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Activation Energy for the Disproportionation of $HBrO_2$ and Estimated Heats of Formation of $HBrO_2$ and BrO_2

Jesús Alberto Ágreda B.[†,‡] **and Richard J. Field***[,†]

Departamento de Química, Universidad Nacional de Colombia, Bogotá, Colombia, and Department of Chemistry, The University of Montana, Missoula, Montana 59812

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The kinetics of the reaction $HBrO_2 + HBrO_2 \rightarrow HOBr + BrO_3^- + H^+$ is investigated in aqueous $HClO_4$ (0.04−0.9 M) and H_2SO_4 (0.3−0.9 M) media and at temperatures in the range 15−38 °C. The reaction is found to be cleanly second order in $[HBrO_2]$, with the experimental rate constant having the form $k_{exp} = k + k'[H^+]$. The half-life of the reaction is on the order of a few tenths of a second in the range $0.01 \text{ M} < [HBrO_2]_0 < 0.02 \text{ M}$. The detailed mechanism of this reaction is discussed. The activation parameters for k are found to be $E^{\ddagger} = 19.0 \pm 0.9$ kJ/mol and $\Delta S^{\ddagger} = -132 \pm 3$ J/(K mol) in $HClO_4$, and $E^{\ddagger} = 23.0 \pm 0.5$ kJ/mol and $\Delta S^{\ddagger} = -119 \pm 1$ J/(K mol) in H_2SO_4. The activation parameters for k' are found to be $E^{\ddagger} = 25.8 \pm 0.5$ kJ/mol and $\Delta S^{\ddagger} = -106 \pm 1$ J/(K mol) in $HClO_4$, and $E^{\ddagger} = 18 \pm 3$ kJ/mol and $\Delta S^{\ddagger} = -130 \pm 11$ J/(K mol) in H_2SO_4. The values $\Delta_f H_{298}{}^0\{BrO_2(aq)\} = 157$ kJ/mol and $\Delta_f H_{298}{}^0\{HBrO_2(aq)\} = -33$ kJ/mol are estimated using a trend analysis (bond strengths) based on the assumption $\Delta_f H_{298}{}^0\{HBrO_2(aq)\}$ lies between $\Delta_f H_{298}{}^0\{HOBr(aq)\}$ and $\Delta_f H_{298}{}^0\{HBrO_3(aq)\}$ as $\Delta_f H_{298}{}^0\{HClO_2(aq)\}$ lies between $\Delta_f H_{298}{}^0\{HOCl(aq)\}$ and $\Delta_f H_{298}{}^0\{HClO_3(aq)\}$. The estimated value of $\Delta_f H_{298}{}^0\{BrO_2(aq)\}$ agrees well with calculated gas-phase values, but the estimated value of $\Delta_f H_{298}{}^0\{HBrO_2(aq)\}$, as well as the tabulated value of $\Delta_f H_{298}{}^0\{HClO_2(aq)\}$, is in substantial disagreement with calculated gas-phase values. Values of $\Delta_r H^0$ are estimated for various reactions involving BrO_2 or $HBrO_2$.

Introduction

The Belousov−Zhabotinsky (BZ) reaction[1−4] is the oscillatory, metal-ion [e.g., Ce(IV)/Ce(III)]-catalyzed oxidation of an organic substrate [e.g., $CH_2(COOH)_2$] by BrO_3^- in an aqueous, strongly acid medium. Elucidation of the mechanism of the BZ reaction starting with the work of Field, Körös and Noyes[4] has led to considerable information concerning the rate and thermodynamic parameters[5−9] of reactions 1−7. Reactions 1−7 are

$$Br^- + HOBr + H^+ \rightleftarrows Br_2 + H_2O \qquad (1,-1)$$

$$Br^- + HBrO_2 + H^+ \rightleftarrows HOBr + HOBr \qquad (2,-2)$$

$$Br^- + BrO_3^- + 2H^+ \rightleftarrows HBrO_2 + HOBr \qquad (3,-3)$$

$$HBrO_2 + HBrO_2 \rightleftarrows HOBr + BrO_3^- + H^+ \qquad (4,-4)$$

$$HBrO_2 + BrO_3^- + H^+ \rightleftarrows 2BrO_2 + H_2O \qquad (5,-5)$$

$$Ce(III) + BrO_2 + H^+ \rightleftarrows Ce(IV) + HBrO_2 \qquad (6,-6)$$

$$Ce(IV) + BrO_2 + H_2O \rightleftarrows Ce(III) + BrO_3^- + 2H^+ \qquad (7,-7)$$

the core of the mechanism[4,5] of the autocatalytic oxidation of Ce(III) to Ce(IV) by BrO_3^-, a critical phase of the BZ reaction. Values of $\Delta_f G^0$ for aqueous Br^-, Br_2, HOBr, and BrO_3^- are tabulated.[6] A complete set of thermodynamically and kinetically consistent rate constants for reactions 1−7, as well as values of $\Delta_f G^0(aq)$ in 1 M H_2SO_4 for $HBrO_2$ and BrO_2, have been estimated by Field and Försterling[5] (FF) on the basis of a large but diverse (being from a number of different sources) body of kinetic and thermodynamic data and the indirectly determined values $K_5 \approx 10^{-6}$ and $pK_a\{HBrO_2\} \approx 4.9$. The FF values might be revised on the basis of a more reliable $pK_a\{HBrO_2\}$ value of 3.4 due to Faria et al.[7,8] at relatively low ionic strength and acidity. However, there is sufficient variability (e.g., in temperature, acidity, ionic strength) in this and other quantities involved in the FF estimates that it does not seem worthwhile to do so at the present time. The existing parameters do work well in simulations of the BZ reaction.[9,10]

