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Production of 5-hydroxy-4-keto-2-pentenoic acid by photo-oxidation of 5-hydroxymethylfurfural with singlet oxygen: A kinetic investigation

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ABSTRACT

5-Hydroxy-4-keto-2-pentenoic acid (HKPA) is characterized by the presence in its chemical structure of four different chemical groups (hydroxyl, keto, carboxylic and unsaturated groups) that render it a possible intermediate or monomer in the chemical industry. The production of this compound is studied by the sensitized photo-oxidation of 5-hydroxymethylfurfural (5-HMF) in aqueous solution at acidic pH. 5-HMF can be easily obtained through the degradation of saccharides such as fructose or inulin.

The system reactivity is influenced by the concentration of methylene blue (BM) which is used as the photosensitizer and the oxygen dissolved in the solution. Only moderate consumptions of the sensitizer are recorded during the oxidation experiments thus suggesting the possibility to recover and reuse it in new runs. No differences in the reactivity of the system and/or selectivity for HKPA are observed as a result of changes in the starting concentration of the substrate and/or pH.

A simplified reaction scheme of photo-oxidation of 5-HMF is proposed. Two kinetic models are developed according to this scheme to simulate the photo-oxidation processes of the substrate in the absence and in the presence of methylene blue. A validation of these models is carried out by means of the experimental data, collected at pH = 6.0, at different initial concentrations of 5-HMF and BM.

1. Introduction

The continuous oscillation of oil price and mainly the awareness of the shortage of its world supplies stimulated during the last three decades the search of new renewable sources for both the chemicals and fuels. Many studies have been up to now carried out to explore the possibility to convert biomasses and particularly carbohydrates – which are the most abundant fractions of them – into valuable chemical intermediates and fuels [1–3]. 5-Hydroxymethylfurfural (5-HMF) is an example of these intermediates, produced through the degradation of hexoses [4]. Investigations at pilot plant level to produce it from D-fructose or inulin have been documented in the past [5]. Moreover, improved performances in the production of 5-HMF from fructose and inulin, particularly in terms of productivity [6], have been reported for catalysts based on vanadyl phosphate, even modified by the addition of different metals.

A new process to obtain 5-HMF from fructose by means of a biphasic system has been also recently proposed [7].

5-HMF and 2,5-disubstituted furans are expected to become in near future the interesting intermediates in the chemical industry capable in some cases to replace important “chemical building blocks” which are actually produced from oil. Numerous versatile intermediate chemicals, which could replace other petrochemical compounds, can be generated from 5-HMF in simple large-scale transformations. For example, the possibility has been suggested to substitute terephthalic acid with 2,5-furandicarboxylic acid, which could be obtained from 5-HMF through a direct oxidation process [8].

Nowadays a great interest is recorded for new processes capable of transforming 5-HMF into more valuable chemical intermediates and products [2].

Among the available indications in the literature, it is reported that the photo-oxidation of 5-HMF in an aqueous solution, in the presence of methylene blue (BM) or rose bengale (RB) as photosensitizers, results in the formation of 5-hydroxy-4-keto-2-pentenoic acid (HKPA) following the attack of singlet oxygen to the substrate [9].

HKPA is characterized by the presence of four different chemical groups (hydroxyl, keto, carboxylic and unsaturated groups) in its chemical structure which indicates it as a possible intermediate in chemical synthesis or as a monomer for polymerization.

At present no indications have been reported in the literature about the effect of some variables such as the starting concentrations of the substrate and BM, wavelengths of radiation, pH, temperature and oxygen concentration dissolved in the solution

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Nomenclature

H	Henry's law constant for O_2
I°_{305}, I°_{313}, I°_{366}	incident power lamp at wavelengths 305 nm (4.5×10^{-6} E s^{-1}), 313 nm (1.0×10^{-6} E s^{-1}) and 366 nm (7.5×10^{-6} E s^{-1}), respectively (measured in this work)
I_a^A	radiant power absorbed by the solution in the absence of BM (E s^{-1})
I_a^{BM}	radiant power absorbed by the solution in the presence of BM (E s^{-1})
l	Reactor optical length (1.1 cm) (measured)
k	kinetic rate constant
k_d	rate constant for $^1O_2$ decay to ground state oxygen in water (2.5×10^{-5} s^{-1}) [15]
P	total pressure (atm)
V	volume of the solution (0.28 L) (measured)
x	liquid-phase mole fraction for O_2

Greek letters

ε^A_{305}; ε^A_{313}; ε^A_{366}	molar extinction coefficients of 5-HMF at wavelengths 305 nm (5.49×10^3 L mol^{-1} cm^{-1}), 313 nm (1.95×10^3 L mol^{-1} cm^{-1}) and 366 nm (3.00 L mol^{-1} cm^{-1}), respectively (measured in this work)
ε^{BM}_{305}; ε^{BM}_{313}; ε^{BM}_{366}	molar extinction coefficients of BM at wavelengths 305 nm (1.72×10^4 L mol^{-1} cm^{-1}), 313 nm (9.57×10^3 L mol^{-1} cm^{-1}) and 366 nm (5.66×10^2 L mol^{-1} cm^{-1}) (measured in this work)
λ	wavelength
σ	percentage standard deviation (%) (estimated in this work)
Φ_A	quantum yield of substrate direct photolysis (1.057 mol E^{-1}) (estimated in this work)
Φ_{BM}	quantum yield of $^1O_2$ production by direct photolysis of BM (mol E^{-1}) (0.52 mol E^{-1}) [19]

on the reactivity and yield of HKPA. Moreover, no results of kinetic assessments on the photo-oxidation of 5-HMF to produce HKPA have been so far published.

