A Kinetic Study of the Reduction of Bromate Ion by Oxovanadium(IV) in Perchlorate Solution

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The reaction $BrO_3^- + 5VO^{2+} + 2H_2O = 0.5Br_2 + 5VO_2^+ + 4H^+$ in perchloric acid solution obeys the rate expression $-d[BrO_3^-]/dt = k'[BrO_3^-][VO^{2+}]$ for 1–3 half-lives. However, the deviation past this stage and the values of k' are consistent with an increase in the magnitude of the rate parameter with increasing $[VO^{2+}]_0/[BrO_3^-]_0$ ratios. This result is interpreted in terms of a competition between disproportionation of a bromous acid intermediate to produce bromate ion as one product and reduction of bromous acid by oxovanadium(IV). The stoichiometry in the presence of the scavengers bromide ion plus allyl alcohol is $BrO_3^- + 2VO^{2+} = $ products, and the value of the second-order rate parameter is independent of initial reactant concentration ratios.

Introduction

Studies of the reduction of the bromate ion in acid solution by the potentially multiequivalent reducing agents bromide ion,[1] hydrogen peroxide,[2] and hydrazoic acid[3] have been interpreted by the reaction sequence

$$Red + Br(V) = Oxid + Br(III)$$

$$Red + Br(III) = Oxid + Br(I)$$
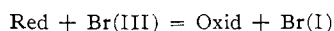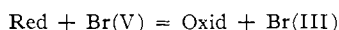
where Red is the particular reducing agent and Oxid its oxidized form. The first reaction is rate determining and exhibits a positive hydrogen ion dependence. Hypobromous acid is also very reactive in the bromide ion and hydrogen peroxide systems. We thought it would be of interest to employ the one-electron reducing agent oxovanadium(IV), thereby necessarily generating additional bromine intermediates. These intermediates may be reduced in a stepwise fashion or interact with one another, as has occasionally been observed in the corresponding chlorine system.[4] An additional feature of interest is the form of the rate law. We have found the rate expression $-d[Np(V)]/dt = k[BrO_3^-]^2$ to be operative in the neptunium(V)–bromine(V) system in 2.0 M perchloric acid.[5]

Experimental Section

Reagents.—Reagent grade sodium bromide, allyl alcohol, and perchloric acid were used without further purification. Reagent grade sodium bromate was either used directly or recrystallized three times; both sources yielded identical results. The lithium perchlorate and sodium perchlorate were recrystallized three times after preparation by the neutralization of the reagent grade carbonate salt with perchloric acid. The water was doubly distilled in an all-glass apparatus after distillation of deionized water from an alkaline permanganate still. The source of the oxovanadium(IV) was CP vanadyl sulfate. Solutions of this reagent were converted to the perchlorate form by addition of the requisite amount of reagent grade barium carbonate; the resulting barium sulfate precipitate was removed by centrifugation. A second preparation utilized ion-exchange procedures. A vanadyl sulfate solution was placed on a column of purified Dowex 50WX-8 resin, the sulfate ion eluted with dilute perchloric acid, and the oxovanadium(IV) eluted with 2 M per-

chloric acid. Only the center fraction was collected. A third preparation followed the same procedure, except that the vanadyl sulfate solution was prepared by reduction of vanadium(V) perchlorate with sulfur dioxide. The preparation of the vanadium-(V) perchlorate has been described previously.[6] The positions and molar extinction coefficients were as follows: λ 7625 Å, VO^{2+} (17.1), VO_2^+ (0), Br_2 (0); λ 3130 Å, VO^{2+} (9.3), VO_2^+ (389), Br_2 (10); λ 2800 Å, VO^{2+} (74), VO_2^+ (734), Br_2 (26). These values are in good agreement with published values.[6-8] Bromate ion is transparent at the wavelengths used.