However, enthalpic and activation energy data for reactions 1−7 remain incomplete, even though there is need of these parameters for understanding various aspects of the BZ reaction potentially dependent on thermal effects[11−13] and in response to current interest in bromine-containing species in the atmosphere.[14,15] Values of $\Delta_f H^0(aq)$ for Br^-, Br_2, HOBr, and BrO_3^- are tabulated.[6] Thus completion of the set of thermodynamic parameters for reactions 1−7 requires only $\Delta_f H^0(aq)$ values for $HBrO_2$ and BrO_2. Although recent values (theoretical[16] and experimental[17]) of $\Delta_f H^0\{BrO_2(g)\}$ are available, we are aware of no literature value of $\Delta_f H^0\{BrO_2(aq)\}$. Several computational values of $\Delta_f H^0\{HBrO_2(g)\}$ are available,[18−22] and a value of $\Delta_f H^0\{HBrO_2(aq)\}$ may be estimated from an experimental value of $\Delta_f H^0\{BrO_2^-(aq)\}$ due to Kennedy and Lister.[23] We estimate here values of $\Delta_f H^0\{HBrO_2(aq)\}$ and $\Delta_f H^0\{BrO_2(aq)\}$ by a trend analysis[24] based on tabulated values of $\Delta_f H^0\{HClO_2(aq)\}$ and $\Delta_f H^0\{ClO_2(aq)\}$.[6] This result allows estimation of $\Delta_r H^0$ values for reactions 1−7.

Only quite crude measurements of activation energies of a few members of reactions 1−7 are available.[25,26] We further report here an experimental investigation of the kinetics of

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* To whom correspondence should be addressed. E-mail: richard.field@umontana.edu. Telephone: (406) 243-6374. Fax: (406) 243-4227.

[†] The University of Montana.

[‡] Universidad Nacional de Colombia. E-mail: jaagredab@unal.edu.co.

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disproportionation of $HBrO_2$ (reaction 4) at various temperatures and acidities and derive its activation parameters.

Kinetics of $HBrO_2$ Disproportionation

The rate of disproportionation of aqueous Br(III) to Br(I) and Br(V) as exemplified by reaction 4 is strongly pH dependent because reaction rates are very different depending upon the protonation state of Br(III), i.e., whether it is present as $BrO_2^-(aq)$, $HBrO_2(aq)$, or $H_2BrO_2^+(aq)$. The observed overall kinetics also may be complicated by further reaction of Br(I) in analogues of reactions 1−3, in which species also may be present in various protonation states depending upon pH. However, the reaction seems always to be initiated by a second-order process, e.g., a simple oxygen-atom transfer or (in strongly acid media) possibly a more complex process involving formation of the intermediate $\{{}^+Br{=}O \leftrightarrow Br{-}O^+\}$ from $HBrO_2$.

Lee and Lister[27] investigated the very slow (near 25 °C)[28] decomposition of $BrO_2^-(aq)$ in the pH range 12.8−13.2 and at temperatures of 76.6 and 86.0 °C and suggested the mechanism below to rationalize their results, which included a rate dependence on Br^- also noted by others.[28,29]

$$BrO_2^- + BrO_2^- \rightarrow BrO^- + BrO_3^- \qquad (8)$$

$$BrO^- + BrO_2^- \rightarrow Br^- + BrO_3^- \qquad (9)$$

$$Br^- + BrO_2^- \rightleftarrows 2BrO^- \qquad (10)$$

Reaction 8 is slow, and most BrO_2^- decomposition seems to occur via cycling of Br^- in reactions 9 and 10.

Faria et al.[8] studied the decomposition of aqueous BrO_2^-/$HBrO_2$ in the pH ranges 5.9−8.0 in phosphate-buffered and 3.9−5.6 in acetate-buffered media and interpreted their results in terms of reactions 4, 11, and 12 involving $HBrO_2$ and BrO_2^-.

$$BrO_2^- + H^+ \rightleftarrows HBrO_2 \qquad (11)$$

$$HBrO_2 + BrO_2^- \rightarrow HOBr + BrO_3^- \qquad (12)$$

Disproportion is much faster under these more acidic conditions, and no kinetic effect of Br^- was noted by Faria et al.,[8] presumably because of the greater speed of reaction 12 as compared to that of reactions −3 followed by 10. Ariese and Nagy[30] suggested that the well-known[4,5] rapid bimolecular reaction between Br(III) and Br^- in a strongly acid medium (reaction 2) passes through $H_2BrO_2^+$ rather than BrO_2^- or $HBrO_2$ and thus is expected to be unimportant at this moderate acidity. Faria et al.[8] detected no effects attributable to reaction 8.

Försterling and Varga[31] and Noszticzius et al.[32] also investigated the disproportionation of $HBrO_2$ under quite acidic conditions, e.g., in the range 0.3 M ≤ $[H_2SO_4]$ ≤ 3.0 M, where it is quite rapid even at 25 °C. Essentially all Br(III) is present as $HBrO_2$ or $H_2BrO_2^+$ under these conditions. They interpreted their results in terms of reactions 13−15. The occurrence of reaction 13 was also inferred by Faria et al.[8] Reactions 13−15 are also compatible with our experimental results mostly at pH ≈ 0 to 1.

$$HBrO_2 + HBrO_2 \rightarrow HOBr + BrO_3^- + H^+ \qquad (13)$$

$$HBrO_2 + H^+ \rightleftarrows H_2BrO_2^+ \qquad (14)$$

$$HBrO_2 + H_2BrO_2^+ \rightarrow HOBr + BrO_3^- + 2H^+ \qquad (15)$$

Experimental Section

Materials. All reagents were made up using deionized water. Fisher H_2SO_4 (96%) and $HClO_4$ (69−72%) were used without additional purification. All experiments were carried out in the ranges 0.04 M ≤ $[HClO_4]$ ≤ 0.9 and 0.3 M ≤ $[H_2SO_4]$ ≤ 0.9 M. $NaBrO_2$ was prepared according to the procedure of Noszticzius et al.[32] The purity of the product obtained was monitored both by spectrophotometry[32] and by titration.[33] The concentration of the resulting stock solution was found to be 0.13 M BrO_2^- in 0.1 M NaOH. Solutions were prepared for experiments with $[BrO_2^-] \approx 0.002$ M and ≈ 0.02 M in 0.1 M NaOH.