Therefore, in the present paper, the production of HKPA from 5-HMF through a photo-oxidation process in aqueous solution is investigated with the aim of assessing the effect on the system reactivity and the yield of HKPA of operative variables such as pH of the solution, concentration of the substrate, sensitizer and dissolved oxygen. The reaction kinetics are also studied.

2. Materials and methods

The experimental runs were carried out at 298 K in a batch cylindrical glass jacketed reactor with an outer diameter of 5.6 cm and a height of 40 cm wrapped with an aluminium foil. At the top, the reactor had two inlets for feeding reactants and gas stream and an outlet for withdrawing samples.

The reactor was equipped with a 125 W (power input) high-pressure lamp (by Helios Italquartz), mainly emitting at 305, 313 and 366 nm (manufacturer's data), enclosed in a glass sleeve, which was immersed in the solution in the center of the reactor. The reactor was equipped with a magnetic stirrer placed at the bottom. pH measurements were performed by means of an Orion 960 pH-meter. The pH of solutions was regulated with perchloric acid and sodium hydroxide.

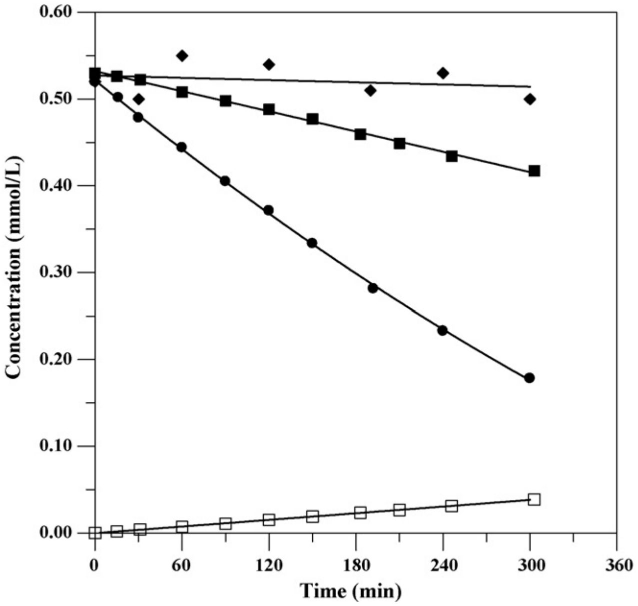


Fig. 1. Concentration profiles of 5-HMF and HKPA against the reaction time for different experimental conditions: O_2 bubbling at dark (◆ 5-HMF); O_2 bubbling and radiation (■ 5-HMF; □ HKPA); N_2 bubbling and radiation (● 5-HMF). T = 25 °C; pH = 6.0.

The samples, taken from the reactor, were analyzed immediately after sampling. The concentrations of 5-HMF and HKPA were evaluated by HPLC analysis. For this purpose, the HPLC apparatus (HP 1100) was equipped with a UV–vis detector (λ: 284 nm for 5-HMF and 210 nm for HKPA) and Alltech OA-100 organic acid column, using H_2SO_4 (0.01 mol L^{-1}) solution as mobile phase, flowing at 0.5 ml min^{-1}.

HKPA (not purchasable as chemical standard) was purified and isolated by means of preparative HPLC by using the mobile phase previously described. Its structure was identified by LC–MS analysis with a Sinergy Polar column (eluent: mixture of 75% formic acid (0.1% by volume) and 25% acetonitrile at flow rate of 0.7 ml/min). The mass fragmentation (m/e) for HKPA was: 130 [M], 112 [M$-$H$_2$O], 85 [M$-$HCOOH], where M indicates the molecular peak.

The molar extinction coefficients for 5-HMF and HKPA were calculated by measuring the absorbance with UV–vis spectrophotometer (HP 8452 A) with quartz cells (path length = 1 cm).

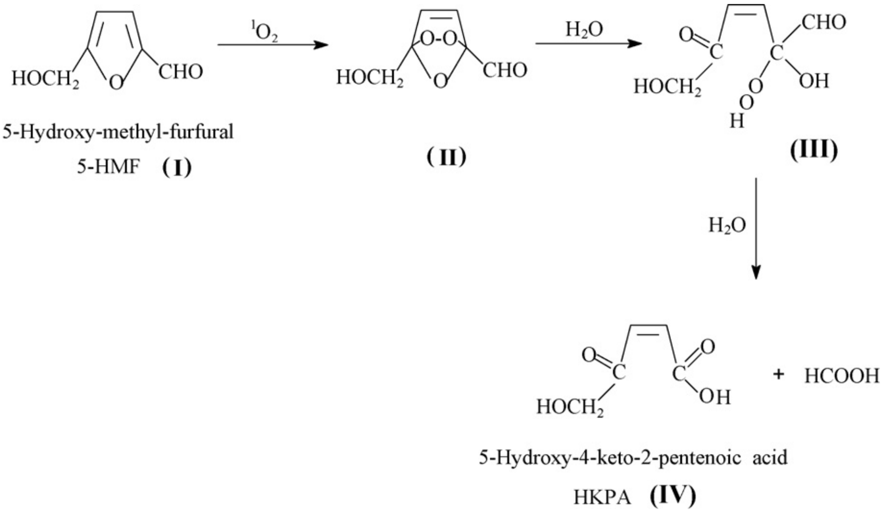
The power of lamp at 366 nm (I°_{366}) was 7.50×10^{-6} E s^{-1} (measured using a UV radiometer), at 313 nm (I°_{313}) 1.00×10^{-6} E s^{-1} (valerophenone actinometry [10]) and at 305 nm (I°_{305}) 4.50×10^{-6} E s^{-1} according to Kuhn et al. [11]. 5-HMF, BM, sodium hydroxide and perchloric acid were purchased from Sigma–Aldrich and used as received.

