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This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/1543002> since 2016-10-07T10:57:02Z

Published version:

DOI:10.1039/c5ra10523d

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This is an author version of the contribution published on:

Questa è la versione dell'autore dell'opera:

RSC Advances, 5, 2015, 54589-54604

DOI: 10.1039/c5ra10523d

The definitive version is available at:

La versione definitiva è disponibile alla URL:

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Influence of electron acceptors on the kinetics of metoprolol photocatalytic degradation in TiO₂ suspension. A combined experimental and theoretical study[§]

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2014,
Accepted 00th January 2014

DOI: 10.1039/x0xx00000x

www.rsc.org/

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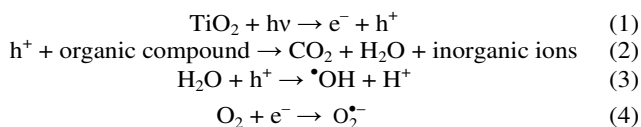
Metoprolol (MET) belongs to a group of frequently used β_1 -blockers, which often occur in waste waters. The objective of this work was to employ liquid chromatography (LC) and total organic carbon methods to study the photocatalytic degradation of MET in UV irradiated aqueous suspensions of TiO₂ (Wackherr's "Oxyde de titane standard" and Degussa P25), in the presence of different electron acceptors such as molecular oxygen, hydrogen peroxide, potassium bromate, and ammonium persulfate. The degradation rates were found to be strongly influenced by the kind of electron acceptor and the type of catalyst. The optimal amount of hydrogen peroxide and potassium bromate was investigated as well. MET photocatalytic degradation was fastest in the presence of O₂ and potassium bromate with TiO₂ Degussa P25, while mineralization was most efficient in the presence of molecular oxygen alone. In all investigated cases, degradation followed a pseudo-first order kinetics. Reaction intermediates of MET degradation in the presence of different electron acceptors with both catalysts were studied in detail and a number of them were identified using LC-ESI-MS/MS. The interactions with MET of reactive radical species relevant to this study ($O_2^{\bullet-}$, $\bullet OH$, BrO_2^{\bullet} , and $SO_4^{\bullet-}$) were theoretically investigated by means of density functional theory (DFT) computations.

1. Introduction

Studies dating more than 30 years ago dealt with photocatalytic reactions, which irrupted into the scientific literature when they were proposed as a suitable tool to promote separation of molecular H₂ and molecular O₂ from water using solar irradiation.^{1,2} Heterogeneous photocatalysis using TiO₂ powders has become a subject of increasing interest during the past twenty years, mainly in the field of environmental protection and wastewater decontamination.³ Photocatalysis in the presence of semiconductors is triggered by the interaction of electrons and holes, generated in a photochemically activated solid, with the surrounding medium. Activation is the consequence of light absorption: the irradiation of the photocatalytic material with sufficient energy leads to the formation of holes (h⁺) in the valence band and electrons (e⁻) in the conduction band.

The two species can either recombine or participate in reductive and oxidative reactions that lead to the decomposition of contaminants.⁴

The h⁺ can either directly oxidize pollutants, or oxidize water (preferably the OH⁻ groups adsorbed on the solid surface) to produce $\bullet OH$. In contrast, e⁻ reduces surface-adsorbed O₂. The oxidative and reductive reaction steps taking place with the irradiated photocatalyst (TiO₂) are expressed as follows:⁵⁻⁸



A practical problem in using TiO₂ as a photocatalyst is the energy waste due to the e⁻-h⁺ recombination, which results in lower degradation efficiency. The prevention of recombination is thus very important, and it can be achieved by adding proper electron acceptors. In the simplest systems, in aerated solution, molecular O₂ acts as electron acceptor to prevent e⁻-h⁺ recombination.⁹ Additional oxidants, such as H₂O₂, S₂O₈²⁻, and BrO₃⁻, can act as electron acceptors to enhance the photodegradation efficiency. These electron acceptors can have several effects including: (I) avoidance of e⁻-h⁺ recombination because of scavenging of conduction-band electrons; (II) increase of the concentration of $\bullet OH$ and (III) production of other oxidizing species that can enhance the oxidation rate of the substrate and of its intermediate compounds.¹⁰

By employing computer simulations within the framework of the density functional theory (DFT), it is possible to gain insight into the changes of the investigated structures as a

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[§] Electronic supplementary information (ESI) available: Influence of electron acceptors on the kinetics of metoprolol photocatalytic degradation in TiO₂ suspension. A combined experimental and theoretical study.

consequence of the presence of other molecules in the system.^{11,12} The information thus obtained is very important to further understand the degradation mechanisms of the investigated compounds.^{13,14}

Fukui functions and Fukui indices are often used as local quantum-molecular descriptors. Fukui functions describe the changes in the molecular electron density as a consequence of the addition or removal of charge, while Fukui indices represent scalar values for each atom. Fukui functions are visualized as iso-surfaces, and larger Fukui values indicate higher reactivity.^{15,16} It should be emphasized that values of Fukui functions are sensitive to changes in basis sets and population analysis. Therefore, one shouldn't use these values as absolute but rather as comparative parameters.

The molecular electrostatic potential (MEP) is related to the charge distribution and it is a very useful descriptor to determine potential sites prone to electrophilic attack and nucleophilic reactions.^{14,17,18} In the field of pollutant degradation, MEP enables the localization of parts of a molecule that are prone to various types of attacks, also giving information on how molecules interact with other molecules or radicals. The MEP (hereafter indicated as $V(r)$), when neglecting polarization and nuclear rearrangement effects due to the presence of a unit test charge at the distance r , is given as follows:

$$V(\vec{r}) = \sum \frac{Z_A}{|\vec{R}_A - \vec{r}|} - \int \frac{\rho(\vec{r}')}{|\vec{r}' - \vec{r}|} d\vec{r}' \quad (5)$$

where the summation runs over all nuclei A with charge Z_A and coordinate \vec{R}_A , while $\rho(r')$ is the electron density of the molecule. $V(r)$ represents the potential exerted at the coordinate r by the nuclei and the electrons. The sign of $V(r)$ at any point depends on whether the effects of the nuclei or the electrons are dominant.^{19,20}

Natural bond order (NBO) can be used for efficient investigation of intra- and inter-molecular bonding and interactions. It is a convenient basis for the investigation of charge transfer or conjugative interactions in molecular systems.^{21–23} NBO analysis is carried out by examining all possible interactions between 'filled' (donor) NBOs and 'empty' (acceptor) NBOs, estimating their energetic importance by 2nd-order perturbation theory. In this way one obtains the energies of delocalization of electrons from filled NBOs into empty NBOs, *e.g.* stabilization energies gained by donation from the donor NBO to the acceptor NBO. For each donor NBO (i) and acceptor NBO (j), the stabilization energy associated with $i \rightarrow j$ delocalization can be estimated on the basis of the second-order perturbation theory:^{24–26}

$$E(2) = \Delta E_{ij} = q_i \frac{F(i, j)^2}{\varepsilon_i \varepsilon_j} \quad (6)$$

where q_i is the donor orbital occupancy, ε_i , ε_j are diagonal elements (orbital energies) and $F(i, j)$ is the off-diagonal NBO Fock matrix element.

Metoprolol (MET) is a selective β_1 -blocker of the cardiac adrenergic receptors.²⁷ Due to the frequent use, MET is present in sewage waters, in rivers from Netherlands (25–100 ng L⁻¹),²⁸ Poland (51–155 ng L⁻¹),²⁹ UK (7–11 ng L⁻¹),³⁰ Sweden (60–70 ng L⁻¹),³⁰ and Germany (exceeding 1000 ng L⁻¹).³¹

Previous work has shown that the rate of MET photocatalytic degradation tended to a plateau at about 0.5–1.0 mM initial

concentration of the substrate, and that photodegradation was most efficient at a photocatalyst loading of 1.0 mg mL⁻¹.¹³ The aim of this work was to compare the kinetics of photodegradation of MET, sensitized by TiO₂ Wackherr or Degussa P25 in aqueous suspension under the same experimental conditions, in the presence of different electron acceptors (O₂, H₂O₂, S₂O₈²⁻, and BrO₃⁻). To monitor MET removal and mineralization, liquid chromatography (LC) and total organic carbon (TOC) analysis were used, respectively. An attempt has also been made to identify the intermediates formed during the photooxidation of MET in the presence of different electron acceptors with both catalysts, and a number of them were identified using LC–ESI–MS/MS. Employing DFT computations, the interactions of radical species (O₂⁻, •OH, BrO₂[•], and SO₄^{•-}) with MET and their possible effects on its degradation were investigated from the aspect of structural considerations, charge distribution, NBO analysis, Fukui functions and Fukui indices.

2. Materials and methods

2.1. Chemicals and solutions

All chemicals were of reagent grade and were used without further purification. The drug (±)-Metoprolol(+)-tartrate salt (Sigma-Aldrich) was used as received ($\geq 99\%$ purity); 85% H₃PO₄ was purchased from Lachema, Neratovice; acetonitrile (ACN) was a product of J.T. Baker. Other chemicals were as follows: 30% H₂O₂ from Sigma-Aldrich; KBrO₃ and (NH₄)₂S₂O₈ from Merck. All solutions were made using doubly distilled water. The used catalysts were TiO₂ Degussa P25 (75% anatase and 25% rutile, surface area 50 ± 1.0 m² g⁻¹, crystallite size about 20 nm, non-porous) and TiO₂ Wackherr's "Oxyde de titane standard" (100% anatase, surface area 8.5 ± 1.0 m² g⁻¹, crystallite size 300 nm, hereafter "TiO₂ Wackherr"), produced by the sulfate process.³²

2.2. Photodegradation procedures

Photocatalytic degradation was carried out in a cell made of Pyrex glass (total volume of ca. 40 mL, liquid layer thickness 35 mm), with a plain window on which the light beam was focused. The cell was equipped with a magnetic stirring bar and a water circulating jacket. A 125 W high-pressure mercury lamp (Philips, HPL-N, emission bands in the UV region at 304, 314, 335 and 365 nm, with maximum emission at 365 nm) together with an appropriate concave mirror was used as the radiation source. The output of the mercury lamp was calculated to be ca. 8.8×10^{-9} Einstein mL⁻¹ min⁻¹ (potassium ferrioxalate actinometry).

Experiments were performed using 20 mL of 0.05 mM MET containing 1.0 mg mL⁻¹ of TiO₂ (Wackherr or Degussa P25), except for the study of direct photolysis. The aqueous suspension of TiO₂ was sonicated (50 Hz) in the dark for 15 min before irradiation, in order to uniformly disperse the photocatalyst particles and to attain adsorption equilibrium. Before irradiation, the suspension thus obtained was thermostated at 25 ± 0.5 °C in a stream of O₂ (3.0 mL min⁻¹), except for a control run in the absence of electron acceptors when N₂ was bubbled (3.0 mL min⁻¹) to remove dissolved oxygen. During irradiation, the mixture was stirred at a constant rate under continuous gas flow. All experiments were performed at the natural pH which changed during the photodegradation, from pH 7 to pH 4 in the case of TiO₂

Wackherr and from pH 7 to pH 5 in the case of Degussa P25. In the investigation of the influence of electron acceptors, apart from constant O₂ bubbling, solutions of H₂O₂, KBrO₃ or (NH₄)₂S₂O₈ (at typical 3.0 mM initial concentration) were added to the MET solution.