Methods. Stopped-flow kinetic experiments were carried out using an Aminco-Morrow apparatus upgraded by On-Line Instrument Systems (Route 2, Jefferson, GA 30549). Solutions of BrO_2^- in 0.1 M NaOH were rapidly mixed with ∼1 M solutions of $HClO_4$ or H_2SO_4 to yield $HBrO_2$, whose disappearance was then monitored spectrophotometrically. Acidities reported here are after neutralization of BrO_2^-. Digital data-acquisition methods were used, and the data were manipulated using standard PC methods and software. Experiments were carried out with spectrophotometric monitoring at 230 nm with $[NaBrO_2]_0 \approx 0.002$ M and at 295 nm with $[NaBrO_2]_0 \approx 0.01-0.02$ M. The results obtained are very similar at the two wavelengths, but the results at 295 nm have less scatter. All data reported here are for 295 nm adopting[27,30,31] $\epsilon_{295}\{HBrO_2\} = 66$ M^{-1} cm^{-1}, $\epsilon_{295}\{HOBr\} = 63$ M^{-1} cm^{-1}, and a path length (l) of 0.864 cm. Stoichiometries 13 and 15 with these values of ϵ_{295} require absorbance to fall by about one-half in the course of reaction 4, as is observed (Figure 1, top). The entire stopped-flow apparatus, as well as stock solutions, were located in a thermostated glovebox with temperature control to ±0.1 °C. Experiments were carried out over 15.0−38.0 °C.

Results and Discussion

Figure 1 shows absorbance at 295 nm vs time for a typical stopped-flow kinetic experiment.

We assume that the only absorbing species present are $HBrO_2$ and HOBr on the quite rapid (<1 s) time scale of this experiment. The secondary formation of Br_2 via reactions −2, −3, and 1 is expected to occur on a substantially longer time scale. Thus the initial absorbance (A_0) is assumed to be due entirely to $[HBrO_2]_0$, and the final absorbance (A_∞) is assumed to be entirely due to $[HOBr]_\infty$, with $2[HOBr]_\infty = [HBrO_2]_0$ according to the stoichiometry of reaction 4. The instantaneous $[HBrO_2]$ at time t is then related to the absorbance at that time (A_t) by eq 16 with $[HBrO_2]_0 = A_0/(\epsilon_{295}\{HBrO_2\}l)$. Reactions

$$[HBrO_2] = [HBrO_2]_0\left(\frac{A_t - A_\infty}{A_0 - A_\infty}\right) \qquad (16)$$

13−15 may be interpreted as consisting of two parallel rate-determining steps, reactions 13 and 15, with reaction 15 preceded by the protonation equilibrium, reaction 14, suggesting eq 17. Equation 17 becomes pseudo-second-order in $[HBrO_2]$

$$\frac{d[HBrO_2]}{dt} = -2(k_{13} + k_{15}K_{14}[H^+])[HBrO_2]^2 \qquad (17)$$

under the present conditions in which $[H^+] > [HBrO_2]/2$. We

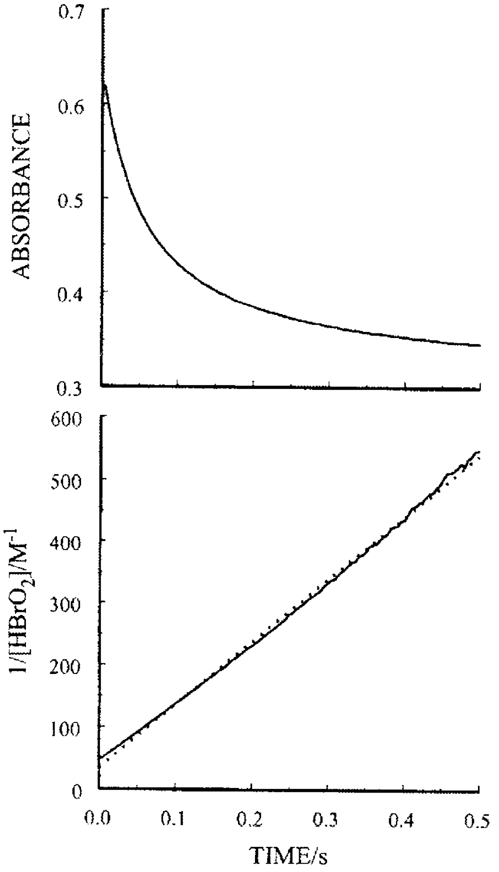


Figure 1. Disproportionation of $HBrO_2$ with $[HClO_4]_0 = 0.50$ M and $[HBrO_2]_0 \approx 0.011$ M. Top: absorbance vs time. Bottom: $1/[HBrO_2]$ vs time. $k_{exp} = 1011 \pm 5\ M^{-1}\ s^{-1}$ from dotted least-squares line; ≈95% reaction; temperature = 15 °C.

thus fit our experimental data to

$$\frac{1}{[\mathrm{HBrO_2}]} = \frac{1}{[\mathrm{HBrO_2}]_0} + k'_{\mathrm{exp}}t \qquad (18)$$

with

$$k_{\mathrm{exp}} = k'_{\mathrm{exp}}/2 = (k_{13} + k_{15}K_{14}[\mathrm{H^+}]) \qquad (19)$$

Figure 1 (bottom) shows that typically plots of $1/[HBrO_2]$ vs t are linear at high $[H^+]$ to well over 95% completion of reaction, although some curvature occurs at long reaction times in the lowest acidity measurements. This linearity supports our assumptions that $HBrO_2$ and HOBr are the only absorbing species present (eq 16) and that the kinetics of the reaction is governed by eq 17.

