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Photocatalytic Degradation of Hexaethylene Glycol

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Abstract Polyethylene glycol (PEG) photodegradation
was studied in water under UV irradiation in the presence
of catalytic amount of TiO_2 using hexaethylene glycol as
a model compound. Full conversion was achieved in 7 h
with an average quantum yield around 1%. Formic acid
was found to be the main intermediate and was slower to
oxidize into CO_2 (traces remains after 24 h). The other
intermediates [lower PEG, oxidized PEG (formates, alde-
hydes and acids, acetic acid)] of the photodegradation have
also been identified and quantified. A mechanism based on
previous literature but also taking into account these new
observations is proposed.

Graphical Abstract
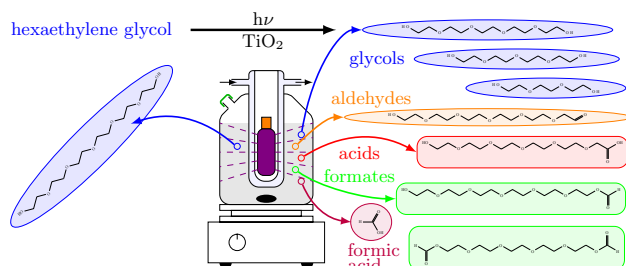
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1 Introduction

Photocatalysis, especially with TiO_2 as the catalyst is very
effective for the abatement of organic pollutants in water
but much less for the degradation of polymers mainly due
to the hydrophobic nature of the latter [1]. On the con-
trary polyethylene glycols (PEGs) constitute a family of
mostly water-soluble polymers available over a wide range
of molecular weights from 300 to 10,000,000 Da used in
many areas such as additives in the plastic industry, excipi-
ents in pharmaceuticals, surfactants or lubricants. PEG are
generally considered non toxic and biocompatible, however
they may become potential contributors to environmental
problem if discarded after use into solid waste or as aque-
ous solutions [2, 3]. The smaller oligomers with a few gly-
col units, especially the monodisperse ones are good model
molecules to use in order to describe the degradation of the
larger ones.

Some studies of PEG oxidation are reported but very
few using photocatalysis with TiO_2. The degradation of
tetraethylene glycol, choosen as a model of PEG, under
thermal conditions is reported by Glastrup [4]. The oxida-
tion of ethylene glycol using various advanced oxidation
processes such as ozone [5], or Fenton's reagent and H_2O_2
/UV [3, 6] have also been reported. Wu et al. [7–9] report
the photocatalytic degradation of PEG with TiO_2 nanopar-
ticles as the photocatalyst. They observed the formation of
esters and other intermediates and a zero order reaction.
Vijayalakshmi and Madras [10] report the photocatalytic
degradation of high molecular weight PEG in solution and
propose a random mode of chain scission. Yuan et al. [1]
studied the photocatalytic degradation of heavy PEG (PEG-
4000–10000) in solid phase where the catalyst (TiO_2 or
Fe–TiO_2) is dispersed in a PEG matrix. The degradation
was monitored by gel permeation chromatography and no

mechanism is reported. Formic acid is known as the more stable intermediate produced in high quantities. Many other intermediates are usually detected, including PEG of lower molecular weight and their derivatives.

The aim of the present work is to study the degradation of a light water-soluble PEG, hexaethylene glycol (noted G6 later in the text) in an aqueous solution, to identify the degradation intermediates and to update the mechanism of degradation.

2 Experimental

2.1 Reagents

TiO_2 P25 was purchased from Acros. Hexaethyleneglycol (97%, ref. 259268) was obtained from Aldrich. n-Eicosane (99%, ref. 219274) used as an internal standard was provided by Aldrich. Deionized water (18 MΩ) was used as solvent.

2.2 Analysis

Analysis was performed on concentrated solutions of by-products in ethanol using eicosane (n-C_{20}) as internal standard. Water was evaporated from the samples (20 mL) taken during the reaction, then 400 µL of an eicosane solution (3 g/L) in ethanol, was added. This solution was then analyzed by GC-FID using a DB50 column (10 m × 0.1 mm × 0.1 µm). Calibration was performed with PEG 400 solutions for each individual oligomer and aldehydes and formates were assumed to have similar response factors. GC–MS (same DB50 phase) is used in order to identify the products of the photocatalytic degradation. LC–MS (on a grafted-C_{18} column) is also used to identify the product which do not elute in GC such as the mono- and dicarboxylic acids. Ionic chromatography (IC) is used to determine the amount of lighter acidic (formic acid, acetic acid,···) compounds not measurable by GC, a Dionex ICS-1000 system fitted with a Dionex AS 25 anionic column was used. Calibration were performed using different acids in the ranges of concentration used in the experiments.

