

Elemental Bromine Production by TiO₂ Photocatalysis and/or Ozonation

Francesco Parrino,* Giovanni Camera Roda, Vittorio Loddo, and Leonardo Palmisano

Abstract: Significant production of elemental bromine (Br₂) was observed for the first time when treating bromide containing solutions at acidic pH, with TiO₂ photocatalyst, ozone, or a combination thereof. Br₂ selectivities up to approximately 85 % were obtained and the corresponding bromine mass balance values satisfied. The process is general and may be applied at a laboratory scale for green bromination reactions, or industrially as a cheap, safe, and environmentally sustainable alternative to the currently applied bromine production methods.

Soon after the discovery of bromine (Br₂) in 1825 by Balard,^[1] (the element was casually distilled during studies of seawater) Br₂ became an industrially relevant chemical. World Br₂ production capacity in 2003 was estimated to be approximately 600 000 tons^[2] and figures are continuously growing. A large variety of brominated compounds are usually prepared by application of liquid Br₂ to addition or substitution reactions. Br₂ is used for the synthesis of flame retardant compounds, dyestuffs and dye intermediates, drugs (for example, naproxene, antihistamines, anticancer drugs, anti-Alzheimer agents, antiseptics, and narcotics), disinfectants for water purification, agricultural and mining chemicals, and polymeric compounds, among others.

Br₂ is industrially obtained by oxidation of bromide (Br[−]) ions. The oxidation process can be carried out with oxo-compounds,^[3] electrochemical methods,^[4] catalytic methods,^[5] or various oxidizing species.^[6] However, the two most widespread Br₂ extraction processes are steaming out- and air blowing-processes. Both technologies use gaseous chlorine as the oxidizing agent, according to Equation 1.



Although problems related to transportation and handling of this expensive, highly corrosive, and toxic gas, must be faced, its use is justified because Cl₂ is a co-product of the chloralkali industry, which also uses brine as the primary feedstock. However, there is a long-felt need for a more

eco-friendly and economic process.

Over a number of decades, photocatalysis has attracted interest as a powerful advanced oxidation process. Various applications have been proposed, especially in the field of environmental remediation.^[7] Indeed, the mild operative conditions, the possibility of solar light exploitation,^[8] the versatility in tailoring the properties of catalysts,^[9] and the use of safe, cheap, and chemically stable semiconductors,^[10] make photocatalysis a competitive technology in view of sustainability. However, photocatalytic applications in the field of synthetic chemistry still remain rare, mainly because of the poor selectivity of reactions that proceed with highly oxidizing species such as hydroxyl radicals. Nevertheless, some examples of highly selective photocatalytic reactions are reported.^[11]

Ozone (O₃) is a strong oxidizing agent mainly used for water purification and disinfection. Coupling of O₃ and photocatalysis has been investigated intensely in the field of environmental remediation.^[12] The influence of light or O₃ on the formation of halogen molecules in the atmosphere is reported in the relevant literature.^[13,14] This mechanism is of paramount importance in atmospheric phenomena, such as O₃ layer depletion, or the formation of halogen-derived molecules. However, all of these studies, which were carried out with laboratory set-ups that simulate atmospheric conditions, only allow recovery of micromoles of Br₂. While this research is of great scientific and environmental importance, process applications for Br₂ synthesis have never been considered. Herein, the first preparative synthesis of Br₂ by means of TiO₂ photocatalysis, ozonation, or a combination thereof, is reported. The three processes are separately presented for the benefit of the reader.

Formation of Br₂ was observed when a TiO₂ (P25-Evonik) aqueous suspension containing KBr and HNO₃ was irradiated under near-UV light in the presence of O₂. The produced Br₂ was stripped from the 40 °C suspension and trapped in a set of ice cold CCl₄ traps. The experimental set-up is shown in Figure S1 (Supporting Information).

