

Hydroxyl radical induced decomposition of aliphatic acids in oxygenated and deoxygenated aqueous solutions

Nathalie Karpel Vel Leitner*, Marcel Dore

Laboratoire de Chimie de l'Eau et des Nuisances, URA 1468, Ecole Supérieure d'Ingénieurs de Poitiers, 40 av. du Recteur Pineau, 86022 Poitiers Cedex France

Received 5 January 1996; accepted 28 March 1996

Abstract

The aim of this work was to study the oxidation of aliphatic acids by hydroxyl radicals resulting from the photolysis of hydrogen peroxide. Experiments carried out in dilute aqueous solutions (pH = 2.9–3.5) of mono and dicarboxylic acids with 1 to 4 carbon atoms showed (i) the oxidation of the carboxylic group is slow, (ii) the hydroxyl group of hydroxylated acids activates the adjacent C–H bond and leads, after hydrogen atom abstraction, O₂ addition and HO₂ removal, to the carbonyl group, (iii) a C–C bond cleavage occurs after hydrogen atom abstraction and oxygen addition for unsubstituted dicarboxylic acids. Except for oxalic acid, the mechanism of oxidation into CO₂ of the acids studied involves oxygen consumption and O₂⁻/HO₂ release.

Keywords: Hydroxyl radicals; Carboxylic acids; Hydrogen peroxide; UV irradiation; Oxygen; Organic peroxy

1. Introduction

Simple aliphatic acids are often found among oxidation by-products of more complex molecules. Most of the data available concerning the mechanism of oxidation of organic acids by hydroxyl radicals have been obtained with the use of radiolysis. It has been shown that hydroxyl radicals from the radiolysis of N₂O/O₂ (4:1 V/V) -saturated aqueous solutions react with aliphatic acids by H-abstraction at the carbon atom furthest from the carboxyl group [1,2]. This reaction would represent the rate-determining step in the reactions of OH[•] radicals with aliphatic compounds according to Anbar et al. [3]. When present in solution, oxygen rapidly adds to the radicals produced to give peroxy radicals [4,5]. Using pulse radiolysis with optical and conductivity detection, it was shown that α-hydroxyalkylperoxy radicals derived from primary and secondary alcohols undergo a rapid HO₂ elimination [6–10]. The rate of this reaction depends on the nature of the flanking substituents. The peroxy radicals derived from unsubstituted carboxylic acids, unlike the α-hydroxyalkylperoxy radicals derived from primary and secondary alcohols, cannot undergo an HO₂ elimination reaction. The fate of peroxy radicals derived from unsubstituted aliphatic acids and from β-hydroxyalkylperoxy radicals has been found to undergo a head-to-head termination reaction to form

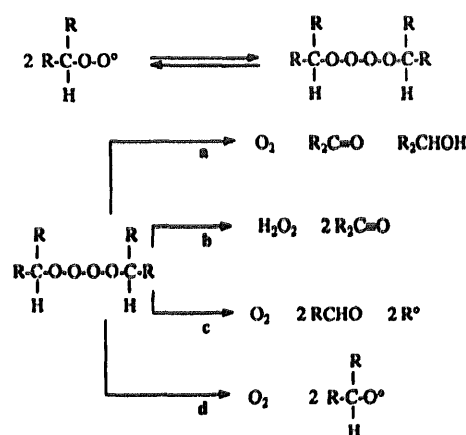


Fig. 1. Proposed scheme for the evolution of peroxy radicals during pulse radiolysis according to Von Sonntag and Schuchmann [12].

intermediate tetroxides which have been observed during some pulse radiolysis experiments in aqueous solution [11,12]. These tetroxides can be broken down by various routes (Fig. 1):

- The best known reaction is the Russell reaction [13], in which two primary or secondary peroxy radicals undergo an electrocyclic reaction to give molecular oxygen, a product with a C=O function and one with an OH function (reaction a).
- The formation of H₂O₂ and two carbonyl compounds (reaction b) represents another decomposition pathway.

* Corresponding author.

- Another well-established decomposition mode of peroxy radicals leads to oxygen and to oxyl radicals (reaction d) followed mostly for primary and secondary oxyl radicals by reactions releasing similar products as routes a and b.
- Reaction c is responsible for a C–C bond cleavage.

However, reactions which occur subsequently to first oxidation steps are usually not discussed. Radiation-chemical methods have not yet been used to study them. In the present work, we have investigated the oxidation of carboxylic acids by hydroxyl radicals resulting from the photolysis of hydrogen peroxide up to CO₂. Moreover, the oxygen consumption and the role of HO₂ in the oxidation process have been presented.

