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A Kinetic Study of the Two-Stage Oxidation of the Tantalum Halide Cluster Ion $(Ta_6Br_{12})^{2+}$ by Vanadium(V)[1]
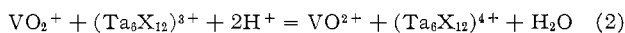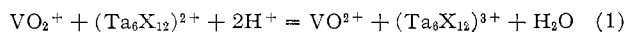
By JAMES H. ESPENSON

Vanadium(V) oxidizes $(Ta_6Br_{12})^{2+}$ in perchloric acid solution in two steps to $(Ta_6Br_{12})^{3+}$ and to $(Ta_6Br_{12})^{4+}$. The second-stage reaction follows the rate equation $-d[(Ta_6Br_{12})^{3+}]/dt = [(Ta_6Br_{12})^{3+}](k_{34} + k'_{34}[H^+][VO_2^+])[VO_2^+]$; at 25.0° and $\mu = 0.500\ M$, $k_{34} = 1.14 \pm 0.07\ M^{-1}\ sec^{-1}$ and $k'_{34} = 1.17 \pm 0.05 \times 10^4\ M^{-3}\ sec^{-1}$. The novel second term in this rate expression suggests either participation of a rapidly equilibrating vanadium(V) dimer or else involvement of a cluster species of net ionic charge greater than $4+$. The relative law for the first step of oxidation is $-d[(Ta_6Br_{12})^{2+}]/dt = k_{23}[(Ta_6Br_{12})^{2+}][VO_2^+][H^+] + k_c[(Ta_6Br_{12})^{3+}]$ with $k_c = (k_{34} + k'_{34}[H^+][VO_2^+])[VO_2^+]$. A method based on the Guggenheim procedure was developed for treating the autocatalytic kinetic data. The value of k_{23} is $2.1 \times 10^2\ M^{-2}\ sec^{-1}$ at 25.0° and $\mu = 0.50\ M$. Autocatalysis results from a pathway involving the rate-determining oxidation of the product $(Ta_6Br_{12})^{3+}$ by VO_2^+, followed by the rapid reproportionation reaction of $4+$ and $2+$ cluster ions.

Introduction

Cluster ions composed of tantalum and halogen atoms have the general form $(Ta_6X_{12})^{n+}$, with the species having $n = 2$, 3, and 4 being well characterized for bromine and chlorine compounds.[2] Conversion from one oxidation state to another can be accomplished readily be common oxidizing and reducing agents. The cluster unit remains intact during the course of these reactions, and a quantitative recovery of $(Ta_6X_{12})^{2+}$ is achieved upon adding Cr^{2+} or V^{2+} to a previously oxidized solution. Prolonged treatment with an excess of strong oxidizing agent will, however, result in disruption of the cluster framework, eventually leading to precipitation of Ta_2O_5.

In acid solution both $(Ta_6Cl_{12})^{2+}$ and $(Ta_6Br_{12})^{2+}$ are oxidized by vanadium(V), VO_2^+, in two distinct stages, as shown in eq 1 and 2. The two stages of

$$VO_2^+ + (Ta_6X_{12})^{2+} + 2H^+ = VO^{2+} + (Ta_6X_{12})^{3+} + H_2O \quad (1)$$

$$VO_2^+ + (Ta_6X_{12})^{3+} + 2H^+ = VO^{2+} + (Ta_6X_{12})^{4+} + H_2O \quad (2)$$

oxidation are known to be well separated in potential,[3] and the reproportionation reaction (eq 3) lies well

$$(Ta_6X_{12})^{2+} + (Ta_6X_{12})^{4+} = 2(Ta_6X_{12})^{3+} \quad (3)$$
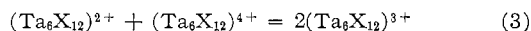
toward the right. Despite the much greater reducing strength of $(Ta_6X_{12})^{2+}$ over $(T_6X_{12})^{3+}$, we find that reaction of the latter with V(V) constituted a major

pathway for the reaction of $(Ta_6X_{12})^{2+}$ with V(V). The additional pathway of this unusual type caused a number of complications in treating the kinetic data. A procedure not unlike the Guggenheim approach for first-order kinetics was developed that allowed treatment of the autocatalytic kinetic data.

