The Kinetics of the Aqueous Vanadium(II)–Halogen Reactions

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The kinetics of the vanadium(II)–triiodide, –iodine, and –bromine reactions were studied. In each case a first-order rate dependence on the concentrations of vanadium(II) and of the halogen oxidant was found. The rate constants and activation parameters are (oxidant, $k_{25°}$, $\Delta H^{\pm}$, and $\Delta S^{\pm}$): I_3^-, $(9.7 \pm 0.2) \times 10^2 \ M^{-1} \ \text{sec}^{-1}$, 9.1 ± 0.2 kcal/mol, and -14 ± 1 eu; I_2, $(7.5 \pm 0.5) \times 10^3 \ M^{-1} \ \text{sec}^{-1}$, 5.9 ± 0.5 kcal/mol, -21 ± 2 eu; and Br_2, $(3.0 \pm 0.4) \times 10^4 \ M^{-1} \ \text{sec}^{-1}$, 3.5 ± 1.2 kcal/mol, -26 ± 4 eu. The mechanism for these reactions is discussed.

Introduction

The mechanisms by which aqueous vanadium(II), $V(H_2O)_6{}^{2+} \equiv V^{2+}$, acts as a reducing agent have been discussed in some detail.[1,2] It has been concluded that for many of the reactions studied the replacement of a water molecule in the first coordination sphere of the V^{2+} by the oxidizing agent is the rate-determining step. That conclusion is based on the similarity between the rate constants[3-5] and activation parameters[5] for the complexation reaction between V^{2+} and SCN^-, and those for the oxidation–reaction reactions.[1,2] This paper reports the results of complete kinetic studies of the aqueous V^{2+}–triiodide (I_3^-), –iodine (I_2), and –bromine (Br_2) reactions. Some results on the V^{2+}–tribromide (Br_3^-) and –chlorine (Cl_2) reactions are also reported.

Experimental Section

Materials.—Vanadium(II) perchlorate solutions were prepared by reducing vanadium(IV) perchlorate in solution at known concentrations using zinc amalgam. The vanadium(IV) concentration was determined spectrophotometrically using the extinction coefficient $\epsilon_{VO^{2+}}$ 17.17 $M^{-1} \ \text{cm}^{-1}$ at 758 mμ.[6] To make vanadium(IV) perchlorate solutions, solid vanadium(IV) hydroxide was dissolved in perchloric acid. Vanadium(IV) hydroxide was precipitated from solutions of Fisher purified vanadyl sulfate by dropwise addition of saturated ammonium carbonate solution.[7] Precipitation was carried out repeatedly until the vanadium(IV) perchlorate solution showed the absence of sulfate ion when tested with 1 M barium perchlorate.

The free acid concentration in vanadium(II) solutions was calculated from the known free acid concentration in the original vanadium(IV) solution assuming consumption of 2 mol of hydrogen ion per mole of vanadium(IV) reduced. The free acid concentration in solutions of vanadium(IV) perchlorate was determined using a Beckman Expandomatic pH meter equipped with a Beckman general purpose glass electrode and a Leeds and Northrup calomel electrode. The saturated KCl solution of the calomel electrode was replaced with 4 M LiCl. The pH meter was calibrated using solutions of known hydrogen ion concentration whose ionic strength was adjusted with zinc perchlorate.

Ionic strength was maintained by the addition of lithium perchlorate solution. Saturated lithium perchlorate solution, 4.47 M,[8] was made by maintaining saturated lithium perchlorate solution in equilibrium with solid lithium perchlorate at 25°. Lithium perchlorate, which was recrystallized, was prepared by the addition of Baker and Adamson 70% perchloric acid to Mallinkrodt 99.5% lithium carbonate.

Solutions of vanadium(II) and of the halogens were prepared in a nitrogen atmosphere. Any residual oxygen in the nitrogen was removed by passing the nitrogen stream through a chromium(II) scrubbing solution which was kept in contact with zinc amalgam.

Elemental chlorine was obtained in cylinders (Matheson) and was passed through an acidified sodium chloride solution before use. Reagent grade liquid bromine and solid, resublimed iodine obtained from Mallinkrodt Chemical Works and Baker and Adamson Chemical Co., respectively, were used without further purification.

