Oxidation of Bromide by Tert-Butyl Hypochlorite

CRISTINA PASTORIZA, JUAN MANUEL ANTELO, JUAN CRUGEIRAS

Departamento de Química Física, Facultad de Química, Universidad de Santiago de Compostela, 15782 La Coruña, Spain

Received 24 October 2012; revised 16 April 2013; accepted 20 April 2013

DOI 10.1002/kin.20799

ABSTRACT: The kinetics of the oxidation reaction of bromide by tert-butyl hypochlorite (^{t}BuOCl) was studied at 25°C, ionic strength 0.5 M, and under isolation conditions. A stopped-flow spectrophotometer was employed for monitoring the reactions. Kinetic studies show that the reaction is first order with respect to $[Br^-]$ and $[^t\text{BuOCl}]$. Linear dependences of the proton concentration, in perchloric acid medium, and the buffer solution concentration were found on the rate constant. The activation parameters were calculated using the Arrhenius and Eyring equations from the kinetic studies performed to analyze the influence of temperature on the rate constant. The results are consistent with a reaction mechanism of general acid catalysis. The catalytic constants were obtained for the oxidation of bromide by tert-butyl hypochlorite. The slope obtained for the Brönsted relationship was 0.36. © 2013 Wiley Periodicals, Inc. Int J Chem Kinet 45: 629–637, 2013

INTRODUCTION

The chlorinating agents that have an atom of Cl^+ are important molecules because they have a high bactericidal capacity, so they are often used as agents for the disinfection of drinking water [1–3]. However, their use in water treatment can cause problems when other chemical compounds are present, since these compounds are usually highly reactive and have a high capacity as oxidants [4–8]. The halides are an example of compounds that can be easily oxidized by chlorinating agents, especially in acid medium [9–14]. Some of these reactions involving halides can be used to assess the amount of the chlorinating agent, but above all they must be taken into account because the presence of easily oxidizable species contributes to decrease the Cl^+ amount existing in the medium. This may be an inconvenience during disinfection processes [1,15].

This paper summarizes the kinetic results obtained in the study of the reaction of Br^- ions with tert-butyl hypochlorite (^{t}BuOCl) in acid medium. The reaction was carried out using an excess of the Br^- concentration, at least 30 times higher than the ^{t}BuOCl concentration. In these conditions, the reaction that takes place is presented in Scheme 1.

To obtain kinetic information about the reaction process and to discuss a possible reaction mechanism, a set of experiments were designed. These experiments allowed us to determine the reaction order with respect to each one of the reagent concentrations and the influence of the concentrations of Br^- and that of protons. Also, the influence of ionic strength and temperature was studied as well as the possible catalytic processes when different buffer solutions were used to control the proton concentrations.

EXPERIMENTAL

Reagents

^{t}BuOCl was obtained by passing a stream of chlorine through a solution of NaOH, tert-butanol, and

---

Correspondence to: C. Pastoriza; e-mail: cinecris@gmail.com.

Supporting Information is available in the online issue at www.wileyonlinelibrary.com.

Scheme 1

water [16,17]. The product obtained was purified by distillation and stored at 0°C in a topaz flask to avoid the decomposition by action of light. Its concentration was determined iodometrically, and its purity was close to 100%. The solution used in the kinetic experiments was prepared every day, from ^{t}BuOCl synthesized in the laboratory, using acetonitrile as a solvent.

Aqueous solutions of NaBr, $HClO_4$, and $NaClO_4$ were prepared using Aldrich commercial products, A.C.S. reagent. Several buffer solutions, prepared with Aldrich commercial products, A.C.S. reagent, were used to control medium pH: $H_3PO_4/H_2PO_4^-$, $Cl_2CHCOOH/Cl_2CHCOO^-$, $ClCH_2COOH/ClCH_2COO^-$, CH_3COOH/CH_3COO^-, and CH_3OCOOH/CH_3OCOO^-.

Instrumental

A spectrophotometer (Varian Cary 1 Bio) was used for the previous studies. It was supplied with a thermostated cell holder and was equipped with quartz cells with 1-cm path length and a capacity of 3 cm^3. A stopped-flow spectrophotometer (Applied Photophysics DX.17MV) was used for monitoring of the kinetics of the reactions. A system of mixed asymmetric (1:25) was used with the purpose of minimizing the solvent effect. The thermostate was used (Selecta Frigiterm S-382) to ensure consistency in temperature of ± 0.1°C. A workstation allowed obtaining the absorbance–time data, which were collected by a computer equipped with a program to analyze the data.

pH measurements were made with a pH meter PHM 82 Standard, Radiometer Copenhagen, equipped with a combined electrode GK2401C, thermostated at 25°C. The pH meter was calibrated using standard solutions supplied by Crison of pH 4.01, 7.00, and 9.26.

RESULTS

Previous Studies: To Select the Wavelength

To select the most suitable wavelength to monitor the kinetics of the reaction, spectrophotometric studies of all reagents and of the reaction mixture were carried out in the range between 200 and 360 nm. The comparison of these studies has allowed us to confirm that the absorption band of the reaction mixture shows a maximum at 266 nm, which corresponds to the absorption maximum of the Br_3^- species formed in the reaction ($\lambda_{max} = 266$ nm, $\varepsilon_{max} = 40{,}900 \pm 400$ M^{-1} cm^{-1}) [18]. This is the wavelength selected for monitoring of the reaction.

