

# Elucidation of the degradation mechanism of 2-chloroethanol by hydrogen peroxide under ultraviolet irradiation

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## Abstract

Oxidation of 2-chloroethanol by  $H_2O_2$  under UV irradiation has been studied. Analysis of reactants and products was performed by gas and ion chromatography. In this study we have compared the disappearance of 2-chloroethanol with the contemporaneous appearance of  $Cl^-$  ions and conductivity changes of the solution. It was found that the oxidation of 2-chloroethanol yields quantitative amounts of  $Cl^-$  ions. Moreover, the rate of change of the solution conductivity is comparable with the rate of formation of  $Cl^-$ . Acetic, glycolic and formic acids and acetaldehyde were formed in the reaction although at low concentrations.

## 1. Introduction

Although there are several chemical water purification methods for organic pollutants, involving diverse process techniques (hydrolysis, oxidation, etc.), none of these processes is devoid of secondary pollution effects. For example, to remove pollutants present in low concentrations, a high concentration of reagent is necessary. A real difficulty arises in the elimination of numerous substances by appropriate chemical agents, owing to the low toxicity levels displayed (even fractions of ppb), since the conversion rate of a substrate at very low concentrations may be extremely small. Oxidation of aqueous pollutants is a widely used method. The oxidizing ability of the reagent, albeit high, may not be sufficient to eliminate the trace pollutant, as dictated by the

Nernst equation relating the potential of a redox couple to the concentration ratio of the species involved. This difficulty might be overcome by choosing an oxidant that will oxidize not only the initial reduced substrate but also its oxidized form resulting from the first oxidation stage. The  $\cdot OH$  radical potential ranks among the highest available, its value being only lower than that of fluorine. Moreover, its reaction rates with organic compounds are very high (of the order of  $10^9 M^{-1} s^{-1}$ ) [1–6]. Table 1 lists the standard redox potentials of some oxidants.

The reaction with  $\cdot OH$  radical appears to be the major route for the oxidative degradation of organic compounds in many processes (atmospheric or ozone-promoted degradation, etc.) [7–12]. The reaction products are, generally, small oxygenated compounds that are easily biodegradable.

For a hydrocarbon, a viable conversion would

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Table 1  
Standard redox potentials of some oxidants

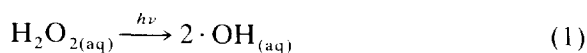
Species	$E^\circ$ (V)
Fluorine	3.03
Hydroxyl radical	2.80
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.78
Perhydroxyl radical	1.70
Hypobromous acid	1.59
Chlorine dioxide	1.57
Hypochlorous acid	1.49
Chlorine	1.36
Bromine	1.09
Iodine	0.54

be its complete mineralization to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . By oxidation with superoxide anion,  $\text{O}_2^-$ , polyhalogenated aromatic hydrocarbons and chlorinated organic compounds are completely transformed to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and HX [13–16].

Oxidation with the 'Advanced Oxidation Process',  $\text{H}_2\text{O}_2$ -UV irradiation, is an attractive method for the oxidation of organic pollutant compounds in aqueous media: photolysis of  $\text{H}_2\text{O}_2$  is one of the simplest ways to produce hydroxyl radicals (reaction 1).

In the present work we have studied the interaction of the radical  $\cdot\text{OH}$  with 2-chloroethanol in water. The substrate chosen can be taken as a model for the study of simplified reaction mechanisms thanks to its simple structure and its high solubility in water.

The data we have gathered may be of help in dealing with more complex mechanisms such as the interaction of  $\cdot\text{OH}$  with aromatic polycyclics, pesticides, etc. Hydrogen peroxide in diluted aqueous solution is known to produce  $\cdot\text{OH}$  radicals by photolysis under UV irradiation ( $\lambda < 370$  nm) [3,6,10,17,18]:



At high light intensities the photolysis rate is proportional to  $I_{\text{abs}}$  and, thus, to the concentration of  $\text{H}_2\text{O}_2$  ( $I_{\text{abs}} \propto I_0 [\text{H}_2\text{O}_2]$  where  $I_0$  is the

incident light intensity). At low intensities the photolysis rate is proportional to  $(I_{\text{abs}})^{1/2} \cdot [\text{H}_2\text{O}_2]$ . Under these conditions the rate is proportional to  $[\text{H}_2\text{O}_2]^{1.5}$  [17].