Concentrations of the halogens in acidic perchlorate solution were determined spectrophotometrically. Values of the extinction coefficients ϵ of the various halogen species were as follows [oxidant; ϵ, $M^{-1} \ \text{cm}^{-1}$; (wavelength, mμ)]: Cl_2,[9] 5.0 (254), 26.3 (289), 75.3 (325); Cl_3^-,[9] 3311 (254), 180 (289), 192 (325); Br_2,[10] 145 (365), 127 (436); Br_3^-,[10] 974 (365), 183 (436); I_2,[11] 121 (270), 746 (460); I_3^-,[11] 26,400 (353), 40,000 (287).

Reagent grade sodium and lithium halide salts were obtained from Fisher Chemical Co. and J. T. Baker Chemical Co.

Measurements.—To determine the extent of vanadium(IV) formation in mixtures of halogen species with excess vanadium(II), solutions of vanadium(II) were mixed with halogen solutions in spectrophotometer cells which had been capped with Parafilm, sealed with rubber septum caps, and vented with purified nitrogen.

Spectrophotometric data were obtained using a Cary Model 14 recording spectrophotometer (Applied Physics Corp.). Reaction rates were followed spectrophotometrically using a Gibson-Durrum stopped-flow device (Durrum Instrument Co., Palo Alto, Calif.). The instrument has a minimum 99.5% mixing time of 2 msec and can be thermostated to ±0.5°. The course of the chemical reaction was followed by changes in light transmission.

In all mixing experiments involving the consumption of trihalide ion, the two solutions to be mixed were prepared having the same halide ion concentration. The assumption of lability in the equilibria forming the trihalide species from aqueous halogen and the halide ion was checked in the iodine and bromine cases. All attempts to measure by stopped-flow technique the rate of equilibration at low concentrations of the species involved were defeated by the lability of the equilibria. Previous workers have shown that iodine–triiodide equilibration is very rapid.[12,13]

(1) H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968).
(2) N. Sutin, *Accounts Chem. Res.*, **1**, 225 (1968).
(3) B. R. Baker, M. Orhanovic, and N. Sutin, *J. Am. Chem. Soc.*, **89**, 722 (1967).
(4) W. Kruse and D. Thusius, *Inorg. Chem.*, **7**, 464 (1968).
(5) J. M. Malin and J. H. Swinehart, *ibid.*, **7**, 250 (1968). Note: $\Delta S^{\pm}$ for the $V^{2+} + SCN^-$ reaction should be -7 ± 4 eu.
(6) M. Barrett, Ph.D. Thesis, Stanford University, 1968.
(7) F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, **9**, 1177 (1955).

(8) J. P. Simmons and C. D. L. Ropp, *J. Am. Chem. Soc.*, **50**, 1650 (1928), quoted in "Solubilities of Organic and Metal-Inorganic Compounds," A. Seidell, Ed., Vol. 2, 4th ed, American Chemical Society, Washington, D. C., 1965, p 408.
(9) G. Zimmerman and F. C. Strong, *J. Am. Chem. Soc.*, **79**, 2063 (1957).
(10) A. C. Rutenberg and H. Taube, *ibid.*, **73**, 4426 (1951).
(11) A. D. Awtrey and R. E. Connick, *ibid.*, **73**, 4426 (1951).
(12) O. E. Myers, *J. Chem. Phys.*, **28**, 1027 (1958).
(13) M. Eigen and K. Kustin, *J. Am. Chem. Soc.*, **84**, 1355 (1962).

Values of k_1, the observed pseudo-first-order rate constant for disappearance of halogen species, were calculated as the slopes of plots of ln $[(A_\infty - A_0)/(A_\infty - A)]$ vs. time. A_∞ was the measured absorbance after at least 10 half-lives, A_0 was the initial absorbance, and A was the absorbance at time t. In the reactions of V^{2+} with I_2, I_3^-, and Br_2, these plots were linear over at least 3 half-lives indicating pseudo-first-order consumption of those halogen species in tenfold or greater excess vanadium(II).

Estimated errors in the activation parameters were calculated using the regression analysis method described by Laitinen.[14] Student's t values for a 50% confidence limit were applied.

