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Degradation of melamine in aqueous systems by vacuum UV-(VUV-) photolysis. An alternative to photocatalysis

Alessandra Bianco Prevot[a,*], Valter Maurino[a], Debora Fabbri[a], André M. Braun[b], Mónica C. Gonzalez[c]

[a] University of Torino, Department of Chemistry, Via P. Giuria 5, 10125, Torino, Italy
[b] Karlsruhe Institute of Technology, 76131, Karlsruhe, Germany
[c] Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), (1900) La Plata, Argentina

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ABSTRACT

VUV-irradiation experiments with aqueous solutions of melamine and related triazine derivatives were carried out in the presence or absence of molecular oxygen. Substrate degradation, total organic carbon and evolution profiles of intermediates were monitored. Relevant mineralization of the substrates was observed, in particular for melamine, its extent depending on the concentration of dissolved O_2 and on the number of amino substituents at the *s*-triazine moiety of the substrate. In all experiments, cyanuric acid was found to be the only persistent final product. Experimental results indicate that the route of reactions leading to mineralization is independent of that leading to amino group substitution. Mechanistic hypotheses are proposed and compared with findings coming from TiO_2-based photocatalysis.

1. Introduction

The environmental impact of the wide and unrestricted use of pesticides during the last decades [1] and a suboptimal control of industrial effluents disposal/treatment is reflected in the present level of pollution of surface and ground waters. Adequate chemical, i.e. abiotic, processes (Advanced Oxidation Processes (AOPs)) can be used for the oxidative degradation of biocidal and/or biorefractory pollutants. AOPs are mostly light-induced or (photochemically) catalyzed oxidation processes where highly reactive intermediates (mainly hydroxyl radicals, $HO^{\cdot}$) are generated to initiate the oxidative degradation of organic pollutants [2].

Vacuum-ultraviolet (VUV-) photolysis of water generates HO· radicals, hydrogen atoms (H) and, to a lower extent, solvated electrons (reactions (1)) [3,4] and has been successfully used for the oxidative degradation of organic pollutants in water [5]. Moreover it has been demonstrated that VUV-irradiation can remarkably increase the photocatalytic efficiency, for instance in processes using TiO_2, a widely employed photocatalyst [6]. The high absorbance cross-section of water and quantum-yields of H_2O homolysis of 0.3 to 0.5 (for wavelengths of excitation between 185 to 140 nm [7]) lead to very high local concentrations of HO radicals and H atoms [8]. Oxidative degradation of organic pollutants is initiated by HO radicals, either by hydrogen abstraction (reaction (2)), by electrophilic addition to π-systems (reaction (3)) or by electron transfer reactions (Eq. (4)). For an efficient oxidative degradation of the pollutants, dissolved molecular oxygen contributes to convert C-centered radicals into peroxyl radicals (ROO), (reaction (5)) that may be considered as key intermediates of a complex manifold of oxidation reactions leading eventually to the complete mineralization of the dissolved organic material [2]. In parallel, H atoms are trapped by O_2 to generate perhydroxyl radicals ($HO_2^{\cdot}$), (reaction (6)), and a rather important concentration of H_2O_2 is produced by deprotonation (equilibrium (7)) and disproportionation of $O_2^{\cdot -}$ and HO_2 (reactions (8) [9,10].

$$H_2O \xrightarrow{h\nu} H^{\bullet} + HO^{\bullet} \tag{1a}$$

$$H_2O \xrightarrow{h\nu} H^{+} + e^{-} + HO^{\bullet} \tag{1b}$$

$$HO^{\bullet} + RH \rightarrow H_2O + R^{\bullet} \tag{2}$$

$$HO^{\bullet} + RR'C = CR''R''' \rightarrow RR'C(OH) - C^{\bullet}R''R''' \tag{3}$$

$$HO^{\bullet} + RH \rightarrow HO^{-} + HR^{\bullet +} \rightarrow H_2O + R^{\bullet} \tag{4}$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \tag{5}$$

$$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet} \tag{6}$$

$$O_2^{\bullet -} + H_3O^{+} \leftrightarrows HO_2^{\bullet} + H_2O \tag{7}$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \tag{8a}$$

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[*] Corresponding author.
E-mail address: alessandra.biancoprevot@unito.it (A. Bianco Prevot).

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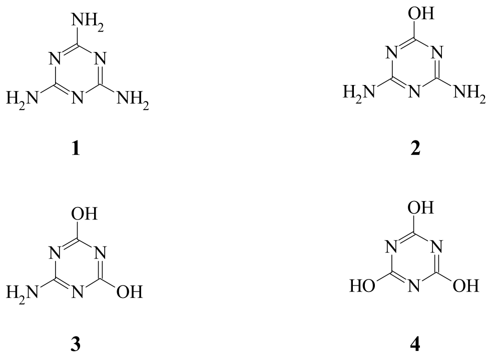


Scheme 1. Chemical structures of the investigated substrates.

$$HO_2^{\bullet} + O_2^{\bullet -} \rightarrow HO_2^{-} + O_2 \quad (8b)$$

$$O_2^{\bullet -} + O_2^{\bullet -} \rightarrow O_2^{2-} + O_2 \quad (8c)$$

In a previous work the VUV-technique was used to degrade atrazine [11], a widely used, highly persistent herbicide and potential carcinogenic [12,13]; following this approach aqueous solutions of atrazine yielded a definitely lower amount of cyanuric acid, the fully hydroxylated s-triazine derivative (**4**, Scheme 1), than that reported in detailed studies using TiO_2 photocatalysis [14] or Fenton processes [15]. So far, there is no AOP known that could be employed to eliminate **4** by oxidative degradation, but the extent of its production could be dramatically diminished by working with VUV-radiation under conditions of O_2 exclusion [11]. Up to the present time no other AOP has been demonstrated capable to mineralize a s-triazine moiety, they rather yield to the total conversion to cyanuric acid.