2.3. Analytical procedures

The photodegradation of MET was monitored by liquid chromatography–photodiode array detection (LC–PDA). To do so, aliquots of 0.30 mL were taken from the reaction mixture at the beginning of the experiment and at regular time intervals. Aliquot sampling caused a maximum volume variation of ca. 10% in the reaction mixture. The suspensions were filtered through Millipore (Millex-GV, 0.22 µm) membrane filters to eliminate the photocatalyst. Lack of adsorption of MET on the filters was preliminarily checked. Afterwards, a 10-µL sample was injected and analyzed using a Shimadzu UFLC–PDA, equipped with an Eclipse XDB-C18 column (150 mm × 4.6 mm i.d., particle size 5 µm, 25 °C). The UV/vis PDA detector was set at 225 nm (wavelength of MET maximum absorption), as well as at 210, 260, 270 and 280 nm for the monitoring of the intermediates. The mobile phase (flow rate 0.8 mL min⁻¹) was a mixture of ACN and water (the latter acidified with 0.1% H₃PO₄), with the following gradient: 15% ACN at 0 min, which was increased to 30% ACN in 5 min, after which 30% ACN was constant for 5 min; post time was 3 min. The retention time for MET was 6.0 ± 0.1 min. Reproducibility of repeated runs was around 3–10%.

Concerning TOC analysis, 10 mL aliquots of the reaction mixture were taken at regular time intervals, diluted to 25 mL and analyzed after filtration on an Elementar Liqui TOC II analyzer, according to Standard US 120 EPA Method 9060A. For the LC–ESI–MS/MS evaluation of intermediates after 10 min irradiations, 100-µL samples were analyzed on an Agilent Technologies 1200 series LC with Agilent Technologies 6410A series electrospray ionization triple-quadrupole MS/MS, using Agilent Technologies Zorbax XDB-C18 column (50 × 4.6 mm i.d., particle size 1.8 µm, 40°C). The mobile phase (flow rate 0.5 mL min⁻¹) consisted of 0.05% aqueous formic acid and MeOH (gradient, 0 min 20% MeOH, 10 min 60% MeOH, 12 min 100% MeOH, post-time 3 min). Analytes were ionized using the electrospray ion source, a capillary voltage of 4.0 kV and with nitrogen as the drying gas (temperature 350°C, flow 10 L min⁻¹) and nebulizer gas (45 psi). High-purity nitrogen was used as the collision gas. Full scan mode (*m/z* range 50–800, scan time 100 ms, fragmentor voltage 100 V) in positive ion mode was used to select precursor ions for the starting compound and each degradation intermediate, as well as to examine isotopic peak distribution. Then, the product ion scan MS² mode (fragmentor voltage 135 V, scan time 200 ms, collision energy 10–40 V in increments of 10 V) was used to elucidate the structure of each degradation intermediate.

2.4. Computational details

All DFT calculations were carried out using the Gaussian 03 software package,³³ except for Fukui functions and Fukui indices that were calculated at the same level of theory using Jaguar, version 8.4,³⁴ as implemented in the Schrödinger Materials Suite, release 2014-2. For the purpose of NBO analysis, it was used the NBO 3.0 program as implemented in Gaussian 03. For all systems, calculations were performed employing the B3LYP exchange and correlation functional with 6-31 G+(d) basis set.³⁵ Two stages took place for all configurations. Firstly, equilibrium geometry of the

investigated systems was located using default convergence criteria and, secondly, the harmonic vibrational spectrum was checked to assure that the true minimum of potential energy, characterized by positive frequencies, was located.

In this work we investigated five systems: MET, MET/O₂^{•-}, MET/O₂^{•-}/•OH, MET/O₂^{•-}/BrO₃^{•-}, and MET/O₂^{•-}/SO₄^{•-}. To make the simulations more realistic, solvent effects of water were taken into account using the default Polarizable Continuum Model (PCM). Initially, in all cases O₂^{•-} was placed above the hydroxyl group located at the tail of MET, while •OH, BrO₃^{•-} and SO₄^{•-} were placed above the aromatic ring.

Interesting sites containing a significant amount of charges were located through MEP surfaces, which were obtained using Molekel after geometry optimization and frequency check.³⁶

3. Results and discussion

3.1. Effect of electron acceptors

Apart from O₂, which is the most frequently applied electron acceptor, in this work we also investigated the influence of H₂O₂, BrO₃⁻, and S₂O₈²⁻. These compounds operate as e⁻ scavengers and should be able to prevent e⁻–h⁺ recombination, thereby enhancing the formation of •OH and other reactive species.^{5,6} However, compounds such as H₂O₂ are also able to scavenge the photogenerated transients.³⁷

Fig. 1 and Table 1 show the time trend and degradation kinetics of MET, upon irradiation in the presence of TiO₂ (Wackherr, 1a, and Degussa P25, 1b) and several electron acceptors. In all investigated cases, the degradation process followed a pseudo-first order kinetics. Note that the role of O₂ as electron acceptor was investigated by comparing the system in air (blue triangles) with the one in which oxygen was bubbled to create an O₂ atmosphere (purple stars; in such a system, the concentration of both gas-phase and dissolved O₂ is expected to be ~5 times higher than in the case of air equilibrium). For further comparison, the behaviour of the deoxygenated system (N₂ bubbling, pink triangles) was also studied.

As expected, all the studied electron acceptors increased the efficiency of MET photocatalytic removal. It was determined that the influence of electron acceptors on the efficiency of degradation followed the order: O₂/H₂O₂ > O₂ ≈ O₂/S₂O₈²⁻ ≈ O₂/BrO₃⁻ using TiO₂ Wackherr, and O₂/BrO₃⁻ > O₂/H₂O₂ > O₂/S₂O₈²⁻ > O₂ using Degussa P25 (Fig. 1, Table 1). The added oxidants (H₂O₂, BrO₃⁻, S₂O₈²⁻) did not cause MET transformation in the dark.

Moreover, MET degradation using TiO₂ under N₂ atmosphere was very slow, and only marginally faster compared to the direct photolysis (MET irradiation in air without TiO₂). As reported in Fig. 1 and Table 1, a considerable enhancement of MET degradation was observed, with irradiated TiO₂, in air compared to N₂ atmosphere: the increase of the pseudo-first order rate constant *k'* was around 7 times with TiO₂ Wackherr and around 12 times with Degussa P25.

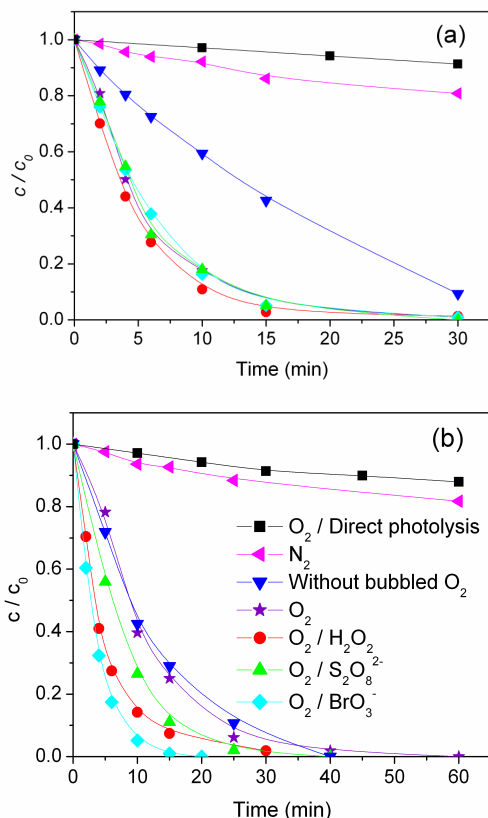


Fig. 1 Kinetics of the photolytic/photocatalytic removal of MET using TiO_2 Wackherr (a) and Degussa P25 (b) under UV irradiation, in the absence/presence of different electron acceptors.

Table 1. Values of the first-order decay constant, k' , for the photolytic/photocatalytic removal of MET (initial concentration 0.05 mM) using TiO_2 (where applicable) and UV radiation, as a function of the absence/presence of different electron acceptors

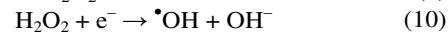
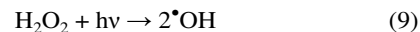
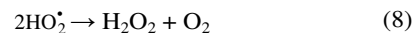
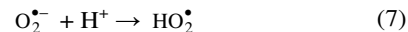
	$k' \text{ (min}^{-1}\text{)}^*$	
	0.0029	
Direct photolysis	TiO_2 Wackherr	Degussa P25
N_2	0.008	0.007
Without bubbled O_2	0.054	0.086
O_2	0.184	0.092
$\text{O}_2/\text{H}_2\text{O}_2$	0.224	0.199
$\text{O}_2/\text{BrO}_3^-$	0.172	0.299
$\text{O}_2/\text{S}_2\text{O}_8^{2-}$	0.180	0.133

* k' determined after 10 min of irradiation.

