viz., that involving a simultaneous in-phase, out-of-plane "umbrella" vibration involving all and only the radial halogens. As suggested by studies of octahedral anions $[MCl_6]^{n-}$, such modes invariably fall *below* (usually significantly below) 200 cm^{-1}.

(10) The theory of resonance Raman scattering predicts that the resonance involving a single electronic transition enhances a single element of the Raman scattering tensor,[11] and if that element dominates the intensity, then the depolarization ratio, ρ_l, for a totally symmetric vibration (A_g) approaches 1/3 at that resonance.[12]

(11) A. C. Albrecht and M. C. Hutley, *J. Chem. Phys.*, **55**, 4438 (1971).

(12) R. E. Hester, *Raman Spectrosc.*, Chapter 4 (1967).

(13) Reference 2, p 26.

(14) Although the crystal structure of $K_4[Ru_2OCl_{10}]$ does not indicate a difference between the lengths of the terminal and radial chlorine–ruthenium bonds, such differences were frequently unobserved in early x-ray crystal structures. Indeed, a recent single-crystal x-ray determination has revealed such a difference exists in the ion $[Os_2OCl_{10}]^{4-}$ (see text). In light of the close similarity between the Raman spectra of $[Ru_2OCl_{10}]^{4-}$ and $[Os_2OCl_{10}]^{4-}$, it is likely that a more accurate redetermination of the structure of $K_4Ru_2OCl_{10}$ will reveal that the terminal chlorine–ruthenium bond is significantly longer than the radial chlorine–ruthenium bond. Thus, the longer and, therefore, presumably weaker $Ru-Cl_t$ bond is assumed to absorb at a lower frequency than the shorter $Ru-Cl_r$ bond.

(15) K.-F. Tebbe and H. G. von Schnering, *Z. Anorg. Allg. Chem.*, **396**, 66 (1973).

(16) We were repeatedly unsuccessful in our efforts to prepare the bromo analogue $Cs_4[Os_2OBr_{10}]$.

(17) O. Olsson, *Ber. Dtsch. Chem. Ges.*, **46**, 566 (1913); E. König, *Inorg. Chem.*, **2**, 1238 (1963).

(18) R. Colton and G. G. Rose, *Aust. J. Chem.*, **21**, 883 (1968).

(19) E. König, *Inorg. Chem.*, **8**, 1278 (1969).

(20) R. Colton and R. H. Farthing, *Aust. J. Chem.*, **21**, 589 (1968).

(21) R. Saillant, J. L. Hayden, and R. A. D. Wentworth, *Inorg. Chem.*, **6**, 1497 (1967).

(22) E. Pedersen, *Acta Chem. Scand.*, **26**, 333 (1972).

(23) (a) A. Feltz, *Z. Anorg. Allg. Chem.*, **358**, 21 (1968); (b) *ibid.*, **335**, 304 (1965).

(24) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Wiley, New York, N.Y., 1972, p 842.

(25) F. W. B. Einstein and B. P. Penfold, *Acta Crystallogr.*, **17**, 1127 (1964).

(26) H. Stammreich, D. Bassi, O. Sala, and H. Siebert, *Spectrochim. Acta*, **13**, 192 (1958); D. V. Luu and M. Abenoza, *C. R. Hebd. Seances Acad. Sci., Ser. B*, **269**, 208 (1968), and references therein.

(27) S. Schneider and R. L. Collin, *Inorg. Chem.*, **12**, 2136 (1973).

(28) E. Steger and B. Kassner, *Z. Anorg. Allg. Chem.*, **355**, 131 (1967).

(29) J. Behringer, *Raman Spectrosc.*, Chapter 6 (1967); W. Holzer, W. F. Murphy, and H. J. Bernstein, *J. Chem. Phys.*, **52**, 399 (1970); W. Kiefer and H. J. Bernstein, *Mol. Phys.*, **27**, 835 (1972); J. San Filippo, Jr., and H. J. Sniadoch, *Inorg. Chem.*, **12**, 2326 (1973); R. J. H. Clark and P. D. Mitchell, *J. Chem. Soc., Chem. Commun.*, 762 (1973); R. J. H. Clark and P. D. Mitchell, *J. Am. Chem. Soc.*, **95**, 8300 (1973); T. Kamisuki and S. Maeda, *Chem. Phys. Lett.*, **21**, 330 (1973); A. Ranade and M. Stockburger, *Chem. Phys. Lett.*, **22**, 257 (1973); H. Hamaguchi, I. Harada, and T. Shimanouchi, *Chem. Lett.*, 1049 (1973); Y. M. Bosworth and R. J. H. Clark, *Chem. Phys. Lett.*, **28**, 611 (1974); M. Booth, R. J. Gillespie, and M. J. Morton, *Adv. Raman Spectrosc.*, **1**, 364 (1973); G. J. Kubas and T. G. Spiro, *Inorg. Chem.*, **12**, 1797 (1973); T. G. Spiro and T. C. Strekas, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 2622 (1972); L. A. Nafie, M. Pezolet, and W. L. Peticolas, *Chem. Phys. Lett.*, **20**, 563 (1973); R. J. H. Clark and M. L. Franks, *J. Am. Chem. Soc.*, **97**, 2691 (1975); T. C. Strekas and T. G. Spiro, *Inorg. Chem.*, **14**, 1421 (1975), and references therein.

(30) J. San Filippo, Jr., R. L. Grayson and H. J. Sniadoch, in preparation.