Aiming at a more detailed description of the reaction manifold of s-triazines degradation induced by the VUV-photolysis of water, in comparison to other AOPs, and with specific emphasis on the widely studied and applied TiO_2-based photocatalysis, the present work deals with the VUV photochemically initiated degradation of different s-triazine compounds, exhibiting the same structure than atrazine but with different substituents (melamine, **1,** ammeline, **2,** ammelide, **3** and cyanuric acid, **4,** Scheme 1).

Melamine was chosen as the starting compound, because amino substituents of the s-triazine moiety are also present in intermediates of the oxidative degradation of atrazine, and compounds **2** and **3** were already found as intermediates of the oxidative degradation of atrazine and of **1** [11,14–16]. Furthermore, when applying AOPs to melamine degradation, cyanuric acid was obtained as the stable final product [15,16].

Moreover melamine based polymers find wide application, and even if melamine is not classified as a health risk, its chronic toxicity is still object of in-depth investigations [17].

Melamine has been implicated in diagnoses of urinary tract stones and sand like calculi due to contamination of milk products [18].

Recently melamine degradation by means of TiO_2-based photocatalysis has been deeply investigated in order to give insights into the mechanism of oxidation, and in particular into the role of hydroxyl radical vs direct hole oxidation mechanisms [16]. Indeed the role of bound or free HO· mediated oxidation vs direct hole transfer oxidation has been largely debated in TiO_2-photocatalysis studies [19] and the elucidation of the significance of these pathways has a fundamental importance in the understanding and control of photocatalytic processes. In addition to previously reported evidences in support of both mechanisms [20,21], the photodegradation of melamine resulted as an efficient tool to evaluate the direct hole transfer ability of a photocatalyst, since it was demonstrated that melamine is not able to directly react with HO· radicals under H_2O_2-UV irradiation or Fenton conditions.

The present work aims firstly to evaluate the possibility to attain melamine mineralization by means of VUV-irradiation and secondly to assess the degradation mechanisms in comparison with the findings obtained in TiO_2-photocatalysis.

2. Materials and methods

2.1. Chemicals

Melamine (2,4,6-triamino-1,3,5-triazine, **1**), Fluka, Steinheim, Germany, and cyanuric acid (2,4,6-trihydroxy-1,3,5-triazine, **4**), Merck, Darmstadt, Germany, were used as received. Ammeline (2,4-Diamino-6-hydroxy-1,3,5-triazine, **2**) and ammelide (2-amino-4,6-dihydroxy-1,3,5-triazine, **3**) were previously prepared [22]. Didodecyldimethylammonium bromide (DDDMAB), Eastman Kodak Co., Rochester, NY, and sodium dodecylsulphate (SDS), Darmstadt, Germany, were used as received. All other reagents were at least analytical grade (Merck or Fluka). Pure water was provided by an UHQ II System (Millipore, > 18 mΩ cm^{-1}, < 20 ppb organic carbon). Ar and synthetic air were of 99.99% quality (Messer, Sulzbach, Germany).

2.2. Irradiation experiments

2.2.1. Light source

A cylindrical Xe-excimer radiation source (length: 25 cm, external diameter: 3 cm [23]) emitting at 172 nm ± 14 nm was operated at 100 W and 175 (± 10%) kHz, using a high frequency, high voltage power supply (ENI, Model HPG-2).

2.2.2. Reactor

A 500 mL annular reactor (Pyrex, length: 30 cm, external diameter: 5 cm, Mangels, Bornheim, Germany) adapted for the immersion of the Xe-excimer radiation source and equipped with an external electrode [24] and a purging system was used. A built-in circulation system ensured efficient stirring of the solution. Experiments were performed by irradiating 350 mL of solution within a temperature range of 25 to 30°C, without adjusting the initial pH value of ca. 7.5.

2.2.3. Analyses

HPLC analyses were carried out using a HP model 1090 liquid chromatograph with multiwavelength UV–vis detector (wavelength of analysis: 220 nm); column: Lichrospher C_{18}, length: 250 mm, i.d.: 4 mm, 10 μm packing (Merck, Darmstadt, Germany,).

2, **3** and **4** were analysed by Ion Interaction Chromatography using the Immobilised Reagent Technique (IIIR). The column was loaded with a 1×10^{-2} M DDDMAB solution in acetonitrile/water (25%/75%) at 1 mL/min and washed with 30 mL of water; a 5×10^{-3} M phosphate buffer solution at pH 7.7 was used as eluent at 1 mL/min. For **1**, the eluent was a solution of 1×10^{-3} M SDS and 0.1 M of NaCl in 15% ethanol, adjusted to pH 3.06 with glacial acetic acid. Before the analysis, the column was equilibrated for two hours with the eluent at 1 mL/min.

TOC (total organic carbon) analyses were carried out with a Rosemount Analytical Instrument, Dohrmann DC-190.

3. Results and discussion

3.1. VUV-photolysis versus UVC-photolysis of H_2O_2, photochemically enhanced Fenton process and TiO_2-photocatalysis: mechanistic and kinetic aspects

Abiotic AOPs, and in particular those initiated by photochemical means, relay on the generation of hydroxyl radicals, HO, to initiate manifolds of oxidative degradation of organic compounds (pollutants) dissolved in aqueous systems [2]. However, there are important differences as far as the generation of reactive intermediates and their (local) concentrations are concerned.

Investigating on the UVC-photolysis of H_2O_2 or on the (photochemically enhanced) Fenton process, H_2O_2 is added to the reaction system and is used to generate $HO^{\cdot}$ radicals. While for the first, HO radicals are generated by the photochemical homolysis of H_2O_2 (reaction 28), HO· radicals appear in the second upon reduction of H_2O_2 by $Fe^{2+\cdot}$(reaction 29).

