Communications to the Editor

Reduction of Bromine(V) by Cerium(III), Manganese(II), and Neptunium(V) in Aqueous Sulfuric Acid

Sir:

There have been several reports of oscillating redox systems recently.[1a–e] A typical one is the oscillatory appearance of Ce(IV) in a solution of Ce(III), Br(V), and a variety of dicarboxylic acids such as malonic acid in aqueous sulfuric acid. Fruehbeis and Roeder[1e] found that Mn(II) can be substituted for Ce(III), at least if malic acid is used. A knowledge of the rate law governing the bromate–metal ion reaction is fundamental to the understanding of any of these systems. To date, however, all attempts to describe the kinetic behavior of this complex reaction have led to only qualitative results.[1d,2]

We wish to report on results obtained when Br(V) is reduced by Np(V) or large excesses of Ce(III) or Mn(II) in 3 *M* sulfuric acid. The reactions were monitored by conventional spectrophotometric techniques (a Zeiss PMQII instrument equipped with a rapid mixing sample compartment was employed). The stoichiometry observed was

$$5H^+ + 4M^{n+} + BrO_3^- = 4M^{n+1} + HOBr + 2H_2O \qquad (1)$$

where M is the particular metal ion. All of these reactions exhibit rather poorly reproducible induction periods. The duration of the induction period (1) increases with decreasing bromate concentration and temperature, and (2) increases in the order Np(V) < Mn(II) < Ce(III) for a given initial bromate concentration. After approximately 10% reaction, the behavior of all three systems is accurately described by the empirical rate law

$$-\mathrm{d}(BrO_3^-)/\mathrm{d}t = k_1(BrO_3^-)^2 \qquad (2)$$

Other studies[3] in this laboratory on the Np(V)–Br(V) reaction in perchloric acid indicate that this rate law holds for at least 3 half-lives irrespective of reactant concentration ratios. The Ce(III) and Mn(II) systems, however, exhibit very complicated kinetic behavior when large excesses of the reducing agent are not employed.

Values of the rate parameter k_1 for the three systems are summarized in Table I. The startling result is that not only do all three redox reactions obey the same rate expression, but also they yield rate parameters that are identical within the experimental uncertainty. Thus, the reaction rate is solely governed by the bromate concentration under the experimental restraints outlined. Values of $\Delta H^{\ddagger} = 18.5 \pm 0.2$ kcal/mol and $\Delta S^{\ddagger} = 7.0 \pm 0.6$ eu were calculated from the combined data in Table I.

Table I. Values of k_1 (M^{-1} sec^{-1}) in 3 M H_2SO_4[a]

Temp, °C	k_1, Np(V)[b]	k_1, Mn(II)[c]	k_1, Ce(III)[d]
32.0		11.9 ± 0.3 (5)[e]	12.1 ± 0.1 (4)
25.0	6.08 ± 0.09 (5)	5.95 ± 0.18 (6)	5.85 ± 0.13 (8)
17.0	2.54 ± 0.02 (4)	2.38 ± 0.06 (4)	2.40 ± 0.03 (4)
10.0	1.02 ± 0.06 (4)		

[a] Uncertainties are average deviations. $(BrO_3^-)_0 = 0.43–1.30 \times 10^{-3}$ *M*. [b] $[Np(V)]_0 = 6.00–7.50 \times 10^{-4}$ *M*. [c] $[Mn(II)]_0 = 0.12–0.40$ *M*. [d] $[Ce(III)]_0 = 0.026–0.052$ *M*. [e] Number of experiments.

