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On the Oxybromine Chemistry Rate Constants with Cerium Ions in the Field–Körös–Noyes Mechanism of the Belousov–Zhabotinskii Reaction: The Equilibrium $HBrO_2 + BrO_3^- + H^+ \rightleftharpoons 2BrO_2^{\cdot} + H_2O$

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A revised set of rate constants at 20 °C and in 1 M H_2SO_4 is developed for the Field–Körös–Noyes mechanism of the $4Ce(III) + BrO_3^- + 5H^+ \rightleftharpoons 4Ce(IV) + HOBr + 2H_2O$ component of the oscillatory Belousov–Zhabotinskii reaction. The mechanism involves 10 species and 8 reversible reactions. Our results are based on the recognition that the reaction $HBrO_2 + BrO_3^- + H^+ \rightleftharpoons 2BrO_2^{\bullet} + H_2O$ is strongly reversible and is in fact close to equilibrium under normal Belousov–Zhabotinskii conditions where $[Ce(III)] \ll [BrO_3^-]$. This is not true if $Fe(phen)_3^{2+}$ is substituted for Ce(III). We find the equilibrium constant to be about 1×10^{-6} M^{-1}. This value leads to $\Delta G_f^\circ(HBrO_2) \cong -0.4 \pm 1$ kJ/mol and $pK_a(HBrO_2) \cong 4.9$. The species $HBrO_2$ is thus considerably more stable than has been assumed previously. This value of $\Delta G_f^\circ(HBrO_2)$ is combined with other thermodynamic data, several recent determinations of the rate constants of individual component reactions, and data on the overall process to yield a complete set of rate constants that is thermodynamically consistent and in essential agreement with all known direct kinetic measurements. The resulting values are very close to the "Lo" values derived by Tyson except that k for $HBrO_2 + BrO_3^- + H^+ \rightarrow 2BrO_2^{\bullet} + H_2O$ is somewhat higher than proposed by him. They are able to simulate very accurately simultaneous data on [Ce(IV)] and $[BrO_2^{\bullet}]$ in the overall reaction of Ce(III) with bromate even when the reactant concentrations are varied over factors of several hundred. This agreement supports both the essential form of the mechanism and the derived rate constant values, which we believe to be accurate to within a factor of 2. Propagation of the revised rate constants into the Oregonator reduction of the Field–Körös–Noyes mechanism is discussed.

An important benefit of the continued interest over the past 15 years in the oscillatory Belousov–Zhabotinskii (BZ) reaction[1,2] has been the development of considerable systematic understanding[1-5] of the reactions and thermochemistry in ~1 M H_2SO_4 of the oxybromine compounds BrO_3^-, $BrO_2^{\bullet}$, $HBrO_2$, and HOBr, as well as their reactions among themselves and with the ions Ce(III) and Ce(IV). The basic form of this chemistry was presented by Field, Körös, and Noyes[1] (FKN) in 1972 and now seems universally accepted.[2,3,6] It is given by reactions R1–R7, which are numbered after FKN.

$$\mathrm{Br^- + HOBr + H^+ \rightleftharpoons Br_2 + H_2O} \qquad \text{(R1)}$$

$$\mathrm{Br^- + HBrO_2 + H^+ \rightleftharpoons 2HOBr} \qquad \text{(R2)}$$

$$\mathrm{Br^- + BrO_3^- + 2H^+ \rightleftharpoons HOBr + HBrO_2} \qquad \text{(R3)}$$

$$\mathrm{HBrO_2 + HBrO_2 \rightleftharpoons HOBr + BrO_3^- + H^+} \qquad \text{(R4)}$$

$$\mathrm{HBrO_2 + BrO_3^- + H^+ \rightleftharpoons Br_2O_4 + H_2O} \qquad \text{(R5}')$$

$$\mathrm{Br_2O_4 \rightleftharpoons 2BrO_2^{\bullet}} \qquad \text{(R5}'')$$

$$\mathrm{HBrO_2 + BrO_3^- + H^+ \rightleftharpoons 2BrO_2^{\bullet} + H_2O} \qquad \text{(R5} = \text{R5}' + \text{R5}'')$$

$$\mathrm{Ce(III) + BrO_2^{\bullet} + H^+ \rightleftharpoons Ce(IV) + HBrO_2} \qquad \text{(R6)}$$

$$\mathrm{Ce(IV) + BrO_2^{\bullet} + H_2O \rightleftharpoons Ce(III) + BrO_3^- + 2H^+} \qquad \text{(R7)}$$

A thermodynamically consistent set of rate constants for these reactions (which are essentially the mechanism of the reaction $4Ce(III) + BrO_3^- + 5H^+ \rightleftharpoons 4Ce(IV) + HOBr + 2\ H_2O$, in the presence of significant initial concentrations of Br^- and Br_2) also incorporating all kinetic data known at that time was deduced by FKN. It was later refined and extended by Barkin et al.[4] These are called the FKN values and are given in Table I. The FKN rate constants have been remarkably successful at reproducing in computer simulations[7-10] a wide variety of observed behaviors of both the BZ reaction and the overall reaction of Ce(III) with BrO_3^-. Perhaps their most striking accomplishment is the prediction[11] and experimental realization[12,13] of the minimal BrO_3^- oscillator.

However, quantitative problems have appeared suggesting that the FKN rate constants need to be modified. Tyson[3,14,15] pointed out problems that develop when the FKN values are propagated into the Oregonator model[16] of the BZ reaction and suggested that the FKN rate constants seem much too large. Discrepancies are particularly apparent in reproducing BZ-like traveling wave velocities.[3,17-19] Noszticzius et al.[20] presented direct experimental evidence that both k_2 and k_4 are much smaller than quoted by FKN. These results have now been confirmed by Ariese and

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TABLE I: FKN Rate Constants

reactn	k_{forward}	k_{reverse}	K_{equil}
R1	$k_1 = 8 \times 10^9$ M^{-2} s^{-1}	$k_{-1} = 110$ s^{-1}	7.3×10^7 M^{-2}
R2	$k_2 = 2 \times 10^9$ M^{-2} s^{-1}	$k_{-2} = 5.0 \times 10^{-5}$ M^{-1} s^{-1}	4.0×10^{13} M^{-1}
R3	$k_3 = 2.1$ M^{-3} s^{-1}	$k_{-3} = 1 \times 10^4$ M^{-1} s^{-1}	2.1×10^{-4} M^{-2}
R4	$k_4 = 4 \times 10^7$ M^{-1} s^{-1}	$k_{-4} = 2 \times 10^{-10}$ M^{-2} s^{-1}	2.0×10^{17} M
R5 = R5′ + R5″	$k_5 = 1 \times 10^4$ M^{-2} s^{-1}	$k_{-5} = 2 \times 10^7$ M^{-1} s^{-1}	5.0×10^{-4} M^{-1}
R6	$k_6 = 6.5 \times 10^5$ M^{-2} s^{-1}	$k_{-6} = 2.4 \times 10^7$ M^{-1} s^{-1}	2.7×10^{-2} M
R7	$k_7 = 9.6$ M^{-1} s^{-1}	$k_{-7} = 1.3 \times 10^{-4}$ M^{-3} s^{-1}	7.4×10^4 M^2

TABLE II: Revised Rate Constants and Thermodynamic Data[a]

reactn	k_{forward}	k_{reverse}	K_{equil}	$\Delta G°$ (±1),[b] kJ/mol
R1	$k_1 = 8 \times 10^9$ M^{-2} s^{-1}	$k_{-1} = 110$ s^{-1}	7.3×10^7 M^{-2}	−44
R2	$k_2 = 3 \times 10^6$ M^{-2} s^{-1}	$k_{-2} = 2 \times 10^{-5}$ M^{-1} s^{-1}	1.5×10^{11} M^{-1}	−63
R3	$k_3 = 2$ M^{-3} s^{-1}	$k_{-3} = 3.2$ M^{-1} s^{-1}	0.6 M^{-2}	+1
R4	$k_4 = 3000$ M^{-1} s^{-1}	$k_{-4} = 1 \times 10^{-8}$ M^{-2} s^{-1}	3×10^{11} M	−64
R5′	$k_{5'} = 42$ M^{-2} s^{-1}	$k_{-5'} = 2.2 \times 10^3$ s^{-1}	1.9×10^{-2} M^{-2}	+10
R5″	$k_{5''} = 7.4 \times 10^4$ s^{-1}	$k_{-5''} = 1.4 \times 10^9$ M^{-1} s^{-1}	5.3×10^{-5} M	+24
R5 = R5′ + R5″	$k_5 = 42$ M^{-2} s^{-1}	$k_{-5} = 4.2 \times 10^7$ M^{-1} s^{-1}	1×10^{-6} M^{-1}	+34
R6	$k_6 = 8 \times 10^4$ M^{-2} s^{-1}	$k_{-6} = 8.9 \times 10^3$ M^{-1} s^{-1}	9 M^{-1}	−5
R7	$k_7 \simeq 0$	$k_{-7} \simeq 0$	1.2×10^5 M^2	−29

