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VUV-photolysis of aqueous solutions of hydroxylamine and nitric oxide. Effect of organic matter: phenol†

Mónica C. Gonzalez *[a] and André M. Braun [b]

VUV-irradiation of aqueous solutions containing hydroxylamine (NH_2OH) in its acid form (NH_3OH^+) and phenol (C_6H_5OH) results in the simultaneous mineralization of the organic substrate and the almost quantitative reduction of NH_3OH^+ to ammonium ions (NH_4^+). Irradiation of aqueous solutions of NH_3OH^+ in the absence of organic substrates showed the formation of nitrate (NO_3^-) and nitrite (NO_2^-) and minor quantities of NH_4^+. In line with these experiments, VUV-irradiation of aqueous solutions of nitrogen monoxide ($NO^•$) yields NH_4^+ only when C_6H_5OH is simultaneously mineralized. A possible reaction mechanism is discussed, where reactions of $NO^•$ and NH_3OH^+ with hydrogen atoms ($H^•$), hydroxyl radicals ($HO^•$) and hydrated electrons (e^-_{aq}), all generated by the VUV-photochemically initiated homolysis of water, are of great importance to the observed results. In the presence of phenol, competition between phenol and either $NO^•$ or NH_3OH^+ for these reactive intermediates in the primary volume of reactions strongly determines the oxidation state and nature of the N-containing products. C-Centered radicals and intermediate products of reactions may also have an important effect on the overall mechanism. The present results are discussed in relation to the actual state of knowledge presented in the literature.

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Introduction

VUV-photolysis of water produces hydrogen atoms ($H^•$), hydroxyl radicals ($HO^•$) and, with minor efficiency, hydrated electrons (e^-_{aq}).[1] These photochemically generated reactive species initiate a series of diffusion controlled secondary reactions yielding reduced and oxidized intermediates and products ($HO^•$, $H^•$, e^-_{aq}, hydroperoxyl radicals ($HO_2^•$), superoxide anion ($O_2^{•-}$), molecular hydrogen (H_2), molecular oxygen (O_2), hydrogen peroxide (H_2O_2), hydroperoxide (HO_2^-), protons (H^+), hydroxide (HO^-) and H_2O) that must be taken into account to describe the VUV-photolysis of pure water.[1–3] The primary reactive species $H^•$, $HO^•$ and e^-_{aq} are able to initiate a series of reactions leading to the mineralization of organic substrates.[4–6] The ratio of the concentrations of $HO^•$ to $H^•$ ($[HO^•]/[H^•]$) or to e^-_{aq} ($[HO^•]/[e^-_{aq}]$) to react with the organic and/or inorganic substrates depends strongly on the experimental conditions, with the concentration of dissolved O_2 being one of the important parameters.[1,7,8]

Xenon excimer (Xe_2*) lamps used for irradiating aqueous solutions present an emission band at 172 nm (MHW: 12 nm). The absorption coefficient of water in this spectral range varies from 6000 to 200 cm^{-1}.[1] Therefore, VUV-photolysis of water is the main photochemical reaction in aqueous systems containing concentrations of dissolved organic matter of 1000 ppm or lower.

Reported investigations on the depletion of NO_3^- induced by the VUV-irradiation of aqueous solutions under different experimental conditions showed the formation of NH_4^+ or nitrous oxide (N_2O) depending on the presence of organic substrates.[9–11] Nitrite (NO_2^-), peroxynitric anion (O_2NOO^-) and N_2O were identified as reaction products and nitric oxide ($NO^•$), nitrogen dioxide ($NO_2^•$) and nitroxyl (HNO) were postulated as key intermediates in the overall reaction mechanism in experiments in the absence of organic substrates.[9] The one-electron reduction potentials of $NO^•$ to the first excited ($^1NO^-$) and to the ground state nitroxyl anion ($^3NO^-$) are $-1.7(\pm0.2)$ and $-0.8(\pm0.2)$ V *vs.* NHE, respectively.[12,13] Because of its high reduction potential, $NO^•$ reduction to $^1NO^-$ by a superoxide ($O_2^{•-}$) is not a viable reaction in physiological systems. However, the reaction cannot be discarded for hydrated electrons $\left(E_{\mathrm{aq}/e^-_{\mathrm{aq}}} : \sim -2.8\,\mathrm{V}\,vs.\,\mathrm{NHE}\,(\mathrm{ref.}\,14)\right)$ in VUV-irradiation experiments. The re-evaluated pK_a of $^3NO^-$ of 11.6(±3.4) implies that nitroxyl exists almost exclusively in its protonated form (HNO) in acidic and low alkaline media.[15] Therefore, a

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[a] *Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), (1900) La Plata, Argentina. E-mail: gonzalez@inifta.unlp.edu.ar*
[b] *Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany. E-mail: andre.braun@kit.edu*

† Dedicated in memory of Professor Ugo Mazzucato (Università degli Studi di Perugia, Italy), 1929–2017.

reduction of $NO^•$ and subsequent reaction of HNO to yield N_2O as the final product ($2HNO \rightarrow N_2O + H_2O$) seem unlikely in biological systems but has to be taken into account if $^1NO^-$ is generated in VUV-photochemical experiments.