Mixture of the Reaction

In previous studies, it has been found that this reaction is very fast, so to perform the kinetic study it was necessary to use a stopped-flow spectrophotometer. The ^{t}BuOCl solution used in the kinetic experiments was prepared every day, using acetonitrile as a solvent to prevent decomposition and its hydrolysis. A system of mixed asymmetric (1:25) was used with the purpose of minimizing the solvent effect in the reaction medium. The Br^- concentration was always kept at least 30 times higher than the concentration of ^{t}BuOCl. All the experiments were carried out at 25°C, except a set of experiments in which the influence of temperature was studied. In all experiments, the ionic strength (I) was maintained constant by adding the necessary volume of 2 M $NaClO_4$ solution.

The concentration of protons is a parameter that has a great influence on the reaction rate, for this reason it was necessary to maintain its concentration in each experiment. This was achieved by adding a known volume of a perchloric acid titrated solution or using buffer solutions. In the latter case, it was also necessary to study the possible catalytic effect of the species used for the preparation of the buffer solutions.

Reaction Order

Taking into account the stoichiometric equation for the studied reaction, the rate equation can be written as

$$\begin{aligned} v &= -\frac{\mathrm{d}\left[{}^t\mathrm{BuOCl}\right]}{\mathrm{d}t} = \frac{\mathrm{d}\left[\mathrm{Br}_3^-\right]}{\mathrm{d}t} \\ &= k\left[\mathrm{Br}^-\right]^a\left[\mathrm{H}^+\right]^b\left[{}^t\mathrm{BuOCl}\right]^c \end{aligned} \tag{1}$$

As indicated above, all experiments were carried out in conditions in which the concentrations of Br^- and H^+ were practically constant during each experiment, so that

$$\begin{aligned} v &= -\frac{\mathrm{d}\left[{}^t\mathrm{BuOCl}\right]}{\mathrm{d}t} = \frac{\mathrm{d}\left[\mathrm{Br}_3^-\right]}{\mathrm{d}t} \\ &= k_{\mathrm{obs}}\left[{}^t\mathrm{BuOCl}\right]^c \end{aligned} \tag{2}$$

where k_{obs} represents the experimental rate constant.

To make sure that the reaction is first order with respect to the ^{t}BuOCl concentration, $c = 1$,

Table I Rate Constants in Perchloric Acid Medium

T (°C)	[^{t}BuOCl] (M)	[H$^+$] (M)	I (M)	[Br$^-$] (M)	k_{obs} (s^{-1})	k_{2nd} (× 10^3 M^{-1} s^{-1})
25	5×10^{-5}	0.01	0.5	0.0025	26 ± 1	10.4 ± 0.4
25	5×10^{-5}	0.01	0.5	0.0050	50 ± 4	10.0 ± 0.8
25	5×10^{-5}	0.01	0.5	0.010	102 ± 4	10.2 ± 0.4
25	5×10^{-5}	0.01	0.5	0.025	254 ± 7	10.2 ± 0.3
25	5×10^{-5}	0.0050	0.5	0.0050	38 ± 2	7.6 ± 0.4
25	5×10^{-5}	0.0075	0.5	0.0050	55 ± 4	11.0 ± 0.8
25	5×10^{-5}	0.010	0.5	0.0050	50 ± 1	10.0 ± 0.2
25	5×10^{-5}	0.015	0.5	0.0050	90 ± 4	18.0 ± 0.8
25	5×10^{-5}	0.025	0.5	0.0050	139 ± 3	27.8 ± 0.6
25	5×10^{-5}	0.050	0.5	0.0050	304 ± 15	60.8 ± 3
25	5×10^{-5}	0.02	0.225	0.0050	116 ± 2	23.2 ± 0.4
25	5×10^{-5}	0.02	0.425	0.0050	109 ± 9	22 ± 2
25	5×10^{-5}	0.02	0.625	0.0050	114 ± 8	23 ± 2
25	5×10^{-5}	0.02	0.825	0.0050	102 ± 7	20 ± 1
25	5×10^{-5}	0.02	1.025	0.0050	111 ± 7	22 ± 1
15	5×10^{-5}	0.01	0.5	0.0050	37 ± 1	7.4 ± 0.2
25	5×10^{-5}	0.01	0.5	0.0050	53 ± 2	10.6 ± 0.4
35	5×10^{-5}	0.01	0.5	0.0050	69 ± 2	13.8 ± 0.4
45	5×10^{-5}	0.01	0.5	0.0050	90 ± 5	18 ± 1

the absorbance–time data were fitted to the integrated equation written exponentially. In all cases, the experiments were performed under isolation conditions and the results were adjusted perfectly to this equation:

$$A_t = A_\infty + (A_o - A_\infty) \cdot e^{-k_{obs} t} \tag{3}$$

where A_0, A_t, and A_∞ are the absorbance reading at zero, t, and infinite times, respectively, and k_{obs} is the pseudo–first-order rate constant.

All the experiments were repeated between six and 10 times, and the deviation of the values obtained with respect to the average value was less than 3%. The mean values obtained for each experiment are presented in the tables.

Reaction in Perchloric Acid

The results summarized in Table I show an increase in the rate constant by increasing the Br$^-$ concentration, so that the reaction order with respect to the bromide concentration is $a = 1$. This table also includes the second-order rate constant, $k_{2nd} = k_{obs}/[\mathrm{Br}^-]$.

Another group of experiments allows us to confirm the increase in the rate constants k_{obs} and k_{2nd} with increasing the proton concentration (Table I). A linear relationship between k_{obs} and the proton concentration can be observed, and thus the reaction order with respect to proton concentration is $b = 1$.