(31) A. B. Hoffman et al., *J. Am. Chem. Soc.*, **94**, 3620 (1972).

(32) W. Kiefer and H. J. Bernstein, *Appl. Spectrosc.*, **25**, 500, 609 (1971).

(33) J. L. Woodhead and J. H. Fletcher, Report No. 4123, A.E.R.E., Harwell, England, 1962.

(34) F. P. Dwyer and J. W. Hogarth, *J. Proc. R. Soc. N.S.W.*, **84**, 194 (1950).

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Mechanistic Studies on the Vanadium(II) and Vanadium(III) Reductions of Iodate and Bromate

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Received July 21, 1975 AIC50517D

The kinetics of the vanadium(III) reduction of iodate have been investigated over a wide range of conditions, $\mu = 1.0\ M$ ($LiClO_4$). Rate constants, $[H^+] > 0.25\ M$, are dependent on the ratio of reactants R ($=[V(III)]_i/[I(V)]_i$) implying that disproportionation of an intermediate oxidation state, probably I(III), is effective at low V(III). The dependence of rate constants on $[H^+]$ indicates that the reaction proceeds by paths $V^{3+} + IO_3^-$ and/or $VOH^{2+} + HIO_3$, and the temperature dependence has been studied, 3–35°C. The V(II) reduction of iodate proceeds in 1-equiv steps. Rate constants obtained from consecutive reaction treatment, $[H^+] = 0.5$–$1.0\ M$, suggest that the pathway $V^{2+} + HIO_3$ ($k \geq 360\ M^{-1}\ sec^{-1}$ at 25°) is dominant. Brief studies of the V(II) and V(III) reductions of bromate have also been made. With V(II) small (0.07%) contributions from a 2-equiv process giving VO^{2+}, and hence the highly absorbing V^{III}_2 species as an intermediate, were detected.

Iodate and bromate function as 2-equiv oxidants in the reaction with hydrazine and sulfite.[1] Although many studies have been made of reactions of chlorate and bromate with metal complexes,[2-12] the reactions of iodate have with one exception[13] been neglected. Bromate is known to undergo a 2-equiv change in the oxidation of the mercury(I) dimer,[14] but 1-equiv changes are effective in other cases. We consider here the iodate and bromate oxidations of V(II) and V(III), both of which might be regarded as potential 2-equiv reductants. The single-stage change $V^{2+} \rightarrow VO^{2+}$ has been observed previously[15-17] and is clearly a possibility. The single-stage $V^{3+} \rightarrow VO_2^+$ change has not been detected, however,[18,19] and is more difficult to bring about because of the extensive change in degree of hydrolysis. The studies with iodate which we report are more extensive than those with bromate, which amount to little more than semiquantitative observations.

Experimental Section

Solutions of vanadium(II), vanadium(III), and vanadium(IV) perchlorates, lithium perchlorate, and perchloric acid were prepared as described previously.[15] Iodic acid (BDH Analar) and potassium bromate (Fisons Analytical Reagent) were used without further purification. A nitrogen gas stream was used to deoxygenate all solutions. Atlas nylon syringes, stainless steel needles, and rubber serum caps were used to maintain air-free conditions. Ionic strengths were adjusted to $\mu = 1.00\ M$ ($LiClO_4$). Unless otherwise stated reactions were followed spectrophotometrically using a Durrum-Gibson stopped-flow spectrophotometer.

Results

The Reaction of V(III) with Iodate. With a large excess of V(III) products VO^{2+}, λ_{max} 760 nm (ϵ 17.2 $M^{-1}\ cm^{-1}$), and I_2, λ_{max} 460 nm (ϵ 746 $M^{-1}\ cm^{-1}$),[20] are obtained in the first stage. Stopped-flow measurements indicate that 0.46 ± 0.05 mol of I_2 and 5.02 ± 0.4 mol of VO^{2+} are formed for each mole of iodate present initially. On completion of a second stage no I_2 remains and 6.0 ± 0.1 mol of VO^{2+} is produced for each mole of iodate. The two stages of the reaction can thus be summarized as in (1) and (2). The second stage has

$$5V(III) + I(V) + 2H_2O \rightarrow {}^1/_2I_2 + 5VO^{2+} + 4H^+ \qquad (1)$$

$$V(III) + {}^1/_2I_2 + H_2O \rightarrow I^- + VO^{2+} + 2H^+ \qquad (2)$$

been studied independently by Ramsay and Heldman[21] and from their data the half-life at 25°, $[H^+] = 0.5\ M$, [V(III)]

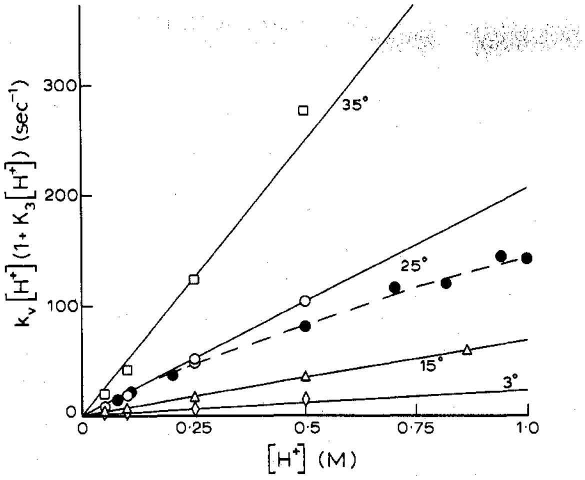

Figure 1. Dependence of the function $k_V[H^+](1 + K_3[H^+])$ on $[H^+]$ with $[V(III)] = 0.012\,M$, $[I(V)] = 2.5 \times 10^{-4}\,M$, and $\mu = 1.00$ ($LiClO_4$) (open points) and with $[V(III)] = 1.38 \times 10^{-3}\,M$, $[I(V)] = 3.23 \times 10^{-3}\,M$ and $\mu = 1.00\,M$ ($LiClO_4$) (solid points, 25°).

