N_2. UCl_4 and $AlCl_3$ were weighed out on a microbalance and transferred to an optical cell in a helium drybox whose water content was <3 ppm.

In order to permit spectral measurements to be made over as large a temperature and pressure interval as possible, heavy-walled cylindrical cells (wall thickness 2–3 mm) and 10- or 20-cm path lengths were used, with volumes ranging between 30 and 75 cm^3. The cells were fabricated from quartz tubes by fusing 3-mm thick quartz windows on the ends making sure that the entire window thickness was employed in making the seal. Several cells ruptured before this procedure in making the seals was adopted. Cell volumes were determined to within 0.2% by pycnometric weighing and the path length was measured with a caliper to ±0.03 cm. The cells, after addition of measured amounts of UCl_4, Al_2Cl_6, and Cl_2 gas, were sealed off under vacuum at the side arm.

The cells were placed in a cylindrical furnace of a type previously described.[29] Spectra were generally measured in the temperature range 400–700°K and total pressures of 1–5 atm.

In order to prevent condensation of $AlCl_3$ or UCl_4 on the windows and to minimize heat losses, small auxiliary Pt heaters were placed in both end portions of the furnace and the ends of the furnace were fitted with outer quartz windows. The voltage of the Pt heaters was kept constant over a run. With this arrangement, the temperature at the cell windows was about 40° higher than the middle of the cell at 500°K and only a few degrees higher at 800°K. Calibration curves for the temperature distribution along the cells were obtained as a function of temperature with a dummy cell in the furnace. In order to vary the position of the thermocouple within the cell, a small hole was drilled through the furnace and cell windows. Heat losses were found to be somewhat less during an actual run so that the average temperatures T, determined in the calibration runs, are estimated to be within 5° of the actual temperature.

During the runs, the temperature was measured with the thermocouple situated near the middle of the furnace adjacent to the cells. It was found that this temperature was within ±0.5° of the minimum temperature $T_{\min}$, measured inside the cell during a calibration run.

A Cary 14 H spectrophotometer with the sequence: light source → chopper → sample → monochromator → detector → ac amplifier → recorder was used for the spectral measurements. The usefulness of this arrangement for high-temperature measurements has been described elsewhere.[30]

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Kinetics and Mechanism of the Oxidation of Vanadium(II) by Vanadium(V) in Aqueous Perchlorate Solutions[1a]

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The reaction of V^{2+} and VO_2^+ in perchloric acid solution occurs mainly to produce V^{3+} and VO^{2+}, although both the rate and stoichiometry are affected to some extent by a side reaction between V^{3+} and VO_2^+. After correction for that effect, the main reaction was found to follow the rate expression $-d[VO_2^+]/dt = \{a + b[H^+]\}[V^{2+}][VO_2^+]$. At $\mu = 1.00\ M$ and 25.0°, $10^{-3}a = 2.58 \pm 0.10\ M^{-1}\ sec^{-1}$ and $10^{-3}b = 2.16 \pm 0.15\ M^{-2}\ sec^{-1}$. The rate constants were evaluated at other temperatures giving the following activation parameters: $\Delta H_a^{\ddagger} = 1.9 \pm 0.4$ kcal mol^{-1}, $\Delta S_a^{\ddagger} = -36.8 \pm 1.4$ eu, $\Delta H_b^{\ddagger} = 1.8 \pm 0.9$ kcal mol^{-1}, and $\Delta S_b^{\ddagger} = -37.3 \pm 3.1$ eu. The reaction was also studied in the presence of thiocyanate ion; very rapid oxidation of $VNCS^+$ to $VNCS^{2+}$ by VO_2^+ was noted with a rate constant of $(4 \pm 1) \times 10^5\ M^{-1}\ sec^{-1}$. Possible reaction mechanisms are discussed.

Introduction

Vanadium is known in four oxidation states in acidic aqueous solution, representing oxidation numbers +2 through +5. Each of the ions $V(H_2O)_6^{2+}$, $V(H_2O)_6^{3+}$, VO^{2+}, and VO_2^+ is stable with respect to disproportionation since the ions become uniformly better oxidizing agents as the oxidation state increases.[2] The lower two ions must be protected from oxygen oxidation,[3,4] and both reduce perchlorate ion at appreciable rates,[5] rendering them metastable with respect to oxidation by the perchlorate salts that usually constitute the preferred reaction media.

The rates of the electron-exchange reactions of adjacent ions have been measured: V^{2+} and V^{3+},[6] V^{3+} and VO^{2+},[7] and VO^{2+} and VO_2^+.[8] The net reactions between oxidation states differing by two electrons have also been studied: the conversion of V^{2+} and VO^{2+} to V^{3+}, which occurs in part by way of the unstable intermediate VOV^{4+},[9] and the reaction of V^{3+} and VO_2^+ to form VO^{2+}.[10]

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[1] (a) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2599. (b) Fellow of the Alfred P. Sloan Foundation, 1968–1970.