2. Materials and methods

Experiments were carried out in a 4-liter cylindrical batch reactor, previously described [14], and equipped with a low pressure mercury vapour lamp (Hanau NN15/20) placed on the axis of the reactor in a quartz sleeve. This lamp emitted a monochromatic radiation at 253.7 nm (photonic flux = 5.8 10⁻⁶ E.s⁻¹).

During oxygen-free experiments, oxygen was removed from the solutions by bubbling with ultrapure nitrogen. During the experiments carried out in the presence of dissolved oxygen, O₂ gas was introduced in solution if necessary.

Solutions were prepared in unbuffered ultrapure water delivered by the Millipore Milli RO - Milli Q system (resistivity = 18 MΩ.cm, TOC < 0.1 mg.l⁻¹). The pH of the organic acids and H₂O₂ aqueous solutions was in the range 2.9–3.5.

Hydrogen peroxide and organic acids (analytical grade) were used without further purification.

Hydrogen peroxide was analysed by the TiCl₄ colorimetric method. Organic acids were determined by HPLC with an anionic column (Supelco C 610H) eluted with 0.1% of H₃PO₄ in water. Total Organic Carbon analyses were performed with the Carbon analyzer Dohrmann DC 80. Dissolved oxygen was measured with an oxygen sensitive electrode (Consort Z621, Schott Gerate 9009/2).

Some organic by-products formed during the experiments carried out in oxygen-free solutions have been identified by gas chromatography–mass spectrometry after derivation of the extracts. Before extraction, residual hydrogen peroxide in aqueous samples was neutralised with sodium sulfite. Freeze-drying of 250-ml aqueous solutions was then performed over a period of 24 h. The extract was dissolved in 20-ml *tert*-butyl methyl ether (MTBE) by mixing for 1 h and concentrated to 1-ml before methylation with diazomethane. A total of 1-μl of each extract was injected into a DB 1701 capillary column (30 m × 0.25 mm I.D.; J & W Scientific) using a Varian Model 3400 gas chromatograph operated in the splitless injection mode. The temperature program was 50 °C isothermal for 5 min, rising to 270 °C at 4 °C/min, held at 270 °C for 8 min. The separated products were identified

using a Finnigan ITS 40 Mass Spectrometry detector. Compound identifications were performed in both electron impact and chemical ionization (with methane) mode. By following this procedure, extraction yields determined with solutions of standards were found to range from 3 to 30%.

3. Results and discussion

The hydroxyl radicals generation process chosen for this work is the photolysis of hydrogen peroxide. Photoirradiation of hydrogen peroxide solutions gives hydroxyl radicals as the main primary photoproducts:



In pure water this primary step is followed by:



$$k = 2.7 \times 10^7 \text{ l.mol}^{-1}.\text{s}^{-1}$$



$$k \approx 8.3 \times 10^5 \text{ l.mol}^{-1}.\text{s}^{-1}$$

In order to examine the mechanism and the kinetics of oxidation of aliphatic acids with that radical process, experiments have been conducted in oxygenated and deoxygenated conditions on carboxylic acids containing 1 to 4 carbon atoms of various oxidation degree: formic acid, glycolic, glyoxylic and oxalic acids, malonic, hydroxymalonic and ketomalonic acids, succinic, malic and tartaric acids. We have gathered, in Table 1, the rate constants for the reaction of hydroxyl radicals with some of the organic acids studied.

3.1. Formic acid

Preliminary experiments carried out on dilute aqueous solutions of formic acid and hydrogen peroxide (C₀ = 0.1–1 mM) showed that in the presence of oxygen, during the oxidation of the acid, hydrogen peroxide concentration doesn't vary and the concentration of dissolved oxygen decreases. The removal of both formic acid and hydrogen peroxide is enhanced in oxygen-free solutions (Fig. 2). These results can be explained by the pathway presented in Fig. 3.

The reaction of OH[·] radicals with formic acid produces COOH/CO₂ radicals. When oxygen is present in solution, the latter react preferentially with O₂ yielding HO₂/O₂⁻ radicals and CO₂. The recombination of two hydroperoxyl radicals, which leads to the formation of hydrogen peroxide, explains that the concentration of this compound is unchanged during oxidation. Under the experimental conditions studied, the reaction between H₂O₂ and OH[·] (k = 2.7 × 10⁷ M⁻¹.s⁻¹) can be neglected [14]. Moreover, the stoichiometry observed for the oxygen consumption during the experiments (0.5 mole of O₂/mole of formic acid decomposed) agrees with the mechanism proposed.

