Bromine Production

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Elemental Bromine Production by TiO_2 Photocatalysis and/or Ozonation

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Abstract: *Significant production of elemental bromine (Br_2) was observed for the first time when treating bromide containing solutions at acidic pH, with TiO_2 photocatalyst, ozone, or a combination thereof. Br_2 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 (Br_2) in 1825 by Balard,[1] (the element was casually distilled during studies of seawater) Br_2 became an industrially relevant chemical. World Br_2 production capacity in 2003 was estimated to be approximately 600000 tons[2] and figures are continuously growing. A large variety of brominated compounds are usually prepared by application of liquid Br_2 to addition or substitution reactions. Br_2 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.

Br_2 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 Br_2 extraction processes are steaming out- and air blowing-processes. Both technologies use gaseous chlorine as the oxidizing agent, according to Equation 1.

$$2\,Br^- + Cl_2 \rightarrow Br_2 + 2\,Cl^- \qquad (1)$$

Although problems related to transportation and handling of this expensive, highly corrosive, and toxic gas, must be faced, its use is justified because Cl_2 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 (O_3) is a strong oxidizing agent mainly used for water purification and disinfection. Coupling of O_3 and photocatalysis has been investigated intensely in the field of environmental remediation.[12] The influence of light or O_3 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 O_3 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 Br_2. While this research is of great scientific and environmental importance, process applications for Br_2 synthesis have never been considered. Herein, the first preparative synthesis of Br_2 by means of TiO_2 photocatalysis, ozonation, or a combination thereof, is reported. The three processes are separately presented for the benefit of the reader.

Formation of Br_2 was observed when a TiO_2 (P25-Evonik) aqueous suspension containing KBr and HNO_3 was irradiated under near-UV light in the presence of O_2. The produced Br_2 was stripped from the 40 °C suspension and trapped in a set of ice cold CCl_4 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 Br_2, along with the mass balance of Br atoms. Br^- conversion continuously increased during irradiation, reaching approximately 30% after five hours. As the reaction proceeded, Br_2 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 Br_2 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 Br_2.

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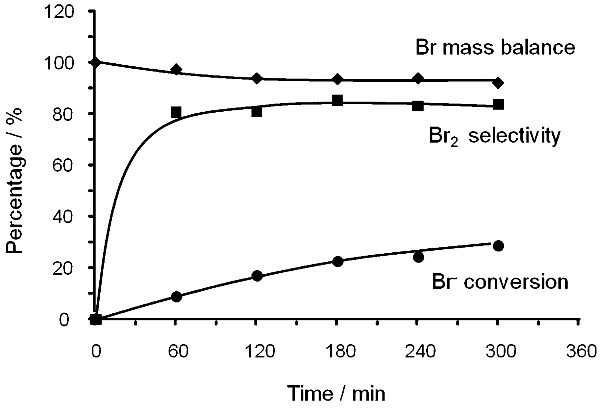


Figure 1. Br^- conversion (——●——), selectivity towards Br_2 (——■——), and Br atom mass balance (——◆——) vs. reaction time. Reaction conditions: volume (500 cm^3), initial Br^- (2 mM) and HNO_3 (4 mM), TiO_2 (P25-Evonik; 1 $g\,L^{-1}$), temperature (40 °C), O_2 flow rate (0.1 $L\,min^{-1}$).

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 Br_2 concentration affected selectivity values much more than the mass balance. Notably, no bromate ions (BrO_3^-) were detected in the reacting mixture. In the absence of TiO_2 only negligible amounts of Br_2 (ca. 1 μmol after 5 h) were detected, indicating the photocatalytic nature of this reaction. The reaction was strongly influenced by O_2 concentration in the liquid phase. In particular, under N_2 atmosphere no Br^- oxidation was achieved, while increasing O_2 concentration produced higher reaction rates. Figure 2 reports the concentration of Br^-, NO_3^-, and Br_2 in the reacting mixture during irradiation.

Notably, the amount of Br_2 in the aqueous phase reached a maximum and then decreased. Indeed, once produced, Br_2 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, NO_3^- concentration was virtually constant and the pH of the suspension (≈pH 2.7) did not significantly change after 5 h irradiation. In the absence of HNO_3 the reaction did not proceed and no Br_2 production was observed. Substituting HNO_3 with equivalent amounts of $NaNO_3$ produced only traces of Br_2 (in this case the suspension presented pH 5.2, mainly because of the presence of the TiO_2 photocatalyst). The use of equivalent amounts of H_2SO_4, instead of HNO_3, resulted in production of negligible amounts of Br_2. These results clearly indicate that both the acidic pH and the NO_3^- ions are necessary for the present reaction to occur. An increase of initial HNO_3 led to higher Br_2 production, until a plateau was reached at HNO_3 concentrations higher than 4 mM (Figure S2, Supporting Information). Different pathways are hypothesized to tentatively explain the above reported results.

