

Revisiting the Kinetics and Mechanism of Bromate-Bromide Reaction

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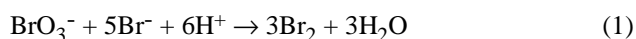
A reação bromato-brometo, em meio de ácido perclórico, foi observada numa faixa de acidez até então não estudada. A reação foi acompanhada através da medida da absorvância no ponto isosbético para as espécies Br_2 e Br_3^- ($\lambda = 446 \text{ nm}$). Observou-se um comportamento de primeira ordem para o bromato e para o brometo e um comportamento de segunda ordem para o H^+ , levando à lei de velocidade $v = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$. Esta lei de velocidade sugere um mecanismo envolvendo duas protonações sucessivas do íon bromato, formando o H_2BrO_3^+ , que então reage com o íon brometo. Estes resultados discordam de outros estudos que verificaram um comportamento de segunda ordem para o íon brometo, bem como um comportamento de primeira ordem para o H^+ , que levaram a propor a existência de intermediários tais como $\text{H}_2\text{Br}_2\text{O}_3$ e HBr_2O_3^- . O comportamento de segunda ordem observado para o H^+ na faixa de concentração $0,005 \leq [\text{H}^+] \leq 2,77 \text{ mol L}^{-1}$ permite afirmar que o pK_a do ácido brômico, HBrO_3 , deve ser menor do que $-0,5$ a $25 \text{ }^\circ\text{C}$, diferentemente de todas as propostas existentes até agora na literatura para o valor deste pK_a .

The bromate-bromide reaction was investigated in an acidity range not studied yet. The reaction was followed at the $\text{Br}_2/\text{Br}_3^-$ isosbestic point ($\lambda = 446 \text{ nm}$). It was observed a first-order behavior for bromate and bromide ions and a second-order behavior for H^+ ion that results in the rate law $v = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$. This rate law suggests a mechanism involving two successive protonation of bromate followed by the interaction of the intermediate species H_2BrO_3^+ with bromide. These results disagree with the obtained by other authors who observed a second-order behavior for the bromide and first-order for H^+ , and have proposed intermediate species like $\text{H}_2\text{Br}_2\text{O}_3$ and HBr_2O_3^- . The second-order for $[\text{H}^+]$ observed in the range $0.005 \leq [\text{H}^+] \leq 2.77 \text{ mol L}^{-1}$ sets down that the pK_a of bromic acid, HBrO_3 , must be lower than -0.5 ($T = 25 \text{ }^\circ\text{C}$), different from all other values for this pK_a proposed in the literature.

Keywords: bromic acid, pK_a , bromate, bromide, kinetics

Introducion

Judson and Walker¹ were the first to study the reaction between bromate and bromide (equation 1) and concluded that it follows a fourth-order rate law (equation 2).



$$-d[\text{BrO}_3^-]/dt = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2 \quad (2)$$

This rate law was confirmed by several authors²⁻⁸ which observed that the rate constant decreases with the increase of the ionic strength, I , for $I \leq 1 \text{ mol L}^{-1}$ and increases with the

increase of I for $I > 1 \text{ mol L}^{-1}$. In addition, the possibility of a fifth-order rate law at high ionic strength with second-order on bromide was pointed out by some authors⁵.

Rábai *et al.*⁹ were the first to use ultraviolet spectroscopy to follow this reaction at the $\text{Br}_2/\text{Br}_3^-$ isosbestic point. They measured the initial rate for a wide range of bromide concentration ($0.1 < [\text{Br}^-] < 2.0 \text{ mol L}^{-1}$) at low concentrations of H^+ and bromate. To explain the observed behavior, especially at high $[\text{Br}^-]$, they proposed a rate law with three terms, as indicated in equation 3, and a mechanism with six elementary steps including the intermediate species H_2BrO_3^+ , HBr_2O_3^- and $\text{H}_2\text{Br}_2\text{O}_3$.

$$-d[\text{BrO}_3^-]/dt = k'[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2 + k''[\text{BrO}_3^-][\text{Br}^-]^2[\text{H}^+] + k'''[\text{BrO}_3^-][\text{Br}^-]^2[\text{H}^+]^2 \quad (3)$$

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Burgos *et al.*¹⁰ followed this reaction at the λ_{\max} of Br_2 , using UV-Vis spectroscopy. They found a significant increase in the rate constant of this reaction at high values of ionic strength especially when it was controlled by NaClO_4 . Domínguez *et al.*⁸ have followed this reaction at the λ_{\max} of Br_3^- in a wide range of ionic strengths. They found a decrease, followed by an increase in the rate constant with the increase of the ionic strength.

