**X-Ray[7] Diffraction.**—Powder patterns (Cr K$\alpha$ and Cu K$\alpha$) of $K_2ReH_9$ and potassium technetium hydride are very similar. Table I compares the observed $d$-spacings and relative intensities of the lines in the powder patterns of the two compounds. Also shown in Table I are the indices ($hkl$) and $d$-spacings calculated on an IBM 7094 computer using the single crystal lattice constants of $K_2ReH_9$ ($a$ = 9.607, $c$ = 5.508 Å.).[3,7] It is clear from the table that the Re and Tc compounds are isostructural. The lattice constants for potassium technetium hydride are calculated to be $a$ = 9.64, $c$ = 5.56 Å., and the volume of the hexagonal unit cell is 447.5 Å.[3], an increase of 1.7% over the unit cell volume of $K_2ReH_9$ (440.24 Å.[3]).

According to the X-ray results, technetium hydride is isostructural with $K_2ReH_9$. Hence, the K:Tc ratio and the arrangement of the K and Tc atoms may be regarded as established, but it is conceivable, although un-

likely, that the stoichiometry and geometry of the technetium hydride anion is not thereby determined, since the hydrogen atoms do not *directly* make an observable contribution to the X-ray diffraction pattern. However, when we consider the X-ray results together with the infrared spectrum, which *is* characteristic of the structure of the hydride anion, any doubt as to the nature of the anion is removed. The infrared spectra of $K_2ReH_9$ and potassium technetium hydride, in the solid state, differ only by small displacements of the bands, and since the metal atom arrangement in the two compounds is the same, we may conclude that the Re and Tc hydride anions are isostructural. Thus, the formula of potassium technetium hydride must be $K_2TcH_9$. In view of the results in ref. 3, there are six H at the corners of a trigonal prism with the Tc at its center and three H beyond the centers of the rectangular prism faces (point group symmetry $D_{3h}$).

# The Intermediate in the Reaction between Vanadium(II) and Vanadium(IV)[1]

By T. W. NEWTON and F. B. BAKER

When V(II) and V(IV) are mixed in acid perchlorate solutions, a highly colored substance forms which has been shown to be an intermediate in the reaction $V^{+2} + VO^{+2} + 2H^+ = 2V^{+3} + H_2O$ and to be $VOV^{+4}$, a hydrolytic dimer of V(III). The rate of formation of $VOV^{+4}$ is given by $k_1[V^{+2}][VO^{+2}]$ and its rate of reaction with acid is given by $k_2[VOV^{+4}][H^+]$. At 0° and unit ionic strength $k_1$ is about 0.067 $M^{-1}$ sec.$^{-1}$ and $k_2$ is about 0.33 $M^{-1}$ sec.$^{-1}$. Also $k_2$ = 4.054 × $10^4 T$ exp ($-9400/RT$). About 65% of the over-all oxidation–reduction reaction involves the intermediate; the rest goes directly to the final products, probably by way of an outer-sphere activated complex.

## Introduction

During a study of the kinetics of the reaction between V(II) and V(IV) in aqueous perchlorate solutions,[2] evidence was obtained for an intermediate. It was observed that when V(II) and V(IV) were mixed in acid solutions, a brown color developed much more rapidly than the rate of the over-all reaction to produce aquo V(III). The over-all reaction was found to have the rate law: $-d[V(IV)]/dt = (k' + k''[H^+])[V(II)][V(IV)]$. The $k'$ term accounts for nearly all of the rate and values of $\Delta H^*$ and $\Delta S^*$ for this path were found to be 12.3 kcal./mole and $-16.5$ cal./deg. mole. In the work to be reported here the intermediate has been investigated further in order to compare its properties with those of the intermediates which have been observed[3] or postulated[4] in other oxidation–reduction reactions.

## Experimental

The system was studied spectrophotometrically using a Cary Model 14 recording spectrophotometer. The reactions were started by injecting V(II) into appropriate solutions of V(IV) in stirred absorption cells which were positioned in a small water-filled thermostat in the light beam of the spectrophotometer. The details of this arrangement, as well as the methods for the preparation of the various solutions, have already been described.[2,4a]

A Beckman Model G pH Meter was used for the pH determinations. The calomel electrode was separated from the experimental solutions, which contained perchlorate, by means of a fiber-tipped glass sleeve which contained 1 $M$ NaNO$_3$. The meter was calibrated using carefully diluted HClO$_4$ in LiClO$_4$ at unit ionic strength.