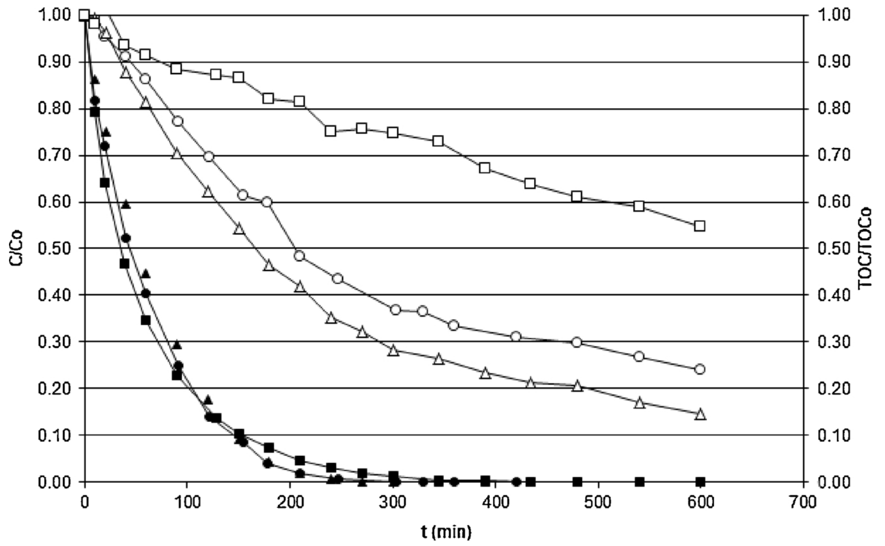


Fig. 1. Normalized results of the consumption of melamine (**1**) (solid symbols) and of the diminution of TOC (empty symbols) upon VUV-irradiation. Experiments performed in: (■, □) = air saturated solution; (●, ○) aerated solution; (▲,△) = Ar saturated solution. Initial melamine concentration 5.5 × 10^{-4} M.

$$H_2O_2 \xrightarrow{h\nu} 2HO^{\bullet} \tag{28}$$

$$Fe^{2+} + H_2O_2 \rightarrow HO^{\bullet} + HO^{-} + Fe^{3+} \tag{29}$$

Photochemical enhancement of the second consists in fact of the photochemical reduction of Fe^{3+} (reaction 30, D: electron donor), and the process might be classified as photocatalyzed.

$$Fe^{3+} + D \xrightarrow{h\nu} D^{\bullet +} + Fe^{2+} \tag{30}$$

Electronic excitation of TiO_2 (TiO_2-based photocatalysis) generates a charge separation between the conduction and the valence band of the semiconductor (reaction 31) The high oxidation potential of the electron deficient valence band generates HO radicals from mostly surface adsorbed H_2O (reaction 32), while the electron excessive conduction band is acting as a reductant, e.g. of molecular oxygen present and adsorbed to the photocatalyst surface (reaction 33)

$$TiO_2 \xrightarrow{h\nu} TiO_2(e^{-} + h^{+}) \tag{31}$$

$$TiO_2(h^{+}) + H_2O \rightarrow TiO_2 + HO^{\bullet} + H^{+} \tag{32}$$

$$TiO_2(e^{-}) + O_2 \rightarrow TiO_2 + O_2^{\bullet -} \tag{33}$$

While for the first two mentioned AOPs, reductants like HO_2 and O_2^{-} are generated by reaction (34), the TiO_2-based photocatalysis produces the species by reduction from the electron excess conduction band (reaction 33). Overall and local concentrations of H_2O_2 and of HO_2 and O_2-, respectively, depend on experimental conditions, mainly on the concentration (absorbance) of H_2O_2 for the UVC-photolysis of H_2O_2 and on the concentration (absorbance) of Fe^{3+} for the photochemically enhanced Fenton process, whereas for the TiO_2-based photocatalysis, the reductants are generated at or close to the photocatalyst surface, and H_2O_2, being a product of the subsequent disproportionation (reaction 8), is present all over the liquid part of the suspension.

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \tag{34}$$

$$TiO_2(h^{+}) + H_2O_2 \rightarrow TiO2 + HO_2^{\bullet} + H^{+} \tag{35}$$

Hydroperoxide radicals, HO_2·, might also be generated by oxidation of H_2O_2 at the electron deficient surface of TiO_2 (reaction 35). They may be considered the main reductant species in all three processes mentioned for the oxidative degradation of organic compounds in aqueous systems (AOPs).

Hydroxyl radicals, HO·, may also be generated by VUV-photolysis of H_2O (reactions 1). At the mostly used wavelength of excitation of 172 nm (Xe_2* excimer), the molar absorption coefficient of H_2O places the total absorption (A = 2) at a fraction of mm of radiation penetration. H· atoms will either recombine or react with dissolved O_2 within the extremely restricted volume of irradiation, and it has been shown that, depending on the incident photon flux, a more or less important deficiency of O_2-concentration will occur [29]. Consequently, beside the diffusion of HO· radicals and even under conditions of macroscopically air-saturated solutions, reductant species, such as e_{aq}-, O_2^{-} and HO_2 might escape from the irradiated volume and affect the subsequent paths of reactions of the oxidative degradation.

The VUV-photolysis of pure H_2O yields H_2O_2 only in the presence of O_2 [31], hence, giving evidence of the importance of the observed differentiation between irradiated and total reactor volume and between O_2-deficient and macroscopically saturated volumes. It remains to explore reactions systems where comparative investigations would not only confirm the superior kinetics of the primary oxidation (reaction 2) of the VUV-photolysis but also discrepancies in the percentage of mineralization.

3.2. VUV-photolysis of aqueous solutions of melamine (1), ammeline (2), ammelide (3) and cyanuric acid (4)

The study of the melamine degradation was carried out by establishing the evolution of the concentrations of substrate and intermediates and of the TOC as a function of irradiation time. The effect of the concentration of dissolved oxygen concentration was investigated by working with air-equilibrated stirred solutions or with solutions purged continuously with synthetic air or with Ar.

