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Kinetics and Mechanism of Bromate–Bromide Reaction Catalyzed by Acetate

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The initial rate of the bromate–bromide reaction, $BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$, has been measured at constant ionic strength, $I = 3.0$ mol L^{-1}, and at several initial concentrations of acetate, bromate, bromide, and perchloric acid. The reaction was followed at the Br_2/Br_3^- isosbestic point ($\lambda = 446$ nm) by the stopped-flow technique. A very complex behavior was found such that the results could be fitted only by a six term rate law, $\nu = k_1[BrO_3^-][Br^-][H^+]^2 + k_2[BrO_3^-][Br^-]^2[H^+]^2 + k_3[BrO_3^-][H^+]^2[\text{acetate}]^2 + k_4[BrO_3^-][Br^-]^2[H^+]^2[\text{acetate}] + k_5[BrO_3^-][Br^-][H^+]^3[\text{acetate}]^2 + k_6[BrO_3^-][Br^-][H^+]^2[\text{acetate}]$, where $k_1 = 4.12$ L^3 mol^{-3} s^{-1}, $k_2 = 0.810$ L^4 mol^{-4} s^{-1}, $k_3 = 2.80 \times 10^3$ L^4 mol^{-4} s^{-1}, $k_4 = 278$ L^5 mol^{-5} s^{-1}, $k_5 = 5.45 \times 10^7$ L^6 mol^{-6} s^{-1}, and $k_6 = 850$ L^4 mol^{-4} s^{-1}. A mechanism, based on elementary steps, is proposed to explain each term of the rate law. This mechanism considers that when acetate binds to bromate it facilitates its second protonation.

Introduction

Aqueous bromine chemistry received a new impetus with the discovery of chemical oscillators.[1−6] Oscillating reactions that employ bromate, such as the Belousov−Zhabotinsky reaction and other reactions derived from this, require a deep comprehension of an intricate set of reactions involving several bromine oxyacids, oxyanions, and oxides.[7−10] The starting reaction for all proposed mechanisms is the bromate−bromide, reaction 1. In the FKN mechanism[7] and other mechanisms based on it, this reaction is proposed to proceed via formation of bromous and hypobromous acids as shown in reaction 2.

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \qquad (1)$$

$$BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + HOBr \qquad (2)$$

In the first study of reaction 1, Judson and Walker[11] found that it follows the fourth-order rate law, eq 3. This rate law

$$-d[BrO_3^-]/dt = k[BrO_3^-][Br^-][H^+]^2 \qquad (3)$$

has been confirmed by several authors.[12−22] In addition, the possibility for a fifth-order rate law at high bromide concentration arising from a second-order term in bromide was pointed out by Skrabal[15] and by Bray and Liebhafsky.[16] A higher order for bromide ion was also found by Rábai et

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al.,[23] who were the first to use visible spectroscopy to follow this reaction at the Br_2/Br_3^- isosbestic point. They measured the initial rate for a wide range of bromide concentration ($0.1 < [Br^-] < 2.0$ mol L^{-1}) at low concentrations of H^+ and bromate. To explain the observed behavior, especially at high $[Br^-]$, they proposed a rate law with three terms, as indicated by eq 4.

$$-d[BrO_3^-]/dt = k'[BrO_3^-][Br^-][H^+]^2 + k''[BrO_3^-][Br^-]^2[H^+] + k'''[BrO_3^-][Br^-]^2[H^+]^2 \quad (4)$$

In addition to these kinetic studies, only a few systems containing oxyhalogen compounds have been proved to be catalyzed by acetate ion. For oxyanions with halogen(V), only the reactions bromate−iodide[24] and iodate−iodide[25] have been observed to be catalyzed by acetate and follow the rate laws eqs 5 and 6, respectively, where B^- can be $CH_3CO_2^-$, $ClCH_2CH_2CO_2^-$, or $ClCH_2CO_2^-$.

$$-d[BrO_3^-]/dt = k_0[BrO_3^-][I^-][H^+]^2 + k_b[BrO_3^-][I^-][H^+]^2[B^-] \quad (5)$$

$$-d[IO_3^-]/dt = k_0[IO_3^-][I^-]^2[H^+]^2 + k_b[IO_3^-][I^-]^2[H^+]^2[B^-]/(1 + k'[I^-]) \quad (6)$$

More recently, the disproportionation of HOI has been shown to be catalyzed and suppressed by the acetic acid-acetate buffer.[26]

In this paper we present evidence for acetate catalysis on reaction 1 and we fit the experimental initial rate values to a six term rate law, showing that this catalytic effect is much more complex than it has been previously supposed.

Experimental Section

Analytical grade chemicals $NaBrO_3$ and sodium acetate (VETEC), acetic acid, $HClO_4$, and $NaClO_4$ (Merck), and NaBr (Grupo Química) were used without further purification. Water was obtained by a Milli-Q Plus purification system and had 18 MΩ resistivity.

Kinetics experiments were carried out by the stopped-flow technique performed by the use of the Hi-Tech dual mixing microvolume stopped-flow SF-61DX2. Temperature was maintained at 25.0 ± 0.1 °C by a circulating bath, and the ionic strength, I, was adjusted to 3.0 mol L^{-1} with $NaClO_4$ considering the concentrations of all ionic species present in the solution.

The reaction was followed at the isosbestic point of the mixture Br_2 and Br_3^- ($\lambda = 446$ nm, $\epsilon = 111$ L mol^{-1} cm^{-1}). The wavelength and the extinction coefficient for this isosbestic point were obtained by fitting a second degree polynomial to the experimental absorbance data for Br_2 and Br_3^- determined by Raphael[27] in 2 mol L^{-1} perchloric acid solution.

The initial rate of reaction, ν_0, was determined by fitting a second degree polynomial, $at^2 + bt + c$, to the curve of total bromine concentration versus time. The coefficient b is the initial rate. All experimental kinetic data presented here are averages of a minimum of five determinations.

