4^0 and $\text{PbH}_2\text{PO}_4^+$. From an investigation of the hydrolysis of secondary and tertiary lead orthophosphates in the pH range 3-10, the ΔG_f° values for the solid phases $\text{Pb}_3(\text{PO}_4)_2$, $\text{Pb}_3(\text{PO}_4)_2\text{OH}$, and $\text{Pb}_4\text{O}(\text{PO}_4)_2$ were calculated to be -565.0 , -902.0 , and $-617.3 \text{ kcal mol}^{-1}$, respectively. The stability of these phosphates in the system $\text{PbO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ is discussed.

Introduction

The solubility and stability of lead orthophosphates are of considerable importance in environmental geochemistry, agriculture, and in the mineralization of biological hard tissues. Thus, as combustion products

of leaded gasoline¹ and constituents of phosphate fertilizers,² lead phosphates play an important role in the dispersion and fixation of lead and phosphorus

(1) S. P. Mattarella and R. L. O'Neil, *J. Gen. Motors Eng.*, **9**, 16 (1962).

(2) M. K. John, *Environ. Sci. Technol.*, **5**, 1199 (1971).