

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

Role of Hydroxyl, Superoxide, and Nitrate Radicals on the Fate of Bromide Ions in Photocatalytic TiO₂ Suspensions

This is a pre print version of the following article:

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/1768427> since 2021-01-22T17:08:48Z

Published version:

DOI:10.1021/acscatal.0c02010

Terms of use:

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)

The role of hydroxyl, superoxide, and nitrate radicals on the fate of bromide ions in photocatalytic TiO₂ suspensions

F. Parrino^{*a \diamond} , S. Livraghi^{b \diamond} , E. Giamello^b, R. Ceccato^a, L. Palmisano^c

^a Department of Industrial Engineering, University of Trento, Via Sommarive 9, 38123 Trento, Italy

^b Department of Chemistry and NIS, University of Torino, Via P. Giuria 7, 10125 Torino, Italy

^c Department of Engineering, University of Palermo, Viale delle Scienze Ed. 6, 90128 Palermo, Italy

\diamond These authors equally contributed to this work

*corresponding author: francesco.parrino@unitn.it

Abstract

The influence of bromide ions on systems containing highly reactive radical species is of great interest for environmental remediation, atmospheric chemistry and green synthesis of high added value compounds. In this regard, irradiated TiO₂ suspensions are simple and suitable systems to highlight some mechanisms of general validity in the above mentioned research fields. In this work the spin-trapping technique has allowed to highlight the concurrent action of hydroxyl and superoxide radicals towards bromide ions. In fact, hydroxyl radicals oxidize bromide ions to bromine atoms which in turn can be reduced back to bromide ions by superoxide radicals. Results suggest that this relais mechanism, mainly based on secondary redox products (such as reactive oxygen species, ROS) rather than on direct interfacial electron transfer, is responsible for the generally observed constant concentration of bromide ions in irradiated TiO₂ suspensions. The presence of nitrate ions in the system significantly alters this equilibrium. In fact, nitrate radicals generated by hole induced oxidation of nitrate ions, selectively oxidize bromide ions to elemental bromine even in anoxic conditions, but in the presence of bromate as an opportune electron scavenger. This result not only reveals the importance of nitrate radicals towards the photocatalytic production of elemental bromine but confirms the active role of nitrate ions in irradiated photocatalytic suspensions.

Keywords: reactive oxygen species, photocatalysis, bromine, nitrate radicals.

1. Introduction

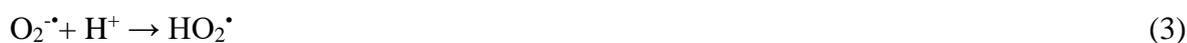
Bromide ion is a ubiquitous species in natural aqueous systems. Its concentration is quite low in rain water, ranging from 0 to $110 \mu\text{g}\cdot\text{L}^{-1}$ [1], but reaches considerable values in groundwater, between 0.01 and $2 \text{ mg}\cdot\text{L}^{-1}$ [2], and in seawater, typically about $70 \text{ mg}\cdot\text{L}^{-1}$. Moreover, in specific areas such as the Dead Sea, or the Salt lakes in USA, bromide concentration is in the order of several grams per liter. Coastal or estuarine areas where seawater could come in contact with surface water usually present higher bromide concentration with respect to inland areas [3], therefore, bromide ions concentration has been often considered as an indicator of seawater intrusions in soil water [4]. Bromide is present in almost every drinking water at concentrations ranging from ca. 0.01 up to 3 mg L^{-1} [5]. Notably, the presence of bromide ions *per se* does not represent a threat to living organisms. However, bromide ions are easily involved in oxidation reactions of natural or anthropogenic origin, giving rise to not negligible side effects for environmental and human safety.

As far as natural oxidations are concerned, bromide ions play a key role in sea water and in the atmosphere, where they are transported in seawater droplets which constitute the most important aerosol type in the atmosphere. In fact, in the troposphere seawater particles accounts for ca. 27 Tg on a dry mass basis [6]. These particles, not only are efficient centers of cloud condensation [7], but are important sites for SO_2 oxidation to sulphuric acid [8,9], and constitute a source of reactive Br_2 and BrCl species. The latter ones, in turn, trigger oxidation reactions involving ozone and hydrocarbons [10]. As a matter of fact, the depletion of tropospheric ozone largely depends on reactions involving halogen species [11]. In this regard, the interaction of bromine species with reactive oxygen species (ROS) such as hydroxyl ($\cdot\text{OH}$) or superoxide radicals ($\text{HO}_2\cdot$) is of paramount importance. These radicals are also known as “atmospheric cleansers” because they are mainly responsible for the self-cleaning ability of the troposphere during day time [12]. ROS can be also generated within dispersed seawater particles via direct photolysis of light absorbing species (nitrate, nitrite, hydrogen peroxide, ozone) or redox reactions induced by excited chromophores, involving water and oxygen molecules [13]. Therefore, the interplay between ROS and bromide species is a “hot topic” of atmospheric chemistry. Similarly, bromide ion is usually considered the main $\cdot\text{OH}$ scavenger in seawater affording bromine radical ($\text{Br}\cdot$), which in turn, mainly reacts with another bromide ion giving rise to dibromide radical, $\text{Br}_2\cdot^-$ [14]. Bromine centered radicals are able to react with dissolved organic compounds producing bromoderivatives which are usually persistent and toxic pollutants [15].

As far as the human activities are concerned, it has been evidenced that ozonation of bromide containing water, besides the desired effects of water remediation and pollutant degradation, quantitatively induces oxidation of bromide to bromate ion. The latter has been classified by the International Agency for the Research on Cancer (IARC) as a potentially carcinogenic species, and the World Health Organization (WHO) [16] guidelines reported that a concentration of bromate of $3 \mu\text{g}\cdot\text{L}^{-1}$ is associated with an upper-bound excess lifetime cancer risk of 10^{-5} . By considering that the bromide ion concentration in drinking water ranges from less than 0.01 to nearly $3 \text{ mg}\cdot\text{L}^{-1}$ [17], it is necessary to avoid or control the formation of bromate ions, whose accumulation can be extremely dangerous in particular in closed recirculated systems [18]. TiO_2 photocatalysis has been proposed as a tool to control bromate formation when coupled with ozonation [19-21]. In fact, under irradiation of suitable energy, photogenerated electrons are able to reduce bromate ions, while avoiding further oxidation of bromide ions.

Recently, production of elemental bromine through oxidation of bromide ions has been reported in irradiated aqueous TiO_2 suspensions containing catalytic amounts of nitric acid [22,23]. This process, driven by light irradiation and without using strong oxidants, is a green alternative to the currently applied industrial ones which instead employ toxic and harmful gaseous chlorine as the oxidant.

Photocatalysis is based on the capability of irradiated semiconductors such as TiO_2 , to produce (Eq. 1) in their conduction and valence band, respectively photogenerated electrons (e^-_{CB}) and holes (h^+_{VB}), which can undergo interfacial electron transfer and induce useful redox reactions [24]. In particular, electrons can reduce oxygen to superoxide radical anion (Eq. 2) which in turn gives rise to hydroxyl radicals (Eqs. 3-5).



