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Effect of temperature on hydrogen peroxide photolysis in aqueous solutions

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Abstract

The photolysis of hydrogen peroxide in dilute aqueous solution (1×10^{-4} M) at various temperatures (15–85 °C) and pH (pH 2.5–7) was studied by flash photolysis. The rate of oxygen production under continuous photolysis conditions was measured at room temperature. The rate constants and activation parameters are reported. Evidence for the formation of complexes between hydrogen peroxide and intermediate radicals is presented. The liquid phase data are discussed and compared with those available for the gas phase. © 1997 Elsevier Science S.A.

Keywords: Hydrogen peroxide; Photolysis; Temperature

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1. Introduction

The application of UV/H_2O_2 methods to the study of the photodegradation of organic substances in aqueous solution has received considerable attention [1–5]. Advanced oxidative procedures (AOPs), in which H_2O_2 or intermediates such as HO, HO_2 and O_2^- are involved, have developed rapidly in recent years. However, there is a lack of information on the initial stages of the photodegradative processes of organic matter [6].

Flash photolysis studies have been infrequently applied to obtain information on the kinetic rate constants and activation parameters associated with the UV/H_2O_2 method [7]. Several processes involving light, organic matter and H_2O_2 can only be detected in the millisecond range. In order to obtain the rate constants of the reactions observed in these systems, information corresponding to the photolysis of pure hydrogen peroxide solutions is required. Most of the information available in the literature involves pulse radiolysis studies performed at room temperature [7–11]. The determination of the activation parameters at different temperatures is necessary for basic studies performed within the framework of UV/H_2O_2 methods.

The flash photolysis of hydrogen peroxide has been mainly used to produce OH radicals [12,13]. In these systems, the kinetic analysis of the decay rate of oxidation processes has been limited to the initial rate [12,13] and no effect of the temperature has been reported.

In this paper, flash photolysis studies performed at various hydrogen peroxide concentrations and temperatures in acidic medium are reported.

2. Experimental details

2.1. Materials and methods

The water used in this study was of Milli-Q quality. Electrochemical studies revealed the presence of ions (such as Fe^{III} and Cu^{II}) at concentrations no higher than 10 nM. Hydrogen peroxide (30%) was obtained from Aldrich and Merck (perihydrol). The pH was controlled with $HClO_4$ (Merck). Oxygen of chromatographic quality was employed. The hydrogen peroxide concentration was controlled by titration with $KMnO_4$ standards.

Absorbance measurements were performed on a Cary 3 spectrophotometer. pH measurements were made using a Radiometer pH meter.

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Conventional flash photolysis experiments were performed using a Xe Co. model 720C apparatus, whose optics and electronics were modified to increase the sensitivity. The flash energy was varied between 800 and 7200 kV. This equipment has been reported previously [14].

Two collinear quartz–xenon lamps (Xe Co. FP-5-100C) and quartz cells of 10 and 18 cm were employed. Mercury lamps (HBO 100 W/2) and Xe–halogen lamps (XBO 75 W/1) were used for the analysis of the variation in the optical density of the solutions.

The pH of the solutions was varied between pH 2.5 and 7. The temperature was changed from 15 to 85 °C. Total organic carbon (TOC) measurement and ionic chromatography were used to control the presence of organic matter in the samples of hydrogen peroxide at the desired concentration. The concentration of organic matter (TOC) was lower than the detection limit of the equipment (1 ppm).

Some experiments were performed with O_2 or N_2 bubbling. In order to measure the rate of oxygen production, photolysis experiments were performed with continuous irradiation of the hydrogen peroxide solutions. An HP 125 W lamp was used as the radiation source. The hydrogen peroxide concentration was varied from 5×10^{-4} M to 1 M. Some experiments were performed in the presence of ethylenediaminetetraacetic acid (EDTA). The oxygen produced was measured with an O_2 selective electrode (Orion, model 37-08-99).

3. Results

3.1. Flash photolysis experiments

The time-resolved spectra of the intermediates detected at pH 2.5 and pH 7.0 are shown in Fig. 1. The initial amplitude increases from pH 2.5 to pH 7.0 and the absorption maximum shifts to the red from 235 to 240 nm. The spectral shape and the absorption maxima do not change during the decay and are temperature independent (Fig. 2). The observed decays are unaffected by the presence of oxygen.

