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Removal of hydroxylamine by processes generating $OH^{\bullet}$ radicals in aqueous solution

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Abstract

The oxidation of hydroxylamine in aqueous solution ($[NH_2OH]_o = 1$ mM, pH = 7) by $OH^{\bullet}$ radicals was studied using H_2O_2/UV and γ-irradiation as radicals generation processes. Nitrites and nitrates were identified as the major by-products in the aqueous phase. Their concentration depends on the experimental conditions, i.e. the presence or the absence of oxygen, and the concentration of hydrogen peroxide(H_2O_2). For the smallest initial concentrations of H_2O_2 studied (below 10 mM), hydroxylamine was oxidized into gases of low solubility. It is assumed that these gases are mainly constituted of N_2 and N_2O. Subsequently to the H-abstraction from the molecule of hydroxylamine by $OH^{\bullet}$ radicals, $^{\bullet}NHOH$ radical recombinations are favored in the absence of oxygen and H_2O_2 and would lead to N_2. In the presence of oxygen, NOH can be produced and can dimerise into N_2O or react with NH_2OH to form N_2. Reactions involving O_2 and H_2O_2, or $O_2{}^{\bullet -}$ can account for nitrites then nitrates. ©1999 Published by Elsevier Science S.A. All rights reserved.

Keywords: Hydroxylamine; $OH^{\bullet}$ radicals; H_2O_2/UV process; γ-irradiation; By-products

1. Introduction

Oxidation processes involving $OH^{\bullet}$ radicals, also called advanced oxidation processes, are used for the treatment of aqueous solutions, principally for the removal of organic pollutants. Since inorganic compounds are often present in high concentration with regard to the micropollutants, their influence must be taken into consideration. Therefore, the mechanisms induced by $OH^{\bullet}$ radicals on inorganic molecules merit examination.

Data are available on the rate constants of $OH^{\bullet}$ radicals towards inorganic compounds [1], but the mechanisms relative to the decomposition of certain classes are much less known. That's the case for 'inorganic' nitrogen. Concerning the oxidation of ammonia, several authors [2,3] stated the formation of nitrites and nitrates as end products with the presence of hydroxylamine as intermediate. Hydroxylamine, used as antioxidant for fatty acids and soaps, can therefore be found in small amount in the environment. Our work consisted in the study of the oxidation of hydroxylamine (NH_2OH) by $OH^{\bullet}$ radicals. In particular, the objective was to examine if this molecule could be a source of nitrates. The radical generation processes used were the H_2O_2/UV combination on one hand and γ-irradiation in the presence of N_2O on the other hand.

2. Materials and methods

2.1. Reactors

Experiments with the H_2O_2/UV system were realized in a 4 l cylindrical batch reactor equipped with a low pressure mercury vapor lamp (Hanau NN 15/20) in axial position as previously described [4]. The photon flux, emitted essentially at the 253.7 nm wavelength, was 5.9×10^{-6} Einstein s^{-1} (2.78 J s^{-1}). The device allowed a continuous bubbling of nitrogen during irradiation for oxygen-free experiments. Introduction of oxygen in solution before the experiments was performed to study the influence of O_2 concentration.

For several experiments, hydroxyl radicals were generated from a ^{60}Co source (Gammacell). In water, ionization and electronic excitation lead to the formation of solvated electrons e^-_{aq}, $OH^{\bullet}$ radicals and H atoms as the primary radicals, with small amounts of H_2 and H_2O_2. N_2O alone or

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with oxygen ($N_2O/O_2 = 80/20$) was introduced continuously in 1 l solution during γ-irradiation. Under these conditions, all the solvated electrons produced simultaneously to the hydroxyl radicals by the radiolysis of water are converted into these latter oxidant species according to the reaction

$$e^-_{aq} + H_2O + N_2O \rightarrow N_2 + OH^\bullet + OH^-$$

2.2. Solutions

Hydrogen peroxide (30%, Fluka) and hydroxylamine (NH_2OH, HCl; purity >99%; Fluka) were used without further purification.

