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Communication

Formation of High Concentrations of BrO_2 in Acidic Bromate Solutions

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A new procedure to produce the BrO_2 transient species allowed time-resolved UV–vis spectra that show a structured band ($\lambda_{max} = 502$ nm) in dichloromethane to be obtained. In water, because of the increase of the dielectric constant, the λ_{max} presents a blue shift to 474 nm and the species decomposes much faster. The time-resolved spectra show evidence for its equilibrium with a nonidentified colorless form. This route opens new possibilities to the study this species in solution.

Treinin and Yaacobi[1] were the first to suggest that the transient species ($\lambda_{max} = 460$ nm) formed during the flash photolysis of aqueous bromate solution should be assigned to BrO_2. Buxton and Dainton[2] were the first to estimate its molar absorption coefficient, ϵ, as 1×10^3 L mol^{-1} cm^{-1} ($\lambda_{max} = 475$ nm). Since then, many authors[3] observed the same spectra generated, in aqueous solution, by pulse radiolysis or flash photolysis of bromate solutions or by reacting bromate with bromite or Ce^{3+} in acidic solutions. In this Communication we show the formation of this transient species during the decomposition of acidic bromate solution, its UV−vis spectra in dichloromethane, acetonitrile, and water, the evidence for its equilibrium with a colorless form, and its decay in solution.

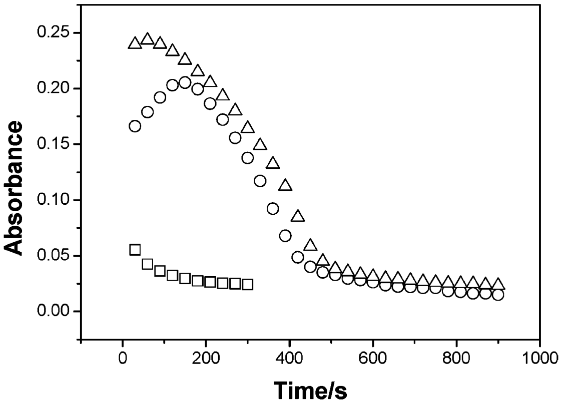

Figure 1. Appearance of BrO_2 by the increase of temperature up to 25 °C and its decay at 25 °C, in dichloromethane solution ($\lambda = 502$ nm). See text for additional experimental conditions. Symbols ○ and △ indicate two similar experiments. ○ indicates an experiment in which the solution initial temperature, at the time it was transferred to the cuvette, was approximately 15 °C; for △ the initial acquisition temperature is approximately 20 °C. Decay of BrO_2 in water ($\lambda = 474$ nm) is shown by the curve □.

To produce this very unstable and elusive transient species we have followed an experimental procedure that comprises the addition of three parts (by volume) of 2.5 mol L^{-1} sodium bromate solution to five parts of 70% $HClO_4$ with stirring at, approximately, −10 °C. This mixture is then extracted with 30 parts of dichloromethane and transferred to a round-bottom flask in which argon is bubbled to reduce the volume until approximately half of the initial. All these steps take no more than, approximately, 10 min. The dichloromethane solution is then transferred to a standard size quartz cuvette (1 cm path length) tightly closed by a Teflon plug and inserted in the UV−vis single beam diode-array spectrophotometer HP 8452A. The sample compartment was maintained at 25 °C by a circulating bath. Analytical grade reagents were used without any additional purification.

At the end of the argon bubbling step the dichloromethane solution presents a characteristic pink color that after some time disappears completely. This can be followed by UV−vis spectroscopy as shown in Figures 1 and 2. The $\lambda_{max} = 502$ nm, which can be seen in Figure 2, allow this pink color to be attributed to BrO_2, as all other known bromine species absorb at significantly lower wavelength. The use of other gases such as hydrogen or nitrogen or even not bubbling a

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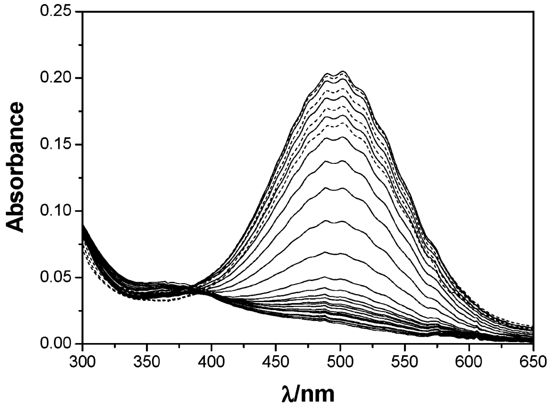

Figure 2. Time series spectra for the formation and decay of BrO_2 in dichloromethane (same experiment indicated by ○ in Figure 1). Broken lines indicate that the band at 502 nm is increasing as the time is running. Full lines indicate that intensity of the band is decreasing as time goes. Spectra were taken at each 30 s. See text for experimental conditions.

gas does not change the speed of disappearance of the color. When the dichloromethane solution was concentrated under vacuum, the same behavior was observed.