Results

Stoichiometry and VO^{2+} Production.—For all of the reactions of halogens (X_2) or trihalides (X_3^-) with excess V^{2+} the stoichiometries were

$$2V^{2+} + X_2 = 2V^{3+} + 2X^-$$
$$2V^{2+} + X_3^- = 2V^{3+} + 3X^-$$
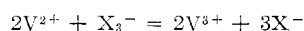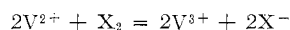
If any VO^{2+} was produced in the reaction between V^{2+} and X_2 or X_3^-, it would be consumed in excess V^{2+} by the reactions[15]

$$V^{2+} + VO^{2+} \rightleftharpoons VOV^{4+}$$
$$VOV^{4+} + 2H^+ \longrightarrow 2V^{3+} + H_2O$$
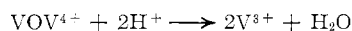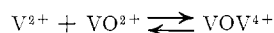
It has already been shown that the intermediate in the V^{2+}–VO^{2+} reaction, VOV^{4+}, can be used as a sensitive probe of the production of VO^{2+} in the reactions between excess V^{2+} and O_2 and H_2O_2.[16] Table I contains

Table I
Oxidation of V^{2+} to VO^{2+} by Halogens[a]

X_2	$[X^-]$, M	10^3[oxidizing agent],[b] M	10^2 $[V^{2+}]$,[c] M	ΔD^d	10^{-3} $\Delta D^{e,g}/$ $[V^{2+}]\cdot$ $[VO^{2+}]$	Q^f
Cl_2	0.70	4.2	5.3	0.14	0.63	7
Cl_2	0.01	1.2	3.5	0.03	0.72	8
Cl_2	...	10.1	5.3	0.11	0.21	2
Br_2	0.23	2.2	7.1	0.04	0.25	3
Br_2	...	0.8	5.3	0.02	0.47	5
I_2	0.23	0.9	7.1	0.01	0.16	2
I_2	...	0.9	7.1	0.01	0.16	2
VO^{2+}	0.70 (Cl^-)	0.5	8.8	0.38	8.5	...
VO^{2+}	0.10 (Br^-)	1.1	8.8	0.90	9.3	...
VO^{2+}	0.23 (I^-)	1.5	3.5	0.48	9.1	...
VO^{2+}	...	1.5	3.5	0.48	9.1	...
VO^{2+}	0.01 (Cl^-)	1.2	7.1	0.72	8.5	...

[a] Temperature 22°; $\mu = 1.0$ (HClO$_4$, LiClO$_4$, Zn(ClO$_4$)$_2$, and LiX); $[H^+] = 0.3\ M$. [b] Initial concentration of oxidizing agents. [c] $[V^{2+}]$ corrected for amount consumed by oxidizing agents X_2 and X_3^-. [d] Difference in absorbance at 425 mμ between the zero-time extrapolation of the absorbance vs. time curve and the absorbance contributions from V^{2+} and VO^{2+}. [e] $[VO^{2-}]$ is taken to be $\{[X_2] + [X_3^-]\}$. [f] Q is percentage of V^{3+} produced by the reaction of V^{2+} with VO^{2+}. [g] The quantity $0.693\Delta D/$ $[V^{2+}][VO^{2+}]t_{1/2}$, where $t_{1/2}$ was calculated to be 1.74 sec from a measured $[H^+]$ of 0.3 M, is 3500 ± 100 M^{-2} sec^{-1}. The value at 22° extrapolated from the data of Newton and Baker[16] is 3100 M^{-2} sec^{-1}. The difference between the values may result from errors in the measurement of $[H^+]$ or ΔD.

the data obtained for the reactions of various halogens and/or trihalides with V^{2+}. When V^{2+} was mixed with outgassed solutions containing no oxidizing agents,

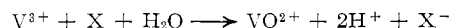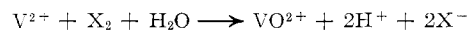(14) H. A. Laitinen, "Chemical Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 563–570.
(15) T. W. Newton and F. B. Baker, *Inorg. Chem.*, **3**, 569 (1964).
(16) J. H. Swinehart, *ibid.*, **4**, 1069 (1965).