[a] All calculations were carried out at 293.15 K. [b] These $\Delta G°$ values were calculated from the equilibrium constant in the preceding column using $\Delta G° = -RT \ln K$. Because of roundoff errors (and in the cases of reactions R1 and R3 corrections for nonideality) they will differ slightly from $\Delta G°$ values calculated directly from the following $\Delta G_f°$ values. Free energies of formation in kJ/mol used are, Br^- = −102.8,[c] Br_2 = +4.1,[c] HOBr = −83.3,[c] $BrO_2^\bullet \simeq 144 \pm 1$,[c] BrO_2^- = 27,[c] $HBrO_2 \simeq -0.4 \pm 1$,[d] BrO_3^- = 18,[c] BrO_4^- = 118.3,[e] H_2O = −237.1.[c] The values for $BrO_2^\bullet$ and $HBrO_2$ are estimated from kinetic measurements and must be uncertain by at least ±1 kJ/mol. [c] Tyson, J. J. In *Oscillations and Traveling Waves in Chemical Systems*"; Field, R. J., Burger, M., Eds.; Wiley-Interscience: New York, 1985. [d] This work. [e] Schreiner, F.; Osborne, D. W.; Pocius, A. V.; Appleman, E. H. *Inorg. Chem.* **1970**, *9*, 2320. This quantity is not used in the calculations reported here but is included for completeness. Reaction R5′ is assumed to be rate determining for reaction R5 in both the forward and the reverse directions.

Nagy-Ungvârai.[21,22]

The source of the problem was identified by Tyson,[3] who emphasized that the absolute magnitude of the FKN rate parameters is dependent on the assumption $pK_a(HBrO_2) \cong 2$, which allowed FKN to estimate $\Delta G_f°(HBrO_2)$ and thus to assign values to k_2 and k_5. The values of other rate constants were then calculated with equilibrium constants (also dependent on $\Delta G_f°(HBrO_2)$) and experimentally determined ratios of $k_{5'}/k_2$ and $k_{5'}^2/4k_4$. Unfortunately, all experimental constraints known to FKN were used by them to arrive at their internally consistent set of rate constants. No other information remained to be used as a cross-check for external consistency, especially of their assumed value of $pK_a(HBrO_2)$.

While $pK_a(HBrO_2) \cong 2$ is in keeping with known[23] pK_a values of other HXO_2 acids, there is evidence[24] that the true value is closer to 6 than to 2. Tyson also pointed out other experiments[25] in which the lifetime of $HBrO_2$ seems longer than is possible if k_4 is as large as the FKN value.

Tyson then went on to develop a new set of values for k_2, k_4, and k_5 (the important rate constants for the Oregonator, his major interest). These values are $k_2 = 1 \times 10^6$ M^{-2} s^{-1}, $k_4 = 2 \times 10^3$ M^{-1} s^{-1}, and $k_5 = 10$ M^{-2} s^{-1} and are referred to as the "Lo" values as they are considerably smaller than the FKN values. Tyson also presented a "Hi" set of values based on $k_4 = 4 \times 10^8$ M^{-1} s^{-1} inferred by Lamberz.[26] This value of k_4 is even higher than the FKN value.

It is difficult to determine which of the competing sets of rate constants is most accurate by investigation of the overall reaction of Ce(III) with BrO_3^- or of the BZ reaction. Thus Bar-Eli and Ronkin[9] found that the FKN values typically reproduce experiment better than either the "Hi" or the "Lo" values, and Field and Boyd[10] concluded that the "Lo" value of k_5 was much too small, at least at 29 °C. The latter authors also found that the FKN values simulated the Ce(III)/Ce(IV)–BrO_3^-–H_2SO_4–oxalic acid–acetone oscillator well. They did report, however, that a set of rate constants much smaller than the FKN values also was able to reproduce the experimentally observed oscillations.

The reason for the success of the FKN rate constants is that the most apparent features of the BZ reaction and of the overall Ce(III)–bromate reaction itself are determined by the values of k_1 and by the ratios $k_{5'}/k_2$, $k_{5'}^2/4k_4$, and k_6/k_{-6}. The FKN values are thermodynamically consistent and maintain k_1, $k_{5'}/k_2$, and $k_{5'}^2/4k_4$, which can be independently determined, at their correct values. The remaining parameter, k_6/k_{-6} is then adjusted to reproduce experiment. Even if the absolute values are grossly incorrect, agreement with experiment is good if these ratios are correct. The large discrepancies observed between calculated and experimental traveling wave velocities[3,17–19] likely arise because $Fe(phen)_3^{3+}/Fe(phen)_3^{2+}$ rather than Ce(III)/Ce(IV) is used as the metal-ion catalyst in these experiments. Reaction R6 is much faster[27,28] with $Fe(phen)_3^{2+}$ than with Ce(III), causing $k_{5'}$ alone rather than $k_{5'}^2/4k_4$ to be rate determining in the wavefront.[19,29] While the "Lo" values are much closer to the correct absolute magnitudes than the FKN values, they assume $k_{5'}^2/4k_4 \cong 0.01$ M^{-3} s^{-1} rather than the correct value of $\cong$0.15 M^{-3} s^{-1} and thus do not reproduce experiment as well as the FKN values.

We report here that some experiments due to Försterling et al.[30] may be interpreted by assuming that (R5) is at equilibrium with $K_5 \cong 1 \times 10^{-6}$ M^{-1} and that $pK_a(HBrO_2) \cong 4.9$. We then develop a set of rate constants that is consistent with all known kinetic and thermodynamic data in 1 M H_2SO_4 at 20 °C. These rate constants are given in Table II and are much closer to the Tyson "Lo" values than to the FKN values.

The Equilibrium $HBrO_2 + BrO_3^- + H^+ \rightleftharpoons 2BrO_2^\bullet + H_2O$

Försterling et al.[30] investigated the injection of small aliquots (~200 μL) of $NaBrO_2$ in 0.1 M NaOH into 120-mL solutions of 1 M BrO_3^- in 1 M H_2SO_4. It is expected that the BrO_2^- will

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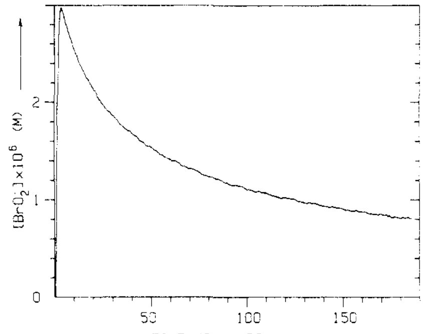

Figure 1. Concentration of $BrO_2^\cdot$ calculated from the absorbance at 488 nm and $\epsilon_{488}(BrO_2^\cdot) = 975$ M^{-1} cm^{-1} after injecting 1 mL of a 1.74×10^{-3} M $NaBrO_2$ solution into 136 mL of a deoxygenated 1 M solution of $NaBrO_3$ in 1 M H_2SO_4 (leading to an initial concentration $C_0 = 1.3 \times 10^{-5}$ M of $HBrO_2$): optical pathlength, 10.8 cm; temperature, 20.0 °C; monitoring wavelength, 488 nm (spectral bandwidth 10 nm, double-interference filter arrangement); reference wavelength, 670 nm (dual-wavelength method). Further details of the experimental method are given in ref 30.

be protonated quickly to yield $HBrO_2$, which will react in (R5) to yield $BrO_2^\cdot$. They assumed that (R5) is only slowly reversible, a reasonable assumption based on the FKN rate constants.

