

# Hydrogen peroxide evolution during V-UV photolysis of water

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Received 5th January 2005, Accepted 6th April 2005

First published as an Advance Article on the web 18th April 2005

Hydrogen peroxide evolution during the vacuum-ultra-violet (V-UV, 172 nm) photolysis of water is considerably affected by the presence of oxalic acid (employed as a model water pollutant) and striking differences are observed in the absence and in the presence of dioxygen.

Water pollution due to toxic organic compounds remains a serious problem worldwide. In the last two decades, advanced oxidation processes<sup>1</sup> (AOP) have been developed for the treatment of wastewaters, and most of these processes are based on the production of hydroxyl radicals (HO•) as highly oxidizing species. V-UV photolysis of water is a particularly interesting and powerful source of HO•.<sup>2,3</sup> Indeed, absorption of water increases steadily from approx. 190 to 120 nm,<sup>4</sup> and its electronic excitation in this spectral region leads to its homolysis with the production of hydrogen atoms and hydroxyl radicals ( $\Phi_{\text{HO}} = 0.42$  at 172 nm).<sup>5</sup> The quantum yield for the production of hydrated electrons is lower than 0.05.



This technique presents the advantage of producing HO• without addition of any supplementary oxidant (e.g. hydrogen peroxide or ozone) or catalyst. V-UV irradiation employing Xe-excimer<sup>6</sup> radiation sources (quasi-monochromatic emission at 172 nm) has been applied to water treatment,<sup>1,3,7</sup> and more recently to the treatment of gaseous streams<sup>8</sup> and adsorbent regeneration.<sup>9</sup>

In this work, we have investigated the production of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) during irradiation of water at 172 nm in the absence and in the presence of dioxygen and/or oxalic acid. The latter compound is one of the intermediates most often found during the oxidative degradation of organic water contaminants. To the best of our knowledge, no detailed investigation of the H<sub>2</sub>O<sub>2</sub> production during V-UV irradiation of water has been published so far, although such an investigation might provide a better understanding of the mechanistic pathways involved in the oxidative process induced by V-UV photolysis of aqueous solutions.

## Irradiation of pure water free from dioxygen

In a first step, pure water free from dioxygen was irradiated at 172 nm using a Xe-excimer radiation source,<sup>†</sup> and the formation of hydrogen peroxide was analyzed during irradiation.<sup>‡</sup> Fig. 1 (open symbols) shows that the concentration of H<sub>2</sub>O<sub>2</sub> increased regularly until a quasi-stationary concentration ( $[\text{H}_2\text{O}_2]_{\text{s}}$ ) of  $6.10 \times 10^{-5} \text{ mol L}^{-1}$  was reached after approx. 60 minutes of irradiation. Under our experimental conditions, the main reactions involved, that may explain the experimental observations, are the following:<sup>10,11</sup>

### H<sub>2</sub>O<sub>2</sub> formation.

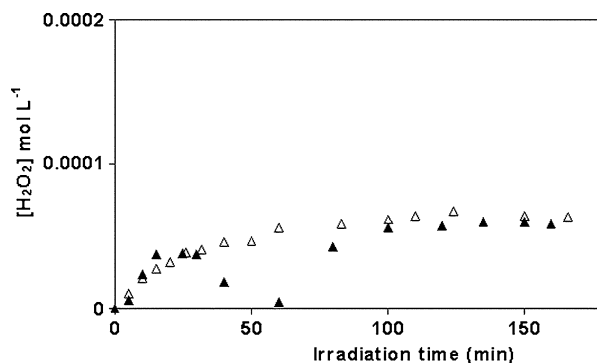
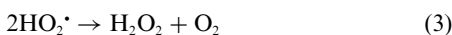
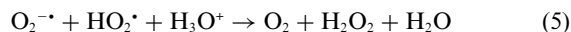
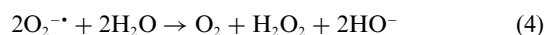
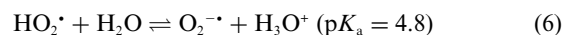


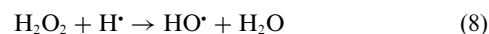
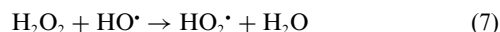
Fig. 1 Formation of hydrogen peroxide during V-UV irradiation in the absence of dioxygen: (Δ) in pure water and (▲) in an aqueous solution of oxalic acid ( $9.54 \times 10^{-3} \text{ mol L}^{-1}$ ).