Kinetic Studies.—A Zeiss PMQ-11 spectrophotometer equipped with a thermostated, rapid-mixing sample compartment (mixing time <1 sec) was used to monitor the reaction. Measurements were made either at 7625 Å where VO^{2+} is the only absorbing species or at 3130 Å (and occasionally 2800 Å) where VO_2^+ is the principally absorbing species. A solution containing the desired amounts of perchloric acid, perchlorate salt, and one of the reactants was allowed to reach temperature equilibrium ($\pm 0.1°$) in a 2-cm absorption cell in the sample compartment. The reaction was initiated by rapid injection of the other reactant. In the experiments that employed scavengers, the allyl alcohol was added after temperature equilibration, and the reaction was initiated by rapid injection of a neutral solution containing the desired amounts of sodium bromate and sodium bromide. The output of the detector tube was recorded on a strip chart recorder with a chart speed of 24 cm/min. The first observation was made within 2 sec after mixing, and the reaction was followed to completion. VO^{2+} concentrations were determined from the spectral data (corrections were applied for all absorbing species), and the BrO_3^- concentrations were calculated from these data according to the stoichiometry.

Results

Stoichiometry.—The ratio $\Delta[VO^{2+}]/\Delta[BrO_3^-]$ was determined to be 4.97 ± 0.06 in 0.20–2.00 M perchloric acid. This result indicates that the stoichiometry is

$$5VO^{2+} + BrO_3^- + 2H_2O = 5VO_2^+ + 0.5Br_2 + 4H^+$$
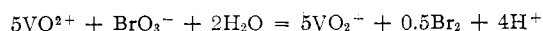
The rate of oxidation of VO^{2+} by Br_2 is much slower than that by BrO_3^- under the conditions employed in this study. Only in experiments with excess VO^{2+} and low [H$^+$] was further oxidation by the Br_2 product competitive with the BrO_3^- reaction and then only after more than *ca.* 3 half-lives.

Due to complexities encountered in the kinetic studies (*vide infra*), additional experiments were conducted in the presence of scavengers to remove various intermediates formed in the reaction. Allyl alcohol reacts rapidly with hypobromous acid through addition at the double bond but reacts very slowly with bromate

(1) (a) W. C. Bray and H. A. Liebhafsky, *J. Amer. Chem. Soc.*, **57**, 51 (1935); (b) M. Sclar and S. C. Reisch, *ibid.*, **58**, 667 (1936); (c) C. N. Hinshelwood, *J. Chem. Soc.*, 694 (1947).

(2) (a) W. C. Bray and P. R. Davis, *J. Amer. Chem. Soc.*, **52**, 1427 (1930); (b) H. A. Young, *ibid.*, **72**, 3310 (1950); (c) C. J. O'Connor, *Int. J. Appl. Radiat. Isotop.*, **18**, 790 (1967).

(3) R. C. Thompson, *Inorg. Chem.*, **8**, 1891 (1969).

(4) For a recent discussion, see B. Z. Shakhashiri and G. Gordon, *J. Amer. Chem. Soc.*, **91**, 1103 (1969), and the references cited therein.

(5) C. G. Knight and R. C. Thompson, unpublished results, 1970.

(6) E. H. Appelman and J. C. Sullivan, *J. Phys. Chem.*, **66**, 442 (1962).

(7) K. M. Davies and J. H. Espenson, *J. Amer. Chem. Soc.*, **92**, 1884 (1970).

(8) R. H. Betts and A. N. MacKenzie, *Can. J. Chem.*, **29**, 655 (1951).

ion and vanadium(V). Sclar and Reisch[1b] found that in the presence of allyl alcohol the reaction between bromate and bromide ions apparently stops at hypobromous acid; the stoichiometry observed was

$$BrO_3^- + 2Br^- + 3H^+ = 3HOBr$$

$$3HOBr + 3CH_2\!\!=\!\!CHCH_2OH = products$$
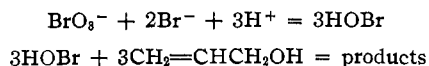
In the present system the ratio $\Delta[VO^{2+}]/\Delta[BrO_3^-]$ was determined to be 3.93 ± 0.04 in the presence of allyl alcohol at an initial concentration slightly in excess of the bromate ion concentration ultimately consumed ($\Delta[BrO_3^-]$). The simplest interpretation of this result is that the reaction stops at hypobromous acid under these conditions.