Table II Values of Activation Parameters for the Reaction of Oxidation of ^{t}BuOCl by Br$^-$ in Perchloric Acid Medium

Arrehnius Parameter	Eyring Parameter
$A = (8 \pm 3) \times 10^9$ M^{-2} s^{-1}	$\Delta S^{\neq} = (-63 \pm 3)$ J mol^{-1} K^{-1}
$E_a = (22.4 \pm 0.8)$ KJ mol^{-1}	$\Delta H^{\neq} = (19.8 \pm 0.9)$ KJ mol^{-1}

On the other hand, we have studied the influence of the ionic strength (I) on the rate constant in acid medium. The results indicate that the rate constant is independent of the ionic strength under the conditions studied (Table I). This seems to indicate that at least one nonionic species must be involved in the transition state.

A study of the influence of temperature on the rate constant was performed to complete the study of the reaction of Br$^-$ with ^{t}BuOCl in perchloric acid medium. This study was carried out at 15, 25, 35, and 45°C. The results listed in Table I show an increase in the rate constant with increasing the temperature. These experimental results are in compliance with the Arrhenius equation and the equation derived from the Eyring theory activated complex. This allows us to obtain the activation parameters for the reaction in perchloric acid medium (Table II).

Table III Influence of the Concentrations of Br^- and ^{t}BuOH, in the Presence of Buffer Solution

Buffer Solution	$[{}^t\mathrm{BuOH}]$ (M)	pH	$[BR^-]$ (M)	k_{obs} (s^{-1})	k_{2nd} ($\times 10^3$ M^{-1} s^{-1})
$[H_3PO_4/H_2PO_4{}^-]_T = 0.05$ M, $I = 0.425$ M	–	1.85	0.005	71 ± 2	14.2 ± 0.4
	–	1.86	0.015	224 ± 4	14.9 ± 0.3
	–	1.85	0.030	404 ± 20	13.5 ± 0.7
$[ClCH_2COOH/ClCH_2COO^-]_T = 0.2$ M, $I = 0.4$ M	–	2.58	0.005	23 ± 1	4.6 ± 0.2
	–	2.57	0.010	47 ± 1	4.7 ± 0.1
	–	2.43	0.025	116 ± 4	4.6 ± 0.2
	–	2.40	0.035	161 ± 2	4.60 ± 0.06
$[H_3PO_4/H_2PO_4{}^-]_T = 0.2$ M, $I = 0.4$ M	0.010	2.09	0.005	38 ± 2	7.6 ± 0.4
	0.025	2.13	0.005	45 ± 1	9.0 ± 0.2
	0.050	2.14	0.005	41 ± 1	8.2 ± 0.2
	0.075	2.12	0.005	41 ± 1	8.2 ± 0.2
	0.10	2.11	0.005	39 ± 2	7.8 ± 0.4
	0.25	2.12	0.005	48 ± 2	9.6 ± 0.4
	0.35	2.12	0.005	44.3 ± 0.8	8.9 ± 0.2
	0.50	2.16	0.005	39 ± 2	7.8 ± 0.4

$T = 25°C$, $[{}^t\mathrm{BuOCl}] = 5 \times 10^{-5}$ M.

The calculated enthalpy value shows that the process corresponds to a chemical control for the reaction. The negative activation entropy value indicates that the transition state is more orderly than the reactants.

Kinetics Studies in the Presence of Buffer Solutions

To study the influence of pH on the kinetics of the oxidation reaction of bromide by tert-butyl hypochlorite, the kinetic studies were carried out using different buffer solutions to control the proton concentration in the medium.

The results obtained with different concentrations of bromide, for each buffer solution, are included in Table III. A linear increase in the rate constant with an increase in the bromide concentration can be observed. This confirms that the reaction is first order with respect to the bromide concentration.

Another group of experiments allows us to confirm that the presence of the ^{t}BuOH does not significantly alter the rate constant (Table III).

Influence of the Buffer Solution Concentration

A set of experiments were carried out to study the effect of different concentrations of buffer solutions on the reaction medium. In these experiences, the pH of the medium was modified using different buffer solutions: $Cl_2CHCOOH/Cl_2CHCOO^-$, $ClCH_2COOH/ClCH_2COO^-$, CH_3COOH/CH_3COO^-, and CH_3OCOOH/CH_3OCOO^-.

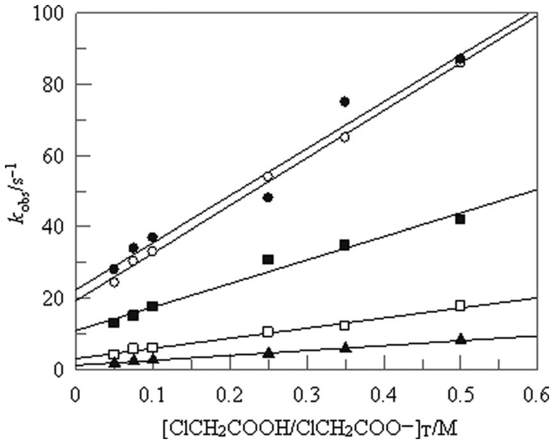


Figure 1 Influence of $[ClCH_2COOH/ClCH_2COO^-]_T$ on k_{obs}. $T = 25°C$, $I = 0.5$ M, $[{}^t\mathrm{BuOCl}] = 5 \times 10^{-5}$ M, $[Br^-] = 5 \times 10^{-3}$ M. ●: $pH_m = 1.85$, ○: $pH_m = 2.31$ (dash line), ■: $pH_m = 2.68$, □: $pH_m = 3.27$, ▲: $pH_m = 3.65$.