Försterling et al.[30] identified $BrO_2^\cdot$ by its spectrum as the product of (R5). The kinetics of $BrO_2^\cdot$ (followed by the absorbance at 488 nm) in a typical experiment is shown in Figure 1. The $BrO_2^\cdot$ disappears slowly after its rapid formation. It was initially assumed that (−R5) is rate determining for this disappearance, again a reasonable assumption if k_4 were as large as suggested by FKN.

There is a problem in these experiments, however, with the amount of $BrO_2^\cdot$ produced. It is expected from the stoichiometry of (R5) that $[BrO_2^\cdot]_{max} = 2[HBrO_2]_0$, but this amount of $BrO_2^\cdot$ is approached only when $[HBrO_2]_0$ falls to approximately 10^{-8} M. This discrepancy was ascribed to two sources. (1) At higher $[HBrO_2]_0$ considerable $HBrO_2$ disappears during mixing by disproportionation in (R4) before it can react with BrO_3^- in (R5). (2) The observed $BrO_2^\cdot$ is in equilibrium with its dimer, Br_2O_4, in (R5″). The first assumption is supported by the large FKN value of k_4. The second assumption is supported because it is clear from the Försterling et al. results that the $BrO_2^\cdot$ is in equilibrium with other species. A double-injection experiment was designed that eliminated problems from the initial reaction of $HBrO_2$ in (R4) and led to an apparent equilibrium constant of about 1×10^{-6} M^{-1}. However, this value is about 50 times smaller than the value of $K_{5''} = 5.3 \times 10^{-5}$ M^{-1} determined directly by Buxton and Dainton[31] in a pulse radiolysis experiment. This difference was ascribed to the fact that Buxton and Dainton worked in neutral solution rather than in 1 M H_2SO_4, although $K_{5''}$ is not expected to be strongly medium dependent.

The Försterling et al.[30] interpretation is not valid if (R4) is as slow as implied by the direct measurements of Noszticzius et al.[20] and Ariese and Nagy-Ungvárai.[21] Assigning $k_{5'}$ a value commensurate with the rapid appearance of $BrO_2^\cdot$ and $k_4 = 3000$ M^{-1} s^{-1}, it is more reasonable to assume that (R5′) and (R5″) are both at equilibrium. Thus the equilibrium constant measured by Försterling et al.[30] must be $K_5 = K_{5'}K_{5''}$ rather than $K_{5''}$. This assumption is verified by experiments[27] in which BrO_2^- is added to solutions with varying $[BrO_3^-]$. The amount of $BrO_2^\cdot$ present at equilibrium in these experiments depends upon $[BrO_3^-]^{1/2}$.

If (R5) is at equilibrium, the slow decay of $BrO_2^\cdot$ evident in Figure 1 can be interpreted in terms of (R4) and (R5). The disappearance of $BrO_2^\cdot$ is governed in this case by the stoichiometric relationship[32]

$$2C_0 = [BrO_2^\cdot] + 2[HBrO_2] + 4[HOBr] \qquad (I)$$

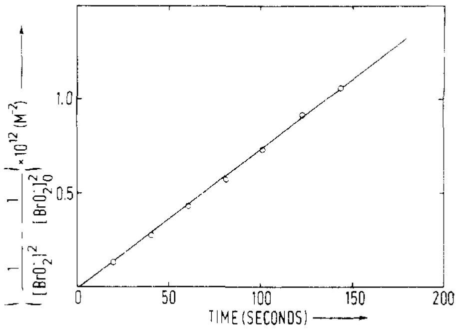

Figure 2. Plot of the experimental $[BrO_2^\cdot]$ vs. time data in Figure 1 according to eq III. The slope yields $2k_4/(K_5[BrO_3^-][H^+]) = 7.1 \times 10^9$ M^{-2} s^{-1}.

where C_0 is the initial $[HBrO_2]$. With the assumptions that (R5) is at equilibrium and that (R4) is rate determining for the disappearance of $HBrO_2$, differentiation of eq I leads to eq II. Under

$$\frac{d[BrO_2^\cdot]}{dt} = \frac{-4k_4[BrO_2^\cdot]^4}{K_5[H^+][BrO_3^-](K_5[H^+][BrO_3^-] + 4[BrO_2^\cdot])} \qquad (II)$$

the condition $4[BrO_2^\cdot] \gg K_5[H^+][BrO_3^-]$ (which for $K_5 \cong 1 \times 10^{-6}$ M^{-1}, $[H^+] = [BrO_3^-] = 1$ M, is true when $[BrO_2^\cdot] > 10^{-6}$ M), integration of eq II leads to eq III. A plot of the data shown

$$\frac{1}{[BrO_2^\cdot]^2} - \frac{1}{[BrO_2^\cdot]_0^2} = \frac{2k_4}{K_5[H^+][BrO_3^-]}t \qquad (III)$$

in Figure 1 according to eq III is shown in Figure 2. This plot and four others with 5×10^{-6} M $\leqslant [HBrO_2]_0 \leqslant 2.2 \times 10^{-5}$ M and $[H_2SO_4] = [BrO_3^-] = 1$ M are linear with an average slope (equal to $2k_4/(K_5[H^+][BrO_3^-])$) of $(7 \pm 2) \times 10^9$ M^{-2} s^{-1}.

With the assumption that $k_4 = 3000$ M^{-1} s^{-1}, in keeping with the direct measurements of Noszticzius et al.,[20] Ariese and Nagy-Ungvárai,[21] and Försterling,[27] a value of $K_5 = 0.9 \times 10^{-6}$ M^{-1} is obtained from the slope of Figure 2. This result is in agreement with that obtained directly by Försterling et al.[30] in their double-injection experiment.

Plots such as that in Figure 2 are linear only for $[BrO_2^\cdot] \gtrsim 5 \times 10^{-6}$ M. At lower $BrO_2^\cdot$ concentrations its rate of disappearance does not decrease as rapidly as in eq III. This problem becomes worse if the approximation $K_5[H^+][BrO_3^-] \ll 4[BrO_2^\cdot]$ is not made. There is apparently a first-order component of the disappearance of $HBrO_2$ at lower concentrations. A similar result has been noted[27] in direct experiments on the disproportionation of $HBrO_2$ at low concentrations. The concentration of $HBrO_2$ is usually too high in both the BZ reaction and the overall reaction of Ce(III) with bromate for this effect to be important.

The reversibility of (R5) can be confirmed by using simultaneous measurements of [Ce(IV)] and $[BrO_2^\cdot]$ during the overall reaction of Ce(III) with bromate. Such data are shown for [Ce(IV)] in Figure 3a and for $[BrO_2^\cdot]$ in Figure 3b. In Figure 3a [Ce(IV)] initially increases exponentially before entering a period of linear growth that is followed by a sharp decrease in d[Ce(IV)]/dt as (−R6) becomes competitive with (R5), and the final state is approached asymptotically. In Figure 3b $[BrO_2^\cdot]$ grows exponentially before reaching a maximum that appears a little later (presumably due to $BrO_2^\cdot$ production in (−R6)) than the period of linear growth of [Ce(IV)]. The $[BrO_2^\cdot]$ then decays as d[Ce(IV)]/dt falls to near zero.

We assume that in the region of constant d[Ce(IV)]/dt the reaction is at a pseudo-steady state in which $HBrO_2$ production from (R5) followed by (R6) is balanced by its destruction in (R4). We further assume that Ce(IV) production is by (R6). Thus $k_6 = [d[Ce(IV)]/dt]/([BrO_2^\cdot][Ce(III)][H^+])$ should be valid in the region of linear [Ce(IV)] growth. Division of d[Ce(IV)]/dt in the linear region of each experiment by the corresponding values of [Ce(III)] and $[BrO_2^\cdot]$ at the midpoint of the linear region yields

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(31) Buxton, G. V.; Dainton, F. S. *Proc. R. Soc. London, A* **1968**, *304A*, 427. It should be noted that $K_{5''}$ was miscalculated in this paper as 0.053 M^{-1} rather than the correct value of 5.3×10^{-5} M^{-1}.