Table 1
pK_a values and rate constants for the reaction of OH[•] radicals with the organic acids studied

Organic Compound	pK _a	Rate constants k _(OH[•]) (l.mol ⁻¹ .s ⁻¹) [15]
Formic Acid; HCOOH	3.75	k _{HA} = 1.3 × 10 ⁸ ; k _{A⁻} = 3.2 × 10 ⁹
Acetic Acid; H ₃ C-COOH	4.75	k _{HA} = 1.6 × 10 ⁷ ; k _{A⁻} = 8.5 × 10 ⁷
Glycolic Acid; HOH ₂ C-COOH	3.8	k _{HA} = 6.0 × 10 ⁸ ; k _{A⁻} = 8.6 × 10 ⁸
Oxalic Acid; HOOC-COOH	pK _{a1} = 1.23 pK _{a2} = 4.19	k _{H₂A} = 1.4 × 10 ⁶ ; k _{HA⁻} = 4.7 × 10 ⁷ k _{A⁻} = 7.7 × 10 ⁶
Malonic Acid; HOOC-CH ₂ -COOH	pK _{a1} = 2.85 pK _{a2} = 5.69	k _{H₂A} = 2.0 × 10 ⁷ k _{A⁻} = 3.0 × 10 ⁸
Ketomalonic Acid; HOOC-C(O)-COOH	pK _{a1} = 1.6 pK _{a2} = 3.9	k _{HA⁻} = 5.7 × 10 ⁷ k _{A⁻} = 1.0 × 10 ⁸
Succinic Acid; HOOC-(CH ₂) ₂ -COOH	pK _{a1} = 4.16 pK _{a2} = 5.61	k _{H₂A} = 3.1 × 10 ⁸
Malic Acid; HOOC-CH ₂ -CH(OH)-COOH	pK _{a1} = 3.4 pK _{a2} = 5.11	k _{H₂A} = 7.3 × 10 ⁸ k _{A⁻} = 8.6 × 10 ⁸
Tartaric Acid; HOOC-CH(OH)-CH(OH)-COOH	pK _{a1} = 3.22 pK _{a2} = 4.82	k _{H₂A} = 7.0 × 10 ⁸ k _{A⁻} = 6.8 × 10 ⁸

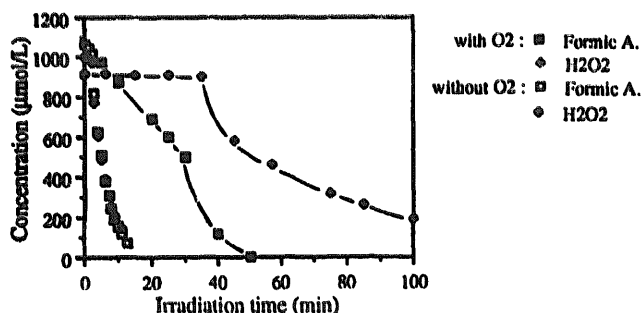


Fig. 2. Formic acid (FA) and hydrogen peroxide removal during irradiation in oxygenated ([FA]₀ = 1060 µmol.l⁻¹; [H₂O₂]₀ = 919 µmol.l⁻¹; pH₀ = 3.4) and in oxygen-free aqueous solutions ([FA]₀ = 1060 µmol.l⁻¹; [H₂O₂]₀ = 999 µmol.l⁻¹; pH₀ = 3.3).

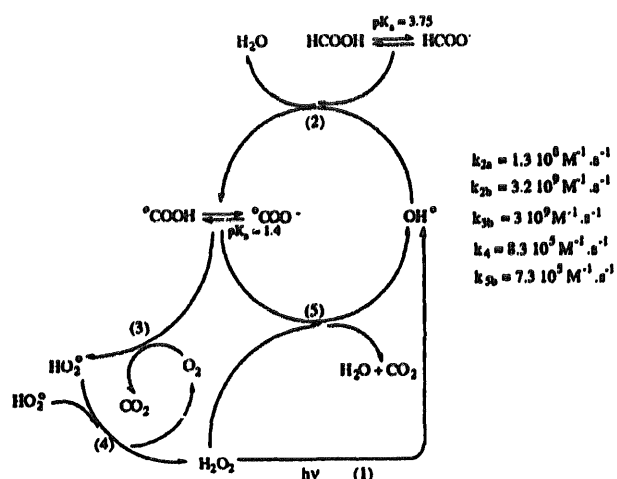


Fig. 3. Proposed pathways for the oxidation of formic acid by hydroxyl radicals during hydrogen peroxide photolysis.

In oxygen-free solutions, the [•]COOH/CO₂⁻ radicals react with hydrogen peroxide to form CO₂ to regenerate OH[•] radicals. The decomposition of formic acid is increased by this OH[•] catalysis.

These results indicate that when involved in a mechanism, the [•]COOH/CO₂⁻ radicals will have an influence on the

concentration of hydrogen peroxide depending on the presence or the absence of dissolved oxygen.