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

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Rate measurements on the last of the possible oxidation–reduction reactions among the vanadium ions have been made for the purpose of characterizing the kinetics and mechanism of the reaction of V^{2+} and VO_2^+ shown in the reaction

$$V^{2+} + VO_2^+ + 2H^+ = V^{3+} + VO^{2+} + H_2O \qquad (I)$$

The kinetics study undertaken was complicated by the occurrence of two side reactions between the products of reaction I and the reactants. These are the previously studied net reactions[9,10] between different oxidation states cited above, represented by the reactions

$$V^{2+} + VO^{2+} + 2H^+ = 2V^{3+} + H_2O \qquad (II)$$

$$V^{3+} + VO_2^+ = 2VO^{2+} \qquad (III)$$

Based on the published rate data,[9] reaction II occurs sufficiently slowly that it will not interfere with the study of reaction I; this was confirmed in the present work by the lack of effect addition of considerable concentrations of VO^{2+} had on the present studies of kinetics and stoichiometry between V^{2+} and VO_2^+.

On the other hand, the reaction of V^{3+} and VO_2^+ according to reaction III was of at least minor concern in all experiments and quite significant in some. The variability of stoichiometry and rate, dependent upon the relative rates of reactions I and III and upon concentration conditions, complicated the evaluation of the rate parameters for I. The complications in the kinetic data were shown to be ascribable to reaction III rather than to other processes. A digital computer was used to provide numerical solutions to the differential rate equations permitting resolution of the kinetics of reaction I.

Experimental Section

Materials.—Vanadium pentoxide was made by hydrolysis of fractionally distilled $VOCl_3$, igniting the ammonium vanadate to the oxide.[11] Vanadium(V) solutions were made by dissolving the oxide in excess perchloric acid. The resulting solution was filtered through a fine sintered-glass frit and proved to be *ca.* 0.01 *F* vanadium(V)–0.1 *F* perchloric acid.

Oxovanadium(IV) perchlorate solutions were made by electrolysis of a slurry of vanadium pentoxide in perchloric acid; electrolysis was performed at an applied potential of *ca.* 9 V, using platinum electrodes.[12]

Vanadium(II) solutions were prepared immediately before use by reduction of acidified vanadyl ion solutions with amalgamated zinc. The solutions were continuously swept with a stream of nitrogen from which any traces of oxygen had been removed by passage through scrubbing towers containing chromium(II) solutions over amalgamated zinc.

Vanadium(III) solutions were prepared according to reaction II, using a slight excess of vanadium(II). The solutions were allowed to stand for a time adequate for reaction II to proceed to completion.[9] The vanadium(III) solutions were prepared and stored under purified nitrogen.

Lithium perchlorate was synthesized from the carbonate and perchloric acid and was recrystallized twice. Other materials were reagent grade chemicals used without further purification. Conductivity water was used in all solutions.

Analyses.—Vanadium(V) solutions were analyzed by reaction with a known excess of iron(II) sulfate solution and back-titration with cerium(IV) to a ferroin end point in *ca.* 1 *F* sulfuric acid. Vanadium(IV) stock solutions were titrated with cerium(IV) in an acetic acid medium also using ferroin as indicator.[13]

The dilute vanadium(II) for each rate run was made up from the stock solution as needed at the time; samples for analysis of V^{2+} were taken during the course of the experiment. The V^{2+} analytical samples were withdrawn from the 200-ml volumetric flask used as the solution reservoir in the stopped-flow apparatus by means of a syringe and a 30-cm Teflon needle and were delivered under the surface of a solution of $[Co(NH_3)_5Br]Br_2$ in dilute perchloric acid, which was being purged with nitrogen. After an additional 20-min period under nitrogen, ammonium thiocyanate (0.1 g/ml) was added and the solution was diluted with acetone and water to a final 50 vol % acetone composition. The absorbance of the cobalt(II) was measured at 623 nm and the vanadium(II) concentrations were calculated from this analysis based on the 1:1 stoichiometry of the V^{2+}–$Co(NH_3)_5Br^{2+}$ reaction and a molar absorptivity of the cobalt(II) thiocyanate species of 1842 M^{-1} cm^{-1}.

In runs where both vanadium(II) and -(III) were present in the starting solutions, the vanadium(II) content was analyzed as above. The concentration of vanadium(III) was computed from the difference of total vanadium and vanadium(II), the former determined spectrophotometrically after oxidation to vanadium(V) and addition of hydrogen peroxide.[14,15]

Rate Procedures and Kinetic Data.—The stopped-flow apparatus with a 0.3-cm optical path was quite similar to that of Dulz and Sutin[16] and has been described previously.[17] The light source for uv measurements was a deuterium lamp (Beckman 96280); the conventional lamp power supply was replaced by one with a dc filament supply (Gilford Model 205) to eliminate excessive ac noise. A few experiments were also performed using a Durrum stopped-flow spectrophotometer equipped with a Kel-F mixing chamber and a 2-cm optical path. The agreement in rate constants between the two instruments was within the scatter of repeat determinations. Generally, three or four rate determinations were made with every set of solutions, with the individual runs showing typically $\leqslant 4\%$ average deviation from the mean.