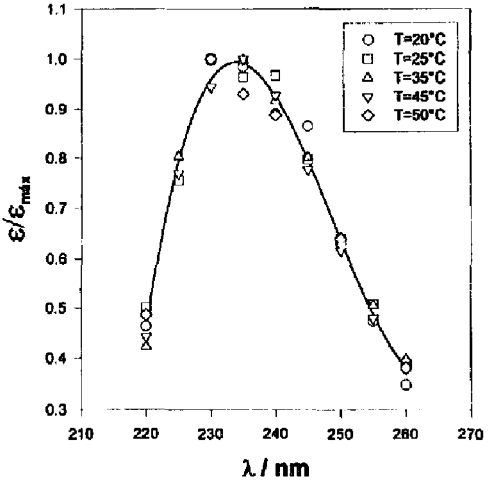


Fig. 2. Spectrum of the intermediate formed at pH 4 at different temperatures. Within experimental error, the spectrum is temperature independent.

The concentration of the generated intermediates increases linearly with the flash intensity. A careful analysis of the time-resolved profiles shows complex kinetics: both second- and first-order decays are required to describe the observed kinetics. As shown in Fig. 3, the plot of $1/A$ vs. time departs from linearity after a few milliseconds and the linear behaviour of ln A vs. time can be seen at the end of the observation. The analysis of the rate $\Delta A/\Delta t$ at different times as a function

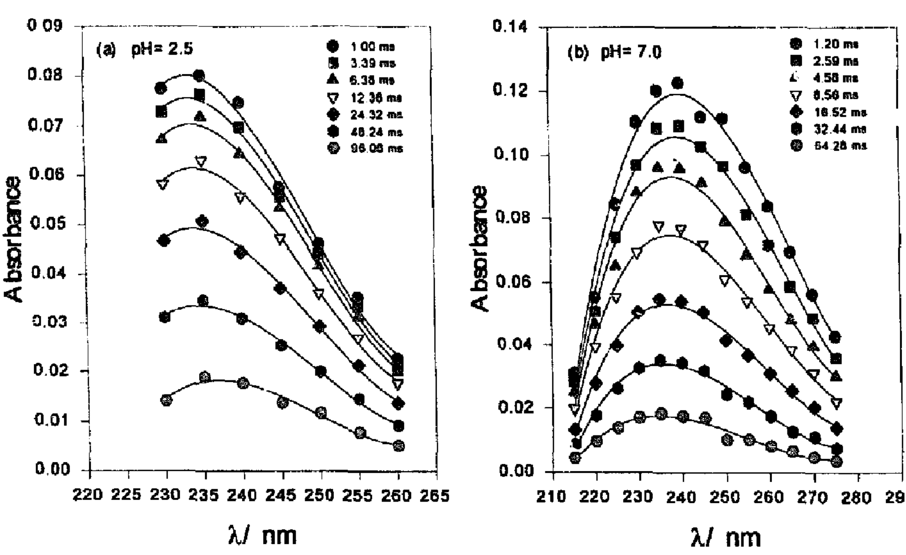


Fig. 1. Time-resolved spectra at pH 2.5 (a) and pH 7 (b) at different times.

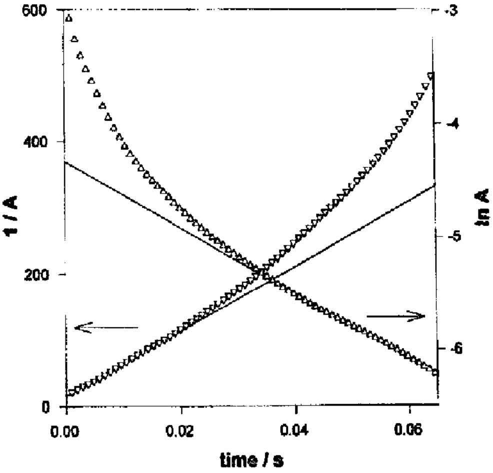


Fig. 3. Experimental behaviour of the observed absorbances considering first-order (ln A, right ordinate) and second-order ($1/A$, left ordinate) kinetics.

of the observed absorbance indicates the presence of both first- and second-order rates (see Fig. 4). However, under our experimental conditions, a simple mixed-order mechanism cannot reproduce the entire set of observed decays.