The solutions were prepared in ultra pure water delivered by a Milli RO-Milli Q purification system. The pH was set with NaOH at an initial value of 7.

2.3. Analytical procedures

Hydroxylamine ($pK_{aNH_3OH^+/NH_2OH} = 6.2$; 20°C), nitrite and nitrate ions were analyzed by a capillary electrophoresis apparatus (C.I.A. Waters) equipped with an automatic injector and a data acquisition system (Millennium 2010 software Waters). For the hydroxylamine determination, the samples were eluted with the UV CAT 3 (Waters) electrolyte at a fixed pH value of 4.8. The run potential was 20 kV with a migration time of 30 s in the hydrostatic mode and with a run sample of 5 kV in the electromigration mode. For nitrite and nitrate ions, the electrolyte is made of OFM-OH^- (Waters) and sulfate ions. The run potential was set on 12 kV with a migration time of 50 s in the hydrostatic mode. Chloride ions are used as internal standard for anions and lithium ions for cations.

Total and 'inorganic' nitrogen in solution were determined with a nitrogen analyzer DORHMANN DN 1900 based on chemiluminescence detection as described below. The different species likely to be involved during our experiments, and classified according to decreasing oxidation degree of the nitrogen are: NO_3^-, N_2O_4 ($2NO_2$), HNO_2/NO_2^-, NO, N_2O, N_2, NH_3OH^+/NH_2OH, $N_2H_5^+/N_2H_4$, NH_4^+/NH_4OH. In the course of the analyses of the nitrogen content by the DORHMANN DN 1900 apparatus, nitrates and nitrites are converted to NO by chemical reduction using VCl_3 at 80°C in the presence of concentrated sulfuric acid. This part is referred to as the 'inorganic' nitrogen fraction in this method. Based on this procedure, hydroxylamine is not taken into account as 'inorganic' nitrogen. For total nitrogen measurement, the sample (and therefore hydroxylamine and ammonia) is first oxidized by catalytic oxidation at 850°C in the presence of oxygen, and then all the species are reduced into NO by vanadium chloride. Finally, the reaction of ozone with NO leads to NO_2^* in an excited state which emits photons that are detected by a photomultiplier. It must be noted, we found that hydroxylamine was only partly quantified by this method of total nitrogen analysis.

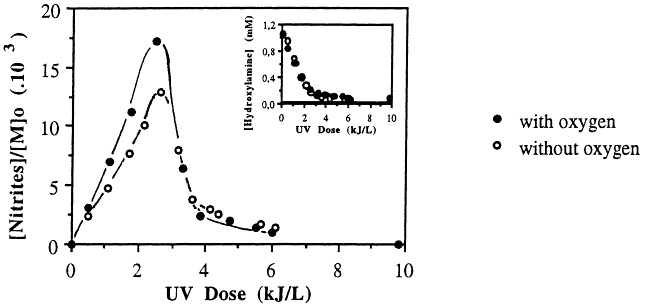

Fig. 1. Concentration of nitrite ions during the removal of hydroxylamine induced by hydrogen peroxide photolysis in the presence ($[O_2]_o = 0.99$ mM) and in the absence of oxygen. ($[M]_o$ represents $[NH_2OH]_o = 1.05$ mM, $[H_2O_2]_o = 0.97$ mM, $pH_i = 6.9$, $pH_f = 3.9$) Insert: Evolution of hydroxylamine.

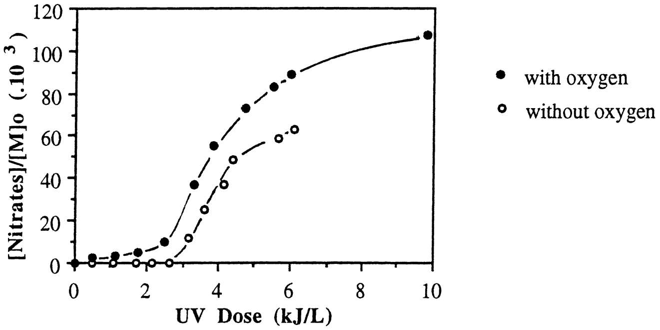

Fig. 2. Production of nitrate ions during the removal of hydroxylamine induced by hydrogen peroxide photolysis in the presence and absence of oxygen. (Initial conditions, see Fig. 1).