Experimental Section

Materials.—Aqueous solutions containing the tantalum cluster cations $(Ta_6Cl_{12})^{2+}$ and $(Ta_6Br_{12})^{2+}$ were prepared by dissolving in water purified samples of $Ta_6Cl_{14}\cdot 8H_2O$, $K_4Ta_6Cl_{18}$, or Ta_6Br_{14}.[4] Such solutions were used without further purification. Some preparations were additionally recrystallized from water one or two times. The recrystallization had no effect on the rate measurements and we concluded that catalytic impurities probably were absent.

Vanadium(V) perchlorate solutions were prepared by dissolving the purified pentoxide in excess perchloric acid. An alternate source of the material was commercial V_2O_5, and such solutions gave identical rates.

Lithium perchlorate was recrystallized twice before use. Conductivity water, redistilled from alkaline permanganate, was used throughout.

Procedures.—The reactions were monitored by spectrophotometry, generally following the decrease in $[(Ta_6X_{12})^{2+}]$ at its intense peak at 6370 Å. Further oxidation of $(Ta_6Br_{12})^{3+}$ to $(Ta_6Br_{12})^{4+}$ could be studied most conveniently using the 7150-Å peak of the 3+ cluster. A Cary Model 14 recording spectrophotometer equipped with a water-filled constant-temperature compartment[5] was used for these studies.

$(Ta_6X_{12})^{2+}$ **Analyses.**—Solutions of $(Ta_6X_{12})^{2+}$ were analyzed by

(1) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission; Contribution No. 2203.

(2) P. J. Kuhn and R. E. McCarley, *Inorg. Chem.*, **4**, 1482 (1965).

(3) J. H. Espenson and R. E. McCarley, *J. Am. Chem. Soc.*, **88**, 1063 (1966).

· (4) These preparations were carried out according to published recipes.[2] We are grateful to Dr. R. E. McCarley, Mr. J. L. Meyer, and Mr. J. G. Converse for these materials.

(5) J. H. Espenson, *J. Am. Chem. Soc.*, **86**, 5101 (1964).

a procedure that amounted to a spectrophotometric titration at fixed wavelength. Varying amounts of an oxidizing agent were added to a given volume of $(Ta_6X_{12})^{2+}$ solution in a series of volumetric flasks. The absorbance of each solution was read at 6370 Å. A plot of absorbance (D) vs. moles of oxidizing agent was linear below the equivalence point. The break was quite sharp, and from its position the number of moles of $(Ta_6X_{12})^{2+}$ was computed, assuming a 1:1 stoichiometry for the oxidation reaction. This assumption was confirmed for $(Ta_6Br_{12})^{2+}$ by use of three independent reactions using independently analyzed solutions. The oxidizing agents used were Ce^{IV}, VO_2^+, and Fe^{3+}, as perchlorates, in perchloric acid. The analyses were identical within experimental error $(\pm 3\%)$; we took such agreement as a check on the analysis method and on the assumed stoichiometry. A fourth analysis of the same solution was carried out by first converting it to $(Ta_6Br_{12})^{3+}$. The same type of spectrophotometric analysis procedure was employed, using the reduction of $(Ta_6Br_{12})^{3+}$ with Cr^{2+} to $(Ta_6Br_{12})^{2+}$. This result was again in agreement with the other three methods. Each analysis also afforded values of the molar absorptivities of $(Ta_6X_{12})^{2+}$. At the 6370-Å maximum, the values are: Cl, ϵ 6200 M^{-1} cm^{-1}; Br, ϵ 7100 M^{-1} cm^{-1}. Most subsequent solutions of $Ta_6X_{12}^{2+}$ were analyzed on the assumption of these values, and the more tedious titration procedure was used only rarely.

Since most rate experiments had a large excess of vanadium(V) over $(Ta_6X_{12})^{2+}$, knowledge of the precise starting concentration of the latter was not necessary in most cases.