## Results and Discussion

**The Intermediate.**—Typical results obtained on mixing V(II) into solutions of V(IV) are shown in Fig. 1. Absorbance, $D$ (defined as log $[I_0/I]$), was determined as a function of time at 4250 Å. The solutions were at 0° and 0.5 $M$ in HClO$_4$, 0.0023 $M$ in V(II), while the V(IV) concentrations varied from 0.0134 to 0.100 $M$. The ionic strength was held constant at 0.8 $M$ using Zn(ClO$_4$)$_2$. The optical path length, $b$, was 2.20 and 2.19 cm. for the two cells used. The initial rise in $D$ followed by a subsequent decrease shows that the

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(1) Work done under the auspices of the U. S. Atomic Energy Commission, and presented in part at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(2) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **68**, 228 (1964).

(3) T. W. Newton and F. B. Baker, *Inorg. Chem.*, **1**, 368 (1962).

(4) (a) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **67**, 1425 (1963); (b) *ibid.*, **62**, 943 (1958).

<div align="center">

Table I

The Dependence of $\Delta D$ on the Reactant Concentrations

Part A.   Conditions: 0°, 0.5 $M$ HClO$_4$, $\mu$ = 0.8 (Zn(ClO$_4$)$_2$), path length, $b \cong 2.2$ cm.

</div>

| V(II), $M \times 10^3$ | V(IV), $M \times 10^2$ | $\Delta D$ | $\Delta D/[\text{V(II)}][\text{V(IV)}]b$, $M^{-2}$ cm.$^{-1} \times 10^{-3}$ | $t_{1/2}$, sec. |
|---|---|---|---|---|
| 2.26, 2.30 | 1.34 | 0.167, 0.163 | 2.51, 2.42 | 5.0, 4.9 |
| 2.29, 2.31 | 3.34 | 0.414, 0.414 | 2.46, 2.45 | 5.0, 5.1 |
| 2.31, 2.28 | 6.68 | 0.842, 0.835 | 2.49, 2.49 | 5.1, 5.1 |
| 2.31, 2.29 | 10.0 | 1.281, 1.267 | 2.53, 2.51 | 5.4, 5.2 |

<div align="center">

Part B.   Conditions: 0°, 0.7 $M$ HClO$_4$, $\mu$ = 1.3 (Zn(ClO$_4$)$_2$), $b \cong 2.2$ cm.

</div>

| V(II), $M \times 10^2$ | V(IV), $M \times 10^3$ | $\Delta D$ | $\Delta D/[\text{V(II)}][\text{V(IV)}]b$, $M^{-2}$ cm.$^{-1} \times 10^{-3}$ | $t_{1/2}$, sec. |
|---|---|---|---|---|
| 1.51 | 2.97 | 0.195 | 1.98 | 3.1 |
| 2.51 | 2.97 | 0.326 | 1.99 | 3.0 |
| 5.03 | 2.97 | 0.664 | 2.03 | 3.1 |
| 7.53 | 2.97 | 1.004 | 2.05 | 3.1 |
| 10.0 | 2.97 | 1.351 | 2.08 | 3.1 |

reactants do not go directly to products and thus indicates the presence of some additional species. It will be shown later that this species is an intermediate in the oxidation–reduction reaction and not merely a complex which forms between V(II) and V(IV). The slow decrease in $D$ is due to the consumption of the intermediate as V(II) and V(IV) react to form the final products. The latter portions of the curves were extrapolated to the time of mixing to give $D_0'$, the values the absorbance would have had if the intermediate had formed instantaneously. The extrapolations were made on plots of log $(D - D_\infty)$ vs. time, which were essentially linear. The absorbance at zero time, $D_0$, is equal to the sum of the absorbances of the V(II) and V(IV), both of which are small at 4250 Å. The absorbance change due to the hypothetical instantaneous formation of the intermediate, $D_0' - D_0 = \Delta D$, was found to be essentially proportional to the V(IV) concentration. This is shown in part A of Table I which summarizes the results of the runs shown in Fig. 1. The fact that the quantity $\Delta D/[\text{V(II)}]\cdot[\text{V(IV)}]b$ is essentially constant shows that $\Delta D$ is proportional to the concentration of V(IV). $\Delta D$ is also proportional to the concentration of V(II), as is shown in part B of Table I. If the concentration of the intermediate were as large as $10^{-4}$ $M$ in the solutions which were 0.1 $M$ in either V(II) or V(IV), a significant departure from proportionality would have occurred. The values found for $\Delta D/[\text{V(II)}][\text{V(IV)}]b$ show a slight trend but in the opposite direction to that expected if significant concentrations of intermediate had formed.

