# 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

$$5H^+ + 4M^{n+} + BrO_3^- = 4M^{n+1} + HOBr + 2H_2O \quad (1)$$
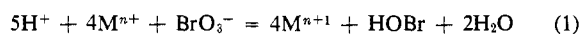
where M is the particular metal ion. All of these reactions exhibit rather poorly reproducible induction periods. The duration of the induction period (1) increases with decreasing bromate concentration and temperature, and (2) increases in the order Np(V) < Mn(II) < Ce(III) for a given initial bromate concentration. After approximately 10% reaction, the behavior of all three systems is accurately described by the empirical rate law

$$-d(BrO_3^-)/dt = k_1(BrO_3^-)^2 \quad (2)$$

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.

(1) (a) A. M. Zhabotinskii, *Dokl. Akad. Nauk SSSR*, **157**, 392 (1964); (b) V. A. Vavilin, A. M. Zhabotinskii, and V. I. Krupyanko, Symposium on Periodic Processes in Biological and Chemical Systems, Nauka, 1967, p 199; (c) H. Degn, *Nature (London)*, **213**, 589 (1967); (d) G. J. Kasperek and T. C. Bruice, *Inorg. Chem.*, **10**, 382 (1971); (e) H. Fruehbeis and A. Roeder, *Angew. Chem., Int. Ed. Engl.*, **10**, 192 (1971).

(2) V. A. Vavilin and A. M. Zhabotinskii, *Kinet. Katal.*, **10**, 83 (1969).

(3) C. G. Knight and R. C. Thompson, unpublished observations.

Table I. Values of k_1 (M^{-1} sec^{-1}) in 3 M H$_2$SO$_4$[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. $(BrO_3^-)_0 = 0.43$–1.30×10^{-3} M. [b] $[Np(V)]_0 = 6.00$–7.50×10^{-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$_2$O$_2$,[5] and HN$_3$[6] yields simple, mixed second-order rate laws and exhibits no induction period.

(4) (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).

(5) (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. Isotopes*, **18** (II), 790 (1967).

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

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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