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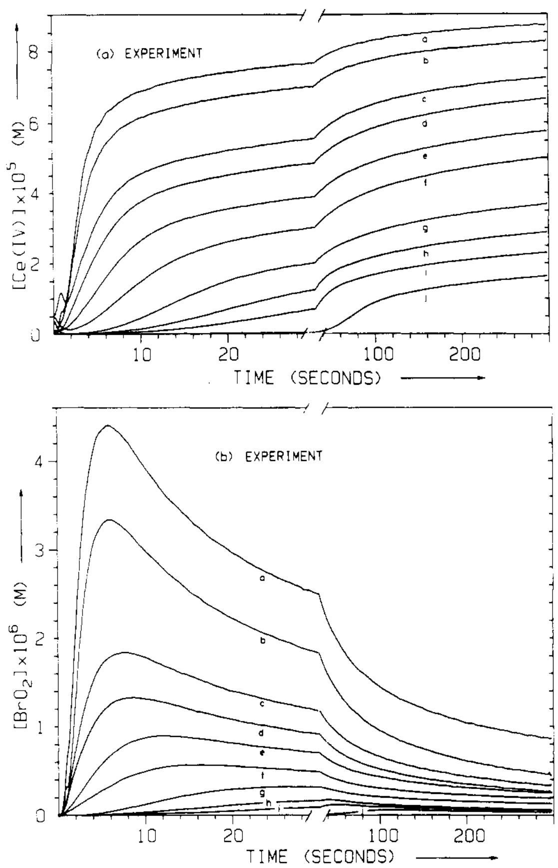

Figure 3. Experimental [Ce(IV)] (a) and [$\mathrm{BrO_2^\bullet}$] (b) during the reaction of Ce(III) with an excess of $\mathrm{BrO_3^-}$. The [Ce(IV)] is calculated from the measured absorbance at 401 nm with ϵ_{401}(Ce(IV)) = 800 $\mathrm{M^{-1}\ cm^{-1}}$, and [$\mathrm{BrO_2^\bullet}$] is calculated from the measured absorbance at 549 nm with $\epsilon_{549}(\mathrm{BrO_2^\bullet})$ = 387 $\mathrm{M^{-1}\ cm^{-1}}$ (optical path length 10.8 cm). At t = 0 Ce(III) was injected (initial concentration $C_0 = 1 \times 10^{-4}$ M) into 1 M $\mathrm{H_2SO_4}$ solutions containing varying concentrations of $\mathrm{NaBrO_3}$. The $\mathrm{BrO_3^-}$ concentrations are (a) 1 M, (b) 0.75 M, (c) 0.35 M, (d) 0.2 M, (e) 0.1 M, (f) 0.05 M, (g) 0.02 M, (h) 0.01 M, (i) 0.005 M, and (j) 0.002 M. The bromate solutions were deoxygenated; the temperature was 20 °C. The irregularities within the first 2 s are due to the processes of injecting and mixing. Further experimental details are given in ref 33.

$k_6 = 8 \pm 2 \times 10^4\ \mathrm{M^{-2}\ s^{-1}}$, in very good agreement with the value obtained in a more direct experiment by Försterling et al.[33]

With the assumption that (R5) is at equilibrium and that a pseudo-steady state is reached between $\mathrm{HBrO_2}$ production by (R6) and $\mathrm{HBrO_2}$ destruction by (R4), eq IV is obtained. A plot of

$$[\mathrm{BrO_2^\bullet}] = (K_5^2k_6/2k_4)^{1/3}[\mathrm{Ce(III)}]^{1/3}[\mathrm{BrO_3^-}]^{2/3}[\mathrm{H^+}] \tag{IV}$$

ln $\{[\mathrm{BrO_2^\bullet}]/([\mathrm{Ce(III)}]^{1/3}[\mathrm{H^+}])\}$ vs. ln [$\mathrm{BrO_3^-}$] should then be linear with a slope of $^2/_3$ and an intercept of $^1/_3$ ln $(K_5^2k_6/(2k_4))$. Such a plot is shown in Figure 4. It is linear with a slope of $^2/_3$ and an intercept of −9.86, leading to $(K_5^2k_6/(2k_4))^{1/3} = 5.22 \times 10^{-5}$ $\mathrm{M^{-1}}$. The value of this quantity calculated from the parameters developed here (see Table II) is $2.37 \times 10^{-4}\ \mathrm{M^{-1}}$, about a factor of 4 higher than the experimental value. This discrepancy occurs because eq IV does not take into account the fact that the concentrations of $\mathrm{HBrO_2}$ and $\mathrm{BrO_2^\bullet}$ are comparable in these experiments. Thus the approximation $K_5[\mathrm{BrO_3^-}][\mathrm{H^+}] \ll 4[\mathrm{BrO_2^\bullet}]$ implicitly made in deriving eq IV is not true here as it is for the data shown in Figure 2.

We assume the parameters in Table II and point out the conclusion that under the conditions of the Ce(III)/Ce(IV)-catalyzed BZ reaction ([Ce(III)] $\cong 10^{-4}$ M, [$\mathrm{BrO_3^-}$] $\geq$ 0.01 M, and [$\mathrm{BrO_2^\bullet}$] $\cong 10^{-6}$ M) (R6) is slower than (−R5) and that (R5) is thus generally close to equilibrium or at least substantially reversible. This is not true if [Ce(III)] > 10^{-3} M, especially at low [$\mathrm{BrO_3^-}$], where (R6) may in fact dominate[34,35] (−R5). On the other hand, (R6) is substantially faster[27] with $\mathrm{Fe(phen)_3^{2+}}$ than with Ce(III) (Field et al.[28] find k_6 to be about $2 \times 10^9\ \mathrm{M^{-1}}$ $\mathrm{s^{-1}}$ with $\mathrm{Fe(CN)_6^{4-}}$), and (R5) is seldom reversible with this or other low-redox-potential catalysts.[19,36] Furthermore, (R6) is also not appreciably reversible with these catalysts.[19,36] The reagents used in traveling wave experiments[3,17-19] normally use such low-redox-potential catalysts and may behave substantially different from Ce(III)/Ce(IV)-catalyzed systems.

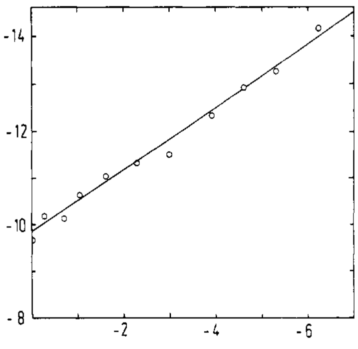

Figure 4. Test of eq IV by plotting ln ([$\mathrm{BrO_2^\bullet}$]/([Ce(III)]$^{1/3}$[$\mathrm{H^+}$])) vs. ln ([$\mathrm{BrO_3^-}$]). The [$\mathrm{BrO_2^\bullet}$] were taken from Figure 3b at the time of the midpoint of the region of linear [Ce(IV)] growth in Figure 3a. The slope is 0.66 and the intercept is −9.86.

Derived Value of $\Delta G_f°(\mathrm{HBrO_2})$

We assume that $K_5 = 1 \times 10^{-6}\ \mathrm{M^{-1}}$. Previously developed[1-3,5] thermodynamic data (see Table II) then allows $\Delta G_f°(\mathrm{HBrO_2})$ to be calculated from eq V. The result obtained is $\Delta G_f°(\mathrm{HBrO_2})$

$$-RT \ln K_5 = \Delta G_f°(\mathrm{H_2O}) + 2\Delta G_f°(\mathrm{BrO_2^\bullet}) - \Delta G_f°(\mathrm{BrO_3^-}) - \Delta G_f°(\mathrm{HBrO_2}) - \Delta G_f°(\mathrm{H^+}) \tag{V}$$

$\cong -0.4 \pm 1$ kJ/mol. Combining this result with $\Delta G_f°(\mathrm{BrO_2^-})$ = 27 kJ/mol leads to pK_a($\mathrm{HBrO_2}$) $\cong$ 4.9, which is much higher than the value assumed by FKN and close to the value of 6 suggested by Massagli et al.[24] and used by Tyson.[3]

The Reaction $4\mathrm{Ce(III)} + \mathrm{BrO_3^-} + 5\mathrm{H^+} \rightleftharpoons 4\mathrm{Ce(IV)} + \mathrm{HOBr} + 2\ \mathrm{H_2O}$

Reactions R1–R7 are the mechanism of the above reaction. We now use the value of $\Delta G_f°(\mathrm{HBrO_2})$ derived above as well as previously available and recently reported kinetic data to suggest revisions in both the FKN and the "Lo" rate constants. There is no further need to consider the "Hi" rate constants as they are based on the clearly incorrect value $k_4 = 4 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$. We treat the component reactions in a logical rather than in numerical order.