In this work we extend the $[\text{H}^+]$ to the high acidity range of 0.005 to 2.77 mol L⁻¹, at low concentrations of bromate and bromide. The obtained kinetic results posed some questions to the rate law proposed by Rabay *et al.*⁹ and allowed us to establish that the $\text{p}K_a$ of HBrO_3 must be lower than -0.5.

Experimental Section

Analytical grade chemicals NaBrO_3 (Riedel-deHaën), HClO_4 (Merck), NaClO_4 (Riedel-deHaën; Vetec), and NaBr (Grupo Química) were used without further purification. Water used had 18 M Ω resistivity and was obtained by a Milli-Q Plus purification system.

Kinetics experiments were carried out by two methods. The first method (to be assumed when not indicated) employed the UV-Vis diode array spectrophotometer HP 8452-A and Suprasil standard quartz cuvette with 1.00 cm optical path (Hellma 110-QS). After the reagents were transferred to the cuvette using a fast delivering digital pipette (Transferpette), the cuvette was closed tightly with a round Teflon plug. The total volume of the solution in the cuvette was 2.0-3.0 mL. The cuvette containing a 3 x 5 mm Teflon coated cylindrical stirring-bar was placed inside a jacketed cuvette holder equipped with a water powered magnetic stirrer. The stirring rate was about 900 rpm and no vortices were observed inside the cuvette. Experimental points were taken at each 0.1 s for the faster experiments. The estimated dead time after mixing the reagents was about 2 s. The second method was the stopped-flow technique performed by the use of the Hi-Tech Dual Mixing Microvolume Stopped-Flow SF-61DX2. For both methods the temperature was maintained at 25.0 \pm 0.1 °C by a circulating bath and the ionic strength of all solutions was adjusted with NaClO_4 .

The reaction was followed at $\lambda = 446$ nm that corresponds to the isosbestic point of the mixture of Br_2 and Br_3^- ($\epsilon = 111$ L mol⁻¹ cm⁻¹). The extinction coefficient at the isosbestic point was obtained by fitting a second degree polynomial to the experimental absorbance data for Br_2 and Br_3^- obtained by Raphael in 2 mol L⁻¹ perchloric acid solution¹¹. Our value for the extinction coefficient ($\epsilon = 111$ L mol⁻¹ cm⁻¹) of the isosbestic point of Br_2 and Br_3^- is in the middle of the values found by Lengyel *et.*

*al.*¹² ($\epsilon = 130$ L mol⁻¹ cm⁻¹, $\lambda = 441$ nm, in perchloric acid solution) and Rábai *et al.*⁹ ($\epsilon = 83$ L mol⁻¹ cm⁻¹; $\lambda = 544$ nm cannot be right because bromine solutions do not absorb at this wavelength¹³).

In the case of HP results the initial rate of reaction, v_0 , was determined by fitting a second degree polynomial, $at^2 + bt + c$, to the total bromine concentration *versus* time curve. The coefficient b is the initial rate. In the case of stopped-flow experiments, v_0 was determined by linear regression fitting to the initial time experimental data. All experimental kinetic data presented here are the average of a minimum of five determinations.

Data treatment and curve fitting for kinetic data were carried out by using the LOTUS 1-2-3¹⁴.

Results and Discussion

Table 1 presents the first-order rate constants obtained at different bromide concentrations, keeping constant the initial bromate concentration, acid concentration and ionic strength. Since the bromide and acid concentration are both much higher than bromate concentration, a pseudo-first-order condition is satisfied and pseudo-first-order rate constants could be obtained from plots of $\log(A_{t+\Delta t} - A_t) \times t$ (Guggenheim method)¹⁵. These plots have shown excellent linear behavior, confirming the first-order for bromate. The plot $\log k_{\text{obs}} \times \log [\text{Br}^-]_0$ produced a good straight line ($R^2 = 0.998$) with slope 0.984 ± 0.022 , indicating a first-order behavior for the bromide too.

Table 1. First-order rate constants for the determination of the bromide order. Constrains: $[\text{BrO}_3^-]_0 = 1.00 \times 10^{-3}$ mol L⁻¹; $[\text{HClO}_4]_0 = 0.1137$ mol L⁻¹; $I = 0.55$ mol L⁻¹ (adjusted with NaClO_4); $T = 25.0$ °C.