At each total acetic acid−acetate buffer concentration, the free concentrations of H^+ and acetate ions were calculated on the basis of the acetic acid dissociation. The value of this constant, K_a, which is equal to 1.778×10^{-5} (pK_a = 4.750) at zero ionic strength (25 °C), was corrected to 1.124×10^{-5} (pK_a = 4.949) for $I = 3.0$ mol L^{-1}.[28]

Experiments using the highest acetate buffer concentration together with the highest bromate concentration employed in this work did not show any significative modification in the UV−vis spectra, up to 10 min. This ensures that if some reaction between bromate and the acetate buffer occurs, it is outside the time scale used in our bromate−bromide reaction, which was studied by the measurement of the initial velocity using the stopped-flow technique in a time scale maximum of 100 s.

Data treatment and curve fitting for kinetic data were carried out by using LOTUS 1-2-3.[29] The Solver facility of this program, found in other spreadsheets,[30] was employed to obtain some of the rate constants.

Results

The Supporting Information presents all the initial rate values determined for reaction 1 at 25 °C and $I = 3.0$ mol L^{-1}. This encompasses 44 sets of results, each one showing the effect of the variation of the concentration of only one species on the rate constant. Some experiments were carried out using an excess of bromide (see Supplemental Material 1, Supporting Information) and others using an excess of bromate (see Supplemental Material 2, Supporting Information). In Tables 1 and 2 we present a résumé of each set of results included in the Supporting Information.

Bromate Order. From the experiments to determine the effect of the variation of bromate concentration, in the presence of acetate and with an excess of bromide (first entry in Table 1), we obtained a very good linear plot of log $\nu_0 \times$ log $[BrO_3^-]_0$ ($R^2 = 0.9999$) with a slope equal to 1.000. This clearly points to a first-order term in bromate. Additionally it shows that the first-order term in bromate is not affected by the acetate concentration. When an excess of bromate is used either in the absence (first entry in Table 2) or in the presence of acetate (second entry in Table 2), the results still point to a first-order in bromate.

Bromide Order in the Absence of Acetate. The second entry in Table 1 is concerned with the variation of the initial rate with the variation in the bromide concentration in the absence of acetate. On the basis of eq 7, the plot of $\nu_0/[BrO_3^-]_0[H^+]_0^2[Br^-]_0 \times [Br^-]_0$ (see Figure 1) is linear ($R^2 = 0.993$) and indicates the rate law shown in eq 8, where k_1

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Table 1. Résumé of the Initial Rate Values for Reaction 1 Using an Excess of Bromide at $I = 3.0$ mol L^{-1} and $T = 25.0$ °C

effect of	$[BrO_3^-]_0$/M	$[Br^-]_0$/M	$[H^+]_0/10^{-3}$ M	$[\text{acetate}]_0/10^{-3}$ M	plot	slope (R^2)
BrO_3^-	0.100−0.250	2.50	0.372	29.3	log ν_0 × log $[BrO_3^-]$	1.000 ± 0.005 (0.9999)
Br^-	0.0200	0.100−2.50	118		eq 7	see text (0.993)
Br^-	0.0200	0.100−2.50	0.373	102	log ν_0 × log $[Br^-]$	0.80; 1.36[a]
Br^-	0.250	2.00−2.30	0.373	1.75	log ν_0 × log $[Br^-]$	2.0 ± 0.3 (0.96)
Br^-	0.250	2.00−2.30	0.373	2.34	log ν_0 × log $[Br^-]$	1.98 ± 0.10 (0.994)
Br^-	0.250	2.00−2.50	0.373	2.93	log ν_0 × log $[Br^-]$	1.95 ± 0.04 (0.999)
Br^-	0.250	2.00−2.50	0.373	14.9	log ν_0 × log $[Br^-]$	2.00 ± 0.02 (0.999)
Br^-	0.250	2.00−2.40	0.373	23.5	log ν_0 × log $[Br^-]$	2.01 ± 0.07 (0.997)
Br^-	0.250	2.00−2.50	0.373	29.3	log ν_0 × log $[Br^-]$	1.79 ± 0.01 (0.9998)
Br^-	0.250	2.00−2.50	0.373	44.1	log ν_0 × log $[Br^-]$	1.67 ± 0.01 (0.9999)
Br^-	0.250	2.00−2.30	0.373	58.5	log ν_0 × log $[Br^-]$	1.62 ± 0.01 (0.9998)
Br^-	0.250	2.00−2.30	0.373	73.1	log ν_0 × log $[Br^-]$	1.57 ± 0.04 (0.999)
Br^-	0.250	2.00−2.30	0.373	102	log ν_0 × log $[Br^-]$	1.553 ± 0.005 (0.99998)
acetate	0.250	0.500	0.373	1.75−102	log ν_0 × log [acetate]	0.61; 1.79[b]
acetate	0.250	2.00	0.373	2.34−102	log ν_0 × log [acetate]	0.63; 1.67[b]
acetate	0.250	2.10	0.373	1.75−102	log ν_0 × log [acetate]	0.55; 1.66[b]
acetate	0.250	2.20	0.373	1.75−102	log ν_0 × log [acetate]	0.59; 1.64[b]
acetate	0.250	2.30	0.373	1.75−102	log ν_0 × log [acetate]	0.54; 1.63[b]
acetate	0.250	2.50	0.373	1.75−102	log ν_0 × log [acetate]	0.56; 1.61[b]
H^+	0.250	2.50	0.175−0.405	27.0	log ν_0 × log $[H^+]$	2.16 ± 0.02 (0.9998)
H^+	0.250	2.50	0.103−0.182	44.2	log ν_0 × log $[H^+]$	2.04 ± 0.04 (0.999)
H^+	0.250	2.50	0.724−0.131	60.1	log ν_0 × log $[H^+]$	2.03 ± 0.06 (0.998)
H^+	0.250	2.50	0.560−0.103	74.8	log ν_0 × log $[H^+]$	1.98 ± 0.05 (0.999)

[a] Slope for the four lowest bromide concentration data points; slope for the four highest bromide concentration data points. [b] Slope for the four lowest acetate concentration data points; slope for the four highest acetate concentration data points.

