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The Kinetics of Bromate-Cerium(III) and -Iron(II) Reactions

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The bromate-cerium(III) and -iron(II) reactions in acidic media were examined with special reference to their induction periods and reaction rates. In the bromate-cerium(III) reaction, the induction period is followed by a burst of cerium(IV) formation and then a gradual formation of cerium(IV). In the bromate-iron(II) reaction, a slow decrease occurs only in acidic media, even without bromate, so it may differ from the decrease in the tris(1,10-phenanthroline)iron(II) concentration based on the oxidation by bromate. It was interpreted as the dissociation from $[Fe(phen)_3]^{2+}$ to $[Fe(phen)_2]^{2+}$ and phen. This is the induction period for iron(III) formation, which follows as the burst. The induction period and the rates of cerium(IV) or iron(III) formation can be interpreted on the basis of the mechanism for the Belousov oscillatory and the present redox reactions proposed by Noyes and his co-workers.

The Belousov reaction,[1,2] a typical oscillating reaction, is the oxidation of malonic acid with potassium bromate catalyzed by cerium(III) and (IV) ions. The mechanism of the reaction was investigated by Field and Noyes,[3] who suggested that the reaction involves both the oxidation of the cerium(III) ion by potassium bromate and an autocatalytic reaction with respect to bromous acid. This suggestion has led us to take an interest in the redox reactions between potassium bromate and cerium(III) sulfate or tris(1,10-phenanthroline)iron(II).[4]

The reactions between bromate and various reducing agents, Ce(III), $[Fe(phen)_3]^{2+}$, Co(II), Mn(II), Np(V), and V(V), had been examined qualitatively.[3,5,6] The kinetic behaviour of these systems could be described experimentally by this rate law: $-d[BrO_3^-]/dt = k_0[BrO_3^-]^2$. However, to date all attempts to understand these systems adequately in this quantitative aspect have been unsuccessful.

If the mechanism suggested by Noyes and his coworkers[3] is applied to the oxidation of cerium(III) and iron(II) with no bromide ion involved, the following set of elementary reactions are obtained:

$$BrO_3^- + HBrO_2 + H^+ \rightleftharpoons 2BrO_2^{\cdot} + H_2O, \quad (1)$$

$$BrO_2^{\cdot} + M^{n+} + H^+ \rightleftharpoons HBrO_2^{\cdot} + M^{(n+1)+}, \quad (2)$$

$$BrO_2^{\cdot} + M^{(n+1)+} + H_2O \rightleftharpoons BrO_3^- + M^{n+} + 2H^+, \quad (3)$$

$$2\,HBrO_2 \rightleftharpoons BrO_3^- + HOBr + H^+, \quad (4)$$

where M^{n+} and $M^{(n+1)+}$ are the reducing agent and its oxidized form respectively.

The observation that an induction period is followed by a burst of oxidation suggests that there is at least one elementary autocatalytic reaction, and that it corresponds to the following reaction (5). It is obtainable from two of the elementary reactions above, (1) and (2), and it contains $HBrO_2$ as the vital species:

$$\begin{aligned} &BrO_3^- + HBrO_2 + 2M^{n+} + 3H^+ \\ &= 2HBrO_2 + 2M^{(n+1)+} + H_2O. \end{aligned} \quad (5)$$

Considering that the bromate-cerium(III) and -iron(II) reactions are characterized by an induction period, the rapid formation of cerium(IV) or iron(III) at the inflection point on a kinetic curve and the slow formation of cerium(IV) had been examined in connection with the above suggestion by Noyes *et al.*[3] The purposes of this paper are to present our results on the reduction of bromate by cerium(III) or $[Fe(phen)_3]^{2+}$ ions and to explain these systems, as in a previous paper.[7]

Experimental

The potassium bromate, $Ce_2(SO_4)_3 \cdot 8H_2O$, $FeSO_4 \cdot 7H_2O$, and 1,10-phenanthroline monohydrate of a guaranteed reagent grade were obtained from the Wako Pure Chemical Industries, Ltd., Japan. Especially, the $[Fe(phen)_3]^{2+}$ stock solution was prepared by mixing $FeSO_4 \cdot 7H_2O$ and 1,10-phenanthroline monohydrate in a 1 : 3 mole ratio. The ionic strengths of the aqueous reaction solutions were usually controlled by means of a 1.5 mol dm^{-3} portion of sulfuric acid for cerium(III) and a 0.5 mol dm^{-3} portion of sulfuric acid for iron(II) in such a way that their concentrations were far higher than the concentration of either the potassium bromate or the cerium sulfate and $[Fe(phen)_3]^{2+}$ employed. Each sulfuric acid solution was degassed before use.