Ionic strength in all of the rate studies was maintained at 1.00–1.03 *M*, and it consisted largely of lithium perchlorate and perchloric acid. In all of the experiments vanadium(II) was in excess, and the increase in uv transmittance due primarily to vanadium(V) was followed with time. In a typical run with $[VO_2^+]_0 = 1.0 \times 10^{-4}$ *M*, the measurements were made at λ 250 nm ($\epsilon(VO^{2+})$ 36, $\epsilon(VO_2^+)$ 960 M^{-1} cm^{-1}). The kinetic data were evaluated in the usual manner,[12,18] with first-order or second-order rate plots being made depending on the ratio of starting concentrations.

Results

Rate Studies at High $[H^+]$.—The kinetics of reaction I in solutions with 1.00 *M* H^+ will be considered first. The rate studies at high $[H^+]$ are least subject to interference from reaction III, since the main rate term of the latter reaction[10] is proportional to $[H^+]^{-1}$. Kinetic data were obtained with $[V^{2+}]$ and $[H^+]$ both considerably greater than $[VO_2^+]$. At 1.00 *M* H^+, the rate experiments covered the following ranges of initial concentration: $3.3 \times 10^{-4} \leq [V^{2+}]_0 \leq 5.1 \times 10^{-3}$ *M*, and $1.0 \times 10^{-5} \leq [VO_2^+]_0 \leq 5.0 \times 10^{-4}$ *M*.

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[11] We are grateful to Professor R. E. McCarley for this vanadium pentoxide.

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The linearity of the first- or second-order rate plots, whichever was appropriate for the run in question, confirmed that the reaction followed a mixed-second-order rate expression. The value of k_{25}, eq 1, was

$$-d[VO_2^+]/dt = k_{25}[V^{2+}][VO_2^+] \tag{1}$$

computed for each experiment. Table I summarizes all of the rate experiments at 1.00 M H^+, except those to which V(III) was added initially. The average value of k_{2i} is $(4.69 \pm 0.17) \times 10^3$ M^{-1} sec^{-1}.

TABLE I

RATE CONSTANTS FOR THE REACTION OF V(II) AND V(V) AS A FUNCTION OF CONCENTRATION AT 1.00 M H^+, 25.0°, AND $\mu = 1.0$ M

Initial concn, $M \times 10^4$		$10^{-3}k_{25}$, M^{-1} sec^{-1}	
V^{2+}	VO_2^+	Obsd	Cor[a]
3.26	1.00	4.85	4.81
4.12	0.500	4.94	4.93
6.4	0.100	4.89	4.89
6.4	0.250	4.93	4.93
6.4	0.500	4.51	4.50
7.10	1.00	4.79	4.77
9.4	0.500	5.09	5.08
11.0	1.00	4.66	4.65
14.3	1.00	4.61	4.60
14.3	1.98	4.78	4.76
14.3	2.98	4.64	4.60
14.4	4.95	4.77	4.65
18.8	1.00	4.67	4.66
26.9	1.00	4.54	4.53
43.6	1.98	4.47	4.47
50.8	1.98	4.22	4.21

[a] Corrected for interference by reaction III, using the computer solution as explained in the text.

Effect of V(III) at High $[H^+]$.—Inspection of reactions I and III indicates that if they occur in sequence, the ratio of VO_2^+ to V^{2+} consumed will exceed unity, and the apparent rate of consumption of VO_2^+ will be greater than that given by I above. The values of the rate constants at 1.00 M H^+ also indicate, however, that this will not be a substantial factor: for I, $k_{25} = 4.7 \times 10^3$ M^{-1} sec^{-1}, and for III, $k_{35} = 2.2 \times 10^2$ M^{-1} sec^{-1} under the same conditions.[10]

Addition of V(III) to the initial reaction solution, however, can enhance the importance of III relative to I, even at 1 M H^+. In an effort to establish the magnitude of this effect and to confirm that the known rate constants k_{25} and k_{35} can quantitatively account for the effect, several runs were carried out with the initial addition of V^{3+} to the V^{2+} solution before it was mixed with VO_2^+ in the stopped-flow apparatus. In each of these experiments a pseudo-first-order rate plot was constructed, which was found to be linear. Apparent values of k_{25} were computed from the slopes of such plots according to the expression

$$k_{25,\mathrm{app}} = -[V^{2+}]_{\mathrm{av}}^{-1}(d \ln [VO_2^+]/dt) \tag{2}$$