3. Results

Preliminary experiments have shown that under our working conditions, hydroxylamine was neither removed by gas stripping nor by direct UV irradiation at 253.7 nm. Moreover, hydroxylamine aqueous solutions were stable in the presence of hydrogen peroxide.

3.1. Influence of oxygen

3.1.1. H_2O_2/UV process

The removal of hydroxylamine during the photolysis of hydrogen peroxide ($[NH_2OH]_o = 1.05$ mM, $[H_2O_2]_o = 0.97$ mM, pH = 7) leads first to the formation of nitrite ions (Fig. 1). A maximum concentration is reached and then, simultaneously to the decrease of nitrites concentration, nitrate ions appear in the solution (Fig. 2).

Like the decay of hydroxylamine shown in Fig. 1, the rate of hydrogen peroxide removal is similar in the presence and in the absence of oxygen. The production of nitrites and nitrates is smaller in oxygen-free solutions. Under both conditions, the formation of nitrites and nitrates is weak compared to the amount of hydroxylamine removed. The sum of nitrites and nitrates concentrations is always below 12% of the hydroxylamine removed. A decrease of the

Table 1
Evolution of total 'inorganic' nitrogen[a] (N_T and N_I) measured during the removal of hydroxylamine induced by hydrogen peroxide photolysis in the presence and absence of oxygen (Initial conditions of Fig. 1)

UV dose ($kJ\,l^{-1}$)	With oxygen			Without oxygen		
	(N_T/N_{To})	(N_I/N_T)	% of unidentified compound within N_I	(N_T/N_{To})	(N_I/N_T)	% of unidentified compound within N_I
0	1	0	0	1	0	0
0.42	0.74	<0.03	0	–	<0.03	–
0.83	0.51	<0.04	0	0.52	<0.04	–
1.67	0.27	0.24	81.7	0.13	0.14	0
2.50	0.23	0.34	51.4	0.15	0.19	0
3.75	0.23	0.47	18.0	0.19	0.42	2.9
5.00	0.23	0.51	4.5	0.24	0.58	28.3
6.255	0.22	0.56	0	0.22	0.81	35.9
7.51	0.23	0.56	0	0.21	0.94	38

[a] N_I: Nitrogen referred to by the Nitrogen analyser as 'inorganic' nitrogen, i.e. NO_3^-, NO_2^-, NO_2, NO and any intermediate which could be reduced into NO by VCl_3, see Section 2.3.

pH was observed during irradiation. When present, approximately 0.5 mol of dissolved oxygen was consumed per mole of hydroxylamine removed.

The analysis of total nitrogen in solution (N_T, Table 1) indicates that the total nitrogen mass balance is not constant. Hence, hydroxylamine is probably partly converted into byproducts that diffuse from the solution to the gas phase. From the measurements of the 'inorganic' nitrogen (N_I, as defined above in Section 2.3), the occurrence of unidentified 'inorganic' nitrogen was shown, in addition to the presence of nitrites and nitrates, during the reactions under both oxygen and oxygen-free conditions. In the presence of oxygen, the concentration of these unidentified oxidized species reaches rapidly a maximum value for the UV dose around $1.67\,kJ\,l^{-1}$, thus, representing a higher yield than nitrites and nitrates, and then decreases. In oxygen-free solutions, unidentified 'inorganic' nitrogen appears with higher UV doses. Considering the principles of nitrogen determination by the DORHMANN DN 1900 analyzer, these non-identified species could be the nitrogen dioxide (NO_2). But neither NO nor NO_2 was detected by Dräger-type tubes placed at the gas outlet of the reactor. The progressive increase of the 'inorganic' nitrogen associated with the decrease of the concentration of the total nitrogen means that total nitrogen in solution becomes mostly constituted by the 'inorganic' nitrogen at the end of the experiment (Table 1).