In all cases, correlation coefficient was higher than 0.95

Moreover, while MET degradation with Degussa P25 was little influenced by a further increase of the oxygen concentration (compare the runs with and without bubbled O_2), a further significant increase of the MET rate constant (over three times) was observed with TiO_2 Wackherr. Interestingly, in the case of TiO_2 Wackherr the degradation of MET did not undergo a further important enhancement upon addition of other e^- scavengers. In contrast, with Degussa P25 the additional effect of the scavengers was substantial. The differences between the two photocatalysts may be connected with the different surface area (much larger for Degussa P25) and different crystal

structure (presence of the rutile phase in Degussa P25). These issues could lead to differences in the interaction of O_2 and other e^- scavengers with the photocatalyst surface. In the case of TiO_2 Wackherr, it appears that O_2 bubbling already brought the reaction to its optimum and that any further enhancement was difficult. The situation was very different for Degussa P25. As far as the role of O_2 as electron acceptor is concerned, photoelectrons can be captured by O_2 to produce $\text{O}_2^{\bullet-}$, H_2O_2 (reactions 4, 7, and 8) and then eventually hydroxyl radicals (reactions 9-11):^{8,10,38}



When comparing the systems O_2 and $\text{O}_2/\text{H}_2\text{O}_2$ (oxygen bubbling in both cases, reported as purple stars and red circles, respectively, in Fig. 1), one can notice a small acceleration (by a factor of 1.2) caused by H_2O_2 addition in the case of TiO_2 Wackherr, and a more marked H_2O_2 effect (2.2 times) with Degussa P25. Despite the more important role of H_2O_2 , MET degradation with Degussa P25 and $\text{O}_2/\text{H}_2\text{O}_2$ was still a bit slower compared to TiO_2 Wackherr with otherwise identical conditions. The fact that a photocatalyst with lower surface area (TiO_2 Wackherr) could induce faster MET degradation compared with Degussa P25 is most likely accounted for by lower radiation scattering, which allows a better use of the incoming photons.¹³

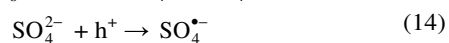
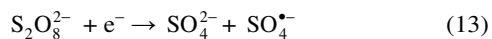
The increase of MET degradation rate upon addition of H_2O_2 to Degussa P25 (Table 1) was likely due to increased generation of $^{\bullet}\text{OH}$. Indeed, H_2O_2 can enhance $^{\bullet}\text{OH}$ production through the following pathways: (I) direct photolysis of H_2O_2 under UV irradiation (reaction 9); (II) reaction between H_2O_2 and e^- : H_2O_2 is a more effective electron acceptor than oxygen because its reaction with e^- yields $^{\bullet}\text{OH}$ and OH^- (reaction 10), while the corresponding process with O_2 produces the weaker oxidant $\text{O}_2^{\bullet-}$ (reaction 4); (III) reaction with $\text{O}_2^{\bullet-}$, also yielding $^{\bullet}\text{OH}$ (reaction 11).^{8,10,38}

In the presence of Degussa P25, the $\text{O}_2/\text{BrO}_3^-$ system was the most efficient for the degradation of MET. In contrast, the addition of BrO_3^- did not have an important effect on MET degradation with TiO_2 Wackherr. When operational, the enhancement of photodegradation efficiency would likely be a consequence of the reaction between BrO_3^- and conduction-band electrons. A first effect is the inhibition of e^- - h^+ recombination, which prolongs the life time of the photogenerated holes. One should additionally consider the formation of the reactive species BrO_2^{\bullet} (reaction 12).^{38,39} The possible role of BrO_2^{\bullet} in MET degradation was investigated with DFT methods (*vide infra*).



The addition of persulfate to the O_2 -bubbling system (to obtain $\text{O}_2/\text{S}_2\text{O}_8^{2-}$) had a limited enhancement effect in the case of Degussa P25 (1.4 times) and practically no effect with TiO_2 Wackherr. The reaction (13) between $\text{S}_2\text{O}_8^{2-}$ and e^- yields the

strong oxidant $\text{SO}_4^{\bullet-}$, but SO_4^{2-} is also formed and it can act as a hole scavenger (reaction (14)).^{10,38} The trade-off between h^+ and $\text{SO}_4^{\bullet-}$ could result into a limited enhancement effect, or even into no effect.¹⁰



Another issue is that sulfate, formed in reaction (13), can be adsorbed on the TiO_2 surface and decrease the photocatalytic activity of the oxide.¹⁰ Since $\text{S}_2\text{O}_8^{2-}$ turned out to be quite ineffective as electron acceptor in the removal of MET, it was not subjected to further investigation. The very low interaction between $\text{SO}_4^{\bullet-}$ and MET, compared to other systems, was confirmed through theoretical analysis as well (*vide infra*).

The results reported, and in particular the much faster transformation of MET with O_2 compared to N_2 bubbling, highlight the importance of electron acceptors in the degradation process. The addition of further electron acceptors may enhance degradation, but the reaction pathways are probably modified as well. Fig. 2 reports chromatograms obtained using TiO_2 Wackherr and Degussa P25 in the presence of the studied electron acceptors, showing that the occurrence of certain intermediates (represented by unassigned peaks) significantly depended on the applied electron acceptor and catalyst. Moreover, according to literature data,^{10,38,40,41} it is suggested that the application of an optimal concentration of electron acceptors is of great importance to achieve the maximum removal of organic compounds from the system. For this reason, the effects of the acceptor concentrations were studied in this case as well.

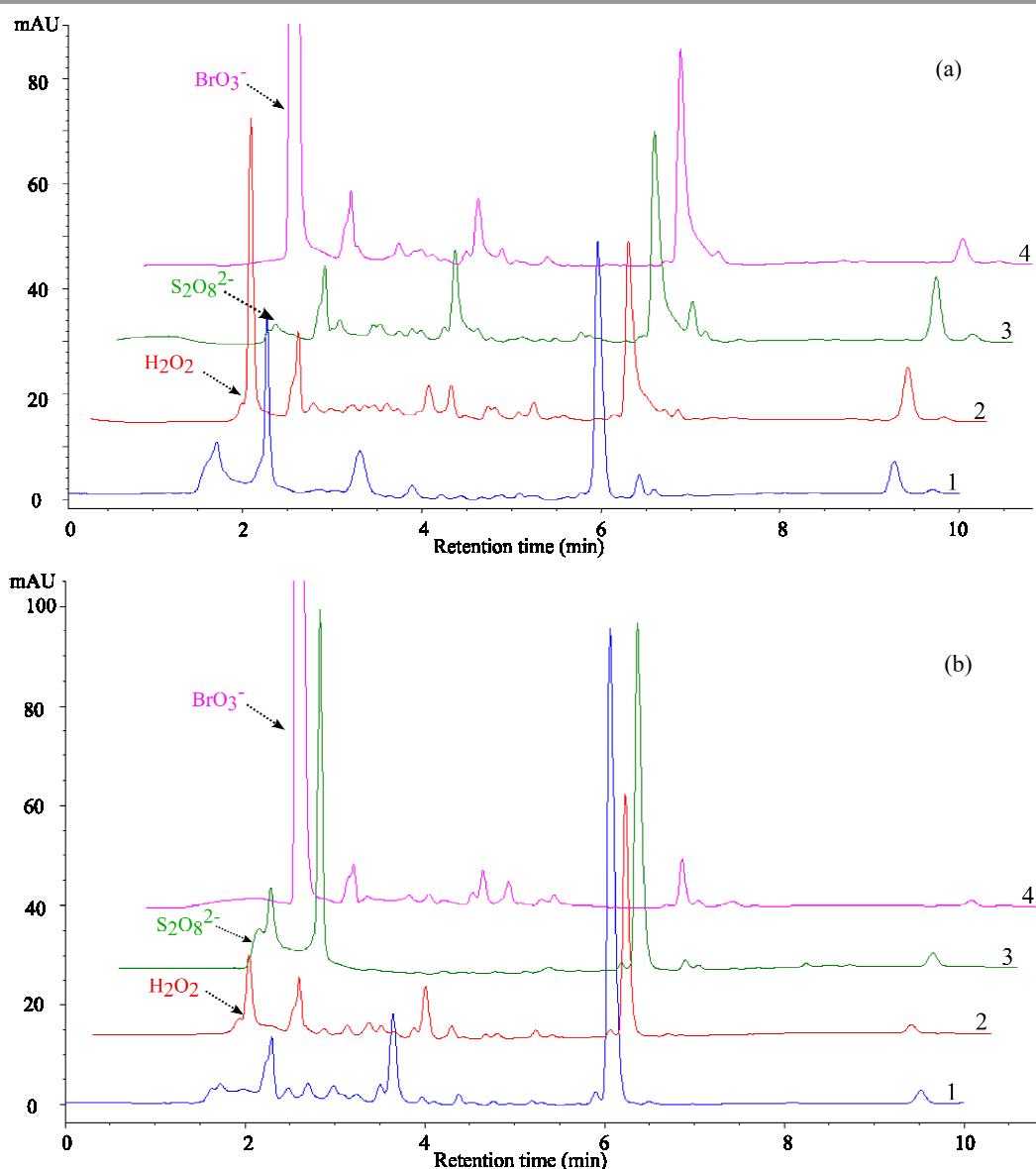


Fig. 2 Chromatograms obtained after 10 min of MET exposure to UV irradiation in the presence of TiO_2 Wackherr (a) and Degussa P25 (b), using different electron acceptors (1: O_2 ; 2: H_2O_2 ; 3: $\text{S}_2\text{O}_8^{2-}$; 4: BrO_3^-). $\lambda_{\text{det}} = 225 \text{ nm}$

3.2. Effect of the initial concentration of hydrogen peroxide

The influence of the concentration of H_2O_2 on the efficiency of MET removal was investigated in the range of 1.0 to 5.0 mM (Fig. 3). For both Degussa P25 and TiO_2 Wackherr, the optimal concentration of H_2O_2 was 3 mM. Under such conditions, after 10 min irradiation of the $\text{O}_2/\text{H}_2\text{O}_2$ system, the degradation of MET reached 89% with TiO_2 Wackherr and 86% with Degussa P25 (Fig. 3).

The presence of H_2O_2 at concentration values above 3 mM resulted in lower MET degradation compared to the optimal conditions. The most likely reason is that H_2O_2 acts as an $\cdot\text{OH}$ scavenger, generating the much less reactive hydroperoxyl/superoxide radicals ($\text{HO}_2^\cdot/\text{O}_2^{\cdot-}$, reaction 15).

Moreover, HO_2^\cdot can further react with $\cdot\text{OH}$ to form oxygen and water, which are not directly involved into MET degradation (reaction 16).^{10,40}

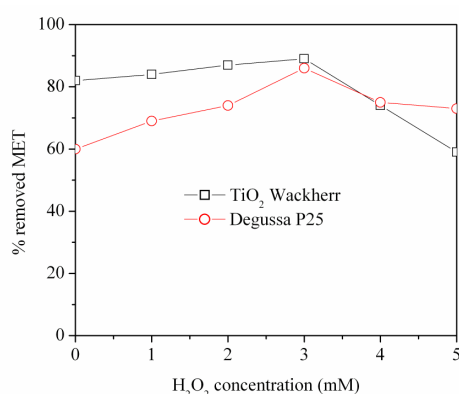
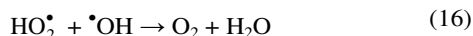
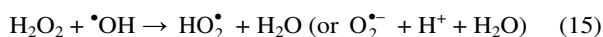


Fig. 3 Effect of the initial concentration of H_2O_2 on MET removal using $\text{O}_2/\text{UV}/\text{TiO}_2$ for the first 10 min irradiation.