2.3 Photocatalytic Degradation

The reaction was carried out in a batch reactor fitted with a central source of UV (cf. Fig. 1) allowing for the irradiation of 0.5 L of suspension of TiO_2 P25 in an aqueous solution of G6.

The UV-source used was a HPK 125W high-pressure mercury vapor lamp from Heraeus inserted inside a water-cooled jacket. The lamp provides a discrete emission
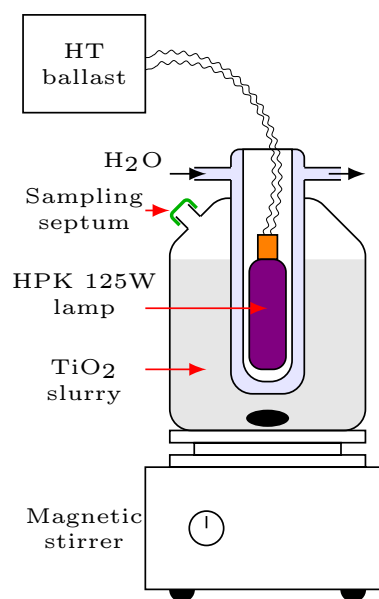

Fig. 1 Scheme of the photoreactor

spectrum with lines at 365, 334, 313 and 302 nm, lower wavelengths being cut off by the Pyrex® envelope. The irradiance of the main line 365 nm was measured (Vilber-Lourmat VLX-3W radiometer fitted with a 365 nm probe) to be of 60 W/m^2 at the surface of the cooling jacket. The photon number ratio, i.e., the fraction of the total number of photon, emitted at each band for the 365/334/313/302 nm bands were around 52/6/26/16%, respectively. A magnetic stirrer is used assuming sufficient stirring to provide an uniform composition of the reaction mixture.

3 Results and Discussion

3.1 Identification of the Products

GC-FID of the reaction mixture at intermediate time (i.e., before complete degradation) shows a regular pattern of the products formed during the degradation of G6 (cf. Fig. 2), indicating the formation of compounds with homologous structure. GC–MS and LC–MS analysis allowed for the identification of most of the components present in the reaction mixture during the photocatalytic degradation of G6. Figure 3 presents the structure of the most abundant products detected. It is worth noticing that although the functional groups present in these compounds are well defined by their fragmentation scheme, the molecular peak is generally not observable and thus neither is their formula weight.

The identified products can be classified into different families:

Fig. 2 A typical GC-FID chromatogram of the reaction mixture
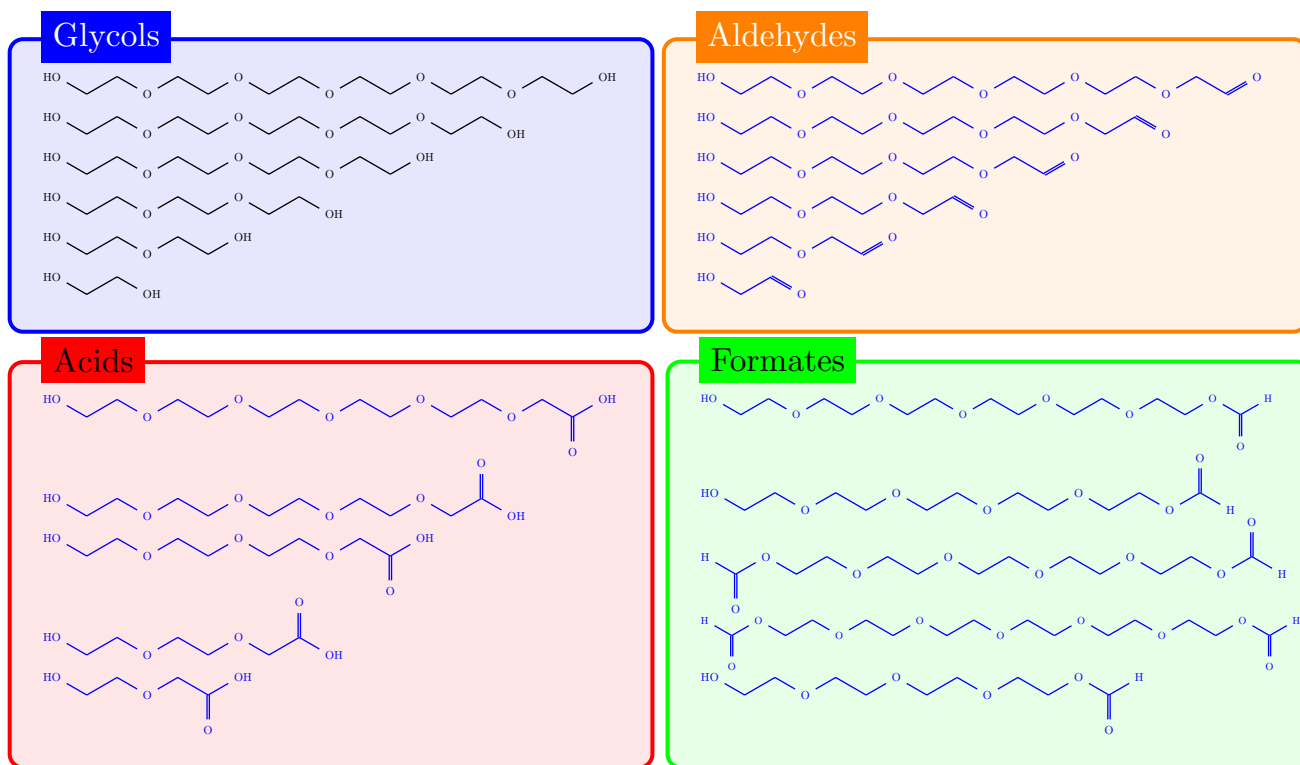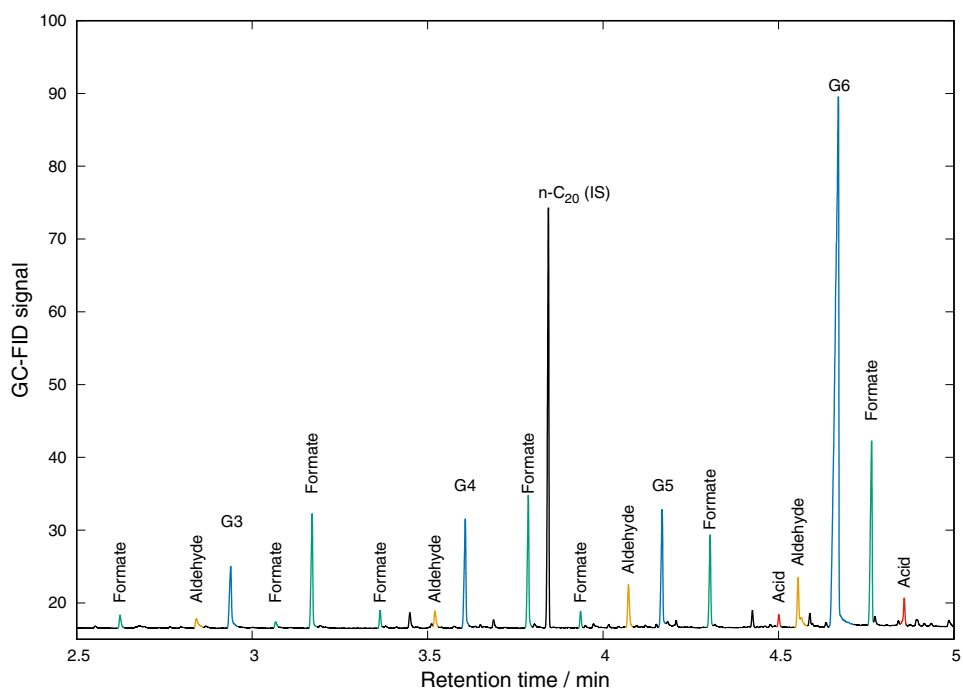
Fig. 3 Products identified (*black*) and postulated (*blue*)

– lower homologues of G6, i.e., penta-, tetra-, tri-, and diethylene glycol that will be called G5, G4, G3 and G2, respectively,

– aldehydes corresponding to the oxidation of one of the terminal hydroxyl,

- carboxylic acids corresponding to further oxidation of the previous compounds,
- formates of the glycols of different lengths,
- other compound with oxidated groups (aldehydes or carboxylic acids) at both extremities of the molecules, among them diacids have been detected by LC–MS.