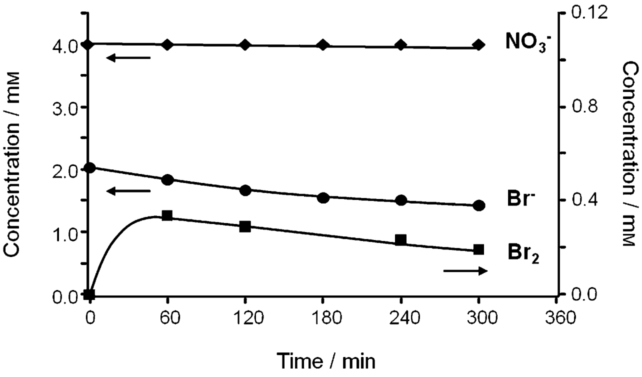


Figure 2. Concentration of NO_3^- (——◆——), Br^- (——●——), and Br_2 (——■——) in the reacting mixture during irradiation. Reaction conditions: volume (500 cm^3), initial Br^- (2 mM) and HNO_3 (4 mM), TiO_2 (P25-Evonik; 1 $g\,L^{-1}$), temperature (40 °C), O_2 flow rate (0.1 $L\,min^{-1}$).

The impinging light is absorbed by TiO_2, which in turn photogenerates electron–hole pairs [Eq. (2)].[7]

$$TiO_2 + h\nu \rightarrow TiO_2\,(e^-_{CB}/h^+_{VB}) \tag{2}$$

Electrons reduce O_2 into superoxide radical anion ($O_2^{-\bullet}$) [Eq. (3)], which is easily protonated to $HO_2^{\bullet}$ in the acidic reaction medium [Eq. (4)]. Finally, $HO_2^{\bullet}$ further reacts according to Equations (5) and (6), eventually producing hydrogen peroxide (H_2O_2) and hydroxyl radicals ($HO^{\bullet}$).

$$O_2 + e^- \rightarrow O_2^{-\bullet} \tag{3}$$

$$O_2^{-\bullet} + H^+ \rightarrow HO_2^{\bullet} \tag{4}$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \tag{5}$$

$$H_2O_2 + e^-_{CB} \rightarrow HO^{\bullet} + OH^- \tag{6}$$

On the other hand, the photogenerated holes may directly or indirectly oxidize H_2O and Br^- into hydroxyl ($HO^{\bullet}$) and bromine ($Br^{\bullet}$) radicals, respectively, according to Equations (7) and (8).[15]

$$H_2O + h^+_{VB} \rightarrow HO^{\bullet} + H^+ \tag{7}$$

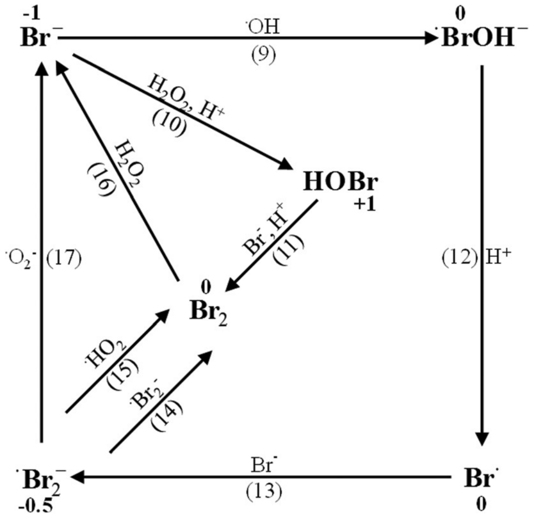
$$Br^- + h^+_{VB} \rightarrow Br^{\bullet} \tag{8}$$

The radicals produced according to Equations (2)–(8) induce chain reactions in turn, which eventually give rise to Br_2 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.

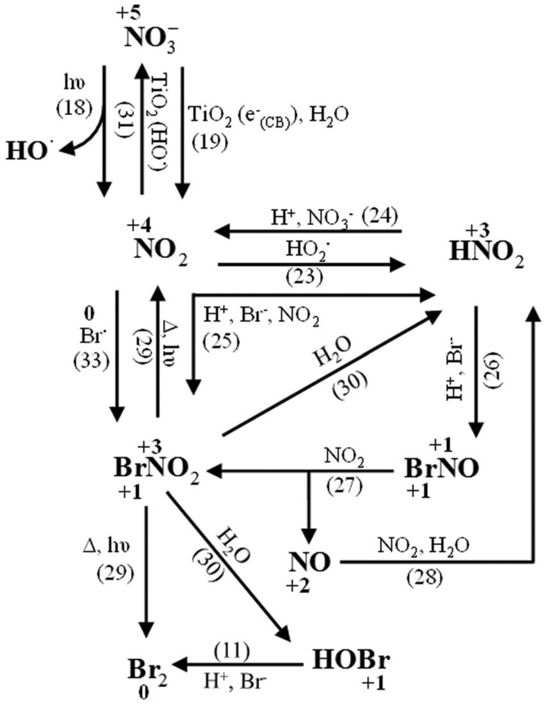
Br^- can be oxidized by direct hole oxidation [Eq. (8)], or indirectly with $HO^{\bullet}$ [Eq. (9)][16] or H_2O_2[14b] (H_2O_2 mediated Br^- oxidation gives rise to hypobromous acid (HOBr)) [Eq. (10)]. HOBr oxidizes Br^- into Br_2 [Eq. (11)].[17] Eventually, the hydroxyl radical path produces $Br_2^{-\bullet}$ as a key intermediate [Eqs. (12), (13)].