Figure 1 reports the time evolution in terms of conversion of Br[−] and selectivity towards Br₂, along with the mass balance of Br atoms. Br[−] conversion continuously increased during irradiation, reaching approximately 30 % after five hours. As the reaction proceeded, Br₂ selectivity values of up to 85 % were maintained. The Br atom mass balance was calculated at fixed intervals of time as a percentage of the ratio between the sum of the moles of residual Br[−] in the reactor and Br₂ produced multiplied by two, and the initial moles of Br[−]. This value, ranging between 90 and 95 %, was almost constant during the reaction, indicating that virtually all the reacted Br[−] was selectively transformed into Br₂.

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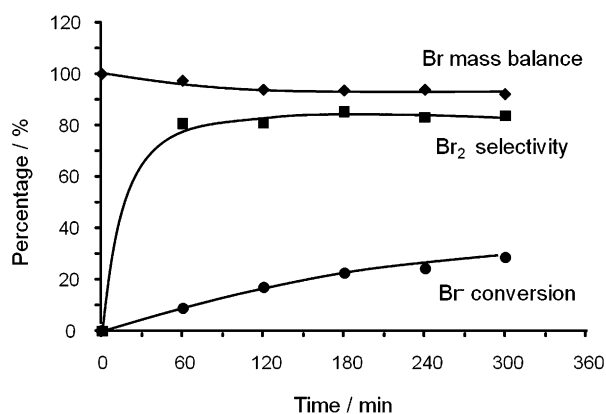


Figure 1. Br⁻ conversion (—●—), selectivity towards Br₂ (—■—), and Br atom mass balance (—◆—) vs. reaction time. Reaction conditions: volume (500 cm³), initial Br⁻ (2 mM) and HNO₃ (4 mM), TiO₂ (P25-Evonik; 1 g L⁻¹), temperature (40 °C), O₂ flow rate (0.1 L min⁻¹).

A discrepancy of about 10% between mass balance and selectivity can be ascribed primarily to the fact that, for the low conversion values reported, quantification errors in Br₂ concentration affected selectivity values much more than the mass balance. Notably, no bromate ions (BrO₃⁻) were detected in the reacting mixture. In the absence of TiO₂ only negligible amounts of Br₂ (ca. 1 μmol after 5 h) were detected, indicating the photocatalytic nature of this reaction. The reaction was strongly influenced by O₂ concentration in the liquid phase. In particular, under N₂ atmosphere no Br⁻ oxidation was achieved, while increasing O₂ concentration produced higher reaction rates. Figure 2 reports the concentration of Br⁻, NO₃⁻, and Br₂ in the reacting mixture during irradiation.

Notably, the amount of Br₂ in the aqueous phase reached a maximum and then decreased. Indeed, once produced, Br₂ was stripped out of the reactor because of its low solubility in water and the temperature of the reacting mixture (40 °C). While Br⁻ concentration continuously decreased, NO₃⁻ concentration was virtually constant and the pH of the

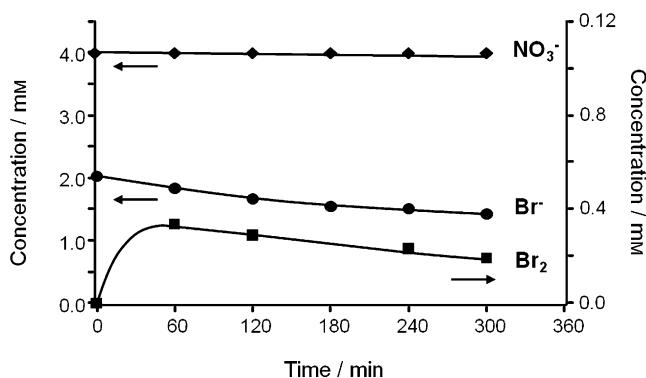


Figure 2. Concentration of NO₃⁻ (—◆—), Br⁻ (—●—), and Br₂ (—■—) in the reacting mixture during irradiation. Reaction conditions: volume (500 cm³), initial Br⁻ (2 mM) and HNO₃ (4 mM), TiO₂ (P25-Evonik; 1 g L⁻¹), temperature (40 °C), O₂ flow rate (0.1 L min⁻¹).

suspension (≈ pH 2.7) did not significantly change after 5 h irradiation. In the absence of HNO₃ the reaction did not proceed and no Br₂ production was observed. Substituting HNO₃ with equivalent amounts of NaNO₃ produced only traces of Br₂ (in this case the suspension presented pH 5.2, mainly because of the presence of the TiO₂ photocatalyst). The use of equivalent amounts of H₂SO₄, instead of HNO₃, resulted in production of negligible amounts of Br₂. These results clearly indicate that both the acidic pH and the NO₃⁻ ions are necessary for the present reaction to occur. An increase of initial HNO₃ led to higher Br₂ production, until a plateau was reached at HNO₃ concentrations higher than 4 mM (Figure S2, Supporting Information). Different pathways are hypothesized to tentatively explain the above reported results.