Several reports have appeared on the use of  $\cdot\text{OH}$  to remove organic pollutants from aqueous solutions [1–5,12], and numerous methods for the kinetic study of these reactions have been described, involving electron paramagnetic resonance spectrometry, chromatographic techniques, etc. [1–5,10–12,19]. In order to measure the degradation rate of an organic compound we have devised a procedure that will allow a correlation between the changes in the organic substrate concentration and  $\text{H}_2\text{O}_2$ ,  $\text{Cl}^-$  and the conductivity, as will be described in the following sections.

## 2. Experimental

### 2.1. Irradiation apparatus

The photolysis reactions were carried out in a glass apparatus of the type shown in Fig. 1 with a volume of 1825 ml equipped with a Helios Italquartz 13F 125-W high-pressure mercury vapour lamp with inner water cooling (emission radiation in the range 280–380 nm). The entire equipment (shielded with aluminium foil) was immersed in a thermostat at  $25.0 \pm 0.1^\circ\text{C}$ . Measurements were carried out in 10-ml solution aliquots in order not to cause significant changes in the total volume and, hence, in the irradiation conditions of the solution.

### 2.2. Materials

All reagents were of analytical grade and used as received. Hydrogen peroxide solutions (Prolabo, 30% with 0.0005% sodium stannate as stabilizer) were used as received without further treatment. Titration with cerium sulphate indicated a 32% titre. Water was obtained from a Millipore deionizer and filtered on 0.2- $\mu\text{m}$  cellulose filters.

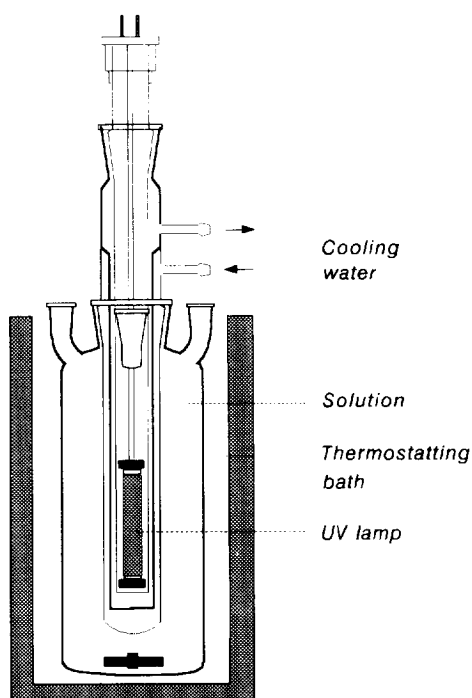


Fig. 1. Schematic drawing of the thermostatted photochemical reactor with magnetic stirrer.

### 2.3. Analyses

Hydrogen peroxide was determined photometrically by the neocuproine method [20]. 2-Chloroethanol was determined with a Hewlett-Packard 5890 gas chromatograph equipped with an HP-3392A integrator (FFAP-packed column; injection temperature, 200°C; flame ionization detector, 250°C; nitrogen gas carrier, 60 p.s.i.; oven temperature, 150°C).

Analysis of  $\text{Cl}^-$  and other reaction products was performed by ion chromatography (IC) with a Dionex DX 300 instrument (column, IonPac AS4A-SC, 250 × 4 mm; guard column, IonPac AG4A-SC, 50 × 4 mm; eluent, 5.0 mM  $\text{Na}_2\text{B}_4\text{O}_7$ ; flow-rate, 2.0 ml/min; detection, conductivity). The aldehydes were analyzed by HPLC through conversion to their 2,4-dinitrophenylhydrazones (column, Erbasil S 5-C<sub>18</sub>, 250 × 4 mm; eluent, acetonitrile–water; gradient: 35 to 85% acetonitrile in 12 min; detec-

tion, UV–visible (380 nm)). The conductivity of the solution during the irradiation was measured with a Radiometer CDM 83 conductimeter.