The bromate-cerium(III) reaction was allowed to run in a nitrogen atmosphere and in the dark; the potassium bromate and cerium(III) sulfate were each dissolved in a degassed sulfuric acid solution. Mixing the two solutions initiated the bromate-cerium(III) reaction, the progress of which was followed by recording the absorbance at 320 nm for the cerium(IV) ion, the molar absorptivity at this wavelength being 5520 mol^{-1} dm^3 cm^{-1}.[8] The bromate-iron(II) reaction was also allowed to run in a nitrogen atmosphere and in the dark; the $[Fe(phen)_3]^{2+}$ stock solution was diluted in a degassed sulfuric acid solution. The mixing of the bromate and the iron(II) solutions initiated the bromate-iron(II) reaction. The concentration of the $[Fe(phen)_3]^{2+}$ stock solution was determined spectrophotometrically at 509 nm, at which point the molar absorptivity of $[Fe(phen)_3]^{2+}$ is 11100 mol^{-1} dm^3 cm^{-1},[9] but some correction of this molar absorptivity was needed based on that of $[Fe(phen)_3]^{3+}$, about 500 mol^{-1} dm^3 cm^{-1}. The wavelength of the maximum absorption of $[Fe(phen)_3]^{3+}$ was found to be 590 nm.[10] The progress of this reaction was followed by recording the absorbance at 509 nm for the iron(II) ion. A Hitachi Model 125 spectrophotometer equipped with a temperature controller was used. The reaction vessel was directly connected to the cell of this spectrophotometer by tubing with a circulating pump.

The duration of the induction period was highly dependent on the ages of both the bromate- and cerium(III)-sulfuric acid solutions, but after the induction the change in cerium(III) was almost independent of the ages of either solution. Reproducible results for the duration of the induction period were obtained by the use of a cerium(III)-sulfuric acid solution which had been aged for 1 h and a potassium bromate-sulfuric acid solution which had been aged for 24 h. On the other hand, the dilution of the $[Fe(phen)_3]^{2+}$ stock solution was carried out before use. All these solutions were prepared in a nitrogen atmosphere and in the dark. The reaction rate was not affected by stirring.

Results and Discussion

The progress of the bromate-cerium(III) reaction consists of three stages: (1) An induction period, (2) a burst in cerium(IV) formation, and (3) a gradual formation of cerium(IV).7,11) The duration of the induction period is inversely proportional to the initial bromate concentration, and the rate of the fast formation of cerium(IV) is proportional to the square of the initial bromate concentration, whereas both quantities are independent of the initial cerium(III) concentration. In the slow formation of cerium(IV), the steady-state treatment can be applied with success, even to the concentration of the bromous ion, as well as to those of radical species.7) The details of the kinetic behaviour of the bromate-cerium(III) reaction were reported in a previous paper.7)

Dissociation of $[Fe(phen)_3]^{2+}$. After the mixing of the bromate and the iron(II) solution, a slow decrease of the absorbance at 509 nm occurs in the beginning only in acidic media, and this decrease occurs also without bromate. If only $[Fe(phen)_3]^{2+}$, without bromate, is left alone in acidic media for 22 h at 25 °C, the absorbance in the range from 800 to 370 nm disappears completely. The spectra of the products in the reaction without bromate and in the reaction with bromate were identical. This decrease is independent of the acid concentration, at least in the range from 0.1 to 1.0 mol dm^{-3} sulfuric acid.10,12) It has been postulated as the dissociation from $[Fe(phen)_3]^{2+}$ to $[Fe(phen)_2]^{2+}$ and phen,5,10) and its mechanism has been postulated to be the step-by-step dissociation of the ligand from the complex. For the bromate-iron(II) reaction, this dissociation is considered to be in progress during the burst of $[Fe(phen)_3]^{3+}$ formation. Therefore, it must be considered to be parallel to the $[Fe(phen)_3]^{3+}$ formation. This rate of decrease based on the dissociation to $[Fe(phen)_2]^{2+}$ is proportional to the concentration of $[Fe(phen)_3]^{2+}$ and is independent of the bromate and acid concentrations. The rate-determining step for the dissociation of the complex can be postulated to be the loss of the first ligand molecule.10)