The values obtained were larger than those found in the experiments where V^{3+} was not initially present, but not appreciably larger, until concentrations of V^{3+} were reached that were in considerable excess over those formed as products of the former runs. The effect of V^{3+} can be seen by the following expression, which gives the total rate of loss of VO_2^+ by reactions I and III

$$-d[VO_2^+]/dt = \{k_{25}[V^{2+}] + k_{35}[V^{3+}]\}[VO_2^+] \tag{3}$$

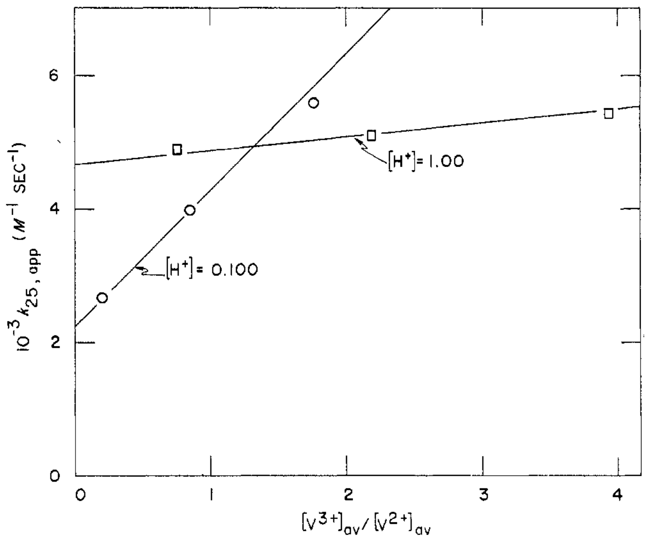

Figure 1.—Illustrating the increasing degree of interference by reaction III with increasing $[V^{3+}]$ and decreasing $[H^+]$ in a plot of $k_{25,\mathrm{app}}$ *vs.* $[V^{3+}]/[V^{2+}]$. The slopes are the known values[10] of k_{35} at 25.0° under the conditions indicated.

Considering that k_{35} at 1.00 M H^+ is 220 M^{-1} sec^{-1} at 25.0°,[10] whereas k_{25} is nearly 20 times larger (Table I), the small effect of V^{3+} at 1.00 M H^+ is not unexpected. According to eq 3, one would expect that the apparent value of k_{25} (eq 2) would vary linearly with the ratio $[V^{3+}]/[V^{2+}]$, giving as intercept the true k_{25} and as slope k_{35}, each referring to 1.00 M H^+. The experiments are presented in Table II, and the agreement of the data with this model is shown by Figure 1, in which the experimental apparent second-order rate constant is plotted *vs.* $[V^{3+}]/[V^{2+}]$, using for the latter quotient the average value during the run. The intercept of this plot is 4.66×10^3 M^{-1} sec^{-1}, in good agreement with the experimental values of k_{25} found in the absence of additional V^{3+}. The slope, although not accurately evaluated owing to the small rate effect, is 200 ± 50 M^{-1} sec^{-1}, in satisfactory

TABLE II

EFFECT OF V(III) ON THE REACTION OF V(II) AND V(V) AT 25.0° AND $\mu = 1.0$ M

Initial concn,[a] $M \times 10^4$			$10^{-3}k_{25}$, M^{-1} sec^{-1}	
$[H^+]$, M	V^{2+}	V^{3+}	Obsd[b]	Cor[c]
1.00	12.8	8.95	4.89 ± 0.13	4.71
1.00	12.8	29.2	5.10 ± 0.10	4.59
1.00	12.5	46.6	5.44 ± 0.26	4.63
0.100	12.4	2.0	2.66	2.30
0.100	12.2	9.6	3.99	2.45
0.100	11.8	19.4	5.6 ± 0.4	~2.2

[a] $[VO_2^+]_0 = 1.00 \times 10^{-4}$ M in all these experiments. [b] Defined by eq 2; uncertainty represents average deviation of three or four repeat determinations using the same set of solutions. [c] Corrected for interference by reaction III using the computer solution, as explained in the text.

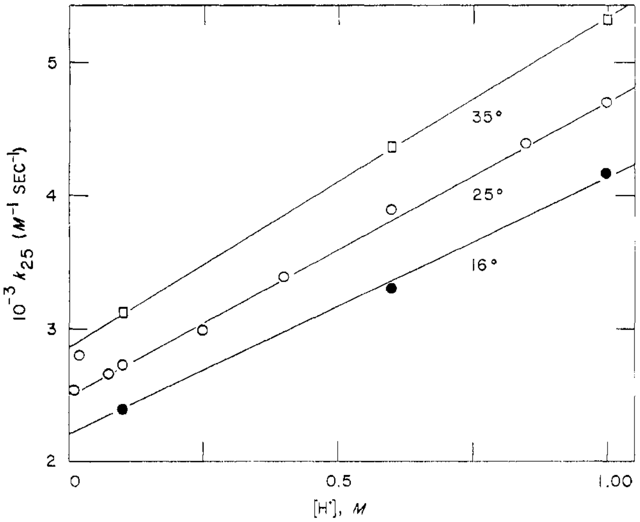

Figure 2.—Illustrating the linear dependence of k_{25} upon [H$^+$] at the three temperatures studied. The lines shown are those resulting from the simultaneous least-squares fit of the [H$^+$] and T dependences.

agreement with Daugherty and Newton's value[10] of 220 M^{-1} sec^{-1} for k_{35} at 1.00 M H$^+$ and 25.0°.

