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Journal of Molecular Catalysis A: Chemical 117 (1997) 439–447

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Olefin oxidation by the system H_2O_2/MoO_4^{2-}: competition between epoxidation and peroxidation

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Received 12 May 1996; accepted 13 August 1996

Abstract

The oxidation of tiglic acid by the catalytic system hydrogen peroxide/molybdate ions is investigated in water under varying conditions of pH. Using similar conditions of temperature and concentrations, we show that two different reaction pathways compete leading either to an epoxide in acidic medium or to an allylic hydroperoxide in alkaline medium. These results are interpreted in terms of the involvement of two peroxomolybdates. Epoxidation probably proceeds via the tetraperoxodimolybdate $Mo_2O_3(O_2)_4^{2-}$ whereas peroxidation involves singlet oxygen, $^1O_2$, ($^1\Delta_g$), formed as a result of the decomposition of the triperoxomolybdate $MoO(O_2)_3^{2-}$. Finally, experimental conditions are given to obtain selectively the epoxide or the hydroperoxide.

Keywords: Peroxomolybdates; Singlet oxygen; Epoxidation; Peroxidation

1. Introduction

Organic peracids are currently used for the epoxidation of olefins [1]. Although the rate of epoxidation is not very sensitive to steric hindrance, it strongly depends on the electron density of the alkene: electron-donating substituents anchored to the carbon–carbon double bond enhance the reaction rate whereas electron-withdrawing substituents have the opposite effect [2].

On the other hand, the combination of hydrogen peroxide with catalysts based on molybdenum(VI) or tungsten(VI) are well known to epoxidize olefins in acidic medium [3–6]. Two mechanisms have been proposed and are still much debated: either the alkene directly interacts with one of the peroxygens [7] or it coordinates in a first step to the metal *center* leading then to a five-membered peroxo metallacycle [8]. Anyway, this procedure allows the epoxidation of electron-deficient olefins, such as α,β-unsaturated acids whereas peracides do not react efficiently with such substrates [2,5–11]. Although both metals exhibit similar behaviors, tungstate ions are more frequently used because they induce the disproportionation of H_2O_2 to a lesser extent [9,12] and because they are more efficiently extracted in organic solvents by phase-transfer catalysts [12–15]. Thus, in spite of a considerable amount of literature available about epoxidation catalyzed with transition met-

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PII S1381-1169(96)00357-3

als, very little work dealing with epoxidation by the system H_2O_2/MoO_4^{2-} in pure aqueous solutions has been published [9,16,17].

Recently, we showed that the disproportionation of hydrogen peroxide catalyzed by molybdate ions in alkaline media quantitatively leads to the formation of singlet oxygen, $^1O_2$ ($^1\Delta_g$) (Eq. (1)) [18].

$$2H_2O_2 \xrightarrow[\text{pH 9–12}]{MoO_4^{2-}} 2H_2O + {}^1O_2\ (100\%) \qquad (1)$$

Therefore, the same system, H_2O_2/MoO_4^{2-}, could act either as an epoxidizing agent or as a peroxidizing agent via the generation of $^1O_2$. In the present paper, we show how a carefully chosen substrate, tiglic acid **A**, may be simultaneously (or selectively) epoxidized or peroxidized by the catalytic system H_2O_2/MoO_4^{2-} under similar conditions of concentrations and temperature only by varying the pH value. Moreover, the recent identification by ^{95}Mo NMR of the different peroxomolybdates formed according to pH and to hydrogen peroxide concentration [19] allows us to propose structures for the complexes responsible for each pathway.

2. Experimental section

2.1. Instrumentation

High performance liquid chromatographic (HPLC) analyses were carried out with a reverse-phase column (Spherisorb RP 18-5ODS) using a Gilson model 303 pump, a mixture of CH_3OH 50/H_2O 50/H_3PO_4 0.2 as eluent and a UV detection at 210 nm with an Holochrom H/MD Gilson detector. Nuclear magnetic resonance ^{1}H (NMR) spectra were recorded in D_2O on a Bruker AC 300P FT-spectrometer. All chemical shifts were referenced with respect to $TSPd_4$ signal ($\delta = 0$ ppm). For the ^{95}Mo NMR spectra, the procedure was described in detail before [19]. The pH were measured with a combined glass-calomel electrode (Schott Geräte, type H6280) and the values obtained in D_2O were uncorrected.