= 0.01 M, is ca. 40 min. For the first stage the rate of appearance of I_2 and VO^{2+} exhibits good first-order kinetics. Allowing for the 10:1 stoichiometry factor, rate constants are equal; thus

$$\frac{2\mathrm{d}[I_2]}{\mathrm{d}t} = \frac{1}{5}\frac{\mathrm{d}[VO^{2+}]}{\mathrm{d}t} = \frac{-\mathrm{d}[I(V)]}{\mathrm{d}t} = k_V'[I(V)]$$

The pseudo-first-order rate constant k_V' is proportional to V(III) and decreases in a complex manner as $[H^+]$ increases. It is known that IO_3^- is protonated in strong acid solution ($K_3 \approx 2\,M^{-1}$, 25°, $\mu = 1.0\,M$,[22] (3), and that V^{3+} undergoes acid

$$H^+ + IO_3^- \overset{K_3}{\rightleftharpoons} HIO_3 \tag{3}$$

dissociation ($K_4 \approx 3 \times 10^{-3}\,M$, 25°C, $\mu = 1.0\,M$),[23] (4).

$$V^{3+} + H_2O \overset{K_4}{\rightleftharpoons} VOH^{2+} + H^+ \tag{4}$$

There are therefore four possible formulations, (5)–(8), of the

$$V^{3+} + HIO_3 \xrightarrow{k_5} \tag{5}$$

$$V^{3+} + IO_3^- \xrightarrow{k_6} \tag{6}$$

$$VOH^{2+} + HIO_3 \xrightarrow{k_7} \tag{7}$$

$$VOH^{2+} + IO_3^- \xrightarrow{k_8} \tag{8}$$

rate-determining step. From this scheme, assuming $K_4 \ll [H^+]$, the predicted $[H^+]$ dependence of the second-order rate constant k_V is

$$k_V = \frac{k_5K_3[H^+]}{1 + K_3[H^+]} + \frac{k_6 + k_7K_3K_4}{1 + K_3[H^+]} + \frac{k_8K_4}{[H^+](1 + K_3[H^+])}$$

The relative importance of the three terms can be investigated by plotting $k_V[H^+](1 + K_3[H^+])$ against $[H^+]$, where k_8K_4 is the intercept, $k_6 + k_7K_3K_4$ is the slope, and k_5K_3 causes nonlinearity. Such plots are shown in Figure 1 (open points). Within the limits of experimental error the plots are linear and pass through the origin, from which it can be concluded that the only important term is $k_6 + k_7K_3K_4$. From the temperature dependence of k_V, using a nonlinear least-squares program with weighting $1/k_V^2$, and values $\Delta H_3 = 0.709$ kcal mol^{-1} and $\Delta S_3 = -3.78$ cal K^{-1} mol^{-1},[22] activation parameters (25°) $\Delta H^{\ddagger} = 15.2 \pm 0.9$ kcal mol^{-1}, $\Delta S^{\ddagger} = 2.7 \pm 3.0$ cal K^{-1} mol^{-1} were obtained for $k_6 + k_7K_3K_4$. Experimental values of k_V are compared with calculated values, Table I. It is not possible to distinguish further between contributions from (6) and (7).

Table I. $[H^+]$ and Temperature Dependence of Rate Constants (λ 760 nm) for the Reaction of V(III) (0.012 M) with I(V) ($2.5 \times 10^{-4}\,M$), $\mu = 1.0\,M$ ($LiClO_4$)

Temp, °C	$[H^+]$, M	k_V M^{-1} sec^{-1}	k_V(calcd),[a] M^{-1} sec^{-1}
3.0	0.05	19.9	20.6
	0.10	19.5	19.0
	0.25	16.7	15.4
	0.50	15.4	11.7
15.0	0.05	53.9	67.7
	0.10	58.1	62.2
	0.25	48.1	50.0
	0.50	36.3	37.7
	0.86	26.3	27.9
25.0	0.05	150	170
	0.10	160	155
	0.25	136	124
	0.25	127	124
	0.50	104	92.9
	0.86	78.1	68.3
	0.86	77.0	68.3
35.0	0.05	358	401
	0.10	336	366
	0.25	325	290
	0.5	264	216

[a] Calculated from the expression $(k_6 + k_7K_3K_4)/(1 + K_3[H^+])$ where activation parameters for the composite term $(k_6 + k_7K_3K_4)$ are given by $\Delta H^{\ddagger} = 15.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = 2.7$ cal K^{-1} mol^{-1}, and $\Delta H_3 = 0.709$ kcal mol^{-1} and $\Delta S_3 = -3.78$ cal K^{-1} mol^{-1}.