Figure 2 shows the dependence of k_{exp} on $[HClO_4]_0 = [H^+]_0$ in the range 0.04−0.7 M plotted according to eq 19.

This plot is linear supporting the form of eqs 17 and 19, and the least-squares line yields $k_{13} = 781 \pm 6\ M^{-1}\ s^{-1}$ and $K_{14}k_{15} = 1013 \pm 16\ M^{-2}\ s^{-1}$.

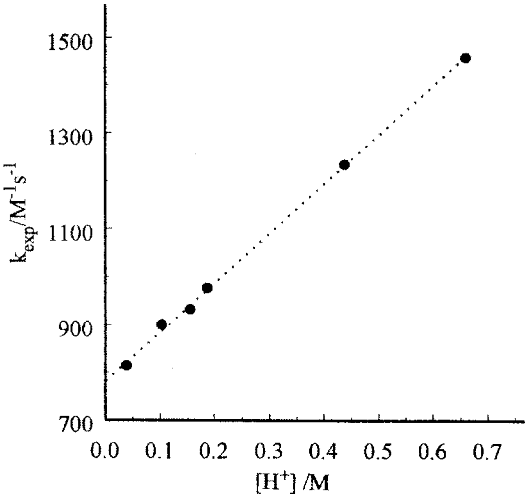


Figure 2. Plot of k_{exp} vs $[H^+]_0$ from $HClO_4$ at 25.0 °C. The dotted line is the least-squares fit to the six experimental points.

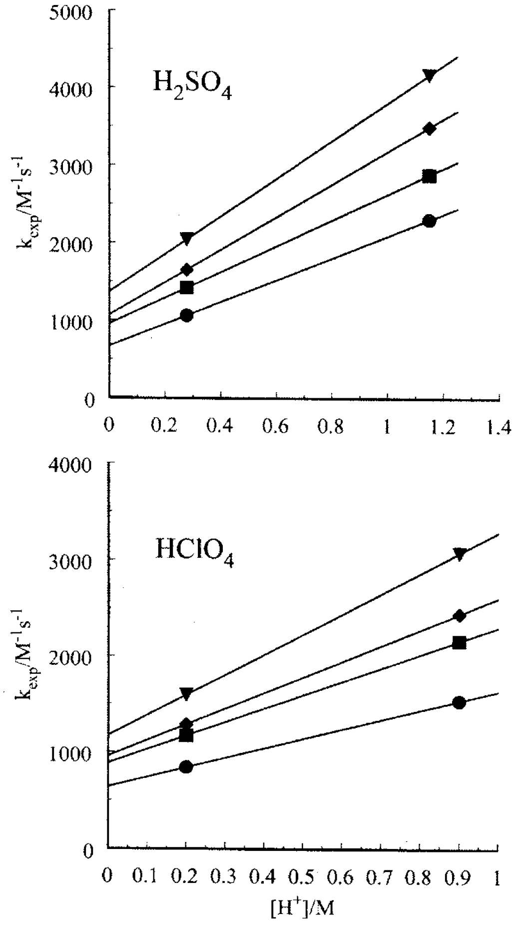


Figure 3. Plots of k_{exp} vs $[H^+]$ at various temperatures: (●) 15.0 °C; (■) 25.7 °C; (◆) 30.0 °C; (▼) 38.0 °C. The slopes are interpreted as $K_{14}k_{15}$ and the intercepts are interpreted as k_{13}. Bottom: $[H^+] = [HClO_4]$. Top: $[H^+]$ calculated from $[H_2SO_4]$ according to the data of Robertson and Dunford.[34]

Faria et al.[7,8] inferred $k_{13} = 800 \pm 100\ M^{-1}\ s^{-1}$ from their work at pH near $pK_a(HBrO_2) = 3.43$, $[HBrO_2]_0 = (2-5) \times 10^{-3}$ M, and 25 °C, in excellent (likely fortuitous) agreement with the above value of 781 $M^{-1}\ s^{-1}$ at 25 °C. Ariese and Nagy[30] report $K_{14}k_{15}[H^+] = 2200\ M^{-1}\ s^{-1}$ for $[H_2SO_4] = 0.5$ M, $[HBrO_2]_0 = 2.1 \times 10^{-3}$ M, and 24 °C, in reasonable agreement with the equivalent value of ≈1700 $M^{-1}\ s^{-1}$ read off Figure 3 for 0.5 M H_2SO_4 and 24.7 °C. Försterling and Varga[31] report the value $K_{14}k_{15}[H^+] = 2200\ M^{-1}\ s^{-1}$ at $[H_2SO_4] = 0.5$ M, $[HBrO_2]_0 \approx 10^{-5}$ M, and 20 °C, again somewhat larger than the present value. Finally, Noszticzius et al.[32] report $K_{14}k_{15}[H^+] \approx 2000\ M^{-1}\ s^{-1}$ at $[H_2SO_4] = 0.5$ M, $[HBrO_2]_0 \approx 10^{-5}$ M, and 24 °C. In general, our results seem to be about 25% smaller than previously reported values. Our raw absorbance (A) vs time data scale to k_{exp} ($M^{-1}\ s^{-1}$) by $\epsilon_{295}[HBrO_2]l/A_0$. Because there is little uncertainty in $\epsilon_{295}[HBrO_2]$, l, or A_0, this difference likely reflects an actual difference in rate.