2.2. Reagents

Tiglic acid (98%), sodium molybdate dihydrate (99%) ($Na_2MoO_4 \cdot 2H_2O$), potassium molybdate (98%) (K_2MoO_4), sodium carbonate (99%), sodium hydrogenocarbonate (99%) were purchased from Aldrich-Chemie. Hydrogen peroxide (50% Rectapur), sodium hydroxyde (98% Normapur), sodium dihydrogenophosphate dihydrate (99%), disodium hydrogenophosphate dihydrate (98%), acetic acid and EDTA were obtained from Prolabo (Paris). Deuterium oxide (99.8% D) was obtained from the CEA (Commissariat à l'Energie Atomique, Saclay).

2.3. Competition between epoxidation and peroxidation of tiglic acid

Tiglic acid **A** (86 mg, 0.86 mmol, 0.20 M) was dissolved into 4 ml of an aqueous solution (D_2O) of sodium molybdate dihydrate (105 mg, 0.43 mmol, 0.10 M), EDTA (2.5 mg, 6.7×10^{-3} mmol, 1.6×10^{-3} M) and sodium hydroxide (34.5 mg, 0.86 mmol, 0.20 M). Different pD values were obtained by addition of acetate (pD 5), phosphate (pD 6 to 8) or carbonate (pD 9 to 10.0) buffers. Finally, 245 μl of hydrogen peroxide 50% (4.3 mmol, 1.01 M) were added and the temperature was maintained at 25°C throughout the reaction. The reaction mixtures were analyzed by ^{1}H NMR after 5 h and after 24 h.

2.4. Epoxidation of tiglic acid

258.6 mg (2.58 mmol, 0.5 M) of tiglic acid **A** were added to 5 ml of an aqueous solution (D_2O) containing sodium molybdate (281.5 mg, 1.16 mmol, 0.225 M) and sodium hydroxide (51.8 mg, 1.3 mmol, 0.25 M). After the addition of 150 μl of hydrogen peroxide 50% (2.6 mmol, 0.5 M), the solution became yellow. Throughout the reaction, the temperature was maintained at

20°C. The reaction was followed by ^1H NMR. The spectrum obtained after 50 min was compared with the values given in the literature and showed that the solution contained 8% of residual tiglic acid **A**, 80% of the epoxide **B**, 9% of the diol **D** and 3% of unassigned products.

2-epoxy-2-methylbutanoic acid **B**. ^1H NMR (D_2O, 300 MHz): 1.33 (d, 3H, CH_3-CH–), 1.46 (s, 3H, CH_3-C–), 3.20 (q, 1H, CH_3-CH–). ^{13}C NMR (D_2O, 300 MHz): 15.38 (CH_3-CH–), 16.59 (CH_3-C–), 61.90 (–CH-O–), 64.43 (–C-O–), 181.90 (–C-COOH).

2,3-dihydroxy-2-methylbutanoic acid **D**. ^1H NMR (D_2O, 300 MHz): 1.21 (d, 3H, CH_3-CH–), 1.49 (s, 3H, CH_3-C–), 3.87 (q, 1H, CH_3-CH–).