3.1.2. Ionizing radiation process

The treatment of hydroxylamine aqueous solutions by the γ-irradiation/N_2O combined system for the generation of $OH^\bullet$ radicals has been performed with and without simultaneous introduction of oxygen. Results relative to the evolution of nitrites and nitrates concentration (Fig. 3) are comparable to those obtained from the H_2O_2/UV process, i.e. formation of nitrites up to a maximum value followed by the decrease of NO_2^- concentration with production of nitrates, both species being favored when oxygen is present.

Unfortunately, during these experiments, the determination of hydroxylamine was not possible. But in the γ-irradiation process with N_2O, a radiation dose of $8\,kJ\,kg^{-1}$ corresponds to the production of $4.4\,mmol\,l^{-1}$ of $OH^\bullet$ (from $G(OH^\bullet) = 2.9 \times 10^{-7}$ and $G(e^-) = 2.8 \times 10^{-7}\,mol\,J^{-1}$, [5], and if recombination reactions are neglected) which is higher than the maximum production allowed from the H_2O_2/UV system with an initial concentration of H_2O_2 of 1 mM (2 mol of $OH^\bullet$ are produced per mole of H_2O_2). Therefore, NH_2OH must be totally removed for the radiation doses applied Fig. 3.

3.2. Influence of H_2O_2 concentration in the H_2O_2/UV process

In the H_2O_2/UV process, the hydrogen peroxide which is the source of $OH^\bullet$ radicals can also react with intermediate species and have an influence on the by-products. Figs. 5 and 6 indicate that, increasing the H_2O_2 concentration in the H_2O_2/UV process leads to an increase of nitrites and nitrates formation. Thus, an almost complete nitrogen mass balance was observed from an initial H_2O_2 concentration, around 48 mM. Simultaneously, due to the competitive effect of H_2O_2 towards $OH^\bullet$ radicals, the rate of hydroxylamine removal becomes slower for the two highest H_2O_2 concentrations (48 and 143 mM, Fig. 4).

4. Discussion

Opposite to the H_2O_2/UV process which produces $OH^\bullet$, but also $HO_2^{\,\bullet}/O_2^{\,\bullet -}$ radicals, the γ-irradiation of aqueous solutions in the presence of N_2O is a pure $OH^\bullet$ radical generation system. Most of the data relative to the oxidation of hydroxylamine by $OH^\bullet$ radicals originate from pulse radiolysis studies. It is assumed that the first attack of $OH^\bullet$ radicals consists in H-abstraction from NH_2OH and $^+NH_3OH$ yielding $^\bullet NHOH$ and $^{\bullet +}NH_2OH$ (reactions 1a and 1b) with rate

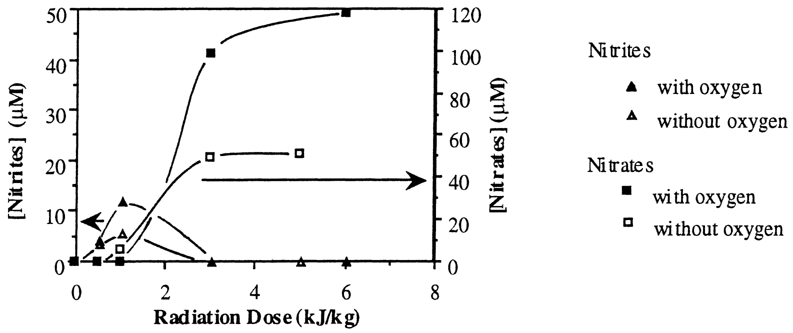

Fig. 3. Evolution of nitrite and nitrate ions during the removal of hydroxylamine by γ-irradiation with N_2O and $N_2O + O_2$ (80/20). ($[NH_2OH]_o = 1\,mM$, $pH_i = 7.0$, $pH_f = 4.6$ and 3.9 without and with oxygen respectively).