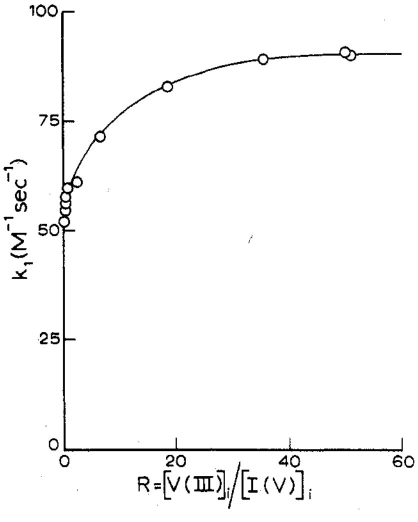

Figure 2. Dependence of k_1(25°) on R ($=[V(III)]_i/[I(V)]_i$) with $[H^+] = 0.82\,M$ and $\mu = 1.00\,M$ ($LiClO_4$).

With a large excess of iodate the reaction products are VO^{2+} and I_2, and 1.0 ± 0.1 mol of I_2 is produced for each 10 mol of V^{3+} consumed. No subsequent reaction between VO^{2+} and IO_3^- is observed. The rates of formation of I_2 and VO^{2+} are first order in $[V^{3+}]$ and $[I(V)]$, where k_I can be defined as

$$\frac{2\mathrm{d}[I_2]}{\mathrm{d}t} = \frac{\mathrm{d}[VO^{2+}]}{5\mathrm{d}t} = \frac{-\mathrm{d}[V(III)]}{5\mathrm{d}t} = \frac{-\mathrm{d}[I(V)]}{\mathrm{d}t} = k_I[V(III)][I(V)]$$

At 25° and $[H^+] = 0.82\,M$, rate constants k_I ($\equiv k_V$ or k_I) are dependent on the ratio of initial reactant concentrations, $R = [V(III)]_i/[I(V)]_i$, Figure 2. A similar dependence on R has been observed previously in the reaction of VO^{2+} and Br(V),[9] where it is believed to arise from competition between disproportionation of an intermediate oxidation state (Br(III)) and reaction of the same intermediate with VO^{2+}. A scheme, (9)–(11), involving I(III), can be invoked in the present case.

$$2V(III) + I(V) \rightarrow 2V(IV) + I(III) \qquad (9)$$

$$I(III) + I(III) \rightarrow I(V) + I(I) \qquad (10)$$

$$2V(III) + I(III) \rightarrow 2V(IV) + I(I) \qquad (11)$$

The precise identity of the intermediate dose not affect the discussion. As the relative concentration of V(III) drops (R decreases), reaction 10 becomes more important compared with (11), and the observed rate constant decreases as reaction 10 re-forms I(V). In the limit as $R \rightarrow 0$, the observed rate constant should approach half of the rate constant observed when V(III) is in large excess and reaction proceeds through (9) and (11). From Figure 2 it can be seen that although the upper limit is apparently reached, a lower limit is not and the ratio of intercept to limiting values is approximately 1:1.7. The possibility that for a given R value k_1 is dependent on actual values of the reactant concentrations used was not investigated.

At low [H$^+$] the ratio effect becomes less significant. Thus in Figure 1 we compare data $R = 50$ already discussed (open circles) with the further set of data $R = 0.42$ (closed circles). At [H$^+$] = 0.82 M the dependence on R is significant and is as illustrated in Figure 2, but at low [H$^+$] (<0.2 M) the difference disappears. This implies that the protonated form of the intermediate (HIO$_2$) disproportionates more rapidly than the unprotonated form and hence that competition as in (10) and (11) becomes significant only at the higher [H$^+$] values. This behavior is well-known in the disproportionation of Cl(III),[24] where alkaline solutions are stable almost indefinitely.

Although the initially observable products of the reaction of V(III) with I(V) are VO^{2+} and I$_2$, this does not necessarily rule out formation of VO$_2^+$ as a primary product in a 2-equiv reaction, (12). The subsequent reaction of V(III) with VO$_2^+$,

$$5V(III) + 2I(V) \rightarrow 5V(V) + I_2 \qquad (12)$$

(13) (k_{13} = 243 M^{-1} sec^{-1}, [H$^+$] = 1.0 M, 25°C, I = 2.00

$$V(III) + VO_2^+ \rightarrow 2VO^{2+} \qquad (13)$$

M),[25] is more rapid than (12). No evidence for VO$_2^+$ formation was obtained.

The Reaction of V(III) with Bromate. With a large excess of bromate the reaction gives VO$_2^+$ and Br$_2$ as final products, (14). The reaction proceeds in two discernible stages, the first

$$5V(III) + 2Br(V) \rightarrow 5V(V) + Br_2 \qquad (14)$$

one (in the stopped-flow range) producing V(IV). This is followed by the slower reaction of VO^{2+} and Br(V) to produce VO$_2^+$. The latter has already been studied.[9] With a large excess of V(III) the products are VO^{2+} and Br$^-$ in the ratio 6:1, (15). Under these conditions the production of VO^{2+}

$$6V(III) + Br(V) \rightarrow 6V(IV) + Br^- \qquad (15)$$

monitored at 760 nm does not follow a simple pseudo-first-order rate law but exhibits two stages, the first being about twice as fast as the second under typical conditions [V(III)] = 0.0119 M, [Br(V)] = 5 × 10^{-4} M, [H$^+$] = 0.83 M, and 25°C. If a first-order dependence on V(III) is assumed and the primary reaction of V(III) with Br(V) corresponds to one of the observed stages, it can be estimated that k_{15} is in the range 3–6 M^{-1} sec^{-1}. In view of the various complications, and those observed for the V(III) reduction of iodate, no further attempts were made to investigate the system.