3.2. Oxalic and ketomalonic acids

Solutions of hydrogen peroxide and carboxylic acids containing carbon atoms with a high degree of oxidation (carboxyl and carbonyl groups) have been irradiated. Figs. 4 and 5 represent results obtained from aqueous solutions of oxalic acid (Fig. 4) and ketomalonic acid (Fig. 5) under oxygenated and deoxygenated conditions.

The experiments carried out with oxalic acid solutions indicate a very small difference between the removal of

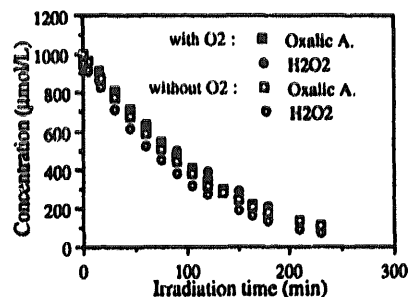


Fig. 4. Oxalic acid (OA) and hydrogen peroxide removal during irradiation in oxygenated and in oxygen-free aqueous solutions ([OA]₀ = 1000 µmol.l⁻¹; [H₂O₂]₀ = 940 µmol.l⁻¹; pH₀ = 2.9)

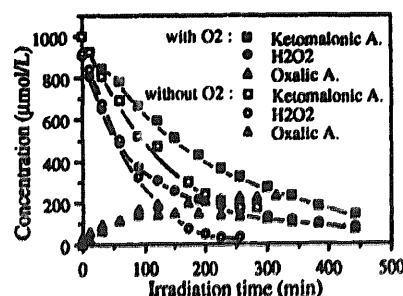


Fig. 5. Ketomalonic acid (KA), hydrogen peroxide removal and evolution of by-products during irradiation in oxygenated and in oxygen-free aqueous solutions ([KA]₀ = 1000 µmol.l⁻¹; [H₂O₂]₀ = 910 µmol.l⁻¹; pH₀ = 2.9).

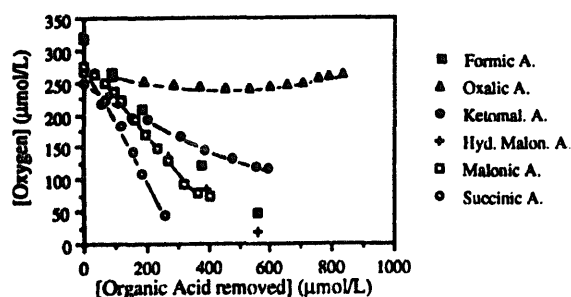
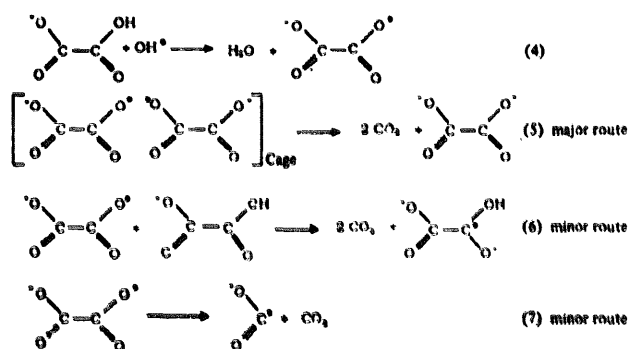
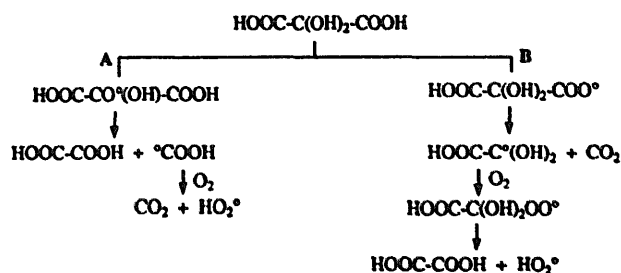
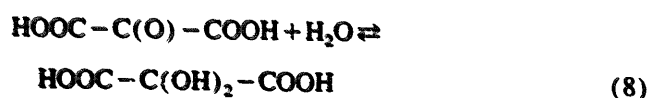


Fig. 6. Evolution of dissolved oxygen during oxidation of organic acids with the $\text{H}_2\text{O}_2/\text{UV}$ process in aqueous solutions ($[\text{Organic acid}]_0 = 1000 \mu\text{mol.l}^{-1}$).