The reactions of $NO^•$, $NO_2^•$ and nitroxyl with organic (*e.g.* C-centered) radicals generated during the simultaneous mineralization of organic substrates were thought to induce advanced reduction to NH_2^+ without the evolution of N_2O and with hydroxylamine (NH_2OH) as a key reaction intermediate.[10,11] In fact, it is well documented that the radical oxidants $NO_2^•$ and $NO^•$, and peroxynitrite anion (O_2NO^-) efficiently react with the organic matter.[15,16] In particular, $NO^•$ has been shown to react with other radical species to yield molecules of higher reactivity and toxicity[17,18], *e.g.*, the reaction between $NO^•$ and $NO_2^•$ yielding dinitrogen trioxide (N_2O_3) exhibiting higher reactivity than $NO^•$ towards organic matter, and the reaction of $NO^•$ with the superoxide ($O_2^{•-}$) to yield the oxidant O_2NO^-.[19] In both reaction manifolds, the nitrogen containing intermediates promote oxidation of the organic substrates. However, experimental evidence is needed to probe that a simultaneous multielectron reduction of the nitrogen containing intermediates to NH_2OH or NH_4^+ takes place in the presence of organic matter.[10]

The present report deals with the VUV-irradiation of aqueous solutions containing $NO^•$ and NH_2OH in the presence and absence of organic substrates (phenol) in an attempt to further investigate their reduction/oxidation reactions. These studies are expected to elucidate in more detail the reaction mechanisms of the VUV-photochemically induced reduction of NO_3^- to NH_4^+ in the presence of organic substrates.

Experimental

Materials

Hydroxylammonium chloride ($NH_3(OH)Cl$) and phenol (C_6H_5OH, p.a. quality, Merck) were used without further purification. Pure water was provided by using a UGH II system (Millipore, >18 MΩ cm, 20 ppb of organic carbon). Compressed air and Ar were purchased from Messer. Nitrogen monoxide ($NO^•$) (Messer) was used without further purification and, thus, $NO_2^•$, dinitrogen tetroxide (N_2O_4) and dinitrogen trioxide (N_2O_3) may be potential contaminants.

Apparatus

Irradiation source: A cylindrical Xe_2* excimer lamp of 25 cm length and 3 cm external diameter (ABB, Baden, Switzerland) emitting at 172 nm (MHW: 12 nm) was used.[20] The lamp was operated with an electrical power of 150 W and a frequency of 200–220 kHz by using an ENI Model HPG-2 power supply.

The photochemical reactor was of annular geometry (volume: 220 mL, DEMA, Bornheim-Roisdorf) adapted for the Xe_2* excimer lamp and fitted with a magnetic stirrer and an external electrode.[21] A picture of the used photochemical reactor is given in the Graphical Abstract.

Experiments were performed maintaining the solutions at 25 °C. However, it was not possible to control and measure the temperature in the irradiated volume (approximately 100 μm optical path length).

Analytical methods

The analysis of C_6H_5OH and its oxidation products was performed by liquid chromatography (HPLC, Hewlett-Packard liquid chromatograph model 1090 with multiwavelength detection), column: ODS Hypersil (particle size 5 μm, 4.6 mm i.d. x 100 mm), eluent: methanol/water 1 : 1, temperature: 30 °C.

Anion analysis was performed by ion chromatography (IC, Hewlett-Packard liquid chromatograph model 1050 (Ti series)) with multi-wavelength detection. Detection limits were normally 1×10^{-6} M. The evolution of NH_4^+ was followed using an ion selective electrode (Ecotest-110, ECONIX Ltd, Russia) with a detection limit of 1×10^{-5} M.

DOC (dissolved organic carbon) analysis was carried out with a Rosemount Analytical Instrument, Dohrmann DC-190. The lowest detection limit was 0.5 ppm.

The pH of the samples was periodically controlled with a Metrohm-Herisau pH meter model E512.

Experimental procedure

The following procedure was standard for experiments performed with NH_2OH: approximately 250 mL of the aqueous solution were placed into the reactor and purged with air or Ar for twenty minutes before being irradiated. Gas flow and magnetic stirring ensured good mixing of the solution during the entire period of irradiation. Samples (3 mL) were taken periodically and kept in capped vials for analysis.

For experiments with $NO^•$, samples were purged with Ar for thirty minutes and then saturated with $NO^•$ in order to avoid oxidation of $NO^•$ by O_2.[22] The concentration of $NO^•$ in water at 25 °C and 1 atm of the gas was $<2 \times 10^{-3}$ M.