The whole reaction (Eqs. 1-5) is a 3-electron reduction of O_2 to a hydroxyl ion and a hydroxyl radical. Hydroxyl radicals can be also formed by hole-induced water oxidation (Eq. 6). In the presence of nitrate ions, however, a further reaction can occur that is, as recently proposed [25], the formation of nitrate radicals (Eq. 7).





Therefore, it is evident that photocatalytic water suspensions are suitable platforms to evidence and simulate the complex chemistry occurring in nature involving bromide ions and oxygen active species, which can be thereby quantitatively produced and easily detected.

In this paper the spin-trapping technique (based on the detection of stable adducts of OH radicals by Electron Paramagnetic Resonance, EPR) and UV-vis spectroscopy have been employed to investigate the evolution as a function of time of hydroxyl and superoxide radicals, respectively, in irradiated suspensions of TiO₂. This was done both in the presence and in the absence of bromide and nitrate ions and at different pH values. Understanding the mechanisms of the reactions occurring in the irradiated system has a twofold value since it allows to shed light into a delicate process of environmental chemistry and, at the same time, to gain further evidence on a possible, more benign, alternative route for bromine production.

2. Materials and methods

5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) employed for the hydroxyl radical detection was purchased from Alexis and nitroblue tetrazolium (NBT) employed for the analysis of the superoxide radical, was purchased from Sigma-Aldrich. Nitric acid (HNO₃ 70%), sulfuric acid (H₂SO₄ 98%), potassium sulfate (K₂SO₄, p.a.), potassium nitrate (KNO₃, p.a.), potassium bromide (KBr, p.a.), potassium bromate (KBrO₃, p.a.), were purchased from Sigma-Aldrich and used as received. Commercial titanium dioxide (TiO₂ P25-Evonik, 20% Rutile and 80% Anatase, specific surface area: 50 m²·g⁻¹) was used as the photocatalyst.

Electron Paramagnetic Resonance (EPR) spectra were run using a X-band CW-EPR Bruker EMX spectrometer equipped with a cylindrical cavity operating at 100 kHz field modulation.

UV-vis spectra were recorded by means of a UV-vis spectrophotometer (Uvikon, Kontron Instruments). Spectra were acquired in the range 200-600 nm by using suprasil quartz cells.

“*In situ*” irradiation experiments for the hydroxyl radical detection were carried out directly in the EPR cavity by using a 1600W Hg lamp (Newport Instruments) with a light beam output set at 800W and equipped with a IR water filter, while “*ex situ*” irradiation experiments to monitor the formation of superoxide radicals were performed irradiating by means of a 500W Xe/Hg lamp (Oriental Instruments) equipped with a IR water filter.

In each experiment the light beam also passed through a filter (Oriental 320FG01-50S) aimed to exclude the deep UV components ($\lambda < 320$ nm) in order to avoid the onset of a radical chemistry caused by

direct interaction between the DMPO molecule and the UV light [26]. The incident irradiation for the UV component was ca. $350 \text{ W}\cdot\text{m}^{-2}$ and $250 \text{ W}\cdot\text{m}^{-2}$ for the “*in situ*” and “*ex situ*” experiments, respectively. The incident light irradiance in the UVA region for each experiment was measured by a Deltahom instrument equipped with a detector operating in the in the UV-A range (315-400 nm). Radical species were generated via UV irradiation of four sets of TiO_2 aqueous suspensions ($1 \text{ g}\cdot\text{L}^{-1}$) at different pH values. The first set of suspensions, characterized by the presence of nitrate ions (4 mM) at pH 2.5, 4.0, and 6.5, was prepared by mixing the appropriate amount of HNO_3 and KNO_3 . A second group of solutions containing sulphate ions (4mM) was prepared by mixing the appropriate amount of H_2SO_4 and K_2SO_4 , in order to afford a sulphate concentration equal to that of nitrate in the first set of suspensions by maintaining the same pH values. Other two sets of suspensions were prepared by adding potassium bromide (2 mM) to the above mentioned ones. In this way it was possible to evidence separately the effect of nitrate and bromide ions. Table 1 reports the various suspensions prepared and the related label.

Table 1. Features and labelling of the various TiO_2 suspensions considered in this work.

Suspension	Ion content	pH	Label
1	NO_3^- 4mM	2.5	N2.5
		4.0	N4.0
		6.5	N6.5
2	SO_4^{2-} 4mM	2.5	S2.5
		4.0	S4.0
		6.5	S6.5
3	NO_3^- 4mM, Br^- 2mM	2.5	NBr2.5
		4.0	NBr4.0
		6.5	NBr6.5
4	SO_4^{2-} 4mM, Br^- 2mM	2.5	SBr2.5
		4.0	SBr4.0
		6.5	SBr6.5

Hydroxyl radicals were detected with the spin trapping technique by using the DMPO molecule as the trapping agent according to Eq. 8 that leads to a stable, EPR detectable, radical adduct [27]:



In a typical experiment 3 ml of a TiO₂ suspension containing DMPO (8.8 mM) was stirred in the dark for 5 minutes. A portion of this suspension (50 µL) was then transferred into the spectrometer cavity and the EPR spectra were recorded, at regular time intervals, during “*in situ*” irradiation and after turning off the irradiation source. The signal intensity of the DMPO-OH adduct has been obtained via double integration of the corresponding EPR signal. The amount of trapped radicals was evaluated by spin counting comparing the intensities of the various signals with those of 2,2-diphenyl-1-picrylhydrazyl radical (DPPH) standard solutions in toluene.

Superoxide radicals were detected via UV-vis spectroscopy according to a method reported by Goto et al. [28]. In a typical experiment 50.0 ml of the TiO₂ suspension containing NBT (20 µM) was stirred in the dark for 15 minutes in order to establish the adsorption–desorption equilibrium. A fraction of this suspension was filtered with an INCOFAR nylon syringe filter (diameter 13mm, pore diameter 0.2 µm) and the initial NBT concentration retrieved by UV-vis spectroscopy. Thereafter, the suspension was irradiated “*ex situ*” for 15 minutes and a fraction was filtered and immediately analyzed by means of UV-vis spectroscopy. In order to exclude undesired radical reactions under dark, the remaining suspension was stirred in the absence of irradiation for further 15 minutes, filtered, and finally analyzed by UV-vis spectroscopy.

This method is based on Eqs. 9-10.



in which the water soluble yellow NBT reacts with superoxide radicals (with both the protonated and unprotonated form) to produce NBTH₂ (formazan), an insoluble purple compound. Therefore, the decrease of the absorption band of NBT, is proportional to the amount of superoxide radicals photocatalytically produced during irradiation of the TiO₂ suspension.

Photocatalytic generation of bromine was performed by using an experimental set up elsewhere reported [22,23] and here briefly described.