$[\text{Br}^-]_0 / \text{mol L}^{-1}$	$k_{\text{obs}} / 10^{-3} \text{ s}^{-1}$
0.400	14.36
0.200	7.213
0.100	3.802
0.0800	2.816
0.0600	2.250

Table 2 presents the initial rate values for a wide range of $[\text{H}^+]$. The initial bromate and bromide concentrations were adjusted to allow a convenient time scale to follow the reaction.

Plots of $\log v_0 \times \text{p}[\text{H}]$, where $\text{p}[\text{H}] = -\log [\text{H}^+]$, from data in Table 2 (which is equivalent to a pH-rate profile¹⁶, plot of $\log k_{\text{obs}} \times \text{p}[\text{H}]$) present slopes very close to -2 for all four sets of experiments (see Table 3). These results point out the second-order in $[\text{H}^+]$ as stated by equation 2. Dividing v_0 by the initial concentrations of bromate and bromide it is possible to put all experimental data in the same plot, as shown in Figure 1.

Table 2. Initial rate values at 25.0 °C.

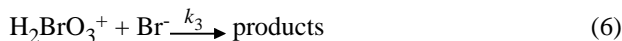
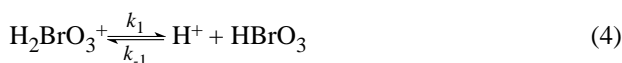
$[\text{BrO}_3^-]_0 / \text{mol L}^{-1}$	$[\text{Br}^-]_0 / \text{mol L}^{-1}$	$I / \text{mol L}^{-1}$	$[\text{H}^+]_0 / \text{mol L}^{-1}$ (a)	$v_0 / (10^{-6} \text{ mol L}^{-1} \text{ s}^{-1})$			
1.00×10^{-3}	1.00×10^{-1}	0.201	0.00500	0.00467			
			0.0100	0.0179			
			0.0150	0.0470			
			0.0250	0.112			
			0.0500	0.473			
			0.0750	1.07			
			0.100	2.13			
7.00×10^{-4}	5.00×10^{-2}	1.05	0.0361	0.107			
			0.0516	0.242			
			0.0734	0.513			
			0.0988	0.917			
			0.148	2.60			
			0.197	4.13			
			0.247	6.90			
			0.296	9.00			
			0.347	10.1			
			0.572	26.0			
			2.00×10^{-4}	1.00×10^{-3}	3.50	1.032	0.760
						1.296	1.37
1.552	1.99						
1.772	2.98						
2.004	3.60						
2.406	4.53						
2.772	5.53						
7.00×10^{-4}	5.00×10^{-2}	1.05	0.105	1.32 ^(b)			
			0.200	4.49 ^(b)			
			0.301	9.53 ^(b)			
			0.409	16.6 ^(b)			
			0.500	27.8 ^(b)			
			0.600	41.6 ^(b)			
			0.691	55.3 ^(b)			
			0.800	75.5 ^(b)			
			0.900	98.0 ^(b)			
			1.03	124 ^(b)			

(a) adjusted using HClO_4 ; (b) stopped-flow results**Table 3.** Slope of the linear fitting for the plots of $\log v_0 \times \text{p[H]}$. ($T = 25.0$ °C).

$[\text{BrO}_3^-]_0 / \text{mol L}^{-1}$	$[\text{Br}^-]_0 / \text{mol L}^{-1}$	$I / \text{mol L}^{-1}$	$[\text{H}^+]_0 / \text{mol L}^{-1}$ (a)	Slope $\log v_0 \times \text{p[H]}$
1.00×10^{-3}	1.00×10^{-1}	0.201	0.00500 - 0.100	-2.03 ± 0.03
7.00×10^{-4}	5.00×10^{-2}	1.05	0.0361 - 0.572	-2.01 ± 0.06
2.00×10^{-4}	1.00×10^{-3}	3.50	1.032 - 2.772	-2.02 ± 0.14
7.00×10^{-4}	5.00×10^{-2}	1.05	0.105 - 1.03	$-2.02 \pm 0.03^{(b)}$

(a) adjusted using HClO_4 ; (b) stopped-flow results

Considering the mechanism below (equations 4 to 6) the reactive species against bromide is H_2BrO_3^+ .



Using this scheme and considering that the rate-determining step is reaction 6, the rate of reaction, v , can be given as a function of the total bromine(V) concentration.