The depletion of $[NH_2OH]$ and dissolved $[NO^•]$, respectively, could not be followed experimentally with the available equipment for concentrations $<1 \times 10^{-3}$ M, and consequently, only a qualitative description of the reactions taking place during the VUV-irradiation of their aqueous solutions is obtained.

Results

VUV-irradiation of aqueous solutions of hydroxylamine

Air or Ar-saturated aqueous solutions containing 3.5×10^{-4} M of NH_2OH were irradiated at 25 °C. Nitrate (NO_3^-), NH_4^+ and smaller amounts of NO_2^- were detected as final reaction products. Fig. 1A and B show the concentration profiles *vs.* irradiation time for the production of NO_3^-, NO_2^- and NH_4^+. The calculated sums of the concentrations of nitrogen containing ions ($[N] = [NO_3^-] + [NO_2^-] + [NH_4^+]$) and pH profiles *vs.* irradiation time are also shown.

Fig. 1A and B show that NH_4^+ and NO_3^- are almost simultaneously produced until constant concentrations are reached after 20 min of irradiation. Higher $[NO_3^-]/[NH_4^+]$ ratios are

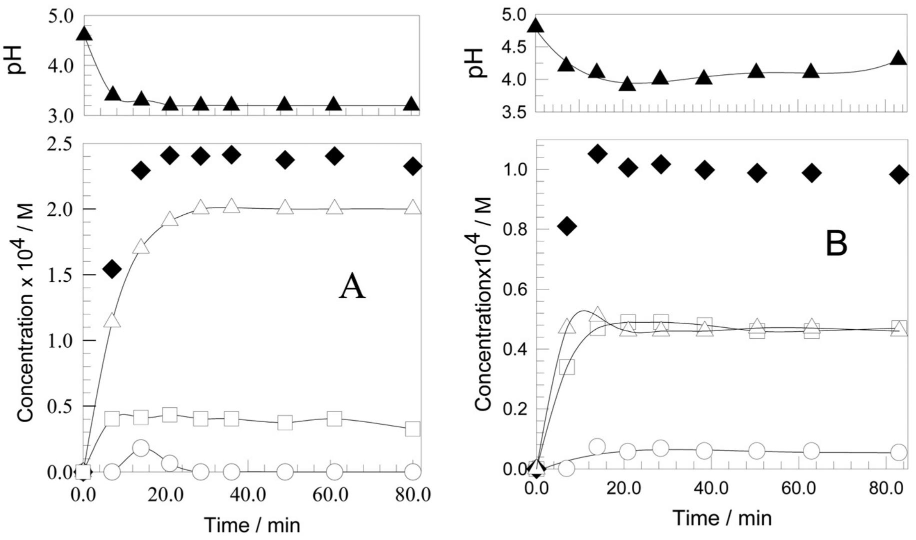

Fig. 1 Concentration profiles *vs*. irradiation time of NO_3^- (△), NO_2^- (○), NH_4^+ (□) and total measured N (◆) during the VUV-irradiation of aqueous solutions containing 3.0×10^{-4} M of NH_3OH^+ at 25 °C in air (A) and Ar- (B) saturated solutions, respectively. Top of figures (A) and (B): pH evolution with irradiation time.

observed in air-saturated experiments. Nitrite (NO_2^-) is also formed, however, its concentration always accounts for less than 10% of the actual concentration of NO_3^-. Under air-saturated conditions, NO_2^- is readily oxidised to NO_3^-. Hence, nitrite (NO_2^-) is an inalienable intermediate in the oxidation of NH_2OH to NO_3^-.

After 20 minutes of irradiation, [N] reaches a constant value depending on the dissolved [O_2]. Final [N] values lower than the starting [NH_3OH^+] strongly indicate the formation of gaseous products during irradiation. The formation of gaseous products is more important for Ar-saturated solutions.

pH profiles *vs*. irradiation time show a pH decrease from initial values of 4.6 to 3.2 or 3.5 depending on the dissolved [O_2], in line with HNO_3 generation.

VUV-irradiation of aqueous solutions containing hydroxylamine and phenol

VUV-irradiation of air and Ar-saturated aqueous solutions containing 6.8×10^{-4} M of C_6H_5OH and 3.3×10^{-4} M of NH_3OH^+ were performed at 25 °C.

Phenol (C_6H_5OH) is readily depleted upon irradiation yielding a mixture of tri and dihydroxybenzenes which finally mineralize to CO_2 and H_2O upon further oxidation, as suggested by the decrease of DOC with irradiation time, see Fig. 2. Depletion rates of DOC are faster in air than in Ar-saturated solutions as also shown in Fig. 2.

Phenol (C_6H_5OH) has a strong effect on the fate of NH_3OH^+. Ammonium (NH_4^+) is the main nitrogen containing inorganic product observed in these experiments, however, smaller amounts of NO_3^- were also formed in experiments in the presence of dissolved O_2. Fig. 3A and B show concentration profiles *vs*. irradiation time for the formation of NO_3^- and NH_4^+ in air and Ar-saturated solutions, respectively. pH profiles *vs*. irradiation time are also shown.