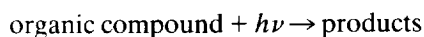
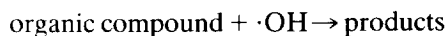
### 2.4. Procedure

In each run, 1825 ml of deaerated  $\text{N}_2$ -saturated aqueous solution of  $\text{H}_2\text{O}_2$  and 2-chloroethanol at the appropriate concentrations were placed in the glass reactor. The water had been irradiated prior to the addition of the reactants. The solution was kept at  $25.0 \pm 0.1^\circ\text{C}$  under a  $\text{N}_2$  flux throughout the irradiation. Different  $\text{H}_2\text{O}_2$ –2-chloroethanol molar ratios (1:1, 1:2, etc.) were employed.

Kinetic runs were also carried out under the same experimental conditions with solutions containing  $\text{H}_2\text{O}_2$  ( $10^{-3}$  M) or 2-chloroethanol ( $10^{-3}$  M) alone as reference blanks.

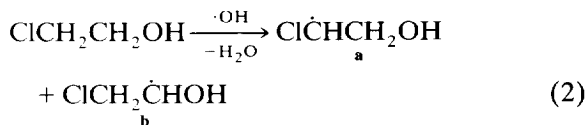
## 3. Results and discussion

When photolysis of  $\text{H}_2\text{O}_2$  is carried out in the presence of 2-chloroethanol, the main chemical reactions of the organic compounds are:



The extent of degradation of 2-chloroethanol by UV irradiation in the absence of  $\text{H}_2\text{O}_2$  is about 6% after 1 h (Fig. 2).

Reaction of  $\cdot\text{OH}$  with chlorinated organic compounds affords mainly hydrogen abstraction. Halogen abstraction by  $\cdot\text{OH}$  is thermodynamically unfavoured [1,2]. Interaction of 2-chloroethanol with  $\cdot\text{OH}$  radicals is believed to yield mainly two different organic radicals:



Radicals **a** and **b** undergo fast conversion with formation of  $\text{Cl}^-$  ions and several degradation products. Globally:

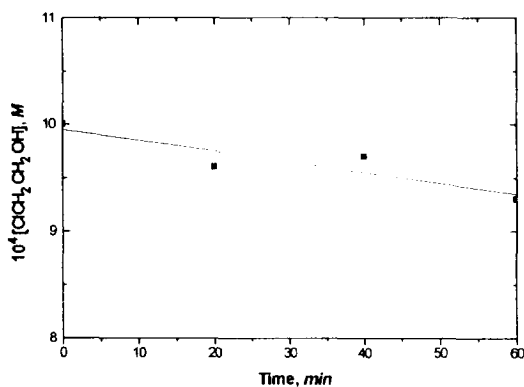
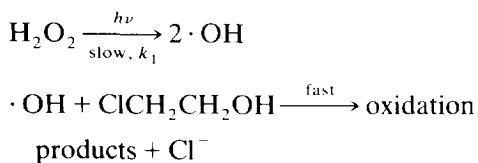


Fig. 2. Degradation of  $10^{-3}$  M 2-chloroethanol by UV irradiation in the absence of  $\text{H}_2\text{O}_2$ .



Scheme 1

The oxidative degradation of 2-chloroethanol was followed by monitoring the disappearance rate of  $\text{H}_2\text{O}_2$  and of the organic substrate along with the formation rate of chloride ion and the companion changes in electric conductivity of the solution. Fig. 3 shows the ion chromatogram versus time, indicating the steady increase of  $\text{Cl}^-$ .

Under our experimental conditions the rate of consumption of  $\text{H}_2\text{O}_2$  has been found to be first order in  $\text{H}_2\text{O}_2$ :

$$-d[\text{H}_2\text{O}_2]/dt = k_1[\text{H}_2\text{O}_2]$$

which reveals in a monoexponential rate law

$$A_t = A_\infty + (A_0 - A_\infty) \exp(-k_1 t)$$

where  $A$  is a physicochemical property with a value proportional to the extent of reaction ([2-chloroethanol],  $[\text{Cl}^-]$ ,  $[\text{H}_2\text{O}_2]$  or conductivity). This corresponds to the monomolecular rate-determining splitting of  $\text{H}_2\text{O}_2$  into  $\cdot\text{OH}$  radicals under irradiation, followed by fast reaction of