The annular Pyrex photoreactor (V = 500 cm³) was equipped with ports in its upper part to withdraw samples and to allow nitrogen bubbling (0.1 L·min⁻¹) through the reacting medium. The photocatalytic aqueous suspension (pH = 2.7) contained 1 g·L⁻¹ of TiO₂ P25 as the photocatalyst, HNO₃ (4 mM) and KBr (2 mM). Tests were performed in the presence or in the absence of KBrO₃ as electron scavenger. Irradiation was performed by a medium pressure Hg lamp (Helios Italquartz, Italy, nominal power 125 W) axially positioned and immersed in the photoreactor. The lamp was cooled by water circulating through a Pyrex thimble. The reacting suspension was maintained at ca. 40°C by means of a heating wire surrounding the outer wall of the reactor, in order to facilitate the

stripping of the bromine produced. Notably, the Pyrex jacket surrounding the lamp cut off radiation wavelengths lower than 320 nm, so to exclude direct photolysis of HNO₃ and to consider TiO₂ the only relevant light absorbing species.

Prior to irradiation, the suspension was maintained in the dark and under nitrogen bubbling for 30 minutes, in order to ensure equilibrium conditions when irradiation started.

The gas flowing outside the photoreactor passed through one ice cold trap containing 50 mL of carbonium tetrachloride (CCl₄ 99.9%, Sigma-Aldrich). The bromine concentration in the trap was measured at fixed time intervals by means of UV-vis spectroscopy, by comparing the intensity of the characteristic bromine absorption band at 415 nm with standard bromine CCl₄ solutions. Runs were repeated at least three times and the standard deviation was always lower than 5%, thus indicating good reproducibility of results.

3. Results and discussion

3.1 The role of hydroxyl radicals

Irradiation of the TiO₂ water suspensions in presence of the DMPO spin trap leads, according to Eq. 8, to the formation of the typical paramagnetic DMPO-OH adduct whose EPR parameters are $a^N=14.6$ G $a^{H\beta}=14.4$, (see Supporting Information Section). Figure 1 compares the evolution with time of the DMPO-OH EPR signal intensity for TiO₂ suspensions in the presence of 4mM sulfate at pH 6.5, 4.0 and 2.5 (blue curves, samples S6.5, A; S4.0, B; S2.5, C). The red curves in each quadrant are obtained in the presence, beside sulphate ions, of bromide ions (2 mM, samples SBr6.5, A; SBr4.0, B; SBr2.5, C). The EPR signals intensities have been monitored in the time range 0-200 seconds under irradiation and for the remaining 200 seconds in dark conditions. Notably, the amount of hydroxyl radicals detected is proportional to the intensity of the EPR signal.

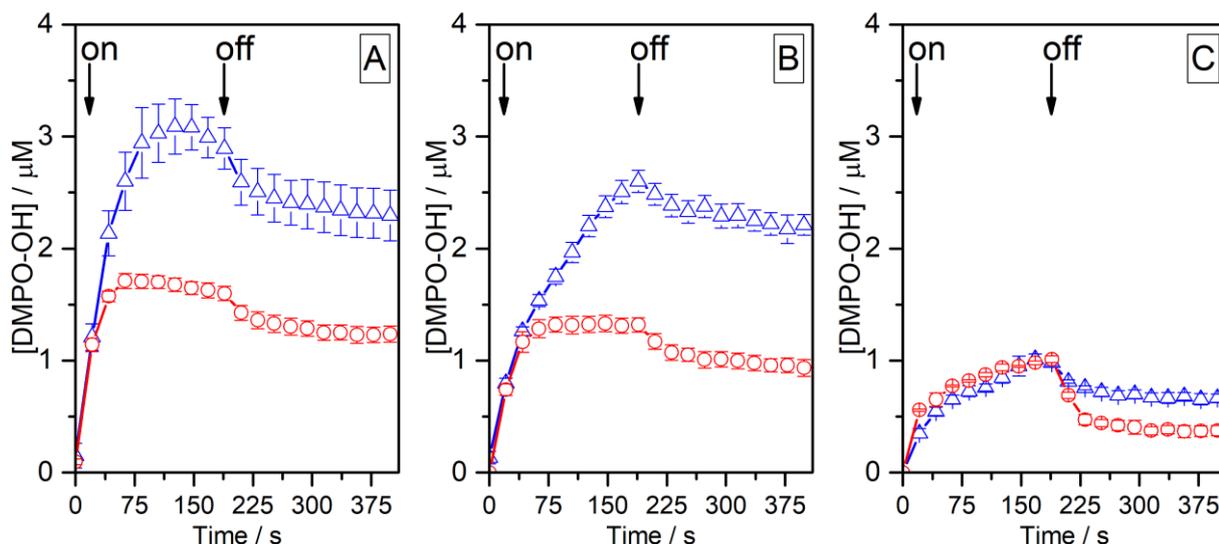


Figure 1. EPR signal intensity of the DMPO-OH adducts for the TiO₂ suspensions containing sulphate ions at three different pH. Blue curves (triangles) and red curves (balls) have been obtained in the absence and in the presence of bromide ions, respectively. Quadrant A: S6.5 and SBr6.5; quadrant B: S4.0 and SBr4.0; quadrant C: S2.5 and SBr2.5 (C).

From the results of spin trapping experiments reported in Figure 1 two main facts are evident:

- the EPR signal intensity (i.e. of OH radical concentration, Eqs. 1-6) steeply increases during the first part of irradiation and, in particular for the suspensions containing bromide, it reaches a constant value within 200 s. Irradiation beyond this limit does not result in a further increase of the EPR signal intensity as the rate of OH generation is equalized by the rate of consumption. The signal intensity slightly decreases after switching off the lamp.
- Except the case of strongly acidic conditions (quadrant C) the amount of OH radicals detected in the case of the presence of Br⁻ ions (red curve) is systematically lower than that recorded in their absence (blue curve)

Decreasing the pH value of the suspension from 6.5 (Figure 1 A) to 2.5 (Figure 1 C) and keeping constant the other conditions, results in weaker EPR signals. This is possibly due both to the lower trapping efficiency of DMPO at acidic pH values [29] and to the reported analysis of OH radical photocatalytic generation that also decreases varying pH from 7 to 3 [30].

The trend of the hydroxyl radical concentration shown in Figure 1 is the result of the interplay between generation and consumption phenomena. In particular, the blue curves, obtained in the absence of bromide ions, express the photocatalytic generation process of OH radicals. On the other hand, the red curves, obtained in the presence of bromide ions, represent the sum of photocatalytic OH generation and of bromide induced OH consumption. Therefore, assuming that the rate of OH

photogeneration is the same in the presence and in the absence of bromide ions, the difference between the two curves reported in each quadrant of Figure 1 expresses the trend of OH radical consumption due to the presence of bromide ions. This procedure leads to the curves shown in Figure 2 which express the bromide induced consumption of OH radicals.

