Kinetics of the Bromate–Bromide Reaction at High Bromide Concentrations

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ABSTRACT: At bromide concentrations higher than 0.1 M, a second term must be added to the classical rate law of the bromate–bromide reaction that becomes $-d[BrO_3^-]/dt = [BrO_3^-][H^+]^2(k_1[Br^-] + k_2[Br^-]^2)$. In perchloric solutions at 25°C, $k_1 = 2.18$ dm^3 mol^{-3} s^{-1} and $k_2 = 0.65$ dm^4 mol^{-4} s^{-1} at 1 M ionic strength and $k_1 = 2.60$ dm^3 mol^3 s^{-1} and $k_2 = 1.05$ dm^4 mol^{-4} s^{-1} at 2 M ionic strength. A mechanism explaining this rate law, with Br_2O_2 as key intermediate species, is proposed. Errors that may occur when using the Guggenheim method are discussed. © 2006 Wiley Periodicals, Inc. Int J Chem Kinet 39: 17–21, 2007

INTRODUCTION

Several authors have studied the kinetics of reaction (1) [1–14].

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \quad (1)$$
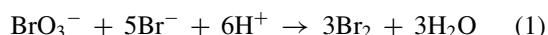
The usually accepted rate law is

$$-d[BrO_3^-]/dt = k[BrO_3^-][Br^-][H^+]^2 \quad (2)$$

but a second term proportional to $[Br^-]^2$ has been suggested [3,4].

$$-d[BrO_3^-]/dt = [BrO_3^-][H^+]^2(k_1[Br^-] + k_2[Br^-]^2) \quad (3)$$

Rabai et al. [13] have proposed rate law (3) with a third term proportional to $[BrO_3^-][Br^-]^2[H^+]$. More recently, Cortes and Faria [14] called this work in question, reinvestigated the kinetics of reaction (1) and concluded that it follows the rate law (2) without additional terms. However, most of their experiments were performed with bromide concentrations lower than 0.1 M, too low to see the term proportional to $[Br^-]^2$ [3,4,13], and we have decided to study once more this venerable reaction using higher bromide concentrations.

EXPERIMENTAL

The reaction was followed using a Spectronic Genesys spectrophotometer and a stopped-flow mixing accessory RX.2000 from Applied Photophysics. The temperature was controlled at $25.0 \pm 0.1°C$. One stopped-flow syringe contained a mixture of NaBrO$_3$, HClO$_4$, and NaClO$_4$ and the other a mixture of NaBr, HClO$_4$, and NaClO$_4$. The concentrations of NaClO$_4$ in the two mixtures were such that their ionic strengths were similar* and that the ionic strength after mixing was exactly 1 or 2 M. Most of the experiments were performed

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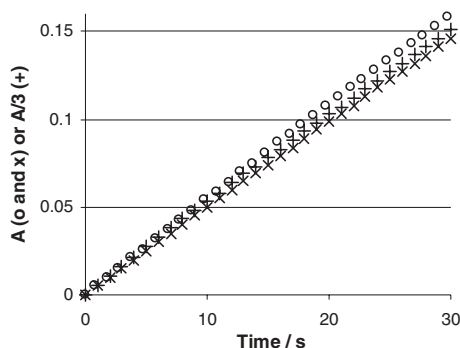*Experiments with $[Br^-] = 3.77$ M and no NaClO$_4$ ($[Br^-] = 1.88$ M and I = 2 M after mixing) gave abnormal results and were discarded.

Figure 1 Differential method. $[BrO_3^-] = 5.00 \times 10^{-3}$ M; $[H^+] = 0.112$ M; $[Br^-] = 0.1$ M, $I = 1$ M ($\times$); $[Br^-] = 0.3$ M, $I = 1$ M (+); $[Br^-] = 0.1$ M, $I = 2$ M ($\circ$).

for $[BrO_3^-] = 5.00 \times 10^{-3}$ M, but experiments with $[BrO_3^-]$ between 2.00×10^{-3} and 1.00×10^{-2} M agreed with the accepted order one. Similarly, most of the experiments were performed for $[H^+] = 0.112$ M, but experiments with $[H^+]$ between 0.056 and 0.280 M agreed with the accepted order two. The bromide concentration was varied from 0.1 to 1 M.