Results and Interpretation

Oxidation of $(Ta_6Br_{12})^{3+}$.—As mentioned earlier, the second stage of oxidation provides one major pathway for the first stage. Appropriate data from the reaction of $(Ta_6Br_{12})^{3+}$ and VO_2^+ were needed to interpret the first stage correctly, and oxidation of $(Ta_6Br_{12})^{3+}$ will be considered first. The stoichiometry given in eq 2 was verified by examining the spectra of the materials produced by treating a given solution of $(Ta_6X_{12})^{3+}$ with an equivalent concentration of several strong oxidizing agents, VO_2^+, $Ce(IV)$, and $HCrO_4^-$. The final spectrum was quantitatively the same, in band positions and intensities, for all solutions. We took this coincidence as strong support for the simple stoichiometry given in eq 2.

Most rate experiments were carried out with the bromide cluster. The excess of VO_2^+ was sufficiently great that its concentration remained nearly constant during reaction. The initial concentration of $(Ta_6Br_{12})^{3+}$ was varied from 1 to 4 × 10^{-5} M. The reaction obeyed pseudo-first-order kinetics for runs that were followed generally to 90% completion. The first-order rate constant so computed is defined by the equation

$$-d[(Ta_6Br_{12})^{3+}]/dt = k'[(Ta_6Br_{12})^{3+}]$$

A series of runs was carried out at 25.0°, $\mu = 0.50$ M, $[H^+] = 0.500$ M over a 30-fold range of initial VO_2^+ concentrations 1.7–49 × 10^{-4} M. The pseudo-first-order behavior persisted over the entire range of concentrations, which spanned half-times of 5.7–1320 sec. The dependence of k' was not a simple linear relation in $[VO_2^+]$, but indicated both first- and second-order paths. The data for 0.500 M H^+ are given in Table I. The last column tabulates values of $k'/[VO_2^+]$, and there is a regular and sizable increase in its value with increasing $[VO_2^+]$. A plot of log k'

TABLE I
KINETIC DATA FOR THE REACTION OF $(Ta_6Br_{12})^{3+}$ AND VO_2^+ AT 25.0°, $\mu = 0.50$ M, AND $[H^+] = 0.500$ M

$10^5[(Ta_6Br_{12})^{2+}]_0$, M	$10^4[VO_2^+]$,[a] M	Obsd $t_{1/2}$, sec	$k'/[VO_2^+]$, M^{-1} sec^{-1}
2.1	1.74	1320	3.0
4.2	3.50	515	3.8
2.1	3.70	484	3.87
4.2	3.80	460	3.96
4.0	4.94	323	4.84
2.0	5.24	294	4.50
2.1	7.90	158	5.55
2.0	13.5	63.0	8.15
2.1	16.1	46, 47.5	9.21
2.0	21.8	26.8	11.9
2.1	32.5	12.3, 12.0	17.5
2.0	32.9	12.4	16.9
2.1	48.9	5.75	24.7

[a] Average $[VO_2^+]$ in each run. The change in $[VO_2^+]$ during a run never exceeded 10%.

vs. log $[VO_2^+]$ is shown in Figure 1; the graph has limiting slopes of $+1$ at low $[VO_2^+]$ and $+2$ at high $[VO_2^+]$.
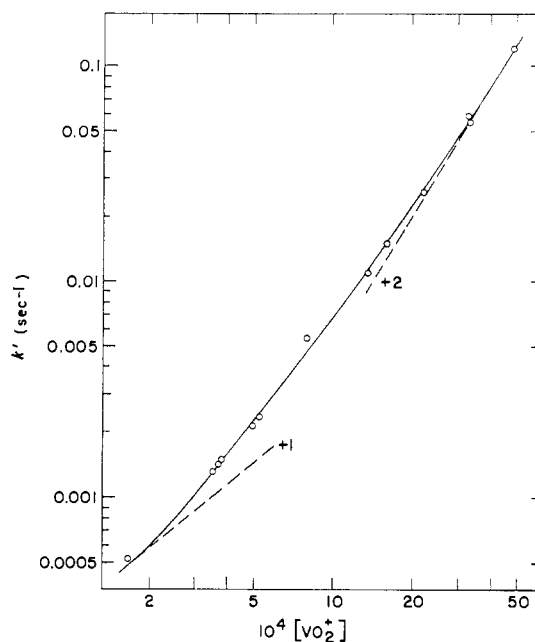

Figure 1.—Illustrating by a log–log plot the changing order with respect to $[VO_2^+]$ in the reaction of VO_2^+ with $(Ta_6Br_{12})^{3+}$. Data refer to 25.0° and 0.500 M H^+ at $\mu = 0.50$ M. The broken lines are drawn with slopes of $+1$ and $+2$.