A second approach to accounting for the effect of reaction III is based on the family of differential equations

$$-\mathrm{d}[\mathrm{V}^{2+}]/\mathrm{d}t = k_{25}[\mathrm{V}^{2+}][\mathrm{VO}_2{}^-] \quad (4)$$

$$\mathrm{d}[\mathrm{V}^{3+}]/\mathrm{d}t = k_{25}[\mathrm{V}^{2+}][\mathrm{VO}_2{}^+] - k_{35}[\mathrm{V}^{3+}][\mathrm{VO}_2{}^+] \quad (5)$$

$$\mathrm{d}[\mathrm{VO}^{2+}]/\mathrm{d}t = k_{25}[\mathrm{V}^{2+}][\mathrm{VO}_2{}^+] + 2k_{35}[\mathrm{V}^{3+}][\mathrm{VO}_2{}^+] \quad (6)$$

$$-\mathrm{d}[\mathrm{VO}_2{}^+]/\mathrm{d}t = k_{25}[\mathrm{V}^{2+}][\mathrm{VO}_2{}^+] + k_{35}[\mathrm{V}^{3+}][\mathrm{VO}_2{}^+] \quad (7)$$

A numerical solution of these equations using the Runge-Kutta method was carried out using a digital computer in a manner similar to that used in earlier work.[15] Using an estimated k_{25} and the literature value[10] of k_{35}, under specified initial concentration conditions, the concentration of each species was calculated at regular time intervals, and an average value of $k_{25,\mathrm{app}}$ (eq 2) was computed from those results. The value so calculated always exceeded the original input estimate of the true k_{25} by at least a small amount. The quotient of the two k_{25} values was then used as a correction factor to be applied to the measured value of $k_{25,\mathrm{app}}$ for runs under those conditions. Owing to the relative unimportance of reaction III at 1.00 M H$^+$, the factors were generally not large except in those runs where V^{3+} was added at the start. The values of k_{25} corrected according to this procedure are tabulated in the last column of Table II and agree well with the values found when V(III) was not initially added. The same computation was then performed for each of the runs with no initial V(III). In every case the correction was quite small at 1.00 M H$^+$ as shown by the results in the last column of Table I.

Rate Studies at Lower [H$^+$].—The rate of reaction I decreased with decreasing [H$^+$], but the interference of reaction III became progressively more important owing to the opposing [H$^+$] effects. The kinetic results for experiments having $0.075 \leq [\mathrm{H}^+] \leq 0.85$ M are summarized in Table III. Included in this compilation are runs in which VO^{2+} was added initially, which proved to be without effect. Runs at 0.100 M H$^+$ with added V^{3+} are also presented in Table II and in Figure 1.

Table III

Rate Constants for the Reaction of V(II) and V(V) as a Function of [H$^+$] at 25.0° and μ = 1.0 M

[H$^+$], M	Initial concn, M × 10^4		10$^{-3}k_{25}$, M^{-1} sec^{-1}	
	V^{2+}	VO$_2{}^+$	Obsd[a]	Cor[b]
0.850	12.6	1.00	4.38	4.37
0.850	16.8	1.00	4.39	4.38
0.600	12.5	1.00	3.88	3.87
0.600	13.8	1.00	4.12	4.11
0.600	16.4	1.49	3.68	3.66
0.600	16.6	1.00	3.84	3.83
0.400	13.0	1.00	3.42	3.41
0.400	17.2	1.00	3.38	3.37
0.250	12.9	1.00	3.08	3.06
0.250	17.2	1.00	2.84	2.82
0.250[c]	17.6	1.00	2.99	2.97
0.250[d]	17.6	1.00	3.09	3.07
0.100	14.2	1.00	2.82	2.75
0.100	16.6	1.49	2.91	2.81
0.075	12.2	0.50	2.94	2.88
0.075	12.2	1.00	2.74	2.63
0.075	12.2	2.00	2.83	2.63
0.075	13.4	1.00	2.88	2.78
0.075	18.7	1.00	2.72	2.65
0.075	39.1	1.00	2.46	2.42
0.020	12.8	1.00	*e*	2.9
0.010	16.9	1.00	*e*	2.6
0.010	13.0	1.00	*e*	2.7

[a] Defined by eq 2. [b] Corrected for interference by reaction III using the computer solution, as explained in the text. [c] VO^{2+} added, 1.0 × 10^{-4} M. [d] VO^{2+} added, 1.0 × 10^{-3} M. [e] Not applicable; a different method was used to evaluate k_{25} at $[\mathrm{H}^+] \leq 0.02$ M; see text.