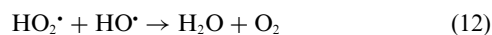
### Acid/Base equilibrium.



### H<sub>2</sub>O<sub>2</sub> decomposition.



### Termination reactions.

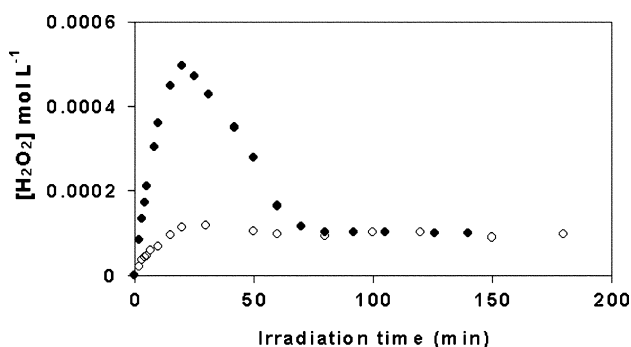


Hydrogen peroxide may be formed by recombination of HO• radicals (reaction (2)) produced by photolysis of water (reaction (1)), as well as by the disproportionation of the perhydroxyl radical (HO<sub>2</sub>•) and its conjugated base, the superoxide anion (O<sub>2</sub><sup>•−</sup>) (reactions (3) to (5), reaction (4) being very slow).<sup>12</sup> Under our experimental conditions, the pH value was 5.5 and therefore both species, HO<sub>2</sub>• and O<sub>2</sub><sup>•−</sup>, were present in solution (reaction (6)). Hydrogen peroxide can be decomposed by reaction with hydroxyl radicals and hydrogen atoms to yield perhydroxyl radicals (reaction (7)) and hydroxyl radicals (reaction (8)), respectively.<sup>13,14</sup> We have not considered the photolysis of H<sub>2</sub>O<sub>2</sub> as its concentration remains very low compared to the water concentration ( $55 \text{ mol L}^{-1}$ ) and photons emitted at 172 nm are totally absorbed by water on less than 100 μm (absorption

coefficient of water:  $550\text{ cm}^{-1}$ ).<sup>5,15</sup> The set of radicals formed are also involved in termination reactions (reactions (9)–(12)).

The photostationary state (Fig. 1, open symbols) is reached when the rate of production of  $\text{H}_2\text{O}_2$  (reactions (2) to (5)) is equal to the rate of its consumption (reactions (7) and (8)), the concentration of  $\text{H}_2\text{O}_2$  at the stationary state ( $[\text{H}_2\text{O}_2]_s$ ) depending on the values of the rate constants and on the concentrations of the various species involved.

#### Irradiation of pure water in the presence of dioxygen



**Fig. 2** Formation of hydrogen peroxide during V-UV irradiation in the presence of dioxygen: (○) in pure water and (●) in an aqueous solution of oxalic acid ( $9.54 \times 10^{-3}\text{ mol L}^{-1}$ ).

The evolution of the  $\text{H}_2\text{O}_2$  concentration when irradiating pure water in the presence of dioxygen (Fig. 2, open symbols) is similar to that observed in the absence of dioxygen (Fig. 1, open symbols), but the  $[\text{H}_2\text{O}_2]_s$  is nearly doubled ( $1.1 \times 10^{-4}\text{ mol L}^{-1}$  vs.  $6.0 \times 10^{-5}\text{ mol L}^{-1}$ ). In a work concerning the oxidative degradation of 4-chlorophenol by V-UV photolysis of water, Jakob *et al.*,<sup>16</sup> indicated that they observed in air-equilibrated water a maximum concentration of  $[\text{H}_2\text{O}_2]$  of  $1.0 \times 10^{-4}\text{ mol L}^{-1}$ .

Under permanent bubbling of dioxygen, reactions (1) to (12) listed above are still valid. However, in this case, dioxygen molecules trap efficiently H atoms (reaction (13), rate constant of approx.  $10^{10}\text{ L mol}^{-1}\text{ s}^{-1}$ )<sup>12</sup> produced by water photolysis (reaction (1)).