3. Results and discussion

3.1. Chemical investigation

Preliminary experimental runs were carried out on aqueous solutions of 5-HMF submitted to oxygen bubbling at dark and in the presence of irradiation (Fig. 1). To throw light on the role of oxygen feeding the photo-oxidation of 5-HMF was carried out also in the absence of this oxidant under nitrogen bubbling.

The data reported in Fig. 1 indicate that 5-HMF undergoes direct photolysis when it was submitted to irradiation at 305–366 nm in the absence of oxygen. No formation of HKPA was observed in this case the substrate being converted to unidentified species



Scheme 1.

as indicated by numerous peaks in the HPLC chromatogram (data not shown). When an oxygen stream was bubbled into the reacting solution, under irradiation, 5-HMF was partially converted into HKPA with a selectivity close to 35%.

No reactivity at all was recorded when the lamp was switched off thus indicating the uncapability of oxygen to directly attack 5-HMF.

The formation of HKPA, starting from 5-HMF under O_2 bubbling and radiation, can be explained assuming the generation of singlet oxygen by an energy transfer from excited state of 5-HMF molecules to dissolved molecular oxygen, since it has been reported that under UV irradiation furanosic ring compounds may favor the formation of singlet oxygen in the solution [12]. An attack of this reactive species to 5-HMF was put forward to explain its conversion into HKPA. A possible reaction pathway for this process is reported in Scheme 1.

The initial singlet oxygen attack to the substrate leads to the formation of the ozonide (II). This species undergoes an hydrolytic cleavage which results into the opening of the ring with the formation of both a ketonic group and an alfa-hydroxyhydroperoxidic one (III). This species easily leads to the formation of HPKA (IV) since it is known that alfa-hydroxyhydroperoxides with carbonylic groups in the alfa position show a rearrangement with a contemporary cleavage of O–O and C–C bonds followed by a rapid hydrolysis, as documented for anomalous ozonolysis mechanism [13]. A similar mechanism was reported for the photo-oxidation of substituted furans in the presence of alcohols [14].

According to these indications it can be stated that the possibility to convert 5-HMF into HKPA is strictly related to the presence in the reacting system of singlet oxygen.

Different species are known from the literature as capable to favor the formation of singlet oxygen when they were added to a system under irradiation. Among them methylene blue is reported as one of the most efficient sensitizers in aqueous media. Fig. 2 shows the data collected with and without BM [15] and it was thus used in the course of the present investigation addition to the aqueous solutions of 5-HMF. It is evident that the addition of this sensitizer renders the system more reactive and increases the selectivity to HKPA from around 35% to about 75%.

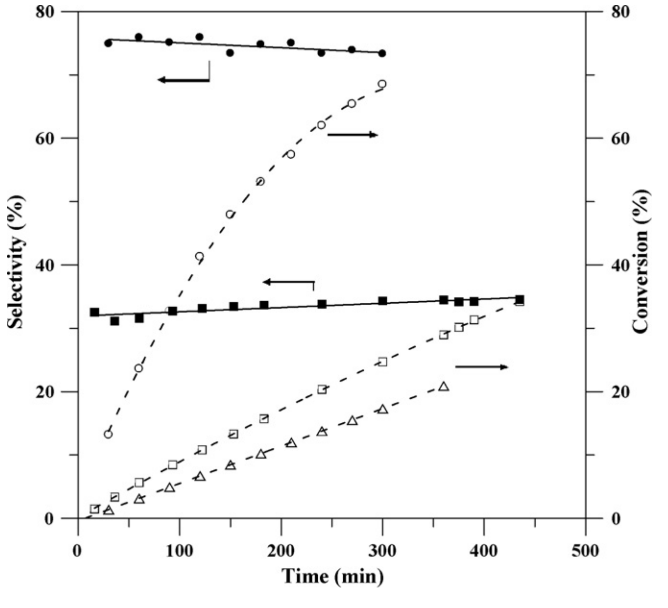


Fig. 2. Conversions of 5-HMF (○, □) and BM (△) and selectivities to HKPA (●, ■) during the photolysis of 5-HMF in the presence (circles) and in the absence (squares) of BM. $T = 25\,^{\circ}C$; pH = 6.0; [5-HMF]$_o$ = 1.0 mmol L^{-1}; [BM]$_o$ = 32.0 μmol L^{-1}.

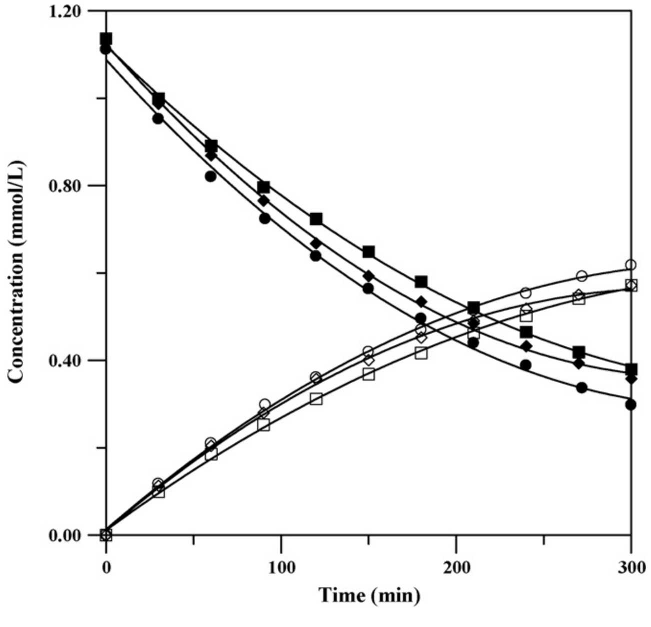


Fig. 3. Concentration profiles of 5-HMF (full symbols) and HKPA (empty symbols) against the reaction time at different pHs: ■: pH = 4.0, ♦: pH = 6.0, ●: pH = 8.0. $T = 25\,^{\circ}C$, [5-HMF]$_o$ = 1.0 mmol L^{-1}; [BM]$_o$ = 32.0 μmol L^{-1}.

