

Vacuum UV photolysis of aqueous solutions of nitrate. Effect of organic matter

II. Methanol¹

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Abstract

Vacuum UV irradiation of aqueous solutions containing NO_3^- and methanol results in the simultaneous mineralization of methanol and depletion of NO_3^- , yielding NO_2^- and NH_4^+ . Moreover, the depletion rates of NO_3^- are two to three orders of magnitude faster in the presence of methanol than in corresponding experiments with pure nitrate solutions.

A possible mechanism is discussed in which the reactions of NO_2^{\cdot} and NO^{\cdot} with the radicals formed during methanol oxidation are proposed to be mainly responsible for the overall behaviour observed. The reactions between these intermediates and NO^{\cdot} seem to follow reduction pathways leading to NH_4^+ formation, whereas a one-electron reduction yielding N_2O is observed in the absence of organic material. The formation of CNO^- as an intermediate product is a clear indication that reactions between nitrogen-containing ions, carbon-centred radicals and/or methanol and its oxidation products occur. The present results are in complete agreement with previously reported data concerning the enhanced reduction of NO_3^- in the presence of phenol, thus suggesting that the behaviour observed may probably be generalized to most organic substrates.

Keywords: Vacuum UV photolysis; Nitrate; Methanol

1. Introduction

Water undergoes homolysis into hydrogen atoms, hydroxyl radicals and, with much less efficiency, hydrated electrons on vacuum UV excitation [1]. Vacuum UV photolysis of aqueous nitrate solutions under different experimental conditions has shown that hydrogen atoms and hydrated electrons initiate a series of reactions partially depleting NO_3^- , N_2O being one of the products [2].

In addition, investigations on the vacuum UV irradiation of aqueous solutions containing NO_3^- and phenol have shown the simultaneous mineralization of phenol and depletion of NO_3^- , yielding mainly NH_4^+ and, to a lesser extent, NO_2^- [3]. A possible mechanism was discussed in which reactions of NO_2^{\cdot} and NO^{\cdot} , formed by depletion of NO_3^- , with phenol and benzyloxy radicals were proposed to be primarily responsible for the overall behaviour observed. Reactions between these organic substrates and NO^{\cdot} seem to favour reduction leading to NH_4^+ formation, whereas one-

electron reduction yielding N_2O is observed in the absence of organic substrates.

In order to determine whether reduction reactions leading to NH_4^+ formation are also favoured by intermediates formed during the oxidative degradation of small aliphatic molecules, investigations on the vacuum UV irradiation of aqueous solutions of methanol and nitrate were undertaken. Methanol was chosen because its oxidative degradation pathways are well reported in the literature [4].

2. Experimental details

2.1. Materials

KNO_3 and methanol (Merck, p.a. quality) were used without further purification. Pure water was provided by a UGH II system (Millipore, greater than $18 \text{ m}\Omega \text{ cm}^{-1}$, less than 20 ppb of organic carbon).

2.2. Preparative irradiation equipment

2.2.1. Light source

A cylindrical Xe excimer lamp (length, 25 cm; external diameter, 3 cm) (ABB, Baden, Switzerland) emitting at 172

¹ Dedicated to Prof. Dr. Stefan Paszyc, Adam Mickiewicz University, Poznan, Poland, on the occasion of his 70th birthday.

nm (MHW, 12 nm) was used [5]. The lamp was operated with an electrical power of 150 W and a frequency of 200–220 kHz by a high frequency, high voltage ENI model HPG-2 power supply.

2.2.2. Photochemical reactor

The photochemical reactor was of annular geometry (volume, 220 ml; DEMA, Bornheim-Roisdorf, Germany) adapted for the Xe excimer lamp and fitted with a magnetic circulation pump and an external grounded electrode [6]. Experiments were performed maintaining the solutions at 25 °C.