Unfortunately, the experimental conditions we have employed are opposite to those necessary in the oscillating systems, where large excesses of bromate must be used. We are currently investigating the Ce(III)–Br(V) reaction over a wide range of reactant concentrations but as yet have been unable to find a general rate law. However, the present results shed some light on the problem. First, the general rate law must reduce to eq 2 when the [Ce(III)] is large. Second, the product Ce(IV) almost certainly must appear in the rate expression when the [Ce(III)] is not large. Compare the Np(V) system, where eq 2 is obeyed irrespective of the reactant concentration ratio, with the Ce(III) and Mn(II) systems where this ratio is critical. A major difference is that the Ce(IV) and Mn(III) products are much stronger oxidants than Np(VI). Indeed, the reaction rates with Ce(III) and Mn(II) decrease sharply with the per cent of reaction if approximately stoichiometric concentrations of reactants are used. Third, the complex kinetic behavior is almost certainly not due to either trace impurities introduced with the reducing agent or complex formation between the cation and bromate. It is possible that impurities in the bromate are important, but we obtain identical results with stock reagent grade sodium bromate and sodium bromate obtained after five recrystallizations.

It is interesting that the complex reactions discussed seem to occur with weak, one-equivalent reducing agents (the case is not so clear with Mn(II), but the data strongly suggest that it is behaving like Ce(III) and Np(V)). On the other hand, the reduction of bromate by potentially multiequivalent reducing agents such as Br^-,[4] H_2O_2,[5] and HN_3[6] yields simple, mixed second-order rate laws and exhibits no induction period.

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Mechanism of Reaction of Bromine(V) with Weak One-Electron Reducing Agents

Sir:

Several weak one-electron reducing agents are oxidized by acid bromate at a rate that is second order in bromate and independent of both the concentration and chemical nature of the reducing agent.[1] This peculiar behavior is observed only after a rather ill-defined induction period and in solutions containing a large excess of reducing agent. When bromate is in considerable excess over cerium(III), Kasperek and Bruice[2] report a very different behavior in which the induction period is followed by a sudden burst of reaction that slows greatly long before the equilibrium concentration of cerium(IV) is approached.

The possible complications of this system are further illustrated by the following potentials for different stages of reduction of bromate based on values in Latimer,[3] on the free energy of formation of bromite ion by Lee and Lister,[4] and on the observation of Buxton and Dainton[5] that $BrO_2\cdot$ is unstable with respect to disproportionation.

$$\begin{aligned} BrO_3^- + 2H^+ + e^- &= BrO_2\cdot + H_2O & E^0 &< 1.24\ V \\ BrO_3^- + 3H^+ + 2e^- &= HBrO_2 + H_2O & E^0 &= 1.24\ V \\ BrO_3^- + 5H^+ + 4e^- &= HOBr + 2H_2O & E^0 &= 1.49\ V \\ BrO_3^- + 6H^+ + 5e^- &= {}^1/_2Br_2 + 3H_2O & E^0 &= 1.51\ V \end{aligned}$$

Since Latimer[3] reports that in 1 M sulfuric acid E^0 = 1.44 V for the reaction $Ce^{4+} + e^- = Ce^{3+}$, it is apparent that cerium(III) can reduce bromate if the overall process involves four or five electrons but that the one- and two-electron processes are thermodynamically unfavorable.

These difficult restrictions can be satisfied by the following mechanism.

$$BrO_3^- + HBrO_2 + H^+ \rightleftharpoons 2BrO_2\cdot + H_2O \qquad (1)$$

$$BrO_2\cdot + Ce^{3+} + H^+ \rightleftharpoons HBrO_2 + Ce^{4+} \qquad (2)$$

$$BrO_2\cdot + Ce^{4+} + H_2O \longrightarrow BrO_3^- + Ce^{3+} + 2H^+ \qquad (3)$$

$$2HBrO_2 \longrightarrow BrO_3^- + HOBr + H^+ \qquad (4)$$

Thompson[1] worked at high concentrations of cerium(III) where step 2 essentially suppressed steps -1 and 3. Then steps 1 and 2 accomplish process A which produces $HBrO_2$ autocatalytically according to the kinetics of eq 5.