TABLE 1. THE DISSOCIATION RATE CONSTANTS TO $[Fe(phen)_2]^{2+}$ FROM $[Fe(phen)_3]^{2+}$ IN 0.10 mol dm^{-3} AQ H_2SO_4

$[Fe(phen)_3]^{2+}_0$ / mol m^{-3}	$k \times 10^5$ / s^{-1}		Temperature / °C
0.153	7.45		25.1
0.118	7.03		25.1
0.101	7.77	7.51±0.35	25.1
0.0512	7.28		25.1
0.0242	8.02		25.1
0.150	16.2		30.7
0.151	4.22		21.7
0.150	0.999		14.7

The details of the dissociation rate are summarized in Table 1. Körös5) and Shakhashiri10) had reported this dissociation rate constant at 25 °C (*k*; first-order dependency to $[Fe(phen)_3]^{2+}$ concentration) to be $(7.54\pm0.42)\times10^{-5}$ and $7.50\times10^{-5}\ s^{-1}$ respectively. Our constant is in good agreement with their values. It is much smaller than the following burst-rate constant for the oxidation to $[Fe(phen)_3]^{3+}$. The activation energy for this dissociation is 123 kJ/mol.

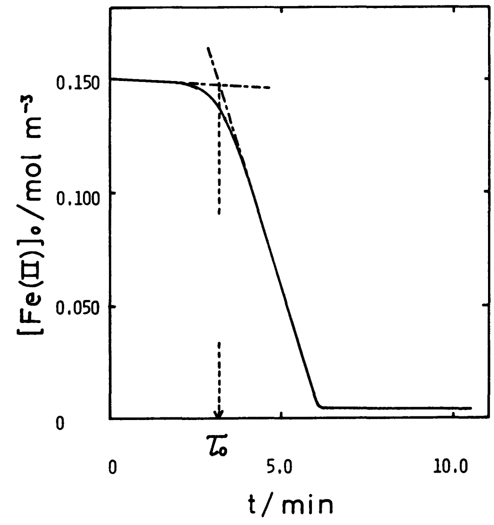

Fig. 1. Kinetic behavior of the bromate–iron system. Reaction-temperature 25 °C, $[BrO_3^-]_0 = 1.53$ mol m^{-3}, $[Fe(II)]_0 = 0.151$ mol m^{-3}, $[H^+] = 1.0$ mol dm^{-3}. Induction period (time, τ_0) defined by a dotted line.

Figure 1 shows the typical behaviour of $[Fe(phen)_3]^{2+}$ concentration with time. Let the induction period, τ_0, be defined as the time of intercept on the initial, slow and decreasing slope (dissociation) by the tangent (burst of iron(III) formation) drawn at the inflection point on the kinetic curve, as is shown in Fig. 1.

Induction Period. For the bromate-cerium(III) reaction, Thompson6) and Kasperek11) obtained a similar but qualitative dependence of the induction period on the initial bromate and acid concentrations. We have previously attempted to explain our quantitative results on the basis of the elementary steps given above.3) The following steps may be considered:

$$BrO_3^- + HBrO_2 + H^+ \xrightarrow{k_1} 2BrO_2^{\cdot} + H_2O, \qquad (1')$$

$$BrO_2^{\cdot} + M^{n+} + H^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HBrO_2 + M^{(n+1)+}, \qquad (2)$$

$$2HBrO_2 \xrightarrow{k_4} BrO_3^- + HOBr + H^+, \qquad (4')$$

where $BrO_2^{\cdot}$ is a radical species. As the amount of unstable $BrO_2^{\cdot}$ is assumed to be extremely small in comparison with those of the other species, the reverse of Step (1) and the slow Step (3) can be disregarded.3) In acidic solutions, HOBr easily converts to Br^-, so the reverse of Step (4) can also be disregarded.12) Moreover, the steady-state treatment is applied to the concentration of unstable $BrO_2^{\cdot}$ for the bromate-iron(II) reaction as:

$$\frac{\mathrm{d}[\mathrm{BrO}_2^{\cdot}]}{\mathrm{d}t} = 2k_1[\mathrm{H}^+][\mathrm{HBrO}_2][\mathrm{BrO}_3^-] - k_2[\mathrm{H}^+][\mathrm{BrO}_2^{\cdot}][\mathrm{Fe(II)}] + k_{-2}[\mathrm{HBrO}_2][\mathrm{Fe(III)}] = 0. \tag{6}$$