The rate equation suggested by these results is given in eq 4, which requires that a plot of $k'/[VO_2^+]$

$$-d[(Ta_6Br_{12})^{3+}]/dt = (k'' + k'''[VO_2^-])[VO_2^+][(Ta_6Br_{12})^{3+}]$$
(4)

vs. $[VO_2^+]$ be linear. This plot is shown in Figure 2, and the data are seen to follow this relation over the entire concentration range, leading to the values $k'' = 2.2$ M^{-1} sec^{-1}, $k''' = 4.6 \times 10^3$ M^{-2} sec^{-1} at 0.500 M H^+ and 25.0°.

Hydrogen Ion Effects on $(Ta_6Br_{12})^{3+}$ Oxidation.—The effect of changes in $[H^+]$ on the rate of oxidation of $(Ta_6Br_{12})^{3+}$ by VO_2^+ were studied in a series of solu-
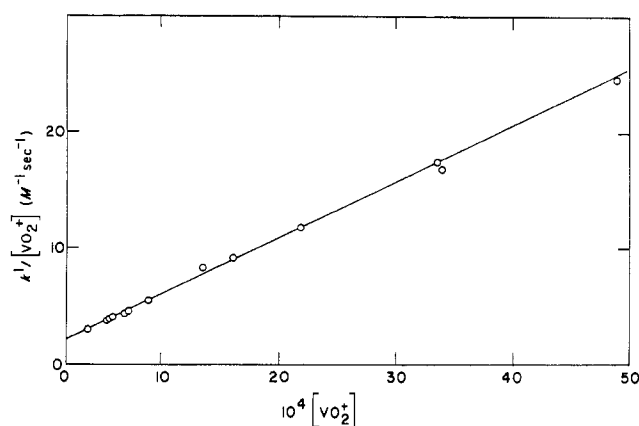
Figure 2.—Illustrating evaluation of k'' and k''' as suggested by eq 5. Data refer to 25.0° and 0.500 M H$^+$.

tions in which ionic strength was held constant at 0.50 M by addition of lithium perchlorate. Rate studies were carried out at [H$^+$] = 0.125, 0.180, and 0.250 M, in addition to those at [H$^+$] = 0.500 M cited earlier. The general trend of the rate behavior was a decrease in rate constant with decreasing [H$^+$]. This dependence could not have been predicted from the net reaction, but the positive order in hydrogen ion is not a surprising result. It has been noted[6] in a large number of reductions of oxo cations that it generally appears profitable to add some but not all of the required protons prior to or at the rate-determining step.

Plots similar to that in Figure 2 were prepared at each [H$^+$] studied. The intercept was roughly constant, but the slope of each varied with [H$^+$]. To a first approximation its value was directly proportional to [H$^+$], suggesting relation 5. The rate parameters k_{34} and k'_{34}, according to eq 4 and 5, are k'' and k'''[H$^+$]. To eliminate the prejudicial fitting of data first to eq 4, and the values so obtained to eq 5, both variables,

$$-d \ln [(Ta_6Br_{12})^{3+}]/dt = (k_{34} + k'_{34}[H^+][VO_2^+])[VO_2^+] \quad (5)$$

[VO$_2^+$] and [H$^+$], were considered simultaneously. The individual data k' ([VO$_2^+$], [H$^+$]) were fitted to the functional form of eq 5 by means of a nonlinear least-squares program,[7] with the result that k_{34} = 1.14 ± 0.07 M^{-1} sec^{-1} and k'_{34} = 1.17 ± 0.05 × 10^4 M^{-3} sec^{-1}.