Bromide ion reacts quantitatively with bromate ion in acid solution to produce bromine[1a,b] in accordance with the rate expression $k[BrO_3^-][Br^-][H^+]^2$. It was found that the competition of moderate concentrations of Br^- for BrO_3^- was negligible relative to that of VO^{2+} at $[H^+] \leq 0.20\ M$. Thus stoichiometric experiments were designed in the presence of added Br^- with the goal of scavenging intermediates generated in the BrO_3^-–VO^{2+} system under conditions where negligible reduction of BrO_3^- by Br^- occurred. The data in Table I indicate that at a $[Br^-]_0/[BrO_3^-]_0$ ratio of 3.00 in

TABLE I
STOICHIOMETRY RESULTS WITH ADDED Br^{-} [a]

$10^2[BrO_3^-]_0$, M	$10^2[VO^{2+}]_0$, M	$10^2[Br^-]_0$, M	$\Delta(VO^{2+})/\Delta(BrO_3^-)$	% Br^- reacted
0.408	2.64	4.08	1.72	32.8
0.415	2.69	2.59	1.75	52.1
0.417	2.70	2.08	1.78	64.5
0.419	2.72	1.57	1.84	84.3
0.420	2.73	1.26	1.96	101
0.065	0.234	0.195	1.98	101
0.422	2.74	0.844	2.90	105

[a] Conditions: 25°, 0.20 M [H+], $I = 2.0\ M$ (LiClO4).

reactions with excess VO^{2+} in 0.20 M perchloric acid, all of the added Br^- reacts with intermediates and the stoichiometry approaches $BrO_3^- + 2VO^{2+}$ = products. At higher $[Br^-]_0/[BrO_3^-]_0$ ratios, additional but incomplete scavenging occurs.

The same 1:2 stoichiometry obtains in $[H^+] \leq 0.20$ M with added $(Br^-)_0 = (1.5–2.0)\ \Delta[BrO_3^-]$ and $[CH_2\!\!=\!\!CHCH_2OH]_0 = 2\Delta[BrO_3^-]$. The ratio $\Delta[VO^{2+}]/\Delta[BrO_3^-]$ was determined to be 1.98 ± 0.03 under these conditions. The combination of allyl alcohol and bromide ion as scavengers in the bromate–oxovanadium(IV) reaction has the important advantage for the kinetic experiments that no buildup of bromine and tribromide ion occurs during the reaction.

Kinetics in the Absence of Scavengers.—It is useful for the subsequent discussion to define the ratio $[VO^{2+}]_0/[BrO_3^-]_0$ as R. At values of $R \leq 0.33$ and near 5.0, plots of ln $([VO^{2+}]/[BrO_3^-])$ vs. time were linear for ca. 90% of the reaction. The apparent rate constant decreases after ca. 2 half-lives when $R = 1.0$–4.3 but increases after 1–2 half-lives when $R \geq 8.8$. The kinetic data were analyzed according to the rate expression $-d[BrO_3^-]/dt = k'[BrO_3^-][VO^{2+}]$. Values of k' were determined from a least-squares adjustment of the integrated form of this expression over the linear region. From 14 to 28 kinetic points were analyzed for each run, and the standard deviation in k' was $\leq 0.9\%$. The results are summarized in Table II.

TABLE II
KINETIC RESULTS[a]

Expt	$10^3[BrO_3^-]_0$, M	$10^3[VO^{2+}]_0$, M	R^b	k', M^{-1} sec^{-1}
1	0.195	14.1	72.3	3.86 ± 0.04
2	0.195	7.10	36.4	3.87 ± 0.08
3[c]	3.13	27.5	8.79	3.40 ± 0.01
4	0.525	3.45	6.57	3.47 ± 0.05
5	4.13	27.2	6.59	3.45 ± 0.03
6[d]	4.24	26.9	6.34	3.36 ± 0.04
7[c]	6.23	26.9	4.32	3.08 ± 0.06
8	6.32	25.7	4.07	3.10 ± 0.04
9[e]	6.32	25.7	4.07	3.10 ± 0.04
10	8.49	21.8	2.57	2.73 ± 0.01
11	1.08	1.11	1.03	2.76 ± 0.02
12[c]	3.21	1.10	0.343	2.34 ± 0.04
13	3.21	1.11	0.346	2.38 ± 0.01
14[d]	3.28	1.08	0.329	2.43 ± 0.01
15	6.38	0.548	0.086	2.21 ± 0.03
16	12.7	0.329	0.026	2.18 ± 0.02
17[f]	4.12	27.5	6.67	3.55 ± 0.03
18[g]	4.12	27.6	6.70	3.70 ± 0.04
19[g]	6.25	26.8	4.29	3.18 ± 0.10
20[g]	2.98	1.11	0.372	2.76 ± 0.01
21[h]	0.195	7.37	37.8	3.68 ± 0.13
22[h]	6.30	2.99	4.75	3.21 ± 0.08
23[h]	3.16	1.10	0.348	2.75 ± 0.01
24[c,i]	6.38	0.590	0.093	1.13 ± 0.01
25[c,j]	6.38	0.590	0.093	0.560 ± 0.001