Table 2. Résumé of the Initial Rate Values for Reaction 1 Using an Excess of Bromate at $I = 3.0$ mol L^{-1} and $T = 25.0$ °C

effect of	$[BrO_3^-]_0$/M	$[Br^-]_0/10^{-2}$ M	$[H^+]_0/10^{-2}$ M	$[\text{acetate}]_0/10^{-3}$ M	plot	slope (R^2)
BrO_3^-	0.00100−0.00500	0.200	107		log ν_0 × log $[BrO_3^-]$	0.98 ± 0.01 (0.9993)
BrO_3^-	0.800−1.00	70.0	0.0373	87.7	log ν_0 × log $[BrO_3^-]$	1.12 ± 0.02 (0.9995)
Br^-	0.0100	0.100−0.500	107		log ν_0 × log $[Br^-]$	0.97 ± 0.02 (0.9992)
Br^-	1.00	3.00−9.00	0.0373	2.34	log ν_0 × log $[Br^-]$	0.91 ± 0.008 (0.9998)
Br^-	1.00	1.00−9.00	0.0373	2.92	log ν_0 × log $[Br^-]$	0.86 ± 0.02 (0.999)
Br^-	1.00	3.00−9.00	0.0373	14.6	log ν_0 × log $[Br^-]$	0.62 ± 0.04 (0.993)
Br^-	1.00	1.00−9.00	0.0373	23.4	log ν_0 × log $[Br^-]$	0.54 ± 0.01 (0.998)
Br^-	1.00	3.00−9.00	0.0373	29.2	log ν_0 × log $[Br^-]$	0.50 ± 0.02 (0.998)
Br^-	1.00	1.00−9.00	0.0373	43.9	log ν_0 × log $[Br^-]$	0.48 ± 0.009 (0.9990)
Br^-	1.00	1.00−9.00	0.0373	58.5	log ν_0 × log $[Br^-]$	0.44 ± 0.005 (0.9996)
Br^-	1.00	3.00−9.00	0.0373	73.1	log ν_0 × log $[Br^-]$	0.43 ± 0.02 (0.996)
Br^-	1.00	1.00−9.00	0.0373	87.7	log ν_0 × log $[Br^-]$	0.43 ± 0.007 (0.9993)
acetate	1.00	1.00	0.0373	2.34−87.7	log ν_0 × log [acetate]	1.16; 1.86[a]
acetate	1.00	3.00	0.0373	2.34−87.7	log ν_0 × log [acetate]	0.98; 1.84[a]
acetate	1.00	5.00	0.0373	2.34−87.7	log ν_0 × log [acetate]	0.89; 1.77[a]
acetate	1.00	7.00	0.0373	2.34−87.7	log ν_0 × log [acetate]	0.84; 1.81[a]
acetate	1.00	9.00	0.0373	2.34−87.7	log ν_0 × log [acetate]	0.81; 1.78[a]
acetate	1.00	10.0	0.0373	2.34−87.7	log ν_0 × log [acetate]	0.67; 1.89[a]
H^+	0.100	0.100	10.0−50.0		log ν_0 × log $[H^+]$	1.99 ± 0.05 (0.998)
H^+	1.00	10.0	0.0175−0.0304	27.1	log ν_0 × log $[H^+]$	2.26 ± 0.03 (0.9997)
H^+	1.00	10.0	0.00560−0.0139	74.9	log ν_0 × log $[H^+]$	2.12 ± 0.08 (0.996)

[a] Slope for the four lowest acetate concentration data points; slope for the four highest acetate concentration data points.

$= 4.12 \pm 0.05$ L^3 mol^{-3} s^{-1} and $k_2 = 0.810 \pm 0.02$ L^4 mol^{-4} s^{-1}. This rate law had been anticipated by Bray and Liebhafsky[16] and shows some agreement with the rate law proposed by Rábai et al.,[23] eq 4, where $k' = 4.37$ L^3 mol^{-3} s^{-1}, $k'' = 1.4 \times 10^{-2}$ L^3 mol^{-3} s^{-1}, and $k''' = 0.56$ L^4 mol^{-4} s^{-1} at the same $I = 3$ mol L^{-1}. As can be seen, there is no necessity to include a first-order term in H^+ as included in eq 4 by Rábai et al.[23] (These authors considered this term to be the more important at low H^+ and high bromide concentrations.) Otherwise, the last term in eq 8 is imperative, differently from what we have found at much lower bromide concentration.[22] It should be noticed that λ and ϵ used by Rábai et al.[23] are significantly different from our values. As expected, at low bromide concentrations, the last term in eq 8 is not important, as can be seen from the bromide order close to 1 (see entry 3 in Table 2). A comparison of the k_1 values is presented in Table 3.

$$\frac{\nu}{[BrO_3^-][H^+]^2[Br^-]} = k_1 + k_2[Br^-] \qquad (7)$$

$$\nu = k_1[BrO_3^-][Br^-][H^+]^2 + k_2[BrO_3^-][Br^-]^2[H^+]^2 \qquad (8)$$

Bromide Order in the Presence of Acetate. Entries 3 to 13 in Table 1 show that the bromide order changes in the presence of acetate. Data from experiments using a wide range of bromide concentrations produced a nonlinear graph of log ν_0 × log $[Br^-]_0$. As indicated by entry 3 in Table 1, the data for low bromide concentrations indicate a bromide order of 0.80 and the data for high bromide concentration indicate a bromide order of 1.36. This suggests that, in the

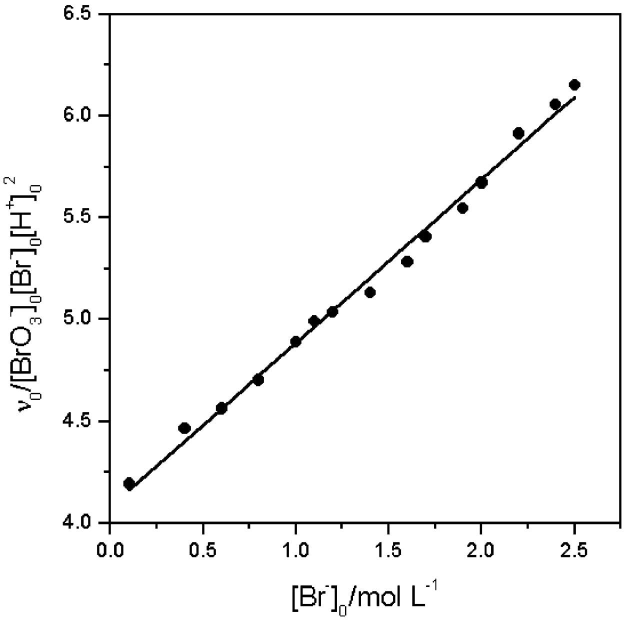

Figure 1. Linear fit of eq 7 to the 15 experimental data corresponding to the second entry of Table 1.