Oxidation of (Ta$_6$Br$_{12}$)$^{2+}$.—The stoichiometry given in eq 1 for the reaction of (Ta$_6$Br$_{12}$)$^{2+}$ and VO$_2^+$ was substantiated on the basis that the same analytical result for (Ta$_6$Br$_{12}$)$^{2+}$ was obtained with this reaction as with several independent methods.[8] The kinetics of the first-stage reaction was considerably more complex. Most runs were studied at 6370 Å, where the high molar absorptivity of (Ta$_6$-Br$_{12}$)$^{2+}$ ensured that the absorbance change was essentially that due to a decrease in (Ta$_6$Br$_{12}$)$^{2+}$. The

(6) T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, **63**, 368 (1959).

(7) Based on a report from Los Alamos Scientific Laboratory, LA 2367 plus addenda. We are grateful to Drs. T. W. Newton and R. H. Moore for supplying these programs.

(8) Note that the spectrophotometric readings at 6370 Å after the end points, say, 1 ≤ [VO$_2^+$]$_0$/[(Ta$_6$Br$_{12}$)$^{2+}$]$_0$ ≤ 1.2, would not be affected appreciably by reaction 2 since both of the higher oxidation states absorb much less than (Ta$_6$Br$_{12}$)$^{2+}$ at this wavelength.

concentrations of VO$_2^+$ were generally at least tenfold higher than that of the tantalum cluster and remained nearly constant during the run. Plots prepared according to a first-order expression were uniformly curved downward. This type of behavior is illustrated by Figure 3 which shows data for a typical experiment plotted as log ($D - D_\infty$) vs. time.
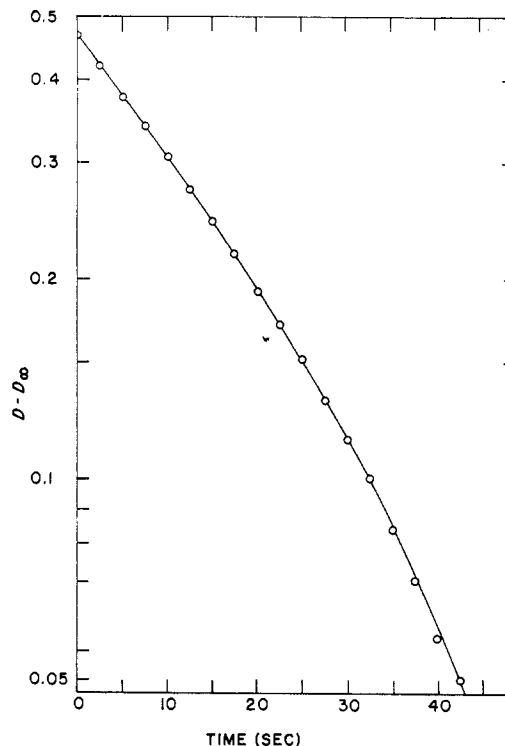

Figure 3.—Conventional pseudo-first-order plot of ($D - D_\infty$) (log scale) vs. time in the reaction of (Ta$_6$Br$_{12}$)$^{2+}$ with VO$_2^+$ studied at 6370 Å. Data refer to 25.0° and 0.500 M H$^+$, fifth entry in Table II.

Curvature in the direction indicated implied either that the apparent reaction order with respect to [(Ta$_6$Br$_{12}$)$^{2+}$] was less than first or that a catalyst was being generated at increasing concentration as the reaction progressed. The former was ruled out by examining the initial rate at various concentrations of (Ta$_6$Br$_{12}$)$^{2+}$, which indicated a first-order dependence on [(Ta$_6$Br$_{12}$)$^{2+}$]. It was then assumed that the oxidized form of the tantalum cluster, (Ta$_6$Br$_{12}$)$^{3+}$, produced an accelerating effect on the reaction. The interpretation tentatively ascribed to the effect influenced the subsequent treatment, and this interpretation will be considered first. It was proposed that the postulated autocatalysis involved the rate-determining reaction of (Ta$_6$Br$_{12}$)$^{3+}$ with VO$_2^+$ (eq 2), followed by rapid reproportionation of 4+ and 2+ cluster ions (eq 3). The former occurs at a known rate, with a known dependence upon [VO$_2^+$] and [H$^+$], eq 5. This model leads to a rate equation (eq 6), valid at constant

$$-d[(Ta_6Br_{12})^{2+}]/dt = k[(Ta_6Br_{12})^{2+}] + k_c[(Ta_6Br_{12})^{3+}] \quad (6)$$

[VO$_2^+$], where eq 7 describes the relation between k_c

$$k_c = k''[VO_2^+] + k'''[VO_2^+]^2 \quad (7)$$

and the rate constants for reaction 2.