The impinging light is absorbed by TiO₂, which in turn photogenerates electron-hole pairs [Eq. (2)].^[7]



Electrons reduce O₂ into superoxide radical anion (O₂^{-•}) [Eq. (3)], which is easily protonated to HO₂[•] in the acidic reaction medium [Eq. (4)]. Finally, HO₂[•] further reacts according to Equations (5) and (6), eventually producing hydrogen peroxide (H₂O₂) and hydroxyl radicals (HO[•]).

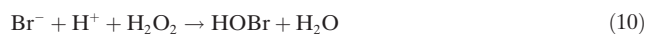


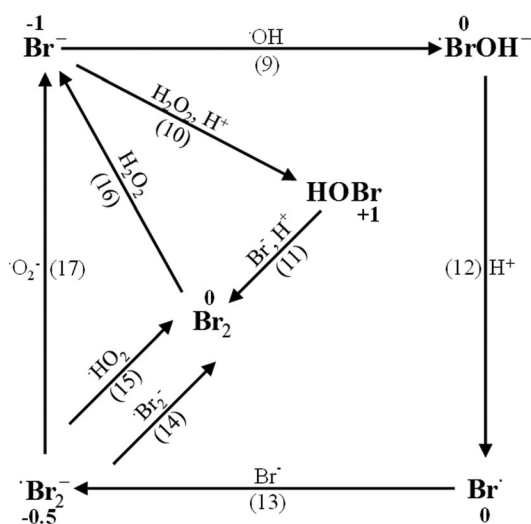
On the other hand, the photogenerated holes may directly or indirectly oxidize H₂O and Br⁻ into hydroxyl (HO[•]) and bromine (Br[•]) radicals, respectively, according to Equations (7) and (8).^[15]



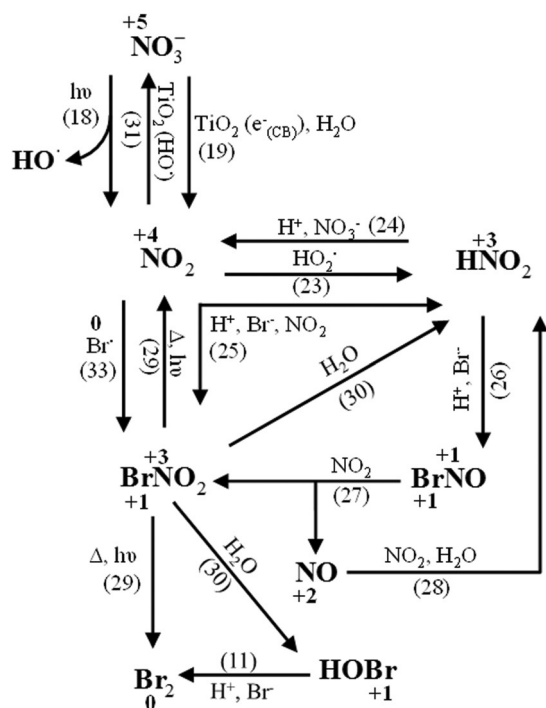
The radicals produced according to Equations (2)–(8) induce chain reactions in turn, which eventually give rise to Br₂ formation. For the benefit of the reader, reactions involving only bromine species are presented in Scheme 1, while reactions involving nitrogen species are summarized in Scheme 2.

Br⁻ can be oxidized by direct hole oxidation [Eq. (8)], or indirectly with HO[•] [Eq. (9)]^[16] or H₂O₂^[14b] (H₂O₂ mediated Br⁻ oxidation gives rise to hypobromous acid (HOBr)) [Eq. (10)]. HOBr oxidizes Br⁻ into Br₂ [Eq. (11)].^[17] Eventually, the hydroxyl radical path produces Br₂^{••} as a key intermediate [Eqs. (12), (13)].