2.3. Analytical methods

The analysis of methanol was performed by gas chromatography (GC; Hewlett-Packard gas chromatograph model 5890 series II with flame ionization detector (FID); column, Hewlett-Packard HP-1 fused silica capillary column; cross-linked phase of 100% methyl silicone). Anion analysis was performed by ion chromatography (IC; Hewlett-Packard liquid chromatograph model 1050 (Ti series), with multi-wavelength detection and a Hewlett-Packard anion chromatography system). Detection limits were normally 1×10^{-6} M. Evolution of NH_4^+ was followed with NH_4^+ ion selective electrodes (Ecotest-110, ECONIX Ltd., Moscow, Russia) with a detection limit of 1×10^{-5} M. Dissolved organic carbon (DOC) 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 Methrom pH meter model E512.

2.4. Experimental procedure

The general procedure followed is strictly the same as that described in Refs. [2] and [3]. In order to correlate the results with those found in experiments with aqueous phenol solutions, the concentration of methanol was chosen for an initial DOC value of approximately 50 ppm. Taking into account that the Xe excimer lamps used for irradiating the aqueous solutions exhibit an emission band at 172 nm (MHW, 12 nm) and that the linear absorption coefficient of water in this spectral range varies from 6000 to 200 cm^{-1} , the photolysis of water is the main photochemical reaction in aqueous systems containing concentrations of nitrate and methanol of the order of 1×10^{-2} M or lower.

3. Results

Air- or argon-saturated aqueous solutions containing 4.2×10^{-3} M of methanol and 3.3×10^{-4} M of NO_3^- were irradiated at 25 °C. Methanol is readily depleted on irradiation. Oxidation of methanol yields CO_2 and H_2O as shown by the decrease in DOC with irradiation time, and the deple-

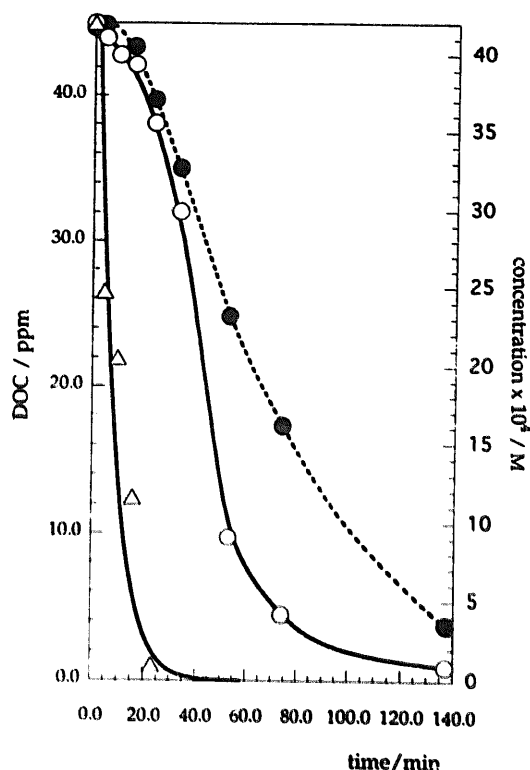


Fig. 1. Depletion of methanol concentration vs. irradiation time for air-saturated aqueous solutions containing 4×10^{-3} M of methanol and 2.7×10^{-3} M of NO_3^- at approximately 25 °C (Δ). Depletion of DOC with irradiation time for air-saturated (○) and argon-saturated (●) aqueous solutions containing 4×10^{-3} M of methanol and 2.7×10^{-4} M of NO_3^- at 25 °C.

tion rates of DOC depend on the concentration of dissolved oxygen (Fig. 1).

The addition of methanol modifies the depletion rate and fate of NO_3^- during the vacuum UV irradiation of corresponding aqueous solutions. The observed behaviour also depends on the presence of dissolved oxygen but, in all cases, NO_2^- , CNO^- and NH_4^+ are the nitrogen-containing ions produced. Figs. 2(a) and 2(b) show the concentration profiles of NO_3^- , NO_2^- , CNO^- and NH_4^+ vs. irradiation time for air- and argon-saturated solutions respectively. The calculated total nitrogen concentrations ($[\text{NT}]_t = [\text{NO}_3^-]_t + [\text{NO}_2^-]_t + [\text{CNO}^-]_t + [\text{NH}_4^+]_t$) vs. irradiation time and the corresponding pH profiles are also given. In general, a similar trend to that reported for the effect of phenol on NO_3^- depletion [3] is found.