With the abbreviation $M = (Ta_6Br_{12})$, the mass balance relation becomes $[M^{3+}] = [M^{3+}]_0 + [M^{2+}]_0 - [M^{2+}]$. Substitution into eq 6 and rearrangement gives an expression (eq 8) that can be inte-

$$-d[M^{2+}]/dt = (k - k_c)[M^{2+}] + k_c([M^{2+}]_0 + [M^{3+}]_0) \quad (8)$$

grated between initial time and any given time. The result is given in eq 9, in which the time-independent term of eq 8 is abbreviated α. As eq 9 stands it is

$$\ln\left[\frac{(k - k_c)[M^{2+}] + \alpha}{(k - k_c)[M^{2+}]_0 + \alpha}\right] = -(k - k_c)t \quad (9)$$

difficult to apply to the data for computation of k since its value enters in the ln expression as well as in the coefficient of t.

An extension of the method Guggenheim[9] developed for simple first-order kinetics appeared capable of handling the situation.[10] Equation 9 was solved for $[M^{2+}]$ at a given time t (eq 10). A second and analo-

$$[M^{2+}]_t = [-\alpha/(k - k_c)] + \{[M^{2+}]_0 + [\alpha/(k - k_c)]\} \times \exp[(-k - k_c)t] \quad (10)$$

gous equation holds for a time later by a constant interval τ. Substraction of the two relations and rearrangement gave the result in eq 11. Only the last member

$$[M^{2+}]_t - [M^{2+}]_{t+\tau} = \{[M^{2+}]_0 + [\alpha/(k - k_c)]\} \times \{1 - \exp(-k - k_c)\tau\} \exp[-(k - k_c)t] \quad (11)$$

on the right is time dependent. Hence a plot of log $(D_t - D_{t+\tau})$ vs. time should be linear with a slope from which the difference $(k - k_c)$ is immediately computed. The plot for a typical experiment is given in Figure 4. Results of experiments under the conditions $[H^+] = 0.50\ M$, $\mu = 0.50\ M$, and 25.0° are given in Table II. The correction term k_c is computed according to eq 7 from the known values of k_{34} and k'_{34}. Values of k so computed are seen to vary directly with $[VO_2^+]$, leading to an expression (eq 12) for the rate

$$-d[Ta_6Br_{12}^{2+}]/dt = k'_{23}[(Ta_6Br_{12})^{2+}][VO_2^+] \quad (12)$$

of direct oxidation of $(Ta_6Br_{12})^{2+}$ by VO_2^+ in solutions with $[(Ta_6Br_{12})^{3+}] = 0$. Under the conditions given above, the value of k'_{23} is $96 \pm 6\ M^{-1}\ sec^{-1}$.

The proposed role of $(Ta_6Br_{12})^{3+}$ as a catalyst for eq 1 was substantiated, and the form of the rate law (eq 6) was subjected to an additional test by a series of experiments carried out on the rate of reaction 1 in the presence of added $(Ta_6Br_{12})^{3+}$. The rate of reaction followed the predicted pattern according to eq 6: at increasing concentrations of added $(Ta_6Br_{12})^{3+}$ the time needed for substantially complete reduction grew shorter. The reactions became so rapid, in fact, that accurate data were obtained for only a few runs. In one experiment at 25.0° and 0.500 M H^+ the starting concentrations were $[(Ta_6Br_{12})^{2+}]_0 = 2.06 \times 10^{-5}\ M$, $[(Ta_6Br_{12})^{3+}]_0 = 5.07 \times 10^{-5}\ M$, and $[VO_2^+]_0 = 4.11 \times 10^{-4}\ M$. The data were treated by the modified Guggenheim procedure. The appropriate plot according to eq 11 led to a value of