The Reaction of V^{2+} with Iodate. The products obtained with excess I(V) are as in (16). The reaction proceeds in two

$$5V^{2+} + 2I(V) \rightarrow 5V(IV) + I_2 \qquad (16)$$

stages which can be distinguished when [H$^+$] > 0.5 M.

Table II. Rate Constants Determined for the Reaction of V^{2+} with Iodate by Consecutive Reaction Treatment (λ 460 nm)[a]

Temp, °C	[H$^+$], M	10^3[V^{2+}], M	10^3[I(V)], M	k_{17}, M^{-1} sec^{-1}	k_{18}, M^{-1} sec^{-1}
0.3	1.0	1.04	12.5	60.5	5.68
	1.0	0.745	7.0	41.7	5.72
	1.0	0.745	14.0	54.0	4.85
	0.82	1.375	3.64	49.5	6.69
	0.70	1.04	12.5	44.0	7.05
	0.60	1.04	12.5	33.6	7.70
	0.50	1.04	12.5	30.5	7.90
	0.50	1.04	12.5	32.6	8.05
25.0	1.0	0.745	7.0	245	43.7
	1.0	0.745	14.0	210	50.1
	1.0	0.745	7.0	201	49.3

[a] The first stage k_{17} corresponds to the V^{2+} reduction of I(V), and the second k_{18}, to the V(III) reduction of I(V), μ = 1.0 M (LiClO$_4$).

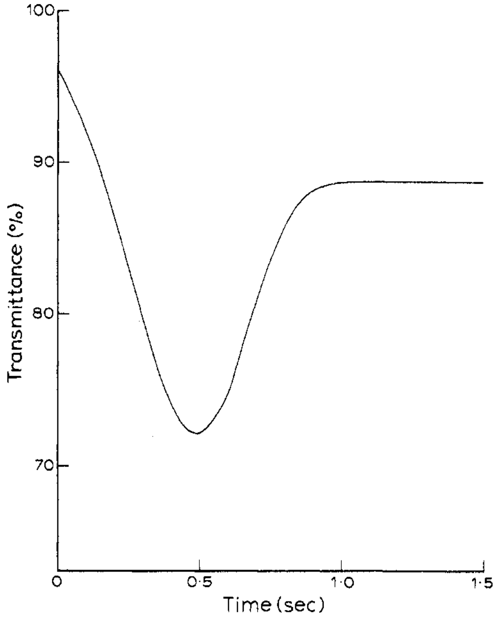

Figure 3. A typical transmittance against time curve for the reaction of I(V) with a large excess of V^{2+} at 20°; [V^{2+}] = 0.012 M, [I(V)] = 5 × 10^{-4} M, [H$^+$] = 0.5 M, μ = 1.00 M (LiClO$_4$), λ 420 nm.

Stopped-flow observations of the I$_2$ produced, λ 460 nm, show that absorbance changes for the two stages are equal (±10%). They can therefore be formulated as (17) and (18). Rate

$$5V^{2+} + I(V) \rightarrow 5V(III) + {}^1/{}_2I_2 \qquad (17)$$

$$5V(III) + I(V) \rightarrow 5V(IV) + {}^1/{}_2I_2 \qquad (18)$$

constants k_{17} and k_{18}, Table II, were obtained by simple consecutive first-order treatment.[26] Values of k_{18} for the second stage are equal to those obtained for the V(III) + I(V) reaction at low R values (intercept, Figure 2). Over the restricted [H$^+$] range k_{17} shows a positive dependence on [H$^+$], but as the mechanism of the reaction with excess I(V) is probably complicated by disproportionation of intermediates (cf. V(III) + I(V)), this observation is of limited significance. If it is assumed that HIO$_3$ is the only reactive species, then from the data at [H$^+$] = 1.0 M, Table II, a rate constant of ca. 360 M^{-1} sec^{-1} at 25° can be estimated for the reaction V^{2+} + HIO$_3$. No investigation of the dependence of the observed rate constants on the ratio [V^{2+}]$_i$/[I(V)]$_i$ was possible because in the presence of excess V^{2+} complications are apparent (see below). If a ratio dependence is observed, then the rate constant for the reaction of V^{2+} with HIO$_3$ could be up to a factor of 2 greater than the apparent rate constant.

A typical transmittance against time curve with a large

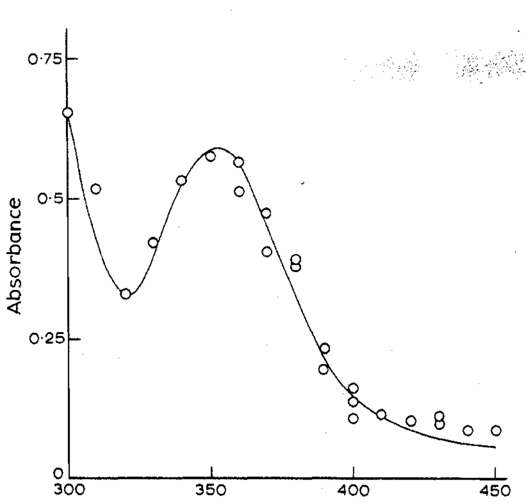

Figure 4. Spectrum of the intermediate in the reaction of I(V) with a large excess of V^{2+} (points), compared with the spectrum of I_3^- (line).