2.5. Peroxidation of tiglic acid

Potassium tiglate (0.77 g, 5.6 mmol, 2.8 M) and potassium molybdate (0.31 g, 1.3 mmol, 0.65 M) were dissolved into 1.43 g of water (H_2O). The volume of the final solution was equal to 2 ml. The solution was immersed in a thermostated bath maintained at 25°C. Then, 0.26 ml (4.55 mmol) of hydrogen peroxide 50% was added and the red brown mixture was stirred for six minutes until the color faded to gold yellow. Twenty two other fractions of 0.13 ml of hydrogen peroxide were allowed to react in the same way and the reaction was monitored by ^1H NMR by diluting 0.02 ml of the reaction medium in D_2O (0.5 ml). Thus, after 3 h, 3.12 ml (54.6 mmol) of hydrogen peroxide 50% had reacted and 98% of the starting organic substrate were oxidized into the hydroperoxide **C** (yield 80%). Its spectroscopic features are identical with those reported by Adam and Griesbeck for a sample photochemically prepared [20].

3-hydroperoxy-2-methylenebutanoic acid **C**. ^1H NMR (D_2O, 300 MHz): 1.31 (d, 3H, CH_3-CH–), 4.92 (q, 1H, CH_3-CH–), 5.58 and 5.89 (s and s, 2H, $-C{=}CH_2$). ^{13}C NMR (D_2O, 300 MHz): 20.7 (CH_3-CH–), 83.7 (CH_3-CH–). 123.2 ($-C{=}CH_2$), 149.0 (=C-COOH), 165.7 (=C-COOH).

2.6. Oxidation of tiglic acid by $K_2Mo_2O_3(O_2)_4 \cdot 4H_2O$

40 mg (0.4 mmol, 0.2 M) of tiglic acid **A** were added to 2 ml of an aqueous solution (H_2O) containing sodium hydroxide (16 mg, 0.4 mmol, 0.2 M) and potassium tetraperoxodimolybdate $K_2Mo_2O_3(O_2)_4 \cdot 4H_2O$ (51.8 mg, 0.1 mmol, 0.05 M). Throughout the reaction, the temperature was maintained at 25°C. The pH of the solution was equal to 5.40. After about 40 min, tiglic acid **A** had completely reacted giving the epoxide **B**.

3. Results and discussion

3.1. Peroxomolybdates generated by the system H_2O_2/MoO_4^{2-}

The reaction between hydrogen peroxide and molybdate ions leads to the formation of different peroxomolybdic intermediates [21,22], recently identified by ^{95}Mo NMR [19]. When the concentration of H_2O_2 is increased in alkaline medium, four mononuclear intermediates, mono- **1**, di- **2**, tri- **3**, and tetra **4** peroxomolybdates of general formulae $MoO_{4-n}(O_2)_n^{2-}$ ($n = 1, 2, 3, 4$), are formed. On the other hand, for decreasing pH values, it appears a broad peak **2a** ($\delta = -265$ to -285 ppm) (Fig. 1) which has been assigned to the dinuclear species $Mo_2O_3(O_2)_4^{2-}$ **2a** by comparison with a genuine sample. This compound may be considered formally as the dimer of the monoprotonated form of the diperoxomolybdate, $HMoO_2(O_2)_2^-$ [19].

From the area of the peaks **1**, **2**, **3** and **4** detected by ^{95}Mo NMR in alkaline medium, the constants K_i ($i = 1$ to 4) of the equilibria established between the four mononuclear peroxomolybdates have been calculated [19]. In the same way, by titration with hydrochloric acid of a solution mainly containing the triperoxomolybdate **3**, the constant K_5 of the equilibrium established between $MoO(O_2)_3^{2-}$ and $Mo_2O_3(O_2)_4^{2-}$ could be determined. By combination of these equilibria, four other equilibrium constants K_j ($j = 6$ to 9) were obtained. All these constants are summarized in Table 1.

By using all these equilibrium constants, a diagram showing the prevalent species as a function of pH and free hydrogen peroxide concentration could be drawn (Fig. 2). The border-lines separating the different domains correspond to conditions for which the concentrations of the complexes located on each side of the line are equal. The inner area correspond to conditions for which the concentration of indicated species is predominant.