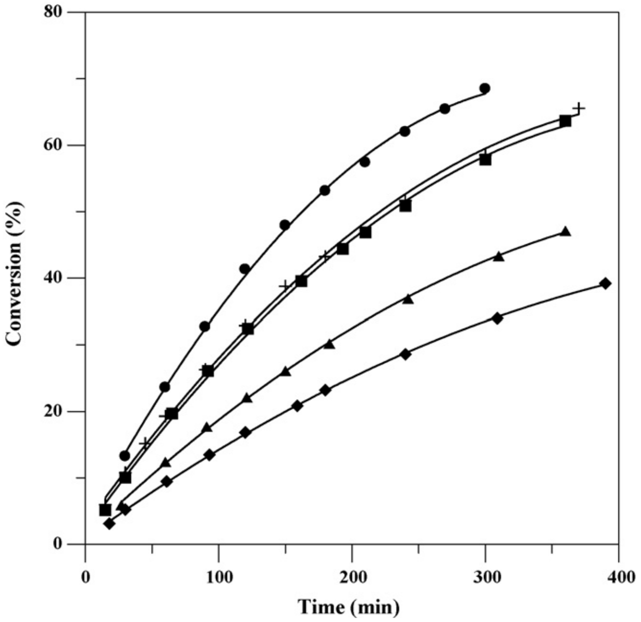


Fig. 4. Photolytic conversions for the photolysis of 5-HMF at different initial concentrations of BM. $[BM]_o$: 80.0 μmol L^{-1} (+), 32.0 μmol L^{-1} (●), 9.0 μmol L^{-1} (■), 4.0 μmol L^{-1} (▲), 1.4 μmol L^{-1} (♦). $T = 25\,^{\circ}$C; pH = 6.0; $[5\text{-HMF}]_o = 1.0$ mmol L^{-1}.

It is noteworthy to observe that only a moderate disappearance of BM (empty triangles) was recorded during the run (Fig. 2) thus suggesting the possibility to recover the photosensitizer at the end of the run (for example by means of a liquid–liquid extraction) and reuse it. Similar results were obtained in all runs.

The effect of some operating variables on the system reactivity and yield of HKPA were also investigated.

The results of some experimental runs at different starting substrate concentrations and at different pHs indicated that these variables have only weak effects, if any, on the reactivity and selectivity of the process. For example, Fig. 3 shows the concentration of 5-HMF and of HKPA in the pH range 4.0–8.0.

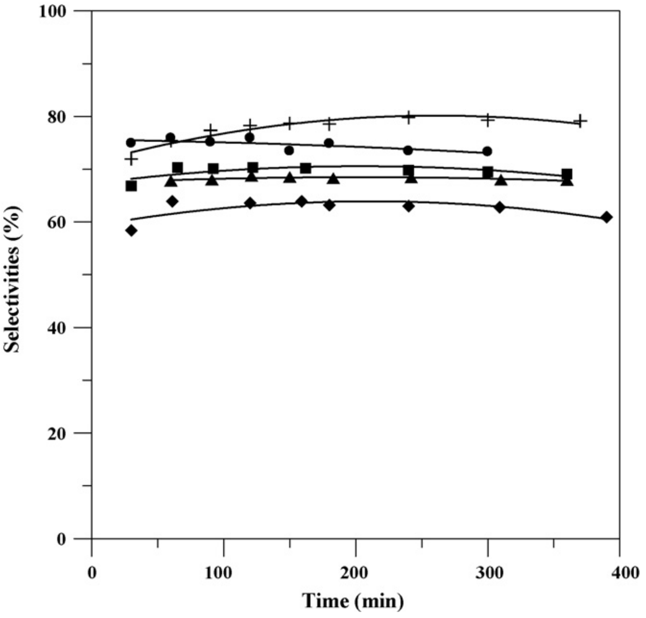


Fig. 5. Selectivities for the photolysis of 5-HMF at different initial concentrations of BM. $[BM]_o$: 80.0 μmol L^{-1} (+), 32.0 μmol L^{-1} (●), 9.0 μmol L^{-1} (■), 4.0 μmol L^{-1} (▲), 1.4 μmol L^{-1} (♦). $T = 25\,^{\circ}$C; pH = 6.0; $[5\text{-HMF}]_o = 1.0$ mmol L^{-1}.

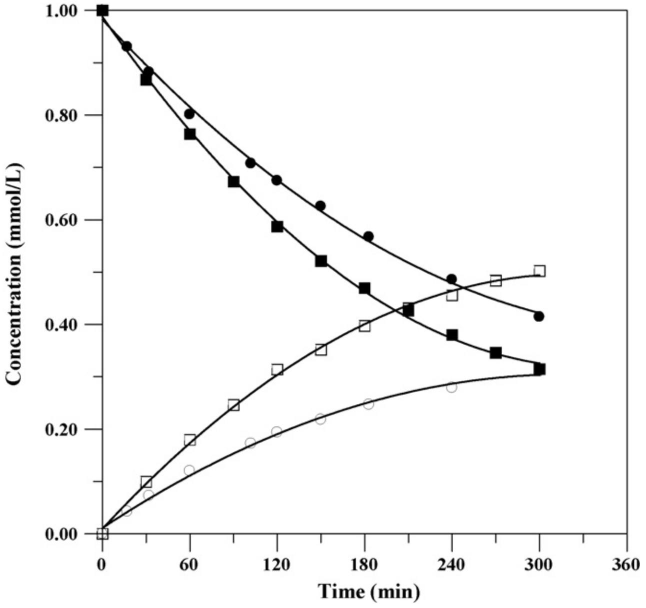


Fig. 6. Concentration profiles against the reaction time for different experimental conditions: with O_2 bubbling (■ 5-HMF; □ HKPA); with air bubbling (● 5-HMF; ○ HKPA). $[5\text{-HMF}]_o = 1.0$ mmol L^{-1}, $[BM]_o = 32.0$ μmol L^{-1}, $T = 25\,^{\circ}$C; pH = 6.0.