Profiles (normalized values) of the consumption of melamine as well as of the diminution of TOC upon VUV-photolysis of melamine aqueous solutions (initial concentration: 5.5 × 10^{-4} M) are shown in Fig. 1. As can be observed, melamine disappearance is not dependent on the concentration of dissolved O_2; at a first glance it is reasonable to postulate that the substrate is reacting with HO generated by reactions (1a) and (1b). Since O_2 is reacting very efficiently with H (reaction (6)), and the rate of consumption of melamine being independent of the concentration of dissolved O_2, a potential reaction of H· with the s-triazine moiety could be considered of minor relevance.

Surprisingly, when compared to previous findings, in particular when applying TiO_2-photocatalysis [15,16], a relevant TOC decrease is observed. In contrast to the kinetics of the melamine consumption, the evolution of the TOC value with irradiation time is significantly affected by the concentration of dissolved O_2, the rate and extent of mineralization being enhanced when decreasing the concentration of dissolved O_2. These findings are in contrast to the generally accepted manifold of oxidation reactions based on an efficient trapping of intermediate C-centered radicals by molecular oxygen [2].

As for intermediate and final products, the amount of melamine not mineralized upon VUV irradiation is yielding ammeline (**2**), ammelide (**3**) and cyanuric acid (**4**), and their evolution in aerated, air saturated and Ar saturated solution is reported in **Figure S1** in the supplementary information. In all cases, **2** and **3** are intermediates of the reaction sequence leading from **1** to **4**, and the percentage of melamine that is not undergoing mineralization is completely transformed into cyanuric acid that accumulates as final product, since it cannot be further degraded and mineralized.

Ammeline is produced by the substitution of one amino group of **1**, and if it is taken as substrate, it is degraded following two routes: i) amino group substitution leading to **3**, and subsequently to **4** (Fig. 2) and ii) mineralization according to TOC decrease (Fig. 3). In contrast to what is observed for melamine, the mineralization efficiency is not affected by the amount of dissolved O_2 and reaches ca.50% of the initial TOC value.

An analogous behavior is featured by ammelide, that upon VUV-photolysis produced **4** with a yield of approximately 50% that did not change in the absence of dissolved O_2 and shown a TOC decay of about 50%.

It is therefore worth to be noticed that the mineralization process is affected severely by the dissolved O_2 only for melamine, whereas its effect is negligible for the other investigated substrates.

3.3. Mechanistic hypotheses concerning melamine (1), ammeline (2) and ammelide (3) degradation/ mineralization

The previously discussed findings regarding substituted s-triazines degradation and mineralization lead to the hypothesis that the substrate transformation is taking place via two different paths: one yielding the formation of cyanuric acid as stable final product and the other leading to a triazine ring opening and the subsequent intermediate mineralization according to the results of the TOC analyses.

HO· radicals generated by the VUV-photolysis of the aqueous medium, could open the sequence of reactions leading to the substitution of the amino groups. This substitution must take place at one of the three C-centers of the aromatic *s*-triazine moiety (Scheme 2), HO being known to add to π-systems as referred to in Eq. (3). The electrophilic addition of HO (reaction (9)) to melamine produces an intermediate radical $\mathbf{A_1}$ with amino and hyroxyl groups in geminal position, prone to either eliminate H_2O (reaction (10)) to yield radical **B** or to eliminate NH_3 (reaction (11a)) to produce radical $\mathbf{C_1}$. Reduction of **B** (reaction (12)) would recycle the substrate, but reduction of $\mathbf{C_1}$ (reaction (13a)) leads to the keto form of **2**. This reaction can be repeated twice to yield **4**.

The VUV-photolysis of aqueous solutions of ammelide (**3**) implies two competing routes of reaction: (i) the substitution of the amino group, to yield **4**, i.e. without subsequent reaction of the product, and (ii) the mineralization of **3**. The photolyses resulted in a quantitaitve consumption of the substrate producing **4** in approx. 50% yield, and TOC-analyses showed that the remaining 50% of the initial substrate concentration were mineralized. The evolution of the concentrations of **3** and **4** as well as of TOC in the presence and absence of dissolved O_2 clearly indicates that the production rate of **4** is not affected by the amount of dissolved O_2, and that the **4** production levels off to the limiting value of approx. 50% (data not shown).

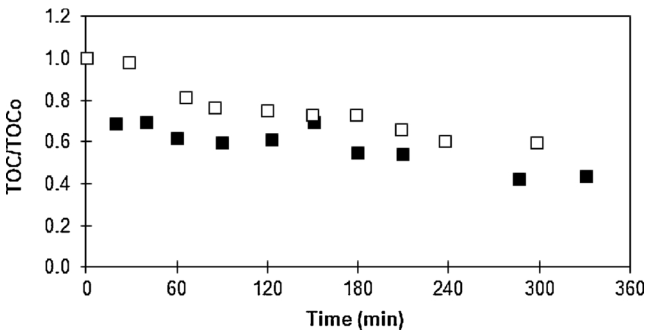


Fig. 3. Normalized TOC decay upon VUV-irradiation of ammeline (initial concentration = 1.0×10^{-4}M). Experiments performed in air (■) and Ar (□) saturated solutions.

A sequence of reactions leading to mineralization necessarily involves the opening of the *s*-triazine moiety. Since mineralization of **3** was found unchanged in the absence of dissolved O_2, oxidation must occur predominantly by the addition of HO· to products of an O_2-independent opening of the *s*-triazine moiety. The latter may occur by the solvolysis of the N-hydroxylated intermediate $\mathbf{D_3}$ producing cyanic acid and hydoxyurea (**5**) (reaction (14c), Scheme 3). $\mathbf{D_3}$ might be generated from radical $\mathbf{E_3}$ either by electron transfer and solvolysis (reactions (15c) and (16c)) or by combination of $\mathbf{E_3}$ and HO· (reaction (17c)). $\mathbf{E_3}$ is obtained by the deprotonation of the radical cation $\mathbf{F_3}$ (reaction (18c)).

Alternatively and according to the general Eq. (4), HO radicals may also react by electron transfer [25–28].