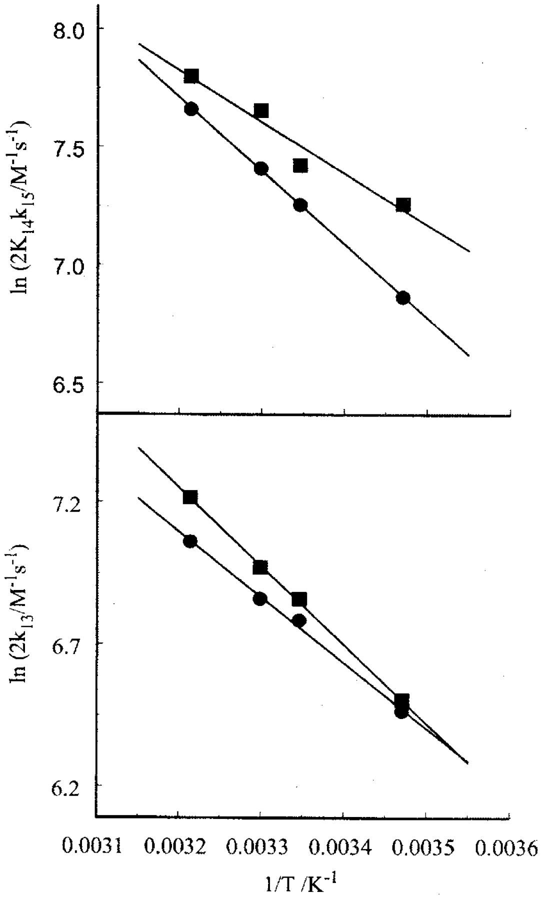


Figure 4. Arrhenius plots constructed from data in Figure 3. Bottom: intercepts (k_{13}). Top: slopes ($K_{14}k_{15}$). Symbols: (●) in $HClO_4$; (■) in H_2SO_4.

TABLE 1: Activation Parameters Derived from Figure 4 for the Reaction $2HBrO_2 \rightarrow HOBr + BrO_3^- + H^+$ in $HClO_4$ and H_2SO_4 Media

	$HClO_4$ medium		H_2SO_4 medium	
	k_{13}	$K_{14}k_{15}$	k_{13}	$K_{14}k_{15}$
$E^\ddagger$ (kJ/ mol)	19 ± 0.9	25.8 ± 0.5	23.0 ± 0.5	18 ± 3
$\Delta S^\ddagger$ [J/(K mol)]	-132 ± 3	-106 ± 1	-119 ± 1	-130 ± 11

Figure 3 shows dissection of k_{exp} into k_{13} and $K_{14}k_{15}$ in $HClO_4$ and H_2SO_4 media of varying acidity and at several temperatures. It is assumed that $[H^+]_0 = [HClO_4]_0$ in perchloric acid media, whereas $[H^+]_0$ in sulfuric acid media is taken from Robertson and Dunford.[34] The values of both k_{13} and $K_{14}k_{15}$ are somewhat higher in H_2SO_4 than in $HClO_4$ media of the same concentration. This effect is also noted in other experiments not reported here.

Figure 4 shows Arrhenius plots constructed on the basis of the data in Figure 3 yielding the activation parameters given in Table 1. Significant medium effects may be noted in Figures 3 and 4 by comparison of measurements in H_2SO_4 and $HClO_4$ media. We attribute the generally higher values of k_{13} and $K_{14}k_{15}$ in H_2SO_4 as compared to $HClO_4$ to general acid catalysis by HSO_4^- and perhaps decrease in a_{H_2O} in H_2SO_4 solutions. The quantities in Table 1 are quoted to misleading precision because the data points in Figure 4 are based on the two-point plots in Figure 3.

Estimation of $\Delta_f H^0\{HBrO_2(aq)\}$ and $\Delta_f H^0\{BrO_2(aq)\}$

The $\Delta_f H^0$ values of HOCl(aq), $HClO_2$(aq), $HClO_3$(aq), as well as of HOBr(aq) and $HBrO_3$(aq), are tabulated.[6] We estimate $\Delta_f H^0\{HBrO_2(aq)\}$ by assuming that $HBrO_2$(aq) lies proportionally between HOBr(aq) and $HBrO_3$(aq) as $HClO_2$(aq) is known to lie between HOCl(aq) and $HClO_3$(aq).[24] We assume the molecular structures HOBr=O and HOCl=O. The procedure involves estimation of the first and second Cl=O and Br=O coordinate-covalent bond strengths in $HClO_2$, $HClO_3$, $HBrO_2$, and $HBrO_3$. We calculate $\Delta_f H^0\{BrO_2(aq)\}$ from $\Delta_f H^0\{HBrO_2(aq)\}$ using an estimate of the H−O bond strength in $HBrO_2$. A summary of the results of this calculation is given in Table 3.

TABLE 2: Computed Values of $\Delta_f H_{298}^0\{HBrO_2(g)\}$ and $\Delta_f H_0^0\{HClO_2(g)\}$ in kJ/mol

isomer			
HOBrO	HOOBr	$HBrO_2$[a]	ref
47.0	29.0	253	19
55.2	33.9	266	20
43.0	11.0	251	21
44.0[c]			22

isomer			
HOClO	HOOCl	$HClO_2$[b]	ref
49.8	8.0	235	41

[a] Contains a Br−H bond. [b] Contains a Cl−H bond. [c] Derived from data in ref 22.

We begin by calculating the bond energy associated with the first Cl=O coordinate-covalent bond formed when HOCl is oxidized to $HClO_2$ by O_2.

$$HOCl(aq) \rightarrow {}^1/_2H_2(g) + {}^1/_2Cl_2(g) + {}^1/_2O_2(g) \tag{20}$$

$$\underline{{}^1/_2H_2(g) + {}^1/_2Cl_2(g) + O_2(g) \rightarrow HClO_2(aq)} \tag{21}$$

$$HOCl(aq) + {}^1/_2O_2(g) \rightarrow HClO_2(aq) \tag{22}$$

Recognizing $\Delta H_{22}^0 = \Delta H_{20}^0 + \Delta H_{21}^0$ with $\Delta H_{20}^0 = -\Delta_f H^0\{HOCl(aq)\} = 120.9$ kJ/mol and $\Delta H_{21}^0 = \Delta_f H^0\{HClO_2(aq)\} = -51.9$ kJ/mol yields $\Delta H_{22}^0 = 69.0$ kJ/mol. The positive value of ΔH_{22}^0 means $HClO_2$ is energetically unstable with respect to HOCl and O_2 and is a better oxidizing agent than is HOCl. The value of ΔH_{22}^0 also can be defined in terms of bond strengths. That is, $\Delta H_{22}^0 = {}^1/_2D(O{=}O) - D(Cl{=}O)_{first}$, where $D(Cl{=}O)_{first}$ is the strength of the first Cl=O bond in $HClO_2$. This yields $D(Cl{=}O)_{first} = {}^1/_2D(O{=}O) - \Delta H_{22}^0 = 498.4/2 - \Delta H_{22}^0 = 180.2$ kJ/mol, not surprisingly, a relatively weak bond.