Table 3. Selected k_1 Values at High Ionic Strength (T = 25.0 °C)

I/M	k_1/M^{-3} s^{-1}	main electrolytes	ref
3.0	38.7	$NaClO_4$	21
3.0	4.37	buffer NaH_2PO_4/H_3PO_4	23
3.0	17.9[a]	buffer NaH_2PO_4/H_3PO_4	23
3.0	4.29	HBr, $NaClO_4$	20
3.0	4.12	$HClO_4$, $NaClO_4$	this work
3.5	4.07 ± 0.40	$HClO_4$, $NaClO_4$	22

[a] Recalculated in ref 22.

presence of acetate, the bromide order depends on its concentration, as it was also noticed in the absence of acetate (see eq 8).

Data from entries 4 to 13 in Table 1 present evidence that acetate, as well bromide, is implicated in the modification of the bromide order. At low acetate concentrations, the bromide order is close to 2 (entries 4 to 8 in Table 1), but as the acetate concentration is increased, this order decreases to values as low as 1.5 (entries 9 to 13 in Table 1). Otherwise, in the presence of an excess of bromate (see entries 3 to 12 in Table 2), the bromide order decreases from 1 to 0.4, as the acetate concentration is increased, showing that at low bromide concentrations even small acetate concentration affect the bromide order (see Figure 2).

Acetate Order. The results in entries 14 to 19 in Table 1 show that acetate order changes significantly with concentration. Plotting log ν_0 × log [acetate]$_0$ does not give a straight line, independent of which bromide concentration is employed. Linear fits using only the four lowest acetate concentration data points gave slopes close to 0.6 for all bromide concentrations (see Table 1). Using only the four highest acetate concentration data points, a linear fit gave slopes from 1.79 ($[Br^-]_0 = 0.500$ mol L^{-1}) to 1.61 ($[Br^-]_0 = 2.50$ mol L^{-1}). A similar finding was obtained with the data obtained using bromate in excess, as can be seen in Table 2 (entries 13 to 18). In this case, the slopes calculated using only data from the four lowest acetate concentrations range from 1.16 ($[Br^-]_0 = 0.01$ mol L^{-1}) to 0.67 ($[Br^-]_0 = 0.1$ mol L^{-1}). Using data from the four highest acetate concentrations, the slopes were close to 1.8 for all bromide concentrations.

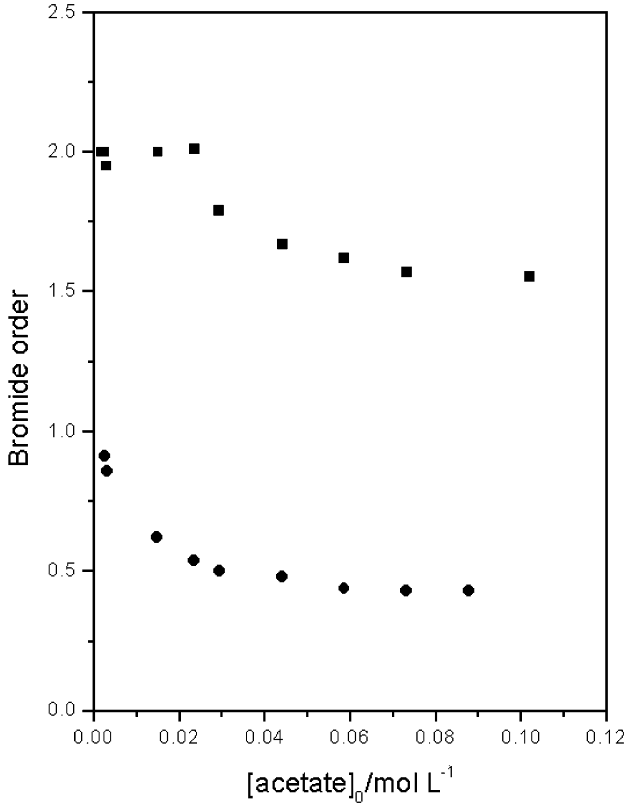

Figure 2. Bromide order as a function of the acetate concentration: (■) data obtained using bromide in excess (see Table 1); (●) data obtained using bromate in excess (see Table 2).

A plot of ν_0 × [acetate]$_0^2$ gave a very good rectilinear graph (see entries 14 to 19 in Table 1 and Figure 3; see entries 13 to 18 in Table 2 and Figure 4). Despite this, it was not possible to obtain a unique value for a rate constant based on a simple rate law such as eq 9, where a and b are integers ranging from 1 to 3. The best result was obtained using $a = 1$ and $b = 3$, which give values for k in the range of 8.3 × 10^7 L^6 mol^{-6} s^{-1} to 5.6 × 10^8 L^6 mol^{-6} s^{-1}.

$$\nu = k[BrO_3^-][Br^-]^a[H^+]^b[\text{acetate}]^2 \qquad (9)$$

H$^+$ Order. The last four entries in Table 1 show that the H$^+$ order is close to 2 for experiments using an excess of bromide in the presence of acetate. At the lowest acetate concentration employed we found an order slightly greater than 2. When bromate is used in excess, the H$^+$ order is still close to 2, and again, the values show a tendency to be slightly higher than this, as can be seen in the last two entries of Table 2.

