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# Green synthesis of bromine by $TiO_2$ heterogeneous photocatalysis and/or ozone: A kinetic study

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ABSTRACT

Elemental bromine is an industrially relevant compound traditionally produced from bromide ions by using chlorine as the oxidizing agent. Problems related to transportation and handling of the corrosive, expensive and toxic chlorine make green synthetic alternatives highly desirable. In this paper the green synthesis of bromine from bromide in aqueous solutions under mild conditions by means of $TiO_2$ photocatalysis and/or ozonation has been investigated from a kinetic point of view. The ozonation in the absence of the photocatalyst follows a first order kinetic with respect to both ozone and bromide. The kinetics of the reactions in the presence of the photocatalyst has been described by means of a Langmuir-Hinshelwood type model and the values of the kinetic constants and of the apparent adsorption constants have been determined. The results obtained constitute the basis for practical applications of this green and novel bromine synthesis and can be used for future reactor engineering and scale up of the process.



## 1. Introduction

Bromine is distributed in nature as bromide salts or organo-bromine compounds, which are produced by various marine organisms. Bromine is present in the hydrosphere, mainly as soluble bromide salts in seawater, inland seas, natural brine wells, salt lakes and in evaporite chloride minerals. Concentrations may vary from 65 mg $L^{-1}$ in seawater up to 6.5 g $L^{-1}$ in the southern basin of the Dead Sea. The world production of bromine in 2015 was more than 600,000 tons being United States, Israel and China the major countries in worldwide bromine production. Bromine compounds are used in fields such as energy storage and generation, fire safety, water treatment, production of pharmaceuticals, reduction of mercury emissions, and enhanced quality rubber. Indeed, bromine used in clear brines increases both the efficiency and productivity of oil and gas wells [1], whereas bromine, present in small amount, is very efficient as a constituent element of flame retardants [2]. Moreover, bromine-based products are ideal solutions for water treatment applications thanks to the bromine ability to kill harmful microorganisms by combining with bacteria and other living organisms [3]. Bromine-based compounds are used also in many prescription drugs, as well as treatments for many different health problems (naproxene, antihistamines, anticancer, anti-Alzheimer, antiseptics, narcotics) [4] and brominated compounds are often used for the preparation of pharmaceutical products, where they are used as catalysts. Bromine-based products can be used to reduce mercury emissions from coal-fired power plants, as bromine additives convert elemental mercury to its oxidized form, which can be easily recovered. Finally, the rubber derived from the combination of butyl rubber with bromine, presents considerable added value with respect to the pristine material as it has strong physical strength, low permeability, and higher resistance to weather and aging.

$Br_2$ can be produced through oxidation of bromide-containing brine. The oxidation process can be carried out by means of electrochemical [5–7] or catalytic [8] methods, by using oxo-compounds [9,10] or various oxidizing species [11]. Anyway, the two most commonly used $Br_2$ extraction processes are the Steaming out- and the Air blowing-process [12]. Both technologies use gaseous chlorine as the oxidizing agent. The use of chlorine is justified as it is a co-product of chloro-alkali industry, which also uses brines as the primary feedstock. However, there is the need to develop cleaner and more economic processes.

Heterogeneous photocatalysis has received increasing interest since some decades, as an efficient advanced oxidation process. This method has been successfully used for wastewater treatment, and is suitable to perform the complete degradation of organic and

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inorganic pollutants, the reduction of metal ions, the inactivation of many aerobic bacteria, etc. [13]. Indeed, the use of chemically stable, cheap and safe semiconductors as photocatalyst [14–17] under mild operating conditions, the versatility in tailoring their properties [18,19], and the possibility of solar light exploitation [20,21] make photocatalysis a competitive technology in view of a sustainable utilization.

However, the applications of photocatalysis in the field of the chemical synthesis are still rare, even if in the literature some examples of highly selective photocatalytic reactions [22–26] are reported.

Ozone ($O_3$) is an oxidising species mainly used for the disinfection and purification of water. The coupling of photocatalysis with ozonation methods has been deeply investigated in the field of wastewater decontamination [27,28].

The mechanism of the formation of halogen molecules in the atmosphere induced by $O_3$ and light has been investigated in the relevant literature [29–31]. This phenomenon is of paramount importance for the $O_3$ layer depletion or for the formation of halogenated compounds in the atmosphere [32–37]. However, all of these studies, carried out in laboratory by using set-ups simulating atmospheric conditions, allowed to recover just micromoles of $Br_2$ and cannot be considered processes aimed to $Br_2$ synthesis.

Recently, $TiO_2$ photocatalysis, ozonation or a combination thereof was found to be effective for the production of elemental bromine from acidic solutions containing bromide [38]. This process could be applied for green bromination reactions even at an industrial scale, because it appears to be a cheap, safe and environmentally sustainable alternative to the current bromine production methods. The knowledge of the kinetics of these reactions is fundamental for the passage from laboratory plants to the design of applications at a production scale.

Therefore, the object of the present work is the kinetic analysis of $Br_2$ formation in the investigated processes: $TiO_2$ photocatalysis, ozonation and their combination.