excess of V^{2+} (λ 420 nm) is shown in Figure 3. The form is complex requiring at least two processes for the formation and one for the decay of the intermediate, maximum concentration in 0.5 sec. The spectrum of the intermediate, Figure 4, was taken point by point from stopped-flow traces at a variety of wavelengths and corresponds to that of I_3^- (λ_{max} 353 nm, ϵ 2.64×10^4 M^{-1} cm^{-1}).[20] Qualitative observations on the rate of formation and removal of the intermediate indicate processes which are first order in $[V^{2+}]$ and, for the removal, approximately independent of $[H^+]$. The rates of reaction of I_2 and I_3^- with V^{2+} have been determined as 7.5×10^3 and 9.7×10^2 M^{-1} sec^{-1}, respectively.[27] The maximum concentration of I_3^- observed in Figure 3 is ca. 1.3×10^{-5} *M* reached after 0.5 sec, but the decay is rapid (from the latter portion of the trace $t_{1/2} < 0.1$ sec). Triiodide exists in equilibrium with I_2 and I^- (19), K_{19} being ca. 782 M^{-1}.[28]

$$I_2 + I^- \rightleftharpoons I_3^- \tag{19}$$

Iodide is not present initially but is built up as I_2 or I_3^- is reduced by V^{2+}, (20). The total concentration of iodine

$$2V^{2+} + I_2 \rightarrow 2V(III) + 2I^- \tag{20}$$

species, $[I^-] + 2[I_2] + 3[I_3^-]$, cannot exceed the initial I(V) concentration. Assuming that all the I(V) is consumed and I_2, I_3^-, and I^- are the only iodine species present in significant amounts, it can be concluded that at maximum $[I_3^-]$ other concentrations are $[I_2] = 4.5 \times 10^{-5}$ *M* and $[I^-] = 3.7 \times 10^{-4}$ *M*. Thus the concentration of I_3^- does not reach a maximum until (20) has gone through 2 half-lives (≡20 msec). As the maximum is reached after 0.5 sec, it can be concluded that the rate of formation of I_3^- is not solely controlled by the rate of formation of I^- from I_2 but that (17) leading to the formation of I_2 from I(V) is probably rate limiting.

With excess V^{2+} any VO^{2+} formed from a 2-equivalent reduction of I(V), or any intermediate species, by V^{2+} would react to produce the V(III) dimer,[29] VOV^+ or $V(OH)_2V^{4+}$, which subsequently decays to give V(III),[30] (21) and (22).

$$V^{2+} + VO^{2+} \rightarrow V^{III}{}_2 \tag{21}$$

$$V^{III}{}_2 + 2H^+ \rightarrow 2V(III) + H_2O \tag{22}$$

The rate of decay of $V^{III}{}_2$ is dependent on $[H^+]$, and although the formation of $V^{III}{}_2$ (λ_{max} 425 nm, ϵ ca. 6800 M^{-1} cm^{-1}) could not be observed due to the intermediate I_3^-, at low $[H^+]$ (<0.1 *M*) any $V^{III}{}_2$ formed should outlast the I_3^- by a considerable amount. Absorbance measurements after the disappearance of I_3^- at low $[H^+]$ correspond to those expected for V^{3+} formed in a 6:1 stoichiometry from I(V). No excess absorbance attributable to $V^{III}{}_2$ was observed. It is concluded that the amount of VO^{2+} formed in the reaction is <0.02% of the V(III) formed.

The Reaction of V^{2+} with Bromate. The reaction was investigated with a large excess of V^{2+}. An important feature is that an increase in absorbance at 420 nm is observed followed by a decrease, the final spectrum corresponding to a stoichiometric mixture of V^{2+}, V^{3+}, and Br^-, (23). Both the

$$6V^{2+} + Br(V) \rightarrow 6V(III) + Br^- \tag{23}$$

rate of formation and the rate of decay of the intermediate increased with increasing $[H^+]$. At low $[H^+]$ (ca. 0.07 *M*) the intermediate was sufficiently long-lived to observe by conventional spectrophotometry. The peak at 420 nm disappeared with a rate constant of 4.67×10^{-3} sec^{-1} at 25°C. This can be compared with the known properties of $V^{III}{}_2$,[29,30] the rate constant for the disappearance being 4.4×10^{-3} sec^{-1} under the same conditions. It is concluded that 0.07% of (23) proceeds via a 2-equiv route, to yield VO^{2+} which reacts as in (21) and (22).

The rate of formation of $V^{III}{}_2$ displays two phases which can be analyzed in terms of consecutive first-order processes with rate constants of 0.135 and 0.062 sec^{-1} ($[V^{2+}] = 0.012$ *M*, $[H^+] = 0.07$ *M*, 25°, $\mu = 1.0$ *M*). The faster process which may correspond to the first or second stage of the reaction producing $V^{III}{}_2$ compares with the rate constant of 0.150 sec^{-1} calculated for the reaction of V^{2+} with VO^{2+} and can be attributed to (21). If the slower step involves Br(V), then it must correspond to the reaction with V^{2+}, having a second-order rate constant of 6.2 M^{-1} sec^{-1}, which increases with increasing $[H^+]$; at $[H^+] > 0.5$ *M* it becomes impossible to separate this reaction from the $[H^+]$-independent reaction of V^{2+} with VO^{2+}.