Additionally, H_2O_2 at elevated concentration could react with TiO_2 to form peroxo compounds, which are detrimental to the photocatalytic action.⁴²

3.3. Effect of the initial concentration of potassium bromate

Fig. 4 reports the MET degradation efficiency in the presence of different initial concentrations of BrO_3^- . In the case of TiO_2 Wackherr, as already discussed, the bromate effect was very limited. In contrast, Degussa P25 showed a degradation increase that quickly tended to a plateau. In the latter case the most effective MET degradation was observed for 3 mM bromate, but very little difference could be detected in the 3-5 mM BrO_3^- concentration range. While e^- scavenging and a potential involvement of BrO_2^\cdot (formed in reaction (12)) could possibly enhance degradation, at elevated BrO_3^- levels the system reactivity could be limited by the formation of bromide (reaction (17)). The latter could both adsorb on the photocatalyst surface and be involved in h^+ and $\cdot\text{OH}$ scavenging.^{10,38,41,43,44}

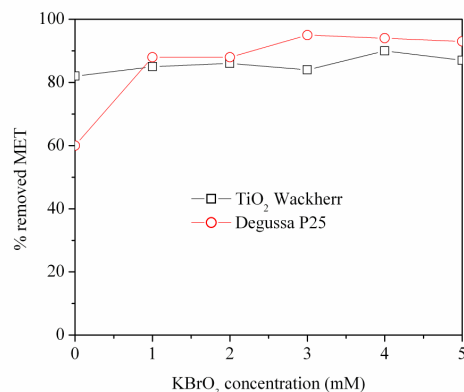


Fig. 4 Effect of the initial concentration of BrO_3^- on MET removal using $\text{O}_2/\text{UV}/\text{TiO}_2$ for the first 10 min of irradiation.

In the studied systems the electron acceptors are expected to inhibit the e^- - h^+ recombination processes, but they could have additional effects (e.g. production of reactive species by photolysis, such as $\cdot\text{OH}$ from H_2O_2 , see reaction (9)). These effects can be highlighted in the absence of TiO_2 . For this reason, MET was irradiated alone and in the presence of $\text{O}_2/\text{H}_2\text{O}_2$ and $\text{O}_2/\text{BrO}_3^-$, without TiO_2 (Fig. 5). The degradation of MET was considerably slower compared to photocatalytic conditions, but in the presence of H_2O_2 around 50% of MET was removed from the system after 60 minutes irradiation. In this case, acceleration of degradation compared to MET direct photolysis would probably be accounted for by $\cdot\text{OH}$, generated by H_2O_2 irradiation. Indeed, the hydroxyl radical reacts rapidly and non-selectively with most organic compounds, either by H-abstraction or by addition to $\text{C}=\text{C}$ unsaturated bonds.⁴⁵ Although slower compared to MET photocatalytic degradation, the use of H_2O_2 under irradiation could be attractive due to its simplicity.

Some enhancement of MET degradation was also observed in the presence of irradiated bromate, in particular at longer irradiation times (> 30 min), in agreement with literature reports.⁴⁶

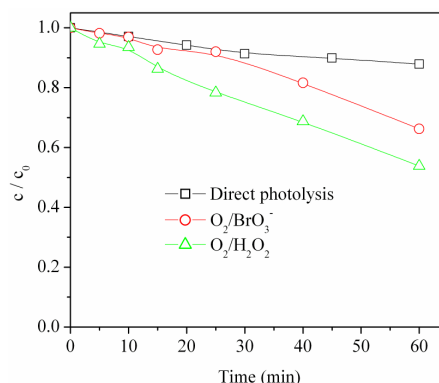


Fig. 5 Kinetics of the direct and indirect photolysis of MET under UV irradiation in the presence of O_2 , $\text{O}_2/\text{BrO}_3^-$ and $\text{O}_2/\text{H}_2\text{O}_2$

3.4. Evaluation of the degree of mineralization

3.4.1 Systems with hydrogen peroxide

H₂O₂ was poorly retained by the analytical column, but its considerable absorption at 225 nm allowed a rough estimation of its concentration to be derived from the chromatograms. By so doing, a considerable decrease of H₂O₂ concentration under photocatalytic conditions could be highlighted with both TiO₂ Wackherr and Degussa P25. Note that such an approach could overestimate H₂O₂ in the degraded systems, because of the possible interference by other poorly retained compounds. Therefore, the extent of H₂O₂ degradation could be underestimated. The chromatograms reported in Fig. 6 also show that the variety and the amount of intermediates depended on the type of photocatalyst. We made similar conclusions also in our previous works, where degradation mechanism¹³ and toxicity of investigated systems⁴⁷ were studied in details. Interestingly, most intermediates formed with both photocatalysts had lower retention times compared to MET: they mainly consisted of ring-hydroxylated compounds and of derivatives arising from oxidative cleavage of the shorter lateral chain of MET (that containing the methoxy group).¹³ The mixture of intermediates with Degussa P25 was considerably more toxic than that obtained with TiO₂ Wackherr.⁴⁷

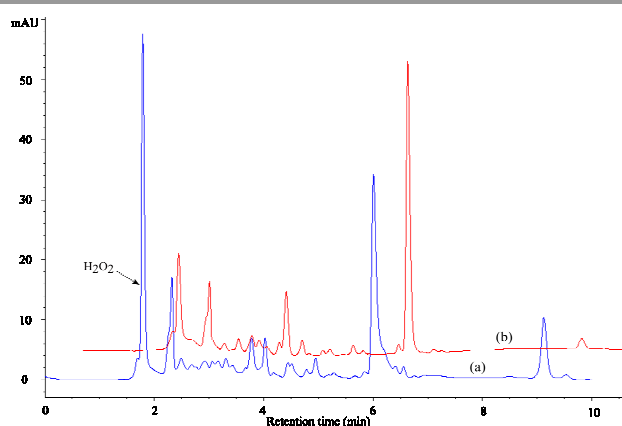


Fig. 6. Chromatograms obtained after 10 min of MET irradiation in the presence of TiO₂ Wackherr (a) and Degussa P25 (b): O₂/H₂O₂ system in both cases (O₂ bubbling, 3 mM H₂O₂), $\lambda_{\text{det}} = 225 \text{ nm}$

Therefore, the ability of the systems to achieve MET mineralization is particularly important in the case of the Degussa P25 photocatalyst. Further experimental results obtained in the present work indicate that the adsorption of MET on the catalysts doesn't differ more than 10%, which leads to conclusion that the adsorption of the investigated compound doesn't have significant influence on the efficiency of photocatalytic degradation. As far as mineralization is concerned, soon after complete removal of MET from the system, 88% of organic compounds (measured as organic carbon) were still present with TiO₂ Wackherr in the absence of H₂O₂, and even 94% (that is, only 6% mineralization) with 3 mM H₂O₂ (Fig. 7a). The degree of mineralization after MET disappearance was significantly higher using Degussa P25, which gave 33% residual organic carbon without H₂O₂ and 72% with H₂O₂ (Fig. 7b). Photonic efficiencies⁴⁸ calculated from data obtained for 60 min of mineralization of MET in the presence of TiO₂ Wackherr and Degussa P25 without H₂O₂ were 0.068%, and 0.223%, respectively. Also, for the systems TiO₂ Wackherr and Degussa P25 in the presence of H₂O₂, the

photonic efficiency was 0.012% and 0.066%, respectively. The better performance of Degussa P25 toward mineralization, compared to TiO₂ Wackherr, could be accounted for by its higher surface area. Indeed, a photocatalyst with low surface area, such as TiO₂ Wackherr, could undergo surface poisoning by the degradation intermediates.¹³ As an alternative or in addition, the mineralization of MET could be connected with reactions involving h⁺. The latter are favoured in the presence of Degussa P25 compared with TiO₂ Wackherr, which induces [•]OH reactions to a higher extent.¹³ This issue would be consistent with the previously discussed finding (Fig. 2) that different chromatographic peaks, corresponding to different intermediates, could be detected with the two photocatalysts.

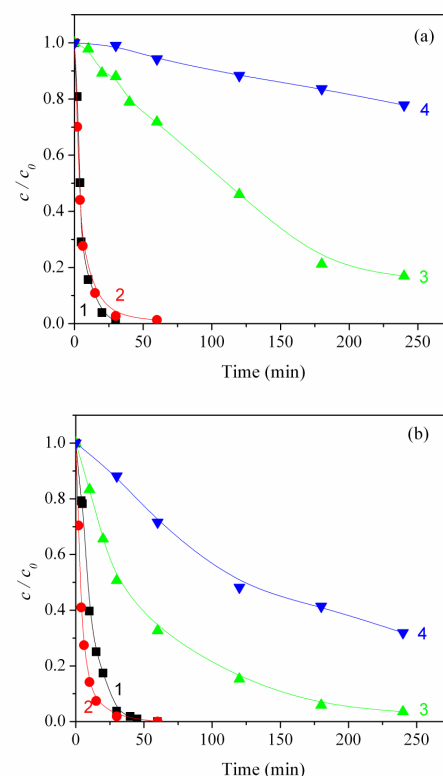


Fig. 7. Kinetics of photocatalytic degradation of MET under UV irradiation and O₂ bubbling, in the presence of TiO₂ Wackherr (a) and Degussa P25 (b): (1) MET trend, no H₂O₂; (2) MET trend, 3 mM H₂O₂; (3) TOC trend, no H₂O₂; (4) TOC trend, 3 mM H₂O₂.

With both TiO₂ types, mineralization further increased up to the longest irradiation time (4 h). However, while H₂O₂ enhanced MET degradation (at least with Degussa P25), it slowed down mineralization with both photocatalysts. If the above hypothesis concerning h⁺ vs. [•]OH is correct, the addition of H₂O₂ would shift the system reactivity towards the hydroxyl radical and the inhibition of mineralization would be automatically explained.

3.4.2 Systems with potassium bromate

In a similar way as H₂O₂, bromate was poorly retained by the analytical column but it could be detected due to significant radiation absorption at 225 nm. An approximate assessment of BrO₃⁻ concentration could thus be obtained from the chromatograms, similarly to H₂O₂ and with the same limitations. Contrary to H₂O₂, for which clear evidence of a

concentration decrease under photocatalytic conditions was obtained, no evidence was available from the chromatograms of a change in bromate concentration. Fig. 8 shows the chromatograms obtained after 10 minutes of MET degradation in the system O_2/BrO_3^- . In addition to the constant area of the peak to which bromate contributes, chromatograms obtained in the presence of TiO_2 Wackherr and Degussa P25 show significant differences in the amount and presence of peaks related to the degradation intermediates. This finding is in general agreement with earlier suggestions that different photocatalysts induce not only different transformation kinetics, but also different degradation mechanisms.¹³ TOC measurements (Fig. 9) show that bromate slightly increased mineralization with TiO_2 Wackherr and slightly decreased it with Degussa P25. After 240 minutes of irradiation without BrO_3^- , the percentage of the residual organic compounds was reduced to 17% for TiO_2 Wackherr and to 4% for Degussa P25. In the presence of BrO_3^- , the corresponding values were 5% for TiO_2 Wackherr and 13% for Degussa P25. Photonic efficiencies of mineralization of MET after 60 min in the presence of TiO_2 Wackherr and Degussa P25 with $KBrO_3$ were 0.096%, and 0.194%, respectively.