The monoperoxomolybdate does not appear on this diagram since it is never prevalent. When mononuclear species such as $MoO(O_2)_3^{2-}$ and $Mo(O_2)_4^{2-}$ are involved, the border-line is calculated from the equality $[MoO(O_2)_3^{2-}] = [Mo(O_2)_4^{2-}]$. On the other hand, when one of the two species is dinuclear, such as for the equilibrium between $MoO(O_2)_3^{2-}$ and $Mo_2O_3(O_2)_4^{2-}$, the equation of the border-line is obtained from the equality $[MoO(O_2)_3^{2-}] = 2 \times$

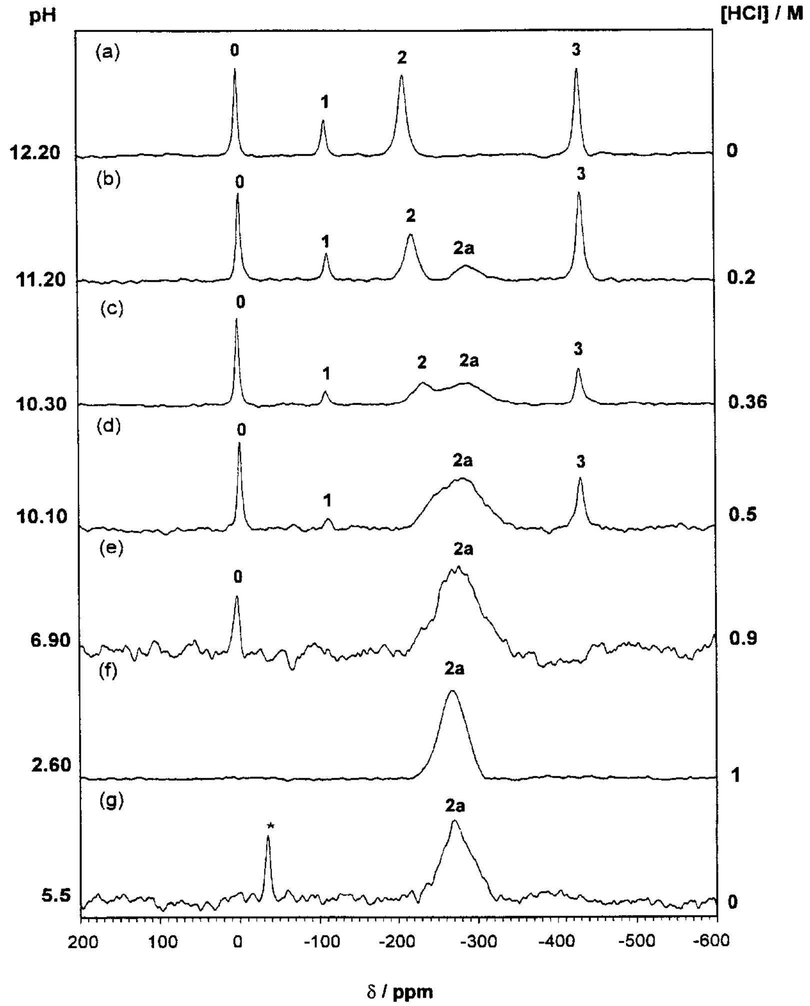


Fig. 1. (a–f) Evolution of the ^{95}Mo NMR spectra as a function of pH for $H_2O_2/Mo = 2$ ($T = 0°C$, $[Na_2MoO_4] = 1$ M, $[H_2O_2] = 2$ M). (g) Spectrum of $K_2Mo_2O_3(O_2)_4 \cdot 4H_2O$ (0.1 M) in H_2O at natural pH (5.5). (*) Non-assigned.

$[Mo_2O_3(O_2)_4^{2-}]$. It is noteworthy that for high pH values, the acid–base equilibrium of hydrogen peroxide ($pK_a = 11.6$) had to be taken into account for the determination of the equation of the border-line [19].