the excess absorbance ΔD (footnote d, Table I) was found to be zero. This indicated that residual oxygen was not present in the solutions. The data in Table I indicate that the primary mechanistic steps in the reaction of V^{2+} with X_2 (or X_3^-) are

$$V^{2+} + X_2 \longrightarrow V^{3+} + X + X^-$$
$$V^{2+} + X \longrightarrow V^{3+} + X^-$$
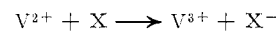
and that steps of the type

$$V^{2+} + X_2 + H_2O \longrightarrow VO^{2+} + 2H^+ + 2X^-$$
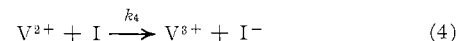$$V^{3+} + X + H_2O \longrightarrow VO^{2+} + 2H^+ + X^-$$
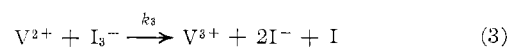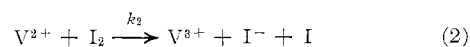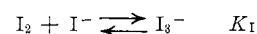
are relatively unimportant.

Vanadium(II)–Iodine Reaction.—Table II presents kinetic data for the reaction at 25.0°. Kinetic measurements were carried out using at least a tenfold excess of V^{2+} over I_2 and/or I_3^-. The disappearance of the iodine-containing species was used to monitor the reaction. The rate constant k_1 which is defined from the equation

$$-\frac{d[I_2]_{total}}{dt} = k_1[V^{2+}][I_2]_{total} \tag{1}$$

is independent of $[I_2]_{total}$, $[H^+]$, and $[I^-]$ in regions of large $[I^-]$ (runs 1–6) and approximately independent of $[I^-]$ in regions of small $[I^-]$ (runs 22–26). However, values of k_1 are rather strongly dependent on the $[I^-]$ in the range 2×10^{-2} M to approximately 2×10^{-4} M (runs 7–21). This behavior is consistent with a mechanism in which I_2 and I_3^- are both reactive toward V^{2+} but are in labile equilibrium with each other

$$I_2 + I^- \rightleftharpoons I_3^- \qquad K_I$$
$$V^{2+} + I_2 \xrightarrow{k_2} V^{3+} + I^- + I \tag{2}$$
$$V^{2+} + I_3^- \xrightarrow{k_3} V^{3+} + 2I^- + I \tag{3}$$
$$V^{2+} + I \xrightarrow{k_4} V^{3+} + I^- \tag{4}$$

Steps involving the oxidation of V^{3+} by I are eliminated since VO^{2+} is not produced. If reactions 2 and 3 are assumed to be rate determining and the iodine–triiodide species equilibrate rapidly,[12,13] the rate equation is

$$-\frac{d[I_2]_{total}}{dt} = \left\{ \frac{k_2 + k_3 K_I(3/2)[I^-]}{1 + K_I(3/2)[I^-]} \right\} [V^{2+}][I_2]_{total}$$
$$= k_1[V^{2+}][I_2]_{total} \tag{5}$$

Thus at large and small $[I^-]$, k_1 approaches k_3 and k_2, respectively. It is clear from the values of K_I[17] [938 (20°), 782 (25°), and 695 M^{-2} (30°)] that the dominant species in runs 1–6, Table II, is I_3^- and values of k_1 obtained at these concentrations of I^- can be equated with k_3 (V^{2+}–I_3^- reaction). Average values of k_3 (M^{-1} sec^{-1}) determined at various temperatures at concentrations of I^- between 0.10 and 0.70 M are: 300 ± 5 (5.7°), 500 ± 10 (12.7°), 970 ± 20 (25.0°), 1900 ± 40 (38.5°). A plot of ln (k_3/T) vs. $1/T$ yields values of $\Delta H^{\pm}$ and $\Delta S^{\pm}$ of 9.1 ± 0.2 kcal/mol and -14 ± 1 eu, respectively.

(17) L. I. Katzin and E. Gebert, *J. Am. Chem. Soc.*, **77**, 5814 (1955).