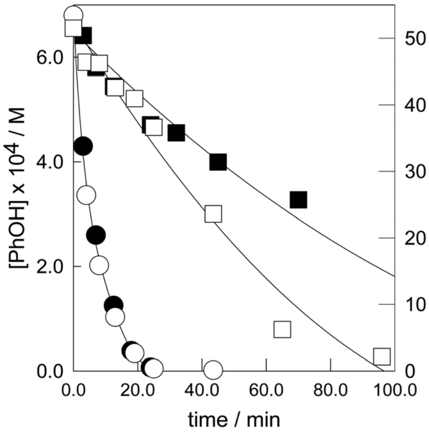

Fig. 2 Depletion of [C_6H_5OH] (○) and DOC (□) *vs*. irradiation time for aqueous solutions containing 6.8×10^{-4} M of C_6H_5OH and 3.3×10^{-4} M NH_3OH^+ at 25 °C in air and Ar-saturated solutions (open and closed symbols, respectively).

The following general observations can be drawn from these figures: Almost quantitative depletion of NH_3OH^+ to yield NH_4^+ is observed in Ar-saturated solutions after more than two hours of irradiation, and quantitative depletion of NH_3OH^+ to NH_4^+ and NO_3^- seems to take place in the presence of dissolved O_2.

pH profiles *vs*. irradiation time show an initial decrease until 15 to 20 min of irradiation, and a subsequent increase at long irradiation times. These profiles might be due to the formation of oxidized organic compounds such as organic acids and their latter elimination from the solution as CO_2.

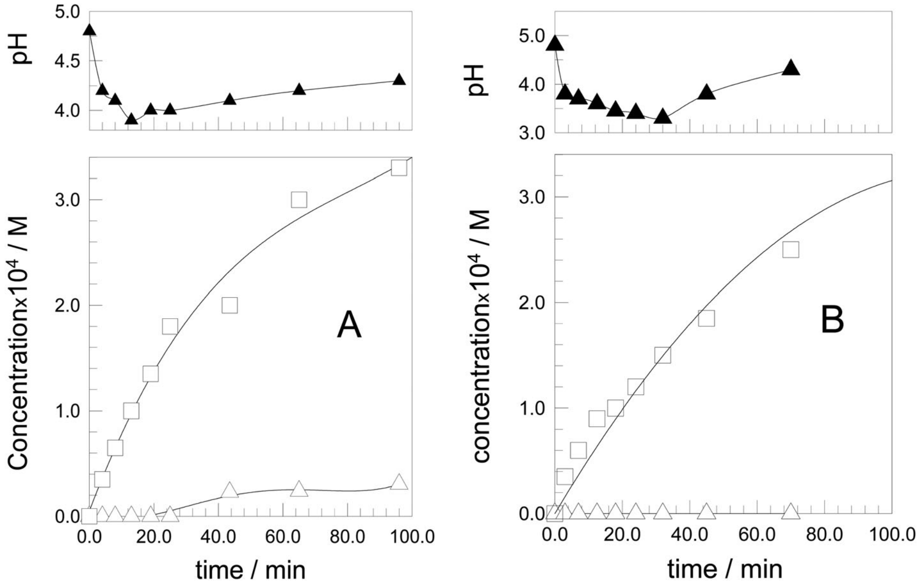

Fig. 3 Concentration profiles *vs.* irradiation time of NO_3^- (△) and NH_4^+ (□) during VUV-irradiation of aqueous solutions containing 3.3×10^{-4} M of NH_3OH^+ and 6.8×10^{-4} M of C_6H_5OH at 25 °C for air (A) and Ar- (B) saturated solutions, respectively. Top of figures (A) and (B): pH evolution with irradiation time.

VUV-irradiation of aqueous solutions of nitric oxide in the presence and absence of phenol

Aqueous solutions containing approximately 2×10^{-3} M of dissolved $NO^•$ were irradiated at 25 °C in the presence and absence of C_6H_5OH (5.3×10^{-4} M). Upon irradiation, phenol is promptly depleted yielding to CO_2 and H_2O after successive oxidation, as supported by the decrease in DOC, see Fig. 4.

Ion analysis of experiments containing dissolved $NO^•$ presents severe experimental errors due to the fact that samples may be coming into contact with air during chromatographic analysis. Dissolved $NO^•$ may react with O_2 to yield NO_2^- and NO_3^- with concentration ratios that strongly depend on particular experimental conditions.[22] Nitrate (NO_3^-) and NO_2^- concentrations thus obtained may not correspond to the real values thus distorting any quantitative analysis. However, some important observations may still be drawn: (i) VUV-irradiation of $NO^•$ leads to the formation of NO_3^- and NO_2^- as reaction products. (ii) However, only experiments in the presence of C_6H_5OH result in the formation of NH_4^+ in concentrations of the order of 3.0×10^{-4} M.