Three runs were carried out at 0.010 and 0.020 M H$^+$, where the interference of reaction III is quite severe (k_{35} = 1.6 × 10^4 and 3.8 × 10^4 M^{-1} sec^{-1} at 0.020 and 0.010 M H$^+$, respectively[10]). In the latter case the deviations from the simple stoichiometry were so great, as were the deviations from an apparent first-order dependence upon [VO$_2{}^+$], that a different procedure was employed. Various estimates of k_{25} were made, and each of these was employed with the known k_{35} to calculate [VO$_2{}^+$] with time using the computer program. The computed results were compared with the observed values, and the process was repeated in an iterative manner to obtain the "best" k_{25} values, which are also presented in Table III.

The variation of k_{25} with [H$^+$] is shown in Figure 2, which establishes the equation

$$-\mathrm{d}[\mathrm{VO}_2{}^+]/\mathrm{d}t = k_{25}[\mathrm{V}^{2+}][\mathrm{VO}_2{}^+] = \{a + b[\mathrm{H}^+]\}[\mathrm{V}^{2+}][\mathrm{VO}_2{}^+] \quad (8)$$

At 25.0° and μ = 1.0 M the values of the rate parameters are $10^{-3}a$ = 2.58 ± 0.10 M^{-1} sec^{-1} and $10^{-3}b$ = 2.16 ± 0.15 M^{-2} sec^{-1}.

Variation of Temperature.—Rate studies to evaluate k_{25} as a function of [H$^+$] at temperatures other than 25.0° were carried out, to permit evaluation of the activation parameters associated with the rate con-

TABLE IV

RATE CONSTANTS FOR THE REACTION OF VANADIUM(II) AND VANADIUM(V) AS A FUNCTION OF TEMPERATURE AT $\mu = 1.0\ M$

		Initial concn, $M \times 10^4$		$-10^{-3}k_{25}$, M^{-1} sec^{-1}-	
Temp, °C	$[H^+]$, M	V^{2+}	VO_2^+	Obsd[a]	Cor[b]
16.0	1.00	12.8	1.00	4.19	4.19
16.0	1.00	13.8	1.49	4.14	4.14
16.0	0.600	13.8	1.00	3.24	3.24
16.2	0.600	16.4	1.49	3.35	3.34
16.2	0.100	14.2	1.00	2.40	2.37
16.2	0.100	16.6	1.49	2.45	2.40
35.0	1.00	12.8	1.00	5.34	5.32
35.0	1.00	13.8	1.49	5.36	5.32
35.0	0.600	13.8	1.00	4.60	4.57
35.0	0.600	16.4	1.49	4.19	4.15
35.0	0.100	14.2	1.00	3.55	3.34
35.0	0.100	16.6	1.49	3.12	2.87

[a] Defined by eq 2. [b] Corrected for interference by reaction III using the computer solution, as explained in the text.

stants. The results are summarized in Table IV. Activation parameters were calculated using a nonlinear least-squares computer program[19] to fit simultaneously the dependence of rate constant upon $[H^+]$ and T. The dependence upon $[H^+]$ was assumed to be as in eq 8, and each of the parameters a and b was assumed to follow the Eyring absolute rate theory equations, with $\kappa = 1$. The resulting activation parameters are summarized in Table V.

TABLE V

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE REACTION OF VANADIUM(II) AND VANADIUM(V) AT $\mu = 1.0\ M$

Rate parameter	Value at 25.0°	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}
a	2580 M^{-1} sec^{-1}	1.9 ± 0.4	-36.8 ± 1.4
b	2160 M^{-2} sec^{-1}	1.8 ± 0.9	-37 ± 3

Effect of Added SCN^-.—The rate and equilibrium behavior of both $VNCS^+$ and $VNCS^{2+}$ are known,[20-23] and a study of the effect of thiocyanate ion on the rate of the V(II)–V(V) reaction offered the promise of providing additional information on the mechanism. The complexation of V(II) by SCN^- is given in reaction IV, for which the rate constants are $k_1 = 28\ M^{-1}$

$$V(H_2O)_6^{2+} + SCN^- \rightleftharpoons (H_2O)_5VNCS^+ + H_2O \quad (k_1, k_2) \qquad (IV)$$

sec^{-1} and $k_2 = 1$ sec^{-1}; the equilibrium constant is $K_{12} = 28\ M^{-1}$. The possible formation of $VNCS^{2+}$ upon mixing[24] of $VNCS^+$ and VO_2^+ was monitored at λ 350 nm, where $VNCS^{2+}$ has an absorption maximum[20] with ϵ 580 M^{-1} cm^{-1}. Experiments were carried out with the following initial concentrations ($M \times 10^4$): $[VO_2^+]$, 1.00, 1.00, 0.20, 2.0; $[VNCS^+]$, 0.85, 0.85, 0.35, 2.3; $[V^{2+}]$, 29, 29, 3.2, 23; $[NCS^-]$, 5.1, 5.1, 200, 18. In every case the absorbance–time trace at λ 350 nm went through a maximum, corresponding to two stages of reaction: formation of $VNCS^{2+}$ in reaction V and subsequent establishment of the V(III)–SCN^- equilibrium in reaction VI. The first three runs gave the