Reaction R4. We use $k_4 = 3000\ \mathrm{M^{-1}\ s^{-1}}$ based on the results of Noszticzius et al.,[20] Ariese and Nagy-Ungvārai,[21] and Försterling[27] and find $K_4 = k_4/k_{-4} = 3 \times 10^{11}$ M and $k_{-4} = 1 \times 10^{-8}\ \mathrm{M^{-2}\ s^{-1}}$. This reaction is very seldom reversible in the BZ reaction.

Reaction R5 = R5′ + R5″. Quantitative treatment of this reaction is complicated because the available data are at several temperatures and in several media. We use data at 20 °C and in 1 M $\mathrm{H_2SO_4}$ where available.

The values $K_{5''} = 5.3 \times 10^{-5}$ M and $k_{-5''} = 1.4 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$ were determined by Buxton and Dainton[31] using pulse radiolysis experiments in neutral solutions. We accept these values in 1 M $\mathrm{H_2SO_4}$ because no other data exist and because (R5″) should not be strongly medium dependent as it does not involve charged species. While it is not possible[28] to reproduce the pulse radiolysis

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[33] Försterling, H.-D.; Lamberz, H.-J.; Schreiber, H. *Z. Naturforsch. A: Phys., Phys. Chem., Kosmophys.* **1985**, *40A*, 368. The value $k_6 = 1 \times 10^5$ $\mathrm{M^{-2}\ s^{-1}}$ was reported in this paper. However, the effect of the reverse reaction, −R6, was not accounted for. Doing so does not affect the first-order kinetics predicted and observed but leads to $k_6 = 8 \times 10^4\ \mathrm{M^{-2}\ s^{-1}}$.

[34] Noyes, R. M.; Field, R. J.; Thompson, R. C. *J. Am. Chem. Soc.* **1971**, *93*, 7315.

[35] Thompson, R. C. *J. Am. Chem. Soc.* **1971**, *93*, 7315.

[36] Kuhnert, L.; Krug, H.-J. *J. Phys. Chem.*, submitted.

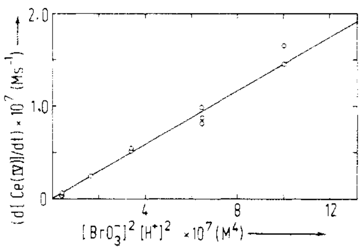

Figure 5. Plot of d[Ce(IV)]/d*t* vs. $[BrO_3^-]$ measured in the region of linear growth of [Ce(IV)] during the reaction of an excess of Ce(III) (0.05 M) with BrO_3^- in the concentration range 2×10^{-4} to 10^{-3} M. All experiments were carried out in deoxygenated 1 M H_2SO_4 solutions at 20.0 °C.

experiments in 1 M H_2SO_4, the equivalent flash photolysis experiments[37] are possible in this medium and have been undertaken.[27] The results are very similar to those of Buxton and Dainton.[31]

If $K_5 = 1 \times 10^{-6}$ M^{-1} and $K_{5''} = 5.3 \times 10^{-5}$ M, then $K_{5'} = k_{5'}/k_{-5'} = K_5/K_{5''} = 0.019$ M^{-2}. Further information is required to separate $k_{5'}$ and $k_{-5'}$. Unfortunately, it is very difficult[27] to measure $k_{5'}$ directly by the addition of $HBrO_2$ to BrO_3^- solutions. The solution volume must be large in order to detect the weak absorbance due to $BrO_2^•$. Thus the mixing time is several seconds. At $BrO_3^- \cong 1$ M, where a substantial fraction of the added $HBrO_2$ is converted to $BrO_2^•$, the half-life of (R5′) is less than a second if $k_{5'} \cong 10$ M^{-2} s^{-1}, the lowest value suggested so far. However, at $BrO_3^- \cong 10^{-3}$ M, where (R5′) is much slower, only about 1% of the added $HBrO_2$ is converted to $BrO_2^•$, and this takes only a second or so. That is, at low $[BrO_3^-]$ the approach to equilibrium is governed by the reverse reactions, which are rapid. Thus at both high and low $[BrO_3^-]$ the maximum $[BrO_2^•]$ is reached during mixing.

Fortunately, a value of $k_{5'}^2/4k_4$ is available from experiments on the overall reaction of Ce(III) with bromate. As mentioned earlier, at high [Ce(III)], e.g., 0.1 M, and low $[BrO_3^-]$, e.g., 10^{-3} M, (R6) is dominant over (−R5). Thus (R5′) becomes rate determining for the production of $HBrO_2$, and a pseudo-steady state develops with $HBrO_2$ being removed by (R4). This is the complementary circumstance to that when (R5) is strongly reversible and eq IV is applicable. Noyes et al.[34] pointed out that under this circumstance eq VI governs the production of Ce(IV).

$$\frac{1}{4}\frac{d[\mathrm{Ce(IV)}]}{dt} = \frac{k_{5'}^2}{4k_4}[\mathrm{BrO_3^-}]^2[\mathrm{H^+}]^2 \qquad \text{(VI)}$$

Thompson[35] showed the form of eq VI to be followed experimentally for Ce(III), Mn(II), and Np(V) in 3 M H_2SO_4 at 25 °C. His results were independent of both the identity and the concentration of metal ion. Noyes et al.[34] deduced from this result that $k_{5'}^2/4k_4 = 0.7$ M^{-3} s^{-1}. Knight and Thompson[38] found $k_{5'}^2/4k_4 = 0.12$ M^{-3} s^{-1} in 1 M $HClO_4$ at 25 °C, and we regard this as clear evidence of a medium effect between 1 M $HClO_4$ and 3 M H_2SO_4.

We have repeated the experiment at 20 °C and in 1 M H_2SO_4. There is a region of linear growth of [Ce(IV)] after the exponential onset of reaction but before significant amounts of BrO_3^- are consumed or Ce(IV) are produced. Figure 5 shows a plot of d[Ce(IV)]/d*t* in the linear region vs. $[BrO_3^-]^2$ in the range 10^{-4}–10^{-3} M BrO_3^-. It is linear and its slope yields $k_{5'}^2/4k_4 = 0.15$ M^{-3} s^{-1}. We use this result to calculate $k_{5'}$, assuming $k_4 = 3000$ M^{-1} s^{-1}. The result is $k_{5'} = 42$ M^{-2} s^{-1}, which yields $k_{-5'} = 2.2 \times 10^3$ s^{-1} from $K_{5'} = 0.019$ M^{-2}.

The value $k_{5'} = 42$ M^{-2} s^{-1} at 20 °C is somewhat larger than suggested by other data. The Knight and Thompson[38] value of $k_{5'}^2/4k_4$ leads to $k_{5'} = 38$ M^{-2} s^{-1}, but this is at 25 °C and $\Delta E_a = 60$ kJ/mol[19] for (R5′). Treatment of radioactive exchange data due to Betts and MacKenzie[39] in 1 M $HClO_4$ at 25 °C leads to $k_{5'} = 10$ M^{-2} s^{-1}. This discrepancy may be due to the medium effect or the complexity of the data treatment, which is very sensitive to the thermodynamic data used. A value $k_{5'} = 30$ M^{-2} s^{-1} was obtained by Kuhnert et al.[19] in 0.613 M H_2SO_4 at 25 °C, but the interpretation that led to this result ignores the effect of (R4), which would make $k_{5'}$ seem somewhat smaller than its true value. We suggest that the value reported here for $k_{5'}$ is probably an upper limit.

The question arises as to whether (−R5′) might be competitive with (R5″). We find $k_{-5'} = 2.2 \times 10^3$ s^{-1} and $k_{5''} = 7.4 \times 10^4$ s^{-1}, which suggests that (R5′) is not at equilibrium unless (R5″) is also. If these reactions were competitive, however, then the number we have assigned to $k_{5'}$ is actually $k_{5'}k_{5''}/(k_{-5'} + k_{5''})$ or even $k_{5''}K_{5'}$. These cases are kinetically indistinguishable.