The spectrum of the intermediate was determined by repetitive scanning of V(II)–V(IV) mixtures and extrapolation to the time of mixing. The result is a single, unsymmetrical band between 3500 and 7600 Å. as shown in Fig. 2.

For the runs in which the rate of the over-all reaction to give final products was low, it was found that plots of log $(D_0' - D)$ vs. time were straight lines. This is consistent with a mechanism in which the intermediate forms at a constant rate but disappears at a rate proportional to its concentration. Where the rate of the over-all reaction is not low the course of $D$ vs. time is more complicated but still consistent with the same

mechanism. In this case a small correction was applied to the time values; the derivation of the correction term will be postponed until after a mechanism is proposed. The half-times reported in Tables I and II were determined using corrected time values. These half-times refer to the pseudo-first-order processes by which the intermediate disappears.

The hydrogen ion dependence of the half-times for the disappearance of the intermediate and for the quantity $\Delta D/[\text{V(II)}][\text{V(IV)}]b$ were determined in solutions of constant ionic strength. The results of a series of runs made at 0° are summarized in Table II. The significance of the last quantity tabulated can be seen from eq. 11.

Plots of $\Delta D/[\text{V(II)}][\text{V(IV)}]b$ vs. $1/[\text{H}^+]$ and of $t_{1/2}$ vs. $1/[\text{H}^+]$ were found closely to approximate
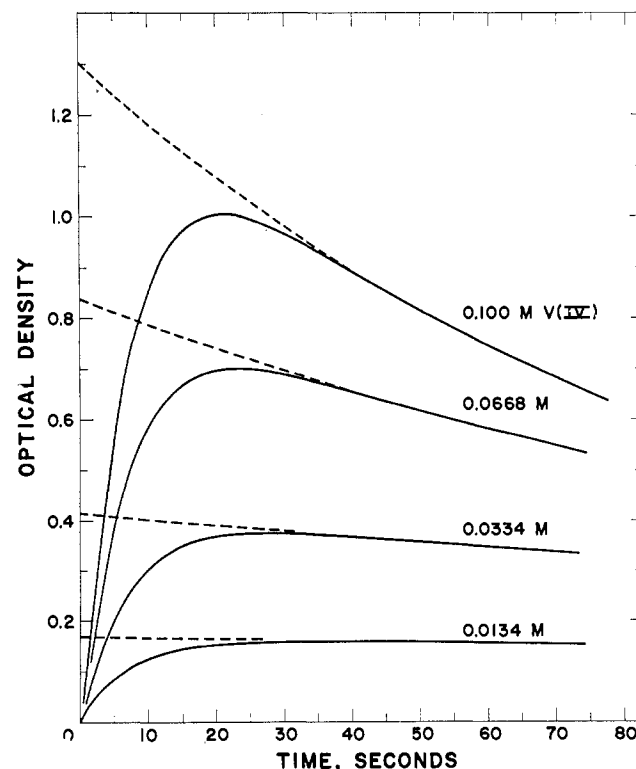


Fig. 1.—Absorbance (optical density) vs. time, showing the formation and disappearance of the intermediate, 0° and 0.5 $M$ HClO$_4$.