Electron transfer from **3** to HO· (reaction (20c)) would generate the radical cation $\mathbf{F_3}$, and, combined with the solvolysis of $\mathbf{F_3}$ (reaction (21c), would represent an alterative reaction path of **3.** A potential polymerization is prevented by the protic medium.

Although, the routes of amino group substitution involving $\mathbf{A_3}$ and of mineralization via $\mathbf{E_3}$ and $\mathbf{D_3}$ seem plausible, the proposals depicted in Schemes 2 and 3 cannot explain (i) how $\mathbf{C_n}$ would be reduced to yield the higher hydroxylated s-triazine, (ii) why the efficiencies of the two competing routes of reaction depend on the concentration of dissolved O_2 (Figs. 1 and S1), and (iii) why mineralization could not be observed, when conventional methods of HO radical generation (e.g. photolysis of H_2O_2 or Fenton

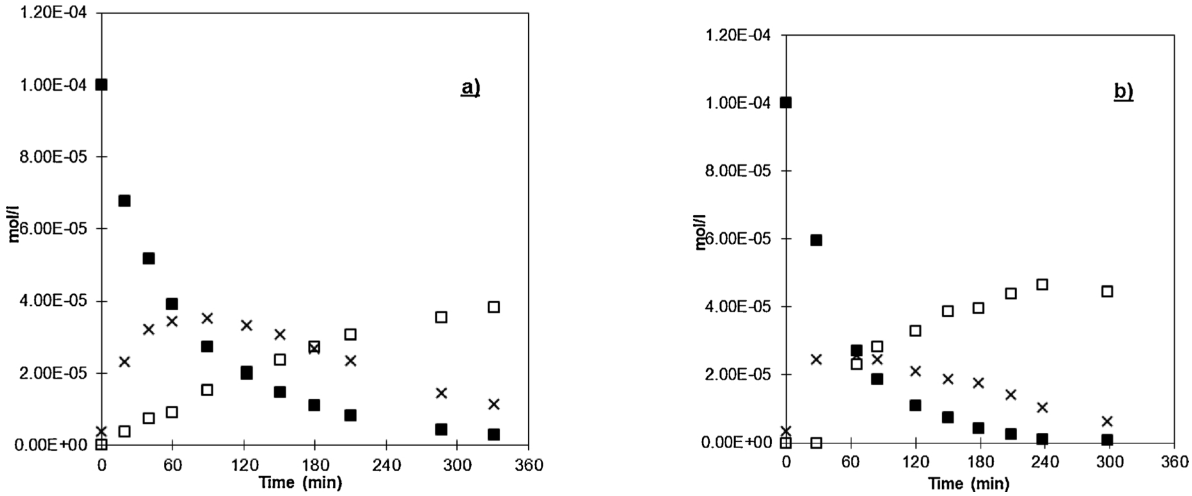
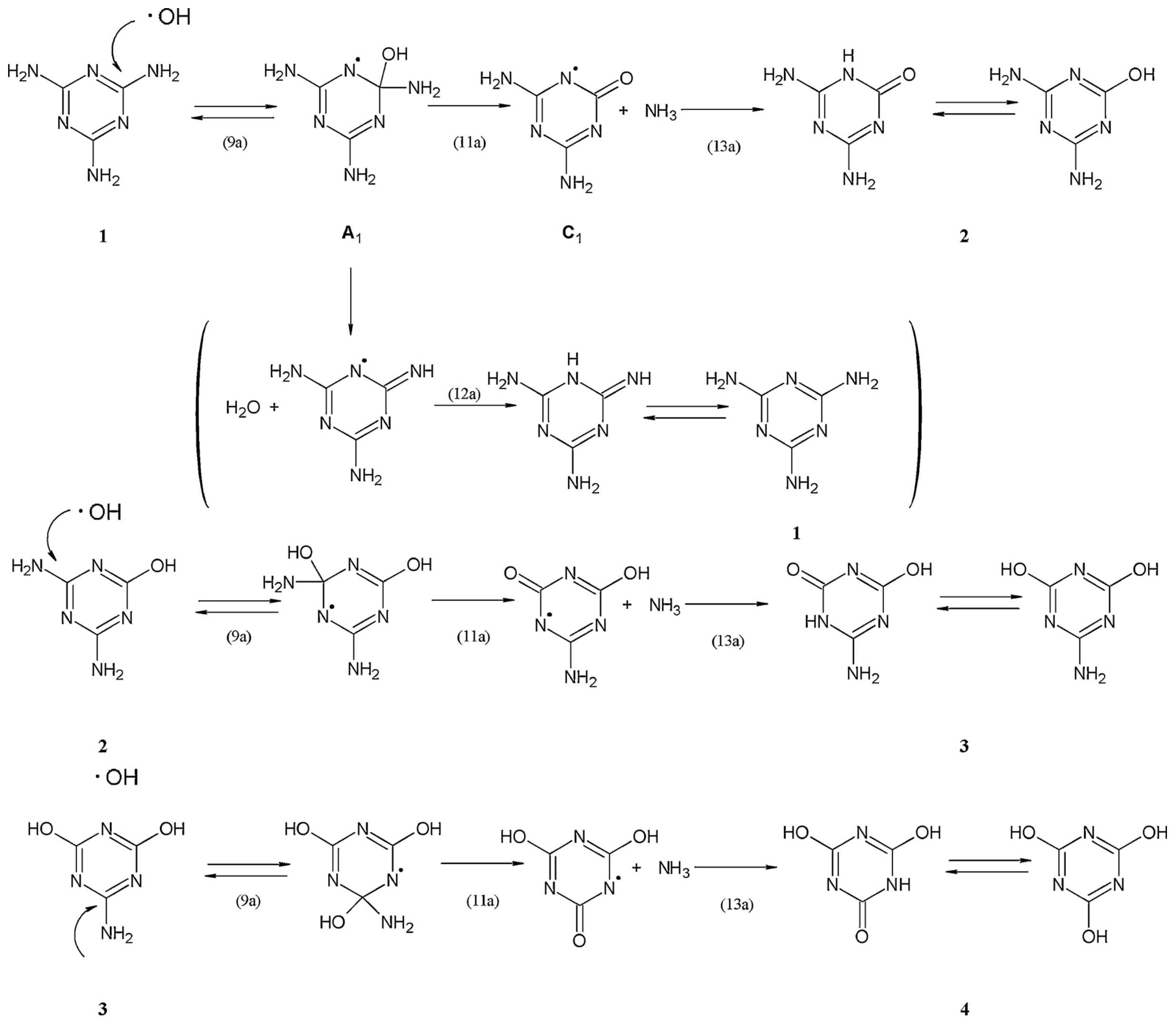