3.2. Oxygen measurements

Complementary measurements of oxygen production were also performed. The amount of oxygen produced on continuous photolysis is plotted against time in Fig. 5.

The rates of oxygen production (ppm s^{-1}) equal to the slopes of the straight lines in Fig. 5 are plotted vs. the hydrogen peroxide concentration in Fig. 6. At low concentrations, the rate is proportional to $[H_2O_2]$ and the intensity of absorbed light, but at concentrations higher than 0.1 M, the slope changes but the rate continues to be almost proportional to $[H_2O_2]$. This hyperbolic behaviour suggests a complex mechanism involved in oxygen production.

The addition of EDTA to the system ($[H_2O_2]$/[EDTA] = 2000) has no effect on the oxygen production rate at $[H_2O_2]$ values lower than 0.01 M. However, at higher

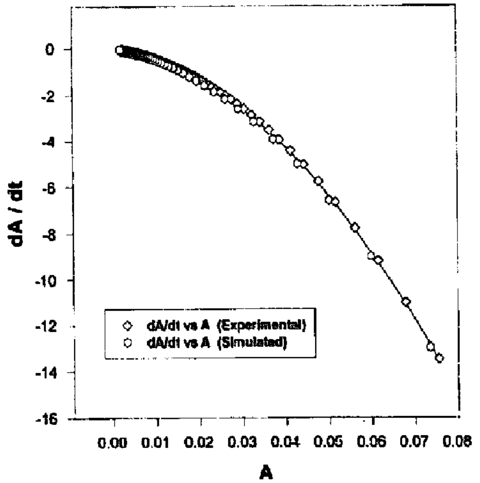


Fig. 4. Experimental dA/dt vs. A and calculated rate on the basis of the concentration profiles obtained from Scheme 1.

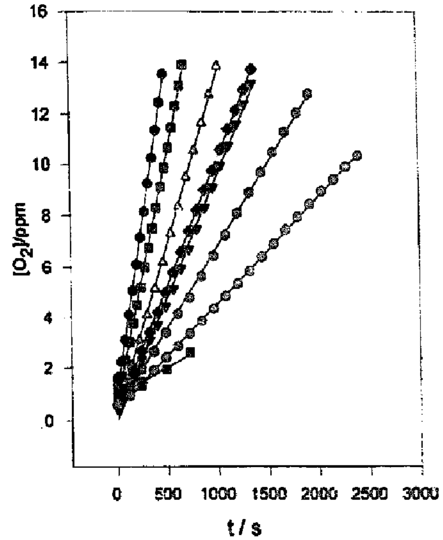


Fig. 5. Oxygen production (ppm) as a function of the irradiation time at different hydrogen peroxide concentrations. The highest slope corresponds to $[H_2O_2]$ = 1 M. In decreasing order, the $[H_2O_2]$ values are 0.4, 0.16, 0.08, 0.032, 0.0128, 0.0512 and 0.00248 M. These experiments were performed in the absence of EDTA.

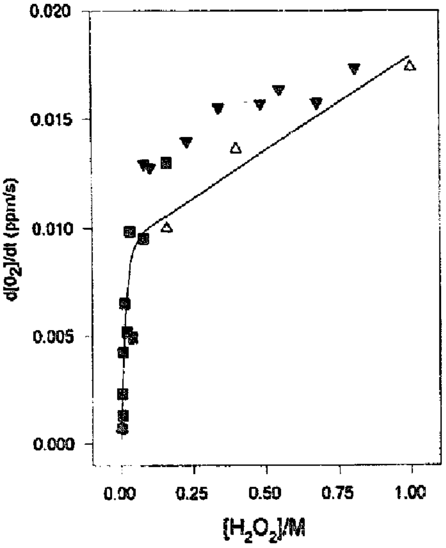


Fig. 6. Rate of oxygen production (ppm s^{-1}) as a function of the hydrogen peroxide concentration: ■, in the absence of EDTA; Δ, in the presence of EDTA; ▼, G_{O_2} data from Ref. [10] and normalized to the present scale; —, calculated rate of oxygen production including the existence of the complex described in the text.