The rate equations for the increase in the iron(III) concentration, the decrease in the bromate concentration, and the change in the bromous concentration are formulated as:

$$\frac{\mathrm{d}[\mathrm{Fe(III)}]}{\mathrm{d}t} = k_2[\mathrm{H}^+][\mathrm{BrO}_2^{\cdot}][\mathrm{Fe(II)}] - k_{-2}[\mathrm{HBrO}_2][\mathrm{Fe(III)}] = 2k_1[\mathrm{H}^+][\mathrm{BrO}_3^-][\mathrm{HBrO}_2], \tag{7}$$

$$-\frac{\mathrm{d}[\mathrm{BrO}_3^-]}{\mathrm{d}t} = k_1[\mathrm{H}^+][\mathrm{BrO}_3^-][\mathrm{HBrO}_2] - k_4[\mathrm{HBrO}_2]^2, \tag{8}$$

$$\frac{\mathrm{d}[\mathrm{HBrO}_2]}{\mathrm{d}t} = k_1[\mathrm{H}^+][\mathrm{BrO}_3^-][\mathrm{HBrO}_2] - 2k_4[\mathrm{HBrO}_2]^2. \tag{9}$$

The concentration of $\mathrm{BrO}_2^{\cdot}$ can be neglected as compared with those of the other species.[3] The following relations are assumed to hold for the initial stage, as based on the simple material and valency balances:

$$[\mathrm{BrO}_3^-]_\circ + [\mathrm{HBrO}_2]_\circ = [\mathrm{BrO}_3^-] + [\mathrm{HBrO}_2], \tag{10}$$

$$[\mathrm{Fe(III)}] = 2\{[\mathrm{BrO}_3^-]_\circ - [\mathrm{BrO}_3^-]\}, \tag{11}$$

where the subscript ∘ indicates the initial value.

The integration of Eq. 7 gives:

$$\ln\left\{\frac{[\mathrm{BrO}_3^-]_\circ(2[\mathrm{HBrO}_2]_\circ + [\mathrm{Fe(III)}])}{[\mathrm{HBrO}_2]_\circ(2[\mathrm{BrO}_3^-]_\circ - [\mathrm{Fe(III)}])}\right\} = k_1[\mathrm{H}^+]\{[\mathrm{BrO}_3^-]_\circ + [\mathrm{HBrO}_2]_\circ\}t. \tag{12}$$

The concentration of the initial bromous acid is negligible as compared with that of the bromate and is at a steady value ($[\mathrm{HBrO}_2]_\circ/[\mathrm{BrO}_3^-]_\circ = C_1$; constant), as established through the aging adopted in the preparation of the reactions.

The induction period is obtained as follows. The relation between the time, t_f, and the concentration, $[\mathrm{Fe(III)}]_\mathrm{f}$, at the inflection point on the kinetic curve in Fig. 1 is obtainable from Eq. 12. On the other hand, $[\mathrm{BrO}_3^-]_\mathrm{f}$ and $[\mathrm{HBrO}_2]_\mathrm{f}$ may be obtained on the basis of $\mathrm{d}^2[\mathrm{Fe(III)}]/\mathrm{d}t^2 = 0$ at the inflection point:

$$[\mathrm{HBrO}_2]_\mathrm{f} = C_2[\mathrm{BrO}_3^-]_\mathrm{f} = \frac{C_2}{C_2+1}[\mathrm{BrO}_3^-]_\circ, \tag{13}$$

where the subscript f denotes the value for the inflection point and where:

$$C_2 = 1 + \frac{k_1[\mathrm{H}^+]}{2k_4} - \sqrt{1+\left(\frac{k_1[\mathrm{H}^+]}{2k_4}\right)^2}. \tag{14}$$

The slope of the tangent drawn at the inflection point on the kinetic curve is determined from Eq. 7 as:

$$\frac{\mathrm{d}[\mathrm{Fe(III)}]_\mathrm{f}}{\mathrm{d}t} = 2k_1[\mathrm{H}^+]_\mathrm{f}\frac{C_2}{(C_2+1)^2}[\mathrm{BrO}_3^-]_\circ^2. \tag{15}$$