TABLE II

HYDROGEN ION DEPENDENCE

Conditions: $0°$, $\mu = 1.0\ M$ (LiClO$_4$), $2.6 \times 10^{-3}\ M$ V(II), optical path, $b = 10$ cm.

| [V(IV)], $M \times 10^3$ | [HClO$_4$], $M$ | $\Delta D$ | $t_{1/2}$, sec. | $\dfrac{\Delta D[\mathrm{H}^+]}{[\mathrm{V(II)}][\mathrm{V(IV)}]b}$ | $t_{1/2}[\mathrm{H}^+]$, $M$ sec. | $\dfrac{0.693\Delta D}{[\mathrm{V(II)}][\mathrm{V(IV)}]bt_{1/2}}$ |
|---|---|---|---|---|---|---|
| 5.25 | 0.500 | 0.375 | 4.18 | 1.36 | 2.09 | 450 |
|  |  | 0.378 | 4.18 | 1.37 | 2.09 | 454 |
|  |  | 0.372 | 4.16 | 1.36 | 2.08 | 454 |
| 5.25 | 0.275 | 0.654 | 7.35 | 1.32 | 2.02 | 452 |
|  |  | 0.660 | 7.30 | 1.33 | 2.01 | 459 |
| 5.25 | 0.140$^a$ | 1.249 | 14.5 | 1.28 | 2.03 | 437 |
| 2.62 | 0.138 | 0.640 | 13.85 | 1.29 | 1.91 | 469 |
| 2.62 | 0.0933 | 0.952 | 20.4 | 1.28 | 1.90 | 468 |
|  |  | 0.947 | 20.7 | 1.28 | 1.93 | 459 |

$^a$ Temp. was $-0.4°$.

straight lines through the origin. This is shown by the near constancy of the quantities listed in the fifth and sixth columns of Table II. The trends with [H$^+$] indicate either a small systematic error in the measurements, a small medium effect, or hydrogen ion dependences which are complicated by the presence of small additional terms.

The effect of temperature on the half-times and on the absorbance due to the complex at 4250 Å. was studied. Determinations were made at various concentrations of HClO$_4$ with $\mu = 1.0\ M$ (LiClO$_4$) at 13 and 25° as well as at 0°. The results of these determinations are summarized in Table III.

TABLE III

THE EFFECT OF TEMPERATURE ON THE INTERMEDIATE

| Temp., °C. | $0.693[t_{1/2}]^{-1}[\mathrm{H}^+]^{-1}$, $M^{-1}$ sec.$^{-1}$ | $\dfrac{0.693\Delta D}{[\mathrm{V(II)}][\mathrm{V(IV)}]bt_{1/2}}$ |
|---|---|---|
| 0 | $0.330 + 0.003/[\mathrm{H}^+]$ | 456 |
| 13 | $0.772 + 0.005/[\mathrm{H}^+]$ | 1370 |
| 25 | $1.54 + 0.03/[\mathrm{H}^+]$ | 3700 |

The results of the rate experiments presented so far show that a colored substance forms, the extrapolated initial concentration of which is proportional to [V(II)][V(IV)], and that the substance disappears at a rate which is predominantly proportional to its own concentration times the hydrogen ion concentration. That this substance is an intermediate in the oxidation–reduction reaction to give aquo V(III) and not merely in equilibrium with V(II) and V(IV) is shown in the next section. Evidence is given that a hydrolytic dimer of V(III) reacts with acid to give aquo V(III) at the same rate that the colored substance reacts with acid.

**A Hydrolytic Dimer of V(III).**—When solutions of V(III) were brought to a pH of about 2.7 a brown color developed similar to that of the intermediate in the V(II)–V(IV) reaction. The spectrum showed a peak at 4250 Å., similar to that of the intermediate. The colored hydrolysis product is not a monomer since the average extinction coefficient, $\bar{\epsilon}$, was found to depend on the total V(III) concentration at constant pH, as shown in Table IV.

The results are consistent with the assumption that a small concentration of highly colored dimer, V$_2$,

TABLE IV

EFFECT OF V(III) CONCENTRATION ON AVERAGE EXTINCTION COEFFICIENT AT CONSTANT pH

CONDITIONS: 23°, pH 2.7

| [V(III)], $M \times 10^3$ | path, $b$, cm. | Absorbance $D$ | $\bar{\epsilon}$, obsd., $M^{-1}$ cm.$^{-1}$ | $\bar{\epsilon}$, calcd.,$^a$ $M^{-1}$ cm.$^{-1}$ |
|---|---|---|---|---|
| 0.675 | 10 | 0.203 | 30.1 | 29.9 |
| 1.35 | 10 | 0.721 | 53.4 | 54.2 |
| 2.70 | 5 | 1.365 | 101 | 100.3 |
| 4.50 | 1 | 0.713 | 158 | 157.1 |
| 5.19 | 1 | 0.925 | 178 | 177.5 |
| 6.75 | 1 | 1.483 | 220 | 220.6 |