In each experiment, we can observe that the rate constant increases with increasing the buffer solution concentration. This suggests the possible existence of a catalysis process. This catalytic effect was observed in all buffer solutions used, and the linear relationships obtained in each experiment between k_{obs} and the buffer solution concentration are shown in Figs. 1–4.

Table IV summarizes the results obtained by least-squares analysis of k_{2nd} versus $[HA_i]_T$ for all series of experiments carried out with different buffer solutions.

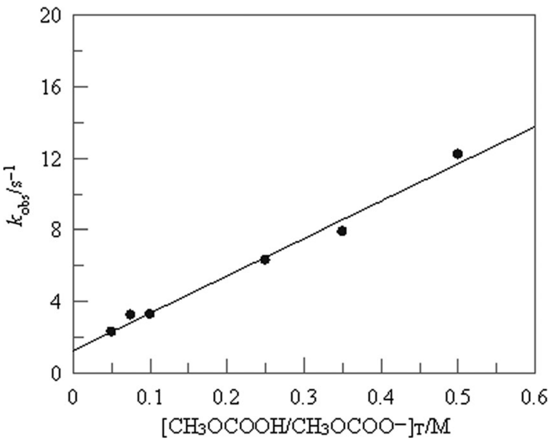


Figure 2 Influence of $[CH_3OCOOH/CH_3OCOO^-]_T$ on k_{obs}. $T = 25°C$, $I = 0.5$ M, $[^tBuOCl] = 5 \times 10^{-5}$ M, $[Br^-] = 5 \times 10^{-3}$ M. ●: $pH_m = 3.59$.

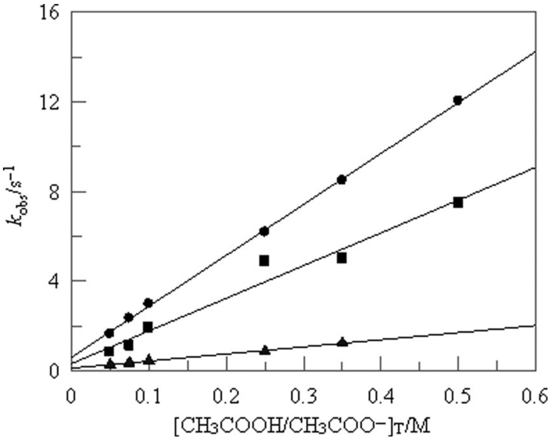


Figure 3 Influence of $[CH_3COOH/CH_3COO^-]_T$ on k_{obs}. $T = 25°C$, $I = 0.5$ M, $[^tBuOCl] = 5 \times 10^{-5}$ M, $[Br^-] = 5 \times 10^{-3}$ M. ●: $pH_m = 3.94$, ▲: $pH_m = 4.62$, ■: $pH_m = 5.37$.

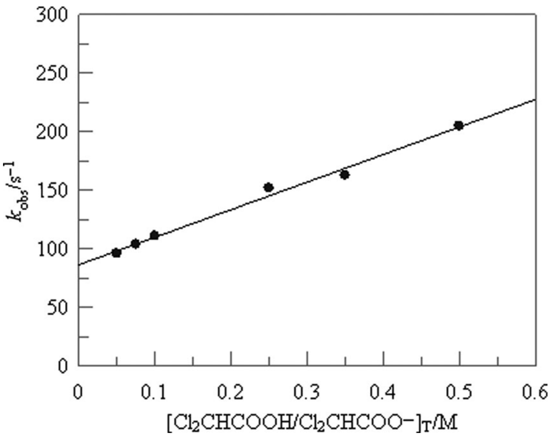


Figure 4 Influence of $[Cl_2CHCOOH/Cl_2CHCOO^-]_T$ on k_{obs}. $T = 25°C$, $I = 0.5$ M, $[^tBuOCl] = 5 \times 10^{-5}$ M, $[Br^-] = 5 \times 10^{-3}$ M. ●: $pH_m = 1.71$.

MECHANISM AND DISCUSSION

When the solutions of ^tBuOCl and Br^- are mixed, the formation of the $Br_3{}^-$ species takes place. Experimentally, the reaction was found to be first order with respect to the concentration of each one of the reagents. Moreover, the possibility that the reaction may be in equilibrium was discarded because the rate constant is not affected by the change in the ^tBuOH concentration.

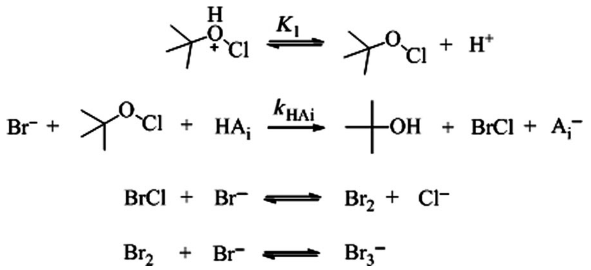
The reaction that occurs is a redox process where the Cl^+, of the ^tBuOCl, will be reduced to Cl^- while the bromide ion (Br^-) is oxidized to Br^0.