Overall Rate Law. As also proposed by Barton and Wright, from a study of the catalysis in bromate−iodide[24] and iodate−iodide[25] reactions, the results above suggest a rate law containing terms additional to those in eq 8. These additional terms should contain acetate, bromide, and H$^+$ in varying orders (as well as the first-order bromate) in such a way as to fit all experimental results. Due to the complexity

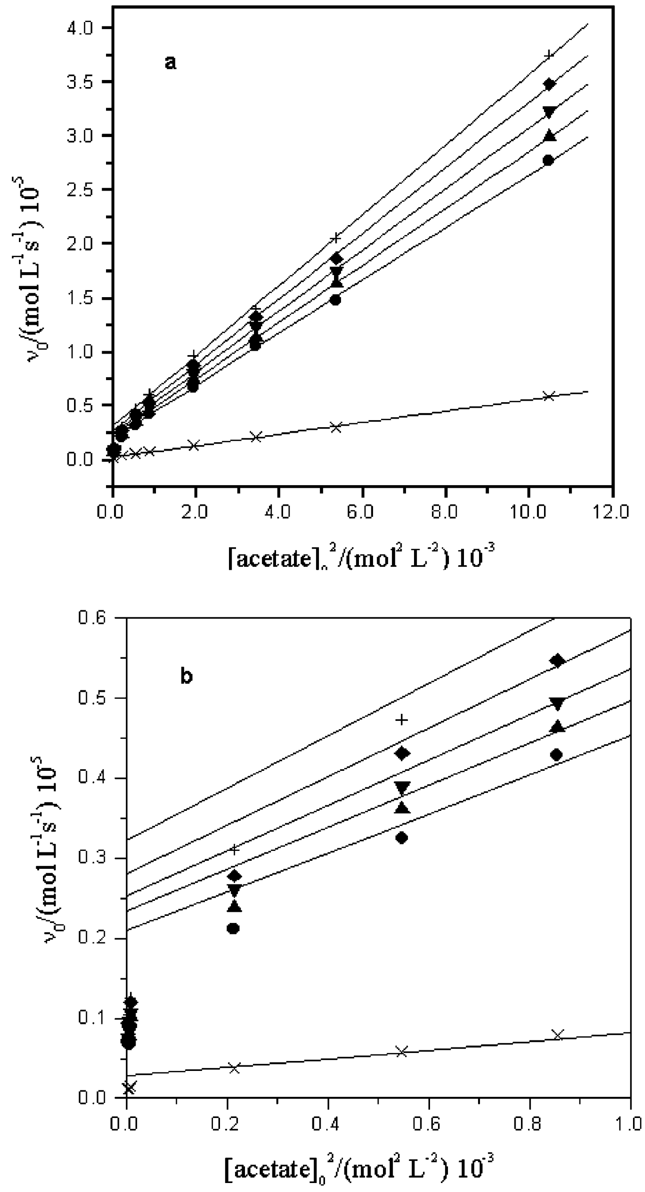

Figure 3. Acetate second-order evidence at several bromide concentrations in bromide excess at 25 ± 0.1 °C: $[BrO_3^-]_0 = 2.50 \times 10^{-1}$ mol L^{-1}, $[H^+]_0 = 3.73 \times 10^{-4}$ mol L^{-1}, $1.75 \times 10^{-3} < [\text{acetate}]_0 < 0.102$ mol L^{-1}; (×) $[Br^-]_0 = 0.500$ mol L^{-1}, (●) $[Br^-]_0 = 2.00$ mol L^{-1}; (▲) $[Br^-]_0 = 2.10$ mol L^{-1}, (▼) $[Br^-]_0 = 2.20$ mol L^{-1}, (◆) $[Br^-]_0 = 2.30$ mol L^{-1}, (+) $[Br^-]_0 = 2.50$ mol L^{-1}, $I = 3.0$ mol L^{-1} (entries 14 to 19 in Table 1); (a) full set of data; (b) [acetate] ≤1.00 mol L^{-1}. Straight lines are the linear fit to each data set.