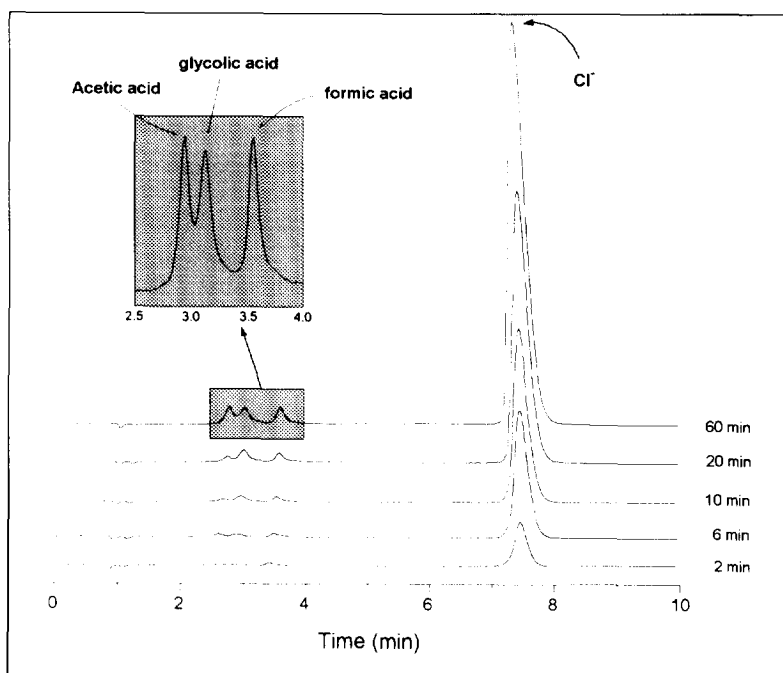


Fig. 3. Ion chromatogram versus time indicating the steady increase of  $\text{Cl}^-$ , and the appearance of traces of organic acids ( $[\text{ClCH}_2\text{CH}_2\text{OH}]/[\text{H}_2\text{O}_2]$  molar ratio = 1).

Table 2  
Rate parameters observed for the reaction between  $\text{H}_2\text{O}_2$  and  $\text{ClCH}_2\text{CH}_2\text{OH}$  under UV irradiation under  $\text{N}_2$  at  $25^\circ\text{C}$

$[\text{ClCH}_2\text{CH}_2\text{OH}]$ ( $10^3 M$ )	$[\text{H}_2\text{O}_2]$ ( $10^3 M$ )	$10^4 k^a_{(\text{H}_2\text{O}_2)}$ ( $\text{s}^{-1}$ )	$10^4 k^b_{(\text{ClCH}_2\text{CH}_2\text{OH})}$ ( $\text{s}^{-1}$ )	$10^4 k^c_{(\text{Cl}^-)}$ ( $\text{s}^{-1}$ )	$10^4 k^d_{(\text{conductivity})}$ ( $\text{s}^{-1}$ )
0	1	$7.8 \pm 0.5$	–	–	–
1	1	$4.0 \pm 0.8$	$8.1 \pm 0.5$	$8.0 \pm 0.3$	$7.8 \pm 0.2$
1	0.5	$3.5 \pm 0.8$	$8.0 \pm 0.8$	$7.3 \pm 0.8$	$6.7 \pm 0.1$
5	1.0	$3.0 \pm 0.3$	$7.7 \pm 0.8$	$4.7 \pm 0.2$	$4.8 \pm 0.2$
50	1.0	$2.8 \pm 0.6$	– <sup>c</sup>	$3.2 \pm 0.2$	$2.0 \pm 0.3$

<sup>a</sup> First-order rate constants for the consumption of  $\text{H}_2\text{O}_2$ .

<sup>b</sup> First-order rate constants for the disappearance of  $\text{ClCH}_2\text{CH}_2\text{OH}$ .

<sup>c</sup> First-order rate constants for the appearance of  $\text{Cl}^-$ .

<sup>d</sup> First-order rate constants for the increase in conductivity.

<sup>e</sup> Value omitted for the not significantly variation of  $[\text{ClCH}_2\text{CH}_2\text{OH}]$ .

radicals with the chlorinated substrate leading to its degradation products and  $\text{Cl}^-$  (Scheme 1).