[a] [H+] = 2.00 M, and temperature is 25° unless otherwise noted. Uncertainties are average deviations of duplicate runs. [b] $R = (VO^{2+})_0/(BrO_3^-)_0$. [c] (H+) = 0.210 M, $I = 2.0\ M$ (LiClO4). [d] Second preparation of VO^{2+} stock solution used (column eluted). [e] Order of mixing reactants reversed. [f] Added $(VO^{2+})_0 = 2.65 \times 10^{-2}\ M$. [g] Added $(Br_2)_0 = \frac{1}{2}\Delta(BrO_3^-)$. [h] Added $[CH_2\!\!=\!\!CHCH_2OH]_0 = 1.05\Delta[BrO_3^-]$; data analyzed according to the stoichiometry $\Delta(VO^{2+})/\Delta(BrO_3^-) = 4.00$. [i] Temperature 17°. [j] Temperature 10°.

The data in Table II indicate that the value of k' increases as R increases with the stipulation that a lower limit is apparently reached and an upper limit is approached. The conclusion that an upper limit has not been experimentally attained is based on the result that even in experiment 1, the apparent rate begins to increase after ca. 65% reaction. Entries 4 and 5 indicate that k' is affected only by the magnitude of R and not the individual concentrations of reactants. The results show that the rate parameter is independent of the hydrogen ion concentration in the range utilized, the wavelength used to monitor the reaction, the source of the oxovanadium(IV) stock solution, and the initial presence of added vanadium(V), a product. The value of k' is slightly increased by the initial presence of bromine. The addition of allyl alcohol to scavenge the hypobromous acid intermediate restricts the range of k' values but does not remove the dependence of k' on R.

A number of more complicated rate expressions were used to analyze the data, but none was successful. For example, the incorporation of $k''[VO^{2+}]^2$ or $k'''\cdot[BrO_3^-][VO^{2+}]^2$ as additional terms in the rate law yielded values of k'' that were very small and increased with increasing $[V(IV)]$ and k''' values that were negative. Further, these more complicated rate laws are not consistent with the lower and apparent upper limits observed for k'.

Since this work was completed, our attention was drawn to a previous study of this system.[9] The condi-

(9) C. W. Fuller and J. M. Ottaway, *Analyst*, **94**, 32 (1969). See C. W. Fuller and J. M. Ottaway, *ibid.*, **95**, 791 (1970), for results on the iodate and chlorate oxidations of oxovanadium(IV). For somewhat conflicting results on the chlorate oxidation, see D. R. Rosseinsky and J. Zlotnick, *J. Chem. Soc. A*, 1200 (1970).

tions used were similar to ours except that all the experiments were conducted with large excesses of bromate ion. The rate law presented was $-d[VO^{2+}]/dt = k_0K_1[BrO_3^-][VO^{2+}]/(1 + K_1[BrO_3^-])$ with $k_0 = 0.125$ sec^{-1} and $K_1 = 88.8$ M^{-1} at 20°, $I = 0.10$ M (LiClO$_4$). The rapid equilibrium

$$BrO_3^- + VO^{2+} \overset{K_1}{=} BrO_3^- \cdot VO^{2+}$$
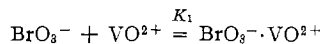
and the rate-determining step