Discussion

This study has shown that the reaction of V^{2+} with I(V) proceeds entirely by 1-equiv changes. A small proportion of the reaction of V^{2+} with Br(V) (0.07%) occurs in a 2-equiv redox step. Such a process need not necessarily occur in the initial redox step but could involve one of the bromine intermediates. The reaction of V^{2+} with Cl(V) has previously been investigated. Tanaka and Nakano[31] suggested from their polarographic study that some VO^{2+} is produced, possibly from the reaction of the hypochlorite intermediate with V^{2+}, but Gordon and Tewari from a spectrophotometric study[2] indicated that V^{3+} is the only product. It can be concluded that 1-equiv reactions are predominant in the reactions of oxyhalogen species with V^{2+}.

Of the halate ions iodate is the only one to show appreciable protonation, (3).[22,32] The reaction of V^{2+} with I(V) exhibits a positive dependence on $[H^+]$ which suggests that $V^{2+} + HIO_3$, $k \geq 360$ M^{-1} sec^{-1} at 25°, is the dominant reaction. Unlike Cl(V)[33] and Br(V),[34] HIO_3 is a labile species,[35,36] and rate constants for the reaction of HIO_3 with two aquo complexes (to give iodato complexes)[37] have been shown to be of the same order of magnitude as for exchange with solvent water, i.e., ca. 10^4 sec^{-1}. The rate constant for substitution on V^{2+} is ca. 10 M^{-1} sec^{-1} for a univalent anion.[38] Thus although substitution of HIO_3 into the V^{2+} coordination sphere cannot precede electron transfer, substitution of V^{2+} into the I(V) coordination sphere is a possibility. The need for the IO_3^- to be protonated is consistent with such an inner-sphere reaction. The V^{2+} reduction of Cl(V) is independent of $[H^+]$,[2] and the rate constant of 4.8 M^{-1} sec^{-1} is sufficiently close to the rate of substitution on V^{2+} to suggest that the redox process is controlled by this substitution. However the enthalpy and entropy of activation are 9.9 kcal mol^{-1} and −23 cal K^{-1} mol^{-1}, compared with values 13.5 kcal mol^{-1} and −2 cal K^{-1} mol^{-1}

Table III. Rate Constants (25°) for Reactions of V(III) with Halate Ions

Reaction	Rate const, M^{-1} sec^{-1}
$V^{3+} + IO_3^-$	189[a]
V^{3+} + Br(V)	3-6[b]
$V^{3+} + ClO_3^-$	2.0[c]

[a] This work; reaction may also be assigned to $VOH^{2+} + HIO_3$ in some part. [b] This work; [H$^+$] dependence not investigated; [H$^+$] = 0.83 *M*, [V(III)] = 0.012 *M*, [Br(V)] = 5 × 10^{-4} *M*. [c] Unpublished work, quoted in ref 4; temperature 20°, [H$^+$] = 0.5–0.6 *M*, μ = 2.0–3.0 *M*.

for the complexing of NCS^- with V^{2+}.[38] It is concluded that substitution of chlorate into the V^{2+} coordination sphere does not occur prior to electron transfer. No conclusions can be drawn regarding the mechanism of the V^{2+} reduction of Br(V) based on present information.

One- and two-equivalent reactions of V^{3+} are less easily distinguished because the reaction of VO_2^+ with V^{3+} is rapid[25] and produces the 1-equiv product VO^{2+}, (13). None of the reactions of I(V), Br(V), or Cl(V), Table III, exceeds the rate of this reaction so that a distinction cannot be made on this basis. If however a 2-equiv process occurred, then extensive hydrolysis of the V(III) would have to precede formation of VO_2^+ or a less hydrolyzed (and therefore less stable) form of V(V) would be produced. In either case relatively high enthalpies of activation would be required. If the k_6 ($V^{3+} + IO_3^-$) step prevails, then there is no prior hydrolysis of the V^{3+} reactant, and it is difficult to envisage a 2-equiv change. For the $k_7K_3K_4$ ($VOH^{2+} + HIO_3$) path the enthalpy of activation for k_7 will be small (ca. 5 kcal mol^{-1}) after allowing for ΔH_3[22] and ΔH_4[23] and hardly seems consistent with a 2-equiv change. Moreover observations on the V(III) reduction of the strong oxidant Tl(III) have indicated that in this instance 1-equiv reactions are favored.[18,19]

Substitution on V^{3+} is thought to proceed by an associative mechanism with rate constants varying between 3 M^{-1} sec^{-1} for Cl^- [39] and 10^3 M^{-1} sec^{-1} for NCS^-.[40,41] The reactions of the halate ions, Table III, lie within this range, and it is therefore possible that they proceed by inner-sphere mechanisms.

Registry No. V(III), 22541-77-1; V(II), 15121-26-3; iodate, 15454-31-6; bromate, 15541-45-4.