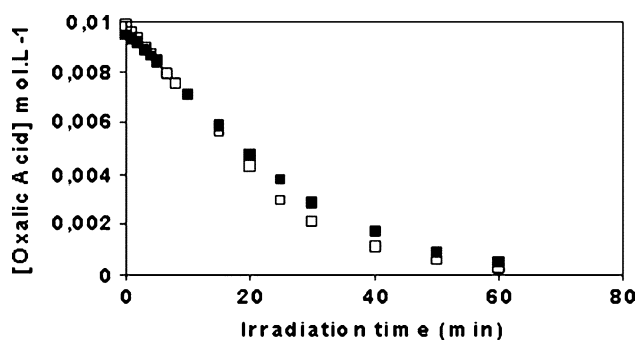


Reaction (13) leads to a high increase of the concentration of  $\text{HO}_2^\bullet$  in the solution and therefore to an increase of the concentration of  $\text{H}_2\text{O}_2$  produced (reactions (3) to (5)).

#### Irradiation of an aqueous solution of oxalic acid free from dioxygen

The evolution of the concentration of oxalic acid (or ethanedioic acid,  $\text{HOOC}\text{COOH}$ ) in an aqueous solution under irradiation at 172 nm, in the absence of dioxygen, is shown in Fig. 3 (open symbols). The acid is totally mineralised after 60 minutes of irradiation. A comparative analysis by mass spectrometry and total organic carbon measurements showed identical concentration decreases, within experimental error.<sup>§</sup> Therefore, it can be concluded that oxalic acid is directly mineralised to carbon dioxide and water, without formation of any stable organic intermediate (*e.g.* formic acid). These results are in agreement with those obtained by Karpel *et al.* in the case of the degradation of oxalic acid by the  $\text{H}_2\text{O}_2$ /UV process.<sup>17</sup> It should be noted that the  $\pi$ – $\pi^*$  absorption band of aliphatic dicarboxylic acids is located at *ca.* 170 nm.<sup>18</sup> However, the fraction of incident radiation at 172 nm absorbed by oxalic acid at the concentration used in this work should not exceed 2%, assuming a molar absorption coefficient of about  $1000\text{ L mol}^{-1}\text{ cm}^{-1}$ .<sup>19</sup>

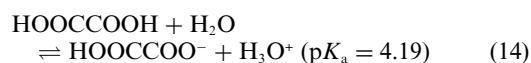
The evolution of the  $\text{H}_2\text{O}_2$  concentration during the irradiation of an aqueous solution of oxalic acid in the absence of dioxygen is shown in Fig. 1 (black symbols). During the first



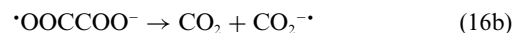
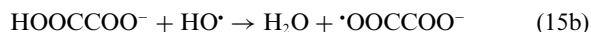
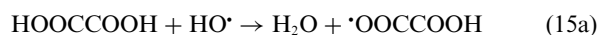
**Fig. 3** Oxalic acid degradation during the V-UV irradiation of a  $9.54 \times 10^{-3}\text{ mol L}^{-1}$  aqueous solution: in the absence (□) and in the presence (■) of dioxygen.

20 minutes, the increase of the amount of  $\text{H}_2\text{O}_2$  is similar to that observed in the absence of oxalic acid (Fig. 1, open symbols). However, in contrast to the further increase of the  $\text{H}_2\text{O}_2$  concentration to reach the plateau value ( $[\text{H}_2\text{O}_2]_s$ ) observed in the latter case, the  $\text{H}_2\text{O}_2$  concentration in the presence of oxalic acid decreases almost to zero between approx. 25 and 60 minutes of irradiation and increases again until the same value of  $[\text{H}_2\text{O}_2]_s$  as in pure water is reached (Fig. 1).

These experimental results may be explained in taking into account, besides reactions (1) to (12), those involving oxalic acid. This compound is a weak acid ( $\text{p}K_a$  4.19, eqn. (14)). Under our experimental conditions, the pH increased from 3.0 to 5.5 during irradiation. Therefore, the acid form of oxalic acid was predominant at the beginning of the reaction ( $\text{pH} < 3.19$ ), then the acid–base pair was present as the reaction proceeded ( $3.19 < \text{pH} < 5.19$ ) and the basic form dominated at the end of the reaction ( $\text{pH} > 5.19$ ).