hydrogen peroxide in the presence and in the absence of dissolved oxygen. The concentration of dissolved oxygen decreases very slowly during oxidation (Fig. 6). These observations allow us to conclude that under our experimental conditions, neither $\cdot\text{COOH}/\text{CO}_2^-$ nor $\text{HOOC-C}(\text{OH})_2$ radicals (suggested by Eiben and Fessenden [16] and by Getoff et al. [17] in N_2O saturated solutions) are formed in the system since both radical would consume oxygen yielding HO_2 radicals and then H_2O_2 [18]. Total Organic Carbon analyses have shown that oxalic acid is oxidized into CO_2 . Data support the following reactions which involve a cage recombination for the radicals $\cdot\text{OOC-COO}$ in the presence and in the absence of dissolved oxygen:



To simplify, in the course of this discussion, the organic acids will be presented by their molecular configuration. Oxalic acid is the only by-product observed during the oxidation of ketomalonic acid with and without dissolved oxygen. The concentration of dissolved oxygen decreases in the course of the oxidation of ketomalonic acid. The removal of both ketomalonic acid and hydrogen peroxide is a little more rapid in oxygen-free solutions. Under these conditions, the amount of oxalic acid produced is larger. Schuchmann et al. [19] have reported that for the protonated acid, the hydrate form is strongly predominant and very little free carbonyl is observed. The oxidation process can thus be depicted by the following reactions:



Under the experimental conditions used, the reaction of O_2^- with the ketomalonate anion, which yields monoperoxalic acid [19,20], can be neglected. Total Organic Carbon analyses show that as far as hydrogen peroxide is present, the curves representing the TOC parameter are similar for aerated and deaerated experiments. According to the experimental data, e.g. the rates of ketomalonic acid and of hydrogen peroxide removal, the evolution of TOC and also the production of oxalic acid, the pathway A which yields $\cdot\text{COOH}/\text{CO}_2^-$ radicals and oxalic acid in the presence and in the absence of dissolved oxygen, seems to be favored. Thus, the oxygen consumption which would occur after the C-C bond cleavage in the mechanism of oxidation of ketoacids by OH^\cdot radicals, would result from the reaction of the $\cdot\text{COOH}/\text{CO}_2^-$ radicals.

3.3. Hydroxylated carboxylic acids

Literature data from radiation experiments indicate that carboxylic acids substituted with one hydroxyl group lead to the formation of the corresponding ketone (or aldehyde) in oxygenated solutions. Material balance considerations allow

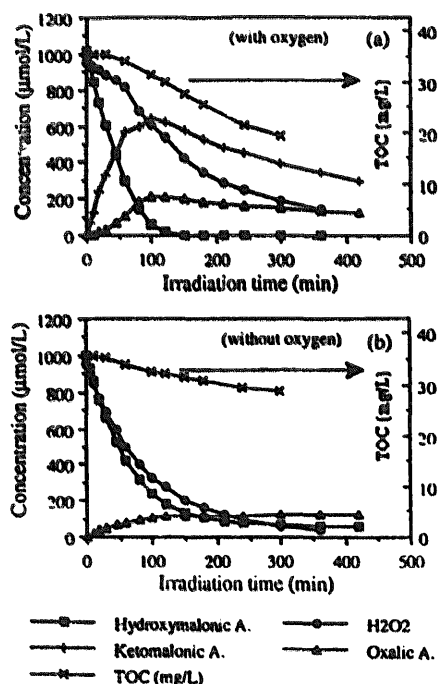
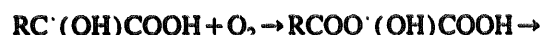


Fig. 7. Hydroxymalonic acid (HA) and hydrogen peroxide removal during irradiation in aqueous solutions, in the presence (a) and in the absence (b) of dissolved oxygen ($[\text{HA}]_0 = 1000 \mu\text{mol.l}^{-1}$; $[\text{H}_2\text{O}_2]_0 = 950 \mu\text{mol.l}^{-1}$; $\text{pH}_0 = 3.0$) and evolution of the by-products.

us to conclude that this also applies to the present system. We have shown that glycolic acid leads to the formation of quantitative glyoxylic acid, which decomposes into oxalic acid [18].

Fig. 7(a) presents, as another example, the evolution of the solutes and of the by-products during the oxidation of hydroxymalonic acid solutions when oxygen is present. The rate constants (Table 1) and the mechanisms proposed for the oxidation of alcohols [8,9] suggest that hydroxyl radicals react mostly with hydroxymalonic acid by H-abstraction to give the radical $\text{HOOC-C}^{\cdot}(\text{OH})\text{-COOH}$ [21]. Oxygen present in the solution adds rapidly to the latter to give the hydroxyperoxyl radical, which is well known to eliminate spontaneously $\text{HO}_2/\text{O}_2^{\cdot-}$. HO_2 radicals, which react with one another to give hydrogen peroxide, explain the slow evolution of the hydrogen peroxide concentration during the initial steps presented by the following reactions:



It should be noted that the removal of these hydroxy acids leads to oxygen consumption (0.5 mol of O_2 consumed/mol of hydroxymalonic acid oxidized into ketomalonic acid; Fig. 6). Following the pathway proposed above, oxalacetic acid was observed as a product of the reaction between malic acid and OH^{\cdot} in the presence of oxygen [22,23].