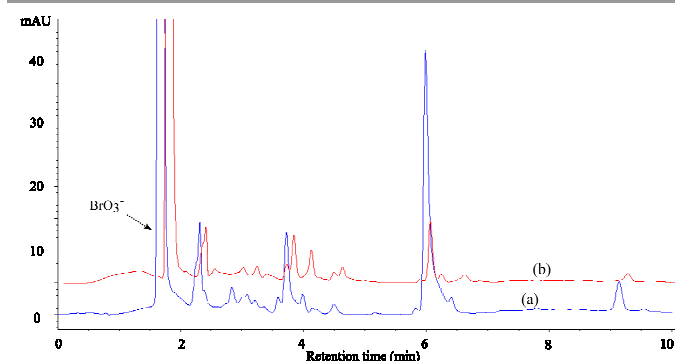


Fig. 8. Chromatograms obtained after 10 min of UV irradiation of MET in the presence of TiO_2 Wackherr (a) and Degussa P25 (b), in the O_2/BrO_3^- system (3 mM bromate, O_2 bubbling); $\lambda_{det} = 225$ nm

3.5. Influence of radicals on MET – DFT insight

3.5.1. Structural and reactivity properties - Fukui functions and indices

To better understand the interaction between MET and the radicals produced by reaction between e^- and electron acceptors, we conducted a DFT computational analysis of the following systems: $MET/O_2^{\bullet-}$, $MET/O_2^{\bullet-}/^{\bullet}OH$, $MET/O_2^{\bullet-}/BrO_2^{\bullet}$, and $MET/O_2^{\bullet-}/SO_4^{\bullet-}$. The optimized molecular geometries of the investigated systems, together with the specific dihedral angles, are given in Fig. 10. The presence of $O_2^{\bullet-}$ (Fig. 10b) modifies dihedral angles, which reduces MET stability. Moreover, the interaction between $O_2^{\bullet-}$ and MET is modified by other electron acceptors (Fig. 10c-d).

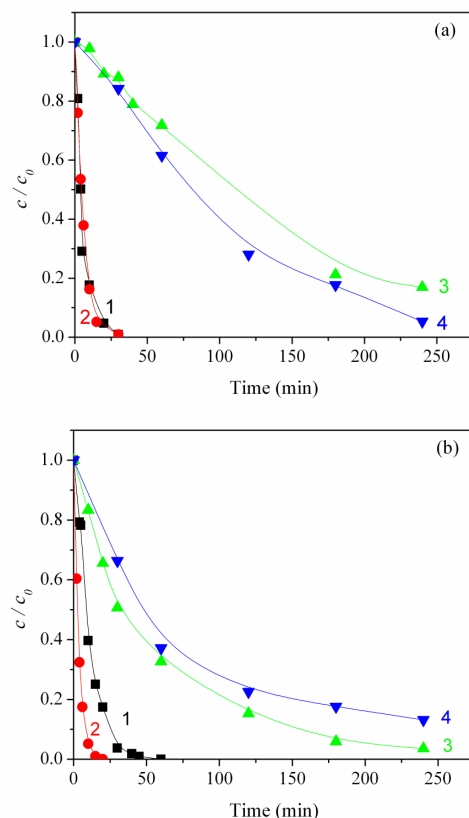


Fig. 9. Kinetics of photocatalytic degradation of MET under UV irradiation with O_2 bubbling, in the presence of TiO_2 Wackherr (a) and Degussa P25 (b): (1) MET trend, no BrO_3^- ; (2) MET trend, 3 mM BrO_3^- ; (3) TOC trend, no BrO_3^- ; (4) TOC trend, 3 mM BrO_3^- .

The interaction distance between $O_2^{\bullet-}$ and MET was the shortest (1.612 Å) when $^{\bullet}OH$ was also present, while it was the longest (3.904 Å) in the presence of $SO_4^{\bullet-}$. Concerning other radicals, the interaction distance with MET was *ca.* 3.4 and 6.4 Å for BrO_2^{\bullet} and $SO_4^{\bullet-}$, respectively. The most interesting situation for the interaction of radicals with MET was found in the case of $^{\bullet}OH$, where a new bond was formed. In various experimental studies carried out with molecules similar to MET, it was concluded that $^{\bullet}OH$ binds to the aromatic ring.^{13,49} However, it was still unclear which carbon atom formed a bond with $^{\bullet}OH$. According to our study, a bond is formed with the carbon atom number 4 (Fig. 10). Structural properties indicate that the highest interaction between MET and radicals takes place in the $MET/O_2^{\bullet-}/^{\bullet}OH$ system. These data are in overall agreement with the experimental results reported before, which emphasized the important role of O_2 vs. deoxygenated systems and the effect of electron acceptors in the enhancement of $^{\bullet}OH$ (and h^+) occurrence, through inhibition of e^-h^+ recombination. This fact is also confirmed by the NBO analysis provided in section 3.5.3 (*vide infra*).

In order to understand the reactive properties of MET, we will refer to Fukui functions and Fukui indices. Fukui functions are presented in Fig. 11, while Fukui indices (f_{NN}^{HOMO} and f_{NN}^{LUMO}) are given in Table 2. Fukui indices are commonly used since they describe the electron density when the molecule is

subjected to a reaction that modifies the electron density itself.^{50–52} Concerning the Fukui functions (f^- and f^+), the red colour corresponds to the negative values while the blue colour corresponds to the positive ones. Negative values of f^- correspond to regions that lose electron density when the molecule is subjected to electrophilic attack, or when the molecule itself acts as a nucleophile. Positive values of f^+ correspond to areas that gain electron density when the molecule is subjected to nucleophilic attack, or when it acts as electrophile.

The f_{NN} HOMO indices are related to the f^- Fukui function, while the f_{NN} LUMO ones are related to f^+ . In other words, a high positive value of f_{NN} HOMO indicates that the relevant

atom can donate electrons, thereby acting as a nucleophile, while an elevated f_{NN} LUMO indicates that the atom can receive electrons, thus acting as an electrophile. Having in mind the fact that a new bond was formed between MET and $\bullet\text{OH}$, special attention was paid to the C4 atom of the MET aromatic ring, namely the atom involved in bond formation. According to positive surface of Fukui f^+ function, the MET molecule has an electrophilic nature on both tail parts. On the other hand, the negative value of f^- located at the aromatic ring, and automatically at the C4 atom, suggests that this atom could act as a nucleophile as well. Significant values of both Fukui functions are located at the oxygen atom O7 (Fig. 11), while its Fukui indices emphasize nucleophilic nature (Table 2).

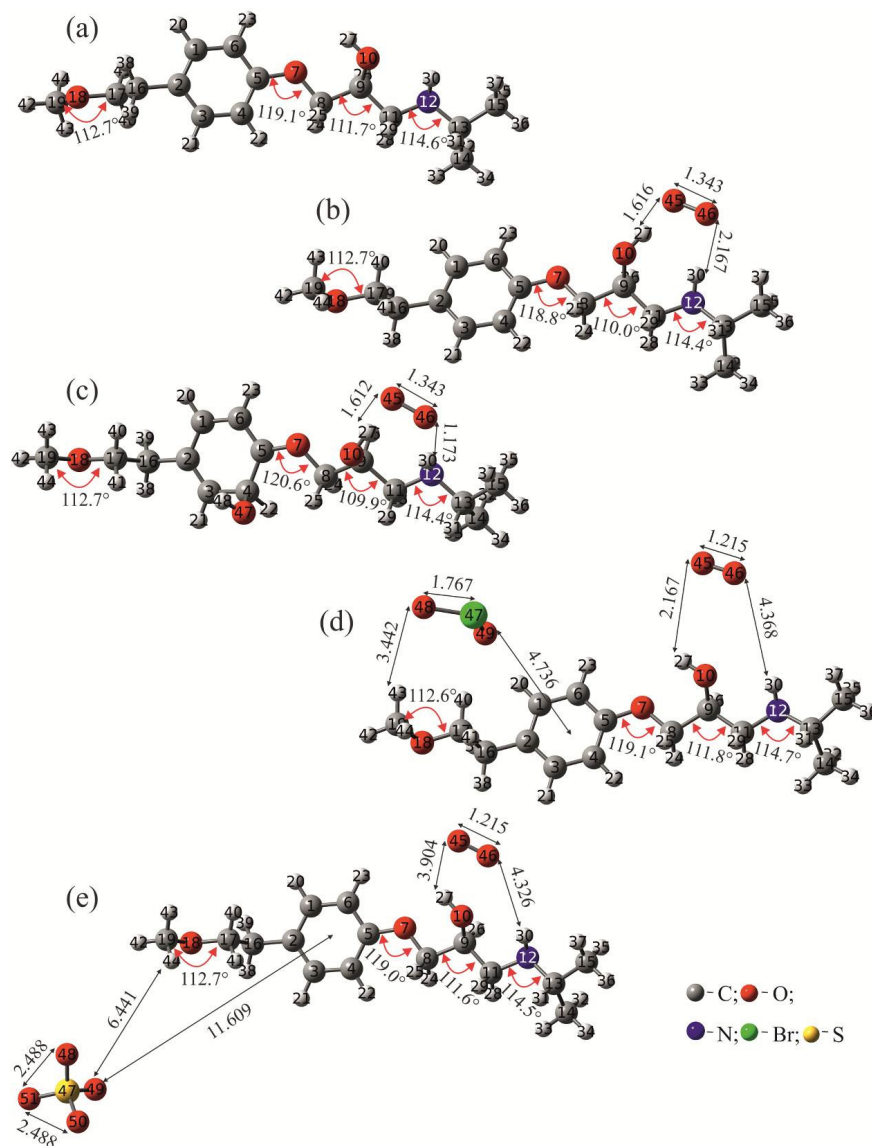


Fig. 10 Optimized geometries of the investigated structures with specific angles (degrees) and distances (Å) for: a) MET; b) MET/ O_2^+ ; c) MET/ O_2^+ / OH ; d) MET/ O_2^+ / BrO_2 ; and e) MET/ O_2^+ / SO_4 .

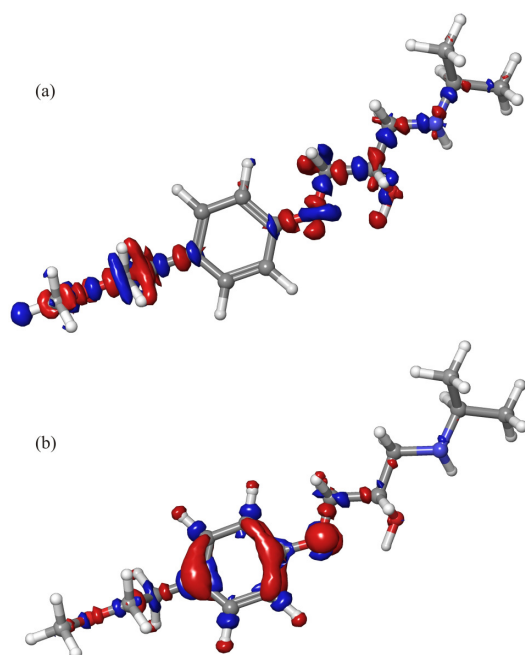


Fig. 11 Fukui functions of MET: a) Fukui f^+ function and b) Fukui f^- function.