Fig. 2. Degradation of ammeline (■) and evolution of, ammelide (X) and cyanuric acid (□) upon VUV irradiation. Initial ammeline concentration = 1.0×10^{-4} M. Experiments performed in (a) air and (b) Ar saturated solutions.



Scheme 2. Mechanistic hypothesis concerning the substitution of amino substituent of the *s*-triazine moiety (e.g. melamine (**1**)) by electrophilic addition of HO radicals.

reaction) are employed [15,16]. Answers to these questions might be found in evaluating alternative routes of generation of these key intermediates.

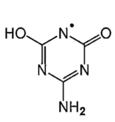
In the absence of dissolved O_2, two species are available, upon VUV-photolysis of H_2O, for the reduction of $\mathbf{C_3}$: H and hydrated electrons (e_{aq}^-). Melamine, though not ammeline or ammelide lead to an important increased mineralization in argon (see Figs. 1 and 2) thus strongly suggesting that either melamine or its subsequent reactive intermediates efficiently react with either H atoms or the hydrated electrons (e_{aq}^-). A reduction by a hydrated electron and melamine would be leading to opened-chain reaction products thus avoiding the formation of ammeline, ammelide and cyanuric acid. Following the reaction mechanisms proposed in the literature for the reactions of e_{aq}^- with nucleobases [29], we propose the reaction manifold shown in Scheme 4 justifying the enhanced mineralization observed when operating under Ar saturation.

The reactivity of ammeline (**2**) seems similar to that of **3** and amino group substitution in **2** might be explained again by the sequence of reactions drawn in Scheme 2. The intermediate product **3** reacts with HO, and production of **4** as well as a decrease of TOC became observable after approx. 40% of substrate conversion and a 20% yield of **3**.

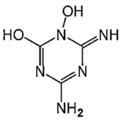
In accordance with the mechanistic hypothesis proposed, the substitution of the amino groups in **1** to yield **3** is independent of the O_2 concentration (Scheme 2). However, summarizing the results concerning the mineralization of **1**,**2** and **3**, the effect of O_2 is highest for **1** and decreasing with decreasing amino substituents.

In accordance with the proposed sequence of reactions implied in the subsitution of the amino groups (Scheme 2), O_2 is not interfering with the N-centered s-triazinyl radicals. Also, there are no reactions of the intermediates (Scheme 3 and 4) with O_2 conceivable that would lead to a relatively stable, most probably oxygenated product that could explain the effects observed.

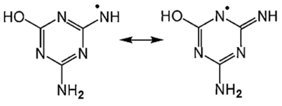
However, during the VUV-photolysis of H_2O, the presence of O_2 is thought to be important for the production of H_2O_2 (Eqs. (6) to (8)) and for the generation of $HO_2^{\cdot}$ and $O_2^{\cdot-}$ (reaction (22)), as these two latter species could readily interact with N-centered s-triazinyl radicals (Schemes 5 and 6). In Scheme 5, enhanced reduction of $\mathbf{C_1}$, by (i) combination with $HO_2\cdot$ and subsequent elimination of O_2 (reactions