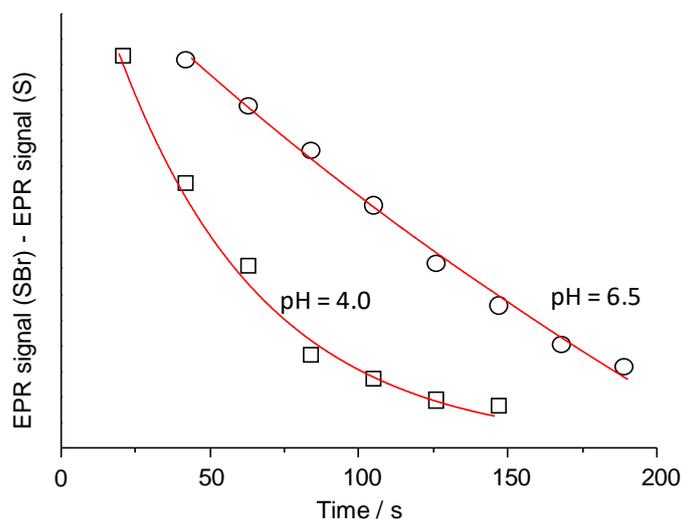


Figure 2. Bromide induced OH radical consumption expressed as the difference between the EPR signals recorded in the presence of sulfate and bromide ions (SBr) and those in the presence of the sole sulfate ions (S), versus irradiation time at pH = 4.0 (squares), and 6.5 (circles).

It is evident that the consumption of OH radicals is slower at pH = 6.5, i.e. close to the point of zero charge of TiO₂. In fact, at the pH of zero-point charge the surface of TiO₂ is nearly neutral while it is positively charged at lower pH values. This implies that the negative bromide ions are strongly interacting with the surface of TiO₂ at pH 4 than at pH 6.5, thus determining a faster decrease of hydroxyl radicals. Moreover, it can be noted that the experimental data present an exponential decay (see red curves in Figure 2) rather than a linear one. A linear decay would imply a zero order kinetics of consumption of hydroxyl radicals. This would be the case, for instance, when bromide ions would be mainly oxidized by the photogenerated holes, i.e. a precursor of hydroxyl radicals (see Eq. 11).



However, the results shown in Figure 2 suggest a kinetics of OH radical consumption of the first order with respect to OH[•], i.e. a direct oxidation of bromide ions by OH radicals according to Eq. 12-13 [31,32].



These results suggest that bromide ions act mainly as OH radical scavengers rather than as traps for the photogenerated hole. Notably, both the paths have been reported in the relevant literature, but bromide ions have been often used as a direct hole scavenger [33]. Therefore, it can be suggested to use more suitable hole scavengers such as melamine [34] for mechanistic studies, instead of bromide ions.

By substituting sulfate with nitrate ions under otherwise identical conditions, the EPR trapping signal under irradiation presents a completely different behaviour as shown in Figure 3. In fact, after an initial maximum (around 50 s), a net decrease of the OH radical concentration is observed till the lamp is switched off. Moreover, in this case, the presence of bromide ions does not significantly affect the evolution of the radical production with time. In fact, only at pH 2.5 (quadrant C) it is possible to observe a significant difference between the signal intensities in the presence and in the absence of bromide ions. Furthermore, similarly to what observed in the presence of sulfate ions, decreasing the pH value of the suspension results in a lower amount of detected hydroxyl radicals.

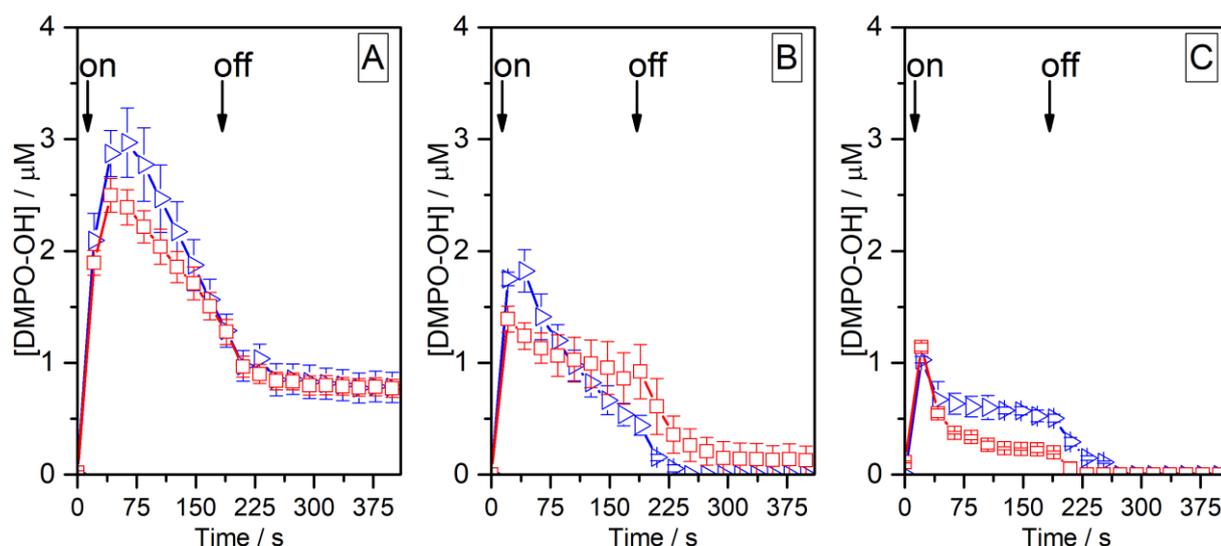


Figure 3. EPR signal intensity of the DMPO-OH adduct for the TiO₂ suspensions containing nitrate ions at three different pH. Blue curves (triangles) and red curves (balls) have been obtained in the absence and in the presence of bromide ions, respectively. Quadrant A: N6.5 and NBr6.5; quadrant B N4.0 and NBr4.0; quadrant C: N2.5 and NBr2.5.

The reason of the behaviour observed for OH evolution in the absence of bromide ions (Figure 2, blue lines) has been proposed in a previous work [25]. Briefly, the observed decrease in the amount of photogenerated OH radicals is due to hole induced oxidation of nitrate ions to nitrate radicals (not trapped by DMPO) which efficiently competes with the formation of OH radicals by water oxidation. This competition seems to take place efficiently after the first 50 seconds of irradiation during which, on the contrary, formation of OH radicals prevails. It can be speculated that, due to the large excess of water, that water molecules constituting the first adsorption layers are firstly oxidized, but then facilitate in a concerted way the oxidation of nitrate ions. In fact, as above mentioned below the zero-point charge of TiO₂, the density of nitrate ions close to the positively charged surface could be significantly high. This hypothesis is supported by an analogous interpretation advanced on the basis of results on surface hopping and DFT calculations [35], that recently highlighted the importance of hydrogen bonding between adsorbed water molecules in stabilizing the hydrated hole (H₂O⁺). This effect could prolong the lifetime of H₂O⁺ which therefore, in the presence of nitrate ions, can promote formation of nitrate radicals (Eq. 7) instead of evolving into hydroxyl radicals. Figure 4 schematically describes this mechanism.