3.2 Reaction Profile

The initial reaction mixture content is reported (at t = 0) in Fig. 4. Commercial G6 was used as received containing some lighter PEG oligomers (G5–G2) and some oxidized species. Concentration for those different species are reported against time in Fig. 4a–c. The carbon mass balance is reported in Fig. 5.

G6 was found to disappear in 5–7 h (Fig. 4a) yielding lower oligomers (Fig. 4b), mostly in the oxidized state (Fig. 4c) and an important amount of formic acid. Formic acid was harder to oxidize and after 24 h, 5–10% of the initial carbon is still in the formic acid form.

In order to visualize the advance of the G6 photocatalytic degradation reaction the sums of the products with the same number of glycolic units (i.e., PEG, aldehyde of PEG, acid of PEG and formate of PEG) is reported in Fig. 5. The missing fraction of this carbon balance is attributed to CO_2, which is not monitored. The total measured quantity of carbon decrease slowly at the beginning of the experiment while the content of the lower oligomers (mostly G3 but also G4 and G5 in some extent) and formic and acetic acid increase rapidly in the solution. A maximum of 30% of the carbon is in the formic/acetic acid form after 7 h of experiment, before becoming slowly oxidized.

The photonic efficiency has been estimated as mentioned in Braslavsky et al. [11] by calculating the ratio between the reaction rate and the incident photon flux. The initial rate of G6 degradation is found to be 2.46e-8 mol/s when the amount of TiO_2 is 0.2 g/L. And the photon flux at 365 nm reaching the solution is estimated to be 1.81e-6 Einstein/s. Thus the photonic efficiency at 365 nm has been found to be $\eta_{365} = 0.014$. This estimation does not take into account the photons at other wavelengths than 365 nm and thus is likely to be an upper value. This value compares well with the literature, for example Emeline et al. [12] reported a value of $\eta_{365} = 0.0057$ for the photodegradation of phenol in the presence of P25 TiO_2. Wang et al. [13] reported a value of $\eta = 0.057$ using P25 TiO_2 for the photocatalytic formation of formaldehyde from methanol using a 310–390 nm source.