$$BrO_3^- \cdot VO^{2+} \overset{k_0}{=} \text{products}$$
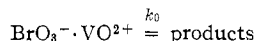
were proposed as a probable reaction path. If one considers only our data that closely simulate the above conditions (experiments 12–16), such a scheme is adequate. We calculate $K_1 = 27$ M^{-1} and $k_0 = 0.49$ sec^{-1} at 25° and $I = 2.0$ M. The linear second-order rate plots mentioned earlier under these conditions are also to be expected, since the percentage of the oxovanadium-(IV) that should be complexed remains constant during a given run. However, this rate law is inadequate if conditions other than excess bromate ion are employed. First, with excess oxovanadium(IV), the apparent second-order rate parameter *increases* at later stages in the reaction. Second, this rate law is not consistent with the results of experiments 4 and 5 which were performed under second-order conditions. An eightfold increase in the initial reactant concentrations produces no change in k'. Third, the variation in k' under conditions of excess bromate ion *and* excess oxovanadium-(IV) are not internally consistent with this rate law. Let k_v' equal the k' value obtained from either experiment 1 or 2 at constant $[VO^{2+}] = [VO^{2+}]_0$ and k_B' equal the k' value obtained from either experiment 12, 13, 14, 15, or 16 at constant $[BrO_3^-] = [BrO_3^-]_0$. Then it follows that $k_v' = k_0K_1/(1 + K_1[VO^{2+}]_0)$ and $k_B' = k_0K_1(1 + K_1[BrO_3^-]_0)$. Elimination of k_0 and rearrangement leads to the expression

$$K_1 = (k_v' - k_B')/(k_B'[BrO_3^-]_0 - k_v'[VO^{2+}]_0)$$

In fact, one calculates negative and varying values of K_1 regardless of which pairs of the above experimental results are used.

Finally, our kinetic results with added scavengers (*vide infra*) are consistent with a simple second-order rate expression over a wide range of reactant concentrations. The results of Fuller and Ottaway[9] performed under similar conditions are in reasonable agreement with the data in Table II. However, the differences in the rate expression lead to markedly different reaction schemes (*vide infra*). The limitations in studying reaction kinetics under pseudo-first-order conditions appear to be amply illustrated in this system.[10]

Kinetics in the Presence of Scavengers.—One possible explanation for the variation in the k' values invokes a rapid interaction between bromine intermediates generated in the system to produce the original reactant bromate ion as one product. This interaction could be the disproportionation of the intermediate bromous acid: $2HBrO_2 = BrO_3^- + HOBr + H^+$. The stoichiometry shown has precedent in the disproportionation of chlorous acid.[11] In order to test this scheme, kinetic experiments were performed with the goal of scavenging the bromous acid intermediate.

(10) See R. Livingston, "Technique of Organic Chemistry," Vol. VIII, Interscience, New York, N. Y., 1953, p 209.

(11) R. G. Kieffer and G. Gordon, *Inorg. Chem.*, **7**, 239 (1968).

Operationally, it was found that a combination of bromide ion and allyl alcohol provides the most satisfactory scavenger. In principle, bromide ion alone could be used, but at the most useful wavelength for monitoring the reaction (3130 Å), spectral interference from the bromine and especially from the tribromide ion formed during the reaction was considerable. The combination of scavengers, however, produces no new absorbing species, and under the conditions outlined in the stoichiometry section, cleanly converts the ratio Δ-$(VO^{2+})/\Delta(BrO_3^-)$ to 2.00.

The results of the kinetic experiments performed in the presence of allyl alcohol and bromide ion are summarized in Table III. The first six entries indicate

TABLE III
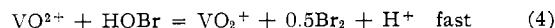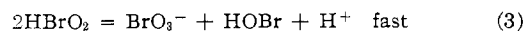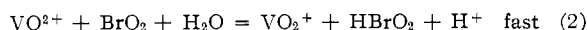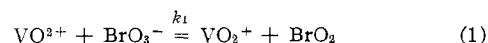KINETIC RESULTS WITH ADDED SCAVENGERS[a]