Scheme 1. Radical chain path giving rise to bromine formation via the contribution of active oxygen and bromine species only. The relationship between Equations (9)–(17) is summarized; equation numbers are indicated in parentheses.



Scheme 2. Radical chain path giving rise to bromine formation via active oxygen, bromine, and nitrogen oxide species. The relationship between Equations (11), (18), (19), (23)–(31), and (33) is summarized; equation numbers are indicated in parentheses.



The latter species gives rise to Br_2 by reaction with another $\text{Br}_2^{\bullet-}$ radical [Eq. (14)] or $\text{HO}_2^{\bullet}$ [Eq. (15)].



According to our experimental evidence, an excess of H_2O_2 decreases the Br_2 production. This finding may be explained after considering that H_2O_2 reduces Br_2 back into bromide [Eq. (16a), (16b)].



Wagner and Strehlow demonstrated that $\text{O}_2^{\bullet-}$ is able to reduce the key intermediate $\text{Br}_2^{\bullet-}$ back into Br^- [Eq. (17)],^[19] whereas the protonated form ($\text{HO}_2^\bullet$) favors the formation of Br_2 [Eq. (15)].^[18]



These considerations may account for the pH dependence of this process. Indeed, negligible Br_2 formation was observed at an approximate pH value of 5, where the amount of $\text{O}_2^{\bullet-}$ is similar to that of $\text{HO}_2^\bullet$ ($\text{p}K_a = 4.8$).

However, the above presented mechanism, which is invoked in the literature to explain the complex radical atmospheric reactions in aerosol or gas phase conditions,^[13,14] may only account for a small part of the Br_2 produced. Accordingly, in the absence of HNO_3 , but with equivalent amounts of H_2SO_4 , only 2 μmol of Br_2 was recovered. Notably, the same amount of bromine was obtained by George and Anastasio in similar conditions;^[14b] that is, in the presence of $\text{HO}^\bullet$ sources such as HNO_3 and H_2O_2 , but in the absence of TiO_2 . This observation implies that the presence of HNO_3 and the absence of TiO_2 cannot justify the significant Br_2 production observed. Therefore, a concerted mechanism, accounting for photocatalytic and HNO_3 -based reactions, must be responsible for the experimental evidence reported herein. This can be tentatively explained as follows: NO_3^- affords $\text{HO}^\bullet$ and NO_2 directly by light (313 nm) absorption^[20] [Eq. (18)].



On the other hand, in the presence of irradiated TiO_2 , NO_3^- may compete with O_2 for the photogenerated electrons, giving rise to NO_2 [Eq. (19)].^[21]



This hypothesis is reasonable in the present conditions because of the HNO_3 concentration used (4 mM) and the acidic conditions, which render the TiO_2 surface positively charged, thus enhancing electrostatic interactions with NO_3^- .

NO_2 and $\text{HO}^\bullet$ radicals may react giving peroxyntrous acid^[22] which in turn decomposes to NO_3^- according to Equation (20).



Equation 20 does not contribute to Br_2 production. On the other hand, NO_2 may dimerize and give rise to N_2O_4 , which produces NO_3^- and HNO_2 by reaction with water [Eqs. (21), (22)].^[21]



Furthermore, $\text{HO}_2^\bullet$ radicals may react with NO_2 , producing HNO_2 [Eq. (23)]^[23] and then NO_2 [Eq. (24)].^[24]



NO_2 and HNO_2 are key intermediates for Br_2 production. It is worth emphasizing that these species are mainly generated by interaction with active oxygen radicals, which are produced by photocatalysis with nitrogen oxide species.

NO_2 and HNO_2 may initiate consecutive reactions, affording nitryl bromide (BrNO_2) by direct [Eq. (25)] or indirect [Eqs. (26), (27)] paths.^[24] The indirect path produces nitrosyl bromide (BrNO) and NO as the intermediates. The former gives rise to BrNO_2 , while the latter may be easily oxidized back to HNO_2 [Eq. (28)].