Rate data in Table 2 indicate that with a  $[\text{ClCH}_2\text{CH}_2\text{OH}]/[\text{H}_2\text{O}_2]$  molar ratio of 1, the disappearance rate of 2-chloroethanol, the formation rate of  $\text{Cl}^-$  and the conductivity increase rate are about twice the rate of  $\text{H}_2\text{O}_2$  consumption. The experimental data for such molar ratios are reported in Fig. 4.

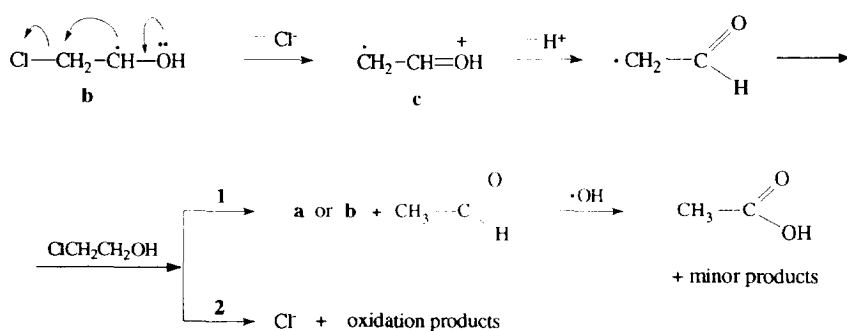
Fig. 4a shows the monoexponential decrease of organic substrate with time, the companion increase in  $[\text{Cl}^-]$  and their sum.

Fig. 4b shows the relationship between increasing  $[\text{Cl}^-]$  and increasing specific conductivity of the reaction solution. It appears that the latter arises virtually from  $\text{Cl}^-$  (as  $\text{HCl}$ ), the contribution from other conducting species (such as weak, undissociated organic acids) being probably negligible. The data in Table 2 are in

agreement with the simple mechanism in Scheme 1, in which the slow decomposition of  $\text{H}_2\text{O}_2$  is followed by rapid degradation of the chlorinated substrate with formation of the conducting chloride ion. On increasing the 2-chloroethanol/hydrogen peroxide molar ratio, the rate of disappearance of 2-chloroethanol is virtually unchanged while that of appearance of chloride decreases. It is likely that other, more complex mechanisms become operative under these conditions, although we are not in a position to suggest any based on the presently available data.

The existence of radical **a** has been proved, whereas radical **b** could only be hypothesized [19]. As a matter of fact, radical **b**, once formed, decomposes rapidly, leading to radical **c** and then  $\text{Cl}^-$  (Scheme 2).