Table 2. Atomic Fukui indices of MET

Atom	$f_{\text{NN}}^{\text{HOMO}}$	$f_{\text{NN}}^{\text{LUMO}}$
C1	0.0344	0.2021
C2	0.2415	0.0115
C3	0.0714	0.2885
C4	0.1006	0.1777
C5	0.1795	0.0070
C6	0.1184	0.2969
O7	0.1739	0.0006
C8	0.0012	0.0014
C9	0.0000	0.0048
O10	0.0007	-0.0026
C11	0.0013	0.0011
N12	0.0061	-0.0008
C13	0.0004	0.0002
C14	0.0002	0.0001
C15	0.0000	0.0001
C16	0.0071	0.0016
C17	0.0219	-0.0035
O18	0.0025	0.0004
C19	0.0018	0.0004

Concerning Fukui indices, the value of $f_{\text{NN}}^{\text{HOMO}}$ for the atom C4 again emphasizes its nucleophilic nature, while the highest value of this index is recorded for the C2 atom. The highest value of $f_{\text{NN}}^{\text{LUMO}}$ is obtained for the atom C6. Overall, Fukui indices have significantly high values for atoms belonging to the aromatic ring.

One should be careful when interpreting the results of Fukui functions and indices, since they are not reliable to absolutely identify the most reactive electrophilic or nucleophilic sites

within a particular molecule. In such a case, they can serve only as qualitative indicators of reactivity. However, according to both Fukui functions and indices, the C4 atom of the MET aromatic ring is a potential reaction site, which is confirmed in the case of the MET/ $\text{O}_2^{\bullet-}$ / OH^{\bullet} system.

3.5.2. Molecular Electrostatic Potential (MEP) surfaces

Representative MEP surfaces of the investigated structures are given in Fig. 12. The blue colour corresponds to the areas with the highest electrostatic potential, the red colour corresponds to the lowest electrostatic potential, while the green colour indicates intermediate values. MEP surfaces clearly indicate that significant changes of charge distribution would occur in MET in the presence of radicals. In particular, the introduction of radical species would change significantly the maximal and minimal MEP values, and the associated change would be the highest for $\text{SO}_4^{\bullet-}$. In the MEP surface of MET alone (Fig. 12) there are two specific sites containing a significant negative charge, located in the near vicinities of oxygen and nitrogen atoms. As expected, these sites would be the centres of reactivity with radicals. In the equilibrium state, $\text{O}_2^{\bullet-}$ was located above the hydroxyl group and the closest adjacent H atom. The hydroxyl radical was bound to the aromatic ring, and the H atom of OH^{\bullet} acquired a significantly positive MEP value.

The situations changed when BrO_2^{\bullet} and $\text{SO}_4^{\bullet-}$ were present in the system. The location of the radical $\text{O}_2^{\bullet-}$ was similar to previous cases, but the MEP values around $\text{O}_2^{\bullet-}$ were much higher than before and also the values around oxygen atoms increased significantly. These different charge distributions indicate interesting chemical interactions between MET and the studied radicals, which will be further discussed in the following section.

3.5.3. Natural Bond Order (NBO) analysis

The nature of molecular interactions can be investigated employing the NBO analysis, specifically based on the observation of the electron delocalization energies between NBO orbitals.^{11,12,53–56} The significance of the chemical or physical interactions between MET and radical species can be assessed by using the total sum of the delocalization energies, $\Sigma E(2)$, obtained by summing the electron delocalization energies of all the significant interactions between the NBO orbitals of interacting molecules.^{57,58} The $\Sigma E(2)$ values are reported in Table 3. A larger $\Sigma E(2)$ means that the interactions, resulting from electron delocalization from donor to acceptor NBO between MET and radicals, are more important. As a consequence, $\Sigma E(2)$ values are a measure of the importance of chemical interaction between the investigated species. On the other side, lower $\Sigma E(2)$ might suggest electrostatic interaction between the studied species.

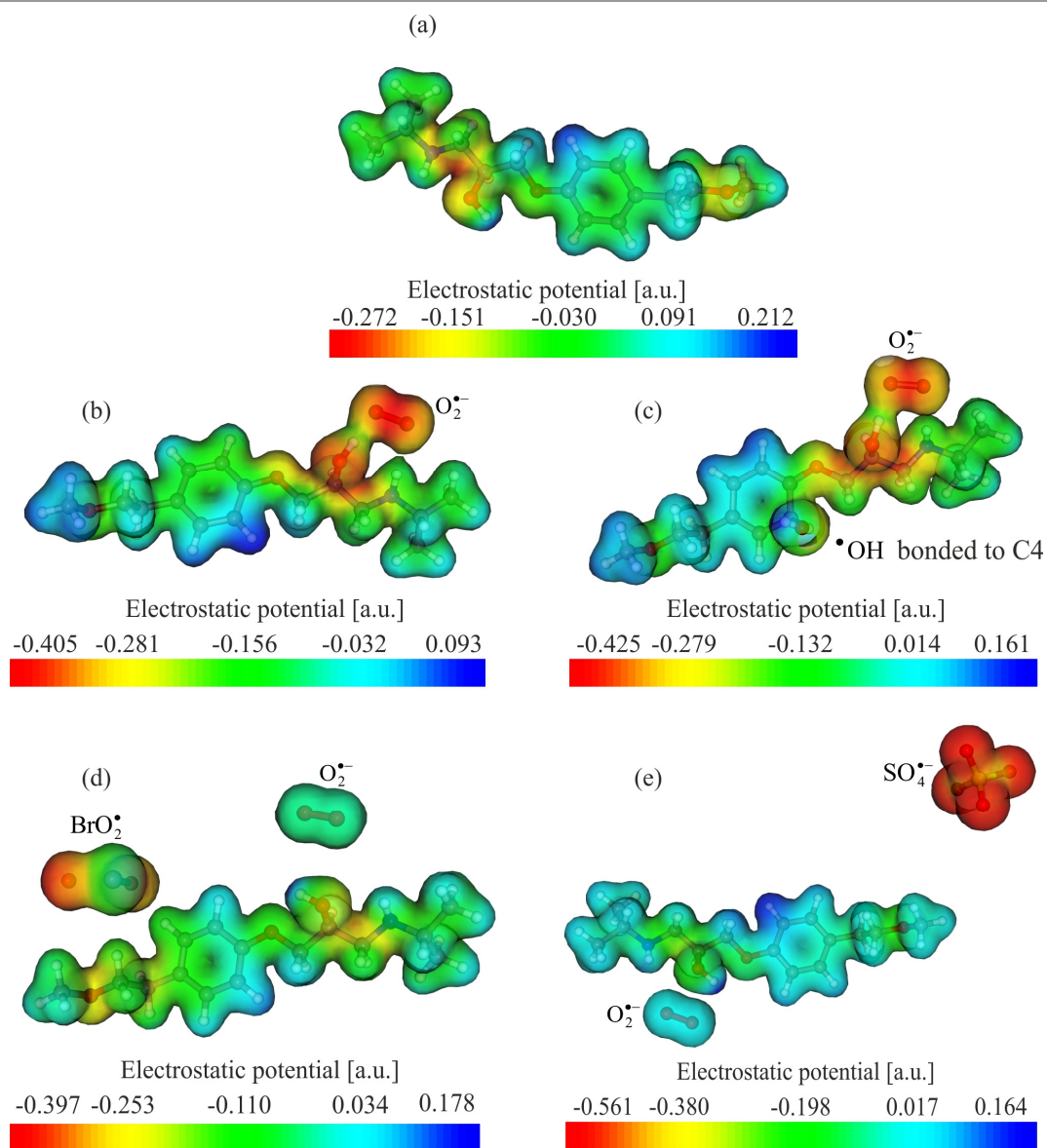


Fig. 12 Representative MEP surfaces of the investigated systems: a) MET; b) MET/ $\text{O}_2^{\bullet-}$; c) MET/ $\text{O}_2^{\bullet-}/\bullet\text{OH}$; d) MET/ $\text{O}_2^{\bullet-}/\text{BrO}_2^{\bullet}$; and e) MET/ $\text{O}_2^{\bullet-}/\text{SO}_4^{\bullet-}$.

According to NBO results, the highest and the most important chemical interactions took place in the MET/ $\text{O}_2^{\bullet-}/\bullet\text{OH}$ system. This is consistent with above findings, which suggested that a new bond was formed in this system between the C4 atom of MET and $\bullet\text{OH}$. The interactions resulting from electron delocalization from $\text{O}_2^{\bullet-}$ to MET NBOs are significant, since $\Sigma E(2) \approx 28 \text{ kcal mol}^{-1}$. In contrast, chemical interactions resulting from electron delocalization from MET to $\text{O}_2^{\bullet-}$ NBOs are insignificant. There is a significant electron delocalization from $\text{O}_2^{\bullet-}$ to MET NBOs in the case of the MET/ $\text{O}_2^{\bullet-}$ system, as suggested by the quite elevated $\Sigma E(2) \approx 34 \text{ kcal mol}^{-1}$. This is the highest value of $\Sigma E(2)$ among all the cases investigated in this work, and it clearly indicates a chemical interaction between $\text{O}_2^{\bullet-}$ and MET. This means that dissolved oxygen, in addition to inhibiting e^-h^+ recombination and enhancing, as a consequence, the occurrence and subsequent reactivity of $\bullet\text{OH}$

and h^+ , could further contribute to MET degradation through the formation of $\text{O}_2^{\bullet-}$.

Table 3. $\Sigma E(2)$ of interacting units between MET and radicals

System	Donor unit (NBOs of)	Acceptor unit (NBOs of)	$\Sigma E(2)$ [kcal mol ⁻¹]
MET/O ₂ ^{•-}	MET	O ₂ ^{•-}	3.14
	O ₂ ^{•-}	MET	34.31
MET/O ₂ ^{•-} /•OH	MET	O ₂ ^{•-}	0.23
	MET	•OH	Bonded
	•OH	MET	Bonded
	O ₂ ^{•-}	MET	28.21
	O ₂ ^{•-}	•OH	<0.05
	•OH	O ₂ ^{•-}	<0.05
MET/O ₂ ^{•-} /BrO ₂ [•]	MET	O ₂ ^{•-}	<0.05
	MET	BrO ₂ [•]	<0.05
	O ₂ ^{•-}	MET	0.64
	BrO ₂ [•]	MET	6.08
	O ₂ ^{•-}	BrO ₂ [•]	<0.05
	BrO ₂ [•]	O ₂ ^{•-}	<0.05
MET/O ₂ ^{•-} /SO ₄ ^{•-}	MET	O ₂ ^{•-}	<0.05
	MET	SO ₄ ^{•-}	<0.05
	O ₂ ^{•-}	MET	<0.05
	SO ₄ ^{•-}	MET	<0.05
	O ₂ ^{•-}	SO ₄ ^{•-}	<0.05
	SO ₄ ^{•-}	O ₂ ^{•-}	<0.05

In the case of MET/O₂^{•-}/BrO₂[•], the $\Sigma E(2)$ of electron delocalization from BrO₂[•] to MET NBOs is ca. 6 kcal mol⁻¹, which suggests weak chemical interaction when compared with previous cases. The chemical interaction between O₂^{•-} and MET in this system turned out to be insignificant, as indicated by a $\Sigma E(2)$ value from O₂^{•-} to MET of only 0.64 kcal mol⁻¹.