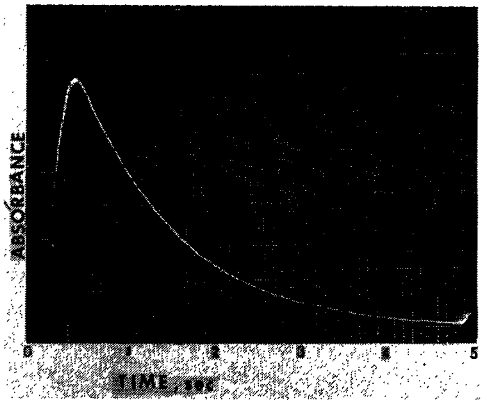

Figure 3.—The absorbance change at λ 350 nm illustrating the effect of SCN^- on the reaction of V(II) and V(V).

$$VNCS^+ + VO_2^+ + 2H^+ = VNCS^{2+} + VO^{2+} + H_2O \qquad (V)$$

$$VNCS^{2+} \rightleftharpoons V^{3+} + SCN^- \quad (k_3, k_4) \qquad (VI)$$

following values for the second-order rate constant for reaction V: $10^{-5}k_V$ (M^{-1} sec^{-1}) = 3, 4, and 4. The second-stage rate constants in the third and fourth experiments were *ca.* 0.9 sec^{-1} in comparison with the rate constants for VI (k_3, 1.0 sec^{-1}; k_4, 117 M^{-1} sec^{-1}) under these conditions. The variations are not considered significant, however, because other possibly competing reactions have been ignored, such as formation of higher V(III)–SCN^- complexes, formation of V^{3+} in reaction II, and the possible reaction of $VNCS^{2+}$ with VO_2^+.

Interpretation and Discussion

Activation Processes.—The rate expression in eq 8 established two independent and parallel reaction pathways that can be represented by the net activation processes[25]

$$V^{2+} + VO_2^+ = [(VO)_2^{3+}]^{\ddagger} \qquad (VII)$$

$$V^{2+} + VO_2^+ + H^+ = [(VO)_2H^{4+}]^{\ddagger} \qquad (VIII)$$

The molar entropies of the transition states can be calculated from the values of $\Delta S^{\ddagger}$ for rate constants a and b as given in Table V and from the molar entropies of V^{2+} and VO_2^+, which are -23 ± 3 and -5 ± 3 eu, respectively. The value for the transition state of 3+ charge in reaction VII is -65 eu, compared to the range -30 to -56 for nine transition states of 3+ charge involving actinide ions.[26] A possible rationalization for this unexpected deviation will be suggested below. In contrast, $S^{\ddagger}$ for the transition state in reaction VIII is also -65 eu, which lies near the average of 13 values lying in the range -60 to -85 eu noted in the tabulated reactions.[26]

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[19] The program was based on the report from Los Alamos Scientific Laboratory, LA2367 + Addenda. We are grateful to Drs. T. W. Newton and R. H. Moore for copies of this program.

[20] B. R. Baker, N. Sutin, and T. J. Welch, *Inorg. Chem.*, **6**, 1948 (1967).

[21] J. M. Malin and J. H. Swinehart, *ibid.*, **7**, 250 (1968).

[22] W. Kruse and D. Thusius, *ibid.*, **7**, 464 (1968).

[23] M. Orhanovic, H. N. Po, and N. Sutin, *J. Am. Chem. Soc.*, **90**, 7224 (1968).

[24] Depending on whether thiocyanate ion is initially mixed with V^{2+} or with VO_2^+, $VNCS^+$ will or will not be present initially. In practice, owing to the oxidation of thiocyanate ion by vanadium(V), the only experiments possible were those in which V^{2+} and SCN^- were placed in the same reservoir of the stopped-flow apparatus.

[25] T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, **63**, 365 (1959).

[26] T. W. Newton and F. B. Baker, Advances in Chemistry Series, No. 71, American Chemical Society, Washington, D. C., 1967, p 268.

Reaction Mechanism.—Based on the similarity of the octahedral hexaaquo ions that are the predominant species for V(II) and V(III) and the structural similarities of the oxo ions that are the predominant V(IV) and V(V) species, it seems most likely that in reaction I V^{2+} is converted to V^{3+} and VO_2^+ to VO^{2+}. This conclusion might be checked with the appropriate radiotracer experiments, but these were not done. Mild support for this assertion also comes from the general preference for one-electron over two-electron changes shown by reactions in which either would be allowed by reason of the stability of the intermediate oxidation states. The very low rate of electron exchange[7] between V^{3+} and VO^{2+}, the products of the reaction in question, also lends support to the conclusion that this is not a two-electron process because in such an exchange (in contrast to the V^{2+}–V^{3+} and VO^{2+}–VO_2^+ reaction) interconversion of aquo and oxo ions is needed.