The reactions of oxalic acid and the oxalate anion with  $\text{HO}^\bullet$  (reactions (15a) and (15b)) generate the radical  $\text{HCO}_2^\bullet$  and the radical anion  $\text{CO}_2^{\bullet-}$  (reactions (16a) and (16b), respectively). These radicals are present in solution as long as the acid is not completely consumed. The reactions of  $\text{HCO}_2^\bullet$  and  $\text{CO}_2^{\bullet-}$  with  $\text{H}_2\text{O}_2$  contribute to the  $\text{H}_2\text{O}_2$  decomposition process (reactions (17a) and (17b)).

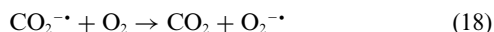


At the beginning of the experiment, when the amount of oxalic acid degraded is relatively small, the mechanism is essentially described by reactions (1) to (12), leading to an increase of the  $\text{H}_2\text{O}_2$  concentration, as in the absence of oxalic acid. As the irradiation proceeds and the concentration of  $\text{CO}_2^{\bullet-}$  ( $\text{HCO}_2^\bullet$ ) increases (reaction (16)), the rate of  $\text{H}_2\text{O}_2$  depletion increases due to reaction (17), and becomes faster than that of its formation. The decrease of the  $\text{H}_2\text{O}_2$  concentration proceeds as long as oxalic acid has not been almost completely mineralized. When mineralization is achieved (after 60 minutes, Fig. 3, open symbols), the  $\text{H}_2\text{O}_2$  concentration increases again to reach the same  $[\text{H}_2\text{O}_2]_s$  value as observed in the absence of oxalic acid (compare Fig. 1, black symbols and Fig. 3).

## Irradiation of an aqueous solution of oxalic acid in the presence of dioxygen

When an aqueous solution of oxalic acid was irradiated at 172 nm in the presence of dioxygen, in contrast to the case of pure water, the  $\text{H}_2\text{O}_2$  concentration showed a fast and important increase from the very beginning of the irradiation (Fig. 2, black symbols). The concentration reached a maximum of  $5.2 \times 10^{-4} \text{ mol L}^{-1}$  after 20 minutes and then decreased at a slower rate until the same quasi-stationary state as in the absence of oxalic acid ( $1.1 \times 10^{-4} \text{ mol L}^{-1}$ ) was reached (Fig. 2).

The above results may be explained by taking into account the trapping of the radical anion  $\text{CO}_2^{\cdot-}$  (and of its conjugated acid  $\text{HCO}_2^{\cdot}$ ) by dioxygen (reaction (18), rate constant of  $2-4 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ ),<sup>20</sup> besides the set of reactions (1)–(17).



In fact, trapping of  $\text{CO}_2^{\cdot-}$  by  $\text{O}_2$  (reaction (18)) competes efficiently with the decomposition of  $\text{H}_2\text{O}_2$  induced by reaction (17). In experiments where hydroxyl radicals were produced by UV photolysis, Karpel *et al.* have shown that the rate constant of reaction (18) should be three orders of magnitude larger than that of reaction (17).<sup>17</sup> Moreover, reaction (18) produces  $\text{O}_2^{\cdot-}$ , leading to the formation of  $\text{H}_2\text{O}_2$  by disproportionation (reactions (3) to (6)). Therefore, the combination of both effects resulting from reaction (18) (efficient trapping of  $\text{CO}_2^{\cdot-}$  and enhanced production of  $\text{O}_2^{\cdot-}$ ) explains the maximum observed in the  $\text{H}_2\text{O}_2$  concentration in the presence of oxalic acid and dioxygen (Fig. 2, black symbols).