While important chemical reaction between MET and BrO₂[•] seems to be excluded, it should be reminded that bromate was able to significantly enhance MET photocatalytic degradation in the case of Degussa P25. In this case, the effect of bromate should probably be ascribed to its mere ability to scavenge e⁻, which inhibits the e⁻-h⁺ recombination and enhances the occurrence and subsequent reactivity of •OH and h⁺. Moreover, the enhancement effect with Degussa P25 combined with no bromate effect on TiO₂ Wackherr suggests that an important role in MET degradation could be played by different properties of the photocatalyst, lifetime of h⁺ and concentration of radical species.

In the case of MET/O₂^{•-}/SO₄^{•-}, the interactions between MET and the corresponding radicals would just be of an electrostatic nature, as suggested by the very low values of the $\Sigma E(2)$ energies, all below the default threshold of 0.05 kcal mol⁻¹. This result excludes chemical reactivity between MET and SO₄^{•-}, and it helps explaining the very limited effect of S₂O₈²⁻ on the photocatalytic degradation of MET. Indeed,

electron scavenging by persulfate would be offset by drawbacks connected with SO₄²⁻ formation (adsorption on the photocatalyst surface, which reduces the photocatalytic activity), while SO₄^{•-} would not be able to favour degradation by significantly reacting with MET.

3.6. LC-ESI-MS/MS identification of degradation intermediates

By using the LC-ESI-MS/MS technique, intermediates of MET degradation in the presence of different electron acceptors (O₂, O₂/H₂O₂ and O₂/KBrO₃) with both catalysts were investigated (see ESI,[§] Fig. S1-S22 and Table S1). Intermediates formed in the absence of electron acceptors (systems with N₂) were not investigated because the rate of MET degradation was very low. Therefore, the concentration of intermediates was low as well and they couldn't be identified. Because the collision-induced dissociation patterns of MET degradation were defined previously,⁵⁹ it was possible to identify the detected peaks by using the product ion MS² spectra. The retention times of all identified degradation intermediates **P1–P10** (1.18–3.98 min) were shorter than that of MET (4.43 min), due to the cleavage of the molecule and the formation of polar moieties.

During the degradation of MET with TiO₂ Wackherr/O₂, a total of seven peaks (labeled **P1–P7**) corresponding to degradation intermediates were detected (ESI,[§] Table S1 and Fig. 13). Intermediate **P1** represents a compound with $M_{mi} = 133$, indicating the presence of a nitrogen atom in its structure. Based on its fragmentation pattern (ESI,[§] Table S1) and literature data, it was concluded that this compound is 3-(propan-2-ylamino)propane-1,2-diol, already identified.¹³ Intermediates **P2** and **P3** both correspond to compounds with $M_{mi} = 253$, but with different MS² spectra. Based on MS² spectra and literature data^{13,60} it could be stated that **P2** is hydroxy derivative 4-[2-hydroxy-3-(propan-2-ylamino)propoxy]benzaldehyde, that was previously identified as MET degradation product. Fragment 212 (C₁₀H₁₄NO₄) present in **P2**, is formed by loss of water and isopropyl moiety, which was further dehydrated to the m/z 177 (i.e., loss of water and methylamine group). Radjenović et al. also identified this compound and they stated that the characteristic fragment ion m/z 133 was detected in the spectrum of the parent compound and degradation products,⁶⁰ which is also in agreement with our results. The herewith provided MS² spectra of **P2** (Table S1) are in very good agreement with those previously reported.^{13,60} It was not possible to determine the positions of the hydroxyls, due to the small number of fragments formed in MS² experiments. However, based on the theoretical results (Table 3 and Figs. 10 and 12), we can assume that •OH might be bonded to the C4 atom of the aromatic ring. Fragment 116 (C₆H₁₄ON), common to many MET degradation products, and observed in the MS² spectrum of **P3**, corresponds to *N*-(1-methylethyl)-2-oxopropan-1-aminium and indicates the intact *O*-bound moiety i.e. hydroxylation of either benzene ring or C₂-chain. Ion 177 fragments by consecutive loss of water ($m/z = 18$) and ethene ($m/z = 28$), indicating the presence of an hydroxyethyl moiety. The presence of ion 159 fragments in MS² spectra of MET and

P3 indicates preserved aromatic ring of MET. Detailed fragmentation of MET is described in the literature, where m/z 159 corresponds to the loss of 109 (18+42+17+32) mass units: water, propene, ammonia are lost from the right side and methanol from the left side of the chain.⁶¹ Thus, **P3** represents either 1-[4-(1-hydroxyethyl)phenoxy]-3-(propan-2-ylamino)propan-2-ol or its 2-hydroxyethyl isomer. This compound was previously identified^{62,63} as the 1-hydroxyethyl isomer.

The three peaks, labelled **P4**, **P5**, and **P6**, corresponding to compounds with $M_{mi} = 281$, were detected. Upon further evaluation of EICs for the observed fragment ions, it was determined that peak **P4** contains two closely-eluting compounds labelled **P4a** and **P4b**. Due to close elution, it was impossible to obtain pure MS² spectra of these compounds. Therefore, EIC traces for each ion had to be checked, to confirm the presence/absence of specific fragments in each chromatographic peak. To ease the comparison of spectra and interpretation, composite MS² spectra were prepared by summing MS² spectra obtained at different collision energies. Molecular mass, higher by 14 units than that of MET, implies the introduction of one oxygen and the abstraction of two hydrogen atoms (i.e. either introduction of an oxo group, or introduction of hydroxyl and oxidation of the existing hydroxyl). Early loss of isopropylamine and water ($\Delta m/z = 77$, yielding fragment 205) and/or propene ($\Delta m/z = 42$, yielding fragment 240) indicate the intact *i*PrNH– moiety. There are five possible isomers of oxo-MET (excluding the one with oxygenated isopropyl), hereby designated A–E. Isomer A: 2-[4-[2-hydroxy-3-(propan-2-ylamino)propoxy]phenyl]ethyl formate, isomer B: methyl {4-[2-hydroxy-3-(propan-2-ylamino)propoxy]phenyl}acetate, isomer C: 1-{4-[2-hydroxy-3-(propan-2-ylamino)propoxy]phenyl}-2-methoxyethanone, isomer D: 4-(2-methoxyethyl)phenyl-2-hydroxy-3-(propan-2-ylamino)propanoate, and isomer E: 2-hydroxy-3-[4-(2-methoxyethyl)phenoxy]-*N*-(propan-2-yl)propanamide. Based on differences in observed spectra, we tentatively assigned structures to detected peaks. The loss of H₂O ($\Delta m/z = 18$, yielding fragment 264), was observable only in peak **P6**, and was followed by subsequent loss of propylamine ($\Delta m/z = 59$, yielding fragment 205). In all the other peaks the latter loss is immediate, and thus only ion 205 is observable, leading to the conclusion that ion 264 is stabilized in **P6**. Thus, we propose that **P6** represents either isomer D or E, that would – after water loss – form an α,β -unsaturated carbonyl compound, stabilized through electron delocalization. Peak **P5** was characterized by the absence of two otherwise common ions for MET and derivatives: 133 (corresponding to ion produced by loss of H₂O, *i*PrNH₂ and phenyl-bound chain) and 116 (corresponding to loss of *p*-substituted phenoxy moiety). Fragment 177, produced by loss of 28 mass units (CO₂/C₂H₄) from ion 205, was also characteristic for this compound only. We concluded that CO loss is to be expected if ion 205 has 1-formyl-2-[4-(2-methoxyethyl)phenoxy]ethenyl structure, i.e. if **P5** could represent the isomer E (in that case, **P6** would be the isomer D). The spectra of **P4a** and **P4b** differ from general pattern observed for **P5** and **P6** by much more pronounced fragments corresponding to loss of propene ($\Delta m/z = 42$) or water and propylamine ($\Delta m/z = 77$), and absence of otherwise common fragment 98 (either due to preferred loss of N-containing part as a neutral molecule, or due to low general abundance). Another common fragment, m/z 121, corresponding to protonated *p*-vinylphenol, was also absent in both peaks, which lead us to the

conclusion that the oxidation possibly occurred at α - and β -position of 2-methoxyethyl moiety, i.e. that peaks **P4a** and **P4b** possibly represent isomers B and C. The presence of abundant fragment 116 (corresponding to intact *N*-(1-methylethyl)-2-oxopropan-1-aminium, formed by cleavage of phenoxy bond) seems to support the assumption. However, at the moment, it was not possible to determine the exact oxygenation site for these two compounds.

In the presence of H₂O₂ three new intermediates were observed (**P8**, **P9** and **P10**), while in the presence of KBrO₃ only **P9** and **P10** were detected. Intermediates **P7** and **P8** both have $M_{mi} = 299$, which is by 32 mass units greater than for MET. This implies that they are dihydroxy MET derivatives.^{13,49} Significant differences in fragmentation patterns of the two compounds allow the determination of the positions of the hydroxyl groups.

Intermediate **P7** was identified as 1-{4-[2-hydroxy-3-(propan-2-ylamino)propoxy]phenyl}-2-methoxyethane-1,2-diol. Initial loss of 62 mass units can be attributed to cleavage of the C-C bond between CHOH and CH(OH)OCH₃ units, leading to loss of methoxymethanol and formation of formyl group on benzene ring. Subsequent loss of propene ($\Delta m/z$ 42) leads to formation of ion 196. This ion further fragments by cleavage of the Ph-O bond, to yield two complementary ions at m/z 74 and 105.

Spectra of **P8** are dominated by a series of fragments characteristic for MET – 159, 133, 116, 74, 72 and 56. Since these ions correspond to preserved C₂-C₆-O-C₃-N moiety (without any additional substitution, compared to MET), we assume that the two hydroxyls are located at peripheral groups – methoxy and/or isopropyl. The value of m/z 282 corresponds to the parent compound after loss of water. However, it was not possible to determine where one or both hydroxyls are bound, due to the lack of any other diagnostic fragments. Intermediate **P9** has $M_{mi} = 273$, namely six mass units higher than MET. This is a consequence of C₃H₆ loss and the attachment of three hydroxyl groups. However, at lower m/z range, a series of fragments was observed – 116 (C₆H₁₄NO), 98 (C₆H₁₂N), 74 (C₃H₈NO), 56 (C₃H₆N) – corresponding to *N*-(1-methylethyl)-2-oxopropan-1-aminium ion and its fragment, indicating a preserved 2-hydroxy-3-[(1-methylethyl)amino]propoxy group. Further fragmentation of ion 116 into 98 by the loss of water ($\Delta m/z = 18$) supports the presumption that the three hydroxyls are bonded to the methoxyethylbenzene moiety. The absence of common ions 159, 133 and 121 supports the oxidative cleavage of benzene ring, with the loss of a C₂ unit. While this reaction was previously described,⁶³ the hereby detected compound **P9** exhibit MS² spectra different from the published ones, indicating differences in the structure and suggesting that there are three OH groups bound to a benzene ring. This leads to the conclusion that the compound is a trihydroxy derivative of 1-amino-3-[4-(2-methoxyethyl)phenoxy]propan-2-ol.