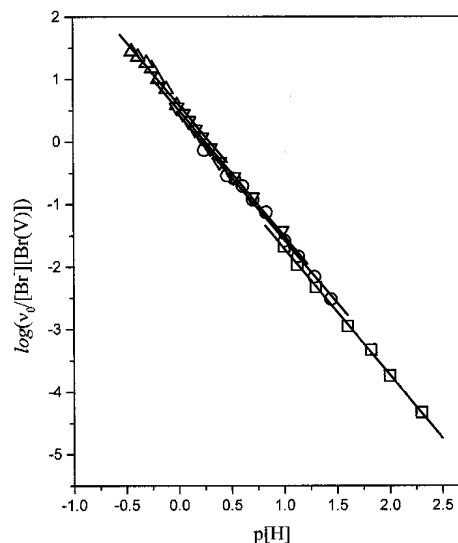
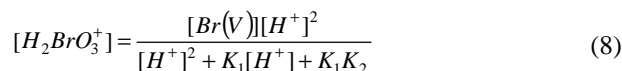


Figure 1. pH-rate profile of Table 2 data as a plot of $\log (v_0/[\text{Br}^-]_0[\text{Br(V)}]_0) \times \text{p[H]}$. (\square) $[\text{BrO}_3^-]_0 = 1.00 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{Br}^-]_0 = 1.00 \times 10^{-1} \text{ mol L}^{-1}$, $I = 0.201 \text{ mol L}^{-1}$; (\circ) $[\text{BrO}_3^-]_0 = 7.00 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{Br}^-]_0 = 5.00 \times 10^{-2} \text{ mol L}^{-1}$, $I = 1.05 \text{ mol L}^{-1}$; (Δ) $[\text{BrO}_3^-]_0 = 2.00 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{Br}^-]_0 = 1.00 \times 10^{-3} \text{ mol L}^{-1}$, $I = 3.50 \text{ mol L}^{-1}$; (∇) same as (\circ) but using stopped-flow technique. $T = 25.0$ °C.



Where $K_1 = k_1/k_{-1}$ and $K_2 = k_2/k_{-2}$. At very low H^+ concentration equation 10 turns into equation 11 that is identical to equation 2, with the fourth-order rate constant, k , equal to k_3/K_1K_2 .



Applying logarithm in both sides one gets equations 12 and 13.

$$\log v = \log \{k_3[\text{Br}^-][\text{Br(V)}]/K_1K_2\} + 2 \log [\text{H}^+] \quad (12)$$

$$\log v = \log \{k_3[\text{Br}^-][\text{Br(V)}]/K_1K_2\} - 2 \text{p[H]} \quad (13)$$

In this way, the linear behavior with slope equal -2 observed in Figure 1 and Table 3 indicates that the order with respect to H^+ is 2. Most importantly, the H^+ concentration is indeed very low compared with K_1 and K_2 , otherwise the approximation that turns equation 10 into equation 11 would not be valid. This indicates that in our reaction medium

we cannot have any protonation equilibrium involving an acid with pK_a higher than, approximately, -0.5 and puts an upper limit for the pK_a of HBrO_3 (pK_2).

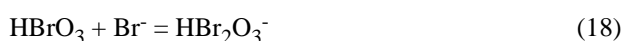
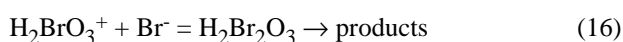
Table 4 shows the fourth-order rate constant, k , at different ionic strengths together with other authors results. Our k values were calculated using the data in Tables 1 and 2 and based on the rate law given by equation 2.

Table 4. Selected values of the fourth-order rate constant, k , for reaction 1. $T = 25.0$ °C.

$I/\text{mol L}^{-1}$	$k/\text{L}^3 \text{ mol}^{-3} \text{ s}^{-1}$	Main Electrolyte	Ref.
0.106	3.59	$\text{HClO}_4, \text{NaClO}_4$	4
0.16	2.75	$\text{HBr}, \text{Mg}(\text{ClO}_4)_2$	5
0.19	1.68	H_2SO_4	3
0.20	1.92 ± 0.12	$\text{HClO}_4, \text{NaClO}_4$	this work
0.20	3.18	$\text{HClO}_4, \text{NaClO}_4$	4
0.23	3.22	$\text{HBr}, \text{NaClO}_4$	8
0.25	2.35	$\text{HBr}, \text{Mg}(\text{ClO}_4)_2$	5
0.25	3.0	NaClO_4	10
0.51	2.42	$\text{HClO}_4, \text{NaClO}_4$	4
0.55	2.83 ± 0.08	$\text{HClO}_4, \text{NaClO}_4$	this work
0.55	2.96	$\text{HBr}, \text{NaClO}_4$	8
0.54	1.10	H_2SO_4	3
0.64	1.55	$\text{HBr}, \text{Mg}(\text{ClO}_4)_2$	5
0.81	1.37	$\text{HBr}, \text{Mg}(\text{ClO}_4)_2$	5
0.81	2.4	$\text{HClO}_4, \text{NaClO}_4$	4
0.91	1.05	HBr	1
1.0	1.18	$\text{HBr}, \text{Mg}(\text{ClO}_4)_2$	5
1.0	2.8	NaClO_4	10
1.0	2.79	$\text{HBr}, \text{NaClO}_4$	8
1.05	2.76 ± 0.36	$\text{HClO}_4, \text{NaClO}_4$	this work
1.05	3.24 ± 0.18	$\text{HClO}_4, \text{NaClO}_4$	this work ^(a)
3.0	38.7	NaClO_4	10
3.0	17.9 ^(b)	$\text{NaH}_2\text{PO}_4/\text{H}_3\text{PO}_4$ buffer	9
3.0	4.29	$\text{HBr}, \text{NaClO}_4$	8
3.5	4.07 ± 0.40	$\text{HClO}_4, \text{NaClO}_4$	this work