Reference solutions of Br_2 and Br_3^- were prepared using reaction (1). The isobestic point of these mixtures was located at $\lambda = 445$ nm, and the kinetic experiments were performed at this wavelength to avoid the effect of the reaction $Br_2 + Br^- \rightleftharpoons Br_3^-$. The extinction coefficient was measured in the stopped-flow cell at the end of experiments giving a total conversion of bromate, and the obtained value was $\varepsilon = 120$ L mol^{-1} cm^{-1}. Cortes and Faria [14] had obtained $\varepsilon = 111$ L mol^{-1} cm^{-1} at $\lambda = 446$ nm, and Rabai et al. [13,15] had obtained $\varepsilon = 83$ L mol^{-1} cm^{-1} at $\lambda = 455$ nm (there is a misprint in [13]). This low ε value can be explained by the location of the isobestic point at a slightly too high wavelength. In this part of the spectrum of Br_2 and Br_3^-, both extinction coefficients decrease when the wavelength increases.

RESULTS

The curves of the absorbance as a function of time were analyzed using two methods, a differential method at low conversions and an integral method. At low conversions, the absorbance A increases nearly proportionally with time. We can measure the slope dA/dt with accuracy and extrapolate it to time zero giving $(dA/dt)_0$ and the reaction rate $(dA/dt)_0/3\varepsilon$. Some examples are presented in Fig. 1. For the experiment with $[Br^-] = 0.3$ M, we have plotted $A/3$ showing clearly that the rate is a little larger than three times the rate if

$[Br^-] = 0.1$ M at the same ionic strength. The analysis of our data by the integral method uses the form (4) of Eq. (3), where x is the extent of reaction.

$$\frac{dx}{dt} = ([BrO_3^-]_0 - x)([H^+]_0 - 6x)^2(k_1[Br^-] + k_2[Br^-]^2) \qquad (4)$$

The excess of Br^- is such that its concentration is practically constant during the reaction, but this is not really true for H^+. The ratio of the initial concentrations $[H^+]_0/[BrO_3^-]_0 = 22.4$ seems high but is only 3.7 times the stoichiometric ratio. The integration of Eq. (4) gives the following expression where b_0 stands for $[BrO_3^-]_0$ and h_0 for $[H^+]_0$:

$$F(x) = (k_1[Br^-] + k_2[Br^-]^2)t$$

where

$$F(x) = \frac{1}{(h_0 - 6b_0)^2} \ln \frac{b_0(h_0 - 6x)}{h_0(b_0 - x)} - \frac{6x}{h_0(h_0 - 6b_0)(h_0 - 6x)}$$

The experimental values of $F(x)$ are calculated as a function of time using $x = A/3\varepsilon$. Figure 2 shows $F(x)$ divided by $[Br^-]$ for some typical experiments. Such plots are linear to more than 80% conversions and their slopes give

$$k_{exp} = k_1 + k_2[Br^-]$$

We see again that the increase in the reaction rate is more than proportional to $[Br^-]$. Figure 3 summarizes our results. The differences between the k_{exp} values obtained with the integral or the differential method
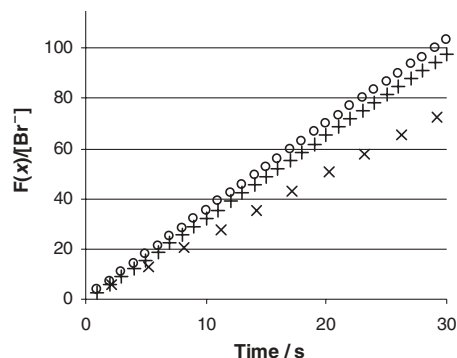

Figure 2 Integral method. $[BrO_3^-] = 5.00 \times 10^{-3}$ M; $[H^+] = 0.112$ M; $[Br^-] = 0.5$ M, $I = 1$ M ($\times$); $[Br^-] = 0.5$ M, $I = 2$ M (+); $[Br^-] = 1$ M, $I = 2$ M ($\circ$).
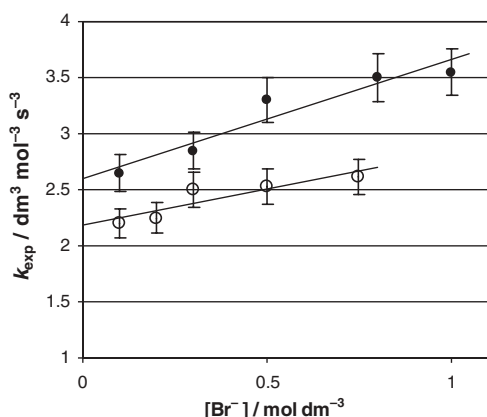
Figure 3   Summary of the results. $I = 1$ M ($\bigcirc$), 2 M ($\bullet$).