Expt	$10^3[BrO_3^-]_0$, M	$10^3[VO^{2+}]_0$, M	R^b	k_1, M^{-1} sec^{-1}
26[c]	0.428	4.62	10.8	4.95 ± 0.08
27[d]	0.428	4.62	10.8	4.90 ± 0.05
28	0.649	2.33	3.59	4.93 ± 0.03
29	3.17	1.17	0.369	4.85 ± 0.02
30	6.34	0.590	0.093	4.94 ± 0.03
31[e]	0.428	4.62	10.8	5.02 ± 0.04
32[e]	3.17	1.17	0.369	4.94 ± 0.05
33[f]	3.17	1.17	0.369	4.73 ± 0.01
34[f,g]	3.17	1.17	0.369	4.11 ± 0.01
35[f,h]	3.17	1.17	0.369	4.23 ± 0.04
36[f,i]	3.17	1.17	0.369	4.44 ± 0.02
37[f,j]	3.17	1.17	0.369	5.28 ± 0.02
38[f,k]	3.17	1.17	0.369	6.80 ± 0.03
39[l]	3.17	1.17	0.369	2.28 ± 0.01
40[l]	0.428	4.62	10.8	2.32 ± 0.04
41[m]	0.428	4.62	10.8	1.18 ± 0.01
42[m]	3.17	1.17	0.369	1.16 ± 0.01

[a] $[H^+] = 0.210$ M, $I = 2.0$ M (LiClO$_4$), $[CH_2=CHCH_2OH]_0 = (2.0-2.1)\Delta[BrO_3^-]$, and $[Br^-]_0 = (1.50-2.00)\Delta[BrO_3^-]$ unless otherwise noted. Uncertainties are average deviations of duplicate runs. [b] $R = [VO^{2+}]_0/[BrO_3^-]_0$. [c] $[Br^-]_0 = 8.56 \times 10^{-4}$ M. [d] $[Br^-]_0 = 6.42 \times 10^{-4}$ M. [e] $[H^+] = 0.114$ M. [f] $[H^+] = 0.071$ M. [g] NaClO$_4$ used to maintain $I = 2.0$ M. [h] $I = 1.00$ M (LiClO$_4$). [i] $I = 0.50$ M (LiClO$_4$). [j] $I = 0.20$ M (LiClO$_4$). [k] $I = 0.071$ M. [l] Temperature 17°. [m] Temperature 10°.

that the observed values of the second-order rate constant k_1 are invariant under varying R values. Further, all the individual runs obeyed the second-order rate law to at least 90% reaction and with standard deviations $\leq 0.4\%$ in k_1.

Discussion

The reaction scheme shown by eq 1–4 is a limiting case that is in accord with the data presented at large initial bromate concentrations. Effective competition for

$$VO^{2+} + BrO_3^- \overset{k_1}{=} VO_2^+ + BrO_2 \qquad (1)$$

$$VO^{2+} + BrO_2 + H_2O = VO_2^+ + HBrO_2 + H^+ \quad \text{fast} \quad (2)$$

$$2HBrO_2 = BrO_3^- + HOBr + H^+ \quad \text{fast} \quad (3)$$

$$VO^{2+} + HOBr = VO_2^+ + 0.5Br_2 + H^+ \quad \text{fast} \quad (4)$$

the bromous acid intermediate by oxovanadium(IV) would diminish the importance of reaction 3 and lead to an increase in the value of the apparent second-order rate constant.[12]

(12) The rate expression $-d[BrO_3^-]/dt = k_1[VO^{2+}][BrO_3^-]$ results from stepwise reduction of BrO$_3^-$ in which reaction 3 is absent. The reaction scheme of eq 1–4 leads to the rate expression $-d[BrO_3^-]/dt = \frac{1}{2}k_1[VO^{2+}] \cdot [BrO_3^-]$ if the steady-state approximation is applied to the concentrations of BrO$_2$ and HBrO$_2$.

Systems in which intermediates present in low concentrations interact are rare. The extreme instability of bromous acid,[13] however, lends some support to this suggestion in the present study. Further, most studies of the reduction of the bromate ion that postulate a very rapid reaction between a bromous acid intermediate and the reducing agent have employed multiequivalent substrates. Bromous acid may disproportionate in the present system due to the fact that its alternative reaction path necessitates reduction by the one-electron reducing agent oxovanadium(IV).

The proposed scheme is not in strict accordance with the kinetic data presented. In the limit, experiments in which bromous acid exclusively disproportionates (at low values of R) should yield k' values only half those observed when the intermediate instead reacts only with VO^{2+} (at high values of R). In fact, $k'_{min} = 0.56 k'_{max}$ at 25°. This result may obtain because the upper limit for k' has not been experimentally attained. However, additional interactions of other intermediates formed in this system would further complicate the interpretation of the data.