$^a$ $\bar{\epsilon}$, calcd. $= 4.98 + 3.75 \times 10^4[\mathrm{V(III)}] - 8.29 \times 10^5[\mathrm{V(III)}]^2$.

is in equilibrium with monomer, V$_1$. Under this assumption the total vanadium concentration is given by [V(III)] = [V$_1$] + 2[V$_2$] and the concentration of dimer is given by [V$_2$] = $K$[V$_1$]$^2$, where $K$ is the dimerization constant. The average extinction coefficient is given by $\bar{\epsilon} = \epsilon_1[\mathrm{V_1}]/[\mathrm{V(III)}] + \epsilon_2[\mathrm{V_2}]/[\mathrm{V(III)}]$, where $\epsilon_1$ and $\epsilon_2$ are the extinction coefficients of the monomer and dimer, respectively. By expanding the solution to these equations in series it can be shown that

$$\bar{\epsilon} = \epsilon_1 + K(\epsilon_2 - 2\epsilon_1)[\mathrm{V(III)}] - 4K^2(\epsilon_2 - 2\epsilon_1)[\mathrm{V(III)}]^2 + \ldots \quad (1)$$
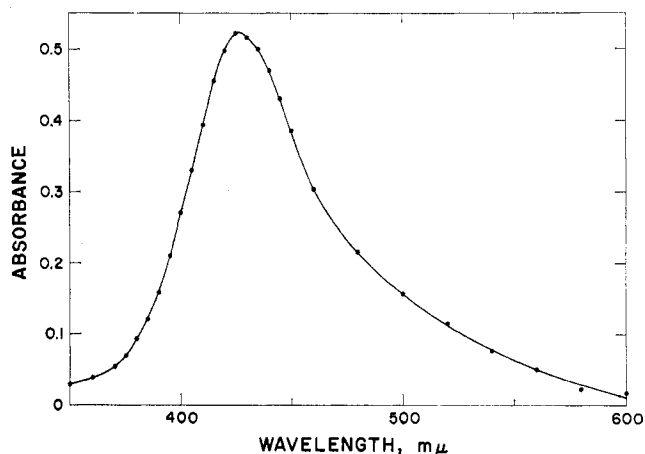


Fig. 2.—The spectrum of the intermediate, determined in 1.5 $M$ LiClO$_4$–0.5 $M$ HClO$_4$; $2.6 \times 10^{-3}\ M$ V(II) and $5.2 \times 10^{-3}\ M$ V(IV) were mixed at 0° in a 10-cm. cell.

Table V

The Reaction between the Dimer and Acid

Conditions: 25°, $\mu = 1.0\ M$ (LiClO$_4$)

| HClO$_4$, $M$ | 0.017 | 0.034 | 0.049 | 0.073 | 0.078 | 0.155 | 0.46 |
|---|---|---|---|---|---|---|---|
| $t_{1/2}$, sec. | 12.8 | 8.8 | 6.8 | 5.1 | 5.6 | 2.6 | ~1 |
| $0.693/t_{1/2}$, sec.$^{-1}$ | 0.054 | 0.079 | 0.102 | 0.135 | 0.124 | 0.267 | 0.69 |
| $0.028 + 1.52[H^+]$ | 0.054 | 0.080 | 0.103 | 0.139 | 0.147 | 0.264 | 0.73 |

The data in Table IV were fit to such an equation by the method of least squares and it was found that $\epsilon_1 = 5.0 \pm 0.6$, $K(\epsilon_2 - 2\epsilon_1) = (3.75 \pm 0.07) \times 10^4$, and $4K^2(\epsilon_2 - 2\epsilon_1) = (8.3 \pm 1.0) \times 10^5$; the uncertainties are the standard deviations. From these values $K = 5.5 \pm 0.7\ M^{-1}$ and $\epsilon_2 = (6.8 \pm 0.8) \times 10^3\ M^{-1}$ cm.$^{-1}$. These values were used for the calculated $\bar{\epsilon}$ in Table IV.