TABLE II
Vanadium(II)–Iodine Rate Data at Various Iodide Concentrations[a]

Run	10^2 [H+], M	10^5 [V²+], M	10^4 [I₂]total, M	[I-],[b] M	kobsd, sec⁻¹	$10^{-3}k_1$, M⁻¹ sec⁻¹	λ, mμ	$10^{-3}k_2$, M⁻¹ sec⁻¹
1	0.30	1.0	2.3	7000	9.7	0.9₇	460	...
2	0.30	1.0	2.3	7000	9.6	0.9₆	460	...
3	0.05	1.0	2.7	5000	10.3	1.0₃	460	...
4	0.23	5.0	2.7	2500	49.0	0.9₈	460	...
5	0.23	5.0	3.7	2500	49.0	0.9₈	460	...
6	0.50	2.0	2.4	1000	19.8	0.9₉	390	...
7	0.50	1.0	1.1	200	12.5	1.2₅	350	7.1₅
8	0.50	1.0	2.5	50.0	19.4	1.9₄	353	7.8₅
9	0.50	1.0	0.6	20.0	30.3	3.0₃	390	7.5₆
10	0.95	1.0	1.1	13.0	40.6	4.0₆	353	8.6₁
11	0.95	1.0	9.7	11.9	36.6	3.6₆	353	7.4₁
12	0.95	1.0	9.7	11.9	44.3	4.4₃	460	9.2₆
13	0.95	1.0	1.0	10.1	48.3	4.8₃	353	9.3₉
14	0.95	1.0	2.1	8.3	50.3	5.0₃	353	8.9₈
15	0.95	1.0	3.4	6.5	45.5	4.5₅	353	7.2₈
16	0.95	1.0	2.3	5.3	60.3	6.0₃	353	9.1₆
17	0.95	0.25	2.3	5.1	12.6	5.0₄	353	7.4₅
18	0.95	1.0	2.7	4.2	53.1	5.3₁	353	7.4₄
19	0.95	1.0	3.1	3.2	52.2	5.2₂	353	6.8₃
20	0.95	1.0	2.6	2.2	52.8	5.2₈	353	6.4₀
21	0.95	1.0	1.5	2.1	60.2	6.0₂	353	7.2₆
22	0.95	1.0	0.9	1.8	55.0	5.5₀	460	6.5₀
23	0.95	1.0	2.0	1.7	66.3	6.6₃	460	7.7₈
24	0.95	1.0	2.0	1.2	55.0	5.5₀	353	6.1₅
25	0.95	1.0	2.0	1,2	62.8	6.2₈	460	7.0₃
26	0.95	1.0	2.0	1.2	64.0	6.4₀	353	7.1₅

[a] Temperature 25.0°; $\mu = 1.0$ (HClO₄, LiClO₄, and LiX).
[b] Average [I-] = ([I-]added + 0.5[I-]produced).

Values of k_2 were determined either from data of the type presented in Table II or by direct measurement of the V²⁺–I₂ reaction. Some values of k_2 are shown in Table II. These were calculated from the values of k_3 determined in runs 1–6, K_I, and the known expression for k_1 (eq 5). Table III lists average values of k_2 determined by this method (runs 40–44) and values determined directly from the V²⁺–I₂ reactions (runs 27–39). Figure 1 shows a plot ln (k_2/T) vs. $1/T$ for the data in Table III. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 5.9 ± 0.5 kcal/mol and −21 ± 2 eu, respectively.

Vanadium(II)–Bromine Reactions.—The reaction between V²⁺ and Br₂ or Br₃⁻ was studied with the expectation that the results would be analogous to those found in the corresponding iodine reactions. The reactions at low Br⁻ concentrations were carried out using at least tenfold excess [V²⁺] and monitored by spectrophotometrically observing the decrease in free Br₂ as a function of time. Table IV presents some typical data that were collected. The data fit the rate law