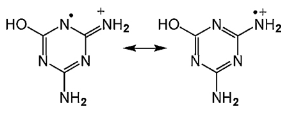
$\mathbf{C_2}$



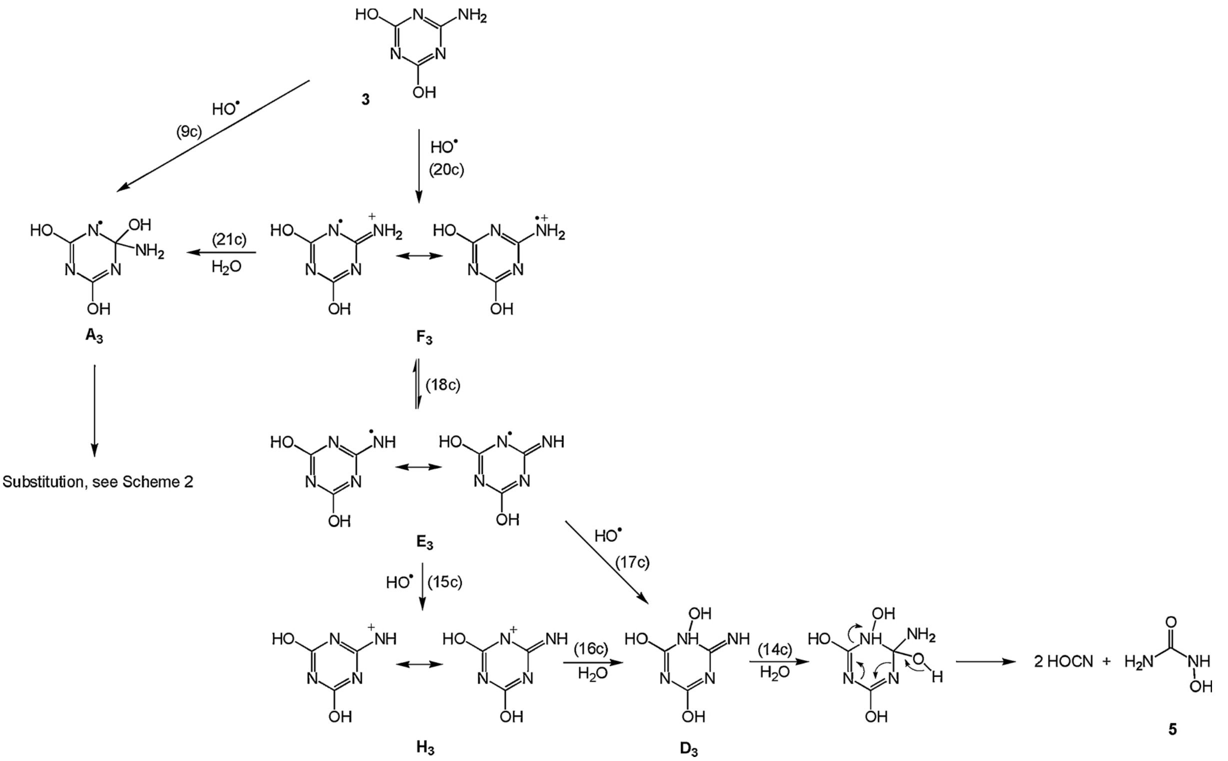
$\mathbf{D_2}$



$\mathbf{E_2}$



$\mathbf{F_2}$



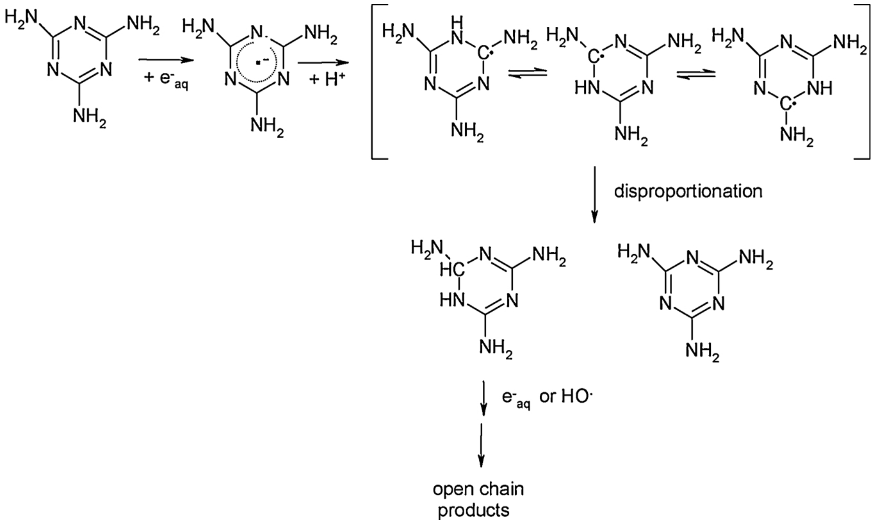
Scheme 3. Mechanistic hypothesis proposing a manifold of reactions upon oxidation of substituted *s*-triazines (e.g. ammelide (**3**)) by HO radicals.

(23a) and (24a) or by (ii) electron transfer from O_2·- and subsequent protonation (reaction (25a)) are proposed to explain the increased extent of amino group substitution in the presence of dissolved O_2.

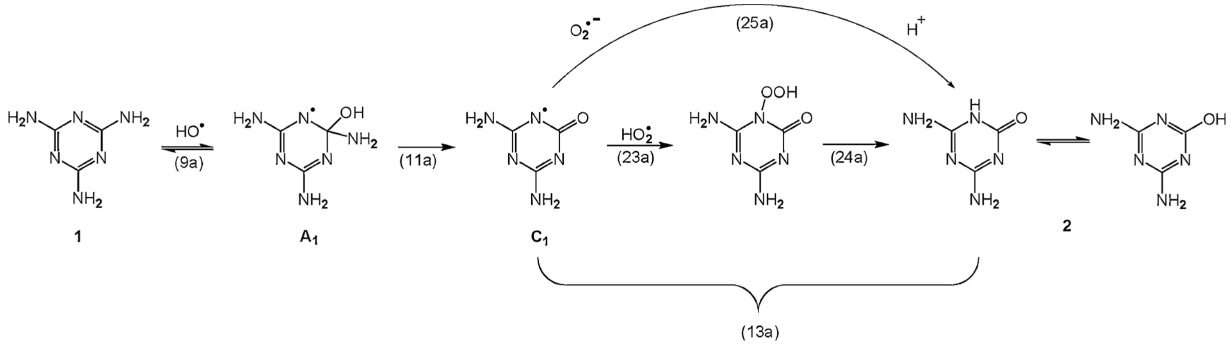
Reductions of $\mathbf{C_1}$ in the presence of HO_2 and $O_2^{\cdot -}$ would compete with the electron transfer from **1** (Scheme 4), and an increasing concentration of dissolved O_2 could affect the extent of mineralization. In addition, HO_2, $O_2^{\cdot -}$ and H_2O_2 may interact with $\mathbf{E_1}$ and $\mathbf{H_1}$, respectively, recycling substrate **1** (Scheme 6). Again, an increase of dissolved O_2 concentration and, hence, of the concentrations of HO_2, $O_2^{\cdot -}$ and H_2O_2 would diminish the importance of the route of reactions leading to mineralization, as observed experimentally.

The experimental results reported in Figs. 1 and 3 reveal that the effect of the O_2^- concentration on mineralization diminishes with the decreasing number of amino substituents.

In most AOPs, relatively high concentrations of H_2O_2 are employed or produced, and air or O_2 saturated reactions systems are maintained. In addition, oxidative degradation being in most cases initiated by HO· radicals, HO_2 and $O_2^{\cdot -}$ are also present in these reaction mixtures. One might therefore understand that mineralization was not observed in earlier work. Nevertheless, VUV-photolyses of air-saturated aqueous systems are leading to partial mineralization of the *s*-triazine derivatives. Based on the paradigm that HO radicals are the initiators and primary oxidants in all AOPs, the mineralization reported here cannot be explained by a different reactivity of the HO radicals. The result found in the case of VUV-photolysis might therefore be due to an exceptionally high local concentration of HO radicals generated in a spatially extremely limited volume of irradiation [30] and to the equally limited volume of subsequent reactions, taking into account the short lifetime of most of the intermediate radical species. The limiting effect of diffusion controlled reactions is clearly observed in comparing



Scheme 4. Mechanistic hypothesis of $\mathbf{C_n}$ reduction in the absence of dissolved O_2.