3.3 Effect of the Amount of Catalyst

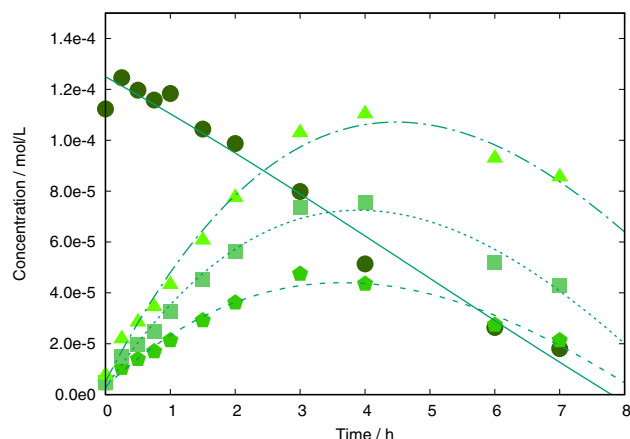The reaction was run with different amount of catalyst, up to 4 g TiO_2/L. Without catalyst no reaction is observed. As
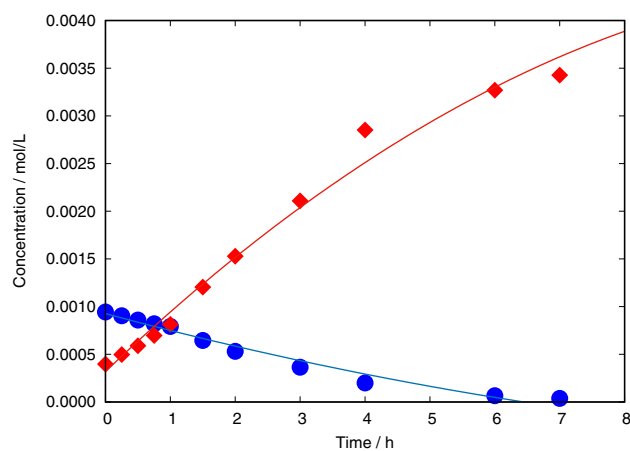
(a) (●) G6 and (◆) formic acid
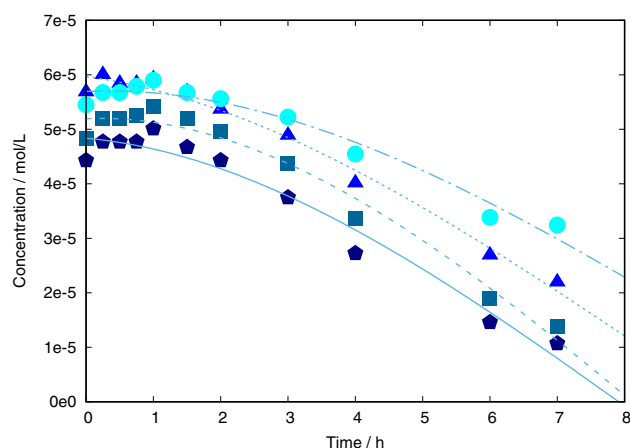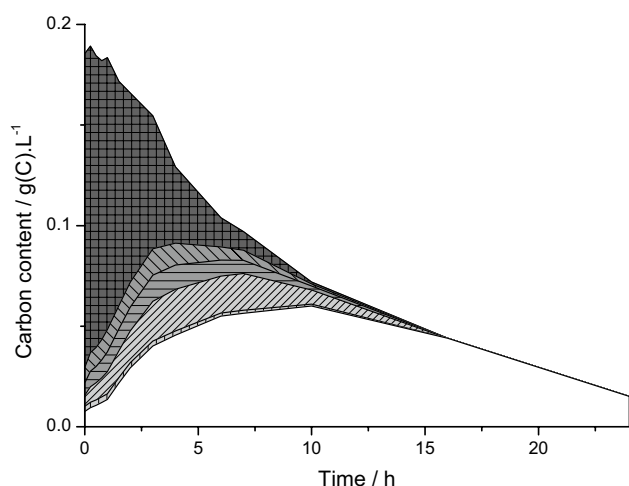

(b) Other PEG: (⬟) G5, (◼) G4, (▲) G3 and (●) G2

(c) Formates of PEG: (●) G6, (⬟) G5, (◼) G4, (▲) G3

Fig. 4 Evolution of the reaction mixture composition during the course of a typical experiment ($[G6]_0 = 0.001$ mol/L, $TiO_2 = 0.2$ g/L)
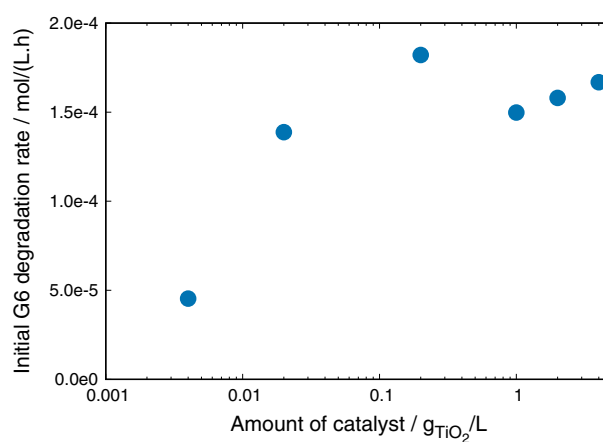
Fig. 5 Balance of C in the reaction mixture during the course of the reaction (▦) G6 and derivatives, (▨) G5 and derivatives, (▭) G4 and derivatives, (▧) G3 and derivatives, (▥) G2 and derivatives, (▭) formic acid (the missing part is CO_2 not measured)