On the basis of this diagram, different reactivities of the system hydrogen peroxide/molybdate ions may be expected according to the pH values. Actually, it has been proved that singlet oxygen is generated quantitatively in alkaline medium [18]. A recent study has shown that the main precursor of this excited species is the unstable triperoxomolybdate $MoO(O_2)_3^{2-}$ which evolves $^1O_2$ at room temperature according to the Eq. (2) [18,19]:

$$MoO(O_2)_3^{2-} \rightarrow MoO_3(O_2)^{2-} + {}^1O_2 \qquad (2)$$

On the other hand, Griffith et al. [23] have prepared organo-soluble salts of $Mo_2O_3(O_2)_4^{2-}$ and have shown that these complexes are efficient epoxidizing agents in organic solvents.

Therefore, in order to show the versatility of the system H_2O_2/MoO_4^{2-}, we have studied the oxidation of an olefin able to react both by epoxidation and peroxidation with $^1O_2$.

3.2. Competition between epoxidation and peroxidation

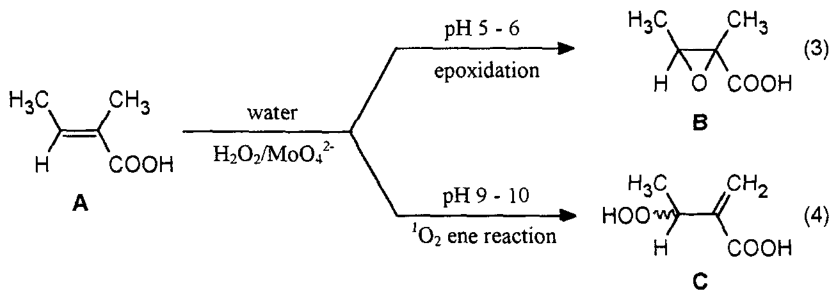
The chosen model was tiglic acid **A** because this α,β-unsaturated acid is water-soluble,

Table 1

Constants of the equilibria established between the different peroxomolybdates and equations of the border-lines separating the domains for which these intermediates are prevalent

Equilibrium	Method	Value	Border-line equation $\log[H_2O_2]_{free}$
$K_1 = \frac{[MoO_3(O_2)^{2-}]}{[MoO_4^{2-}] \times [H_2O_2]}$	^{95}Mo NMR [17]	1.5×10^2	—
$K_2 = \frac{[MoO_2(O_2)_2^{2-}]}{[MoO_3(O_2)^{2-}] \times [H_2O_2]}$	^{95}Mo NMR [17]	1.2×10^3	—
$K_3 = \frac{[MoO(O_2)_3^{2-}]}{[MoO_2(O_2)_2^{2-}] \times [H_2O_2]}$	^{95}Mo NMR [17]	2.1×10^2	$\log(4.7 \times 10^{-3} + 1.2 \times 10^{(pH-14)})$
$K_4 = \frac{[Mo(O_2)_4^{2-}]}{[MoO_2(O_2)_3^{2-}] \times [H_2O_2]}$	^{95}Mo NMR [17]	1.4	$\log(0.7 + 1.8 \times 10^{(pH-12)})$
$K_5 = \frac{[Mo_2O_3(O_2)_4^{2-}] \times [H_2O_2]^2}{[MoO(O_2)_3^{2-}]^2 \times [H_3O^+]^2}$	HCl titration [17]	1.5×10^{16}	$8.09 - pH$
$K_6 = \frac{[MoO_2(O_2)_2^{2-}]}{[MoO_4^{2-}] \times [H_2O_2]^2}$	$K_1 K_2$	1.8×10^5	$\log(2.4 \times 10^{-3} + 5.95 \times 10^{(pH-15)})$
$K_7 = \frac{[Mo_2O_3(O_2)_4^{2-}]}{[MoO_4^{2-}]^2 \times [H_2O_2]^4 \times [H_3O^+]^2}$	$K_5(K_1 K_2 K_3)^2$	2.1×10^{31}	$-7.8 + \frac{pH}{2}$
$K_8 = \frac{[Mo_2O_3(O_2)_4^{2-}] \times [H_2O_2]^4}{[Mo(O_2)_4^{2-}]^2 \times [H_3O^+]^2}$	$K_5(K_4)^{-2}$	7.4×10^{15}	$3.97 - \frac{pH}{2}$
$K_9 = \frac{[MoO_2(O_2)_2^{2-}]^2 \times [H_3O^+]^2}{[Mo_2O_3(O_2)_4^{2-}]}$	$(K_5)^{-1}(K_3)^{-2}$	1.5×10^{-21}	$pH = 10.4$