Table 1
Experimental pK_a values obtained from flash photolysis studies

T (°C)	pK_a
25	4.96
45	4.85
65	5.00

concentrations ($[H_2O_2] > 0.1$ M), the rate is affected by the presence of EDTA. This may indicate the contribution of Fenton-like reactions to O_2 generation, probably due to the presence of metal ions in the H_2O_2 used.

3.3. Spectral analysis

The time-resolved spectra obtained at different pH and temperature indicate that only one independent intermediate is formed under our experimental conditions. According to the information available in the literature, the coupled radicals HO_2 and their conjugated base O_2^- can account for the observed spectra and decays. These species are related through the following equilibrium [15,16]

$$HO_2 \rightleftarrows O_2^- + H^+ \quad K_a$$

The effective extinction coefficient (ε_{eff}) at different pH and temperature can be obtained by applying the mathematical routine analysis described in Section 3.4. It can be easily shown that

$$\varepsilon_{eff} = (\varepsilon_{HO_2}[H^+] + \varepsilon_{O_2}K_a)/([H^+] + K_a)$$

The values of K_a at different temperatures can be obtained from a non-linear regression analysis. Some results are illustrated in Table 1.

The previously reported value for pK_a was 4.85 [7,15], which compares well, within experimental error, with our values. Our results show that the pK_a value is temperature independent, which is consistent with the behaviour of the spectra at different temperatures.

3.4. Mathematical treatment of the kinetic data

The mechanism proposed for this reaction is complex (Scheme 1) and in accordance with the information available in the literature. This mechanism can be used to analyse the experimental behaviour described in Section 3.3. The analysis of the initial rates does not provide sufficient information to explain the whole set of experimental decays shown in Fig. 1. A mathematical procedure adequate to describe this type of complex kinetics has been developed in our laboratory [17]. It combines matrix algebra, a numerical integration procedure (fourth-order Runge–Kutta) and non-linear regression analysis to handle the experimental results. The developed software provides information relevant to kinetic analysis.

A) Reactions				**Reported values ($M^{-1} s^{-1}$)**
$H_2O_2 + h\nu$	$\longrightarrow$	$2\,HO$		-
$HO + H_2O_2$	$\longrightarrow$	$HO_2 + H_2O$	k_1	4.5×10^7
$HO + HO_2$	$\longrightarrow$	$O_2 + H_2O$	k_2	4.85×10^{10}
$HO + O_2^-$	$\longrightarrow$	$O_2 + HO^-$	k_3	1.0×10^{10}
$HO + HO$	$\longrightarrow$	H_2O_2	k_4	5×10^9
$HO_2 + HO_2$	$\longrightarrow$	$O_2 + H_2O_2$	k_5	7.6×10^5; 8.6×10^5
$HO_2 + O_2^- \longrightarrow O_2 + HO_2^-$	$\longrightarrow$	$O_2 + H_2O_2$	k_6	9.7×10^7
$HO_2 + H_2O_2$	$\longrightarrow$	$O_2 + HO + H_2O$	k_7	0.5; 530
$O_2^- + H_2O_2$	$\longrightarrow$	$O_2 + HO + HO^-$	k_8	0.38; 16
B) Equilibria				**Reported values**
HO_2	$\rightleftarrows$	$H^+ + O_2^-$	pK_a	4.8 ± 0.1
H_2O_2	$\rightleftarrows$	$H^+ + HO_2^-$	pK_a	11.6

Scheme 1.

From the simulated profiles of the concentrations of the intermediate radicals [C], the absorbance A ($\varepsilon_{eff}l[C]$) and the rate $\Delta A/\Delta t(\varepsilon_{eff}l \times \Delta[C]/\Delta t)$ can be obtained. These values are compared with the experimental results in Fig. 4. A very good correlation between the experimental and simulated profiles is observed for the entire set of experiments reported in this paper.

The accepted mechanism [7] for the photolysis of H_2O_2 is illustrated in Scheme 1.

Reactions (5)–(8) play a major role within the time interval corresponding to our study. The rate constants at room temperature for reactions (1)–(8) have been reported. However, there is some dispersion in the reported data, as shown in Scheme 1. No information is available in the literature for the rate constants at temperatures other than room temperature. All the rate constants listed in Scheme 1 were obtained from pulse radiolysis studies at concentrations of hydrogen peroxide much higher than those employed in this work. An activation energy of 24.7 kJ mol^{-1} for reaction (5) was estimated from indirect measurements [18].