When V(III) solutions of pH 2.7 were injected into solutions of higher acidity, their absorbances at 4250 Å. were found to decrease at measurable rates. Plots of $\log (D - D_\infty)$ vs. time were found to be linear, showing that the rate of reaction is first power in the concentration of the dimer. Runs with different final acid concentrations showed that the rate is proportional to the hydrogen ion concentration also. The results of a series of such runs are summarized in Table V.
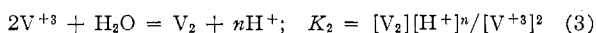
The apparent first-order rate constant is essentially proportional to $[H^+]$ and the second-order rate constant for the reaction between the dimer and $H^+$ is given by $1.52 + 0.028/[H^+]$. Similar runs at 0° gave the expression: $0.31 + 0.005/[H^+]$. Comparison with the results given in Table III shows that these rate constants are in good agreement with those found for the reaction between acid and the intermediate in the V(II)–V(IV) reaction.

This agreement in reaction rate, together with the similarity in the spectra, indicates that the intermediate and the hydrolytic dimer are the same substance.

In order to estimate the charge on the hydrolytic dimer, absorbance vs. pH was determined for a series of solutions at constant total V(III) concentrations. Considering that the principal equilibria are

$$V^{+3} + H_2O = VOH^{+2} + H^+;$$
$$K_1 = [VOH^{+2}][H^+]/[V^{+3}] \quad (2)$$

and

$$2V^{+3} + H_2O = V_2 + nH^+; \quad K_2 = [V_2][H^+]^n/[V^{+3}]^2 \quad (3)$$
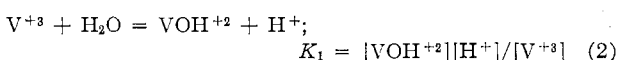
it can be shown that

$$\left[\bar{\epsilon}\left(\frac{[H^+] + K_1}{[H^+]}\right) - \epsilon_0 - \frac{\epsilon_1 K_1}{[H^+]}\right]\left(\frac{[H^+] + K_1}{[H^+]}\right) \cong \frac{\epsilon_2 K_2[V(III)]}{[H^+]^n} \quad (4)$$

where $\epsilon_0$, $\epsilon_1$, and $\epsilon_2$ are the extinction coefficients of $V^{+3}$, $VOH^{+2}$, and $V_2$, respectively. It can be seen that if the log of the left-hand side (LHS) of (4) is plotted against $\log [H^+]$, a straight line should result with slope equal to $-n$. Values for $K_1$ have been published,[5,6] $\epsilon_0$ can be estimated from the limit of $\bar{\epsilon}$

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

(6) F. Brito, to be published. Quoted by L. G. Sillén, Welch Conference, Houston, Texas, 1962.

Table VI

Absorbance vs. pH at Constant V(III) Concentration

Conditions: 0.0093 $M$ V(III), $\mu = 1.0\ M$ (LiClO$_4$), 23°, 2-cm. optical path

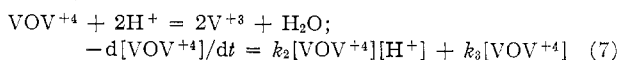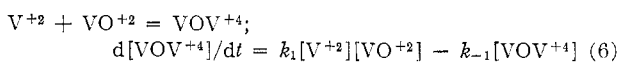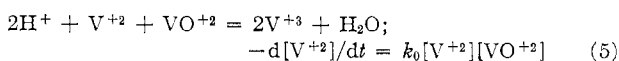| pH | 2.01 | 1.65 | 1.51 | 1.45 | 1.16 | 0.88 | 0.79 |
|---|---|---|---|---|---|---|---|
| Absorbance | 1.070 | 0.380 | 0.264 | 0.215 | 0.145 | 0.119 | 0.114 |
| $\bar{\epsilon}$, $M^{-1}$ cm.$^{-1}$ | 57.8 | 20.5 | 14.3 | 11.6 | 7.8 | 6.4 | 6.2 |
| LHS of eq. 4[a] | 75.9 | 17.8 | 9.95 | 6.8 | 2.2 | 0.86 | 0.68 |

[a] $K_1$ assumed to 0.002 $M$, $\epsilon_0 = 5.5$, and $\epsilon_1 = 5.5\ M^{-1}$ cm.$^{-1}$.

at high acid, and $\epsilon_1$ can be estimated from the results of the experiment described in Table IV.

The results of an experiment designed to use eq. 4 are summarized in Table VI.