commercially available and known to react both by epoxidation (Eq. (3)) and by peroxidation with $^1O_2$ according to an ene reaction leading to an allylic hydroperoxide (Eq. (4)).



The experimental conditions of pH and concentrations of reagents reported in the literature for the oxidation of tiglic acid **A** into either the epoxide **B** or the hydroperoxide **C** are compared with our conditions in Table 2.

Tiglic acid react with photochemically generated $^1O_2$ according to an ene reaction leading to an allylic hydroperoxide (Eq. (3)) [20,26,27]. Adam and Richter have shown that the reaction occurred regioselectively since the hydroperoxide **C** is the sole product of the reaction [27]. McGoran and Wyborney [25] have oxidized tiglic acid into **C** by using H_2O_2 and a resin bound molybdate. However, their method is unsuitable for preparative purpose since the product is irreversibly retained by the resin.

On the other hand, the formation of the epoxide **B** has already been reported by Kirshenbaum and Sharpless [6] who used the system H_2O_2/WO_4^{2-} as a catalyst in the pH range 5.8–6.8 at room temperature. Oguchi et al. [24] improved the yield of epoxide and shortened the reaction time by replacing sodium tungstate with tris(cetylpyridinium)12-tungstophosphate (CPW) and by working at higher temperature (60–65°C) (Table 2).

The aim of our study was to determine the influence of the pH value on the stoichiometric balance of the oxidation reactions. As the epoxidation reaction occurs much faster than the

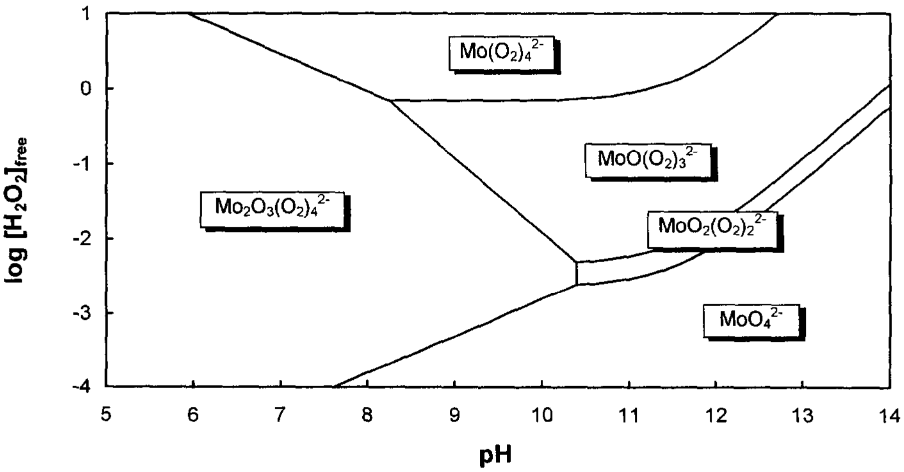


Fig. 2. Prevalent species formed by the interaction between H_2O_2 and MoO_4^{2-} as a function of pH and free $[H_2O_2]$ ($T = 0°C$, $[Na_2MoO_4] = 1$ M).