On the basis of the rate constants in Table II, (R5″) is faster in both directions than (R5′). Reaction R5′ is then rate determining for both directions of the overall process, (R5), and we list in Table II $k_5 = 42$ M^{-2} s^{-1} and $k_{-5} = k_{-5'}/K_{5''} = 4 \times 10^7$ M^{-1} s^{-1}. This value of k_{-5} is about 2 times larger than measured by Buxton and Dainton[31] from the disappearance of $BrO_2^•$ in neutral solutions, where $k_{5'}$ is very small. Reasonable agreement here is of particular importance to the consistency of our arguments as the value of $\Delta G_f°(BrO_2^•)$ listed in Table II and used in the calculation of $\Delta G_f°(HBrO_2)$ is based[3] on the Buxton and Dainton[31] value of k_{-5}.

Reaction R1. The values of k_1 and k_{-1} reported by Eigen and Kustin[41] and adjusted to 1 M H_2SO_4 by FKN have been accepted by all later workers and do not seem to require modification. The value $K_1 = 7 \times 10^7$ M^{-2} s^{-1} at 20 °C has been confirmed in a direct experiment by Lamberz reported by Noszticzius et al.[6]

Reaction R2. The value $k_{-2} = 5 \times 10^{-5}$ M^{-1} s^{-1} has been determined[39] in 1.67 M $HClO_4$ at 25 °C. Assumption of a reasonable activation energy for this very slow reaction suggests that $k_{-2} \cong 2 \times 10^{-5}$ M^{-1} s^{-1} at 20 °C. Combined with $K_2 = 1.5 \times 10^{11}$ M^{-1} as calculated from the thermodynamic data in Table II, this value of k_{-2} yields $k_2 = 3 \times 10^6$ M^{-2} s^{-1}.

A value of k_2 also can be inferred from $k_{5'}$ with the ratio $k_{5'}/k_2 = 1.2 \times 10^{-5}$ in 1 M H_2SO_4 at 25 °C originally determined by Körös and Burger,[40] used by FKN, and recently confirmed by Noszticzius et al.[6] We calculate $k_2 = 3.5 \times 10^6$ M^{-2} s^{-1} assuming $k_{5'} = 42$ M^{-2} s^{-1}. We suggest use of $k_2 = 3 \times 10^6$ M^{-2} s^{-1} at 20 °C. Directly determined values of 1×10^6 M^{-2} s^{-1} $< k_2 < 4 \times 10^6$ M^{-2} s^{-1} and $k_2 = 1 \times 10^6$ M^{-2} s^{-1} have been reported by Noszticzius et al.[20] and Ariese and Nagy-Ungvărai,[22] respectively. The discrepancy between our suggested value of k_2 and that of Ariese and Nagy-Ungvărai is larger than is comfortable. More work needs to be done here.

Reaction R3. The FKN value $k_3 = 2$ M^{-3} s^{-1} seems well established.[1,3] The thermodynamic data in Table II lead to $K_3 = 0.6$ M^{-2} and thus to $k_{-3} = 3.2$ M^{-1} s^{-1}, considerably smaller values than used by FKN. These values lead to $K_3K_4/K_2 = 1$ as required for thermodynamic consistency.

Reaction R6. The value $k_6 = 8 \times 10^4$ M^{-2} s^{-1} was determined directly in 1 M H_2SO_4 at 20 °C by Försterling et al.[33] This value is close to the FKN value and in keeping with the experiments of Field et al.[28] on (R6) with Mn(II). Assuming the thermodynamic data in Table II and $E°$(Ce(IV)/Ce(III)) = 1.44 V, we find $K_6 = 9$ M^{-1} and thus $k_{-6} = 8.9 \times 10^3$ M^{-1} s^{-1}. This value of k_{-6} is in very good agreement with values determined directly by Lamberz[26] and by Sullivan and Thompson.[25]

The values of k_6 and k_{-6} quoted above for the Ce(III)/Ce(IV) redox couple cause (R6) to be substantially reversible as is observed experimentally.[33-35] The situation is substantially different in the case of $Fe(phen)_3^{3+}/Fe(phen)_3^{2+}$ and other low-redox-potential couples.[19,36] With $E°(Fe(phen)_3^{3+}/Fe(phen)_3^{2+}) = 1.06$ V and $K_6 = 3 \times 10^7$ M^{-1}, (R6) is expected to be essentially irreversible when $Fe(phen)_3^{2+}$ is substituted for Ce(III) in the BZ reaction.

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(37) Barat, F.; Gilles, L.; Hickel, B.; Lesigne, B. *J. Phys. Chem.* **1972**, *76*, 302.

(38) Knight, G. C.; Thompson, R. C. *Inorg. Chem.* **1973**, *12*, 63.

(39) Betts, R. H.; MacKenzie, A. *Can. J. Chem.* **1951**, *29*, 655, 666.

(40) Körös, E.; Burger, M. In *Ion-Selective Electrodes*; Pungor, I., Ed.; Hungarian Akademy of Science: Budapest, 1973.

(41) Eigen, M.; Kustin, K. *J. Am. Chem. Soc.* **1962**, *84*, 1355.

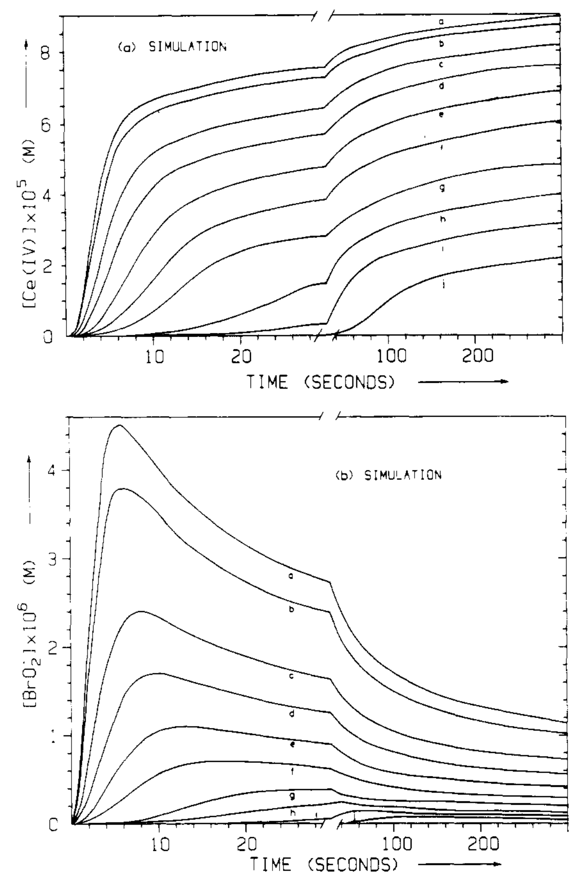

Figure 6. Simulations of the experiments in Figure 3 on the basis of reactions R1–R6 and the rate constant values in Table II. The major reactant concentrations (Ce(III), BrO_3^-, and H_2SO_4) are the same as in Figure 3. Other initial concentrations are $[Br^-] = 6 \times 10^{-13}$ M, $[Br_2] = 1.6 \times 10^{-10}$ M, $[HOBr] = 4 \times 10^{-6}$ M, $[HBrO_2] = 1 \times 10^{-9}$ M, $[BrO_2^\bullet] = 3.3 \times 10^{-9}$ M, $[Br_2O_4] = 2 \times 10^{-13}$ M, and [Ce(IV)] = 0.0 M. These concentrations were calculated on the basis that the $NaBrO_3$ used was contaminated with NaBr at the part-per-million level: (a) [Ce(IV)] and (b) $[BrO_2^\bullet]$.

We suggest that k_6 with $Fe(phen)_3^{2+}$ may be nearly as fast[27] as Field et al.[28] found it to be with $Fe(CN)_6^{4-}$ and that the values $k_6 = 1 \times 10^9$ M^{-2} s^{-1} and $k_{-6} = 33$ M^{-1} s^{-1} be used for the $Fe(phen)_3^{2+}/Fe(phen)_3^{2+}$-catalyzed BZ reaction.

Reaction R7. This reaction is too slow to be important in the BZ reaction.[42] We list $k_7 = k_{-7} \cong 0$ in Table II but calculate $K_7 = 1.2 \times 10^5$ M^2, which yields $K_5K_6K_7 = 1$, as required for thermodynamic consistency.