The data in Table VI give a slope corresponding to $n = 1.8$. This result depends on the values chosen for $K_1$ and $\epsilon_0$, but is essentially independent of $\epsilon_1$. For example, increasing $K_1$ from 0.002 to 0.0025 $M$ increases $n$ to 2.1. Similar experiments gave $n$ in the range of 1.7 to 1.9. Although these experiments are not very accurate, they are sufficient to show that the dimer is predominantly $VOV^{+4}$ corresponding to $n = 2$. This conclusion is in accord with the hydrolysis of Fe(III) where the hydrolytic dimer, $FeOFe^{+4}$, was found.[7]

**Reaction Scheme.**—A reaction scheme which is consistent with the experimental observations is

$$2H^+ + V^{+2} + VO^{+2} = 2V^{+3} + H_2O;$$
$$-d[V^{+2}]/dt = k_0[V^{+2}][VO^{+2}] \quad (5)$$

$$V^{+2} + VO^{+2} = VOV^{+4};$$
$$d[VOV^{+4}]/dt = k_1[V^{+2}][VO^{+2}] - k_{-1}[VOV^{+4}] \quad (6)$$

$$VOV^{+4} + 2H^+ = 2V^{+3} + H_2O;$$
$$-d[VOV^{+4}]/dt = k_2[VOV^{+4}][H^+] + k_3[VOV^{+4}] \quad (7)$$

Since these are net reactions the rate of each has been specified. This formulation has been adopted so that rapid reactions which occur after the rate-determining steps need not be specified.

The $k_{-1}$ and $k_3$ terms are needed if the minor terms in the hydrogen ion dependences are to be accounted for in the mechanism. These minor terms might, however, be due to medium effects. The $k_{-1}$ and $k_3$ terms are quite small at most and in the discussion which follows they have been omitted.

According to this approximation the net rate of formation of $VOV^{+4}$ is

$$d[VOV^{+4}]/dt = k_1[V^{+2}][VO^{+2}] - k_2[VOV^{+4}][H^+]$$

and at the steady state

$$[VOV^{+4}] = k_1[V^{+2}][VO^{+2}]/k_2[H^+]$$

As soon as the steady-state approximation is valid, the apparent second-order rate constant for the over-all reaction, $k'$, is given by $k' = k_0 + k_1$, in agreement with the observation that the hydrogen ion dependence of the over-all reaction is predominantly zero.

The absorption due to the intermediate, $D_I$, is given by $D_I = \epsilon b[VOV^{+4}]$; the total absorption of the solution is $D = D_I + D_0$, where $D_0$ is the absorption due

(7) R. M. Milburn and W. C. Vosburgh, *J. Am. Chem. Soc.*, **77**, 1352 (1957).

to $V^{+2}$ and $VO^{+2}$. We will define a hypothetical absorbance

$$D' = \epsilon b k_1 [V^{+2}][VO^{+2}]/k_2[H^+] + D_0 \qquad (8)$$

This is the absorbance given by extrapolation of the latter portions of the $D$ vs. time plots. When the steady state is reached, $D' = D_I + D_0$, while at time zero the extrapolated value of $D_I$ is given by

$$D_I = \Delta D = D_0' - D_0 = \epsilon b k_1 [V^{+2}]_0 [VO^{+2}]_0 / k_2 [H^+] \qquad (9)$$

Since neither V(II) nor V(IV) is appreciably hydrolyzed in the acid concentration range studied, eq. 9 is consistent with the observation that $\Delta D[H^+]/[V(II)]_0 \cdot [V(IV)]_0 b$ is essentially constant (Table II).

To calculate the approach to the steady state

$$dD/dt = \epsilon b d[VOV^{+4}]/dt = \epsilon b k_1 [V^{+2}][VO^{+2}] -$$
$$\epsilon b k_2 [VOV^{+4}][H^+]$$
$$= k_2 [H^+]\{\epsilon b k_1 [V^{+2}][VO^{+2}]/k_2[H^+] - \epsilon b [VOV^{+4}]\}$$
$$= k_2 [H^+]\{(D' - D_0) - (D - D_0)\} =$$
$$k_2 [H^+]\{(D_0' - D) - (D_0' - D')\}$$

Therefore

$$-\frac{d(D_0' - D)}{(D_0' - D)} \bigg/ dt = k_2[H^+]\left[1 - \frac{D_0' - D'}{D_0' - D}\right]$$

Integrating gives

$$\ln(D_0' - D) = -k_2[H^+]\left[t - \int_0^t \frac{D_0' - D'}{D_0' - D} dt\right] \qquad (10)$$

Thus plots of $\log(D_0' - D)$ vs. the quantity in brackets in (10), the corrected time, will have slopes equal to $-k_2[H^+]/2.303$. The integral in the brackets amounts to a small correction which can be determined with sufficient accuracy graphically. It is this corrected time which was used in determining all of the half-times given in Tables I, II, and III.