Table 2
Comparison of the experimental conditions used for the oxidation of tiglic acid **A** into the epoxide **B** or the hydroperoxide **C**

[Tiglic acid] (M)	$\frac{[H_2O_2]}{[\text{tiglic acid}]}$	Catalyst/solvent	pH	Δt (h)	θ (°C)	Yield (%)		Ref.
						B	**C**	
0.3	1.2	WO_4^{2-}/H_2O	5.8–6.8	1.75	room	81	—	[6]
0.4	1.2	CPW [a]/H_2O	6–7	0.7	60–65	89	—	[22]
0.5	1.0	MoO_4^{2-}/D_2O	5–6	0.85	20	80 [c]	—	[b]
0.85	—	$h\nu$/sensitizer/CCl_4	—	50	0	—	92	[18]
?	20.0?	MoO_4^{2-}/resin/CH_3OH	—	20	20–25	—	[c]	[23]
2.8	9.75	MoO_4^{2-}/H_2O	11–12	3	25	—	80 [c]	[b]

[a] CPW = tris(cetylpyridinium)12-tungstophosphate. [b] Our work. [c] Not isolated.

peroxidation, it appears difficult to observe a competition between the two reaction pathways Eqs. (3) and (4) in the same pot, unless experimental conditions favorable to the latter process are used. Tiglic acid is actually an electron-deficient olefin and its reactivity towards the electrophilic species $^1O_2$ is relatively low [28]. Nevertheless, in alkaline medium, it is expected to be more reactive since the sodium carboxylate group is slightly electron-donating whereas the acid carboxylic group is electron-withdrawing. On the other hand, the reactivity of $^1O_2$ towards organic substrates is much higher in water than in usual organic solvents [29]. It is particularly increased in D_2O since the lifetime of $^1O_2$ is fifteen times longer in deuterated water (67 μs) than in ordinary water (4.4 μs) [30]. Therefore, the mere change of H_2O into D_2O enabled us to observe a competition between the peroxidation and the epoxidation, by using a relatively high concentration of tiglic acid **A** equal to 0.2 M. Moreover, D_2O allows a direct NMR analysis of the reaction medium. Although the process is catalytic and the molybdate is regenerated at the end of the reaction, we have used a relatively high concentration of MoO_4^{2-} (0.1 M) in order to allow the activation of ten-fold H_2O_2 (1 M) in a reasonable time. The stoichiometric balance of oxidized products and residual starting material at various pH was determined by ^1H NMR at the end of the reaction and was represented as a function of the pD value in Fig. 3.

Fig. 3 clearly shows that two different reaction pathways take place according to the pD value. When pD ≤ 7.2, the substrate is completely oxidized giving mainly the epoxide **B**

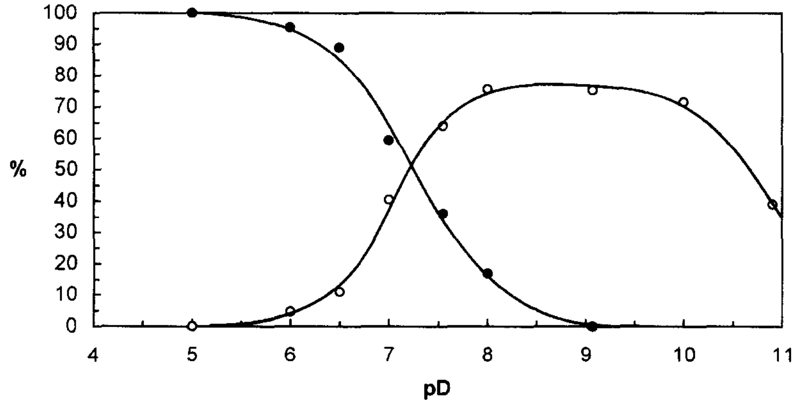


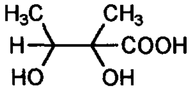
Fig. 3. Stoichiometric balance of oxidized products as a function of pD ([tiglic acid] = 0.2 M, [MoO_4^{2-}] = 0.1 M, [H_2O_2] 1 M, D_2O, T = 25°C). epoxide **B** and diol **D**: ●, hydroperoxide **C**: ○.

whereas when pD ≥ 7.2, the hydroperoxide **C** is prevalent but some tiglic acid remains unchanged. When pD is higher than 10, the percentage of unreacted starting material is increased at the expense of the hydroperoxide **C** due to the occurrence of some spontaneous disproportionation of hydrogen peroxide.