The kinetic results with bromide ion and allyl alcohol present as scavengers appear to be successful in that the rate parameter is invariant with initial reactant concentration ratios. This result is consistent with the reaction scheme presented provided that bromide ion effectively scavenges bromous acid and either allyl alcohol or bromide or both scavenge lower intermediate(s), presumably hypobromous acid. The stoichiometry results are in accord with this provision. In fact, more of a problem was encountered in finding conditions where bromide ion was prevented from also scavenging an additional intermediate, presumably BrO_2 (see Table I).

A problem inherent in utilizing scavengers in kinetic studies is the demonstration that the scavengers and the products they form do not affect the rate-determining step. The high-quality internal precision of the individual kinetic experiments for more than 3 half-lives suggests that the rate constant is not affected by these species. However, the value of k_1 is 4.93 ± 0.04 M^{-1} sec^{-1}, but the maximum value of k' is 3.87 M^{-1} sec^{-1}. The most likely kinetic interference in the scavenged experiments is a bromide ion catalyzed path. The following points suggest that this does not arise under the experimental restraints employed. First, variation of

the bromide ion concentration as much as possible (*ca.* 20%) without altering the stoichiometry in experiments 26 and 27 did not significantly affect the value of k_1. Second, the data in run 30 were analyzed according to the integrated form of the rate expression $-d(BrO_3^-)/dt = k_A(BrO_3^-)(VO^{2+}) + k_B(BrO_3^-)(VO^{2+})(Br^-)$. The least-squares values of the rate parameters were $k_A = 5.26 \pm 0.22$ M^{-1} sec^{-1} and $k_B = -(1.43 \pm 0.59) \times 10^3 M^{-2}$ sec^{-1}.

The results in Table III indicate that the value of k_1 is sensitive not only to the ionic strength but also to the perchlorate salt used to maintain the ionic strength. In the absence of scavengers, the rate parameter is the same at constant R in 2.00 M perchloric acid and in 0.20 M perchloric acid, $I = 2.0$ M (lithium perchlorate). In the limited hydrogen ion concentration range employed in the presence of scavengers, k_1 is also invariant. However, since the bromate ion requires protons to proceed toward products but oxovanadium(IV) requires loss of protons,[14] the absence of a hydrogen ion dependence may well be the result of a net cancellation of effects.

The activation energy calculated from k_1 values over the temperature range employed is 16.0 ± 0.1 kcal/mol. Values of $\Delta H^{\neq} = 15.4 \pm 0.1$ kcal/mol and $\Delta S^{\neq} = -3.6 \pm 0.2$ eu at 25° were calculated in the usual manner by means of absolute reaction rate theory. If the proposed reaction scheme is correct, the values of the activation parameters in the unscavenged kinetic experiments should be nearly the same.[15] Values at 25° of $\Delta H^{\neq} = 14.7 \pm 0.4$ kcal/mol and $\Delta S^{\neq} = -7.5 \pm 0.6$ eu were computed from the k' values for experiments 15, 24, and 25 (Table II). If the rate law proposed for this system were incorrect, major differences in the activation parameters for the scavenged and unscavenged experiments might well have resulted.

(13) (a) J. Breiss, Ing. D. Thesis, University of Strasbourg, Strasbourg, France, 1959; (b) O. Amichai and A. Treinin, *J. Phys. Chem.*, **74**, 3670 (1970), were unable to detect bromous acid as a product of the flash photolysis of bromate ion below pH 5.0, presumably due to its instability.

(14) This method of predicting hydrogen ion dependencies is based on that discussed previously. See, for example, T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, **63**, 365 (1959).

(15) There is an alternative way of viewing this question. In the unscavenged experiments at low values of R, the reaction scheme of eq 1–4 should be operative. Only 2.5 VO^{2+} ions react per net activation process instead of 5.0 as would occur if a completely stepwise reduction of BrO_3^- obtains with the first step rate determining. This requires the computed values of k' to be low by a factor of 2.00, regardless of the temperature. Observed values of k_1/k' at low R values are 2.24, 2.04, and 2.09 at 25, 17, and 10°, respectively.