Now, we obtain τ_0 from t_f, $[\mathrm{BrO}_3^-]_\mathrm{f}$, $[\mathrm{HBrO}_2]_\mathrm{f}$, $[\mathrm{Fe(III)}]_\mathrm{f}$, and the above tangent as follows:

$$\tau_\circ = \frac{1}{k_1[\mathrm{H}^+][\mathrm{BrO}_3^-]_\circ}\{\ln(C_2/C_1) - (C_2+1)\}, \tag{16}$$

which calls for $\tau_\circ$ being inversely proportional to both $[\mathrm{H}^+]$ and $[\mathrm{BrO}_3^-]_\circ$; this is in good agreement with the experimental results shown in Fig. 2. In Fig. 2, results are shown for runs of the reaction with the initial iron(II) concentration of 0.150 mol m^{-3}. The induction period for a burst of iron(III) formation is inversely proportional to the initial bromate concentration, such as that of the cerium(IV) formation.[7] The induction period is independent of the initial iron(II) concentration.

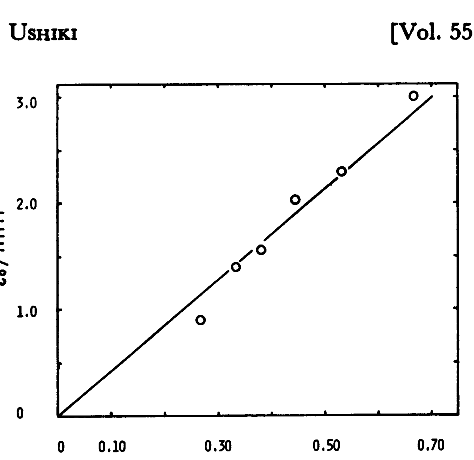

Fig. 2. Kinetic relation between $\tau_\circ$ and the inverse of the initial KBrO_3 concentration.
Reaction-temperature 25 °C, $[\mathrm{Fe(II)}]_\circ = 0.15$ mol m^{-3}, $[\mathrm{H}^+] = 1.0$ mol dm^{-3}.

The Burst of Iron(III) Formation. For the burst of iron(III) formation, the rate of iron(III) formation (R) is defined as the corrected slope of the tangent drawn at the inflection point on the kinetic curve. Figure 3 shows the relation between the corrected slope of the tangent and the square of the initial bromate concentration. The rates of iron(III) formation at 20, 25, and 30 °C are completely proportional to the square of the initial bromate concentration, whereas they are almost independent of the initial iron(II) concentration, shown in Fig. 4. These results are consistent with the interpretation based on Eq. 15. Similar results and a

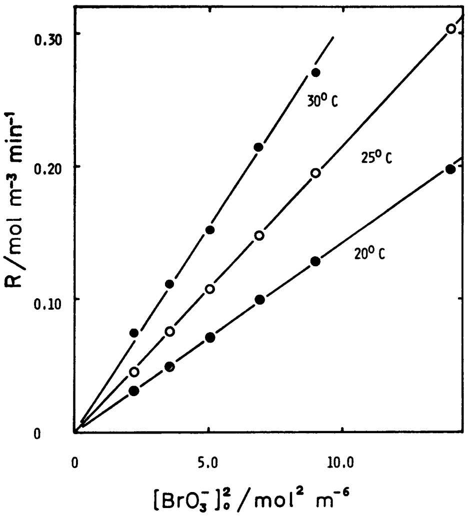

Fig. 3. Kinetic relation between the rate of burst Fe(III) formation (R) and the square of the initial KBrO_3 concentration.
$[\mathrm{Fe(II)}]_\circ = 0.15$ mol m^{-3}, $[\mathrm{H}^+] = 1.0$ mol dm^{-3}. Different reaction-temperatures shown above.