The literature indicates that, for other similar reactions, the formation of bromine may take place through the formation of the BrCl intermediate compound, which in excess of Br^- quickly leads to the formation of Br_2 [11,18,19]. On the other hand, according

Table IV Catalytic Constants for the Reaction of Oxidation of Br^- by ^tBuOCl

Buffer	pH_m	f_{HA_i}	Intercept ($\times 10^3$ M^{-1} s^{-1})	Slope ($\times 10^3$ M^{-1} s^{-1})	r	k_{HA_i} ($\times 10^3$ M^{-2} s^{-1})
$Cl_2CHCOOH/Cl_2CHCOO^-$	1.71	0.26	17.2 ± 0.6	47.0 ± 2.0	0.9952	181 ± 8
$pK_a = 1.26$	1.85	0.85	4.4 ± 0.6	26 ± 3	0.9819	31 ± 3
	2.31	0.66	3.8 ± 0.2	26.6 ± 0.6	0.9988	40.3 ± 0.9
	2.68	0.45	2.2 ± 0.2	13 ± 1	0.9878	29 ± 2
	3.27	0.18	0.6 ± 0.1	5.6 ± 0.2	0.9941	31 ± 1
$ClCH_2COOH/ClCH_2COO^-$	3.65	0.08	0.22 ± 0.02	2.8 ± 0.1	0.9976	35 ± 1
$pK_a = 2.60$						
CH_3OCOOH/CH_3OCOO^-	3.59	0.46	0.24 ± 0.06	4.2 ± 0.2	0.9936	9.1 ± 0.4
$pK_a = 3.53$	3.94	0.81	0.12 ± 0.01	4.54 ± 0.04	0.9997	5.60 ± 0.05
	4.62	0.48	0.06 ± 0.08	3.0 ± 0.2	0.9828	6 ± 2
CH_3COOH/CH_3COO^-	5.39	0.13	0.024 ± 0.004	0.63 ± 0.02	0.9988	4.8 ± 0.1
$pK_a = 4.58$						

$T = 25°C$, $I = 0.5$ M.



Scheme 2

to the literature, when Br_2 is present in solution along Br^-, the Br_3^- species will be formed in a fast equilibrium process that is dissociated from the formation of Br_3^- ($K_e = 16.1$ at 25°C, $I = 1.0$ M) [18].

The experimental results show an increase in the rate constant with increasing the concentration of buffer solution, when the concentrations of the hydrogen ion and bromide ion remain constant. Also, an increase in the rate constant with increasing the proton concentration is observed when the pH of the medium is modified. This behavior is consistent with that observed in other reactions in which the process of general acid–base catalysis takes place [11].

According to the above, the proposed mechanism for this oxidation process of the Br^- ion is shown in Scheme 2.

The estimated value for the dissociation constant of the ${}^t\mathrm{BuOHCl}^+$ is approximately 10^2 [20], so that under the experimental conditions, $[H^+] < 0.05$ M, more than 99.99% of the tert-butyl hypochlorite is present as neutral species (^{t}BuOCl). Therefore, ^{t}BuOCl will be the species involved in the slow step of the reaction. From this mechanism, we obtained a general equation for the rate reaction that is a sum of terms, in which the different species that can act as catalysts of the process are included:

$$\begin{aligned} v &= -\frac{\mathrm{d}\left[{}^t\mathrm{BuOCl}\right]}{\mathrm{d}t} \\ &= \sum_i k_{\mathrm{HA}_i}\,[\mathrm{HA}_i]\left[\mathrm{Br}^-\right]\left[{}^t\mathrm{BuOCl}\right] \qquad (4) \end{aligned}$$

The presented expression of this rate equation can be written as

$$\begin{aligned} v = {} & k_{\mathrm{H_2O}}\,[\mathrm{H_2O}]\left[\mathrm{Br}^-\right]\left[{}^t\mathrm{BuOCl}\right] \\ & + k_{\mathrm{H_3O^+}}\left[\mathrm{H_3O^+}\right]\left[\mathrm{Br}^-\right]\left[{}^t\mathrm{BuOCl}\right] \\ & + k_{\mathrm{HA_i}}\,[\mathrm{HA}_i]\left[\mathrm{Br}^-\right]\left[{}^t\mathrm{BuOCl}\right] \qquad (5) \end{aligned}$$

This includes three terms: (1) a reaction in aqueous solution without a catalyst ($k_{\mathrm{H_2O}}[\mathrm{H_2O}] = k_0$), (2) catalysis due to the presence of protons ($k_{\mathrm{H_3O+}}$), and (3) catalysis due to the acid specie of the buffer solution (k_{HA_i}).

Given that the study has been performed under isolation conditions, ^{t}BuOCl being the limiting reactant and making a material balance, we can express the rate constants k_{obs} and k_{2nd} as a function of the buffer concentration total ($[\mathrm{HA}i]_\mathrm{T}$) and of the acid fraction undissociated from the buffer solution ($f_{\mathrm{HAi}} = [\mathrm{HA}i]/[\mathrm{HA}i]_\mathrm{T}$):

$$\begin{aligned} k_{\mathrm{obs}} = {} & k_0\left[\mathrm{Br}^-\right] + k_{\mathrm{H_3O^+}}\left[\mathrm{H_3O^+}\right]\left[\mathrm{Br}^-\right] \\ & + k_{\mathrm{HA_i}}\,f_{\mathrm{HA_i}}\,[\mathrm{HA_i}]_T\left[\mathrm{Br}^-\right] \qquad (6) \end{aligned}$$

$$\begin{aligned} k_{\mathrm{2nd}} = {} & k_0 + k_{\mathrm{H_3O^+}}\left[\mathrm{H_3O^+}\right] \\ & + k_{\mathrm{HA_i}}\,f_{\mathrm{HA_i}}\,[\mathrm{HA_i}]_T \qquad (7) \end{aligned}$$

These expressions are consistent with the experimental results since they allow us to justify: (1) the first order with respect to the ^{t}BuOCl concentration, (2) the first order with respect to the Br^- concentration, (3) the linear dependence between the rate constant and the proton concentration, and (4) the increase in the rate constant with increasing the buffer concentration.