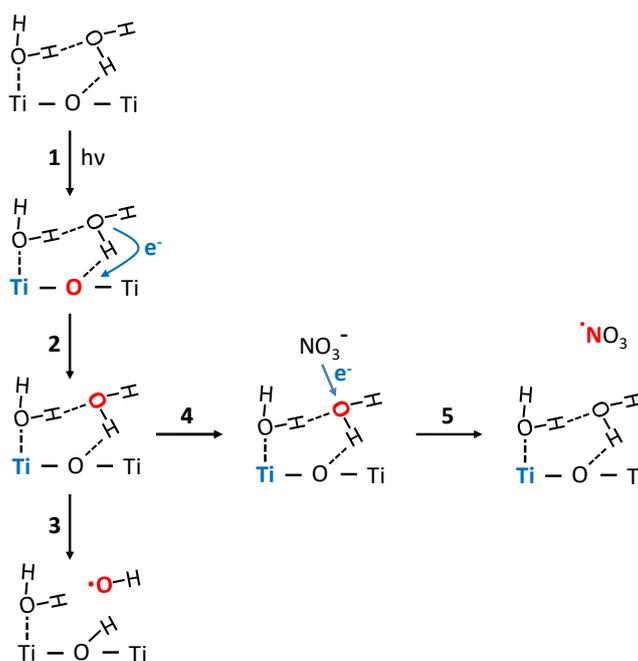


Figure 4. Photogeneration of exciton on vicinal Ti and O atoms (1), formation of H_2O^+ intermediate (2), evolution of OH radical (3), hole induced formation of NO_3 radicals (4 and 5). The color blue and red are used to indicate a localized electron and hole, respectively.

The stabilization of the hydrated hole by hydrogen bonding has been also experimentally observed [36-39]. Scan diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS) evidenced the same effect on anatase TiO_2 (101) with a consequent suppression of charges recombination at the time scale of minutes [38]. The number of water adsorbed layer influences this process as highlighted by means of infrared transient and steady-state absorption spectra of anatase TiO_2 nanoparticles [39]. In fact, the interaction between first-layer water and TiO_2 is lowered by the further water layers, thus reducing the hole trapping capability. As a consequence, the mobility of water onto the surface of TiO_2 plays a key role in this process [40,41].

Furthermore, it must be noted that the one electron oxidation of nitrate ions ($E^0_{\text{NO}_3^-/\text{NO}_3} = 2.4 \text{ V vs NHE}$) is thermodynamically favoured with respect to one electron water oxidation ($E^0_{\text{OH}^\cdot/\text{H}_2\text{O}} = 2.73 \text{ V vs NHE}$).

However, in the presence of nitrate, bromide ions did not significantly affect the EPR signal, especially at pH 6.5 and 4.0. This is possibly due to the fact that the formed nitrate radicals act as efficient scavengers of bromide ions [42] so that the presence of bromide ions does not significantly influence the primary electron transfer steps.

3.2 The role of superoxide radicals

Superoxide radicals exist in the protonated (HO_2^\cdot) or in the deprotonated ($\text{O}_2^{\cdot-}$) form depending on the pH of the irradiated TiO_2 aqueous suspension according to Eq. 14.



The pKa of this equilibrium is equal to 4.8. [43], i.e. superoxide radicals mainly exist in the protonated form at pH 2.5 and 4.0, and in the deprotonated form at pH 6.5.

Figure 5 reports the consumption of the NBT trap by the superoxide radical at different pH values and in the presence of sulfate (S), nitrate (N), and/or bromide ions (Br). Blue bars indicate the NBT consumption measured immediately after irradiation of the TiO_2 suspensions, while red bars indicate the NBT consumption measured after further 15 minutes in the dark. It is worth here to remember that a high height of the bars indicates that superoxide radicals have been consumed by species other than NBT, while low values of the bars indicate that the same have been trapped by NBT whose

concentration decreases. Notably, the blue and red bar heights are always similar, indicating the absence of side radical chain reactions occurring in the dark.

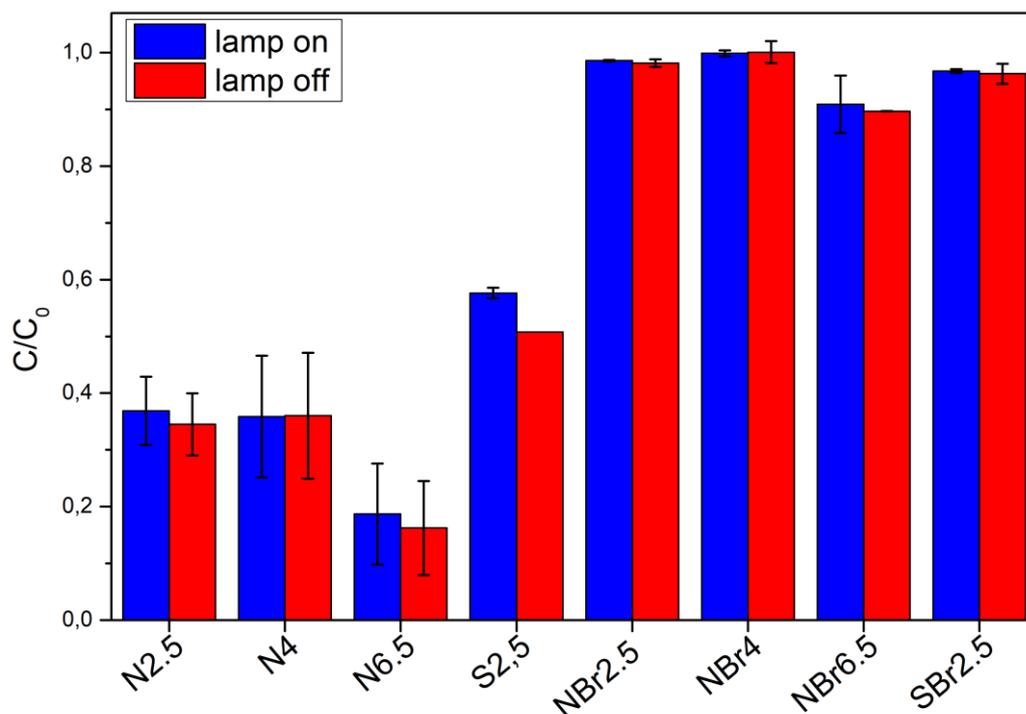


Figure 5. Superoxide radical detection via nitroblue tetrazolium (NBT) reaction. Higher consumption of the NBT target molecule indicates higher amount of the radical species.

The main information from Figure 5 can be summarized and discussed as it follows:

- (i) NBT initial concentration significantly decreases under irradiation in the absence of bromide ions while it remains practically unaffected when the latter are present. This indicates that superoxide radicals (both protonated and deprotonated) are somehow consumed in the presence of bromide ions.
- (ii) At pH 4.0 and 2.5 and in the absence of bromide the NBT concentration is of ca. 60% lower than in the presence of bromide (compare N4.0-N2.5 and NBr4.0-NBr2.5). On the other hand, at pH = 6.5 the above mentioned decrease of NBT concentration is slightly more pronounced (compare N6.5 and NBr6.5). By considering that lower decrease of NBT concentration indicates higher rate of consumption of superoxide, it can be concluded that the effect of bromide in quenching superoxide is slightly more efficient for the protonated form (HO_2^{\bullet}) than for the deprotonated one ($\text{O}_2^{\bullet-}$).