We now estimate the strength of the second coordinate-covalent Cl=O bond formed by the oxidation of $HClO_2$ to $HClO_3$, $D(Cl{=}O)_{second}$.

$$^1/_2H_2(g) + {}^1/_2Cl_2(g) + {}^3/_2O_2(g) \rightarrow HClO_3(aq) \tag{23}$$

$$\underline{HClO_2(aq) \rightarrow {}^1/_2H_2(g) + {}^1/_2Cl_2(g) + O_2(g)} \tag{24}$$

$$HClO_2(aq) + {}^1/_2O_2(g) \rightarrow HClO_3(aq) \tag{25}$$

Recognizing $\Delta H_{25}^0 = \Delta H_{23}^0 + \Delta H_{24}^0$ with $\Delta H_{23}^0 = \Delta_f H^0\{HClO_3(aq)\} = -104.0$ kJ/mol and $\Delta H_{24}^0 = -\Delta_f H^0\{HClO_2(aq)\}$ yields $\Delta H_{25}^0 = -52.1$ kJ/mol. $HClO_3$ is energetically stable with respect to $HClO_2$ and O_2 and is, in fact, found to be a relatively stable species, as is observed experimentally. Representing ΔH_{25}^0 in terms of bond strengths, yields $D(Cl{=}O)_{second}$ in $HClO_3$ as ${}^1/_2D(O{=}O) - \Delta H_{25}^0 = 301.3$ kJ/mol. Thus $D(Cl{=}O)_{second}$ is 121.1 kJ/mol larger than $D(Cl{=}O)_{first}$. The sum $D(Cl{=}O)_{first} + D(Cl{=}O)_{second} = 481.5$ kJ/mol.

TABLE 3: Estimated Values of Δ_rH^0, Δ_rG^0, and Δ_rS^0 for Reactions 1−7, Nominally at 298 K

reaction	Δ_rH^0 (kJ/mol)[a]	Δ_rG^0 (kJ/mol)[b]	Δ_rS^0 [J/(K mol)][c]
(1) $Br^- + HOBr + H^+ \rightleftarrows Br_2 + H_2O$	−54	−44	−34
(2) $Br^- + HBrO_2 + H^+ \rightleftarrows HOBr + HOBr$	−71	−63	−27
(3) $Br^- + BrO_3^- + 2H^+ \rightleftarrows HBrO_2 + HOBr$	43	1	143
(4) $HBrO_2 + HBrO_2 \rightleftarrows HOBr + BrO_3^- + H^+$	−114	−64	−171
(5) $HBrO_2 + BrO_3^- + H^+ \rightleftarrows 2BrO_2 + H_2O$	129	34	324
(6) Ce(IIII) + $BrO_2 + H^+ \rightleftarrows$ Ce(IV) + $HBrO_2$	−31	−5	−89
(7) Ce(IV) + $BrO_2 + H_2O \rightleftarrows$ Ce(III) + $BrO_3^- + 2H^+$	−97	−29	−232

[a] Based on values of $\Delta_fH^0\{HBrO_2(aq)\} = -33$ kJ/mol and $\Delta_fH_{298}{}^0\{BrO_2(aq)\} = 157$ kJ/mol derived here. [b] From ref 5. [c] Calculated from columns a and b.

We now determine the sum $D(Br{=}O)_{first} + D(Br{=}O)_{second}$ for $HBrO_3$ and apportion it between $D(Br{=}O)_{first}$ and $D(Br{=}O)_{second}$ according to the above calculated relative magnitudes of $D(Cl{=}O)_{first}$ and $D(Cl{=}O)_{second}$.

$$^1/_2H_2(g) + {}^1/_2Br_2(l) + {}^3/_2O_2(g) \rightarrow HBrO_3(aq) \qquad (26)$$

$$HOBr(aq) \rightarrow {}^1/_2H_2(g) + {}^1/_2Br_2(l) + {}^1/_2O_2(g) \qquad (27)$$

$$HOBr(aq) + O_2(g) \rightarrow HBrO_3(aq) \qquad (28)$$

Recognizing $\Delta H_{28}{}^0 = \Delta H_{26}{}^0 + \Delta H_{27}{}^0$ with $\Delta H_{26}{}^0 = \Delta_fH^0\{HBrO_3(aq)\} = -67.1$ kJ/mol and $\Delta H_{27}{}^0 = -\Delta_fH^0\{HOBr(aq)\}$ yields $\Delta H_{28}{}^0 = 45.9$ kJ/mol. Expressing $\Delta H_{28}{}^0$ in terms of bond strengths yields eq 29. Thus $D(Br{=}O)_{first} + D(Br{=}O)_{second} = D(O{=}O) - \Delta H_{28}{}^0 = 452.5$ kJ/mol. This value is comparable to the equivalent quantity for $HClO_3$, 481.5 kJ/mol, indicating that the sum of the two coordinate-covalent Cl=O bonds in $HClO_3$ is only a little more than the analogous sum in $HBrO_3$. This result may be rationalized by noting that the different sizes of the central Cl and Br atoms have counteracting effects on bonding to O. The smaller atomic diameter of Cl as compared to Br leads to more tightly held valence electrons, and hence potentially stronger bonds in $HClO_3$ compared to $HBrO_3$. However, it is also more difficult to fit three oxygen atoms around Cl than Br, which tends to destabilize $HClO_3$ relative to $HBrO_3$.

$$\Delta H_{28}{}^0 = D(O{=}O) - D(Br{=}O)_{first} - D(Br{=}O)_{second} \qquad (29)$$

The sum $(D(Br{=}O)_{first} + D(Br{=}O)_{second})$ is now apportioned between $D(Br{=}O)_{first}$ and $D(Br{=}O)_{second}$ by assuming that they are in the same proportion as are $D(Cl{=}O)_{first}$ and $D(Cl{=}O)_{second}$.