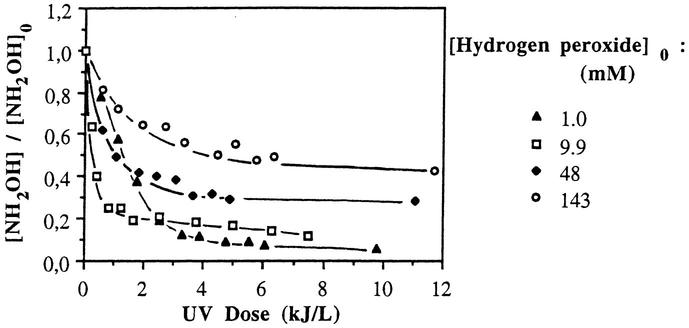

Fig. 4. Evolution of hydroxylamine during the photolysis of different concentrations of hydrogen peroxide in the presence of oxygen. ($[NH_2OH]_o = 1.05\,mM$, $pH_i = 6.9$, $pH_f \approx 3.6$).

constants equal to 9.5×10^9 and below $5.0 \times 10^8\,l\,mol^{-1}\,s^{-1}$ respectively [6,7]. The dissociation constant of the intermediate hydroxylamino radical was determined by Simic and Hayon [7] who found a pK_a value of 4.2 ± 0.1.

$$NH_2OH + OH^{\bullet} \rightarrow {}^{\bullet}NHOH + H_2O \quad (1a)$$

$$^{+}NH_3OH + OH^{\bullet} \rightarrow {}^{\bullet+}NH_2OH + H_2O \quad (1b)$$

4.1. Influence of oxygen in the absence of hydrogen peroxide

In our study, using the γ-irradiation process in the presence of N_2O, i.e. in the absence of H_2O_2 and O_2, the radical $^{\bullet}NHOH$ could dimerise to form N_2 (reaction 2) as proposed by Lefort and Tarrago [6] and Simic and Hayon [7].

$$^{\bullet}NHOH + {}^{\bullet}NHOH \rightarrow [N_2H_2(OH)_2] \rightarrow N_2 + 2H_2O \quad (2)$$

In the presence of oxygen, in relatively high concentration compared with these radicals under our experimental conditions, the competitive reaction of O_2 with $^{\bullet}NHOH$ cannot be excluded (reaction 3). The suggested $^{\bullet}OONHOH$ intermediate could thereafter release $HO_2{}^{\bullet}$ with NOH formation (reaction 4).

$$^{\bullet}NHOH + O_2 \rightarrow {}^{\bullet}OONHOH \quad (3)$$

$$^{\bullet}OONHOH \rightarrow NOH + HO_2{}^{\bullet} \quad (4)$$

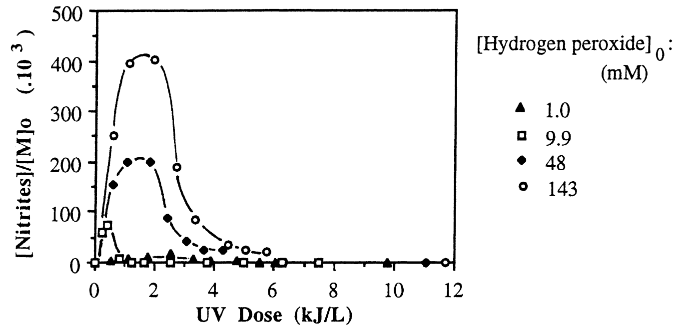

Fig. 5. Evolution of nitrite ions during the removal of hydroxylamine induced by the photolysis of different concentrations of hydrogen peroxide in the presence of oxygen. (initial concentration of NH_2OH, see Fig. 4).