- (iii) In the presence of bromide ions, NBT initial concentration remains virtually unchanged after irradiation regardless of the presence of nitrate or sulfate (compare SBr2.5 and NBr2.5). This indicates that the mechanism of superoxide consumption, involving bromide ions, does not significantly depend on the presence of nitrate.

Bromide ions can be oxidized by hydroxyl radicals as above mentioned according to Eqs. 12-13. Literature reports that in sea water the bromine atom thereby generated reacts with a bromide ion producing the $\text{Br}_2^{\cdot-}$ anion radical according to Eq. 15.



This species is considered the key intermediate for the production of elemental bromine in the atmosphere. Its chemistry with superoxide radicals has been widely investigated [44]. Briefly, $\text{Br}_2^{\cdot-}$ affords elemental bromine by reaction with another $\text{Br}_2^{\cdot-}$ radical (Eq. 16) or with HO_2^{\cdot} (Eq. 17).



The same authors report an apparent kinetic constant of $4.4 \cdot 10^9 \text{ M}^{-1}\text{s}^{-1}$ which suggests as highly probable the occurrence of Eq. 17. On the other hand, reaction of $\text{Br}_2^{\cdot-}$ with the superoxide radical anion ($\text{O}_2^{\cdot-}$) quenches the $\text{Br}_2^{\cdot-}$ radical to bromide ion according to Eq. 18 [45].



This reaction, contrarily, is reported to be of minor importance with respect to Eq. 17.

However, according to the above mentioned results, only slight differences could be observed between the protonated and the not protonated superoxide radicals in the TiO_2 suspensions containing bromide ions. Moreover, at the surface of irradiated TiO_2 , due to the dual nature of the photogenerated excitons, generally oxygen reduction takes place simultaneously with oxidation processes. Therefore, it is more probable that superoxide radicals react with bromine atoms faster than with secondary species such as $\text{Br}_2^{\cdot-}$. Even if the presence of $\text{Br}_2^{\cdot-}$ could not be assessed in the present conditions, it must be considered that according to Eq. 17 and its high kinetic constant, in a photocatalytic suspension at acidic pH (in the absence of nitrate ions) considerable amount of elemental bromine should be produced, while, on the contrary, it has been experimentally proved [22] that only

negligible amount of elemental bromine could be photocatalytically produced. Finally, the role of Br_2^\bullet in these systems could have been overestimated. In fact, BrOH^\bullet intermediate (Eq. 12), i.e. the primary product of the OH radical induced oxidation of bromide ions, possesses virtually the same UV-vis absorption spectrum as Br_2^\bullet , as recently reported by Lampre et al. [32].

For these reasons, according to our results Eq. 19-20 seems to be more plausible in photocatalytic suspension:



This mechanism allows to explain why, in the absence of nitrate ions, the concentration of bromide ions in oxygenated aqueous TiO_2 suspensions under irradiation, does not macroscopically change. In fact, bromide ions can be firstly oxidized mainly by hydroxyl radicals giving rise to bromine atoms (Eq. 12-13) which, in turn, can be reduced back to bromide ions by superoxide radicals. This relais mechanism is schematically depicted in Figure 6.

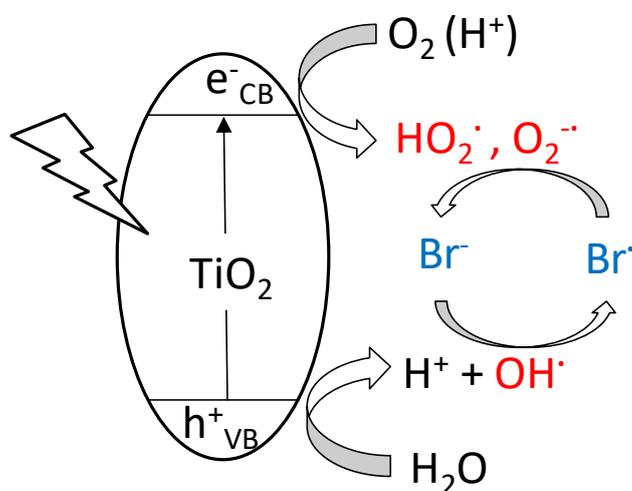


Figure 6. Relais mechanism of OH radicals induced oxidation of bromide ions to bromine radicals and back reduction by superoxide radicals.

3.3 Consequences on the photocatalytic production of elemental bromine

The above presented results on the role of hydroxyl and superoxide radicals allow to clarify some mechanistic aspects related to the photocatalytic production of elemental bromine recently reported [22,23] and briefly below summarized for the benefit of the reader.

Production of elemental bromine has been observed when a TiO₂ (P25-Evonik) aqueous suspension containing bromide ions and catalytic amounts of nitrate ions at acidic pH, was irradiated under UV light in the presence of O₂. In the absence of nitrate ions and/or of oxygen, only negligible amount of bromine could be produced. Therefore, it has been hypothesized that oxygen reduction and nitrate oxidation to nitrate radical were the essential primary steps for the production of Br₂. However, by considering the above mentioned relais mechanism promoted by reactive oxygen species involving bromide ions, it is possible to hypothesize that oxygen behaves as a simple electron scavenger and the reaction could also proceed when substituting oxygen with a species such as bromate, similarly easy to be reduced. Notably, bromate ions are reported to compete with oxygen for the photogenerated electron in photocatalytic suspensions at acidic pH values [20] according to the following Eq. 21.



To this aim we substituted oxygen with bromate ions (4 mM), by bubbling nitrogen (0.1 L·min⁻¹) through the suspension, under otherwise similar experimental conditions ([Br⁻] = 2 mM; [HNO₃] = 4 mM; TiO₂ P25 Evonik: 1 g·L⁻¹; temperature: 40 °C), and monitored the amount of elemental bromine trapped in the CCl₄ cold trap, as described in the experimental part. Results are shown in Figure 7.

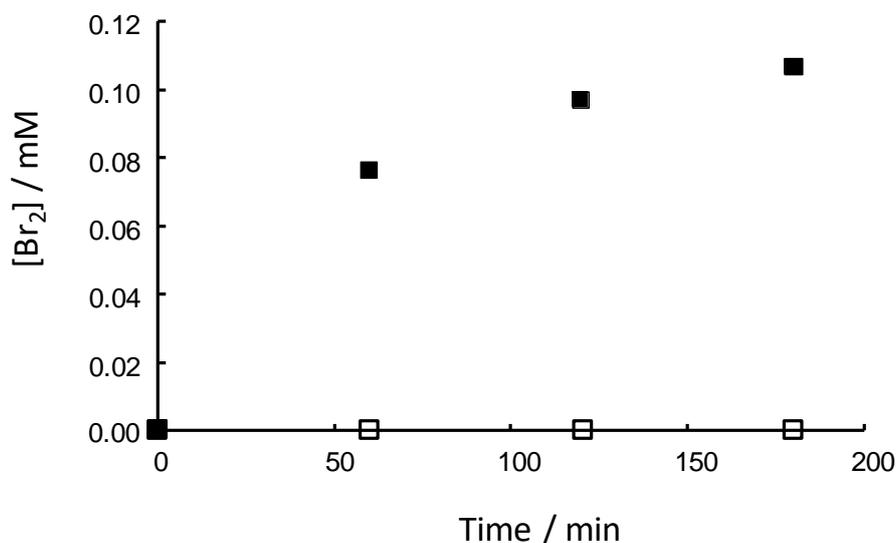


Figure 7. Bromine concentration (mM) in the CCl₄ cold trap as a function of time during irradiation (full squares) and in the dark (empty squares).