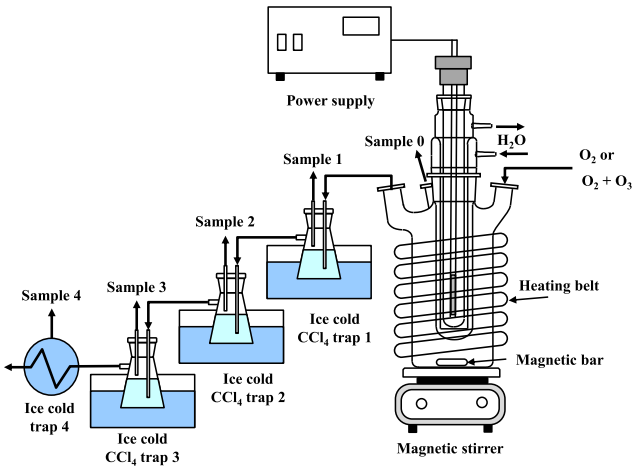


**Fig. 1.** Scheme of the experimental set-up.

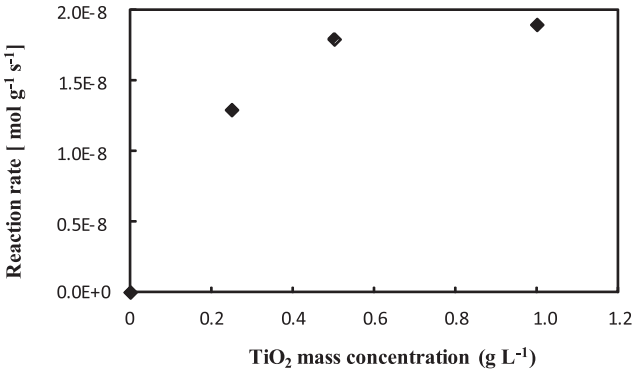


**Fig. 2.** Initial reaction rates of photocatalytic $Br^-$ oxidation in the presence of oxygen at different $TiO_2$ mass concentrations. Initial bromide concentration 2 mM, $HNO_3$ concentration 4 mM, $O_2$ concentration $9.9 \cdot 10^{-4}$ M.

## 2. Experimental

All of the experimental runs were carried out in a 500 $cm^3$ annular Pyrex photoreactor equipped with ports in its upper part for withdrawing samples of the reacting suspension, measuring the pH and allowing the inlet and the outlet of gases ($O_2$, $O_3$ and He). A medium pressure Hg lamp (Helios Italquartz, Italy, nominal power 125 W) was axially positioned in the photoreactor. The lamp was cooled by a Pyrex water-cooling jacket, which constitutes the inner part of the annulus, whereas the outer wall of the reactor was surrounded by a heating wire able to maintain the suspension at about 40 °C, thus facilitating the stripping of the produced bromine. It is worth noting that the Pyrex jacket, which surrounded the lamp, permitted to cut off the radiation with wavelengths lower than ca. 320 nm. Therefore, the direct excitation or photolysis of oxygen or ozone can be excluded and only the absorption of photons by $TiO_2$ can be relevant. However, by considering also that $TiO_2$ is not photoactivated at wavelengths longer than about 380 nm, the fraction of used wavelengths is restricted between 320 and 380 nm. In this range of wavelengths, the emission spectrum of the lamp presents just a peak of emission at 365 nm.

Fig. 1 shows the experimental set up.

During the photocatalytic tests the reacting mixture contained 1 g $L^{-1}$ of $TiO_2$ (P25-Evonik, 20% Rutile and 80% Anatase ca., BET specific surface area: 50 $m^2$ $g^{-1}$) as the photocatalyst, $HNO_3$ (Fluka, 65%), KBr (Sigma-Aldrich p.a.) and distilled water. At this photocatalyst concentration, the observed reaction rate approaches the asymptotic value (see Fig. 2) which is observed in photocatalytic reactors when the photocatalyst is progressively added to the reacting solution [39,40].

The initial concentrations of $HNO_3$ and KBr, if not otherwise specified, were 4 mM and 2 mM, respectively. In these conditions the pH value was around 2.7. In order to avoid the transient regime generated by the gradual dissolution of ozone in the aqueous medium, which takes place after starting the ozonator, bromide was added (few drops of an opportunely concentrated bromide solution) only when saturation by ozone was already reached. Before switching on the lamp, the system was maintained in the dark for 30 min in order to reach the adsorption equilibrium conditions. The suspension was magnetically stirred while a gaseous mixture of $O_2$ and He was continuously bubbled through it. Notably, in order to avoid mass transfer limitations, the mixing of the gas bubbles in the $TiO_2$ suspension was increased until no influence on the reaction rate was observed. The photon flux was measured by a radiometer (Delta Ohm DO9721) with an irradiance probe LP9021 UVA (315–400 nm) at different points on the outer wall of the reactor. The measured average value was 70 W $m^{-2}$ in the absence of the photocatalyst with an almost uniform distribution on the outer wall. For the adopted photocatalyst concentration (1 g $L^{-1}$) the average rate of radiant energy absorption was estimated by solving the radiative transfer equation at about $5.5 \cdot 10^3$ W $m^{-3}$.

The experimental runs usually lasted a few hours and samples of the reacting mixture were withdrawn at fixed time intervals, filtered through a PTFE filter (Millipore, 0.2 μm) and analysed to