$$-\frac{d[Br_2]}{dt} = k_2[V^{2+}][Br_2]$$

A plot of ln (k_2/T) vs. $1/T$ for all of the data obtained for the experiments described in Table IV yields values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of 3.5 ± 1.2 kcal/mol and −26 ± 4 eu, respectively. The reaction between V²⁺ and Br₂ was unaffected by the presence of Br⁻ at concentrations up to 10^{-2} M (see Table IV). At larger concentrations of Br⁻ the kinetics were slower and the kinetic plots showed deviations from pseudo-first-order disappearance of bromide. The fraction of bromine present as Br₃⁻ in these solutions was appreciable. At $\mu = 1.0$ and 25° the equilibrium concentration quotient for Br₂ + Br⁻ ⇌ Br₃⁻ is 17 M⁻¹.[18,19] It was felt that the devia-
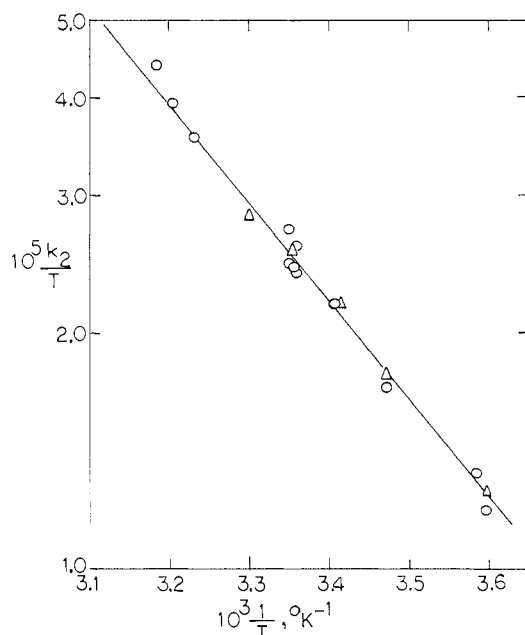

Figure 1.—Plot of ln k_2/T vs. $1/T$ for the V²⁺–I₂ reaction; $\mu = 1.0$. Data were taken from direct measurement (O) or were calculated from experiments with excess I⁻ present (Table II) (Δ).

TABLE III
Values of k_2 Determined from the V²⁺–I₂ Reaction[a] and Data of the Type in Table II[b,c]

Run	[H+], M	10^2[V²+], M	10^5[I₂], M	Temp, °C	$10^{-3}k_2$, M⁻¹ sec⁻¹
27	0.95	0.50	43	5.2	3.3
28	0.50	0.50	2.2	6.2	3.7
29	0.04	0.50	26	15.0	4.9
30	0.04	0.50	26	20.5	6.4
31	0.95	0.50	30	24.7	7.7
32	0.95	0.50	30	24.7	7.1
33	0.95	0.50	2.2	25.0	7.1
34	0.50	1.0	1.8	25.1	7.6
35	0.04	0.50	26	25.5	6.7
36	0.50	0.50	2.2	25.5	8.1
37	0.04	0.50	26	36.5	11.0
38	0.50	0.50	2.2	39.1	12.3
39	0.95	0.50	42	41.0	13.8
40	...	...	...	5.0	3.5
41	...	...	...	15.1	5.1
42	...	...	...	20.0	6.4
43	...	...	...	25.0	7.6
44	...	...	...	30.0	8.5

[a] Runs 27–39. [b] Runs 40–44. [c] $\mu = 1.0$ (HClO₄, LiClO₄); $\lambda = 460$ mμ (runs 28, 31, 34, 36, and 38), 400 mμ (runs 27, 29, 30, 33, 35, 37, and 39), and 360 mμ (run 32).

tion from first-order kinetics might reflect a lack of lability in the Br₂–Br₃⁻ equilibrium. However, the equilibrium was found by experiment to be attained rapidly. An alternate explanation is that at large concentrations of Br⁻ there is an intermediate formed which disappears fairly slowly. This possibility will be considered in the Discussion section.

Vanadium(II)–Chlorine Reaction.—The V²⁺–Cl₂ reaction was found to be quite rapid. The kinetics were

(18) D. B. Scaife and H. J. V. Tyrrell, *J. Chem. Soc.*, 386 (1958).
(19) J. L. Voth, M.S. Thesis, University of California, Davis, Calif., 1954.

Table IV

VANADIUM(II)-BROMINE RATE DATA AT
LOW BROMIDE CONCENTRATION AT VARIOUS TEMPERATURE[a]

$[H^+]$, M	$10^2[V^{2+}]$, M	$10^4[Br_2]$, M	Temp, $^\circ C$	$10^{-4}k_2$, $M^{-1} sec^{-1}$	λ, $m\mu$
1.0	0.5	6.8	4.5	1.5	425
0.5	0.5	3.8	6.0	2.0	420
0.4	1.0	7.0	6.2	2.1	436
1.0	0.5	6.8	13	2.0	425
0.4	1.0	7.0	17	2.6	436
1.0	0.5	6.8	20	2.5	425
0.4	0.5	3.8	22	3.0	420
1.0	0.5	6.8	25	2.9	425
0.4	1.0	7.0	26	3.1	436
1.0	0.5	6.8	32	3.2	425
1.0	0.5	1.3	25	3.5[b]	425
1.0	0.5	3.0	25	3.3[c]	425

[a] $\mu = 1.0$ ($HClO_4$, $LiClO_4$). [b] $[Br^-] = 10^{-3} M$. [c] $[Br^-] = 10^{-2} M$.

not reproducible. The bimolecular rate constant for the reaction is greater than $500 M^{-1} sec^{-1}$.