In the absence of bromate no elemental bromine production could be observed, in agreement to what previously reported [22]. Similarly, no bromine was produced under dark conditions (Figure 7). However, bromine production started under irradiation when bromate ions were present in the deaerated suspension. According to these results it is possible to propose the mechanism depicted in Figure 8 for the formation of elemental bromine.

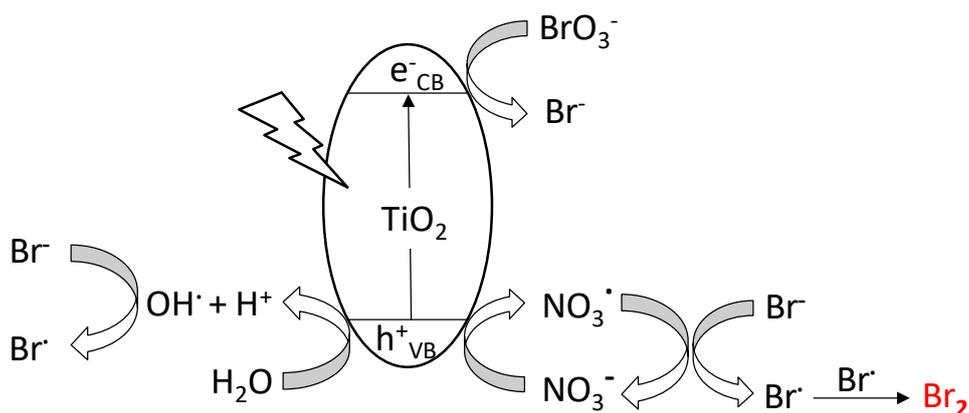


Figure 8. Proposed mechanisms of elemental bromine formation in deaerated TiO₂ suspensions, under UV irradiation and in the presence of nitrate and bromate ions.

Bromate ions act as electron scavengers, while holes mainly oxidize nitrate ions to nitrate radicals which, in turn, oxidize bromide ions to elemental bromine. OH radical formation induced by water oxidation is also represented in Figure 8, even if of minor importance in the presence of nitrate ions, as described throughout the text.

Elemental bromine formation in deaerated TiO₂ suspensions under UV light irradiation and in the presence of nitrate indirectly supports the hypotheses hereby proposed in this work. Further investigation is ongoing because of the technological consequences of this preliminary result. In fact, bromide-bromate mixtures are side products of the industrial ‘‘cold process’’ of bromine production, and green technologies exploiting these mixtures are highly desirable [46].

4. Conclusions

The joint use of EPR and UV-vis spectroscopy allowed to highlight the role of hydroxyl, superoxide and nitrate radicals in TiO₂ aqueous suspensions containing bromide ions. In particular, it is proposed that hydroxyl radicals rather than photogenerated holes oxidize bromide ions to bromine atoms. On the other hand, superoxide radicals are able to reduce back bromine atoms to bromide ions so that the

interplay between these reactive oxygen species does not macroscopically affect the observed concentration of bromide ions in irradiated TiO₂ aqueous suspensions in the presence of oxygen. These findings shine some light on relevant mechanisms in the field of atmospheric chemistry and environmental remediation. Moreover, on the basis of the above mentioned results it is evidenced that the photocatalytic synthesis of elemental bromine relies on the key role of nitrate radicals, while oxygen mainly acts as electron scavenger. The possibility of substituting oxygen with bromate ions in this reaction is proposed as a promising tool to endow with “green” features and to improve the efficiency of the industrial “cold process” for bromine production.

References

- [1] Neal, C., Neal, M., Hughes, S., Wickham, H., Hill, L., Harman, S., 2007. Bromine and bromide in rainfall, cloud, stream and groundwater in the Plynlimon area of mid-Wales. *Hydrol. Earth Syst. Sci.* 11 (1), 301-312.
- [2] Flury, M., Papritz, A., 1993. Bromide in the natural environment: occurrence and toxicity. *J. Environ. Qual.* 22, 747e758.
- [3] Yuita, K., 1983. Iodine, bromine and chlorine contents in soils and plants of Japan. *Soil Sci. Plant Nutr.* 29, 403-428.
- [4] F. Parrino, G. Camera Roda, V. Loddo. L. Palmisano, Three-Dimensional Calibration for Routine Analyses of Bromide and Nitrate Ions as Indicators of Groundwater Quality in Coastal Territories. *Int. J. Environ. Res. Public Health* 2019, 16, 1419.
- [5] Krasner, S.W., McGuire, M.J., Jacangelo, J.G., Patania, N.L., Reagan, K.M., Aieta, E.M., 1989. Occurrence of DBPs in US drinking water. *J. Am. Water Works Assoc.* 81, 41-53.
- [6] Keene, W. C., et al. (1999), Composite global emissions of reactive chlorine from anthropogenic and natural sources: Reactive Chlorine Emissions Inventory, *J. Geophys. Res.*, 104, 8429– 8440.
- [7] Murphy, D. M., J. R. Anderson, P. K. Quinn, L. M. McInnes, F. J. Brechtel, S. M. Kreidenweis, A. M. Middlebrook, M. Posfai, D. S. Thomson, and P. R. Buseck (1998), Influence of sea-salt on aerosol radiative properties in the Southern Ocean marine boundary layer, *Nature*, 392, 62– 65.
- [8] Keene, W. C., R. Sander, A. A. P. Pszenny, R. Vogt, P. J. Crutzen, and J. N. Galloway (1998), Aerosol pH in the marine boundary layer: A review and model evaluation, *J. Aerosol Sci.*, 29, 339– 356.