Thus,

$$\frac{D(Br = O)_{first}}{D(Br = O)_{first} + D(Br = O)_{second}} = \frac{D(Cl = O)_{first}}{D(Cl = O)_{first} + D(Cl = O)_{second}} = \frac{180.2}{481.5} = 0.3742 \qquad (30)$$

Equation 30 leads to $D(Br{=}O)_{first} = 0.3742[D(Br{=}O)_{first} + D(Br{=}O)_{second}] = 169.3$ kJ/mol.

It is now possible to estimate $\Delta_fH^0\{HBrO_2(aq)\}$ via

$$HOBr(aq) + {}^1/_2O_2(g) \rightarrow HBrO_2(aq) \qquad (31)$$

$$^1/_2H_2(g) + {}^1/_2Br_2(l) + {}^1/_2O_2(g) \rightarrow HOBr(aq) \qquad (32)$$

$$^1/_2H_2(g) + {}^1/_2Br_2(l) + O_2(g) \rightarrow HBrO_2(aq) \qquad (33)$$

Recognizing $\Delta H_{33}{}^0 = \Delta_fH^0\{HBrO_2(aq)\} = \Delta H_{31}{}^0 + \Delta H_{32}{}^0$, with $\Delta H_{31}{}^0$ expressed in terms of bond strengths as $^1/_2D(O{=}O) - D(Br{=}O)_{first} = 79.9$ kJ/mol and $\Delta H_{32}{}^0 = \Delta_fH^0\{HOBr(aq)\}$ yields $\Delta_fH^0\{HBrO_2(aq)\} = -33.1$ kJ/mol as compared to the tabulated[6] value $\Delta_fH^0\{HClO_2(aq)\} = -51.9$ kJ/mol.

The value of $\Delta_fH^0\{BrO_2(aq)\}$ can be estimated in a similar fashion using

$$^1/_2H_2(g) + {}^1/_2Br_2(l) + O_2(g) \rightarrow HBrO_2(aq) \qquad (34)$$

$$HBrO_2(aq) \rightarrow BrO_2(aq) + H(aq) \qquad (35)$$

$$H(aq) \rightarrow {}^1/_2H_2(aq) \qquad (36)$$

$$^1/_2H_2(aq) \rightarrow {}^1/_2H_2(g) \qquad (37)$$

$$^1/_2Br_2(l) + O_2(g) \rightarrow BrO_2(aq) \qquad (38)$$

Recognizing $\Delta H_{38}{}^0 = \Delta_fH^0\{BrO_2(aq)\} = \Delta H_{34}{}^0 + \Delta H_{35}{}^0 + \Delta H_{36}{}^0 + \Delta H_{37}{}^0$ with $\Delta H_{34}{}^0 = \Delta_fH^0\{HBrO_2(aq)\}$, $\Delta H_{35}{}^0 = D(OBrO{-}H) = 406.0$ kJ/mol, $\Delta H_{36}{}^0 = -{}^1/_2D(H{-}H) = -218.0$ kJ/mol, and $\Delta H_{37}{}^0 = -{}^1/_2\Delta H_{solvation}{}^0\{H_2(aq)\} = +2.1$ kJ/mol yields $\Delta_fH^0\{BrO_2(aq)\} = 157$ kJ/mol. The value of $D(OBrO{-}H)$ is estimated as $D(HO{-}H)$ adjusted for the ratio $K_w/K_a\{HBrO_2\} \approx 10^{-10}$ via the relationship $D(OBrO{-}H) = D(HO{-}H) - RT \ln 10^{-10} = 463-57 = 406$ kJ/mol. This approximation assumes that the difference between the ΔG^0 values for K_w and $K_a\{HBrO_2\}$ is mainly enthaplic. The derived value of $\Delta_fH^0\{BrO_2(aq)\} = 157$ kJ/mol can be compared with the tabulated[6] values $\Delta_fH^0\{BrO_2(c)\} = 48.5$ kJ/mol and $\Delta_fH^0\{ClO_2(aq)\} = 74.9$ kJ/mol, the latter value in keeping with the observation that ClO_2 is a more stable species than is BrO_2.[35]

The only experimental determination of Δ_fH^0 (BrO_2) we know of is the gas-phase value due to Klemm et al.[17] of $\Delta_fH_0{}^0\{BrO_2(g)\} = 173.4 \pm 4.3$ kJ/mol and $\Delta_fH_{298}{}^0\{BrO_2(g)\} = 163.9 \pm 4.4$ kJ/mol, as compared to our value of $\Delta_fH_{298}{}^0\{BrO_2(aq)\} \approx 157$ kJ/mol. The ≈ 7 kJ/mol difference between these gas-phase and aqueous values of $\Delta_fH_{298}{}^0\{BrO_2\}$ is of the order and direction expected as the solvation energy of BrO_2 in water.