Although reactions (7) and (8) (Scheme 1) have been considered as elementary steps [7,15], earlier studies of this system have shown that this is not valid [9,19,20]. The bond reorganizations required for the release of oxygen should be included in the estimation of the activation energy of the whole process. Therefore, the elementary reactions involved in the depletion of HO_2 and O_2^- by H_2O_2 and the rate of O_2 production are not easily represented by elementary steps.

Taking this mechanism into account, the following rate expressions can be derived

$$d[C]/dt = -k[1,1,1] - k[1,1,2] - k[1,1,3] + k[1,2,3]$$

$$d[OH]/dt = -k[2,1,2] + k[2,1,3] - k[2,2,2] - k[2,2,3]$$

$$d[H_2O_2]/dt = k[3,1,1] - k[3,1,3] + k[3,2,2] - k[3,2,3]$$

where $[C] = [HO_2] + [O_2^-]$

$$k[1,1,1] = k[3,1,1] = 2(k_5\alpha_0^2 + k_6\alpha_0\alpha_1)[C]^2$$

$$k[1,1,2] = k[2,1,2] = (k_2\alpha_0 + k_3\alpha_1)[OH][C]$$

$$k[1,1,3] = k[2,1,3] = k[3,1,3] = (k_7\alpha_0 + k_8\alpha_1)[H_2O_2][C]$$

$$k[1,2,3] = k[2,2,3] = k[3,2,3] = k_1[OH][H_2O_2]$$

$$k[2,2,2] = k[3,2,2] = 2k_4[OH]^2$$

with $\alpha_0 = [H^+]/(K_a + [H^+])$ and $\alpha_1 = K_a/(K_a + [H^+])$.

By applying the previously described mathematical treatment to the experimental data, the following conclusions can be drawn:

1. the hydrogen peroxide concentration is almost constant during all the experiments;
2. the concentration of HO radicals is at least four orders of magnitude lower than that of the other radicals ($HO_2^·$ and O_2^-).

The pH-dependent global rate constants $k[1,1,3]$ and $k[1,1,1]$ are listed in Table 2.

Table 2
Global rate constants for the second-order radical recombination and pseudo-first-order reaction between the intermediates and hydrogen peroxide at different temperatures

T (°C)	pH 2.5	pH 3.2	pH 4.0	pH 5.3	pH 7.2
$10^{-4}k[1,1,3]$ (Ms^{-1})					
15	0.81	0.49		5.42	
20			5.88		
25	1.69		9.64	5.87	1.45
30		0.84	8.32		
35	2.25		10.80	8.75	
40			13.49		
45	2.23	1.14	10.61	9.89	9.98
50			11.91		
55	2.89				
60		1.67		14.70	
65	4.05				16.95
75	4.13	2.88		13.67	
85	4.92			22.35	20.04
$10^{-6}k[1,1,1]$ (Ms^{-1})					
15	2.62	3.42		3.02	
20			4.53		
25	2.35		5.23	3.28	11.83
30		3.39	5.18		
35	3.27		5.25	3.51	
40			5.31		
45	2.81	3.80		3.52	12.26
50			5.85		
55	2.86				
60		2.53	5.83	3.54	
65	2.92				12.62
75	3.02	3.52		3.54	
85	3.82			53.56	12.68

Table 3
Individual rate constants for reactions $HO_2+H_2O_2$ (k_7) and $O_2^-+H_2O_2$ (k_8) at different temperatures

T (°C)	$10^{-4}k_7$	$10^{-4}k_8$
15	0.84	5.95
25	1.23	7.52
35	1.77	9.36
45	2.48	11.50
55	3.42	13.93
65	4.63	16.70
75	6.14	19.81
85	8.07	23.29

Table 4
Individual rate constants for the recombination of HO_2+HO_2 (k_5) and $HO_2+O_2^-$ (k_6) at different temperatures

T (°C)	$10^{-6}k_5$	$10^{-7}k_6$
15	7.61	5.11
25	7.95	5.33
35	8.28	5.55
45	8.60	5.76
55	8.92	5.96
65	9.23	6.36
75	9.53	6.45
85	9.83	6.55

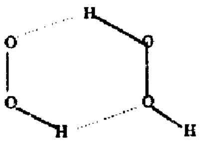
The pseudo-first-order rate constants corresponding to reactions (7) and (8) can be obtained by a non-linear regression analysis (see Table 3), and the values of the activation energies for these reactions are $E_7=27.7$ kJ mol^{-1} and $E_8=16.7$ kJ mol^{-1}.