Numerical Simulations

The rate parameters in Table II were tested by using them to simulate the observed [Ce(IV)] and $[BrO_2^\bullet]$ during the overall reaction of Ce(III) with bromate. Accurate reproduction of the behavior of both a reaction product and an important dynamic intermediate over broad ranges of reactant concentrations is a stringent test of both the form of the mechanism and the rate parameters. Simulations were carried out by numerical integration using the method of Gear[43] of the rate expressions resulting from reactions R1–R6.

Figure 6 shows simulations on the same scales as the experimental [Ce(IV)] and $[BrO_2^\bullet]$ time profiles in Figure 3. Agreement is good between the calculated and experimental amounts of [Ce(IV)] and $[BrO_2^\bullet]$ as well as the trends observed in these as $[BrO_3^-]$ is varied over a factor of 500, i.e., from 0.002 to 1 M, with $[Ce(III)]_0 = 10^{-4}$ M. Similarly good agreement was obtained for other experiments in which $[Ce(III)]_0$ was varied over a factor of 20, i.e., from 1×10^{-5} to 2×10^{-4} M, with $[BrO_3^-] = 0.1$ M.

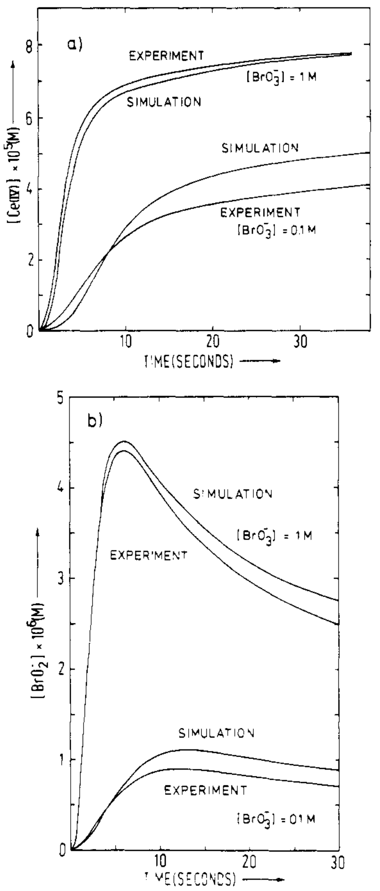

Figure 7. Detailed comparison of the experimental data in Figure 3 and the simulations in Figure 6 for $[BrO_3^-] = 1$ M and 0.1 M: (a) [Ce(IV)] and (b) $[BrO_2^\bullet]$.

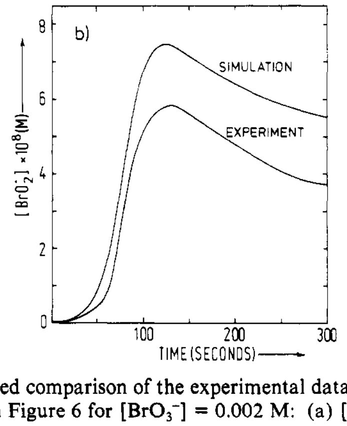

Figure 8. Detailed comparison of the experimental data in Figure 3 and the simulation in Figure 6 for $[BrO_3^-] = 0.002$ M: (a) [Ce(IV)] and (b) $[BrO_2^\bullet]$.

Detailed comparisons of experiment and simulation are displayed in Figures 7 and 8 for the highest, the lowest, and an intermediate $[BrO_3^-]$. Agreement is again good, although there is a tendency at lower $[BrO_3^-]$ for the calculated $[BrO_2^\bullet]$ to be up to 25% higher than observed, which causes the calculated [Ce(IV)] to be too high by about the same amount. Agreement could be made essentially exact within experimental error by

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(42) Ganapathisubramanian, N.; Noyes, R. M. *J. Phys. Chem.* **1982**, *86*, 5158.

(43) Gear, C. W. *Numerical Initial Value Problems in Ordinary Differential Equations*; Prentice-Hall: Englewood Cliffs, NJ, 1971.

modifying rate constants by considerably less than a factor of 2, the nominal accuracy we claim for the rate parameters developed here. Unfortunately, it is not clear exactly which rate constants should be modified. The effects of decreasing $k_{5'}$ as well as increasing k_{-6} or k_4 are very similar and in the correct direction. Thus we have not attempted to make agreement exact by manipulations that may not be the correct ones. We do point out, though, that decreasing $k_{5'}$ improves the quality of the fit and is in keeping with the earlier suggestion that our value of $k_{5'}$ is an upper limit at 20 °C.

The rate constants in Table II also simulate very well the results of Kuhnert et al.[19] at 25 °C on the overall reaction of $\mathrm{Fe(phen)_3}^{2+}$ with bromate if the values of k_6 and k_{-6} suggested above for the $\mathrm{Fe(phen)_3}^{3+}/\mathrm{Fe(phen)_3}^{2+}$ couple are used. The calculated induction period (which is mainly dependent upon k_3) is about half that observed by Kuhnert et al.,[19] but agreement in the region of exponential growth of $\mathrm{Fe(phen)_3}^{3+}$ is very good. Kuhnert et al.[19] extracted a value of $k_{5'}$ from the rate of this exponential growth by assuming that (R4) is unimportant during this phase of the reaction. Our simulations verify the essential validity of their method, which was originally proposed by Rovinskii and Zhabotinskii.[29] However, treatment of our calculated exponential growth of $\mathrm{Fe(phen)_3}^{3+}$ in the same way that they treated their equivalent experimental data retrieves $k_{5'} = 30\ \mathrm{M^{-2}\ s^{-1}}$ rather than the 42 $\mathrm{M^{-2}\ s^{-1}}$ actually used in the calculation. This discrepancy results because (R4) is not entirely unimportant and does slow the rate of exponential growth of $\mathrm{Fe(phen)_3}^{3+}$. We conclude that the Kuhnert et al.[19] value of $k_{5'}$ is essentially correct if a bit low.

The values of k_1–k_3 used do not affect significantly our simulations of the overall reaction of Ce(III) with bromate. They do affect the length of the induction period before this reaction begins, especially in the presence of significant amounts of $\mathrm{Br^-}$ or $\mathrm{Br_2}$. We have not investigated this aspect of the problem in detail.

Implications for Parameterizing the Oregonator

Theoretical treatment of the BZ reaction is usually done with reduced versions[3,44–49] of the FKN mechanism, collectively referred to as the Oregonator.[16] It is appropriate to discuss here the implications of our rate constants on parameterization of the Oregonator.

The simplest Oregonator is given by

$$\mathrm{A + Y \rightarrow X + P} \qquad \text{(O1)}$$

$$\mathrm{X + Y \rightarrow P + P} \qquad \text{(O2)}$$

$$\mathrm{A + X \rightarrow 2X + Z} \qquad \text{(O3)}$$

$$\mathrm{X + X \rightarrow A + P} \qquad \text{(O4)}$$

$$\mathrm{Z} \rightarrow f\mathrm{Y} \qquad \text{(O5)}$$

The usual variable identifications are $\mathrm{A \equiv BrO_3^-}$, $\mathrm{X \equiv HBrO_2}$, $\mathrm{Y \equiv Br^-}$, $\mathrm{Z \equiv 2Ce(IV)}$, and $\mathrm{P \equiv HOBr}$. The quantities X, Y, and Z are dynamic variables corresponding to intermediates, while A and P are reactants and products whose concentrations are usually assumed to be constant. The quantity f is an expendable stoichiometric factor that can be eliminated[10,44] in more complex models with more than three dynamic variables. The use of singular perturbation methods allows reduction of the associated differential equations to two variables[3,15,50] and a form that is particularly tractable mathematically.[18,48,51]

Ignoring reversibility and assuming that (R5′) is rate determining for (R5) and (R6) allow rate constant identifications for $[\mathrm{H^+}] = 0.8$ M and $[\mathrm{CH_2(COOH)_2}] = 0.02$ M to be given

$$k_{\mathrm{O1}} = k_{\mathrm{R3}}[\mathrm{H^+}]^2 = 1.3\ \mathrm{M^{-1}\ s^{-1}}$$

$$k_{\mathrm{O2}} = k_{\mathrm{R2}}[\mathrm{H^+}] = 2.4 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$$

$$k_{\mathrm{O3}} = k_{\mathrm{R5'}}[\mathrm{H^+}] = 34\ \mathrm{M^{-1}\ s^{-1}}$$

$$k_{\mathrm{O4}} = k_{\mathrm{R4}} = 3 \times 10^3\ \mathrm{M^{-1}\ s^{-1}}$$

$$k_{\mathrm{O5}} = 1[\mathrm{CH_2(COOH)_2}] = 0.02\ \mathrm{s^{-1}}$$

The major problem with these parameters involves k_{O3}, quoted as 34 $\mathrm{M^{-1}\ s^{-1}}$. This value ignores the reversibility of (R5) and (R6) (which we have concluded here is significant) and the depletion of Ce(III) by oxidation to Ce(IV). The latter effect should be taken into account[3,15,48,50,51] by explicitly requiring the conservation of cerium ion with a term in the kinetics of (O3) of the form $(\mathrm{C_0 - Z})/\mathrm{C_0}$, where $\mathrm{C_0}$ is total cerium concentration. The value of k_{O3} may also be considered to be an expendable parameter, and a value somewhat less than 34 $\mathrm{M^{-1}\ s^{-1}}$ may be used to obtain good agreement with experiment.