- (1) Irradiation experiments performed with argon-saturated solutions yield the quantitative depletion of NO_3^- , whereas only partial depletion of NO_3^- is observed in experiments with air-saturated solutions. In both cases, the initial depletion rates of nitrate are slower, but almost of the same order of magnitude, as those of methanol.
- (2) NO_2^- is formed immediately after irradiation is started, and its concentration profile follows qualitatively that of NO_3^- , always accounting for less than 10% of the actual concentration of NO_3^- . NO_2^- is therefore an

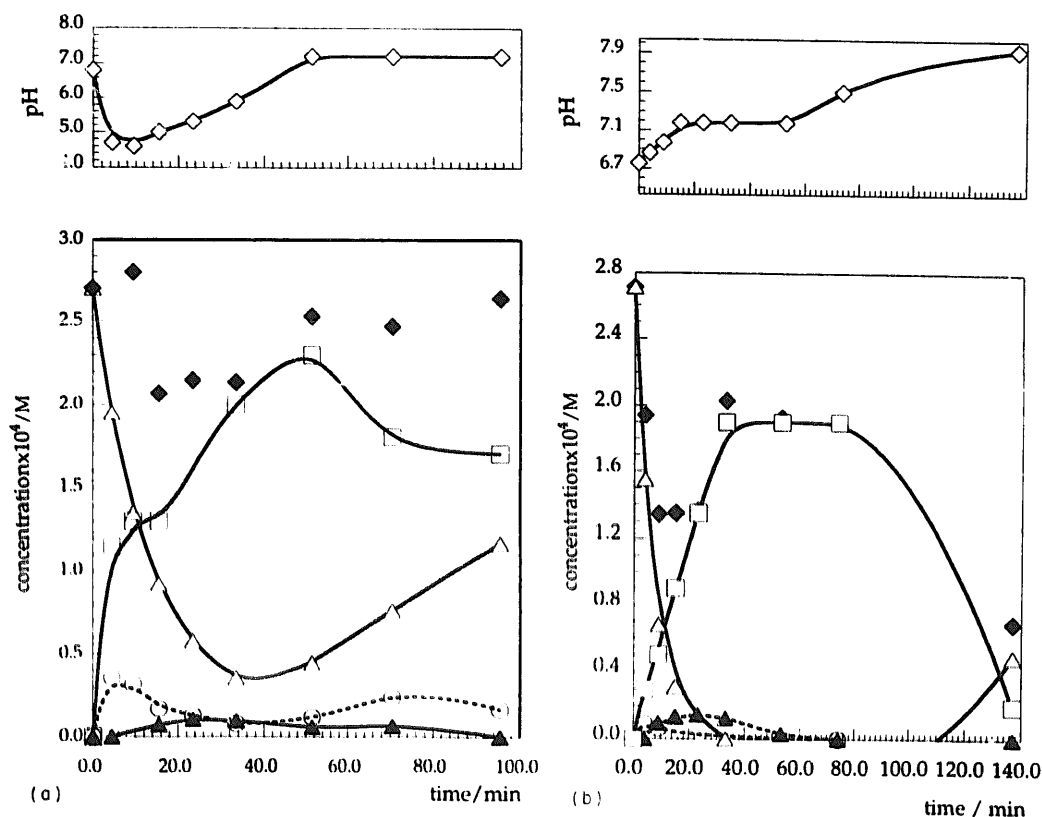


Fig. 2. (a) Concentration profiles vs. irradiation time of NO_3^- (Δ), NO_2^- (\circ), NH_4^+ (\square), CNO^- (\blacktriangle) and $[\text{NT}]$ (\blacklozenge) during vacuum UV irradiation of air-saturated aqueous solutions containing 4.5×10^{-3} M of methanol and 2.7×10^{-4} M of NO_3^- at 25 °C. Top of figure: pH (\diamond) evolution with irradiation time. (b) Concentration profiles vs. irradiation time of NO_3^- (Δ), NO_2^- (\circ), NH_4^+ (\square), CNO^- (\blacktriangle) and $[\text{NT}]$ (\blacklozenge) during vacuum UV irradiation of argon-saturated aqueous solutions containing 4.5×10^{-3} M of methanol and 2.7×10^{-4} M of NO_3^- at 25 °C. Top of figure: pH (\diamond) evolution with irradiation time.