On the other hand, a higher reactivity was shown by the system after the increase of the starting concentration of BM up to 32.0 μM. The adoption of BM concentrations beyond this value resulted into lower reactivity (Fig. 4) although the selectivity to HKPA continued to increase (Fig. 5).

Last data (Figs. 4 and 5) seem to indicate that when the concentration of BM is increased this species exerts a more relevant shielding of radiation which mainly affects the capability of the substrate to undergo direct photolysis thus reducing the overall reactivity of the system.

The effect of oxygen concentration in the reacting solution was investigated by performing some experiments by replacing the oxygen stream with one of air (Fig. 6). A clear decrease of the reactivity was recorded during the run performed with air bubbling.

In fact, the conversions on 5-HMF (at 300 min) pass from 68.5 to 58.6 whereas the selectivities to HKPA decrease from 64.4 to 52.9 when the oxygen stream is replaced by an air one.

3.2. *Kinetic investigation*

According to the results reported above it is clear that the disappearance of 5-HMF under UV irradiation (305–366 nm) and in the presence of an oxygen bubbling with and without BM addition is due to both a direct photolysis of the substrate and its oxidation by singlet oxygen formed in the solution. On the other hand, the formation of the product of interest (HKPA) occurs just according to the oxidation pathway (Scheme 1).

Due to the complexity of a system like this, its kinetic characterization may be better achieved by firstly considering each single subsystem identified in previous paragraphs and finally the complete one.

Table 1
Estimated values of Φ_A along with the percentage standard deviations.

$[5\text{-HMF}]_o$ (mmol L^{-1})	σ_A (%)	Φ_A (mol E^{-1})
0.26	2.42	$1.06 \times 10^{-3} \pm 1.58 \times 10^{-5}$
0.52	3.39	
0.73	1.40	

Table 2
Kinetic parameters and percentage standard deviations for the no-sensitized photo-oxidation of 5-HMF at pH = 6.0.

$[\text{5-HMF}]_o$ (mmol L^{-1})	σ_A (%)	σ_P (%)	k_4 (L mol^{-1} s^{-1})	k_5 (L mol^{-1} s^{-1})
0.53	4.08	22.41	$8.51 \times 10^{-3} \pm 2.55 \times 10^{-4}$	$9.57 \times 10^{7} \pm 5.26 \times 10^{6}$
0.84	1.73	8.99		
1.08	0.18	9.30		
1.35	1.83	15.99		

3.2.1. 5-HMF irradiation in the absence of oxygen (direct photolysis)

As shown above (Fig. 1) 5-HMF is capable to undergo direct photolysis when it is irradiated in a nitrogen bubbled aqueous solution. An attempt to account for this behavior leads to the development of the following reaction scheme:

$$A \xrightarrow{\Phi_A, h\nu} A^* \tag{r$_1$}$$

$$A^* \xrightarrow{k_2} \text{byproducts} \tag{r$_2$}$$

5-HMF (indicated by A) absorbs light to give an excited state molecule (reaction (r$_1$)), A*. The species A*, can decompose to byproducts (reaction (r$_2$)).

According to this scheme the following mass-balance equations can be written for the species A (the substrate) and A* (the substrate in an excited state):

$$\frac{d[A]}{dt} = \frac{I_a^A}{V} \cdot \Phi_A \tag{1}$$

$$\frac{d[A^*]}{dt} = \frac{I_a^A}{V} \cdot \Phi_A - k_2 \cdot [A^*] \tag{2}$$

The light intensity absorbed by the solution may be expressed as:

$$I_a^A = \sum_{i=1}^{3} I_{\lambda_i}^0 \cdot \{1 - \exp[-2.3 \cdot l \cdot (\varepsilon_{\lambda_i}^A \cdot [A])]\} \tag{3}$$

where Φ_A is the quantum yield considered to be constant within range of three wavelengths of emitted by the lamp (305, 313 and 366 nm) due to the lack of any reference in the literature. In Eqs. (1)–(3) two unknown parameters appear Φ_A and k_2 (kinetic constant of reaction (r$_2$)).

However, using the data collected in the experiments in the absence of oxygen only the estimation of Φ_A was possible since neither measurements for the species A* nor for the byproducts arising from the reaction (r$_2$) were available.

The data of a set of three photolytic experiments at different starting 5-HMF concentrations (0.26, 0.52 and 0.73 mmol L^{-1}) were thus used in the optimization procedure in which the minimum of the objective function:

$$\Psi \cong \sum_{i=1}^{n} (Y_i - C_i)^2 \tag{4}$$

was achieved (where Y_i and C_i are calculated and experimental concentrations respectively).

The value obtained for Φ_A along with the percentage standard deviations are reported in Table 1.