(a) Initial rate of degradation of G6

(b) Formation rate of formic acid

Fig. 6 Effect of the catalyst loading upon **a** the degradation rate of G6 and **b** the formation rate of formic acid

reported in Fig. 6a, the degradation rate of G6 increases when the mass of catalyst increases. But as soon as the amount of TiO_2 reaches 0.2 g TiO_2/L the initial degradation rate reaches a plateau. Indeed, an amount of catalyst as low as 0.004 g TiO_2/L is enough to transform 30% of G6 in 7 h (initial rate 0.01 g/L/h). A maximum initial G6 degradation rate of 0.05 g/L/h is achieved with a loading of 0.2 g TiO_2 /L. For higher TiO_2 contents, the rate decreases slightly and remains between 0.04 and 0.05 g/L/h.
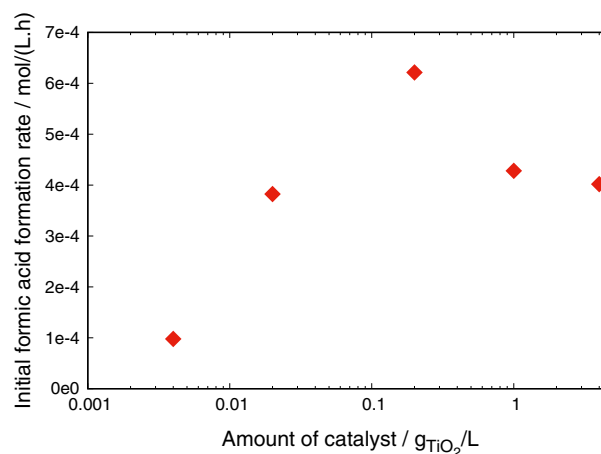
This trend is the same for shorter chain PEGs (G5–G2). A faster rate is obtained for 0.2 g TiO_2/L of catalyst. Nevertheless the general pattern is slightly different as there is an initial increase due to G6 degradation followed by a decrease due to their own degradation. With a very low amount of catalyst (0.004 g TiO_2/L) only the increasing part is observed before 7 h of reaction. It is worth noticing that in the particular case of a loading of 0.2 g TiO_2/L (cf. Fig. 4b) which has the highest initial rate of G6 degradation there is only a decrease in the concentrations of the other glycols which means that their degradation rate is always faster than their formation rate.

As for the formic acid, which is by far the most abundant product formed, only its formation is observed during the first 7 h of reaction. Its degradation takes a longer time and there is still some remaining after 24 h of reaction. The same observation applies to acetic acid. The highest rate of formation of formic acid occurs at 0.2 g TiO_2/L, which is also the catalyst amount at which the higher rate of degradation is observed for the other glycol oligomers.

Some hypotheses could be discussed in order to explain this phenomenon. Firstly, the usual argument for a decrease

of reactivity at high catalyst load (above 2 g/L) is a screening effect due to a high density of catalyst particles. Nevertheless the optimum observed (0.2 g/L) is far below the usual reported values. The effect of catalyst quantity in slurry photocatalysis is well documented [14], although generally the plateau is reached with larger amount of catalyst. Indeed, as reported in the case of dye discoloration in the presence of TiO_2 by Konstantinou and Albanis [15] and the references cited therein the optimum often occurs for an amount of catalyst close to 1 g TiO_2/L. This is also true in the case of other substrates such as sodium dodecyl sulfate [16] or organophosphorous pesticides [17]. In the case of tetracycline antibiotic the optimum catalyst loading is closer to 2 g TiO_2/L [18]. With most of the substrates, a maximum rate of degradation occurs for TiO_2 loading between 1 and 2 g TiO_2/L.

Secondly, the reaction could be mass transfer limited by oxygen; nevertheless the observed reaction rates are one order of magnitude above the usual transfer rate for oxygen

in a small batch reactor, and the optimum would be different for the much slower formate degradation which is definitively not the case here.

Thirdly, significant adsorption of the substrate on the catalyst would also yield such results but this would be visible on GC analysis.

3.4 Mechanism Proposal

A global mechanism is proposed on Fig. 7 based upon our results and degradation mechanisms reported in the literature [3, 10, 19–23].