Intermediate **P10**, eluting at 1.57 min, corresponds to a compound with $M_{mi} = 315$. The short retention time suggests that it is very polar, which would be accounted for by the three hydroxyl groups present in its structure, since its molecular mass is 48 mass units higher than that of MET.¹³ The fragments 116, 98, 74, and 56 in its MS² spectra indicate that the propanylaminopropane moiety stays intact, while the three hydroxyls are bonded to the methoxyethylbenzene part of the molecule. This compound has been previously identified as a trihydroxy derivative of 1-[4-(2-methoxyethyl)phenoxy]-3-(propan-2-ylamino)propan-2-ol.^{13,49}

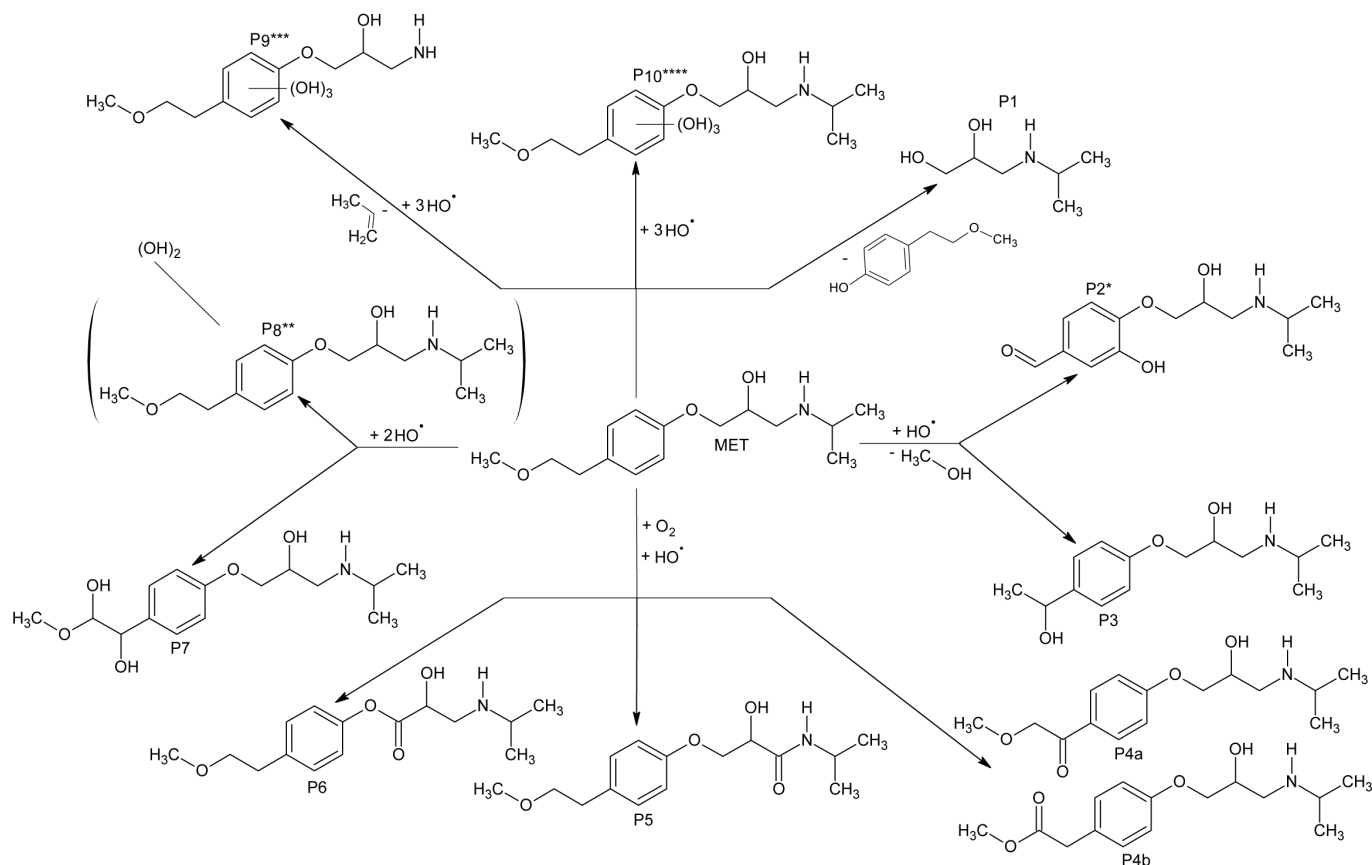


Fig. 13 Degradation intermediates of MET with electron acceptors, in the presence of TiO_2 Wackherr and Degussa P25. P1, P3–P7 were identified in all cases; P2* was identified, in all cases, only with TiO_2 Wackherr; P8** was identified only with TiO_2 Wackherr/ O_2 / H_2O_2 ; P9*** was identified in all cases except TiO_2 Wackherr/ O_2 ; P10**** was identified in all cases except TiO_2 Wackherr/ O_2 and Degussa P25/ O_2 / KBrO_3 .

The occurrence of different intermediates under different conditions could be due to their different stabilities, and/or to differences in the degradation mechanism of MET. One issue could be the interaction of $\text{O}_2^{\bullet-}$ with MET (Table 3). Compared to the case of O_2 alone, the addition of H_2O_2 lowered such interaction by 1.2 times and that of KBrO_3 by 54 times. However, NBO analysis already suggested that in the case of MET degradation with Degussa P25, besides the reactive radicals, the properties of the catalyst and the lifetime of h^+ would play an important role. This issue was confirmed by the analysis of the mechanism. Namely, in the presence of Degussa P25/ O_2 the intermediates **P1**, **P3–P7**, **P9**, and **P10** were identified. Moreover, they were also identified in the presence of H_2O_2 . This issue suggests that H_2O_2 in this case just increased the degradation rate of the parent compound (Fig. 1), which resulted in the faster formation of the intermediates because of an increased occurrence of $\bullet\text{OH}$. The intermediate **P10** was not detected in the presence of KBrO_3 , which might be due to the lower $\bullet\text{OH}$ concentration in the system.

Similarly to our previous work, here it was confirmed that different sets of MET intermediates are formed with different photocatalysts.¹³ Indeed, **P2** and **P8** were not detected in the presence of Degussa P25/ O_2 , while **P8**, **P9** and **P10** were not found with TiO_2 Wackherr/ O_2 . By comparing the O_2 / H_2O_2 systems with Degussa P25, **P2** and **P8** were again not identified, while in the case of TiO_2 Wackherr all intermediates were identified. In the presence of O_2 / KBrO_3 with Degussa P25 the intermediate **P10** was absent, while in the presence of TiO_2 Wackherr **P10** was present, but **P8** was absent.

In the present work, a lower number of intermediates was detected in comparison with previous work.¹³ That is probably a consequence of the significantly lower concentration of MET (by 60 times) used in the present work, which prevented the formation of dimeric species. Moreover, the concentrations (peak areas) of some intermediates in this work were very low and thus their identification was not possible.

4. Conclusions

This study shows that TiO_2 is a very effective photocatalyst for MET degradation, in the presence of electron acceptors such as O_2 , H_2O_2 , and BrO_3^- . The effect of the investigated electron acceptors depends on their initial concentration and on the nature of the photocatalyst. Moreover, while enhancing the transformation of MET (at least with Degussa P25), H_2O_2 decreased the rate of MET mineralization with both TiO_2 types. This contrasting effect might be accounted for by differences in reaction pathways (h^+ vs. $\bullet\text{OH}$) induced by the photocatalysts with and without H_2O_2 , as the $\bullet\text{OH}$ pathway (enhanced by H_2O_2) possibly did not favour the mineralization of the substrate. The same phenomenon could also account for the higher degree of mineralization achieved, without H_2O_2 , by Degussa P25 compared to TiO_2 Wackherr. The higher surface area of Degussa P25 could also be an issue, as it would decrease the probability of photocatalyst poisoning by the degradation intermediates.

DFT calculations and NBO analysis suggested that $\bullet\text{OH}$ and possibly $\text{O}_2^{\bullet-}$ could undergo chemical reaction with MET. It is, therefore, suggested that dissolved oxygen would not only enhance $\bullet\text{OH}/h^+$ reactivity by scavenging e^- and, therefore, inhibiting $e^- - h^+$ recombination; oxygen could additionally favour MET degradation through the formation of $\text{O}_2^{\bullet-}$. In contrast, reaction between MET and BrO_2^{\bullet} or $\text{SO}_4^{\bullet-}$ would be excluded. In the case of $\text{SO}_4^{\bullet-}$, the finding helps explaining the limited effect of $\text{S}_2\text{O}_8^{2-}$ on MET degradation: e^- scavenging by $\text{S}_2\text{O}_8^{2-}$ would be largely offset by the formation of sulfate in addition to $\text{SO}_4^{\bullet-}$. While sulfate decreases the photocatalytic activity by adsorbing on the surface of TiO_2 , $\text{SO}_4^{\bullet-}$ would not be able to take part in MET transformation.

Interestingly, both DFT calculations and the approach based on Fukui functions and Fukui indices consistently suggested that $\bullet\text{OH}$ would react with the MET aromatic ring, and particularly with its C4 atom.

Experimental study by LC-ESI-MS/MS indicated bonding of OH groups to different parts of MET, while results of theoretical analysis obtained in this investigation indicated bonding of OH group to the aromatic ring. According to the theoretical results, bonding of OH group to the C4 atom of benzene ring of **P2** was suggested. It was shown experimentally that the binding of OH groups does not occur on the propanylaminopropane group chain (**P8**, **P9**, and **P10**) and that ring opening doesn't occur as well, which is also in agreement with theoretical analysis. Besides, intermediates that are peculiar for the systems containing H_2O_2 and KBrO_3 were identified as well. Namely, **P8**, **P9**, and **P10** were detected with TiO_2 Wackherr/ $\text{O}_2/\text{H}_2\text{O}_2$ and **P9** and **P10** with TiO_2 Wackherr/ O_2/KBrO_3 . While the same intermediates were identified with Degussa P25/ O_2 and Degussa P25/ $\text{O}_2/\text{H}_2\text{O}_2$, the intermediate **P10** was not identified with Degussa P25/ O_2/KBrO_3 .

Acknowledgements

The authors greatly appreciate the financial support from the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. 172042).

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