3.2.2. 5-HMF irradiation in the presence of oxygen

Since it has been reported that 5-HMF under irradiation may favor the formation of singlet oxygen in the solution, it can be put forward that when 5-HMF was irradiated in the presence of oxygen the system reactivity is the result of both its direct photolysis and its attack by $^1O_2$. A kinetic scheme can be thus written by adding to the reactions already considered for the direct photolysis (reactions (r$_1$) and (r$_2$)) those related to $^1O_2$ generation and consumption (reactions (r$_3$)–(r$_6$)).

Singlet oxygen may be produced by an energy transfer from excited state of 5-HMF to dissolved molecular oxygen:

$$A^* + O_2 \xrightarrow{k_3} {}^1O_2 + A \tag{r$_3$}$$

And, subsequently, can oxidize 5-HMF to produce the product HKPA (P):

$$A + {}^1O_2 \xrightarrow{k_5} P \tag{r$_4$}$$

or can react with molecular oxygen by a photoassisted reaction:

$$A + O_2 \xrightarrow{k_4, h\nu} \text{byproducts} \tag{r$_5$}$$

Moreover it can be also quenched by the aqueous media to its ground state with a kinetic constant k_d (2.5×10^5 s^{-1}) [16]:

$${}^1O_2 \xrightarrow{k_d} {}^3O_2 \tag{r$_6$}$$

The oxygen participation to the reaction (reactions (r$_3$)–(r$_6$)) poses a question related to the regime of absorption with reaction under which the process develops. A simple consideration on the characteristic reaction and saturation times may allow to single out the prevailing regime. In fact, if the pseudo-first order kinetic constant of 5-HMF decay in the most reactive run is evaluated, a value of 5.17×10^{-5} s^{-1} is found. From this result a value of characteristic reaction time equal to 322 min is obtained. This is much greater than the saturation times (1–5 min) reported for reactors similar to that used in the present investigation [17].

Therefore, it can be concluded that the process develops under a kinetic regime of absorption with reaction and the calculation of the enhancement factor, E, gave a value near unity to indicate a "slow kinetic regime". Following these considerations it can be thus assumed that the concentration of oxygen keeps at the saturation value at the operating temperature which can be calculated according to the Henry's law ($P = H \cdot x$) with $H = 4.38 \times 10^4$ atm [18]. If a pure oxygen stream at $P = 1$ atm was used then $x = 2.283 \times 10^{-5}$. A value of 1.267×10^{-3} mol L^{-1} for the concentration of oxygen dissolved in the liquid bulk, $[O_2]$, can be obtained.

According to the reaction schemes proposed (reactions (r$_3$)–(r$_6$)), mass-balance equations may be thus written for A, A*, $^1O_2$ and P species. Since preliminary attempts to estimate unknown kinetic constants indicated a high value of the ratio k_3/k_2, also based

Table 3
Kinetic parameters and percentage standard deviations for the photosensitized oxidation of 5-HMF at pH = 6.0.

$[\text{5-HMF}]_o$ (mmol L^{-1})	$[BM]_o$ (μmol L^{-1})	σ_A (%)	σ_{BM} (%)	σ_P (%)	k_6 (L mol^{-1} s^{-1})	k_7 (L mol^{-1} s^{-1})	k_8 (L mol^{-1} s^{-1})
0.60	32.0	5.24	2.94	15.50	$6.39 \times 10^{3} \pm 2.23 \times 10^{2}$	$2.83 \times 10^{6} \pm 9.90 \times 10^{4}$	$1.42 \times 10^{1} \pm 1.85$
1.09	9.0	3.59	3.41	14.48			
1.07	4.0	4.45	2.63	27.09			
1.08	32.0	7.75	1.46	16.95			