(a) stopped-flow results; (b) recalculated in this work.

Our results do not show any deviation from the first-order for bromide or bromate, in agreement with other authors¹⁻⁸. A closer examination of the data presented by Rábai *et al.*⁹ show that their results agree with this too. Surprisingly, Rábai *et al.* alleged that they observed a deviation from the first-order on bromide when the concentration of this ion was higher than 0.5 mol L^{-1} . For this reason they proposed a rate law (equation 3) that includes additional terms with second-order on bromide and first-order on H^+ , when compared with our rate law equation 2. To explain their rate law Rábai *et al.* proposed the following mechanism:



Indeed, their results present an order in $[\text{H}^+]$ in the range of 1.67 to 1.83. In this way, their results do not agree with the rate law of equation 3. Additionally, we were not able to reproduce their calculated results for the initial rate using their rate constants $k' = 4.37 \text{ L}^3 \text{ mol}^{-3} \text{ s}^{-1}$, $k'' = 0.014 \text{ L}^3 \text{ mol}^{-3} \text{ s}^{-1}$ and $k''' = 0.56 \text{ L}^4 \text{ mol}^{-4} \text{ s}^{-1}$. From their data we calculated rate constants equal to $k' = 17.9 \text{ L}^3 \text{ mol}^{-3} \text{ s}^{-1}$, $k'' = 0.019 \text{ L}^3 \text{ mol}^{-3} \text{ s}^{-1}$ and $k''' = 2.84 \times 10^{-4} \text{ L}^4 \text{ mol}^{-4} \text{ s}^{-1}$ that are quite different from their values, especially for k' and k''' .

On the other hand, we can state that our results support the mechanism represented by equations 4 to 6 that propose that H_2BrO_3^+ is the reactive species to Br^- . In addition, our results did not support the proposal of the existence of the intermediates HBr_2O_3^- and $\text{H}_2\text{Br}_2\text{O}_3$.

As can be seen in Table 4, our values for the fourth-order rate constant are in good agreement with the values obtained by most other authors, especially those of Domínguez and Iglesias⁸. At high I values our results show an increase in the rate constant with the increase of the ionic strength as has been observed by many authors, but not the very strong increase observed by Burgos *et al.*¹⁰. We are not able to explain the reason for this disagreement.

Based on the linear behavior shown in the Figure 1 for all sets of experimental data, we concluded that if there is some fast protonation equilibrium (equations 4 and 5) before the determining step, the pK_a of these acids cannot be in the $p[\text{H}]$ range investigated in this work ($-0.44 < p[\text{H}] < 2.3$). This result is in disagreement with the HBrO_3 pK_a values proposed by other authors (see Table 5).

A comparison of the known bromic acid pK_2 values (see Table 5) shows that they are very different from each other. We have no indication on how the pK_2 value of 0.7 found in the Pourbaix's Atlas¹⁷ was determined. The other pK_2 values of 1.87 and -0.292 were both determined by kinetic experiments and are depend on the proposed mechanism for the reaction. On the other hand, our kinetic results do not allow to determine the pK_2 value, but show that all other values in Table 5 are unacceptable. Unfortunately, all attempts we have made to follow this reaction at a still more acid medium did not give us reproducible results, showing that the reaction is too fast to be followed, even by stopped-flow technique.

Table 5. pK_a values for bromic acid.

pK_2	$T/^\circ\text{C}$	Ref.
0.70	-	17
1.87	27	18
-0.292	40	19

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