intermediate product of the reduction of (and oxidation to) NO_3^- .

- (3) The formation of CNO^- as an intermediate product is observed. It is mineralized in accordance with previous results [7].
- (4) NO_3^- depletion leads to the formation of NH_4^+ . The reduction is, however, not quantitative as NH_4^+ is partially re-oxidized to NO_3^- at long irradiation times.
- (5) $[\text{NT}]_t$ decreases, reaching a minimum value after approximately 10 min of irradiation; it then increases until NH_4^+ reaches a maximum concentration. The minimum in the $[\text{NT}]_t$ profiles clearly indicates the presence of nitrogen-containing intermediates during NO_3^- reduction to NH_4^+ , which our analyses of NH_4^+ , NO_3^- , NO_2^- and CNO^- do not take into account. However, as $[\text{NT}]_t$ returns to its original value at long irradiation times in air-saturated solutions (Fig. 2(a)), we may deduce that all nitrogen-containing intermediates transform into nitrogen-containing ions as final products, the production of N_2O and/or N_2 remaining negligible. The observed re-oxidation of NH_4^+ to NO_3^- should be noted. Interestingly, the pH profile during the irradiation of aerated solutions rapidly decreases to a minimum value after approximately 10 min of irradiation, and then steadily increases to almost its original value at longer

irradiation times. In argon-saturated solutions, partial re-oxidation of NH_4^+ to NO_3^- is observed at long irradiation times, and $[\text{NT}]_t$ decreases steadily (Fig. 2(b)). The decrease in $[\text{NT}]_t$ signals the elimination of nitrogen from the corresponding substrates and intermediates and the formation of gaseous products purged from the solution. The pH evolution during the irradiation of these solutions shows a steady increase from values of pH 6 to pH 8 at long irradiation times. The fact that the pH values of these solutions increase while $[\text{NT}]_t$ is decreasing has already been observed during the irradiation of solutions containing phenol and nitrate [3].

4. Discussion

The vacuum UV photolysis of water produces H^\bullet , HO^\bullet and hydrated electrons. The photolysis of water is the main photochemical reaction in aqueous systems containing organic and/or inorganic substrates [2,3,6-8], and the depletion of methanol is due to reactions with these primary radical intermediates. As indicated in Table 1, reactions between methanol and hydrogen atoms (Eq. (1.2)) or hydrated electrons (Eq. (1.3)) are not very efficient [9] and, consequently, cannot contribute significantly to the overall depletion rate of

Table 1
Reactions of methanol during the vacuum UV irradiation of aqueous solutions

Reaction	Rate constant ($M^{-1} s^{-1}$)	Number
$HO^{\bullet} + CH_3OH \rightarrow \cdot CH_2(OH) + H_2O$	8×10^8	(1.1)
$H^{\bullet} + CH_3OH \rightarrow \cdot CH_2(OH) + H_2$	5×10^6	(1.2)
$e_{aq}^{-} + CH_3OH \rightarrow (CH_2O)^{\bullet-} + H^{\bullet}$	$< 10^4$	(1.3)
$O_2 + \cdot CH_2(OH) \rightarrow CH_2O + HO_2^{\bullet}$		(1.4)
$HO^{\bullet} + CH_2O \rightarrow \cdot CHO + H_2O$	7×10^8	(1.5a)
$HO^{\bullet} + CH_2(OH)_2 \rightarrow \cdot CH(OH)_2 + H_2O$		(1.5b)
$O_2 + \cdot CH(OH)_2 \rightarrow \cdot O_2CH(OH)_2$	4.5×10^9	(1.6a)
$\cdot O_2CH(OH)_2 \rightarrow HCO_2H + HO_2^{\bullet}$		(1.6b)
$\cdot CH_2(OH) + \cdot C^{\bullet}H_2(OH) \rightarrow CH_3OH + CH_2O$	1.5×10^9	(1.7)
$\cdot CH(OH)_2 + \cdot CH(OH)_2 \rightarrow CH_2(OH)_2 + HCO_2^{\bullet} + H^{\bullet}$	3.6×10^8	(1.8)