In oxygen-free aqueous solutions of hydroxymalonic acid (Fig. 7(b)), the TOC decreases slowly and H_2O_2 is rapidly removed; the by-products formed during this experiment have been investigated by GC-MS after extraction and methylation. Table 2 presents the compounds identified in these extracts, but also those obtained from glycolic acid solutions. The by-products observed from the reaction of OH^{\cdot} radicals with glycolic acid in the absence of dissolved oxygen result from:

- dimerization of the $\text{HOOC-C}^{\cdot}\text{H}(\text{OH})$ radical formed by the initial attack of OH^{\cdot} leading to tartaric acid,
- reaction with a second OH^{\cdot} radical producing the hydrated form of glyoxylic acid.

Table 2

By-products identified in the extracts of hydroxylated acid/ H_2O_2 irradiated solutions in the absence of oxygen

	Glycolic acid MW = 76 $\text{HOOC-CH}_2\text{OH}$	
Malonic acid	$\text{HOOC-CH}_2\text{-COOH}$	MW = 104
Glyoxylic acid	HOOC-CHO	MW = 74
Tartaric acid	$\text{HOOC-CH}(\text{OH})\text{-CH}(\text{OH})\text{-COOH}$	MW = 150
	Hydroxymalonic acid MW = 120 $\text{HOOC-CH}(\text{OH})\text{-COOH}$	
Oxalacetic acid	$\text{HOOC-C}(\text{O})\text{-CH}_2\text{-COOH}$	MW = 132
1,1,2-Ethane-tricarboxylic acid	$\text{HOOC-CH}(\text{CH}_2\text{COOH})\text{-COOH}$	MW = 162

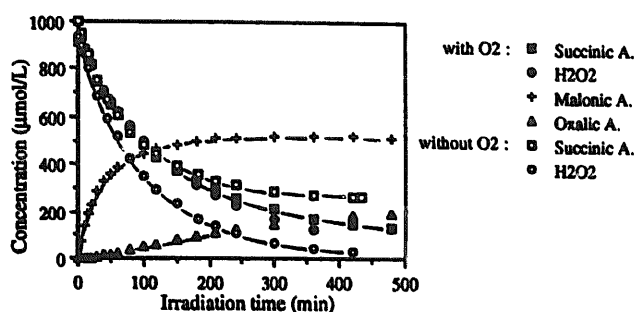


Fig. 8. Succinic acid (SA) and hydrogen peroxide removal, and evolution of by-products during irradiation in oxygenated and in oxygen-free aqueous solutions ($[\text{SA}]_0 = 1000 \mu\text{mol.l}^{-1}$; $[\text{H}_2\text{O}_2]_0 = 930 \mu\text{mol.l}^{-1}$; $\text{pH}_0 = 3.5$).

Malonic acid, which has also been identified, may be due to a minor route not yet clearly elucidated.

Only two by-products have been identified in the extract of hydroxymalonic acid solutions; both result from dimerization reactions. One of them has a tricarboxylic structure. Oxalacetic acid (oxo butanedioic acid) and the enol form (hydroxy butene dioic acid) co-exist. These compounds reveal that the mechanism involves H atom abstraction and C–C bond cleavage, but also OH group elimination.

3.4. Unsubstituted acids

Similar experiments have been carried out with aqueous solutions of acetic acid, malonic acid and succinic acid. Fig. 8 presents the evolution of succinic acid and of its oxidation by-products during irradiation under oxygenated conditions, and the evolution of the solutes under deoxygenated conditions. Material balance indicates that succinic acid is entirely converted into malonic acid during oxidation by hydroxyl radicals in the presence of oxygen. Neither malic acid nor tartaric acid is observed as a by-product. The cleavage of the C–C bond seems then to predominate over the oxidation of the carbon atom.

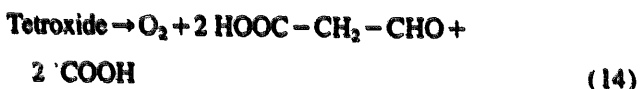
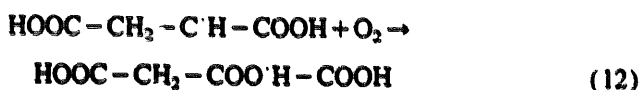
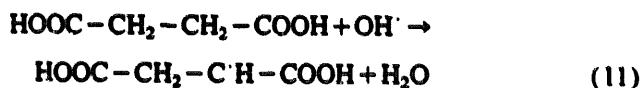
Similarly, hydroxymalonic acid is not observed during oxidation of malonic acid. Oxalic acid is actually the main by-product under our experimental conditions [23]. Behar et al. [24] have established from in situ radiolysis-ESR experiments on acid solutions (0.8 N H_2SO_4) of malonic acid that the main reaction of OH^{\cdot} is abstraction of a C–H hydrogen