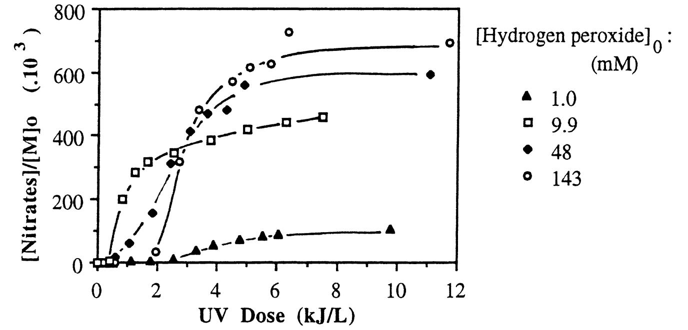

Fig. 6. Evolution of nitrate ions during the removal of hydroxylamine induced by the photolysis of different concentrations of hydrogen peroxide in the presence of oxygen. (initial concentration of NH_2OH, see Fig. 4).

Table 2
Yield of NO_2^- and NO_3^- from hydroxylamine with regards to H_2O_2 contribution in $OH^\bullet$ consumption. $\Omega_{NH_2OH} = 8.3 \times 10^6\ s^{-1}$, $\Omega_{^+NH_3OH} = 8.75 \times 10^4\ s^{-1}$

$[H_2O_2]_o$ (mM)	0.96	9.9	48	143
$\Omega_{H_2O_2}$ (s^{-1})	2.59×10^4	2.7×10^5	1.3×10^6	3.9×10^6
$\Omega_{H_2O_2} / \Omega_{NH_2OH}$	3×10^{-3}	0.03	0.16	0.46
[a]$[NO_2^-]/\Delta[NH_2OH]$	0.021	0.125	0.397	1.0
[b]$[NO_3^-]/\Delta[NH_2OH]$	0.080	0.503	0.796	1.0

[a] Ratio of the maximum nitrite ions concentration with the corresponding amount of hydroxylamine removed.
[b] Production of NO_3^- relative to the hydroxylamine removed for a 5 kJ l^{-1} UV dose (Fig. 6).

Since dimerisation of the unstable NOH is favored in acidic media (reaction 5), under our experimental conditions (pH 7–4), the reaction with hydroxylamine (reaction 6, [6,8]) can be expected.

$$NOH + NOH \rightarrow N_2O_2H_2 \rightarrow N_2O + H_2O \qquad (5)$$

$$NOH + NH_2OH \rightarrow N_2 + 2H_2O \qquad (6)$$

However, all these reactions produce N_2 or N_2O and do not account for the small concentrations of nitrites and nitrates observed in our work. Therefore, additional reactions occur. But, for the smallest concentration of H_2O_2 (1 mM), the H_2O_2/UV system was shown comparable to γ-irradiation.

4.2. Influence of hydrogen peroxide

The experiments with the H_2O_2/UV process have shown that the highest concentrations of H_2O_2 are particularly favorable to the oxidation of NH_2OH into NO_2^- and NO_3^-. We believe that hydrogen peroxide can take part in the mechanism of NH_2OH removal according to two pathways, i.e. from the direct action of H_2O_2 but also from the indirect effect of $HO_2^\bullet$ formed from the reaction of $OH^\bullet$ with H_2O_2 (reaction 7).

Under our experimental conditions, at the beginning of the reaction, for small UV doses (when NO_2^- concentrations are sufficiently weak), mostly NH_2OH and H_2O_2 are competitive for the consumption of $OH^\bullet$ radicals (reactions 1a, 1b, 7).

$$H_2O_2 + OH^\bullet \rightarrow HO_2^{\ \bullet} + H_2O$$
$$k = 2.7 \times 10^7\ l\,mol^{-1}\,s^{-1} \qquad (7)$$

The competitive factor of a compound M, is defined as $\Omega_M = k_{OH^\bullet/M}\ [M]_o$. For the four experiments performed with H_2O_2, concentrations from 0.96 to 143 mM, the competitive factor $\Omega_{H_2O_2}$ is presented in Table 2 with respect to Ω_{NH_2OH}. It appears that, within the range of H_2O_2 concentration studied, the production of nitrite and nitrate ions increases when the contribution of H_2O_2 in $OH^\bullet$ consumption is increased. For the highest initial concentration of H_2O_2 studied (143 mM), 1 mol of NO_3^- was produced per mole of NH_2OH removed, after the formation of NO_2^- as intermediate.