methanol. The reaction of methanol with HO^{\bullet} (Eq. (1.1)) yields $\cdot CH_2(OH)$ radicals, which efficiently react with molecular oxygen to yield formaldehyde (Eq. (1.4)). Further attack of hydroxyl radicals on formaldehyde yields $\cdot CHO$ radicals (Eq. (1.5a)) or their hydrated form $\cdot CH(OH)_2$ (Eq. (1.5b)), which are oxidized by molecular oxygen to formic acid (Eq. (1.6)). Attack of hydroxyl radicals on formic acid eventually leads to the final formation of carbon dioxide [4,9].

In argon-saturated solutions, pathways leading to methanol oxidation should involve reactions independent of the presence of molecular oxygen. Recombination reactions between radicals (Eqs. (1.7) and (1.8)) are very efficient at high radical concentrations [10]; this is found in our experiments due to the extreme heterogeneity between the irradiated and non-irradiated volumes in the photochemical reactor [11].

The vacuum UV irradiation of methanol solutions in the presence of NO_3^- results in the simultaneous depletion of NO_3^- to NO_2^- and NH_4^+ , and complete degradation of the organic matter to CO_2 and H_2O .

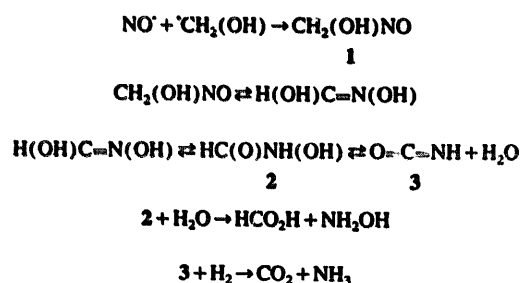
As reported previously [2,3], hydrogen atoms and hydrated electrons produced by the photolysis of water induce a series of reduction reactions partially depleting nitrate from aqueous solutions: NO_3^- reacts efficiently with hydrated electrons and hydrogen atoms yielding $(NO_3)^{\bullet-}$ and $NO_2H^{\bullet-}$, the latter decomposing into NO_2^{\bullet} and hydroxide anion. In the absence of organic substrates, NO_2^{\bullet} in aqueous solution disproportionates into NO_3^- and NO_2^- .

Under conditions of continuous irradiation, NO_2^- reacts with hydrated electrons and hydrogen atoms yielding $(NO_2^{\bullet})^{\bullet-}$ and $NO_2H^{\bullet-}$, the latter decomposing into NO^{\bullet} and

hydroxide anion. The one-electron reduction of NO^{\bullet} in aqueous solution produces NO^- and NOH . Dimerization of NOH yields hyponitrous acid which readily decomposes in water to N_2O and hydroxide anions. However, in the presence of organic substrates, further reduction of NO^{\bullet} will lead to NH_4^+ , but the corresponding reaction mechanisms are not yet resolved.

NO_2^{\bullet} and NO^{\bullet} are key intermediates in the reactions (Table 2). NO_2^{\bullet} is a strong one-electron oxidant in the aqueous phase, the oxidation of organic compounds competing favourably with its disproportionation to NO_2^- and NO_3^- even at low concentrations of organic substrates [12]. Oxidation (Eq. (2.1)) is of particular interest, as it concerns methanol degradation independent of molecular oxygen producing formaldehyde and nitrite [9d]. Extensive investigations of the reactions between NO^{\bullet} and organic radicals have been performed mainly in the gas phase and in liquid media involving organic solvents [13]. Reactions between NO^{\bullet} and $\cdot CH_2(OH)$ or $\cdot CHO$ radicals (Eqs. (2.2) and (2.3)) have been reported in the gas phase [13,14]. Reaction (2.3) explains the presence of CNO^- , an oxidation product of CN^- [7]. The formation of CNO^- during the catalytic reduction of NO^{\bullet} by hydrocarbons in the gas phase has also been reported [15].