The apparent second-order rate constant for the reaction between $VOV^{+4}$ and $H^+$ is given by $k_2 = 0.693/[H^+]t_{1/2}$ and is tabulated in column 2 of Table III. The temperature dependence of this principal, $[H^+]$ independent, term is given by $k_2/T = 4.054 \times 10^4 \exp(-2055/T)$. This equation reproduces the experimental values with a mean deviation of 0.6% and a maximum deviation of 1%. The parameters in the equation correspond to $\Delta S^* = -26.1$ cal./deg. mole and $\Delta H^* = 9.4$ kcal./mole.

The quantity $k_1\epsilon$ can be written in terms of the experimental quantities by substituting for $k_1$ in eq. 9 to give

$$k_1\epsilon = \frac{0.693\Delta D}{[V^{+2}]_0[VO^{+2}]_0 b t_{1/2}} \qquad (11)$$

This is the quantity which is tabulated in the last column of Table II; it is seen to be essentially constant

with an average value of 456 $M^{-2}$ cm.$^{-1}$ sec.$^{-1}$ at 0°. The temperature coefficient of $k_1\epsilon$ is given by $k_1\epsilon/T = 2.97 \times 10^{10} \exp(-2800/T)$. The temperature coefficient of $\epsilon$ is probably negative, so it can be concluded that $\Delta H^*$ associated with $k_1$ is probably greater than 12.8 kcal./mole, slightly larger than the 12.3 kcal./mole which was found for the over-all reaction.

A value for $k_1$ can be estimated from $k_1\epsilon$ by making use of the value of $\epsilon$ found for the hydrolytic dimer: $456/(6800 \pm 800) = 0.067 \pm 0.008\ M^{-1}$ sec.$^{-1}$. At 0° and unit ionic strength, the apparent second-order rate constant for the over-all reaction was found to be 0.106 $M^{-1}$ sec.$^{-1}$,[8] which leaves $0.039 \pm 0.008\ M^{-1}$ sec.$^{-1}$ for $k_0$ since $k' = k_0 + k_1$. In order that $k_0 = 0$ it would have been necessary that $\epsilon = 4300\ M^{-1}$ cm.$^{-1}$, a value considerably smaller than the observed one. It is thus safe to conclude that some of the reaction, probably about 35%, proceeds directly to products (the $k_0$ path) while the rest of the reaction proceeds by way of the intermediate.

The activated complexes for the $k_0$ and $k_1$ paths have the same formulas but differ in that the first decomposes to the final products while the second gives a binuclear intermediate. The second activated complex is almost certainly of the inner-sphere type and it is reasonable to suggest that the other is of the outer-sphere type. In the Fe(II)–Pu(VI) reaction also, two activated complexes were found, one certainly inner-sphere and the other possibly outer-sphere.[4a] The simultaneous involvement of inner- and outer-sphere activated complexes has been demonstrated recently for the oxidation of pentacyanocobaltate(II) by pentaamminecobalt(III) complexes.[9]

It is of interest to compare the V(II)-V(IV) and the Cr(II)-Cr(IV) reactions. Ardon and Plane[10] found that when Cr(II) is oxidized under conditions where Cr(IV) would be expected to form, for example using Tl(III), the product was predominantly $CrOCr^{+4}$. Thus the initial products are quite similar, differing in that $CrOCr^{+4}$ is much more stable in acid solutions than $VOV^{+4}$ and that no direct formation of $Cr^{+3}$ is observed.

(8) Unpublished result, determination made as in ref. 2.

(9) J. Candlin, J. Halpern, and S. Nakamura, *J. Am. Chem. Soc.*, **85**, 2517 (1963).

(10) M. Ardon and R. A. Plane, *ibid.*, **81**, 3197 (1959).