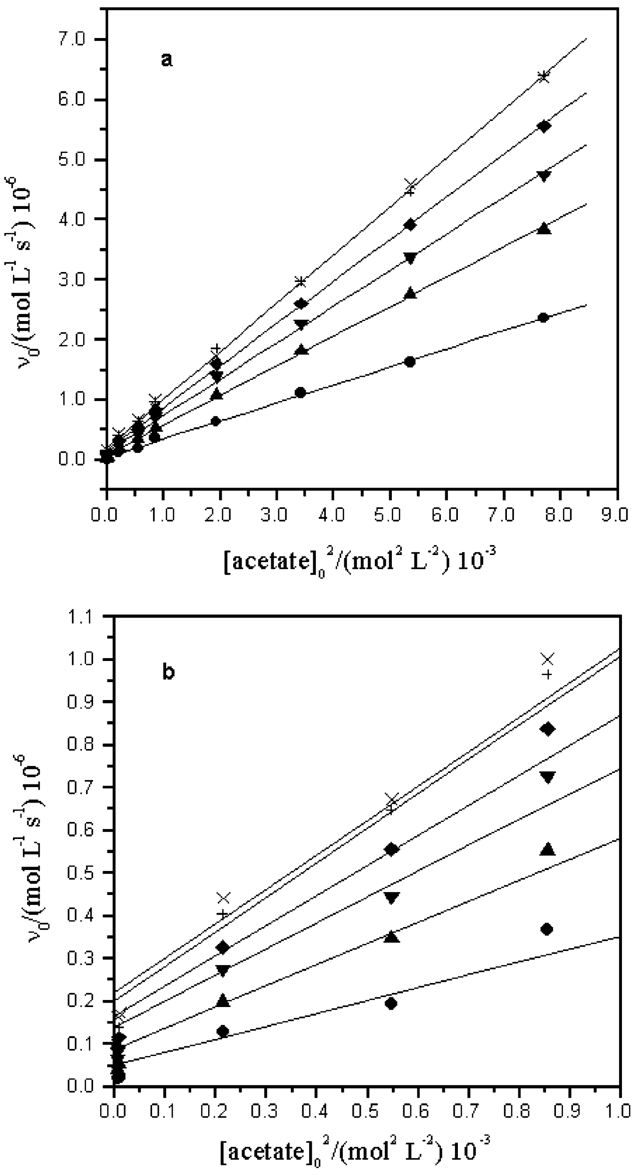

Figure 4. Acetate second-order evidence at several bromide concentrations in bromate excess at 25 ± 0.1 °C: $[BrO_3^-]_0 = 1.00$ mol L^{-1}, $[H^+]_0 = 3.73 \times 10^{-4}$ mol L^{-1}, $2.34 \times 10^{-3} < [\text{acetate}]_0 < 8.77 \times 10^{-2}$ mol L^{-1}; (●) $[Br^-]_0 = 0.0100$ mol L^{-1}; (▲) $[Br^-]_0 = 0.0300$ mol L^{-1}, (▼) $[Br^-]_0 = 0.0500$ mol L^{-1}, (◆) $[Br^-]_0 = 0.0700$ mol L^{-1}, (+) $[Br^-]_0 = 0.0900$ mol L^{-1}, (×) $[Br^-]_0 = 0.100$ mol L^{-1}, $I = 3.0$ mol L^{-1} (entries 13 to 18 in Table 2); (a) full set of data; (b) [acetate] ≤ 1.00 mol L^{-1}. Straight lines are the linear fit to each data set.

of the experimental results, it was not possible to determine these additional rate constant values using a conventional kinetic data treatment, and so we used the SOLVER add-in facility of the Lotus 1-2-3 spreadsheet.

As a demonstration of the SOLVER capability, it was employed to estimate the rate constant values for k_1 and k_2. In doing this, only initial rate values for the experiments without acetate were fed to SOLVER, and the results obtained for k_1 and k_2 were 3.96 L^3 mol^{-3} s^{-1} and 0.87 L^4 mol^{-4} s^{-1}, respectively. These values showed a good agreement with the values determinated by eq 8, revealing the capability of the SOLVER in the rate constant estimation.

To find out the global rate law we have considered the inclusion of several terms containing almost all possible combinations in orders for bromide, acetate, and H$^+$. The starting point was eq 8, and for all attempts we did not change the values of the rate constants k_1 and k_2 determined by fitting eq 7 to the experimental data. After many attempts (see Supplemental Material 3, Supporting Information), a good fit was found using eq 10, where $k_1 = 4.12$ L^3 mol^{-3} s^{-1}, $k_2 = 0.810$ L^4 mol^{-4} s^{-1}, $k_3 = 2.80 \times 10^3$ L^4 mol^{-4} s^{-1}, $k_4 = 278$ L^5 mol^{-5} s^{-1}, $k_5 = 5.45 \times 10^7$ L^6 mol^{-6} s^{-1}, and $k_6 = 850$ L^4 mol^{-4} s^{-1}. A comparison of the calculated initial rate obtained by the use of eq 10 and the experimental values is presented in the Supporting Information (Supplemental Material 1 and 2).

Many other terms should be included to improve the agreement between calculated and experimental data points.

$$\nu = k_1[\mathrm{BrO_3^-}][\mathrm{Br^-}][\mathrm{H^+}]^2 + k_2[\mathrm{BrO_3^-}][\mathrm{Br^-}]^2[\mathrm{H^+}]^2 + k_3[\mathrm{BrO_3^-}][\mathrm{H^+}]^2[\text{acetate}]^2 + k_4[\mathrm{BrO_3^-}][\mathrm{Br^-}]^2[\mathrm{H^+}]^2[\text{acetate}] + k_5[\mathrm{BrO_3^-}][\mathrm{Br^-}][\mathrm{H^+}]^3[\text{acetate}]^2 + k_6[\mathrm{BrO_3^-}][\mathrm{Br^-}][\mathrm{H^+}]^2[\text{acetate}] \quad (10)$$

This rate law is a result of trying to keep a limited number of terms. The rate constants obtained for the terms including acetate (last four terms) have values that are a compromise for a best fit to both data sets (excess of bromide and excess of bromate). If any of these rate constants are changed in order to improve the agreement with one data set, the agreement with the other is reduced. For the data sets obtained with an excess of bromide and an excess of bromate the average errors are 8.5% and 12.3%, respectively.

Discussion

Based on Barton and Wright's results[24] for the bromate−iodide reaction catalyzed by acetate, eq 5, this complex rate law, eq 10, was unexpected, indicating that the catalytic behaviors of acetate in the bromate−iodide and bromate−bromide reactions are very different. A rate law presenting a similar complexity, with five terms, was obtained by Sigalla[31] for the bromate reactions in a medium containing bromide and chloride. Thus, it is reasonable to suppose that the complexity of the rate law obtained by us is a special feature of the aqueous solution chemistry of bromine.

The first two terms in eq 10 have been demonstrated by the results obtained in the absence of acetate, and the values for k_1 and k_2 were determined (see Figure 1) from eq 8. The terms involving the participation of acetate and the rate constants k_3, k_4, k_5, and k_6, which were estimated by SOLVER, find support in the experimental observations. First-order bromate was confirmed for all the experimental conditions used (see Table 1 entry 1 and Table 2 entries 1 and 2).

Figure 2 (■) shows that, in the presence of acetate and with an excess of bromide, the order of bromide remains approximately 2 for concentrations of acetate lower than 23.4 × 10^{-3} mol $\mathrm{L^{-1}}$. At concentration values higher than this, the bromide order decreases to a value between 1 and 2 (approximately 1.5), indicating the possibility of the existence of first- and second-order terms for bromide, and thus the terms containing k_4, k_5, and k_6 in eq 10. When an excess of bromate was used (Figure 2 (●)), it was observed that, when the acetate concentration increases, the bromide order decreases quickly, tending to a value between 1 and 0 (approximately 0.4), indicating the presence of both first- and zero-order terms in bromide and hence the incorporation of a term without bromide, as can be seen in the term containing k_3 in the rate law (see eq 10).

Figure 3a shows that, with an excess of bromide, and for acetate concentrations higher than 23.4 × 10^{-3} mol $\mathrm{L^{-1}}$, there are second-order terms in acetate ion (rate constants k_3 and k_5 in eq 10). At lower acetate concentrations, these second-order terms are negligible, as shown in Figure 3b. The fit of eq 10 to the experimental data indicates that acetate can present a first-order behavior (term containing k_4 in eq 10). Figure 4a shows that, in an excess of bromate, for all acetate concentrations used, the acetate presents a second-order behavior with rate constants k_3 and k_5 in eq 10. In addition, the k_5 term in eq 10 is identical to eq 9 and the value obtained for k_5 in eq 10 has the same order of magnitude as the k value found fitting eq 9.