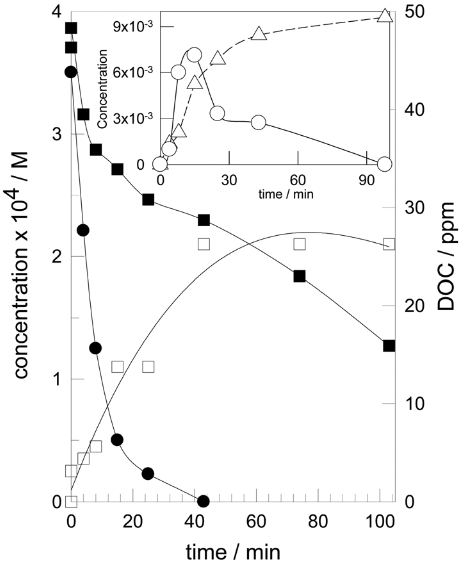

Fig. 4 Depletion of C_6H_5OH (●) and DOC (■) and formation of NH_4^+ (□) *vs.* irradiation time for VUV-irradiation experiments of $NO^•$-saturated aqueous solutions at 25 °C containing 5.3×10^{-4} M of phenol. Insert: Concentration profiles *vs.* irradiation time of NO_3^- (Δ) and NO_2^- (○) in VUV-irradiation experiments of $NO^•$-saturated aqueous solutions at 25 °C.

Discussion

Hydroxylamine (NH_2OH) is a moderately basic compound. In aqueous solution, NH_3OH^+ has $pK_a = 5.9$ (equilibrium (1.1)) and, consequently, it can be considered to be the main reactive species under our experimental conditions with pH values of 3 to 4.[23] Our results show that VUV-photolysis of aqueous solutions of NH_3OH^+ leads to the formation of NO_3^- and NH_4^+ in reactions strongly depending on the presence of O_2. Whereas $[NH_4^+]$ is produced in similar concentrations in both, Ar and air-saturated solutions, $[NO_3^-]$ is highly increased in the presence of O_2. Concentration balances suggest that undefined (gaseous) N-compounds may be produced in Ar-saturated solutions.

Reactions of NH_3OH^+ with $HO^•$ and $H^•$, yielding $NH_2OH^{•+}$ (reactions (1.2) and (1.3))[4,24] and with e^-_{aq} yielding $HO^•$ and

NH_4^+ (reaction (1.4))[24] may initiate the depletion of NH_3OH^+. Reaction (1.4) was also reported to produce amino radicals, $NH_2^•$, and HO^- with lower efficiency (reaction (1.5)).[25] Also, the reaction of NH_3OH^+ with H_2O_2, the latter being formed during the VUV-photolysis of water, leads to the formation of $HO^•$ and $NH_2OH^{•+}$ (reaction (1.6)).[26]

Since $H^•$ and e^-_{aq} efficiently react with molecular oxygen[4] (reactions (1.7) and (1.8)), it may appear at first glance that the formation of NH_4^+ mainly takes place in O_2-free solutions, while the formation of compounds with higher N-oxidation states may take place in both Ar and O_2-purged solutions. However, it should be recalled that the VUV-radiation of 172 nm is totally absorbed within less than 0.1 mm of optical path due to the high absorption cross-section of water and that primary reactive species, $HO^•$, $H^•$ and e^-_{aq} thus generated by the photolysis of water, exhibit very short lifetimes. Therefore, the primary volume of reactions is almost identical to the irradiated fraction of the total reactor volume and the concentration of dissolved oxygen ($[O_2]$) in the volume of primary reactions decreases inversely to the distance from the radiation source.[1,27] Therefore, even under the experimental conditions of strong O_2-introduction into the bulk solution, the volume of primary reactions is characterized by the diffusion controlled reactions of primary reactive species with NH_3OH^+. As a consequence, NH_4^+ is formed by reaction (1.4) independent of the overall $[O_2]$.

Nitrate (NO_3^-) is formed in both Ar and O_2-saturated solutions, though higher concentrations are observed in experiments in the presence of O_2. It may therefore be assumed that $NH_2OH^{•+}$ ($pK_a \approx 4.2$ (equilibrium (1.9))[25]) formed from reactions (1.2), (1.3) and (1.6) could initiate a series of reactions leading to NO_3^- formation.

Hydrogen peroxide (H_2O_2), produced as a secondary species in the VUV-photolysis of water,[28] is reported to react with $NH_2OH^{•+}$ leading to $HO^•$ and nitrosyl hydride (or nitroxyl, HNO, reaction (1.10)).[26] In the presence of O_2, reactions (1.7) and (1.8) lead to the formation of $O_2^{•-}/HO_2^•$ and subsequently to H_2O_2. The reaction of $NHOH^•$, the conjugated base of $NH_2OH^{•+}$, with $O_2^{•-}$ has been reported to lead to NO_2^- (reaction (1.11)),[29] but the recombination of $NHOH^•$ produces N_2 (reaction (1.12)).[25,30] Consequently, in experiments with O_2, reactions (1.10) and (1.11) are favoured with respect to recombination (1.12), in line with the high $[NO_3^-]$ determined in reaction systems containing dissolved O_2. In Ar-saturated solutions, the recombination (1.12) might be favoured compared to reaction (1.10), in line with the higher amounts of undetected N-containing gaseous products and the low $[NO_3^-]$ observed experimentally.