Notably, NO radicals may also be produced by direct NO_2 excitation, followed by homolytic breaking of the N–O bond.

BrNO_2 in turn produces Br_2 by light-induced homolytic cleavage of the Br–N bond [Eq. (29a)],^[25] thermal decomposition [Eq. (29b)],^[26] or hydrolysis [Eq. (30)],^[24] as the HOBr formed can oxidize Br^- into Br_2 [Eq. (11)].



It is evident that nitrogen compounds involved in the mechanism interact with bromine species, being eventually restored and re-oxidized into NO_3^- by means of the radicals generated by photocatalysis [Eq. (31)]:



This is supported by the experimental evidence that NO_3^- is not macroscopically consumed during the reaction.

To confirm the hypothesized key role of HNO_2 , sodium azide (NaN_3) was added to the reacting medium for a standard reaction. In this case pH increased, no Br_2 formation was

observed, and the NO_3^- concentration decreased during reaction. Indeed, NaN_3 selectively reacted with HNO_2 , giving rise to gaseous nitrogen according to Equation (32).^[27]



Notably, formation of BrNO_2 and eventually Br_2 through other radical chain reactions can be hypothesized as follows [Eqs. (33), (34)]:



The unprecedented high conversion and selectivity for Br_2 of the present process is the object of a pending patent.^[28]

Production of Br_2 was also observed in the dark, in the absence of TiO_2 , but in the presence of O_3 and Br^- at acidic pH values. The presence of HNO_3 is not essential in this case, as the Br^- oxidation rate was the same using equivalent amounts of H_2SO_4 in otherwise similar experimental conditions. For this reason a different mechanism was hypothesized. Indeed, O_3 may oxidize Br^- into BrO^- , which exists mainly as HOBr in the acidic pH conditions^[13a,17] [Eqs. (35), (36)]:



This latter species is able to oxidize Br^- into Br_2 [Eq. (11)], as mentioned above. Notably, in the present experimental conditions the indirect oxidation path (through OH radicals formed from O_3 dissociation) is negligible, as it becomes relevant only at higher pH values.^[12] Reaction proceeds selectively to Br_2 (selectivity values of ca. 90 %) with conversions depending on the concentration of O_3 , the acid used, and the amount of Br^- in the liquid phase.

Notably, TiO_2 photocatalysis in the presence of O_3 shows reaction rates higher than the sum of the rates obtained by applying the two technologies separately. This implies the presence of synergy and the effect, hereby reported for a synthetic reaction, is similar to what was observed in the case of degradation reactions for environmental remediation.^[12] Further studies, which are ongoing, elaborate on some aspects of the reaction with O_3 .

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Keywords: bromine · nitric acid · ozonation · photocatalysis · TiO_2