In an experiment where the concentration of oxalic acid was diminished by a factor of 10, a similar behaviour as shown in Fig. 2 (black symbols) was observed for the  $\text{H}_2\text{O}_2$  evolution, but as expected, the decrease in  $\text{H}_2\text{O}_2$  concentration to reach the plateau value occurred at earlier irradiation times. This experiment is in agreement with the absence of significant contribution of the photolysis of oxalic acid to the  $\text{H}_2\text{O}_2$  evolution. The kinetics of oxalic acid disappearance are controlled by reaction (15), and therefore by the rate of production of hydroxyl radicals (reaction (1)) and, as expected, do not depend on the presence of dioxygen within experimental error (Fig. 3).

In summary, the formation of  $\text{H}_2\text{O}_2$  during the irradiation of water in the V-UV spectral region is very sensitive to the presence of  $\text{O}_2$  and organic matter. In air equilibrated solutions, the amount of  $\text{H}_2\text{O}_2$  observed at the quasi-stationary state was approx. double of that produced in Ar-purged solutions, while even higher amounts of  $\text{H}_2\text{O}_2$  were produced when an organic compound (oxalic acid) was being mineralized. The experimental results may be explained by a mechanism involving a series of at least 18 parallel and competitive reactions, involving several radical intermediates ( $\text{HO}^{\cdot}$ ,  $\text{H}^{\cdot}$ ,  $\text{HO}_2^{\cdot}$ ,  $\text{O}_2^{\cdot-}$ ,  $\text{CO}_2^{\cdot-}$ ,  $\text{HCO}_2^{\cdot}$ ), dioxygen, water and  $\text{H}_2\text{O}_2$ . We believe that these results may provide new insights into the V-UV induced oxidative degradation of organic compounds in aqueous solutions.

## Notes and references

† Irradiations were carried out in a DEMA (Mangels, Bornheim-Roisdorf, Germany) 13/12 *Solidex glass* annular photoreactor containing 350 cm<sup>3</sup> of solution. The Xe-excimer radiation source had a cylindrical geometry (25 cm length and 3 cm external diameter), and was positioned in the central axis of the photoreactor. Cooled water was circulated in the lamp jacket. Excitation of the gas (Xe) was provided by a high frequency and high voltage power supply (ENI Model HPG-2, 150 W, 220–230 kHz). The emission band at 172 nm had a half-width of 12–14 nm. The photonic rate was  $(16.4 \pm 0.5) \times 10^{18} \text{ photons s}^{-1}$ . The solution in the reactor was stirred before and during irradiation. For experiments in the absence of dioxygen, the solutions were purged with Ar for four hours before irradiation. The concentration of the model pollutant (oxalic acid dihydrate, 97%, Aldrich) was  $1.2 \text{ g L}^{-1}$  ( $9.54 \times 10^{-3} \text{ mol L}^{-1}$ ) in all experiments. Samples were taken from the photoreactor at regular time intervals during irradiation.

‡ The concentration of hydrogen peroxide was determined by colorimetry after complexation with  $\text{Ti}^{4+}$ .<sup>21</sup> An HP 8452A spectrophotometer

equipped with a diode array detector was employed for registering the absorption spectra. Oxalic acid was analysed by volumetric titration with potassium permanganate ( $\text{KMnO}_4$ , Billault). Taking into account that  $\text{KMnO}_4$  oxidises both oxalic acid and  $\text{H}_2\text{O}_2$  (identical stoichiometric coefficients), the oxalic acid concentration was obtained by subtraction of the  $\text{H}_2\text{O}_2$  concentration known from the colorimetric analysis. Experimental errors were approx. 5%.

§ The electrospray mass spectrometer (Q-TRAP, Applied Biosystem) employed was coupled to a HPLC (Agilent, series 1100, UV/Vis detector, 250 nm, Waters XTERRA RP18 Column). A TurboIon spray source (300 °C, Ion spray potential: –4200 V) was used. The mobile phase (isocratic mode, flow rate:  $0.2 \text{ mL min}^{-1}$ ) contained 95% of an aqueous solution of triethylamine (0.2%) and 5% acetonitrile. The substrate (oxalate ion) was analysed in negative ionisation mode. Detection limit:  $1.4 \times 10^{-4} \text{ mol L}^{-1}$ . Samples of 10 µL were injected. Results were analyzed using the software Analyst 1.3.1 or Analyst 1.4. Total organic carbon (TOC) measurements were carried out using a TOC analyser SHIMADZU 5050A (pyrolysis method). Experimental errors were less than 5%.

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