- [9] Sievering, H., J. Boatman, E. Gorman, Y. Kim, L. Anderson, G. Ennis, M. Luria, and S. Pandis (1992), Removal of sulphur from the marine boundary layer by ozone oxidation in sea-salt aerosols, *Nature*, 360, 571–573.
- [10] von Glasow, R., and P. J. Crutzen (2003), Tropospheric halogen chemistry, in *Treatise on Geochemistry*, edited by R. Keeling, pp. 21– 64, Elsevier, New York.
- [11] K. L. Foster, R. A. Plastridge, J.W. Bottenheim, P. B. Shepson, B. J. Finlayson-Pitts, C.W. Spicer, *Science* 2001, 291, 471 – 474.
- [12] B. J. Finlayson-Pitts, J. N. Pitts Jr., in *Chemistry of the Upper and Lower Atmosphere*, Academic Press, San Diego, 2000.
- [13] Pechtl, S., E. R. Lovejoy, J. B. Burkholder, and R. von Glasow (2006), Modeling the possible role of iodine oxides in atmospheric new particle formation, *Atmos. Chem. Phys.*, 6, 505– 523.
- [14] Neta P, Huie RE, Ross AB. Rate constants for reactions of inorganic radicals in aqueous solution. *J Phys Chem Ref Data* 1988;17:1027–284.
- [15] Steen PO, Grandbois M, McNeill K, Arnold WA. Photochemical formation of halogenated dioxins from hydroxylated polybrominated diphenyl ethers (OH-PBDEs) and chlorinated derivatives (OH-PBCDEs). *Environ Sci Technol* 2009;43:4405–11.
- [16] World Health Organization, 1993. *Guidelines for Drinking Water Quality*. WHO, Geneva, Switzerland.
- [17] Krasner, S.W., McGuire, M.J., Jacangelo, J.G., Patania, N.L., Reagan, K.M., Aieta, E.M., 1989. Occurrence of DBPs in US drinking water. *J. Am. Water Works Assoc.* 81, 41-53.
- [18] G. Camera-Roda, V. Loddo, L. Palmisano, F. Parrino, Photocatalytic ozonation for a sustainable aquaculture: A long-term test in a seawater aquarium *Applied Catalysis B: Environmental* 253 (2019) 69–76.
- [19] F. Parrino, G. Camera-Roda, V. Loddo, G. Palmisano, V. Augugliaro, Combination of ozonation and photocatalysis for purification of aqueous effluents containing formic acid as probe pollutant and bromide ion, *water research* 50 (2014) 189-199.
- [20] F. Parrino, G. Camera-Roda, V. Loddo, V. Augugliaro, L. Palmisano, Photocatalytic ozonation: Maximization of the reaction rate and control of undesired by-products, *Applied Catalysis B: Environmental* 178 (2015) 37–43.

- [21] S. Cataldo, A. Ianni, V. Loddo, E. Mirenda, L. Palmisano, F. Parrino, D. Piazzese, Combination of advanced oxidation processes and active carbons adsorption for the treatment of simulated saline wastewater, *Separation and Purification Technology* 171 (2016) 101–111.
- [22] F. Parrino, G. Camera Roda, V. Loddo, L. Palmisano, Elemental Bromine Production by TiO₂ Photocatalysis and/or Ozonation, *Angew. Chem. Int. Ed.* 2016, 55, 10391-10395.
- [23] F. Parrino, G. Camera Roda, V. Loddo, L. Palmisano, Green synthesis of bromine by TiO₂ heterogeneous photocatalysis and/or ozone: A kinetic study. *Journal of Catalysis* 366 (2018) 167–175.
- [24] H. Kisch, *Semiconductor photocatalysis: principles and applications*, Wiley-VCH Verlag GmbH, Weinheim, 2015.
- [25] F. Parrino, S. Livraghi, E. Giamello, L. Palmisano, The existence of nitrate radicals in irradiated TiO₂ aqueous suspensions in the presence of nitrate ions, *Angew. Chem. Int. Ed.* 2018, 57(33), 10702-10706.
- [26] C.F. Chignell, A.G. Motten, R.H. Sik, C.E Parker, K. Szka, *Photochemistry and Photobiology*, Vol. 59, No. 1, pp. 5-1 I. 1994
- [27] Chapter 8: Spin Trapping (Angelo Alberti and Dante Macciantelli) pag. Xxx in *Electron Paramagnetic Resonance: A Practitioners Toolkit*. M. Brustolon and E. Giamello.
- [28] H. Goto, Y. Hanada, T. Ohno, M. Matsumura, Quantitative analysis of superoxide ion and hydrogen peroxide produced from molecular oxygen on photoirradiated TiO₂ particles. *Journal of Catalysis* 225 (2004) 223–229.
- [29] E. Finkelstein, M. R. Gerald, E. J. Rauckman, *Arch. Biochem. Biophys.* 1980, 200, 1 -16.
- [30] Y. Nakabayashi, Y. Nosaka, *Phys. Chem. Chem. Phys.* 2015, 17, 30570- 30576.
- [31] M. Mozurkewich, *J. Geophys. Res.* 1995, 100, 199 – 207.
- [32] I. Lampre, J.-L. Marignier, M. Mirdamadi-Esfahani, P. Pernot, P. Archirel, M. Mostafavi, Oxidation of Bromide Ions by Hydroxyl Radicals: Spectral Characterization of the Intermediate BrOH^{•-}, *J. Phys. Chem. A* 2013, 117, 877–887.
- [33] J.-M. Hermann, P. Pichat, Heterogeneous Photocatalysis: Oxidation of Halide Ions by Oxygen in Ultraviolet Irradiated Aqueous Suspension of Titanium Dioxide. *J.C.S. Faraday I*, 1980,76,1138-1146.

- [34] V. Maurino, M. Minella, F. Sordello, C. Minero, A proof of the direct hole transfer in photocatalysis: The case of melamine. *Appl. Catal. A: Gen.* 2015 xxx.
- [35] M. Muuronen, S. M. Parker, E. Berardo, A. Le, M. Zwiijnenburg, F. Furche, *Chem. Sci.* 2017, 8, 2179-2183.
- [36] S. Tan, H. Feng, Y. Ji, Y. Wang, J. Zhao, A. Zhao, B. Wang, Y. Luo, J. Yang, J. G. Hou, *J. Am. Chem. Soc.* 2012, 134, 9978–9985.
- [37] T. Ohto, A. Mishra, S. Yoshimune, H. Nakamura, M. Bonn, Y. Nagata, *J. Phys.: Condens. Matter* 2014, 26, 244102-244110.
- [38] A. Litke, Y. Su, I. Tranca, T. Weber, E. J. M. Hensen, J. P. Hofmann, *J. Phys. Chem. C* 2017, 121, 7514-7524.
- [39] K. Shirai, T. Sugimoto, K. Watanabe, M. Haruta, H. Kurata, Y. Matsumoto, *Nano Lett.* 2016, 16, 1323–1327.
- [40] F. Parrino, P. Conte, C. De Pasquale, V. A. Laudicina, V. Loddo, L. Palmisano *J. Phys. Chem. C* 2017, 121, 2258–2267.
- [41] F. Parrino, C. De Pasquale, L. Palmisano, The influence of some surface related phenomena on mechanism, selectivity and conversion of TiO₂ induced photocatalytic reactions, *Chemosuschem*, 12(3), 2019, 589-602.
- [42] S. Seisel, F. Caloz, F. F. Fenter, H. Van den Bergh, M. Rossi, *J. Geophys. Res. Lett.* 1997, 24, 2757-2760.
- [43] B.H.J. Bielski et al., *J. Phys. Chem. Ref. Data*, vol. 14, n° 4, 1985.
- [44] B. M. Matthew, I. George, C. Anastasio, *Geophys. Res. Lett.* 2003, 30, 2297 – 2301.
- [45] I. Wagner, H. Strehlow, *Ber. Bunsenges. Phys. Chem.* 1987, 91, 1317 – 1321.
- [46] S. Adimurthy, G. Ramachandraiah, A. V. Bedekar, S. Ghosh, B. C. Ranu, P. K. Ghosh, Eco-friendly and versatile brominating reagent prepared from a liquid bromine precursor, *Green Chem.*, 2006, 8, 916–922.