Subsequent reactions of HNO generated from reaction (1.10) are also of importance to the present investigation. Nitroxyl (HNO) is a weak acid (pK_a 11.4) and its deprotonation is spin forbidden.[31] Therefore, in the pH range used in our studies, HNO is the main species which may dimerize to hyponitrous acid (HONNOH) that eliminates water leading to the formation of N_2O (reactions (1.13)).[32] However, the reaction of singlet HNO with $HO^•$ to produce higher oxidized N-containing species (reaction (1.14)) is in line with the reported reactions for nitroxyl free radicals ($NO^•$)[33] and cannot be discarded. Finally, the oxidation of $NH_2^•$ by O_2 (reaction (1.15)) is an efficient reaction path leading to higher oxidation states of nitrogen-containing compounds.[34] Moreover, the reaction of $NH_2^•$ with NH_3OH^+ has been postulated to yield NH_4^+ and $NHOH^{•+}$ (reaction (1.16)).[25]

Our studies clearly indicate that organic substrates have an important impact on the quantitative reduction of NH_3OH^+ to NH_4^+. To understand the reaction mechanisms, the reactions of phenol (C_6H_5OH) with the primary reactive species of the VUV-photolysis of water should be discussed. The reactions of phenol with $HO^•$ and $H^•$ were postulated as the primary reactions initiating the depletion of phenol and yielding phenoxyl ($C_6H_5O^•$) and hydroxycyclohexadienyl ($(HO)C_6H_6^•$) radicals (reactions (2.1) and (2.2)), respectively.[4,35,36] The latter radicals may undergo further reaction with O_2, $O_2^{•-}$, and H_2O_2 to yield highly oxidized intermediates and products leading to C_6H_5OH mineralization. The reaction of e^-_{aq} with C_6H_5OH has a much lower rate constant and is not competitive (reaction (2.3)).[1,4]

Considering NH_3OH^+ and C_6H_5OH reactions with the primary reactive species of the VUV-photolysis of water (reactions (1.2) to (1.5) and (2.1) to (2.3), respectively), one possible effect of the presence of C_6H_5OH would be that of competitively and efficiently trapping $HO^•$ and $H^•$. Under such conditions, mainly reactions involving e^-_{aq} (reaction (1.4)) and, with less efficiency, reaction (1.5) would be of significance for NH_3OH^+ depletion in the presence of phenol. Reaction (1.4) and the combination of reactions (1.5) and (1.16) lead to the formation of NH_4^+, in line with the experimental observations. The formation of smaller amounts of NO_3^- at longer irradiation times and only in the presence of O_2 may be rationalized as a consequence of the competition between reactions (1.15) and (1.16) favouring $NH_2^•$ oxidation in the presence of O_2 and a smaller amount of $[NH_3OH^+]$. Reactions between reducing organic radicals and NH_3OH^+ yielding oxidized organic intermediates and $NH_2^•$ (reaction (3)) are thought to contribute to NH_3OH^+ depletion, as reported for $(CH_3)_2C^•OH$ radicals[37]

$$NH_3OH^+ + (CH_3)_2C^•OH \rightarrow NH_2^• + (CH_3)_2CO + H_3O^+ \quad (3)$$

The interpretation of the results obtained with $NO^•$ is more complex because of the experimental limitations. However, the fact that VUV-photolysis of aqueous solutions of $NO^•$ leads to NH_4^+ only in the presence of C_6H_5OH is by itself an important observation.

Both, e^-_{aq} and $H^•$, reduce $NO^•$ to yield the ground-state triplet $^3NO^-$ and singlet ^1HNO (reactions (3.1) and (3.2), respectively), while the reaction with $OH^•$ yields NO_2^- (reaction (3.3)).[4,38] Subsequent reactions of $^3NO^-$ and ^1HNO with $NO^•$ have been shown to ultimately yield N_2O and NO_2^- (reactions (3.4) and (3.5), respectively).[38] Therefore, in the absence of organic matter, VUV-photolysis of aqueous solutions of $NO^•$ is expected to lead to the formation of N_2O and NO_2^-. Nitrite

(NO_2^-) may be ultimately oxidized to NO_3^-, in line with our experimental observations.