(9) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

(10) The identical kinetic situation arose in the oxidation of V^{3+} by Co^{3+} [D. R. Rosseinsky and W. C. E. Higginson, *J. Chem. Soc.*, **31** (1960)], where the data were treated by a procedure involving successive approximations.
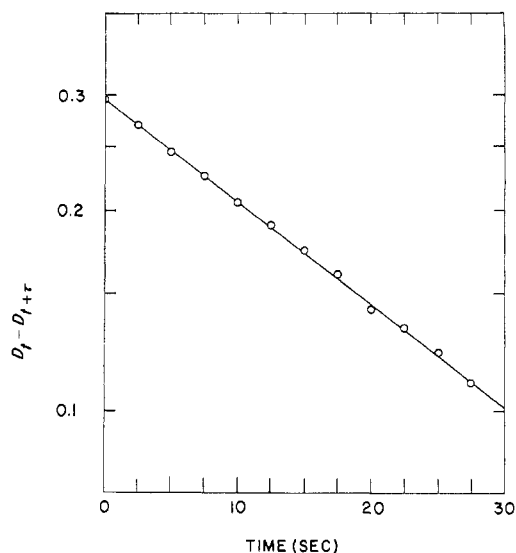

Figure 4.—Plot according to the modified Guggenheim relation (eq 11). Same data as for Figure 3.

TABLE II

KINETIC DATA FOR THE REACTION OF $(Ta_6Br_{12})^{2+}$ AND VO_2^+ AT 25.0°, $\mu = 0.50\ M$, AND $[H^+] = 0.500\ M$

10^5 [$(Ta_6Br_{12})^{2+}]_0$, M	10^4 [VO_2^+],[a] M	$(k - k_c)$[b]/ [VO_2^+], $M^{-1}\ sec^{-1}$	k_c[c]/ [VO_2^+], $M^{-1}\ sec^{-1}$	$k'_{23} = k/[VO_2^+]$, $M^{-1}\ sec^{-1}$
2.1	1.96	83	3.0	86
4.2	3.9	90	3.9	94
2.1	4.0	92	3.9	96
4.2	4.0	102	3.9	106
1.1	4.0	84	3.9	88
2.1	8.1	89	6.1	95
2.1	16.3	97	9.5	106

Av $k'_{23} = 96 \pm 6$

[a] The average value during a run. The change in $[VO_2^+]$ was $\leq 10\%$ in an experiment. [b] The value of $(k - k_c)$ was obtained from the slope of the Guggenheim-type plot suggested by eq 5. [c] The value of k_c was computed according to eq 7, from the known rate constants for the reaction of $(Ta_6Br_{12})^{3+}$ and VO_2^+.

0.0412 sec^{-1} for $k - k_c$. The value of k'_{23} computed was 107 $M^{-1}\ sec^{-1}$, in satisfactory agreement with values from runs in the absence of added $(Ta_6Br_{12})^{3+}$.

Hydrogen Effects on $(Ta_6Br_{12})^{2+}$ Oxidation.—Experiments were carried out to study the effect of $[H^+]$ on the rate of reaction 1. The data were treated by the modified Guggenheim method described earlier, and the value of k'_{23} computed from the slope and the known value of k_c applicable to a given $[VO_2^+]$ and $[H^+]$ according to eq 5 and 7. In addition to the runs at $[H^+] = 0.500\ M$, experiments were carried out at $[H^+] = 0.125$, 0.180, and 0.250 M, in which lithium perchlorate was added to maintain constant ionic strength. The values of k'_{23} ($M^{-1}\ sec^{-1}$) were as follows: 0.125 M H^+, 32 ± 3; 0.180 M, 39 ± 3; 0.250 M, 56 ± 4; and 0.500 M, 96 ± 6. The simplest interpretation of these data one can offer is that they correspond to a single-term rate law (eq 13) with a first-order dependence upon $[H^+]$. Considering the precision of the data a more complicated expression for the variation of k'_{23} with $[H^+]$