For a much more realistic model, especially in view of our major conclusion here that (R5) is significantly reversible under the BZ conditions with cerium ion, one can introduce reversibility as suggested by Field[52] and expanded on by Showalter et al.[45]

$$\mathrm{A + Y \rightleftharpoons X + P} \qquad \text{(S1)}$$

$$\mathrm{X + Y \rightarrow P + P} \qquad \text{(S2)}$$

$$\mathrm{A + X \rightleftharpoons W + W} \qquad \text{(S3)}$$

$$\mathrm{C + W \rightleftharpoons X + Z'} \qquad \text{(S4)}$$

$$\mathrm{X + X \rightarrow A + P} \qquad \text{(S5)}$$

$$\mathrm{Z'} \rightarrow g\mathrm{Y + C} \qquad \text{(S6)}$$

Additional variable identifications are $\mathrm{C \equiv Ce(III)}$, $\mathrm{Z' \equiv Ce(IV)}$, and $\mathrm{W \equiv BrO_2^{\bullet}}$. Of course, S3 and S4 are not reversible in the cases of low-redox-potential catalysts such as $\mathrm{Fe(phen)_3}^{3+}/\mathrm{Fe(phen)_3}^{2+}$. In all cases (S2) and (S5) are seldom reversible, as indicated above.

With the addition of steps S7–S9

$$\mathrm{P \rightarrow Y} \qquad \text{(S7)}$$

$$\mathrm{Y + P \rightleftharpoons U} \qquad \text{(S8)}$$

$$\mathrm{U \rightarrow (Y)} \qquad \text{(S9)}$$

bromine-hydrolysis-controlled[2,10] oscillators can be modeled with $g = 0$ and the additional assignment $\mathrm{U \equiv Br_2}$. The Y in step S9 does not appear in heterogeneous oscillators,[2,10,53] where $\mathrm{Br_2}$ is physically removed rather than removed by reaction with an organic material[10] to yield bromide ion. Rate parameters for these steps can be taken directly from Table II with the identities (S1) ≡ (R3), (S2) ≡ (R2), (S3) ≡ (R5), (S4) ≡ (R6), (S5) ≡ (R4), $k_{\mathrm{S6}} \equiv k_{\mathrm{O5}}$, and (S8) ≡ (R1). The values of k_{S7} and k_{S9} must be chosen according to the particular organic material used[10] or the rate of $\mathrm{Br_2}$ removal by a physical process.

Oscillations in the presence of silver ion[54] or other bromide ion removing metal ions[55] also can be understood by using the Oregonator,[56,57] although the effect of the revised rate constants

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presented here on this work is not yet clear. New experimental results[58,59] on the organic chemistry of the BZ reaction also need to be fitted quantitatively into the framework presented here.

Conclusion

A revised set of rate constants for the oxybromine chemistry portion of the Belousov–Zhabotinskii reaction has been developed at 20 °C in about 1 M H_2SO_4. The suggested values are based on new experiments, recently reported direct rate constant determinations, and a critical reevaluation of previous results. The values ΔG_f° ($HBrO_2$) $\cong -0.4$ kJ/mol and pK_a ($HBrO_2$) $\cong 4.9$ are deduced and used in the generation of the suggested rate constants. A major conclusion is that $HBrO_2$ is considerably more stable than previously thought, causing the reaction $HBrO_2 + BrO_3^- + H^+ \rightleftharpoons 2BrO_2^\bullet + H_2O$ to be significantly reversible under the conditions of the BZ reaction. The suggested rate constants are able to simulate well data on [Ce(IV)] and [$BrO_2^\bullet$] during the overall reaction of Ce(III) with bromate even when the reactant concentrations are varied by factors up to 500. The suggested rate constants are very significantly smaller than the FKN values and quite close to the Tyson "Lo" values. Appropriate propagation of the new rate constants into the Oregonator model is discussed.

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Registry No. Ce, 7440-45-1; BrO_3^-, 15541-45-4; $HBrO_2$, 37691-27-3.

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Comparison of the Field–Körös–Noyes and Field–Försterling Parameterizations of the Bromate–Cerous Reaction

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In 1972, Field, Körös, and Noyes assigned all of the rate constants for the oxidation of cerous ion by bromate. The assignment was based on the minimum permissible number of independent observations, and there was no possibility to test for internal consistency. Field and Försterling have now developed an alternative assignment based on more recent experimental observations. Numerous tests indicate that the FF assignment is internally consistent to within about a factor of 2, but several rate constants in the FF set differ from the FKN set by factors of up to 10^4. These discrepancies have led some people to question the validity of the FKN mechanism itself. A reexamination of the original arguments notes that FKN used the Pauling model for strength of oxyacids in order to assign a pK to bromous acid different by almost 3 units from the value selected by FF. When the FKN set is recalculated with the use of the new pK, the deviations from the FF set are not important. Apparently all of the experimental observations used by FKN were valid and consistent with subsequent measurements. The bromate–cerous component of the oscillatory Belousov–Zhabotinsky reaction now appears to be well understood.

Introduction

In 1972, Field, Körös, and Noyes[1] (FKN) proposed a detailed mechanism for the dramatic Belousov–Zhabotinsky oscillations. Although much of the explanation had to be qualitative, FKN developed an involved argument that permitted them to assign numerical values to all of the kinetic parameters explaining the oxidation of cerous ion by bromate. This oxidation exhibits unusal features such as an induction period followed by very rapid autocatalysis, and it has even been used to generate sustained oscillations in a flow reactor.[2-4]

Although subsequent computations simulated many of these features, evidence began to accumulate suggesting that some of the FKN rate constants might be in error by several orders of magnitude. Such large discrepancies even led some people to question the validity of the FKN mechanism itself.

TABLE I: Rate Constants Exhibiting Major Discrepancies between FKN and FF Assignments

constant	FKN value	FF Value
$k_2/(M^{-2}\ s^{-1})$	2×10^9	3×10^6
$k_{-3}/(M^{-1}\ s^{-1})$	1×10^4	3.2
$k_4/(M^{-1}\ s^{-1})$	4×10^7	3×10^3
$k_{-4}/(M^{-2}\ s^{-1})$	2×10^{-10}	1×10^{-8}
$k_5/(M^{-2}\ s^{-1})$	1×10^4	42
$k_6/(M^{-2}\ s^{-1})$	6.5×10^5	8×10^4
$k_{-6}/(M^{-1}\ s^{-1})$	2.4×10^7	8.9×10^3

Tyson[5] then made a careful analysis that showed that many different parameter assignments might be equally effective at interpreting most of the observations as long as certain key ratios of rate constants were maintained.

Field and Försterling[6] (FF) have now analyzed the accumulated experimental information and have developed a revised set of rate constants for 1 M H_2SO_4 medium at 20 °C. They believe that these rate constants can simulate all known behavior in this system and that any further refinements probably will not need to be by more than a factor of about 2.

Because of the interest in this system and because of the doubts caused by the large discrepancies in the values claimed for some rate constants, it may be useful to summarize the arguments leading to the original FKN set. The reexamination validates all of those arguments and the experimental observations on which

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