Second-order in $\mathrm{H^+}$ was also verified in most experiments. However, orders slightly higher than 2 were found using an excess of bromate (Table 2, last two entries), indicating the possibility of a third-order for this ion, and the inclusion of k_5 term in the rate law (eq 10). This term also appeared when eq 9 was fitted to the results obtained on changing the acetate concentration.

Mechanism for the Terms without Acetate. In the rate law given by eq 10, each term corresponds to a different pathway and rate determining step. In trying to build a mechanism for each term, we considered several possibilities before we arrived at the set of elementary steps presented below.

For the first and second terms of eq 10, which describe the reaction in the absence of acetate, let us start with the following steps, based on the proposition made by Rábai et al.[23]

$$\mathrm{BrO_3^-} + \mathrm{H^+} \underset{}{\overset{K_1}{\rightleftarrows}} \mathrm{HBrO_3} \quad (11)$$

$$\mathrm{HBrO_3} + \mathrm{H^+} \overset{K_2}{\rightleftarrows} \mathrm{H_2BrO_3^+} \quad (12)$$

$$\mathrm{H_2BrO_3^+} + \mathrm{Br^-} \xrightarrow{k'} \text{products} \quad (13)$$

$$\mathrm{H_2BrO_3^+} + \mathrm{Br^-} \overset{K_3}{\rightleftarrows} \mathrm{H_2Br_2O_3} \quad (14)$$

$$\mathrm{H_2Br_2O_3} + \mathrm{Br^-} \xrightarrow{k'''} \text{products} \quad (15)$$

One point worth mentioning is the fact that the reactants in both reactions 13 and 14 are the same but in one case (reaction 13) they react to form product in a slow step and in the other case (reaction 14) they react to form an intermediate species. In addition, on the basis of the very low stability of bromate in strong acid solutions,[32,33] the $\mathrm{H_2BrO_3^+}$ species should not be considered as a stable intermediate. As $\mathrm{HBrO_3}$ is a very strong acid,[33] so the $\mathrm{H_2BrO_3^+}$ species should not be formed at the acid concentrations used to study the bromate−bromide reaction.

Instead, we propose that bromide should be bound to the bromine atom of the bromate assisting the entrance of the $\mathrm{H^+}$ (avoiding the formation of the bromic acid, $\mathrm{HBrO_3}$, or $\mathrm{H_2BrO_3^+}$). In this way, the mechanism goes through other intermediates until $\mathrm{H_2Br_2O_3}$ is formed which suffers a rearrangement to the products, as can be seen in the reactions 16 to 21 written using Lewis structures.[34]

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[32] Fonteyne, R. *Natuurwet. Tijdschr. (Ghent)* **1939**, *21*, 141−144.

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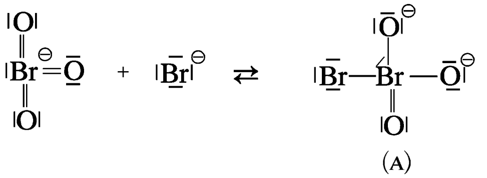

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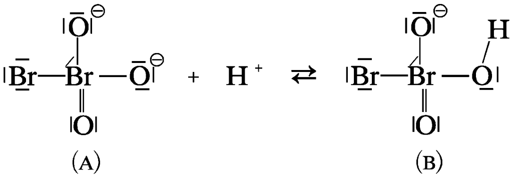
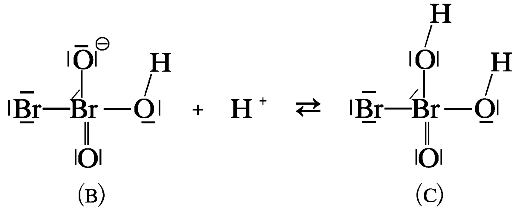


(17)



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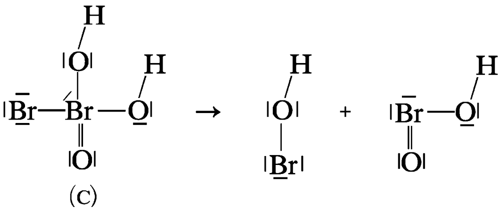


(19)

This mechanism should be contrasted with the mechanism proposed by Agreda B. et al.[35] for the Dushman reaction which goes through $H_2IO_3^+$ and $H_2I_2O_3$ species. Iodic acid is not as strong as bromic acid, and thus the supposition for the formation of the $H_2IO_3^+$ species is reasonable in the Dushman reaction. Otherwise, the Dushman reaction presents only a second-order behavior for the iodide, which suggests that the mechanism for the bromate−bromide reaction should not be the same which is in agreement with our proposal.

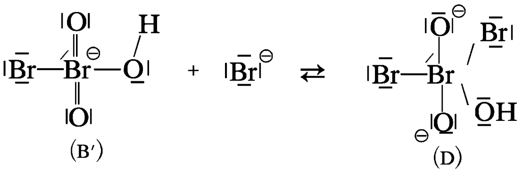
The HOBr formed in reaction 19 will react rapidly with bromide,[36] forming bromine by the very well-known reaction 20.

$$\mathrm{HOBr} + \mathrm{Br}^- + \mathrm{H}^+ \rightarrow \mathrm{Br}_2 + \mathrm{H}_2\mathrm{O} \qquad (20)$$

The $HBrO_2$, formed in reaction 19, will also react rapidly with bromide,[10] forming HOBr (reaction 21).

$$\mathrm{HBrO}_2 + \mathrm{Br}^- + \mathrm{H}^+ \rightarrow 2\mathrm{HOBr} \qquad (21)$$

We propose that bromide attack on bromate is the first step because bromate should be a very weak base and should not attract the H^+ efficiently. Only the A species, which has a double negative charge, should be able to easily attract two H^+ to form the C species, which must be unstable and decomposes to HOBr and $HBrO_2$. Although Lewis structures are not the best way to describe accurately electronic structures, we tried to show with these that the negative charge is hidden inside the bromate ion, making difficult the H^+ attack. In species A, the two negative charges should avoid each other, and because of this we have drawn them in the oxygens. The B species can be represented with the negative charge on the isolated oxygens (which can be represented by two resonant structures) or with the negative charge on the central bromine (which we call BN). In the sequence of steps which represent the mechanism for the second term in eq 10 (reactions 16, 17, 22, and 23), we decided to use BN to emphasize the idea that each bromide, which is added to bromate, contributes to expose the negative charges on the oxygens which thereby attract H^+.