Considering reactions of $NO^{\bullet}$ and C_6H_5OH with the primary reactive species of the VUV-photolysis of water (reactions (2.1) to (2.3) and (3.1) to (3.3), respectively), the presence of C_6H_5OH in the reaction system will lead to an efficient trapping of $HO^{\bullet}$ and, to a lower extent, of $H^{\bullet}$. Under such conditions, mainly reactions involving e^-_{aq} and $H^{\bullet}$ (reactions (3.1) and (3.2)) would be of significance for the depletion of $NO^{\bullet}$ in the presence of phenol in accord with the NH_3OH^+–C_6H_5OH systems. Also, $NO^{\bullet}$ slowly reacts with phenol leading to the formation of ^1HNO and $C_6H_5O^{\bullet}$ (reaction (3.6)).[39] Further reactions of ^1HNO with $NO^{\bullet}$ are very efficient and lead to the formation of $N_2O_2^-/HN_2O_2$ compounds of unknown structure and reactivity which ultimately decompose to NO_2^- and N_2O.[38] Therefore, the formation of NH_4^+ in C_6H_5OH containing reaction systems might be related to the reactions of ^1HNO with organic compounds and/or radicals formed during C_6H_5OH mineralization.

^1HNO is a relatively strong electrophile, as reported for the reaction with thiols leading ultimately to the oxidation of thiolates to disulphides and to the reduction of ^1HNO to $HNOH^{\bullet}$.[40] Therefore, it may be assumed that similar reactions of ^1HNO with radicals of moderate reductive reactivity generated on the pathway of the mineralization of phenol (denoted as $RO^{\bullet}$) may lead to the formation of hydroxyl amine radicals ($H_2NOH^{\bullet+}$/$HNOH^{\bullet}$, $pK_a = 4.2$, reaction (1.9)) and oxidized products (P_{ox}, reaction (3.7)). Further reduction of $H_2NOH^{\bullet+}$/HNOH yields NH_3OH^+/NH_2OH (reaction (3.8)), which may undergo subsequent reducing reactions in the presence of C_6H_5OH leading ultimately to the production of NH_4^+ (*vide supra*).

Conclusions

As discussed in the Introduction and postulated earlier,[9–11] NH_3OH^+ and $NO^{\bullet}$ might be key reaction intermediates during the VUV-photochemical reduction of aqueous NO_3^- and NO_2^- to NH_4^+ and during the corresponding oxidation of NH_4^+ to NO_3^-. Indeed, the experiments presented here show that VUV-irradiation of aqueous solutions of NH_3OH^+ yields quantitative amounts of NH_4^+ as final products only in the presence of organic matter while the formation of N-containing gaseous products such as N_2 or N_2O, NO_2^- and NO_3^- as final products was observed in the absence of organic substrates. A similar observation applies for $NO^{\bullet}$ though, because of experimental limitations, we were not able to probe a quantitative conversion of $NO^{\bullet}$ to NH_4^+ in the presence of organic matter. Our present results corroborate our previous suggestions and define the added organic matter as a necessary sacrificial electron donor.[9–11]

According to the previous reports and to the evidence herein presented, NO_3^-, $NO_2^{\bullet}$, NO_2^-, $NO^{\bullet}$, ^1HNO, NH_2OH/NH_3OH^+ and NH_4^+ are interrelated by many redox reactions, where pH, availability of electrons, presence of proton or hydrogen donors and O_2 determine their occurrence and importance, as indicated by the experimental fact that VUV-irradiation of aqueous solutions of any of these substrates yields NH_4^+ and/or NO_3^- as final products, depending on the particular experimental conditions. Moreover, it is interesting to note that NO_3^- reduction to NH_4^+ by $H^{\bullet}$ and e^-_{aq} seems to be an eight electron sequence implying a complex manifold of predominantly irreversible reactions involving $NO_2^{\bullet}$, NO_2^-, $NO^{\bullet}$ and NH_2OH/NH_3OH^+ as intermediates. These intermediates, as well as ONO_2H and O_2NO_2H formed in the presence of

Table 1 Manifold of reactions depleting NH_3OH^+ during VUV-irradiation of aqueous solutions. See text for the corresponding literature data. Reactions marked in grey are those involving the primary reactive species of the VUV-photolysis of water and may already occur in the primary volume of reactions