Similar reactions will also take place in the aqueous phase, although the nature and distribution of the final products may be different because of the particular properties of water as a solvent. A possible reaction mechanism is shown in Scheme 1



Scheme 1. Postulated reaction mechanism between NO^{\bullet} and $\cdot CH_2(OH)$ radicals.

Table 2
Key reactions between NO_2^{\bullet} , NO^{\bullet} and organic radicals generated during methanol oxidation by HO^{\bullet} radicals

Reaction	Number
$NO_2^{\bullet} + \cdot CH_2(OH) \rightarrow CH_2O + NO_2^- + H^{\bullet}$	(2.1) ^a
$NO^{\bullet} + \cdot CH_2(OH) \rightarrow CH_2O + HNO$	(2.2) ^b
$NO^{\bullet} + \cdot CHO \rightarrow HC(O)NO + HCN + O_2$	(2.3) ^b

^a Aqueous phase.

^b Gas phase.

Table 3
Reactions to be considered in the presence of dissolved oxygen

Reaction	Number
$H^+ + O_2 \rightarrow HO_2^*$	(3.1)
$e_{aq}^- + O_2 \rightarrow O_2^{*-}$	(3.2)
$HO_2^* + NO^* \rightarrow ONOOH$	(3.3)
$HO_2^* + NO_2^* \rightarrow O_2NOOH$	(3.4)

where we postulate a combination of NO^* and $^*CH_2(OH)$ radicals to yield an unstable compound 1 which may undergo isomerization to the corresponding hydroxamic acid 2. There may be a subsequent elimination of water to produce isocyanic acid 3. Both hydroxamic and isocyanic acid readily hydrolyse in aqueous solution to formic acid and hydroxylamine and CO_2 and NH_3 respectively [16]. This reaction scheme is in agreement with our results, since NH_4^+ and CO_2 are confirmed as final reaction products, formic acid is an intermediate of the oxidative degradation of methanol and hydroxylamine is a precursor in the reduction of nitrogen-containing ions to NH_4^+ [17].

Nitrate and methanol depletion rates are of the same order of magnitude and two or three orders of magnitude faster than the depletion of nitrate in corresponding experiments in the absence of organic substrates. The higher rates observed in the presence of organic compounds may be due to an efficient depletion of NO_2^* and NO^* concentrations by organic radicals, thus eliminating competition by oxidation reactions leading to NO_3^- [2,3]. Under such conditions, the depletion rates of NO_3^- should be controlled by the rates of reactions with H^+ and hydrated electrons.

Molecular oxygen diminishes the efficiency of NO_3^- depletion (Table 3) mainly because molecular oxygen competes efficiently for H^+ radicals (Eq. (3.1)) and hydrated electrons (Eq. (3.2)), and the high concentrations of HO_2^* and O_2^{*-} formed in oxygen-saturated solutions compete with organic substrates for NO^* and NO_2^* yielding peroxyxynitrite (Eq. (3.3)) and peroxyxynitrate (Eq. (3.4)), which finally react to give NO_3^- and NO_2^- respectively. The postulated reactions are in accordance with the experimental observation that the pH evolution strongly depends on the presence or absence of dissolved oxygen, as more acidic intermediates are formed in the presence of oxygen.

Since the postulated reaction scheme is extremely complex, the analysis of our experimental results by simple kinetic models is impossible. In an attempt to understand qualitatively in more detail the observed experimental kinetic behaviour, a computer program conceived to simulate ab initio the reaction kinetics during vacuum UV irradiation of aqueous solutions of nitrate at 20–25 °C was used [2].