The radical $HO_2^{\ \bullet}/O_2^{\ \bullet -}$ formed in the H_2O_2/UV process can be also produced during γ-irradiation. Remember that γ-irradiation of water produces small amounts of H_2O_2 ($G(H_2O_2) = 0.8 \times 10^{-7}\ mol\,J^{-1}$ [5]). Moreover, in the presence of O_2, the production of $O_2^{\ \bullet -}/HO_2^{\ \bullet}$ radicals can be assigned to the reaction of the solvated electrons and the $H^\bullet$ atoms with the former. According to Bors et al. [9], the $O_2^{\ \bullet -}$ radical can react slowly with $^\bullet NHOH$ to form NO_2^- (reaction 8).

$$^\bullet NHOH + O_2^{\ \bullet -} \rightarrow NO_2^{\ -} + H_2O \qquad (8)$$

Concerning the direct action of hydrogen peroxide, the reaction of H_2O_2 with $^{\bullet +}NH_2OH$ radicals would yield NOH and the hydroxyl radical (reaction 9) as reported by Lefort and Tarrago [6] and Simic and Hayon [7]

$$^{\bullet +}NH_2OH + H_2O_2 \rightarrow NOH + OH^\bullet + H^+ + H_2O \qquad (9)$$

But NOH would produce N_2O and N_2 (reactions 5 and 6). Since these gases are not expected when the concentration of hydrogen peroxide is increased, the reaction (9) does not probably occur under our experimental conditions.

Another probable route would involve the peroxyl radicals $^\bullet OONHOH$ formed in the presence of oxygen (reaction 3). These $^\bullet OONHOH$ radicals could abstract an H atom from the hydrogen peroxide molecule before decomposition into nitrous acid (reactions 10 and 11). This pathway is in agreement with the pH decrease observed during the experiments.

$$^\bullet OONHOH + H_2O_2 \rightarrow HO_2^{\ \bullet} + [HOONHOH] \qquad (10)$$

$$[HOONHOH] \rightarrow HNO_2 + H_2O \qquad (11)$$

These reactions would explain the higher production of NO_2^- measured when oxygen was present in the H_2O_2/UV experiments with initial concentrations of hydrogen peroxide of 0.97 mM (Fig. 1).

The nitrite ions are rapidly oxidized by hydroxyl radicals ($k = 1.0 \pm 0.1 \times 10^{10}\ l\,mol^{-1}\,s^{-1}$ [10]) according to the reaction (12).

$$OH^\bullet + NO_2^{\ -} \rightarrow NO_2^{\ \bullet} + OH^- \qquad (12)$$

$$NO_2^{\ \bullet} + NO_2^{\ \bullet} \rightleftarrows N_2O_4 \qquad (13)$$

$$N_2O_4 + H_2O \rightarrow NO_2^{\ -} + NO_3^{\ -} + 2H^+ \qquad (14)$$

Reactions 13 and 14 which have been hitherto the accepted mechanism for the hydrolysis of the transients $NO_2^\bullet$ give rise to nitrates with partial regeneration of NO_2^-.

5. Conclusion

The oxidation of hydroxylamine by $OH^{\bullet}$ radicals in aqueous solution was assumed to produce mainly N_2 and N_2O, i.e. gases easily removed from the solution by stripping. Nitrite and nitrate ions were found only as traces excepted in the presence of large amount of hydrogen peroxide where nitrates can constitute the major end-product. These results contribute to the better understanding of the fate of the 'inorganic' nitrogen during $OH^{\bullet}$ induced oxidation and indicate that the nitrogen content of the solutions is expected to decrease after treatment.

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