A number of computational values of $\Delta_fH^0\{BrO_2(g)\}$ have been reported. All are lower than the experimental value of Klemm et al.[17] and include those due to Workman and Francisco[36] of 144 ± 12 kJ/mol, Alcami and Cooper[37] of 156.9 kJ/mol, Lee[16] of 163.9 ± 7.1 kJ/mol, and Klemm et al.[17] of 164 ± 8 kJ/mol. The first two values can be improved to 162.7 and 165.6 kJ/mol, respectively, by inclusion of spin−orbit coupling.[16,17] A value $\Delta_fH_0{}^0\{BrO_2(g)\} = 161.5$ kJ/mol was estimated by Chase[24] using a trend analysis similar to that employed here. Thus we feel that our value of $\Delta_fH_{298}{}^0\{BrO_2(aq)\} \approx 157$ kJ/mol is reasonably reliable, perhaps to within a few kJ/mol.

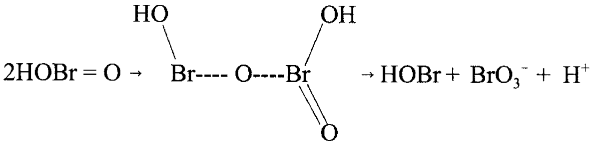
Our estimated value of $\Delta_fH_{298}{}^0\{HBrO_2(aq)\} = -33.1$ kJ/mol is the basis of the above apparently accurate value of $\Delta_fH^0\{BrO_2\}(aq)$ and is comparable to a value of −37 kJ/mol inferred from an experimental value of $\Delta_f H^0\{BrO_2^-(aq)\}$ due to Kennedy and Lister,[23] which is the only pertinent experimental result we know of. The tabulated[6] value $\Delta_f H^0\{HClO_2(aq)\} = -51.9$ kJ/mol is joined by strongly negative experimental estimates of −57.2,[38] −85.2,[39] and −70 kJ/mol, the last value inferred from a value of $\Delta_f H^0\{ClO_2^-(aq)\}$due to Schmitz.[40]

However, unlike the case of BrO_2, where aqueous and computational gas-phase heats of formation agree well, the above negative values of $\Delta_f H_{298}{}^0\{HBrO_2\ (aq)\}$ and $\Delta_f H^0\{HClO_2(aq)\}$ are in substantial disagreement with positive computational $\Delta_f H^0$ (g) values of various of their isomers, as is shown in Table 2. Thus $HClO_2$ and $HBrO_2$ are apparently considerably more stable in water than in the gas phase, apparently having quite significant solvation energies. The computed $HClO_2$ potential surface of Sumanthi and Peyerimhoff[42] shows minima at the covalently bound species HOOCl, HOCl═O, and $HClO_2$, as well as for various complex, loose, hydrogen-bonded minima. Thus we suggest that $HBrO_2$ (and $HClO_2$) are complex, strongly hydrogen bonded species in aqueous solution and indeed may not even have the simple oxyacid structures normally assumed.

Table 3 shows $\Delta_r H^0$ and $\Delta_r S^0$ values for reactions 1−7 calculated on the basis of our estimates of $\Delta_f H_{298}{}^0\{BrO_2(aq)\}$ and $\Delta_f H_{298}{}^0\{HBrO_2\ (aq)\}$. Although these quantities are somewhat crude estimates, they will be of use to people interested in dynamic temperature effects in the Belousov−Zhabotinsky reaction.[11−13]

Conclusion

The kinetics of the disproportionation of $HBrO_2$ to HOBr, BrO_3^-, and H^+ (reaction 4) has been experimentally investigated at various temperatures in aqueous $HClO_4$ and H_2SO_4 media and found to be second-order in [$HBrO_2$], with the experimental rate constant being composed of terms first-order and zero-order in [H^+]. Significant medium effects are found in the two rate constants in $HClO_4$ and H_2SO_4 and their activation parameters. It is suggested that the [H^+]-independent terms reflect reaction via a simple oxygen-atom transfer,



$$2HOBr{=}O \rightarrow \overset{HO\diagdown}{Br}{-}{-}{-}{-}O{-}{-}{-}{-}\underset{\backslash\backslash O}{\overset{\diagup OH}{Br}} \rightarrow HOBr + BrO_3^- + H^+ \qquad (39)$$

whereas the [H^+]-dependent terms reflect something like the more complex route below.

$$H^+ + HO{-}Br{=}O \rightleftarrows [H_2O{-}Br{=}O]^+ \rightleftarrows H_2O + {}^+Br{=}O \qquad (40)$$

$$HOBr{=}O + {}^+Br{=}O \rightleftarrows HOBr\text{- -}O\text{- -}{}^+Br{=}O \rightarrow HOBr + O{=}Br^+{=}O \qquad (41)$$

$$O{=}Br^+{=}O + H_2O \rightarrow 2H^+ + BrO_3^- \qquad (42)$$

Reactions 40−42 offer a number of opportunities for medium effects in aqueous H_2SO_4 arising from general-acid catalysis by HSO_4^-, solvation of charged intermediates by HSO_4^- and SO_4^{2-}, and changes in a_{H_2O}.

The values $\Delta_f H_{298}{}^0\{BrO_2\ (aq)\} \approx 157$ kJ/mol and $\Delta_f H_{298}{}^0\{HBrO_2\ (aq)\} \approx -33$ kJ/mol are estimated using a trend analysis based on the known $\Delta_f H_{298}{}^0$(aq) values of HOCl, $HClO_2$, ClO_2, $HClO_3$, HOBr, and $HBrO_3$. The estimated value of $\Delta_f H_{298}{}^0\{BrO_2(aq)\}$, which is derived from our estimated value of $\Delta_f H_{298}{}^0\{HBrO_2(aq)\}$, is in good agreement with both a recent experimental gas-phase value and recent calculated gas-phase values. However, our value of $\Delta_f H_{298}{}^0\{HBrO_2(aq)\}$, though in agreement with an estimated aqueous experimental value, is much more negative than recent calculated gas-phase values. Thus we conclude that $HBrO_2$ is a complex, heavily solvated species in water.

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