Interaction of 2-chloroethanol with **c** would



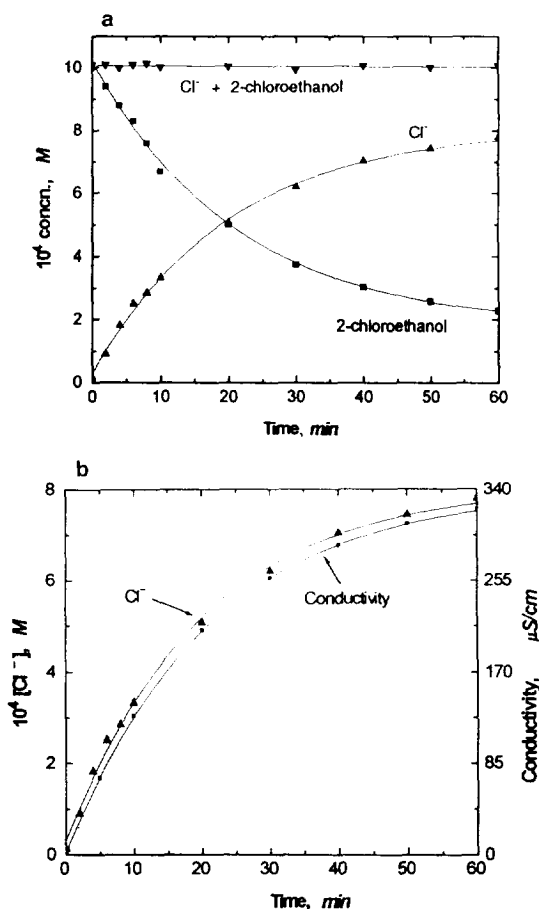


Fig. 4. Experimental data for  $[\text{ClCH}_2\text{CH}_2\text{OH}]/[\text{H}_2\text{O}_2]$  molar ratio of 1. (a) Monoexponential changes with time of  $[\text{ClCH}_2\text{CH}_2\text{OH}]$ ,  $[\text{Cl}^-]$ , and their sum. (b) Relationship between the increase of  $[\text{Cl}^-]$  and the increase of conductivity of the reaction solution.

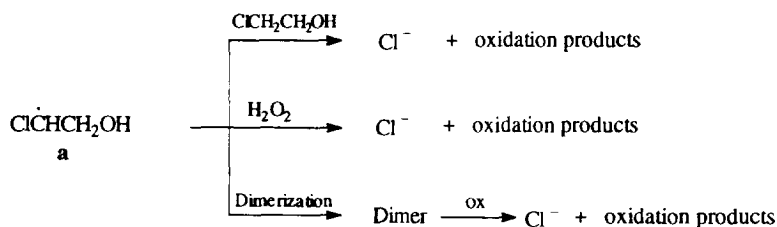
produce  $\text{Cl}^-$ , acetaldehyde and its oxidation products (acetic, formic, glycolic acids, etc.), according to paths 1 and 2 (Scheme 2). Path 1 appears to be less favoured. In fact the acetal-

dehyde intermediate is expected to be easily oxidized to acetic acid. As a matter of fact the concentration of C-2 carboxylic acids was found to be quite low. In a typical run, after 1 h only  $2 \cdot 10^{-3}$  mmol/l  $\text{CH}_3\text{CHO}$  and  $6 \cdot 10^{-2}$  mmol/l  $\text{CH}_3\text{COOH}$  corresponding to ca. 6% of total carbon were obtained. The following other oxidation products were detected, albeit at low concentrations:  $\text{HCOOH}$  ( $7 \cdot 10^{-2}$  mmol/l),  $\text{HOCH}_2\text{COOH}$  ( $2 \cdot 10^{-2}$  mmol/l). To confirm the suggested mechanism, we studied the behaviour of acetaldehyde ( $10^{-3}$  M) under the same conditions ( $\text{H}_2\text{O}_2$   $10^{-3}$  M, UV irradiation). The acetaldehyde was easily oxidized; after 60 min, ca.  $5 \cdot 10^{-4}$  mol/l of  $\text{CH}_3\text{COOH}$  were formed, corresponding to 50% of total carbon. Further  $\text{Cl}^-$  may arise from the intermediate a (Scheme 3).

Reactions of radicals a or b with  $\cdot\text{OH}$  are ruled out. The rate constant for the decomposition of  $\text{H}_2\text{O}_2$  ( $k_1$ ) was measured at different  $\text{H}_2\text{O}_2$  and initial substrate concentrations (Table 2). As can be seen, the presence of 2-chloroethanol causes a marked decrease in the rate of  $\text{H}_2\text{O}_2$  consumption ( $k_1$  for  $\text{H}_2\text{O}_2$  alone =  $7.8 \cdot 10^{-4}$  s $^{-1}$ ). It appears that partial reformation of  $\text{H}_2\text{O}_2$  may be due to reactions of the type suggested by Baxendale and Wilson [21].

#### 4. Conclusions

As shown by Fig. 4a, there is a reverse relationship between the disappearance of 2-chloroethanol and the formation of  $\text{Cl}^-$ . In fact, the sum  $[\text{ClCH}_2\text{CH}_2\text{OH}] + [\text{Cl}^-]$  remains constant throughout the irradiation. Accordingly,



Scheme 3

two interesting observations are possible: (i) the degradation rate of 2-chloroethanol can be followed by monitoring the  $\text{Cl}^-$  ion; (ii) no significant concentrations of chlorinated compounds are formed.

In this work, simple techniques have been devised, involving both HPIC and electric conductivity, which allow the kinetics of a degradation reaction to be easily followed while monitoring at the same time the fate of the halogenated organic substrate.

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