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- [1] F. Yaron in *Bromine manufacture, technology and economic aspects in Bromine and its Compounds* (Ed.: J. E. Jolles), Ernest Benn Limited, London, **1966**, pp. 1–42.
- [2] “Bromine”: P. A. Lyday in *Minerals Yearbook*, Reston, VA: USGS, **2003**.
- [3] a) D. Callihan, E. O. Salant, *J. Chem. Phys.* **1934**, *2*, 317–319; b) S. Adimurthy, G. Ramachandraiah, A. V. Bedekar, S. Ghosh, B. C. Ranu, P. K. Ghosh, *Green Chem.* **2006**, *8*, 916–922.
- [4] a) D. F. Hornig, W. E. Osberg, *J. Chem. Phys.* **1955**, *23*, 662–670; b) A. Anderson, S. H. Walmsley, H. A. Gebbie, *Philos. Mag.* **1962**, *7*, 1243–1245; c) R. C. William, C. D. Kettle, E. E. Stebbins, L. M. McCullough, US Patent 5,254,226 (Cl. 204, 128; C25B1/124), **1993**.
- [5] P. Schubert, A. R. Smith, H. Toube, D. W. Schubert, (Catalytica, Inc.) PCT Int. Appl. WO 93 06 039 (Cl. C01B7/09), **1993**.
- [6] a) S. M. Naudé, H. Verleger, *Proc. Phys. Soc.* **1950**, *63A*, 470–477; b) T. Jagaki, S. Sigeo, S. Matsuoka, Kokai Tokyo Koho, JP 63, 203, 781 [88, 203,781] (Cl. C25B1/46), **1988**; c) N. Ogawa, J. Ozaki, N. Hamada, T. Sato, Tosoh Corp. Jpn. Kokai Tokyo Koho JP 04, 170, 302 [92, 170, 302] (Cl. C01 B7.09), **1992**.
- [7] V. Augugliaro, V. Loddo, G. Palmisano, M. Pagliaro, L. Palmisano, *Clean by Light Irradiation: Practical Applications of Supported TiO₂*, RSC, Cambridge, **2010**.
- [8] a) C. Guarisco, G. Palmisano, G. Calogero, R. Ciriminna, G. Di Marco, V. Loddo, M. Pagliaro, F. Parrino, *Environ. Sci. Pollut. Res.* **2014**, *21*, 11135–11141; b) F. Parrino, A. Ramakrishnan, C. Damm, H. Kisch, *ChemPlusChem* **2012**, *77*, 713–720.
- [9] a) A. Di Paola, M. Bellardita, G. Marci, L. Palmisano, F. Parrino, R. Amadelli, *Catal. Today* **2011**, *161*, 35–40; b) A. Di Paola, M. Bellardita, B. Megna, F. Parrino, L. Palmisano, *Catal. Today* **2015**, *252*, 195–200.
- [10] a) G. Carini, Jr., F. Parrino, G. Palmisano, G. Scandura, I. Citro, G. Calogero, A. Bartolotta, G. Di Marco, *Photochem. Photobiol. Sci.* **2015**, *14*, 1685–1693; b) A. Hamrouni, N. Moussa, A. Di Paola, F. Parrino, A. Houas, L. Palmisano, *Appl. Catal. B* **2014**, *154*, 379–385; c) A. Hamrouni, N. Moussa, F. Parrino, A. Di Paola, A. Houas, L. Palmisano, *J. Mol. Catal. A* **2014**, *390*, 133–141; d) I. Natali-Sora, F. Fontana, R. Passalacqua, C. Ampelli, S. Perathoner, G. Centi, F. Parrino, L. Palmisano, *Electrochim. Acta* **2013**, *109*, 710–715.
- [11] a) M. Bellardita, V. Loddo, A. Mele, W. Panzeri, F. Parrino, I. Pibiri, L. Palmisano, *RSC Adv.* **2014**, *4*, 40859–40864; b) A. Abd-Elal, F. Parrino, R. Ciriminna, V. Loddo, L. Palmisano, M. Pagliaro, *ChemistryOpen* **2015**, online; c) G. Palmisano, V. Augugliaro, M. Pagliaro, L. Palmisano, *Chem. Commun.* **2007**, 3425–3437; d) G. Palmisano, E. García-López, G. Marci, V. Loddo, S. Yurdakal, V. Augugliaro, L. Palmisano, *Chem. Commun.* **2010**, *46*, 7074–7089; e) V. Augugliaro, G. Camera-Roda, V. Loddo, G. Palmisano, L. Palmisano, J. Soria, S. Yurdakal, *J. Phys. Chem. Lett.* **2015**, *6*, 1968–1981.
- [12] a) F. Parrino, G. Camera-Roda, V. Loddo, G. Palmisano, V. Augugliaro, *Water Res.* **2014**, *50*, 189–199; b) F. Parrino, G. Camera-Roda, V. Loddo, V. Augugliaro, L. Palmisano, *Appl. Catal. B* **2015**, *178*, 37–43.