Calculation of Catalytic Constant

Reaction in Perchloric Acid Medium. When the proton concentration of the medium is controlled using a perchloric acid solution, the general equation for the rate experimental constant (Eq. (7)) is simplified as follows: $k_{\mathrm{2nd}} = k_0 + k_{\mathrm{H_3O^+}}\left[\mathrm{H_3O^+}\right]$.

The results summarized in Table I allow us to prove that a linear relationship exists between k_{2nd} and the proton concentration, as shown in Fig. 5.

The value of the intercept allows us to calculate the term: $k_{\mathrm{H_2O}}[\mathrm{H_2O}] = k_0$, $k_0 = (0.0 \pm 0.1) \times 10^4$ $\mathrm{M^{-1}}$ $\mathrm{s^{-1}}$. This term in a strongly acidic medium is almost negligible compared to the term $k_{\mathrm{H_3O+}}$, but it may be important if the pH increases. However, the studies carried out using buffer solutions will make it possible to verify the existence of a process of acid catalysis, so the reaction rate is to be strongly influenced by the catalytic constant.

The slope value corresponds to the proton catalytic constant, $k_{\mathrm{H_3O+}}$, and its value can be calculated from the experimental results:

$$k_{\mathrm{H_3O^+}} = (1.19 \pm 0.05) \times 10^6\ \mathrm{M^{-2}\ s^{-1}}$$

Figure 6 shows the values of the second-order rate constant, k_{2nd} against pH. The values presented in Table I

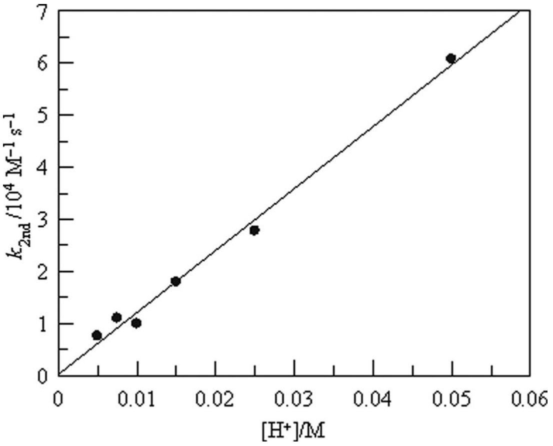


Figure 5 Influence of $[H^+]$ on k_{2nd} (Table I).

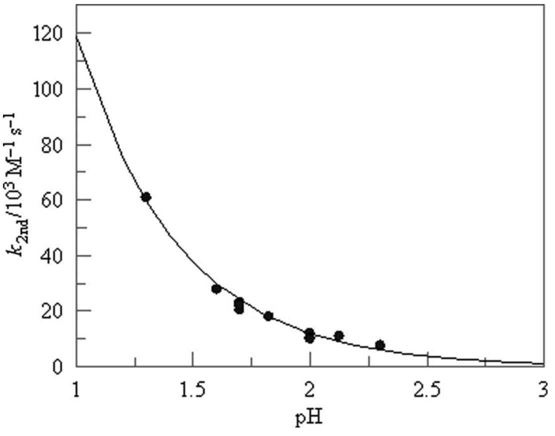


Figure 6 Plot of k_{2nd} against pH in the oxidation of Br^- by ^{t}BuOCl (Table I).

are also included in this figure, which shows that the obtained profile is exponential. This suggests that the second-order rate constant tends to be constant at high pH values. This value would correspond to the value of the term $k_{H_2O}[H_2O]$. As will be seen later, the value of k_{2nd} approaches zero when considering the results obtained with buffer solutions, which allows us to extend the pH range studied.

Reaction in the Presence of Buffer Solutions. A second set of experiments was carried out using different buffer solutions in which the weak acids used to obtain these solutions were H_3PO_4, $Cl_2CHCOOH$, $ClCH_2COOH$, CH_3COOH, and CH_3OCOOH. Thus, the reaction was studied in the range of pH between 1.26 and 4.58.

The experimental results indicate that the reaction rate depends on the nature of the species used for the preparation of the buffer solutions and its concentration. Also, the reaction rate depends on the pK_a of the acids present in the reaction medium. The data shown in Figs. 1–4 allow us to prove for each buffer solution the existence of a linear relationship between k_{2nd} and the total buffer concentration. Table IV presents the results obtained for the intercepts and slopes by adjustments of k_{2nd} versus $[\text{Buffer}]_T$.

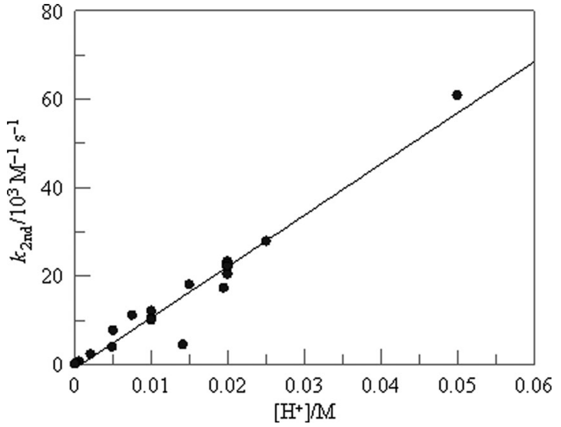


Figure 7 Plot of k_{2nd} against $[H^+]$ in the oxidation of Br^- by ^{t}BuOCl.