The second-order rate constants k_5 and k_6 (pH<7) are listed in Table 4, with the activation energies $E_5=3.1$ kJ mol^{-1} and $E_6=3.0$ kJ mol^{-1}.

4. Discussion

The spectra of the intermediates and their decays are undoubtedly related to the species HO_2 and O_2^-. The molar absorptivities, obtained at different temperatures, imply that the dissociation constant does not change within the temperature range of the experiments.

The data analysis enables the rates of several of the elementary steps to be calculated, especially those associated with the processes within the time interval of our experiments. Steps (5)–(8) are associated with the observed decays. The pH dependence of the second-order reaction is quite similar to that reported in the literature [7], and the low activation energies obtained are consistent with processes involving radicals. Reaction (5) (Scheme 1) has been extensively studied in the gas phase at different temperatures and pressures [19–22]. Below 500 K, the gas phase rate constant varies with pressure and is sensitive to the presence of traces of water. At room temperature, the gas phase reaction presents a temperature coefficient lower than unity, corresponding to a negative activation energy. Lightfoot et al. [21] showed that the gas phase rate constant for the recombination of $HO_2^·$ radicals is well represented in the temperature range from 300 to 1200 K by the sum of Arrhenius terms. The value of −6.8 kJ mol^{-1} has been reported [19,21] for the activation energy at room temperature. Our value obtained for the aqueous phase is $E_5=3.1$ kJ mol^{-1}. The difference may be attributed to the solvation of the radicals in the aqueous phase. The non-Arrhenius behaviour observed in the gas phase has been attributed to a reaction involving a long-lived H_2O_4 intermediate complex [22,23]. Moreover, the presence of water vapour increases the rate constant for this reaction in the gas phase [24]. Ab initio and experimental evidence



Scheme 2.

supports the hypothesis of the formation of a complex between HO_2 and H_2O molecules, which cannot be discounted in the liquid phase.

The pseudo-first-order decays can be related to steps (7) and (8) (Scheme 1). The rate constants k_7 and k_8 obtained from our analysis differ from the values reported in the literature, which range from 10^{-4} to 530 M^{-1} s^{-1} [10]. These values are strongly dependent on the hydrogen peroxide concentration.

Reactions involving hydrogen peroxide are susceptible to the presence of organic matter and/or ions, particularly Cu^{2+} and Fe^{3+} [7,10,25]. These metal ions, normally present in hydrogen peroxide, should be relevant at $[H_2O_2]$ values higher than 0.1 M. However, in our flash photolysis experiments, the metal ion concentration is less than 1 nM. Moreover, there are no significant differences between the rate constants obtained using 8×10^{-4} M hydrogen peroxide solutions at pH 6 and 9. At higher pH, the catalytic properties of Fe^{III} (present mostly as $Fe(OH)^{2+}$ at these pH values) are poor. The mathematical simulation [17] of the reaction kinetics of this system, including the reactions of the radicals with ions such as Cu^{2+} and Fe^{3+} at concentrations lower than 10 nM, shows no difference between the results obtained in the presence and absence of ions. Differences between the decays calculated in the presence and absence of ions appear at ion concentrations higher than 0.1 μM.

Within experimental error, the rate of oxygen production at higher concentrations of H_2O_2 is of the same order of magnitude as those reported in the literature [10]. The reported rates were obtained in radiolysis experiments (at $[H_2O_2] > 0.2$ M). At lower concentrations, the radiolysis of water generates hydrogen peroxide in situ. Therefore, in such experiments, in deaerated solutions, it is not possible to observe that oxygen production decreases with increasing concentration of hydrogen peroxide. This behaviour is clearly observed in our experiments as illustrated in Fig. 6.