1

s not justified. The best value of k_{23} is 2.1×10^2 M^{-2} sec^{-1} at 25.0° and $\mu = 0.50$ M.

$$-d[(Ta_6Br_{12})^{2+}]/dt = k_{23}[VO_2^+][(Ta_6Br_{12})^{2+}][H^+] \quad (13)$$

Discussion

The mechanism of the reaction of $(Ta_6Br_{12})^{2+}$ and VO_2^+ can be represented by the net activation process[6] given in eq 14. This represents the direct pathway for this reaction and the only direct one that we detected under the conditions employed. The reaction

$$(Ta_6Br_{12})^{2+} + VO_2^+ + H^+ = [(Ta_6Br_{12})VO_2H^{4+}]\ddagger \quad (14)$$
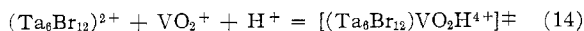
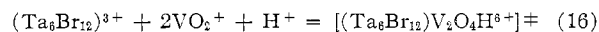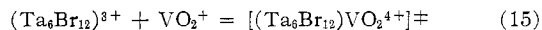appears to be the expected 1-equiv oxidation–reduction process.

Over the range of hydrogen ion concentrations $0.125 \leq [H^+] \leq 0.500$ M at low vanadium(V) concentrations, one singly charged vanadium(V) species predominates,[11] represented by the formula VO_2^+ or $V(OH)_4^+$. A reasonable postulate for the role of hydrogen ion is that the mechanism involves attack of H^+ at a vanadium(V) oxygen, thereby assisting the conversion of $VO_{2,aq}^+$ to $(H_2O)_4VO^{2+}$.

The indirect pathway has been formulated as a product-catalyzed reaction followed by reproportionation (eq 3). For this proposed two-step process to be valid, two requirements must be satisfied. First, the reproportionation process must be rapid relative to the reaction of $(Ta_6Br_{12})^{3+}$ with VO_2^+, which has been verified.[12] Second, the rate constant for the catalytic pathway must agree with the independently known value for the reaction of $(Ta_6Br_{12})^{3+}$ and VO_2^+. In practice we assumed the latter values in treating the data by the modified Guggenheim approach. The residual rate gave constant values for k_{23}, which was taken as evidence that k_c had been correctly related to k_{34} and k'_{34}.

The mechanism of the reaction of $(Ta_6Br_{12})^{3+}$ and

VO_2^+ involves two parallel pathways that differ in the roles of V(V) and H$^+$. In a formal sense the mechanism can be represented by the net activation process[6] for each pathway

$$(Ta_6Br_{12})^{3+} + VO_2^+ = [(Ta_6Br_{12})VO_2^{4+}]\ddagger \quad (15)$$

$$(Ta_6Br_{12})^{3+} + 2VO_2^+ + H^+ = [(Ta_6Br_{12})V_2O_4H^{6+}]\ddagger \quad (16)$$

Existence of a path depending upon $[VO_2^+]^2$ seemed quite remarkable, for the net reaction (eq 2) involves but an over-all 1-equiv change in oxidation state. The step given by eq 16 must be followed by either of two rapid reactions to give a stoichiometry and rate expression that are internally consistent. The activated complex produced in the rate-determining process given in eq 16 must form an unstable intermediate, which might be either a previously uncharacterized tantalum cluster ion $(Ta_6Br_{12})^{5+}$, or a vanadium dimer, $V_2O_4H^{2+}$, with an average oxidation number of 4.5. The second step would then be rapid reduction of the 5+ cluster to $(Ta_6Br_{12})^{4+}$ by reaction with VO^{2+}, or decomposition of the vanadium dimer.

The alternatives presented refer to reactions subsequent to the rate-determining step. Consequently, a distinction between them cannot be obtained from a kinetic study. The hypothetical 5+ cluster may perhaps be implicated since the instability of the cluster framework in the prolonged presence of an excess of strong oxidizing agent has been noted. On the other hand, a precedent for the vanadium dimer model is known. The rate of V(IV)–V(V) electron exchange follows the expression[13] $k[VO^{2+}][VO_2^+]^2$. Present data are not sufficient to allow even a tentative decision in favor of one of the alternatives.

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