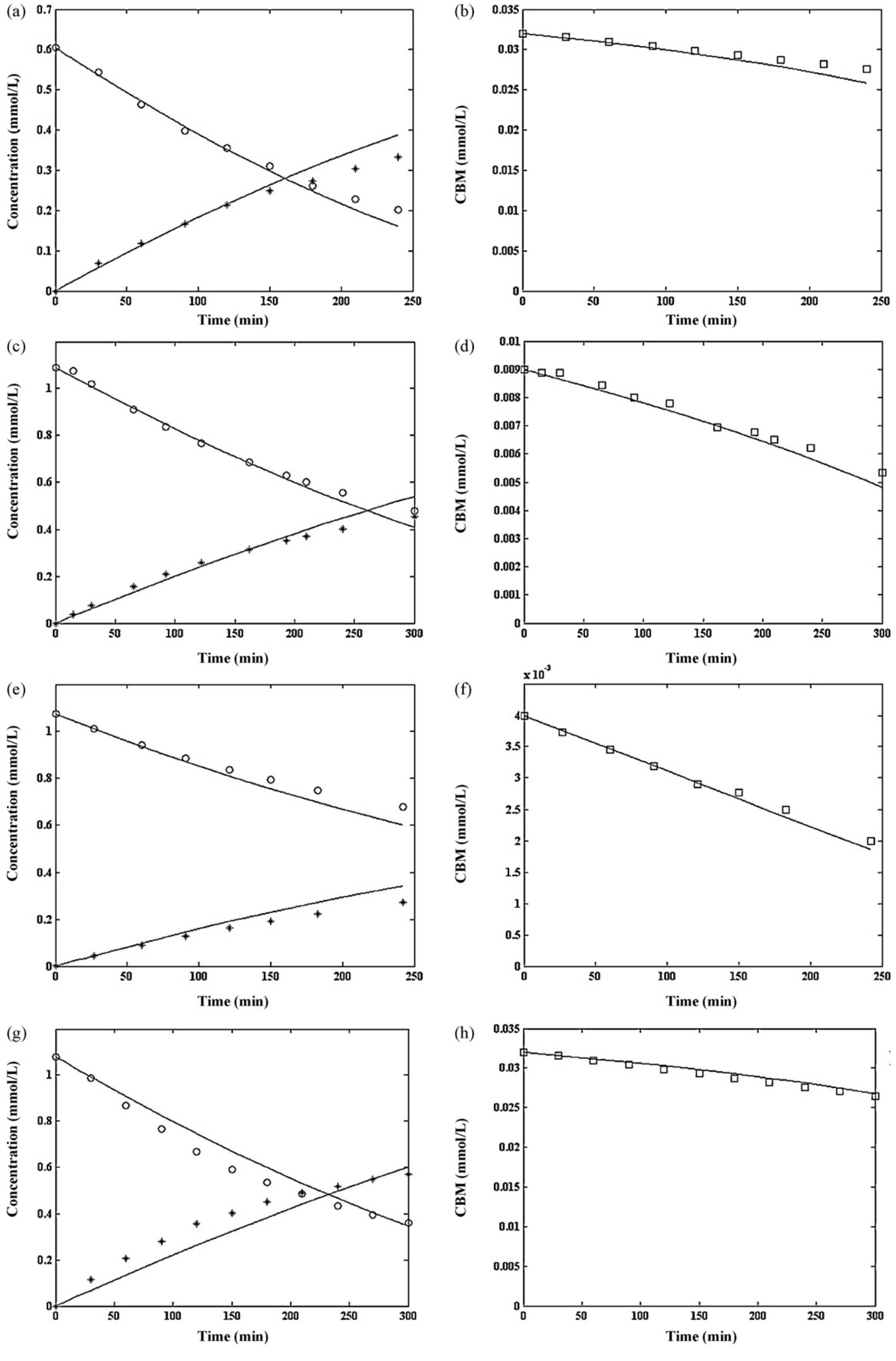


Fig. 7. Predicted (solid lines) and experimental (symbols) concentration–time profiles for 5-HMF (○), HKPA (✱) (a, c, e and g) and BM (□) (b, d, f and h) at pH = 6.0. (a and b): $[5\text{-HMF}]_o = 0.60\ \text{mmol}\ L^{-1}$; $[BM]_o = 32.0\ \mu\text{mol}\ L^{-1}$. (c and d): $[5\text{-HMF}]_o = 1.09\ \text{mmol}\ L^{-1}$; $[BM]_o = 9.0\ \mu\text{mol}\ L^{-1}$. (e and f): $[5\text{-HMF}]_o = 1.06\ \text{mmol}\ L^{-1}$; $[BM]_o = 4.0\ \mu\text{mol}\ L^{-1}$ (g and h): $[5\text{-HMF}]_o = 1.08\ \text{mmol}\ L^{-1}$; $[BM]_o = 32.0\ \mu\text{mol}\ L^{-1}$.

on the discussion reported in previous paragraphs on the difficulty to evaluate k_2 constant, a simplifying assumption was done that the selectivity of reaction (r$_3$) was practically equal to 1.0.

The mass-balance of A*:

$$\frac{d[A^*]}{dt} = \frac{I_a^A}{V} \cdot \Phi_A - k_2 \cdot [A^*] - k_3 \cdot [A^*] \cdot [O_2] \cong \frac{I_a^A}{V} \cdot \Phi_A - k_3 \cdot [A^*] \cdot [O_2] \qquad (5)$$

Moreover, if a steady-state assumption is done for the species A* the following equations are obtained:

$$\frac{d[A^*]}{dt} = \frac{I_a^A}{V} \cdot \Phi_A - k_3 \cdot [A^*] \cdot [O_2] \cong 0 \qquad (6)$$

$$\frac{d[A]}{dt} = -\frac{I_a^A}{V} \cdot \Phi_A + k_3 \cdot [A^*] \cdot [O_2] - k_4 \cdot [A] \cdot [O_2] - k_5 \cdot [A]$$
$$-6pt \cdot [^1O_2] \cong \qquad (7)$$
$$-6pt \cong -k_4 \cdot [A] \cdot [O_2] - k_5 \cdot [A] \cdot [^1O_2]$$

$$\frac{d[^1O_2]}{dt} = \left(\frac{I_a^A}{V} \cdot \Phi_A\right) - k_5 \cdot [A] \cdot [^1O_2] - k_d \cdot [^1O_2] \qquad (8)$$

$$\frac{d[P]}{dt} = k_5 \cdot [A] \cdot [^1O_2] \qquad (9)$$

Eqs. (7)–(9) are integrated starting from the initial conditions ($t = 0$, $[A] = [A]_o$, $[^1O_2] = 0$ and $[P] = 0$) and the unknown parameters k_4, k_5 estimated in an optimization procedure in which four runs at different initial 5-HMF concentrations are simultaneously considered.

The best estimated values of the parameters along with the percentage standard deviations for the substrate (σ_A) and the product (σ_P) are reported in Table 2.

3.2.3. *5-HMF irradiation in the presence of oxygen and BM*

When BM was added to the 5-HMF reacting aqueous solutions, additional reactions have to be taken into account for $^1O_2$ generation.