$$Br^- + HO^{\bullet} \rightarrow {}^{\bullet}BrOH^- \tag{9}$$

$$Br^- + H^+ + H_2O_2 \rightarrow HOBr + H_2O \tag{10}$$



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.

$$HOBr + H^+ + Br^- \rightarrow Br_2 + H_2O \tag{11}$$

$$^{\bullet}BrOH^- + H^+ \rightarrow Br^{\bullet} + H_2O \tag{12}$$

$$Br^{\bullet} + Br^- \rightarrow Br_2^{-\bullet} \tag{13}$$

The latter species gives rise to Br_2 by reaction with another $Br_2^{-\bullet}$ radical [Eq. (14)] or $HO_2^{\bullet}$[18] [Eq. (15)].

$$Br_2^{-\bullet} + Br_2^{-\bullet} \rightarrow Br_2 + 2\,Br^- \tag{14}$$

$$Br_2^{-\bullet} + HO_2^{\bullet} \rightarrow Br_2 + HO_2^- \tag{15}$$

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[14b] [Eqs. (16a), (16b)].

$$Br_2 + H_2O_2 \rightarrow Br_2^{-\bullet} + HO_2^{\bullet} + H^+ \tag{16a}$$

$$Br_2^{-\bullet} + H_2O_2 \rightarrow 2\,Br^- + HO_2^{\bullet} + H^+ \tag{16b}$$

Wagner and Strehlow demonstrated that $O_2^{-\bullet}$ is able to reduce the key intermediate $Br_2^{-\bullet}$ back into Br^- [Eq. (17)],[19] whereas the protonated form ($HO_2\cdot$) favors the formation of Br_2 [Eq. (15)].[18]

$$Br_2^{-\bullet} + O_2^{-\bullet} \rightarrow 2\,Br^- + O_2 \tag{17}$$

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 $O_2^{-\bullet}$ is similar to that of $HO_2^{\bullet}$ ($pK_a = 4.8$).

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 $HO^{\bullet}$ 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 $HO^{\bullet}$ and NO_2 directly by light (313 nm) absorption[20] [Eq. (18)].

$$NO_3^- + H^+ + h\nu \rightarrow HO^{\bullet} + NO_2 \tag{18}$$

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]

$$NO_3^- + H^+ + e^-_{CB} \rightarrow NO_2 + OH^- \tag{19}$$

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

$$NO_2 + HO^{\bullet} \rightarrow HO_2NO \rightarrow H^+ + NO_3^- \quad (20)$$

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]

$$2\,NO_2 \rightarrow N_2O_4 \quad (21)$$

$$N_2O_4 + H_2O \rightarrow H^+ + NO_3^- + HNO_2 \quad (22)$$

Furthermore, $HO_2^{\bullet}$ radicals may react with NO_2, producing HNO_2 [Eq. (23)][23] and then NO_2 [Eq. (24)].[24]

$$NO_2 + HO_2^{\bullet} \rightarrow HNO_2 + O_2 \quad (23)$$

$$HNO_2 + H^+ + NO_3^- \rightarrow 2\,NO_2 + H_2O \quad (24)$$

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)].

$$2\,NO_2 + H^+ + Br^- \rightarrow HNO_2 + BrNO_2 \quad (25)$$

$$HNO_2 + Br^- + H^+ \rightarrow BrNO + H_2O \quad (26)$$

$$BrNO + NO_2 \rightarrow BrNO_2 + NO \quad (27)$$

$$NO + NO_2 + H_2O \rightarrow 2\,HNO_2 \quad (28)$$

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)].

$$2\,BrNO_2 + h\nu \rightarrow Br_2 + 2\,NO_2 \quad (29a)$$

$$2\,BrNO_2 + \Delta \rightarrow Br_2 + 2\,NO_2 \quad (29b)$$

$$BrNO_2 + H_2O \rightarrow HNO_2 + HOBr \quad (30)$$

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)]:

$$NO_2 + HO^{\bullet} \rightarrow NO_3^- + H^+ \quad (31)$$

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]

$$2\,NaN_3 + 2\,HNO_2 \rightarrow 3\,N_2 + 2\,NO + 2\,NaOH \quad (32)$$

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

$$Br^{\bullet} + NO_2 \rightarrow BrNO_2 \quad (33)$$

$$Br_2^{-\bullet} + NO_2 \rightarrow Br_2 + NO_2^- \quad (34)$$

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)]:

$$O_3 + Br^- \rightarrow BrO^- + O_2 \quad (35)$$

$$BrO^- + H^+ \rightarrow HOBr \quad (36)$$

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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