The slopes of these linear relationships (slope = $k_{HA_i} f_{HA_i}$) allow us to calculate the catalytic constant of each of the acids used for the preparation of buffer solutions. These values are also included in Table IV. In this table, we can observe an increase in the catalytic constant k_{HAi} with increasing the acid strength in the following sequence: $Cl_2CHCOOH/Cl_2CHCOO^-$ > $ClCH_2COOH/ClCH_2COO^-$ > CH_3OCOOH/CH_3OCOO^- > CH_3COOH/CH_3COO^-. These results are in concordance with those obtained in previous studies [21,22].

The values of the catalytic constants are summarized in Table V. The results presented in this table, for the buffer solutions of dichloroacetic acid and methoxyacetic acid, were obtained by varying the concentration of buffer at only one pH value. In the case of the buffer solutions of monochloroacetic acid and acetic acid, the values included in this table are the average values of the rate constants obtained in five and three series of different experiments, respectively.

Moreover, the intercept values summarized in Table IV correspond to the rate constant at the zero buffer concentration. This can be interpreted as the rate constant in the absence of buffer at that pH value, which may be analyzed together with the rate constants obtained in perchloric acid medium.

Figure 7 shows the values of the rate constant k_{2nd} obtained in the experiments carried out in perchloric acid medium along with the intercepts obtained in the study of the influence of the buffer concentration (Table IV). The good linear relationship is shown

Table V Catalytic Constants for the Reaction of Oxidation of Br^- by ^tBuOCl

Species	pK_a	k_{HA_i} ($\times M^{-2} s^{-1}$)	k_{HOCl} ($\times M^{-2} s^{-1}$) [a]
H_3O^+	–1.74	$(1.15 \pm 0.05) \times 10^6$	$(1.32 \pm 0.03) \times 106$
$Cl_2CHCOOH/Cl_2CHCOO^-$	1.26	$(1.81 \pm 0.08) \times 10^5$	–
$ClCH_2COOH/ClCH_2COO^-$	2.60	$(3.3 \pm 0.5) \times 10^4$	$(6.11 \pm 0.34) \times 10^4$
CH_3OCOOH/CH_3OCOO^-	3.53	$(9.1 \pm 0.4) \times 10^3$	–
CH_3COOH/CH_3COO^-	4.50	$(5.8 \pm 0.6) \times 10^3$	$(2.09 \pm 0.01) \times 10^4$
H_2O	15.52	–	27.9 ± 5.5

[a] Data obtained from [11] for the reaction $Br^- + HOCl$.

in this figure. The slope value obtained from the least-squares adjustments allows to obtain a value for the catalytic constant, $k_{H_3O^+} = (1.15 \pm 0.05) \times 10^6 \, M^{-2} \, s^{-1}$, which is completely in accordance with that obtained in the experiments performed in perchloric acid medium.

Brönsted Relationship

The acid dissociation constant (K_a) and the rate constants for the reactions catalyzed by a buffer solution (k_{HA}) can be correlated to the Brönsted equation [23], which is shown in the following equation:

$$\frac{k_{HA}}{p} = G_A \left(\frac{K_a q}{p} \right)^{\alpha} \tag{8}$$

where p is the number of acid equivalent positions in the conjugate acid, q is the number of basic equivalent positions in the conjugate base, G_A is the Brönsted proportionality constant, and α is the measurement of the proton transfer in the transition state. The α values are often in the range of $0 < \alpha < 1$ for different reactions in aqueous solution. This equation corresponds to a free-energy relationship between the free energies of activation for proton transfer reactions and free energies of acid ionization.

The compliance of this relationship can be verified if the Brönsted equation is expressed in the logarithmic form.

The values of α and the proportionality constant of Brönsted (G_A) can be obtained from the values of the slope and the intercept obtained by least squares in the log (k_{HA}/p) versus (log ($K_a q/p$)), respectively. Figure 8 shows that the results obtained in this study and the values for the reaction of Br^- with HOCl match with the literature [11].

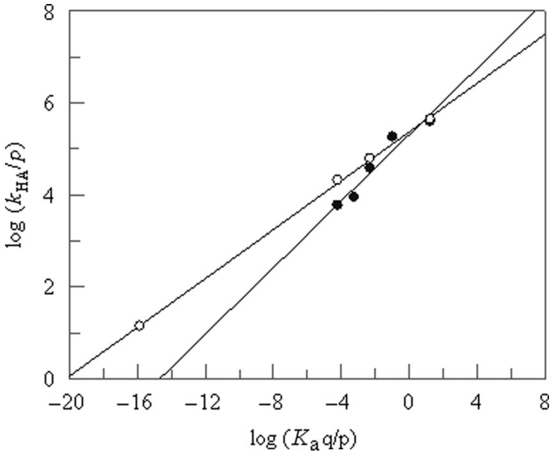


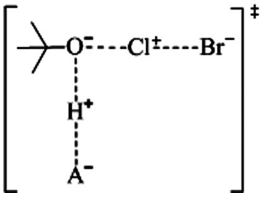
Figure 8 Brönsted plots for the reactions of oxidation of Br^- by ^tBuOCl or by HOCl. ●: Data obtained in this work ($Br^- + {}^tBuOCl$). ○: Data from [11] ($Br^- + HOCl$).