Discussion

Table V summarizes the kinetic data obtained. The enthalpies of activation found for the reaction of V^{2+} with triiodide, iodine, and bromine are not comparable with those found for reactions in which loss of water is thought to be rate determining; $\Delta H^{\ddagger}$ values range from 11 to 13 kcal/mol (see Table I and ref 2). However, this does not preclude the possibility of ligand-assisted water replacement in these V^{2+}-halogen reactions. The large, negative entropies of activation given for all of the reactions in Table V indicate considerable ordering in the activated complexes relative to the reactants. This ordering may, in part, be due to V^{2+}-halogen bond forming giving seven-coordinate vanadium(II) in the activated complex. Since the d electrons in $V(H_2O)_6^{2+}$ are located in t_{2g} orbitals pointing at the faces of the octahedron formed by the vanadium(II) and its associated water molecules, it seems reasonable that the oxidizing agent will attack at these electrophilic centers. However, the possibility exists that the reaction proceeds by an outer-sphere mechanism.

Table V

SUMMARY OF KINETIC DATA FOR V^{2+}-HALOGEN REACTIONS[a]

Oxidant	$k(25^\circ)$, $M^{-1} sec^{-1}$	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
I_3^-	$(9.7 \pm 0.2) \times 10^2$	9.1 ± 0.2	-14 ± 1
I_2	$(7.5 \pm 0.5) \times 10^3$	5.9 ± 0.5	-21 ± 2
Br_2	$(3.0 \pm 0.4) \times 10^4$	3.5 ± 1.2	-26 ± 4
Cl_2	$>5 \times 10^2$	$\cdots$	$\cdots$

[a] $\mu = 1.0$.

The 7-eu difference between the entropy of activation measured in the V^{2+}-I_2 reaction (-14 ± 1 eu) and in the V^{2+}-I_3^- reaction (21 ± 2 eu) can be ascribed to an electrostatic effect. Formation of the activated com-

plex from the oppositely charged V^{2+}-I_3^- species is expected to result in a positive contribution to $\Delta S^{\ddagger}$ produced by an increased electrostatic entropy of activation. Formation of the activated complex from the respective bipositive and neutral species V^{2+} and I_2 should not contribute to $\Delta S^{\ddagger}$ in this way. Contributions of this nature to $\Delta S^{\ddagger}$ can be estimated from the equation[20]

$$\Delta S^{\ddagger}_{el} = \frac{-20Z_aZ_b}{r}$$

which is derived from the Born equation for the electrostatic free energy of a charge sphere in a continuous dielectric. In the equation above, $\Delta S^{\ddagger}_{el}$ is the electrostatic contribution to the entropy of activation, Z_a and Z_b are the charges of the reactants a and b, and r is the distance in ångström units separating them. From the equation, $\Delta S^{\ddagger}_{el}$ for the V^{2+}-I_2 reaction is approximately zero. Therefore the difference of 7 eu between the experimentally observed enthalpies of activation for the V^{2+}-I_2 reaction and the V^{2+}-I_2^- reaction is accountable in terms of $\Delta S^{\ddagger}_{el}$ if the electrostatic radius of the V^{2+}-I_3^- activated complex is assumed to be 2.9 Å.

The reaction of bromine with V^{2+} at high bromide ion concentrations gave a reaction curve which did not indicate first-order kinetics. Similar behavior was observed of the V^{2+}-Cl_2 reaction. The form of the experimentally observed absorbance *vs.* time curves indicated the presence in solution of an intermediate also absorbing light at the wavelengths used to monitor the disappearance of halogen. The data were insufficient for an unambiguous description of the systems, but the existence of an equilibrium involving formation of X_2^- appears to be a likely possibility. Evidence for species of this type has been previously reported.[21-24] Attempts to trap the radical intermediates by adding ethanol and benzyl alcohol to the V^{2+} did not affect the observed kinetics. Experiments with other scavenging agents might be fruitful in simplifying the reactions observed.

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