The initial increase of the color intensity observed for the ○ data in Figure 1 (and only for the first and second △ data points) can be explained if we postulate an equilibrium between a colorless species and the pink transient species. As the dichloromethane solution warms to 25 °C, the equilibrium position shifts from the colorless species to the pink species (notice that the dichloromethane evaporation by argon bubbling decreases the temperature). This proposition is confirmed by the fact that the solution loses its color when it is cooled below −10 °C and the pink color reappears when the solution is warmed again to room temperature. Otherwise, maintaining the reaction mixture at low temperature for a long time reduces the color intensity observed when the solution is warmed. This shows that the colorless transient species is not stable, even at low temperature.

If the transient species formed in the initial aqueous acidic solution is not extracted with dichloromethane, the pink color is fainter and after some time a colorless gas starts to bubble from the solution. After a further few minutes the solution becomes light yellow, indicating bromine formation, which is confirmed by the increase of a band with λ_{max} in the range of 390 nm to 400 nm (Figure 3). After some additional time a huge amount of gas and bromine starts to be released.

The solution of BrO_2 in dichloromethane does not show any evolution of a colorless gas, but the solution goes to a light yellow color, indicating bromine formation, which is confirmed by the UV−vis spectra.

In Figure 2 we can see the UV−vis spectra of the dichloromethane solution at several times as the pink color is forming, reaches a maximum intensity, and then disappears. These spectra show a maximum at 502.0 nm and a sequence of small maxima at 474.4, 489.0, 502.0, 514.4, and 526.9 nm. In aqueous solution (Figure 3), the pink color looks the same but the UV−vis spectra show $\lambda_{max} = 474$ nm and a band without structure. From Figure 1 it is clear that the stability of this species is much lower in water than in dichloromethane. If we change the solvent from dichloromethane to acetonitrile, we observe a band without structure with maximum absorbance at 488 nm. This shows that λ_{max} presents a blue shift with the increase of the dielectric constant of the solvent (78.30 for water, 37.5 for acetonitrile, 9.08 for dichloromethane), as shown in Figure 4.

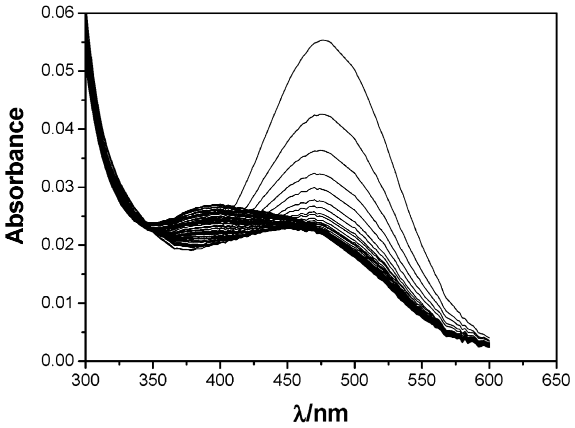

Figure 3. Time series spectra for the decay of BrO_2 in water (same experiment indicated by □ in Figure 1). Spectra were taken at each 30 s. Initial concentrations: $[BrO_3^-] = 0.5$ mol L^{-1}, $[HClO_4] = 5.8$ mol L^{-1}.

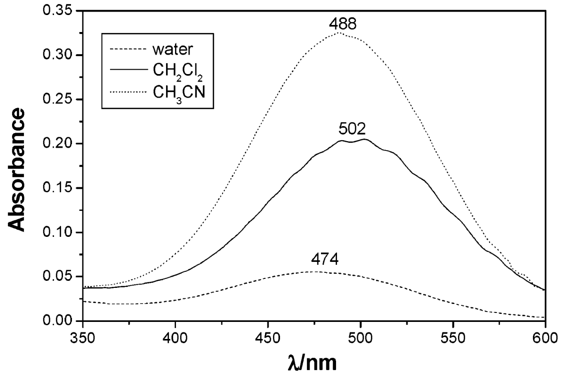

Figure 4. UV−vis spectra of BrO_2 in different solvents, showing the blue shift of the maximum as the dielectric constant increases.