for the same initial concentrations were smaller than the experimental errors, and Fig. 3 include both sets of values. The regression lines give $k_1 = 2.18$ dm^3 mol^{-3} s^{-1} and $k_2 = 0.65$ dm^4 mol^{-4} s^{-1} at 1 M ionic strength and $k_1 = 2.60$ dm^3 mol^{-3} s^{-1} and $k_2 = 1.05$ dm^4 mol^{-4} s^{-1} at 2 M ionic strength.

DISCUSSION

We compare this work with former works and then propose a mechanism explaining the observed rate law. The k_1 values obtained by several authors are presented in Fig. 4. They go through a minimum when the ionic strength increases, an observation qualitatively explained noting that the rate is proportional to $\gamma^2_{\text{HBrO}_3} \gamma^2_{\text{HBr}}$. A quantitative treatment with the Pitzer's equation [16] cannot be performed because the parameters for HBrO$_3$ are unknown. By extrapolation
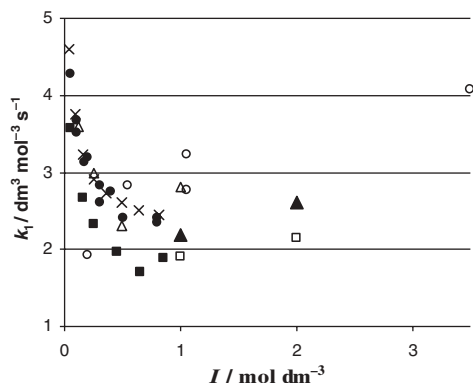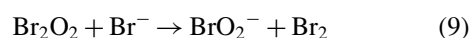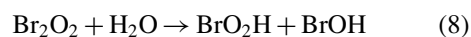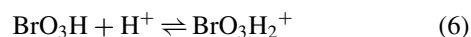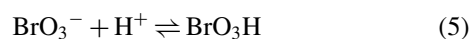

Figure 4   Comparison with other works: Bray and Liebhafsky [3] ($\bullet$), Skrabal and Schreiner [4] ($\square$), Sclar and Riesch [5] ($\times$), Wronska and Wawrzenczyk [8] ($\blacksquare$), Burgos et al. [10] ($\triangle$), Cortes and Faria [14] ($\circ$), and this work ($\blacktriangle$).

at zero ionic strength, the values $k_1(I \to 0) = 9.0$ [2,3] and 9.5 dm^3 mol^{-3} s^{-1} [5] were proposed. In the region of the minimum and above, k_1 depends on the electrolytes used to fix the ionic strength [8,10]. In perchloric solutions with $I = 1$ M, our value $k_1 = 2.18$ dm^3 mol^{-3} s^{-1} is in good agreement with most of the other reported values. Two exceptions are the high values obtained by Burgos [10] and by Cortes [14]. Both authors have analyzed their measurements using the Guggenheim method, and we show in the Appendix that this method gives too high kinetic constants if the excess of H$^+$ and Br$^-$ is not sufficient. We are aware of only three works performed at sufficiently high Br$^-$ concentrations to detect the k_2 term. Bray and Liebhafsky [3] have mentioned this term but without suggesting a value of the rate constant. Skrabal and Schreiner [4] have obtained $k_2 = 0.23$ dm^4 mol^{-4} s^{-1} from only two measurements. The measurements of Rabai et al. [13] deserve a detailed analysis. They were performed at 3 M ionic strength with [H$^+$] fixed between 0.0047 and 0.0458 M with a phosphate buffer and measured with a combined glass electrode. Their data between [H$^+$] = 0.0124 and 0.0458 M can be fitted with rate law (3), and minimizing the sum of squares of the differences between the measured and calculated values we have obtained $k_1 = 4.7$ dm^3 mol^{-3}s^{-1} and $k_2 = 1.1$ dm^4 mol^{-4} s^{-1}. Taking the higher ionic strength and the replacement of perchloric ions with phosphate ions into account, this is an excellent agreement with our results. Their term proportional to [BrO$_3^-$] [Br$^-$]^2[H$^+$] is supported only by their five measurements at [H$^+$] = 0.0047 M, and we do not consider it as firmly established. The response of the glass electrode and the liquid junction potential at this high ionic strength depends on the ions used to fix it, different in the reference solutions (NaBr) and the measured solutions (NaBr + NaClO$_4$ + NaH$_2$PO$_4$). An error of about 3 mV would be sufficient to explain the introduction of the third term in the rate law.