The effect of metal ions in solutions free of organic ligands, such as EDTA, is important at concentrations higher than 0.1 M. The presence of EDTA decreases the participation of Fenton reactions in the overall mechanism. However, under our experimental conditions, the rate of oxygen production is not affected by the presence of EDTA at very low concentrations of hydrogen peroxide. Therefore there is no catalytic effect of ions on the observed pseudo-first-order decay at $[H_2O_2] = 10^{-4}$ M.

The results presented in this paper were obtained from flash photolysis experiments and continuous photolysis at very low concentrations of H_2O_2. The results show that reactions (7) and (8) are complex and no direct information can be obtained from measurements of the oxygen production assuming steady state conditions for the intermediates involved in Scheme 1.

The differences between the values of the rate constants of reactions (7) and (8) (Scheme 1) obtained from flash photolysis experiments and oxygen measurements (continuous photolysis or continuous radiolysis) can be explained by assuming the formation of complexes between the hydroxyperoxide and superoxide anion and H_2O_2. Such complexes have already been postulated in the literature [9,22,26]. In these reports, the formation of an intermediate complex was proposed as a precursor to the formation of the final products. If the following reaction scheme is operative

$$HO_2 + H_2O_2 \xrightarrow{k'} C \xrightarrow{k_C} H_2O + O_2 + OH$$

where C is an intermediate complex, conclusions valid for the gas phase can be drawn from simple molecular orbital calculations. In these calculations, a cyclic complex (complex I, Scheme 2) and a linear complex were considered for C.

The semi-empirical PM3 molecular orbital binding energies for the different participants of this reaction are shown in Table 5. The estimated enthalpies of formation, obtained using the binding energies and the experimental atomic enthalpies of formation, are listed in Table 5 and compared, where possible, with experimental values.

The calculated energy difference for the reaction $HO_2 + H_2O_2 \rightarrow C(\text{cyclic})$ is -8.8 kJ mol^{-1}, whereas that corresponding to the second stage is -28.45 kJ mol^{-1}. The calculated energy change for the whole process is -37.2 kJ

Table 5

Binding energies obtained from semi-empirical PM3 molecular orbital calculations, enthalpy of formation of the atoms and calculated and experimental enthalpies of reactions for the different species analysed in this work. PM3 molecular orbital calculations were performed using a commercial software package

	Binding energy (kJ mol^{-1})	Estimated enthalpy of formation (kJ mol^{-1})	Experimental enthalpy of formation (kJ mol^{-1})
HO_2	−173.9	−2.8	9.3
H_2O_2	−261.15	−40.8	−32.6
Cyclic complex	−440.13	−45.6	
Linear complex	−400.45	−5.9	
H_2O	−217.22	−53.5	−57.8
OH	−108.84	−2.7	2.8
O_2	−115.2	3.9	0

mol^{-1} (the experimental enthalpy change is -78.2 kJ mol^{-1}). The expected activation energy for the formation of the cyclic intermediate complex should not be very high because there is insignificant molecular rearrangement. As two hydrogen bonds are expected to be formed between HO_2 and H_2O_2, the activation energy for activated complex I (see Scheme 2) should be of the order of 20–40 kJ mol^{-1}. Several kinetic studies related to the formation of hydrogen bonds report activation energies of this order of magnitude or even less [27]. This activation energy is similar to the value obtained for the aqueous phase in this study (27.7 kJ mol^{-1}). The second process, however, should involve the concerted rupture of one O–O peroxo and one O–H bond and the transformation of two hydrogen bonds into two O–H bonds leading to the above products. This molecular reorganization may require a higher activation energy. In fact, the experimental bond energies [28,29] associated with the different bonds broken and built during this rearrangement, i.e. O–H (428.4 kJ mol^{-1}), HO–OH (213 kJ mol^{-1}), HO–H (492 kJ mol^{-1}), O=O (497 kJ mol^{-1}) and O_2–H (206.3 kJ mol^{-1}), can be employed for the estimation of the activation energy associated with the process $H_2O + HO + O_2 \rightarrow$ activated complex II $\rightarrow$ C(cyclic). The total energy change associated with these processes is of the order of 70 kJ mol^{-1} or even higher. With all of these values, including the estimated enthalpies of formation of the different species involved in the mechanism, an energy profile, illustrated in Scheme 3, can be deduced. Within this framework, the activation energy for the decomposition along the reaction coordinate should be 42 kJ mol^{-1} or even higher.