The values for the intercept and slope obtained in this representation are 5.3 ± 0.1 and 0.36 ± 0.05, respectively. The term α, corresponding to the slope of the Brönsted, is often interpreted as a measure of the extent of proton transfer in the transition state. The reasoning is the interpretation of whether the transition state is closer to the reactants or products. The value found reflects that the proton transfer is 36%.

It is important to consider that in these processes the proton HA cannot be transferred to ^tBuOCl in a preequilibrium step, because otherwise we would have a specific catalytic process, where the rate constant depends only on the concentration of protons and not on the buffer concentration. This means that the transition state must contain three species: HA, ^tBuOCl, and Br^-.

The oxygen atom of the species ^tBuOCl accepts a proton of HA, whereas the Cl^+ is transferred to Br^-. To reach this transition state, it is not necessary that a trimolecular collision takes place; it is only needed that the species HA approaches to the weakly associated species ($^tBuOCl^+Br^-$) or, perhaps, an approach of the Br^- ion to species (AH^tBuOCl) occurs, always taking into account that the proton transfer cannot be fully carried out before the association of the Cl^+ and Br^- (see Scheme 3).

In this transition state, there are five pairs of electrons around the chlorine atom. This situation is not unusual, taking into account that it appears in a stable species as $Cl_3{}^-$. The valence shell of electron



Scheme 3

pair repulsion theory predicts a bond between O, Cl^+, and Br^-.

CONCLUSIONS

There is information in the literature about the oxidation reaction of Br^- with HOCl, but there is no information for the kinetics of the oxidation reaction of Br^- with ^{t}BuOCl. The results obtained in the present study of the oxidation reaction of Br^- with ^{t}BuOCl have allowed us to prove that its kinetic behavior is totally identical to the behavior found in the reaction of oxidation of Br^- with HOCl.

In general, the results can be summarized as follows:

- first order with respect to the concentration of the Br^- ion,
- first order with respect to the concentration of ^{t}BuOCl,
- the rate constant is not affected by the variation of the concentration of ^{t}BuOH, so the possibility that the reaction is in equilibrium is discarded,
- complex dependence of the rate constant with respect to the H^+ concentration, and
- the reaction catalyzed by acids and bases, so that the species used as pH regulators will act as catalysts for the reaction. The catalytic constants obtained are adjusted to the Brönsted equation.

SUPPORTING INFORMATION

Tables presenting data corresponding to the buffer solution concentration, for each one of the buffers used in this work, are included in the Supporting Information.

BIBLIOGRAPHY

1. White, G. C. The Handbook of Chlorination, 3rd ed.; Van Nostrand Reinhold; New York, 1992; 889–934.
2. Morris, J. C. Water Chlorination Environmental Impact and Health Effects; Ann Arbor Science: Ann Arbor, MI, 1978; Vol 2, pp. 879–890.
3. Jolley, R. L.; Carpenter, J. H. Water Chlorination Environmental Impact and Health Effects; Ann Arbor Science: Ann Arbor: MI, 1983; Vol. 4, Chap. 1, pp. 3–47.
4. Jensen, J. S.; Lam, Yiu-Fai; Helz, G. R. Environ Sci Technol 1999, 33, 3568–3573.
5. Yang, X.; Fan, Chihhao; Shang, C.; Zhao, Q. Water Res 2010, 22, 2691–2702.
6. Donnermair, M. M.; Blantchley, E. R. Water Res 2003, 37, 1557–1570.
7. Liu, S.; Sung, G. Ind Eng Chem Res 2009, 48, 613–618.
8. Rees, M. D.; Pattison, D. I.; Davies, M. J. Biochem J 2005, 391, 125–134.
9. Deborde, M.; von Gunten, U. Water Res 2008, 42, 13–51.
10. Kumar, K.; Day, R. A.; Margerum, D. W. Inorg Chem 1986, 25, 4344–4350.
11. Kumar, K.; Margerum, D. W. Inorg Chem 1987, 26, 2706–2711.
12. Johnson, D. W.; Margerum, D. W. Inorg Chem 1991, 30, 4845–4851.
13. Nagy, J. C.; Kumar, K.; Margerum, D. W. Inorg Chem 1988, 27, 2773–2780.
14. Bichsel, Y.; Von Gunten, U. Environ Sci Technol 2000, 34, 2784–2791.
15. Margerum, D. W.; Huff Hartz K. E. J Environ Monit 2002, 4, 20–26.
16. Teeter, H. M.; Bell, E. W. Org Synth 1963, 4, 125.
17. Walling, C.; Jacknow, B. B. J Am Chem Soc 1960, 82, 6108–6112.
18. Wang, T. X.; Kelley M. D.; Cooper, J. N.; Beckwith, R. C.; Margerum, D. W. Inorg Chem 1994, 33, 5872–5878.
19. Anbar, M.; Ginsberg, D. Chem Rev 1954, 54, 925–958.
20. Anbar, M.; Guttmann, S.; Rein, R. J Am Chem Soc 1959, 81, 1816–1821.
21. Antelo, J. M.; Arce, F.; Campos, J.; Parajó, M. Int J Chem Kinet 1996, 28, 391–396.
22. Antelo, J. M.; Arce, F.; Crugeiras, J.; Miraz, C.; Parajó, M. Gazz Chim Ital 1997, 127, 355–360.
23. Maskill, H. The Physical Basis of Organic Chemistry; Oxford University Press: Oxford, UK, 1985; Chap. 10.