Scheme 5. Mechanistic hypothesis of an enhanced amino group substitution in e.g. **1**, in the presence of HO_2 radicals.

the evolution of mineralization of melamine in air-equilibrated and air-saturated media (Fig. 1).

The fact that the degradation of organic compounds in aqueous solution by VUV-irradiation is strongly influenced by the concentration of dissolved molecular oxygen in the volume of primary reactions, should not be disregarded. In fact, considering that VUV-radiation of 172 nm is totally absorbed within less than 0.1 mm due to the high absorption cross-section of water and that the intermediates thus generated by the homolysis of water show very short lifetimes, the primary volume of reactions is almost identical with the irradiated fraction of the total reactor volume. Braun et al. [31] demonstrated that the concentration of dissolved molecular oxygen in the volume of primary reactions decreases close to the surface of the radiation source. Therefore, even under experimental conditions of strong O_2 gas bubbling in the bulk solution, the volume of primary reactions is characterized by the diffusion controlled reactions of primary radicals (hydroxyl radicals, hydrated electron and H atoms) of very short lifetimes with the organic substrate. The trapping of the C-centered radicals by dissolved molecular oxygen takes place in the remaining major part of the reactor volume in which slower thermal reactions initiated by peroxyl radicals dominate. Therefore, hydrated electron reactions with the organic reactants (such as those shown in Scheme 4) may still take place even under oxygen saturated experimental conditions. This situation is of particular importance for melamine (**1**) and its primary degradation products, ammeline (**2**) and ammelide (**3**), since the reported experiments show that reductive degradation pathways are at least as efficient than oxidative ones. Consequently, the VUV photochemically initiated process is more efficient in mineralizing melamine than TiO_2 mediated oxidative photocatalysis.

4. Conclusion

Advanced oxidation processes (AOP), and in particular TiO_2 mediated photocatalysis, applied to the oxidative degradation of *s*-triazine derivatives, such as melamine, ammeline and ammelide, yield 100% cyanuric acid that under these conditions is not mineralized, while under conditions of VUV-photolysis melamine, ammeline and ammeline undergo mineralization at certain extent. Moreover VUV-photolyses performed in the absence and in the presence of O_2 show that the mineralization of triazine substrates follows a separate sequence of reactions, and the role of hydrated electrons has been claimed to explain the detrimental effect of dissolved oxygen on the melamine mineralization extent. The experimental results exclude that $H\cdot$ or O_2 decisively interfere with the reaction manifold. The results obtained in air-equilibrated reaction media of low turbulence are close to those found under conditions of O_2-exclusion and confirm the strong heterogeneity of the spatial distribution of the concentration of dissolved O_2 during VUV-photolysis and, hence, an important contribution of the reducing species generated during the VUV-photolysis of water.

Acknowledgements

Dedication. The authors dedicate this work to the memory of professor E. Pelizzetti (16 February 1944- 25 July 2017) – University of Torino, Italy - for his pioneering research in advanced oxidation processes and his indefatigable scientific curiosity that he transmitted us with enthusiasm.

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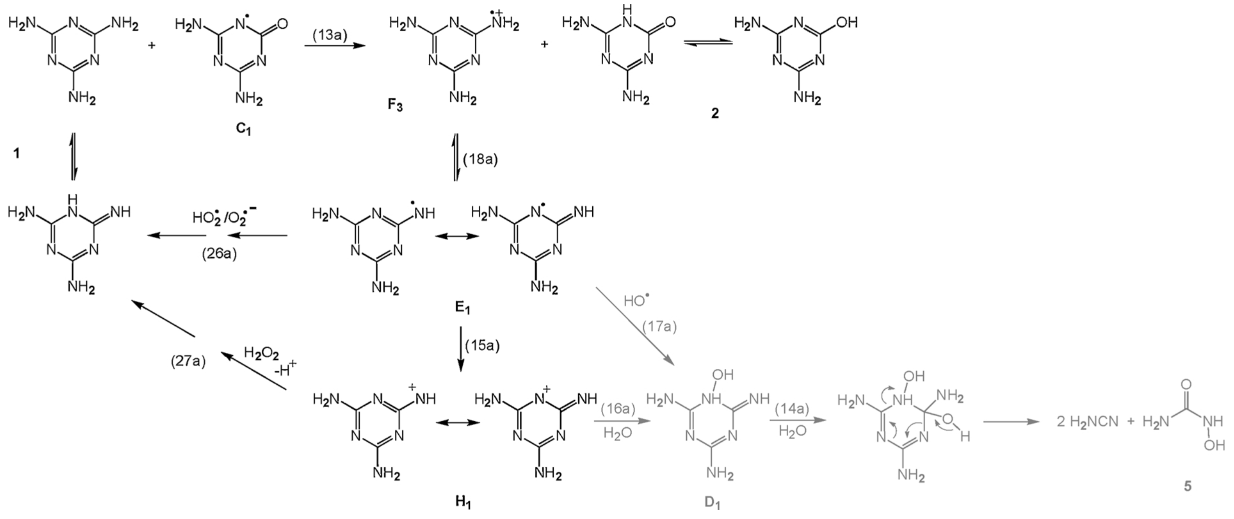

Scheme 6. Mechanistic hypothesis of an enhanced reduction of $\mathbf{E_1}$ and/or $\mathbf{H_1}$ by HO_2, $O_2^{\cdot}$- and/or H_2O_2, to yield **1**, hence, reducing the extent of mineralization.

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