References and Notes

(1) See, e.g., A. G. Sykes, *Adv. Inorg. Chem. Radiochem.*, **10**, 232 (1967).
(2) G. Gordon and P. H. Tewari, *J. Phys. Chem.*, **70**, 200 (1966).
(3) W. S. Melvin and G. Gordon, *Inorg. Chem.*, **11**, 1912 (1972).
(4) B. Z. Shakhashiri and G. Gordon, *J. Am. Chem. Soc.*, **91**, 1103 (1969).
(5) G. Gordon and F. Feldman, *Inorg. Chem.*, **3**, 1728 (1964).
(6) R. C. Thompson and G. Gordon, *Inorg. Chem.*, **5**, 557 (1966).
(7) R. C. Thompson and G. Gordon, *Inorg. Chem.*, **5**, 562 (1966).
(8) J. P. Birk and S. G. Kozub, *Inorg. Chem.*, **12**, 2460 (1973).
(9) R. C. Thompson, *Inorg. Chem.*, **10**, 1892 (1971).
(10) R. C. Thompson, *J. Am. Chem. Soc.*, **93**, 7315 (1971).
(11) G. C. Knight and R. C. Thompson, *Inorg. Chem.*, **12**, 63 (1973).
(12) W. C. E. Higginson and M. E. Simpson, *J. Chem. Soc., Chem. Commun.*, 817 (1974).
(13) Y. Sulfab and H. A. Elfaki, *Can. J. Chem.*, **52**, 2001 (1974).
(14) R. Davies, B. Kipling, and A. G. Sykes, *J. Am. Chem. Soc.*, **95**, 7250 (1973).
(15) M. Green and A. G. Sykes, *J. Chem. Soc. A*, 3221 (1970); 3067 (1971).
(16) F. B. Baker, W. D. Brewer, and T. W. Newton, *Inorg. Chem.*, **5**, 1295 (1966).
(17) J. H. Swinehart, *Inorg. Chem.*, **4**, 1069 (1965).
(18) W. C. E. Higginson, D. R. Rosseinsky, J. B. Stead, and A. G. Sykes, *Discuss. Faraday Soc.*, **29**, 53 (1960).
(19) N. A. Daugherty, *J. Am. Chem. Soc.*, **87**, 5026 (1965).
(20) A. D. Awtry and R. E. Connick, *J. Am. Chem. Soc.*, **73**, 4546 (1951).
(21) J. B. Ramsay and M. J. Heldman, *J. Am. Chem. Soc.*, **58**, 1153 (1936).
(22) J. Ramette, *J. Chem. Educ.*, **36**, 191 (1959); R. Furuichi, I. Matsuzaki, R. Simic, and H. A. Liebhafsky, *Inorg. Chem.*, **11**, 952 (1972).
(23) B. Jezowska-Trzebiatowska and L. Pajdowski, *Proc. Int. Conf. Coord. Chem.*, **5**, Abstract 129 (1959); S. C. Furman and C. S. Garner, *J. Am. Chem. Soc.*, **72**, 1785 (1950).
(24) R. G. Kieffer and G. Gordon, *Inorg. Chem.*, **7**, 235, 239 (1968).
(25) N. A. Daugherty and T. W. Newton, *J. Phys. Chem.*, **68**, 612 (1964).
(26) A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms", 2nd ed, Wiley, New York, N.Y., 1961, p 167.
(27) J. M. Malin and J. H. Swinehart, *Inorg. Chem.*, **8**, 1409 (1969).
(28) L. I. Katzin and E. Geburt, *J. Am. Chem. Soc.*, **77**, 5814 (1955).
(29) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **68**, 228 (1964).
(30) T. W. Newton and F. B. Baker, *Inorg. Chem.*, **3**, 569 (1964).
(31) K. Tanaka and K. Nakano, *J. Electroanal. Chem. Interfacial Electrochem.*, **48**, 399 (1973).
(32) A. Kossiakoff and D. Harker, *J. Am. Chem. Soc.*, **60**, 2047 (1938).
(33) T. C. Hoering, F. T. Ishimari, and H. O. McDonald, *J. Am. Chem. Soc.*, **80**, 3876 (1958).
(34) T. C. Hoering, R. C. Bulter, and H. O. McDonald, *J. Am. Chem. Soc.*, **78**, 4829 (1956).
(35) M. Anbar and S. Guttmann, *J. Am. Chem. Soc.*, **83**, 781 (1961).
(36) R. A. Dwek, Z. Luz, S. Peller, and M. Shporer, *J. Am. Chem. Soc.*, **93**, 77 (1971).
(37) R. K. Wharton, R. S. Taylor, and A. G. Sykes, *Inorg. Chem.*, **14**, 33 (1975).
(38) J. M. Malin and J. H. Swinehart, *Inorg. Chem.*, **7**, 250 (1968).
(39) R. C. Patel and H. Diebler, *Ber. Bunsenges. Phys. Chem.*, **76**, 1035 (1972).
(40) W. Kruse and D. Thusius, *Inorg. Chem.*, **7**, 464 (1968).
(41) B. R. Baker, N. Sutin, and T. J. Welch, *Inorg. Chem.*, **6**, 1948 (1967).

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Comprehensive Study of Satellite Structure in the Photoelectron Spectra of Transition Metal Compounds

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Received August 11, 1975 AIC50598D

A wide variety of different transition metal compounds have been studied for their satellite structure found in photoelectron spectra, with specific emphasis on the 2p shell of the first-row transition metals. In particular, data on halides and cyanide complexes are presented. Results on second- and third-row transition metal compounds are also discussed. The relative roles of electron shake-up and multiplet splitting for producing the satellite structure are evaluated. The behavior of the satellite structure is generalized as a function of metal ion and ligand and the energy spacing of the metal and ligand orbitals. It is ascertained that the large, well-defined satellite peaks are due to electron shake-up involving excitation of electrons from a ligand to a metal orbital.

Introduction

Some satellite structure is commonly observed in most photoelectron spectra. It is the result of the ejected electron created in the photoejection process undergoing some energy loss. This loss can be caused by either internal or external means. In the latter case the photoelectrons undergo inelastic collisions as they pass through the material. Such losses are characteristic of the material but not of the photoionization process. For most insulators the satellite structure due to

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