- [13] For ozone induced reactions, see: a) K. L. Foster, R. A. Plas-tridge, J. W. Bottenheim, P. B. Shepson, B. J. Finlayson-Pitts, C. W. Spicer, *Science* **2001**, *291*, 471–474; b) L. Smoydzin, R. von Glasow, *Atmos. Chem. Phys.* **2009**, *9*, 5057–5072; c) K. Toyota, J. C. McConnell, A. Lupu, L. Neary, C. A. McLinden, A. Richter, R. Kwok, K. Semeniuk, J. W. Kaminski, S.-L. Gong, J. Jarosz, M. P. Chipperfield, C. E. Sioris, *Atmos. Chem. Phys.* **2011**, *11*, 3949–3979; d) H. Herrmann, Z. Majdik, B. Ervens, D. Weise, *Chemosphere* **2003**, *52*, 485–502; e) R. S. Disselkamp, E. G. Chapman, W. R. Barchet, S. D. Colson, C. D. Howd, *Geophys. Res. Lett.* **1999**, *26/14*, 2183–2186; f) K. W. Oum, M. J. Lakin, B. J. Finlayson-Pitts, *Geophys. Res. Lett.* **1998**, *25*, 3923–3926.
- [14] For light induced reactions, see: a) N. K. Richards, B. J. Finlayson-Pitts, *Environ. Sci. Technol.* **2012**, *46*, 10447–10454; b) I. J. George, C. Anastasio, *Atmos. Environ.* **2007**, *41*, 543–553; c) J. Abbatt, N. Oldridge, A. Symington, V. Chukalovskiy, R. D. McWhinney, S. Sjostedt, R. A. Cox, *J. Phys. Chem. A* **2010**, *114*, 6527–6533.
- [15] W. Maurino, M. Minella, F. Sordello, C. Minero, *Appl. Catal. A* **2015**, in press.
- [16] M. Mozurkewich, *J. Geophys. Res.* **1995**, *100*, 199–207.
- [17] R. Vogt, R. Sander, P. J. Crutzen, *Nature* **1996**, *383*, 327–330.
- [18] B. M. Matthew, I. George, C. Anastasio, *Geophys. Res. Lett.* **2003**, *30*, 2297–2301.
- [19] I. Wagner, H. Strehlow, *Ber. Bunsenges. Phys. Chem.* **1987**, *91*, 1317–1321.
- [20] R. G. Zepp, J. W. Hoigné, H. Bader, *Environ. Sci. Technol.* **1987**, *21*, 443–450.
- [21] a) L. G. Forni, V. O. Mora-Arellano, J. E. Packer, R. L. Willson, *J. Chem. Soc. Perkin Trans. 2* **1986**, 1–6; b) A. R. Cook, N. Dimitrijevic, B. W. Dreyfus, D. Meisel, L. A. Curtiss, D. M. Camaioni, *J. Phys. Chem. A* **2001**, *105*, 3658–3666; c) J. Mack, J. R. Bolton, *J. Photochem. Photobiol. A* **1999**, *128*, 1–13; d) K. Doudrick, T. Yang, K. Hristovski, P. Westerhoff, *Appl. Catal. B* **2013**, *136*, 40–47; e) J. A. Navío, G. Colón, M. Trillas, J. Peral, X. Doménech, J. J. Testa, J. Padrón, D. Rodríguez, M. I. Litter, *Appl. Catal. B* **1998**, *16*, 187–196.
- [22] H. Shibata, N. Noda, Y. Ogura, K. Sogabe, Y. Sawa, *Biosci. Biotechnol. Biochem.* **2000**, *64*, 1751–1753.
- [23] M. C. González, A. M. Braun, *Res. Chem. Intermed.* **1995**, *21*, 837–859.
- [24] I. Lengyel, I. Nagy, G. Bazsa, *J. Phys. Chem.* **1989**, *93*, 2801–2807.
- [25] P. Warneck in *Heterogeneous and Liquid Phase Processes: Laboratory Studies Related to Aerosols and Clouds*, Vol. 2, Springer, Berlin, Heidelberg, **1996**, p. 60.
- [26] D. Scheffler, H. Grothe, H. Willner, A. Frenzel, C. Zetzsch, *Inorg. Chem.* **1997**, *36*, 335–338.
- [27] Committee on Prudent Practices for Handling, Storage and Disposal of Chemicals in Laboratories, in *Prudent practices in the Laboratory: Handling and Disposal of Chemicals*, National Academic Press, Washington DC, **1995**, p. 165.
- [28] F. Parrino, G. Camera Roda, V. Loddo, L. Palmisano, Italian Patent Application no. 102016000008715, filed on 28-01-, **2016**.

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