The information contained in the present results does not allow any firm conclusions concerning structural features of the transition states to be drawn. Some features of the detailed mechanism are evident, however. If a hydroxo or oxo anion acts as a bridging group for electron transfer, it is derived from a solvent molecule coordinated to V(II), since the exchange rate of $V(H_2O)_6^{2+}$ and bulk water occurs too slowly to permit either pathway to involve displacement of a V(II) water ligand.[27]

The surprisingly negative value of $S^{\ddagger}$ for the transition state of 3+ charges in VII may reflect the retention in the transition state of *all* of the coordinated solvent molecules.[28] The addition of a proton in the second pathway is a common occurrence[26,29] in reactions where the net structural change converts an oxo ligand to an aquo ligand (*e.g.*, VO_2^+ to VO^{2+}), presumably because the additional proton, by coordination to a VO_2^+ oxygen in the transition state, assists in its conversion into a water molecule. An appropriate concerted motion of protons could give the inner-sphere transition state $[(H_2O)_5V(OH)V(O)(H_2O)_n{}^{4+}]^{\ddagger}$, but the results do not provide a clear indication on this point.

[27] The rate constant for the $V(H_2O)_6^{2+}$–H_2O exchange rate is not known, but the rate constant for anation of $V(H_2O)_6^{2+}$ by SCN^- is 28 M^{-1} sec^{-1},[21] and one can infer from similar comparisons [N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966)] that the solvent rate is probably less than 10-fold higher.

[28] An abnormally positive value of $\Delta S^{\ddagger}$ was used to infer an inner-sphere mechanism: M. J. Nicol and D. R. Rosseinsky, *Chem. Ind.* (London), 1166 (1963). T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **70**, 1943 (1966), have used similar differences in the entropies of activated complexes to suggest inner- and outer-sphere mechanisms for several V^{3+}–MO_2^{2+} reactions.

[29] J. H. Espenson, *Inorg. Chem.*, **7**, 631 (1968).

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Vibrational Analysis for $Nb_6O_{19}^{8-}$ and $Ta_6O_{19}^{8-}$ and the Raman Intensity Criterion for Metal–Metal Interaction[1a]

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Raman and infrared spectra of the octahedral oxyanions $Nb_6O_{19}^{8-}$ and $Ta_6O_{19}^{8-}$ have been subjected to an approximate normal-coordinate analysis. Substantial interaction force constants are required for an adequate fit of the spectra, reflecting the complexity of the force field in these highly condensed complexes. The principal metal–oxygen force constants are quite satisfactory, however, for all three types of oxygen atoms: terminal, bridging, and central. The force constant ratios ~6:3:1 are consistent with a simple bonding scheme in which each oxide ion shares four valence electrons with its neighboring metal ions. As with the structurally analogous $Bi_6(OH)_{12}^{6+}$ a set of cage angles can be replaced in the analysis by a kinetically equivalent set of metal–metal interactions. This internal coordinate is the primary contributor to the lowest frequency A_{1g} fundamental: the "breathing" mode of the metal ions. For $Bi_6(OH)_{12}^{6+}$ this mode produces the most intense band in the Raman spectrum, and metal–metal bonding has been invoked to account for the intensity. For the $M_6O_{19}^{8-}$ complexes, this mode produces one of the weakest Raman bands, consistent with the anticipated absence of metal–metal interaction for these d^0 metal ions. However the "metal–metal" force constants are about the same as for $Bi_6(OH)_{12}^{6+}$. Such force constants evidently have little meaning in bridged polynuclear complexes, and Raman intensity would appear to offer a more reliable criterion for metal–metal interaction.

Introduction

Some years ago Lindqvist and Aronsson showed by X-ray diffraction the existence of discrete polyanions $M_6O_{19}^{8-}$ in crystalline niobates[2] and tantalates.[3] The polynuclear complexes have approximately cubic symmetry, an octahedron of metal atoms being connected by twelve oxygen atoms over the octahedral edges and one in the center of the cage. In addition six peripheral oxygens complete the octahedral coordination shell around each metal. The structure is shown in Figure 1. Alkaline solutions of Nb(V) and Ta(V) also contain hexanuclear anions, as shown by

[1] (a) This investigation was supported by Public Health Service Grant GM-13498, from the National Institute of General Medical Sciences. (b) NIH predoctoral fellow.

[2] I. Lindqvist, *Arkiv Kemi*, **5**, 247 (1953).

[3] I. Lindqvist and B. Aronsson, *ibid.*, **7**, 49 (1954).