The general model we have proposed [17] for this family of reaction, based on the ideas of Bray [18], Skrabal and Schreiner [4], and Sigalla [6], explains the k_2 term in rate law (3). For the bromate–bromide reaction in nonbuffered solutions, it is written

$$BrO_3^- + H^+ \rightleftharpoons BrO_3H \qquad (5)$$

$$BrO_3H + H^+ \rightleftharpoons BrO_3H_2^+ \qquad (6)$$

$$BrO_3H_2^+ + Br^- \rightleftharpoons Br_2O_2 + H_2O \qquad (7)$$

$$Br_2O_2 + H_2O \to BrO_2H + BrOH \qquad (8)$$

$$Br_2O_2 + Br^- \to BrO_2^- + Br_2 \qquad (9)$$

The rate-controlling steps (8) and (9) are followed by the reduction of BrO_2H or BrO_2^- to $BrOH$ and then to Br_2. These reactions are themselves complicated, and their discussion is outside the scope of this work. The rate of bromate reduction is equal to the sum of the rates of the steps (8) and (9), $[Br_2O_2]$ $(k_8 + k_9 [Br^-])$, or with the fast pre-equilibria (5)–(7)

$$-d[BrO_3^-]/dt = K_5 K_6 K_7 [BrO_3^-][H^+]^2[Br^-](k_8 + k_9[Br^-]) \qquad (10)$$

The rate law (3) has the same form as Eq. (10). It has also the same form as the rate law (11) of the iodate–iodide reaction [19].

$$-d[IO_3^-]/dt = [IO_3^-][H^+]^2(k_1'[I^-] + k_2'[I^-]^2) \quad (11)$$

This supports our suggestion that both reactions have the same mechanism, the only difference being the values of the rate constants. The ratio k_1'/k_2' for the iodate–iodide reaction is about 4×10^{-6} M [17,19], and the transition from the fourth to the fifth order occurs when $[I^-] = 4 \times 10^{-6}$ M. The ratio k_1/k_2 for the bromate–bromide reaction is about 3 M, and the transition occurs only when $[Br^-] = 3$ M, so that the purely fifth-order rate law cannot be observed.

The essential of the model is the hypothesis of intermediate species XYO_2 with X and Y = Cl, Br, or I. These species are asymmetric [17] (XYO_2 is different from YXO_2) and may be hydrated. We write Br_2O_2 rather than $Br_2O_3H_2$, a kinetically equivalent species, for simplicity. The existence of these species explains not only rate laws like (3) and (11) but also a large number of experimental observations that would be difficult to explain otherwise. Let us just mention the catalytic effect of chloride on the bromate–bromide reaction [6,8]. Reaction (12), giving the rate law (13), explains these observations. Other possibilities exist starting with $BrO_3H_2^+ + Cl^- \rightleftharpoons ClBrO_2 + H_2O$.

$$Br_2O_2 + Cl^- \rightarrow BrO_2^- + BrCl \qquad (12)$$

$$-d[BrO_3^-]/dt = K_5 K_6 K_7 [BrO_3^-][H^+]^2[Br^-](k_8 + k_9[Br^-] + k_{12}[Cl^-]) \qquad (13)$$

CONCLUSIONS

This work confirms the term proportional to $[Br^-]^2$ in the rate law of the bromate–bromide reaction previously proposed [3,4,13]. It becomes important only at high bromide concentrations and, consequently, can be observed only at high ionic strengths. This raises some problems because the rate is proportional to the fourth power of the mean activity coefficient that depends not only on the ionic strength but also on the ions used to fix it.