	Reaction rates	
$NH_3OH^+ \rightleftarrows NH_2OH + H^+$	$pK_a = 5.9$	(1.1)
$NH_3OH^+ + HO^{\bullet} \rightarrow NH_2OH^{\bullet+} + H_2O$	$<5 \times 10^7\ M^{-1}\ s^{-1}$	(1.2)
$NH_3OH^+ + H^{\bullet} \rightarrow NH_2OH^{\bullet+} + H_2$	$3.6 \times 10^5\ M^{-1}\ s^{-1}$	(1.3)
$NH_3OH^+ + e^-_{aq} \rightarrow NH_3 + HO^{\bullet}$	$1.1 \times 10^{10}\ M^{-1}\ s^{-1}$	(1.4)
$NH_3OH^+ + e^-_{aq} \rightarrow NH_2^{\bullet} + HO^-$	$9.2 \times 10^8\ M^{-1}\ s^{-1}$	(1.5)
$H_2O_2 + H_3NOH^+ \rightarrow H_2NOH^{\bullet+} + HO^{\bullet} + H_2O$		(1.6)
$e^-_{aq} + O_2 \rightarrow O_2^{\bullet-}$	$2 \times 10^{10}\ M^{-1}\ s^{-1}$	(1.7)
$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet}$	$1 \times 10^{10}\ M^{-1}\ s^{-1}$	(1.8)
$NH_2OH^{\bullet+} \rightleftarrows NHOH^{\bullet} + H^+$	$pK_a = 4.2$	(1.9)
$H_2O_2 + H_2NOH^{\bullet+} \rightarrow HNO + HO^{\bullet\bullet} + H_3O^+$		(1.10)
$O_2^{\bullet-} + HNOH^{\bullet} \rightarrow NO_2^- + H_2O$		(1.11)
$NHOH^{\bullet} + NHOH^{\bullet} \rightarrow N_2 + 2H_2O$	$2.4 \times 10^8\ M^{-1}\ s^{-1}$	(1.12)
$HNO + HNO \rightarrow HONNOH \rightarrow N_2O + H_2O$	$8 \times 10^6\ M^{-1}\ s^{-1}$	(1.13)
$HNO + HO^{\bullet} \rightarrow$ oxidized N-compounds		(1.14)
$NH_2^{\bullet} + O_2 \rightarrow NH_2O_2^{\bullet}$	$3 \times 10^8\ M^{-1}\ s^{-1}$	(1.15)
$NH_2^{\bullet\bullet} + NH_3OH^+ \rightarrow NHOH^{\bullet} + NH_4^+$		(1.16)

Table 2 Manifold of reactions depleting phenol (C_6H_5OH) by the primary reactive species of the VUV-photolysis of water. See text for the corresponding literature data

	Reaction rates	
$C_6H_5OH + HO^{\bullet} \rightarrow C_6H_5O^{\bullet}$	$1 \times 10^{10}\ M^{-1}\ s^{-1}$	(2.1)
$C_6H_5OH + H^{\bullet} \rightarrow (HO)C_6H_6^{\bullet}$	$2\text{–}7 \times 10^9\ M^{-1}\ s^{-1}$	(2.2)
$C_6H_5OH + e^-_{aq} \rightarrow C_6H_5(OH)^{\bullet-}$	$1.6 \times 10^7\ M^{-1}\ s^{-1}$	(2.3)

Table 3 Manifold of reactions depleting $NO^{\bullet}$ during VUV-irradiation of its aqueous solutions. See text for the corresponding literature data. Reactions marked in grey are those involving the primary reactive species of the VUV-photolysis of water and may already occur in the primary volume of reactions

	Reaction rates	
$NO^{\bullet} + e^-_{aq} \rightarrow {}^3NO^-$	$2.3 \times 10^{10}\ M^{-1}\ s^{-1}$	(3.1)
$NO^{\bullet} + H^{\bullet} \rightarrow {}^1HNO$	$1.1 \times 10^{10}\ M^{-1}\ s^{-1}$	(3.2)
$NO^{\bullet} + HO^{\bullet} \rightarrow NO_2^- + H^+$	$2 \times 10^{10}\ M^{-1}\ s^{-1}$	(3.3)
${}^3NO^- + NO^{\bullet}(+NO^{\bullet}) \rightarrow N_2O + NO_2^-$		(3.4)
${}^1HNO + NO^{\bullet}(+NO^{\bullet}) \rightarrow N_2O + HNO_2$		(3.5)
$NO^{\bullet} + C_6H_5OH \rightarrow {}^1HNO + C_6H_5O^{\bullet}$	$3.2\ M^{-1}\ s^{-1}$	(3.6)
${}^1HNO + RO^{\bullet} \rightarrow H_2NOH^{\bullet+}/HNOH^{\bullet} + Pox$		(3.7)
$H_2NOH^{\bullet+}/HNOH^{\bullet} + e^-_{aq} + H^+ \rightarrow NH_3OH^+/$ NH_2OH		(3.8)

dissolved O_2, might also be involved in the oxidation of NH_4^+ to NO_3^- by $HO^•$.[11] It should be emphasized here that all reactions proposed in the sequence of reactions depicted in Tables 1–3 have been investigated experimentally and thoroughly studied by different authors. Therefore, the proposed sequences of reduction and oxidation comprise a possible mechanism strongly based on the experimental facts.

VUV-photolysis of aqueous solutions is reported to efficiently mineralize organic compounds due to the formation of $H^•$, $HO^•$ and e^-_{aq} as primary reactive intermediates.[1,41] Herein, we further support that VUV-photolysis of residual waters containing *N*-oxides and their derivatives lead to the formation of NH_4^+ and complete degradation of the organic contaminants, avoiding the formation of gaseous nitrogen compounds as observed here in the presence of phenol.

Conflicts of interest

There are no conflicts to declare.

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