In particular, methylene blue absorbs the UV light to give an excited state:

$$BM \xrightarrow{\Phi_S, h\nu} BM^* \qquad (r_7)$$

Subsequently, singlet oxygen is produced also by an energy transfer from excited state of BM to molecular oxygen:

$$BM^* + O_2 \xrightarrow{k_6} {}^1O_2 + BM \qquad (r_8)$$

BM* molecules are physically quenched by BM ones:

$$BM^* + BM \xrightarrow{k_7} 2BM \qquad (r_9)$$

and rapidly decomposes to give byproducts:

$$BM^* \xrightarrow{k_8} \text{byproducts} \qquad (r_{10})$$

Moreover, a reaction of quenching of singlet oxygen by BM may be written:

$${}^1O_2 + BM \xrightarrow{k_9} BM^* + O_2 \qquad (r_{11})$$

According to the scheme obtained including reactions (r$_7$)–(r$_{11}$), mass-balance equations on the species A, A*, P, $^1O_2$, BM and BM* may be written. If the steady-state hypothesis is done for A*, the following equations may be adopted along with Eqs. (7) and (9):

$$\frac{d[BM]}{dt} = \left(-\frac{I_a^{BM}}{V} \cdot \Phi_{BM}\right) + k_6 \cdot [BM^*] \cdot [O_2] + k_7 \cdot [BM^*] \cdot [BM] - k_9 \cdot [^1O_2] \cdot [BM] \qquad (10)$$

$$\frac{d[^1O_2]}{dt} = \left(\frac{I_a^A}{V} \cdot \Phi_A\right) - k_5 \cdot [A] \cdot [^1O_2] - k_9 \cdot [^1O_2] \cdot [BM] + k_6 \cdot [O_2] \cdot [BM^*] - k_d \cdot [^1O_2] \qquad (11)$$

$$\frac{d[BM^*]}{dt} = \left(\frac{I_a^{BM}}{V} \cdot \Phi_{BM}\right) + k_9 \cdot [^1O_2] \cdot [BM] - (k_6 \cdot [O_2] + k_7 \cdot [BM] + k_8) \cdot [BM^*] \qquad (12)$$

Also in the present case the assumption of slow kinetic regime of absorption with reaction was done and the concentration of oxygen dissolved in the solution calculated according to the equilibrium data.

It is important to observe that since in this case also BM absorbs the UV radiations, the term I_a^A is modified as:

$$I_a^A = \sum_\lambda \left(I_\lambda^0 \cdot \{1 - \exp(-2.3 \cdot l \cdot (\varepsilon_\lambda^A \cdot [A] + \varepsilon_\lambda^{BM} \cdot [BM])\} \cdot \frac{\varepsilon_\lambda^A \cdot [A]}{\varepsilon_\lambda^A \cdot [A] + \varepsilon_\lambda^{BM} \cdot [BM]} \right) \qquad (13)$$

For the term I_a^{BM} the following equation is adopted:

$$I_a^{BM} = \sum_\lambda \left(I_\lambda^0 \cdot \{1 - \exp[-2.3 \cdot l \cdot (\varepsilon_\lambda^{BM} \cdot [BM] + \varepsilon_\lambda^A \cdot [A])]\} \cdot \frac{\varepsilon_\lambda^{BM} \cdot [BM]}{\varepsilon_\lambda^A \cdot [A] + \varepsilon_\lambda^{BM} \cdot [BM]} \right) \qquad (14)$$

In the Legend section all the values of the parameters taken from the literature or previously determined are reported.

The system of equations (Eqs. (7) and (9)–(12)) was numerically integrated starting from the initial conditions ($t = 0$, $[A] = [A]_o$, $[BM] = [BM]_o$, $[^1O_2] = 0$ and $[P] = 0$; $[BM^*] = 0$). The value of kinetic constant k_9 is assumed equal to $3 \times 10^8\ M^{-1}\ s^{-1}$ [19] and that of the quantum yield of methylene blue $\Phi_{BM} = 0.52\ mol\ E^{-1}$ according to Usui and Kamogawa [20]. The values of unknown parameters k_6, k_7 and k_8 were estimated by means of the optimization procedure adopted. Four runs at different initial 5-HMF and BM concentrations are simultaneously considered for the optimization procedure that utilized a weighted least squares method. In Table 3 the calculated values for the unknown parameters along with the percentage standard deviations for the substrate (σ_A), the sensitizer (σ_{BM}) and the product (σ_P) in each single run are reported.

In Fig. 7a–h some examples of the fitting between the experimental data and those calculated by the model are shown.

It is evident that the developed model satisfactorily predicts the concentrations of the substrate and BM. On the other hand less satisfactorily, although still appreciable, prediction of HPKA concentration profile (also confirmed by percentage standard deviations higher than those found for other components) seems to suggest the existence of a model inadequacy probably due to some too simplifying assumptions done.

4. Conclusions

The production of 5-hydroxy-4-keto-2-pentenoic acid (5-HKPA), a possible synthesis intermediate or a monomer for polymerization processes in chemical industry, has been studied by means of the photo-oxidation of 5-hydroxymethylfurfural (5-HMF) by singlet oxygen in aqueous solution at pH = 6.0.

The results of the investigations indicate that the system reactivity is influenced by the concentration of methylene blue (BM), the sensitizer, and the dissolved oxygen, showing a maximum for an initial concentration of sensitizer close to 30 μmol L^{-1} under a pure oxygen bubbling (P = 1 atm). Only small consumptions of the sensitizer have been recorded during the oxidation experiments thus suggesting the possibility to recover it and reuse in new runs. Any change of the starting concentration of the substrate and/or pH values of the solutions did not result into appreciable differences in the reactivity of the system and/or selectivity for HKPA.

Kinetic models have been developed to simulate the processes of photo-oxidation of 5-HMF in the absence and in the presence of BM according to a proposed reaction scheme. These models have been tested with the data collected during the experimental runs at pH = 6.0 at varying initial concentrations of substrate and sensitizer. Moreover, the use of developed models allowed to estimate the kinetic parameters for the proposed reaction scheme and gave satisfactory results for the prediction of the concentrations of 5-HMF and BM. Less satisfactorily results for the prediction of the concentration of HKPA seem to indicate some model inadequacies which require further investigations.

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