The initial step of the degradation is likely to be the H-abstraction by an hydroxyl radical forming a a carbon radical as proposed by Kim and Hoffmann [19] for glycol and by Vijayalakshmi and Madras [10] for PEG. The same initial step is also proposed when the hydroxyl radical derives from hydrogen peroxide splitting [3] . This carbon radical reacts with oxygen to give a peroxy-radical as proposed by Minero et al. [22], then a peroxide and a new radical (route 1). The peroxide rearranges itself to yield a formate and a formaldehyde hemiacetal. Thus the oligomer is cut into two smaller parts with different functionalities. The formaldehyde hemiacetal is unstable and probably gives a PEG and a formaldehyde rapidly oxidized into formic acid. The formate is hydrolysed very slowly under these experimental conditions. This mechanism accounts for the large amount of formate compounds identified through their characteristic ions by GC–MS and the high concentration of formic acid. Thus a n glycol unit oligomer PEG will split into a $n − x$ and a $x − 1$ glycol unit oligomer PEG (one of those with a formate functionalisation) and a free formaldehyde rapidly oxidized into formic acid. Formic acid is then photodegradated on TiO_2 as reported elsewhere [24].

Alternatively the fixation of a second hydroxyl radical could give an other hemiacetal (route 2) which could lead to an aldehyde and a lower glycol as reported by Meichtry et al. [21]. The aldehyde is then further oxidized to the corresponding acid. This route is less probable, which accounts for the fact that in the course of the reaction aldehydes and carboxylic acids are found in smaller amounts as compared with formates produced via route 1. The carboxylic acid of PEG G_n could then be oxidized to give acetic acid and PEG $G_{n−1}$.
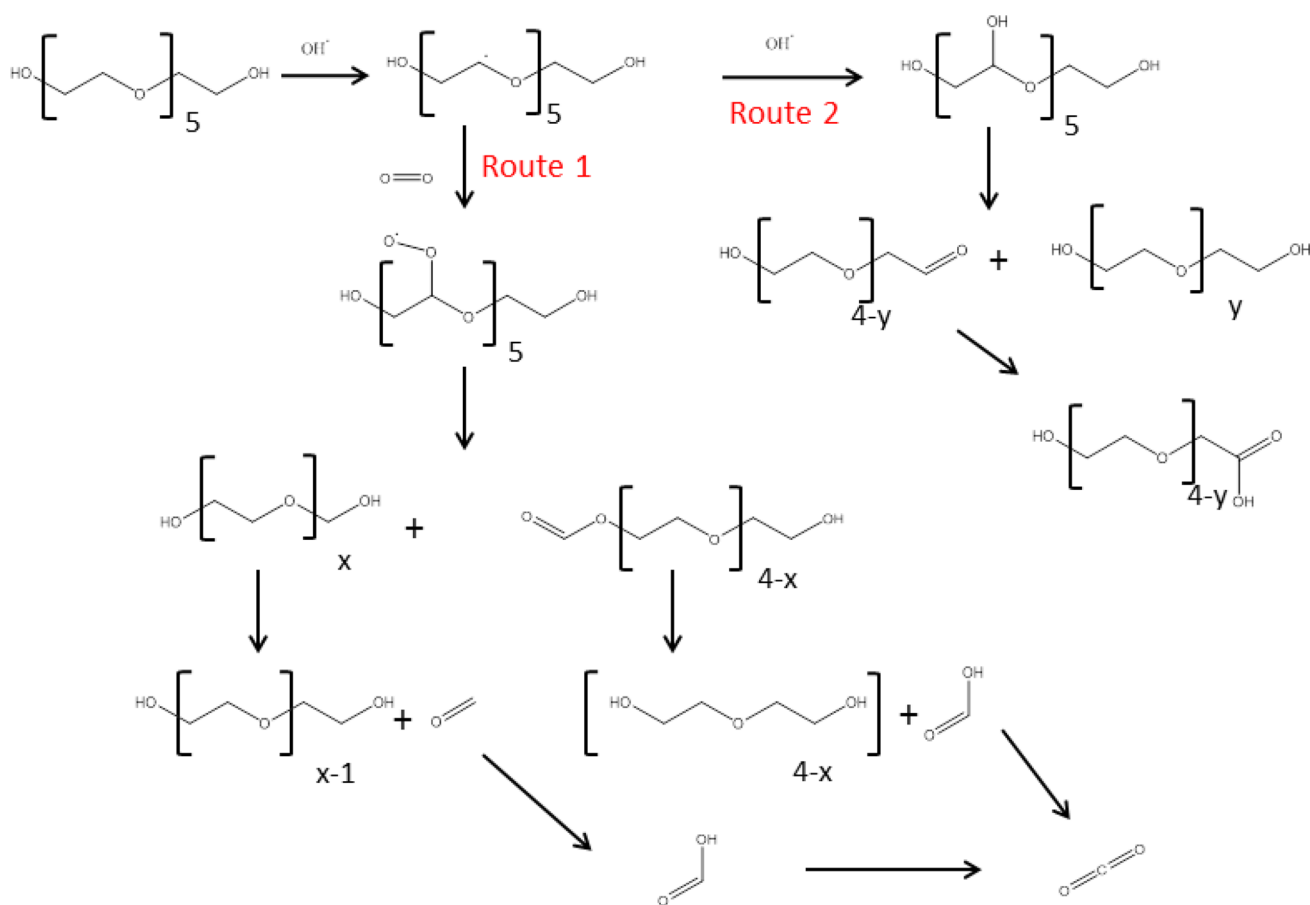
Fig. 7 Proposed degradation mechanism