Comparison of the BrO_2 spectra in Figure 4 with the UV−vis spectra for ClO_2 shows some similarities. Despite the fact that the λ_{max} for ClO_2 is at lower wavelength (in a range of 357 to 360 nm depending on the solvent), the ClO_2 spectrum has a similar sequence of small maxima which is more visible in solvents with low polarity.[4] The λ_{max} for ClO_2 shows a blue shift with the increase of the dielectric constant of the solvent but at much less extension than for BrO_2. Changing solvent from acetonitrile to water causes a blue shift of 14 nm for BrO_2 but only 0.9 nm for ClO_2. This shows that the difference between the polarity of fundamental and excited states for ClO_2 is significantly lower than for BrO_2.

Considering the maximum absorbances shown in Figure 1, equal to 0.25 and 0.055, in dichloromethane and water, respectively, and using the ϵ value determined by Buxton and Dainton in aqueous solution, we found that the maximum concentration we were able to obtain is, approximately, 2.5×10^{-4} mol L^{-1} and 5.5×10^{-5} mol L^{-1} in dichlo-

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romethane and water, respectively. It is worth mentioning that this calculated concentration in dichloromethane was made supposing that the ϵ is the same as in water.

The experimental procedure we have used to obtain the bromine dioxide in solution has some similarities with the procedure used by Noszticzius *et al.*[5] to produce bromine-free HOBr (method b) by reaction 1. In their case, probably because of the lower bromate concentration and higher temperature, the concentration of intermediate BrO_2 was too low and no pink color could be seen, only oxygen formation.

$$BrO_3^- + H^+ \rightarrow HOBr + O_2 \tag{1}$$

The huge amount of gas and bromine, which is observed if the water solution is not extracted with dichloromethane, can be explained by the accumulation of HOBr, followed by the reaction 2, again proposed by Noszticzius *et al.*[5]

$$4HOBr \rightarrow 2Br_2 + 2H_2O + O_2 \tag{2}$$

The abrupt formation of Br_2 can be explained by the reaction between bromine and bromate, reaction 3, studied by Försterling *et al.*,[6] which does not allow bromine accumulation while there is bromate in the medium, only oxygen formation. After bromate is exhausted, HOBr which has been accumulating will decompose by reaction 2.

$$2Br_2 + HBrO_3 + 2H_2O \rightarrow 5HOBr \tag{3}$$

Concerning the formation of BrO_2, it can be explained by the reactions 4 and 5. Reaction 4 is similar to reaction 1 and

$$BrO_3^- + H^+ \rightarrow HBrO_2 + {}^1/_2O_2 \tag{4}$$

$$BrO_3^- + HBrO_2 + H^+ \rightarrow 2BrO_2 + H_2O \tag{5}$$

can be the first step of reaction 1. Reaction 5 is very well-known and has been employed by Försterling *et al.*[3f] to produce BrO_2 at a concentration 10 times less than we were able to produce, in aqueous solution.

As shown in Figure 1, the decomposition of BrO_2 in dichloromethane solution presents a profile similar to some autocatalytic decays.[7] Otherwise, this profile can be explained by the simultaneous processes of its formation (from a colorless form) and decomposition. In this way, no autocatalytic decomposition process can be assured by this time.

The decomposition of BrO_2 in alkaline and neutral solutions was established by Buxton and Dainton[2] on the basis of reactions 6 and 7 being always second order in $[BrO_2]$.

$$2BrO_2 \rightleftarrows Br_2O_4 \tag{6}$$

$$2BrO_2 + H_2O \rightleftarrows BrO_2^- + BrO_3^- + 2H^+ \tag{7}$$

Reaction 6 has an equilibrium constant $K_6 = 1.9 \times 10^4$ at 20 °C, based on the rates $k_6 = 1.4 \times 10^9$ L mol^{-1} s^{-1} and $k_{-6} = 7.5 \times 10^4$ s^{-1}.[8] Reaction 7 is understood as the sum of reaction 6 with reaction 8 and has an equilibrium constant $K_7 = 1 \times 10^6$ and rate constants $k_7 = 4.2 \times 10^7$ L mol^{-1} s^{-1} and $k_{-7} = 42$ L^2 mol^{-2} s^{-1}.[8]

$$Br_2O_4 + H_2O \rightleftarrows BrO_2^- + BrO_3^- + 2H^+ \tag{8}$$

From these reactions, it is quite natural to suppose that the colorless species in equilibrium with BrO_2 is the Br_2O_4 species. Otherwise, until now, there is not any experimental evidence for the existence of the Br_2O_4 dimer,[9] leaving this proposition as a matter to be verified in the future.

Our results show, for the first time, the evidence for an equilibrium between BrO_2 and some colorless form, reinforcing the initial Buxton and Dainton proposition for reaction 6, but the existence of the dimer Br_2O_4 has still to be determined.

As the maximum BrO_2 concentration we obtained is much higher than the concentrations until now reported in the literature, it makes this procedure a new better option for anyone who intends to study this species in solution.

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