By comparing these results with the diagram showing the prevalent peroxomolybdic intermediates as a function of pH and H_2O_2 concentration (Fig. 2), we can assume that the epoxidizing agent is the tetraperoxodimolybdate $Mo_2O_3(O_2)_4^{2-}$ whereas the intermediate responsible for the formation of the hydroperoxide **C** is the triperoxomolybdate $MoO(O_2)_3^{2-}$, precursor of $^1O_2$. From the constant K_5 of the equilibrium established between $MoO(O_2)_3^{2-}$ and $Mo_2O_3(O_2)_4^{2-}$, the pH for which both oxidizing intermediates are in equal amounts could be estimated ($[H_2O_2]_{free}$ is assessed to ≈ 0.75 M) (Fig. 3). The value found (7.7) agrees with the pH value (7.2) obtained in the competition experiments. Actually, the kinetics of the reactions under study are very complex and it is difficult to forecast exactly this pH value only by considering the equilibrium constants. In addition, the constants determined by ^{95}Mo NMR are calculated from experiments performed in a mixture of H_2O/D_2O (80/20) whereas in the present study, the reactions were conducted in D_2O.

As a control experiment, the oxidation of tiglic acid **A** has also been conducted in ordinary water (H_2O) while the pH was maintained at a constant value (pH = 8.0) chosen in such a way that both pathways Eqs. (3) and (4) occurred significantly. A ratio hydroperoxide **C**/epoxide **B** of 0.65 was obtained in H_2O instead of 3.75 in D_2O which confirms that $^1O_2$ is actually the peroxidizing agent in alkaline medium. In the same way, we have oxidized, at pH 5, four equivalents of tiglic acid **A** (0.2 M) with one equivalent of $K_2Mo_2O_3(O_2)_4 \cdot 4H_2O$ (0.05 M), prepared according to the method described by Stomberg [31]. The epoxide **B** was obtained quantitatively showing that the four peroxo bridges of the tetraperoxodimolybdate are used in the epoxidation process. However, the peroxo groups of a single species $Mo_2O_3(O_2)_4^{2-}$ are not reduced successively. It is more likely that when one of the peroxo groups is consumed, the unstable intermediate obtained, $Mo_2O_4(O_2)_3^{2-}$, disproportionates into the more stable MoO_4^{2-} and $Mo_2O_3(O_2)_4^{2-}$. In agreement with this interpretation, we have already shown that a solution of H_2O_2/MoO_4^{2-} in the ratio 1/1 at pH 4–6 does not exhibit other ^{95}Mo NMR peaks than **0** and **2a** [19]. Moreover, Campbell et al. have studied the peroxomolybdates formed in this pH range by Raman and IR spectroscopy and they could not detect other species than the tetraperoxodimolybdate $Mo_2O_3(O_2)_4^{2-}$ [23].

According to these results, by using the system H_2O_2/MoO_4^{2-}, we have oxidized selectively tiglic acid **A** at a preparative level (see Table 2). In acidic medium (pH 5.5–6), we succeeded in oxidizing 0.5 M of tiglic acid giving 80% of the epoxide **B** and 9% of the diol **D** whereas in alkaline medium, 2.8 M of tiglic acid could be oxidized leading to 80% of the hydroperoxide **C**.



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4. Conclusion

By studying the influence of the pH value on the oxidation of tiglic acid, we have shown the double reactivity of the system hydrogen peroxide/molybdate ions. In alkaline medium, the formation of the intermediate $MoO(O_2)_3^{2-}$ allows to obtain the hydroperoxide **C** via the generation of singlet oxygen whereas in acidic medium, the formation of $Mo_2O_3(O_2)_4^{2-}$ leads to the epoxide **B**. Under given conditions, both of these oxidation products can be prepared selectively at a preparative level in good yields.

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