This mechanism accounts for the formation of all compounds detected in the reaction mixture: homologous glycols, formates, aldehydes, carboxylic acids. It also explains the retarded maximum of formic acid as compared with the degradation of G6 and the formation of other PEG since formic acid is produced both at the beginning and at the end of the degradation scheme.

4 Conclusion

The photocatalytic degradation of hexaethylene glycol reported in this work allowed for a nearly quantitative degradation after 24 h:

- the identification of the degradation products which can be classified as a series of homologous compounds; glycols, compounds with terminal aldehydes, compounds with terminal carboxylic acid, "bifunctionalized" glycols and other smaller acids,
- the optimum degradation rate is achieved for an amount of TiO_2 catalyst (0.2 g TiO_2/L), lower than the one generally reported for photocatalytic degradations in slurry reactor,
- the proposal of a degradation mechanism taking into account all the observations.

References

1. Yuan F, Li P, Qian H (2013) Synth React Inorg Met Org Nanomet Chem 43:321
2. Morlat S, Gardette J (2003) Polymer 44:7891
3. Santos LC, Poli AL, Cavalheiro CCS, Neumann MG (2009) J Braz Chem Soc 20:1467
4. Glastrup J (1996) Polym Degrad Stab 52:217
5. Turan-Ertas T, Gurol MD (2002) Chemosphere 47:293
6. McGinnis BD, Adams VD, Middlebrooks EJ (2000) Water Res 34:2346
7. Wu Y, Fan CZ, Si JY (2005) Yingyong Huaxue (Chin J Appl Chem) 22:1253
8. Wu Y, Fan CZ (2007) Huaxue Shijie (Chem World Shanghai) 48:730
9. Wu Y, Chen H, Fan CZ (2007) Fenzi Cuihua (J Mol Catal) 21:144
10. Vijayalakshmi SP, Madras G (2006) J Appl Polym Sci 100:3997
11. Braslavsky SE, Braun AM, Cassano AE, Emeline AV, Litter MI, Palmisano L, Parmon VN, Serpone N (2011) Pure Appl Chem 83(4):931–1014
12. Emeline A, Salinaro A, Serpone N (2000) J Phys Chem B 104(47):11202–11210
13. Wang CY, Rabani J, Bahnemann DW, Dohrmann JK (2002) J Photochem Photobiol A 148(1–3):169
14. Herrmann JM (1999) Catal Today 53:115
15. Konstantinou IK, Albanis TA (2004) Appl Catal B 49:1
16. Lea J, Adesina AA (1998) J Photochem Photobiol A 118(2):111
17. Mengyue Z, Shifu C, Yaowu T (1995) J Chem Technol Biotechnol 64(4):339
18. Luo Z, Li L, Wei C, Li H, Chen D (2015) J Environ Biol 36 Spec No:837
19. Kim KN, Hoffmann MR (2008) Korean J Chem Eng 25:89
20. Santos LC, Schmitt CC, Poli AL, Neumann MG (2011) J Braz Chem Soc 22:540
21. Meichtry JM, Quici N, Mailhot G, Litter MI (2011) Appl Catal B 102:555
22. Minero C, Bedini A, Maurino V (2012) Appl Catal B 128:135
23. Augugliaro V, Bellardita M, Loddo V, Palmisano G, Palmisano L, Yurdakal S (2012) J Photochem Photobiol C 13:224–245
24. Turki A, Guillard C, Dappozze F, Berhault G, Ksibi Z, Kochkar H (2014) J Photochem Photobiol A 279:8–16