$$BrO_3^- + 2Ce^{3+} + 3H^+ \longrightarrow HBrO_2 + 2Ce^{4+} + H_2O \qquad (A)$$

$$d[HBrO_2]_A/dt = k_1[BrO_3^-][HBrO_2][H^+] \qquad (5)$$

Although process A has a somewhat unfavorable $\Delta G°$, the almost irreversible step 4 competes effectively with eq -2 in the initial stages of reaction. The overall process is then described by thermodynamically favored process B.

$$BrO_3^- + 4Ce^{3+} + 5H^+ \longrightarrow HOBr + 4Ce^{4+} + 2H_2O \qquad (B)$$

If rates of formation and destruction of $HBrO_2$ are equal, the steady state of eq 6 is established.

$$[HBrO_2] = (k_1/2k_4)[BrO_3^-][H^+] \qquad (6)$$

We have found that establishment of this steady state can be inhibited by traces of bromide ion, and oxidation of cerium(III) commences only after the bromide has been consumed during the induction period. The reaction then proceeds by kinetic eq 7 in exact agreement with the observations of Thompson.[1]

$$-d[BrO_3^-]/dt = (k_1^2/4k_4)[BrO_3^-]^2[H^+]^2 \qquad (7)$$

The rate is clearly independent of the chemical nature of the one-electron reducing agent in step 2 just as is observed. This interpretation can be combined with the kinetic data of Buxton and Dainton[5] to indicate that E^0 = 1.14 V for the one-electron reduction of acid bromate ion, thereby supporting the observation that only moderately strong one-electron reducing agents will react directly with bromate ion.

Kasperek and Bruice[2] worked at low concentrations of cerium(III) where reversibility of step 2 needed to be considered and where $k_3[Ce^{4+}]$ rapidly became significant with respect to $k_2[Ce^{3+}][H^+]$. If step -1 is still neglected, and if steady-state treatments are applied to the concentrations of $HBrO_2$ and of $BrO_2\cdot$, the kinetic equation becomes 8. This equation explains

$$\frac{-d[BrO_3^-]}{dt} = \frac{1}{4k_4}\{(k_1k_2[BrO_3^-][Ce^{3+}][H^+]^2 - k_1k_3[BrO_3^-][Ce^{4+}][H^+] - k_{-2}k_3[Ce^{4+}]^2)/(k_2[Ce^{3+}][H^+] + k_3[Ce^{4+}])\}^2 \qquad (8)$$

why Kasperek and Bruice[2] observed a very pronounced diminution in rate long before equilibrium was approached. It also explains the observation of Thompson[1] that the stronger reductant Np(V) obeys the simple kinetics of eq 7 until reaction has gone much further than with the very weak reductant Ce(III).

A more complete discussion of the thermodynamic and kinetic features of these complex systems and a mechanistic explanation of the oscillations when malonic acid is also present[6] will be published later.

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Stereospecific Elaboration of the A Ring of Gibberellic Acid by Partial Synthesis

Sir:

Chemists in far-flung laboratories have undertaken the formidable task of reproducing gibberellic acid (gibberellin A_3) (**1**) and related structures by chemical synthesis. The result of their efforts to date has been an almost unprecedented outpouring of ingenious synthetic designs and highly original new synthetic methods.[1] We report herein an efficient reaction se-

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(1) Among these outstanding investigations there may be cited contributions emanating from the schools of (a) H. J. E. Loewenthal [*e.g., Tetrahedron Lett.*, 5333 (1966)]; (b) K. Mori and M. Matsui [*e.g., ibid.*, 2183 (1968)]; (c) F. E. Ziegler [*e.g., ibid.*, 2201 (1971)]; (d) R. A. Raphael [*e.g., J. Chem. Soc.*, 3958 (1961)]; (e) W. Nagata [*e.g., J. Amer. Chem. Soc.*, **92**, 3202 (1970)]; (f) G. Stork [*ibid.*, **87**, 1148 (1965)]; (g) S. Masamune [*ibid.*, **86**, 288 (1964)]; (h) H. O. House [*e.g., J. Org. Chem.*, **34**, 2209 (1969)]; (i) L. J. Dolby [*e.g., ibid.*, **36**, 1277 (1971)];