The analytical forms of the rate laws of the bromate–bromide and iodate–iodide reactions are identical, suggesting a common mechanism. When two halides X and Y are involved (X, Y = Cl, Br, I), similar rate laws are observed with terms proportional to [X], [Y] and/or [X][Y] [4,6,17]. All the rate laws of this family of reaction can be derived from a model represented schematically as follow.

$$XO_3^- + 2 H^+ \rightleftharpoons XO_3H_2^+$$
$$XO_3H_2^+ + Y^- \rightleftharpoons YXO_2 + H_2O$$
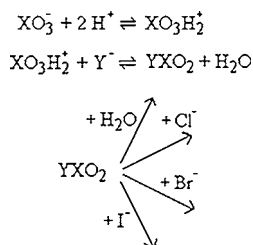
APPENDIX: ERRORS WITH THE GUGGENHEIM METHOD

For simplicity, and some generalization, we represent the bromate–bromide reaction, studied with a large excess of bromide but not necessarily a large excess of acid, by $B + \alpha H \rightarrow$ products with the rate law $-d[B]/dt = k[B][H]^2$. The conversion of bromate is $y = ([B]_0 - [B])/[B]_0$ giving $[B] = [B]_0 (1 - y)$ and, as $[H]_0 - [H] = \alpha([B]_0 - [B])$, $[H] = [H]_0 - \alpha[B]_0 y$. Introducing the initial ratio $\rho = \alpha[B]_0/[H]_0$ and the pseudo-first order rate constant $k' = k[H]_0^2$, the rate law becomes $dy/dt = k'(1 - y)(1 - \rho y)^2$.

The Guggenheim's method applies to a first-order reaction. In our case, it supposes that $\rho \ll 1$ giving the rate law $dy/dt = k'(1 - y)$ with the solution $y = 1 - \exp(-k't)$. The principle of the method is to introduce a constant time lag τ and to subtract the values of y at time t from its value at time $t + \tau$. This gives $y_{t+\tau} - y_t = [1 - \exp(-k'\tau)]^* \exp(-k't)$. A plot of $\ln(y_{t+\tau} - y_t)$ versus t gives a straight line with slope $-k'$. The major advantage of the method is that we do not need to know the value of y but only of any linear function of y. If $z = a + by$, $z_{t+\tau} - z_t = ([1 - \exp(-k'\tau)]/b)^* \exp(-k't)$ and a plot of $\ln(z_{t+\tau} - z_t)$ versus t gives also a straight line with slope $-k'$. For absorbance measurements, the results do not depend on the extinction coefficient. We have applied this method to our measurements but noticed that it gave too high values of k'. The reason was that the condition $\rho \ll 1$ was not sufficiently

strictly fulfilled. The integration of the exact equation $dy/dt = k'(1 - y)(1 - \rho y)^2$ gives

$$\frac{1}{(1 - \rho)^2} \ln \frac{1 - \rho y}{1 - y} - \frac{\rho y}{(1 - \rho)(1 - \rho y)} = k't$$

This equation can be solved for given values of t and $t + \tau$ by an iterative method. Plotting the obtained values of $\ln(y_{t + \tau} - y_t)$ versus t gives a straight line (it is not mathematically but the deviations are not perceptible experimentally) but with a slope higher than k'. In the example of our experiments with $[B]_0 = 5 \times 10^{-3}$ M and $[H]_0 = 0.112$ M giving $\rho = 0.27$, the slope is 20% higher than k' for a final conversion of 50%. The error depends mainly on ρ and decreases slowly when the final conversion increases.

We have found that the Guggenheim's method can nevertheless be indirectly useful. The too high rate constants obtained using it were divided by a correction factor calculated as above with the experimental values of ρ and final conversion. The corrected values agreed perfectly with the values calculated with the integral method. As the Guggenheim's method does not use the value of the extinction coefficient, these calculations support the value used with the integral method.

Similar conclusions would be reached with a large excess of acid but not necessarily a large excess of bromide. The mathematical treatment should include a stoichiometric coefficient increasing from 5 to 8 when $[Br^-]$ increases, and the final product changes from Br_2 to Br_3^-.

We conclude that the Guggenheim's method must be used with great care.

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