The vacuum UV irradiation of air-saturated aqueous solutions containing methanol and nitrate was computer simulated at the initial stages of irradiation, where the depletion of nitrate is less than 10% and where mainly $^*CH_2(OH)$ radicals must be taken into account. The oxidative reaction pathways of methanol to formaldehyde are well reported in

the literature; the reactions involved and the corresponding kinetic parameters are shown in Table 1. In order to account for the interaction between nitrogen oxides and organic substrates, reaction (2.3) and a hypothetical reaction (in the aqueous phase) between NO^* and $^*CH_2(OH)$ leading to nitrogen-containing products which can participate in the reduction manifold producing NH_4^+ were considered. Radical reactions whose kinetic parameters are not reported in the literature were assumed to be diffusion limited in agreement with the reported values for related reactions. These reactions are added to the set of 64 reactions involved during the vacuum UV irradiation of pure aqueous solutions of nitrate [2]. The formation rates of HO^* , H^+ and hydrated electrons were assumed to be of the order of 0.36, 0.33 and 0.03 $M s^{-1}$ respectively for an incident photon flux density P_0 of 7.5×10^{-6} einstein s^{-1} emitted by the Xe excimer light source at 172 nm. Fig. 3 shows the results of simulated experiments for vacuum UV irradiated solutions containing nitrate, methanol and $[O_2]_0 = 2.5 \times 10^{-4}$ M (curve a). The results of simulated experiments with pure nitrate solutions are included for comparison (curve b). In agreement with our experimental results, the simulated depletion of nitrate is faster in irradiated solutions containing organic substrates, supporting the proposed reaction scheme.

The reduction of NO_3^- to NH_4^+ is an eight-electron reduction process involving several intermediates: NO_2^- , NO^* and NH_2OH leading to the formation of N_2O and/or NH_4^+ depending on the experimental conditions [17]. Our experimental results strongly indicate that reactions between organic radicals and NO^* favour a multiple electron reduction

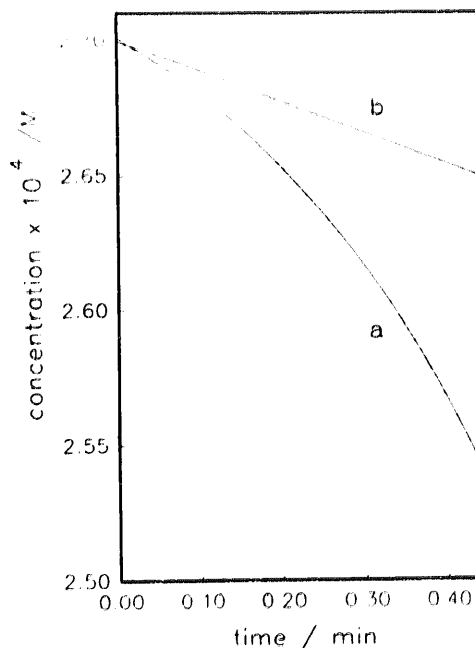


Fig. 3. Computer-simulated depletion of NO_3^- for vacuum UV irradiation experiments in air-saturated solutions at 25 °C with an incident photon flux density P_0 of 7.5×10^{-6} einstein s^{-1} : (a) 2.7×10^{-4} M of NO_3^- and 4.2×10^{-3} M of methanol; (b) 2.7×10^{-4} M of NO_3^- .

of NO^\bullet to hydroxylamine or ammonium, without the evolution of N_2O , with the simultaneous oxidation of the organic substrates. Considering that aromatic compounds can also induce NO_3^- reduction to NH_4^+ [3], the behaviour observed may probably be generalized to most organic substrates. This generalization will be tested by investigations probing other classes of organic substrates.

The oxidation of NH_4^+ to NO_3^- , NO_2^- and probably N_2 is initiated by the reaction between NH_3 (related to NH_4^+ by an acid–base equilibrium) and HO^\bullet radicals, and its importance is discussed in detail in Ref. [3].

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