An estimated value for the rate constant of the global reaction $HO_2(g) + H_2O_2(g)$ in the gaseous phase has been reported in the literature (1.5×10^6 M^{-1} s^{-1} at 1100 K) [30], which is about 10^3 times lower than the experimental value for reaction $HO_2(g) + HO_2(g)$ at the same temperature. The estimated global activation energy under these conditions was 52 kJ mol^{-1} [31], which is similar to that proposed for the unimolecular decomposition of the cyclic complex through activated complex II indicated in Scheme 3. If these estimated values are applied to the liquid phase, the processes observed in flash photolysis may be associated with the formation of the complexes, but in continuous photolysis experiments, the rate-determining step of oxygen production may be ascribed to their decomposition.

$$
\begin{array}{lll}
H_2O_2 \longrightarrow 2\,OH & & I_{abs} = I_0(1-10^{-\varepsilon l\,[H_2O_2]}) \\
HO + H_2O_2 \longrightarrow I + H_2O & & k_1 \\
2\,I \longrightarrow H_2O_2 + O_2 & & k_r = (k_5 + k_6{}^{*}K_a/[H^+])/(1+K_a/[H^+])^2 \\
I + H_2O_2 \rightleftharpoons C & & K_C \\
C \longrightarrow H_2O + O_2 + OH & & k_C
\end{array}
$$

Scheme 4.

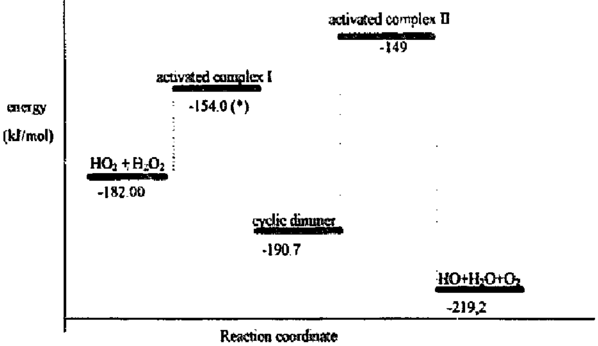
Under continuous irradiation and $[H_2O_2]$ higher than 0.1 M, the rate of oxygen production can be described by the condensed mechanism shown in Scheme 4, where I denotes HO_2 or O_2^-. Under steady state conditions for OH and I, the following steady state concentration of I can be deduced: $[I]_{ss} = (I_{abs}/k_1)^{1/2}$. Then the rate of oxygen production is given by

$$d[O_2]/dt = I_{abs} + k_C K_C (I_{abs}/k_1)^{1/2} [H_2O_2]$$

A simple non-linear regression analysis of all the experimental data obtained from continuous photolysis leads to the following results

$$I_0 = 7.8 \times 10^{-7}\ \mathrm{M\ s^{-1}} \quad k_C K_C (I_0/k_1)^{1/2} = 7.3 \times 10^{-7}\ \mathrm{s^{-1}}$$

Within the experimental range of this work and $[H_2O_2] > 0.1$ M, I_{abs} is almost constant ($\approx I_0$). Therefore the rate of oxygen production is almost linear with $[H_2O_2]$ as illustrated in Fig. 6, where the full line shows the calculated non-linear regression. The behaviour at lower concentration is strongly affected by the dependence of I_{abs} on $[H_2O_2]$. The experiments shown in Fig. 5 were performed at pH 7 in CO_2 free solutions, with $k_1 \approx 3 \times 10^5$ M^{-1} s^{-1}. Taking into account the previous results, the value of $k_C K_C \approx 0.45$ M^{-1} s^{-1} was estimated from our measurements. This value is quite similar to that reported for the Weiss–Haber reaction. In Fig. 6, the



(*) Estimated value for the hydrogen bond activation energy: ≈28 kJ/mol

Scheme 3.

reported experimental data for G_{O2} [10], obtained from continuous radiolysis, are shown. For comparative purposes, these data were normalized to our scale.

In conclusion, the study of the decay of HO_2 and/or O_2^- radicals provides more reliable information on the elementary steps involved in the photolysis of hydrogen peroxide than the analysis of oxygen production.

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