Table 3
By-products identified in the extracts of unsubstituted acid/H₂O₂ irradiated solutions in the absence of oxygen

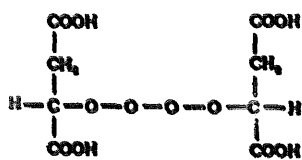
	Acetic acid MW = 60 HOOC-CH ₃	
Glyoxylic acid	HOOC-CHO	MW = 74
Succinic acid	HOOC-CH ₂ -CH ₂ -COOH	MW = 118
	Malonic acid MW = 104 HOOC-CH ₂ -COOH	
Succinic acid	HOOC-CH ₂ -CH ₂ -COOH	MW = 118
One unidentified triacid		MW = 202
	Succinic acid MW = 118 HOOC-CH ₂ -CH ₂ -COOH	
Maleic/Fumaric acid	HOOC-CH=CH-COOH	MW = 116
Malic acid	HOOC-CH(OH)-CH ₂ -COOH	MW = 134
1,2,3-Propane-tricarboxylic acid	HOOC-CH(CH ₂ COOH)-CH ₂ -COOH	MW = 176

to produce $\cdot\text{CH}(\text{CO}_2\text{H})_2$, and that only 10% of the reaction leads to the radical $\cdot\text{CH}_2\text{CO}_2\text{H}$ by decarboxylation.

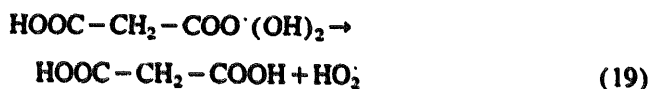
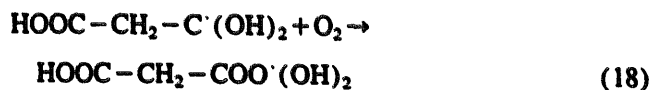
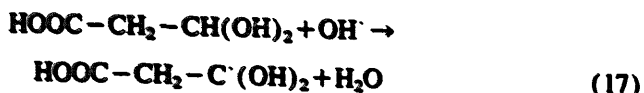
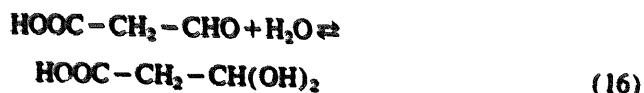
Results indicate that under our experimental conditions, following O₂ addition, the contribution of reactions a and b (Fig. 1) is negligible in the mechanism of decomposition of unsubstituted acids and mostly reaction c would play a role.



Tetroxide



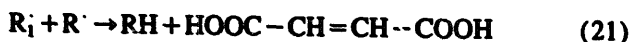
Tetroxide



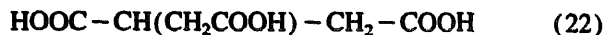
Thus it should be noted that according to this mechanism, the oxidation of succinic acid into malonic acid requires 2 mol of O₂ per mol of succinic acid. As the experimental data showed the consumption of 1 mol of O₂/mol of succinic acid (Fig. 6), we must also take into account the reaction of OH \cdot with hydrogen peroxide, which produces HO₂ \cdot and then O₂ (and H₂O₂).

This mechanism, proposed for the oxidation of unsubstituted dicarboxylic acids, differs from the oxidation of acetic acid, since the first leads to the C-C bond cleavage while acetic acid yields large amounts of two carbon by-products [18,25].

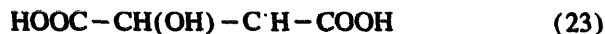
In the course of experiments carried out in oxygen-free solutions, by-product identification has been undertaken using GC-MS analyses of methylated sample extracts (Table 3). From acetic acid and malonic acid, dimerization reactions occur. The by-products identified from succinic acid consisted of unsaturated dicarboxylic acids (maleic and fumaric acid), one hydroxylated derivative and one triacid. Additional experiments have shown that an equilibrium exists between maleic acid and fumaric acid configuration when irradiated at 253.7 nm. These compounds can be produced from the initial radical R₁ = HOOC-C \cdot H-CH₂-COOH: - by abstraction of a second H atom



– by reaction with one radical resulting from the cleavage of succinic acid



but also by reaction of OH^\cdot on the by-products, maleic and fumaric acids



These identified by-products and the weak evolution of the total organic carbon in solution during irradiation indicate that decarboxylation reactions take a small part in the mechanism involved in the absence of oxygen.