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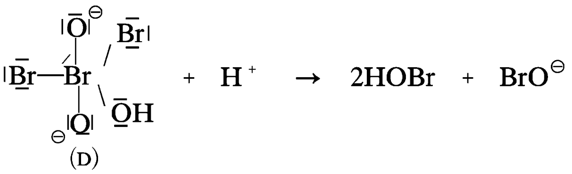

(23)

The way we have written reaction 23 is only one of the possibilities. Similarly, reactions 18 and 19 can be replaced by a single reaction in which species B reacts with H^+ and produces HOBr and HOBrO directly, avoiding the intermediate C. In the same way, another possibility for reaction 23 is the formation of intermediate $H_2Br_3O_3^-$, which would decompose to the same products as in reaction 23. There is no way of distinguishing kinetically these possibilities. Again, our mechanism for the k_2 term in eq 10 (reactions 16, 17, 22, and 23), which considers that bromide attack precedes H^+ attack, is in opposition to that proposed by Agreda et al.[35] for the Dushman reaction, under the second-order halide conditions.

Our proposal for the k_1 and k_2 terms of eq 10 disagree with the mechanism proposed by Rábai et al.[23] too. These authors consider that H^+ attack to bromate, forming $HBrO_3$ and $H_2BrO_3^+$ intermediates, precedes bromide attack. However, their mechanism considers the formation of the same C species which rearranges to products, accounting for their k' term in eq 4 (this accounting the same as the k_1 in eq 10). A similar C species is present in the Agreda et al.[35] mechanism too, with iodine atoms in the place of bromine atoms, but however here it does not rearrange to products. In addition, our mechanism does not consider the participation of the intermediate $BrBrO_2$, which can be considered as a particular case of a general species XYO_2, proposed by many authors[37] in the mechanisms for reactions involving oxyacids or oxyanions of Cl, Br, and I. It does not mean that these species should not exist but only that in our mechanism the $BrBrO_2$ does not play an important role.

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Another point we must consider is the possibility that bromate, after two protonations, loses water and forms the BrO_2^+ species as has been considered by other authors.[19,31] However, this possibility has been ruled out by the results[38,39] on the rate of exchange of isotopic oxygen between the oxy-anions XO_3^- ($X = Cl, Br$) and water as these rates are significantly lower than the reactions of these oxy-anions with X^- ($X = Cl, Br, I$).

Mechanism for Acetate Catalysis. Our proposal for the elementary steps, that accounts for the terms of eq 10 involving the acetate catalysis, follows Barton and Wright[24,25] ideas. In the formulation of the mechanism for each one of the last four terms in eq 10, we have considered that the global reaction, reaction 1, occurs at much lower $[H^+]$ when in the presence of acetate. This suggests that acetate binds to bromate and, in the same fashion as the bromide, it makes easier the protonation of the bromate. After the binding of the bromide, the coordination anion or nonmetal complex rearranges to form the products in the rate determining step. For the terms containing k_4, k_5, and k_6 in eq 10 we propose the following.

$$BrO_3^- + 2Br^- + AcO^- + 2H^+ \rightleftarrows [Br(Br)_2(AcO)(OH)_2O]^{2-} \rightarrow 2HOBr + AcO^- + BrO^- \quad (24)$$

$$BrO_3^- + Br^- + 2AcO^- + 3H^+ \rightleftarrows [Br(Br)(AcO)_2(OH)_3]^- \rightarrow HOBr + 2AcO^- + HBrO_2 + H^+ \quad (25)$$

$$BrO_3^- + Br^- + AcO^- + 2H^+ \rightleftarrows [Br(Br)(AcO)(OH)_2O]^- \rightarrow HOBr + AcO^- + HBrO_2 \quad (26)$$

The formation of intermediates with two acetate bonded to a halogen atom species is not new. One such intermediate has been proposed previously[26] in a mechanism for acetate catalysis in the hypoiodous acid disproportionation reaction.

Again, it is not possible to ensure that the nonmetal complex decomposition is the rate determining step or if it is the last H^+ attack that determines the rate of the reaction. However, from reactions 24 to 26, it appears that bromate may form several different nonmetal complexes with different numbers of bromide, acetate, and OH groups. Our kinetic analysis allowed us to suggest only some of the more important of them.

For the k_3 term in eq 10 we must consider a different route because it is a term independent of the bromide concentration. One of the possibilities, which we consider the most probable, is the formation of the peroxyacetic acid. It means that the rearrangement of the nonmetal complex will bind the OH group with the acetate group in the same way it binds to the bromide to form HOBr in reactions 24 to 26. The peroxyacetic acid should then react with bromide in a fast reaction to form HOBr as shown by reactions 27 and 28.

$$BrO_3^- + 2AcO^- + 2H^+ \rightleftarrows [Br(AcO)_2(OH)_2O]^- \rightarrow BrO^- + 2AcOOH \quad (27)$$

$$AcOOH + Br^- \rightarrow AcO^- + HOBr \quad (28)$$

Until now we do not have any evidence for the formation of the peroxyacetate in this reaction. However, from our kinetic analysis we noticed that the k_3 term is very important for the data obtained with low bromide concentration, but can it be discarded for the data with an excess of this ion.

Comparison of our mechanism (reactions 16 to 28) with the schemes proposed by Barton and Wright[24,25] to explain the acetate catalysis on the bromate−iodide and iodate−iodide reactions shows that our proposal is a step further since we state that protonation of bromate is not the first step in the presence or absence of acetate.

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Supporting Information Available: Tables containing additional rate data. This material is available free of charge via the Internet at http://pubs.acs.org.

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