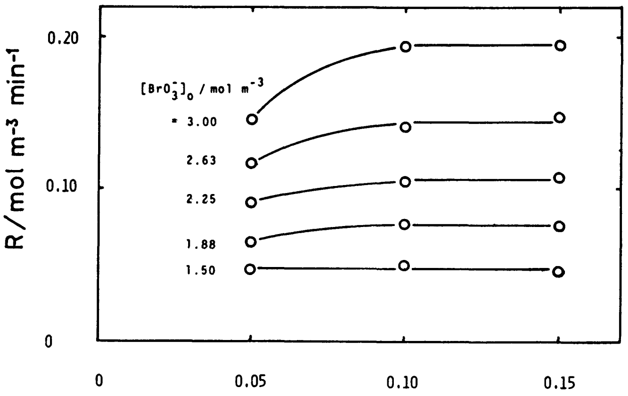

Fig. 4. Kinetic relation between the rate of burst Fe(III) formation (R) and the initial Fe(II) concentration. Reaction-temperature 25 °C, $[H^+]=1.0$ mol dm^{-3}. Various initial $KBrO_3$ concentrations shown above.

similar interpretation have been obtained for the burst of cerium(IV) formation in the previous paper.[7]

Comparison between Bromate-Cerium and -Iron Reactions. For the bromate-cerium(III) reaction, there is an induction period, followed by a burst of cerium(IV) formation, and then a gradual formation of cerium(IV). For the bromate-iron(II) reaction, a slow dissociation to $[Fe(phen)_2]^{2+}$ is observed in the beginning. It is the duration of the induction period for the iron(III) formation, which is followed by the burst of iron(III) formation.

Table 2. Apparent kinetic constants of k_τ and k_r for iron and cerium systems

	k_τ[a]	k_r	Temperature
	s^{-1} mol^{-2} dm^6	s^{-1} mol^{-2} dm^6	°C
Iron(II)	3.22	0.118	20
reaction	3.93	0.180	25
	4.68	0.257	30
Cerium(III)	—	5.44	20
reaction	0.772	7.44	25
	1.98	11.0	30

a) k_τ is equal to $k_1/\{\ln(C_2/C_1)-(C_2+1)\}$. b) k_r is equal to $k_1C_2/(C_2+1)^2$.

For the bromate-cerium(III) and -iron(II) reactions, the details of the apparent kinetic constants are summarized in Table 2: k_τ for the induction period and k_r for the burst oxidation of metal ions, based on Eqs. 16 and 15 respectively. Now, we obtain:

$$k_\tau = \frac{k_1}{\ln(C_2/C_1)-(C_2+1)}, \tag{17}$$

and:

$$k_r = \frac{k_1C_2}{(C_2+1)^2}. \tag{18}$$

The apparent activation energies of k_τ are 27.5 for iron and 140 kJ/mol for cerium. This large difference may result from the different standard electrode potential, the $E°$ values for the $[Fe(phen)_3]^{2+}/[Fe(phen)_3]^{3+}$ and Ce(III)/Ce(IV) couples, and the different ligands of the reaction complexes, which cause dissociation in the iron complex, but not in the cerium one. On the other hand, the apparent activation energies of k_r are 57 for iron and 52 kJ/mol for cerium. These are the same values as we obtained in neptunium from Knight's data (57—70 kJ/mol).[13] This fact may be interpreted well by the behaviour of the $BrO_2^\cdot$ radical if the oxidation rate of metal complex is controlled by the formation of the radical, as is shown in Eq. 1. Since the rate of the bromate-iron(II) ion reaction is faster than that of $[Fe(phen)_3]^{2+}$ dissociation to $[Fe(phen)_2]^{2+}$, we can also conclude that electrode transfer takes place *via* an outer-sphere path.[10]

Let us now consider how the hydrogen ion influences the burst formation of the oxidized metal ion. Knight and Thompson[13] obtained an empirical formation which summarized the variation in $2k_r[H^+]$ with the change in the hydrogen-ion concentration. The two-parameter expression, compared with Eq. 15:

$$2\,k_r[H^+] = \alpha[H^+]^2/(1+\beta[H^+]), \tag{19}$$

fits the data much better for the bromate-Np(V) reaction.[13]

If the $C_2(\simeq k_1[H^+]/2k_4)$ quantity is sufficiently smaller than unity, we obtain, instead of Eq. 15:

$$\frac{d[Fe(III)]_f}{dt} = \frac{\frac{k_1^2}{k_4}[H^+]^2}{1+\frac{k^1}{k^4}[H^+]}[BrO_3^-]_0^2. \tag{20}$$

In the bromate-cerium system, Noyes and his coworkers[3] reported k_1 and k_4 to be 1.0×10^4 mol^{-2} dm^6 s^{-1} and 4.0×10^7 mol^{-1} dm^3 s^{-1} respectively. Therefore, the above assumption seems to be reasonable. Equation 20 is completely consistent with Eq. 19.

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