4. Conclusion

The study of the oxidation of aliphatic acids with the H_2O_2 /UV process, carried out in the presence and in the absence of dissolved oxygen, leads to a wide knowledge about the mechanisms involved. In the presence of dissolved oxygen, the weak consumption of hydrogen peroxide, observed during the oxidation of formic acid and of carboxylic acids with hydroxyl groups, indicates that oxygen consumption is accompanied by $\text{HO}_2^\cdot/\text{O}_2^{\cdot-}$ generation followed by recombination into H_2O_2 . By-product identifications associated with oxygen consumption during the elimination of unsubstituted carboxylic acids show that the oxidation occurs via a C–C bond cleavage. Total Organic Carbon measurements indicated that oxidation into CO_2 is poor in oxygen-free solutions. This study enabled us to present a detailed scheme of the major processes involved in the decay of a class of carboxylic acids during the photolysis of hydrogen peroxide.

References

- [1] W.T. Dixon, R.O.C. Norman and A.L. Buley, *J. Chem. Soc.*, (1964) 3625–3634.
- [2] P. Neta, M. Simic and E. Hayon, *J. Phys. Chem.*, 73 (1969) 4207–4213.
- [3] M. Anbar, D. Meyerstein and P. Neta, *J. Chem. Soc.* (1966) 742–747.
- [4] G.E. Adams and R.L. Willson, *Trans. Faraday Soc.*, 65 (1969) 2981–2987.
- [5] P. Neta, R.E. Huie and A.B. Ross, *J. Phys. Chem. Ref. Data*, 19 (1990) 413–513.
- [6] J. Rabani, D. Klug-Roth and A. Henglein, *J. Phys. Chem.*, 78 (1974) 2089–2093.
- [7] H. Schultze and D. Schulte-Frohlinde, *J. Chem. Soc. Faraday Trans. I*, 71 (1975) 1099–1105.
- [8] E. Bothe, M.N. Schuchmann, D. Schulte-Frohlinde and C. Von Sonntag, *Photochem. Photobiol.*, 28 (1978) 639–644.
- [9] E. Bothe, D. Schulte-Frohlinde and C. Von Sonntag, *J. Chem. Soc. Perkin Trans. II*, (1978) 416–420.
- [10] J. Staehelin and J. Hoigne, *Environ. Sci. Technol.*, 19 (1985) 1206–1213.
- [11] M.N. Schuchmann and C. Von Sonntag, *J. Phys. Chem.*, 83 (1979) 780–784.
- [12] C. Von Sonntag and H.P. Schuchmann, *Angew. Chem. Int. Ed. Engl.*, 30 (1991) 1229–1253.
- [13] G.A. Russell, *J. Am. Chem. Soc.*, 79 (1957) 3871–3877.
- [14] N. Karpel Vel Leitner and M. Dore, *J. Chim. Phys.*, 91 (1994) 503–518.
- [15] G.V. Buxton, C.L. Greenstock, W.P. Helman and A.B. Ross, *J. Phys. Chem. Ref. Data* 17 (1988) 513–886.
- [16] K. Eiben and R.W. Fessenden, *J. Phys. Chem.*, 75 (1971) 1186–1201.
- [17] N. Getoff, F. Schwörer, V.M. Markovic, K. Sehested and S.O. Nielsen, *J. Phys. Chem.*, 75 (1971) 749–755.
- [18] N. Karpel Vel Leitner and M. Dore, *Water Research*, in press (1996).
- [19] M.N. Schuchmann, H.P. Schuchmann, M. Hess and C. Von Sonntag, *J. Am. Chem. Soc.*, 113 (1991) 6934–6937.
- [20] C. Von Sonntag, D.J. Deeble, M. Hess, H.P. Schuchmann and M.N. Schuchmann, in K. Yagi (ed.), *Active oxygens, Lipid peroxides, and Antioxidants*, Japan Sci. Soc. Press, Tokyo/CRC Press, Boca Raton, 1993, pp. 127–138.
- [21] M.N. Schuchmann, H.P. Schuchmann and C. Von Sonntag, *J. Phys. Chem.*, 99 (1995) 9122–9129.
- [22] D.E. Cabelli and B.H.J. Bielski, *Z. Naturforsch.*, 40b (1985) 1731–1737.
- [23] N. Karpel Vel Leitner and M. Dore, *Environ. Technol.*, 16 (1995) 753–763.
- [24] D. Behar, A. Samuni and R.W. Fessenden, *J. Phys. Chem.*, 77 (1973) 2055–2059.
- [25] M.N. Schuchmann, H. Zegota and C. Von Sonntag, *Z. Naturforsch.*, 40b (1985) 215–221.