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The photochemistry of aqueous nitrate ion revisited

Gertraud Mark [a], Hans-Gert Korth [b], Heinz-Peter Schuchmann [a], Clemens von Sonntag [a,*]

[a] *Max-Planck-Institut für Strahlenchemie, Stiftstrasse 34–36, P.O. Box 101365, D-45413 Mülheim, Germany*
[b] *Universität-GH Essen, Institut für Organische Chemie, P.O. Box 103764, D-45117 Essen, Germany*

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Abstract

Aqueous nitrate solutions were photolysed at 254 nm in the absence of oxidizable additives, in the presence of methanol or propan-2-ol and oxygen and in the presence of cyclopentane under anaerobic conditions. The main nitrogen-containing products are nitrite and peroxynitrite. The quantum yields depend on the pH, nitrate concentration, nature of the additive and the light intensity. The intrinsic nitrite yield in alkaline solutions could not be determined directly because, under the conditions of the nitrite assay, the accompanying peroxynitrite decomposes to form nitrite and nitrate; it is smaller than the apparent nitrite yield. In the acidic (pH 4–7) range, the intrinsic nitrite quantum yield is equal to the apparent nitrite yield because there is no buildup of peroxynitrite under these conditions. The apparent nitrite quantum yield increases from 0.01 (no oxidizable additive) to approximately 0.03 (cyclopentane (millimolar range), oxygen free) to 0.06 (methanol (millimolar range), air saturated). At pH 13 and in the absence of oxidizable additives, the apparent nitrite quantum yield increases to about 0.1, whereas from material balance considerations the intrinsic nitrite quantum yield is estimated to be 0.06, twice the oxygen quantum yield of 0.03. Spectrophotometrically, peroxynitrite is detected in the alkaline range only, because its protonated form is unstable.

In the absence of oxidizable additives, the quantum yield of peroxynitrite is about 0.1, i.e. only about two-thirds of the quantum yield in the presence of oxidizable additives. Mechanistic considerations on the basis of the pH dependence of the quantum yields of the products nitrite, peroxynitrite and oxygen, as well as their dependence on the kind of additive, indicate that the decisive factor of photolysis in the absence of additives is the formation of the nitric oxide peroxyl radical, $\mathrm{ONOO}^{\cdot}$, formed by reaction of peroxynitrite with the primarily generated $^{\cdot}\mathrm{OH}$ radical. The decay of $\mathrm{ONOO}^{\cdot}$ is the source of O_2 in this system. Nitric oxide, $\mathrm{NO}^{\cdot}$, the other fragment of this decay reaction, reacts with nitrogen dioxide, which is one of the primarily formed intermediates. The latter reaction is one of the pathways to the product nitrite, particularly in the alkaline range. The formation of $\mathrm{NO}^{\cdot}$ during photolysis has been verified by electron spin resonance (ESR) spectroscopic detection of the nitroxide 1,1,3,3-tetramethyl-isoindolin-2-oxyl, the NO adduct to 7,7,8,8-tetramethyl-*o*-quinodimethane.

Of the three primary processes discussed in the literature, we conclude that reactions (1) and (2) occur with quantum yields of approximately 0.09 and 0.1 respectively

$$\mathrm{NO_3^-} + h\nu \rightarrow \mathrm{NO_2} + \mathrm{O}^{\cdot -} \quad (\mathrm{O}^{\cdot -} + \mathrm{H_2O} \rightarrow {}^{\cdot}\mathrm{OH} + \mathrm{OH}^-) \tag{1}$$

$$\mathrm{NO_3^-} + h\nu \rightarrow \mathrm{ONOO^-} \tag{2}$$

It appears that none of the peroxynitrite anion is formed in a cage reaction through the recombination of the primary fragments from reaction (1). The primary process shown in reaction (3) is of relatively minor importance, with a quantum yield of no more than 0.001

$$\mathrm{NO_3^-} + h\nu \rightarrow \mathrm{NO_2^-} + \mathrm{O} \tag{3}$$

In the presence of methanol (or propan-2-ol) and oxygen under acidic conditions, formaldehyde (or acetone) is formed in an amount equivalent to nitrite via peroxyl radical reactions (quantum yield of approximately 0.06 for both alcohols). In the alkaline range, the apparent formaldehyde quantum yield decreases with increasing pH, while formic acid is produced in increasing amounts. The formation of formic acid is ascribed to the reaction of peroxynitrite anion with photolytically generated formaldehyde. The acetone quantum yield does not decrease with increasing pH over the whole alkaline pH range.

In the presence of cyclopentane under oxygen-free conditions, apart from nitrite (and peroxynitrite when alkaline), the compounds nitrocyclopentane, cyclopentyl nitrate, cyclopentene, cyclopentanol and cyclopentanone are produced. The formation of the organic nitrogen compounds leads to an increase in the pH as photolysis proceeds. This pH shift is particularly pronounced in the neutral range.

Keywords: Nitrate ion; Photochemistry; Peroxynitrite; Nitric oxide peroxyl radical

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[*] Corresponding author. Tel.: +49 208 306 3529; fax: +49 208 306 3951.

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1. Introduction

The question of NO_3^- photolysis has recently acquired a new, practical aspect. In the production of drinking water, UV light is increasingly being used for disinfection [1–4]. Natural waters, apart from those in fossil aquifers, always contain nitrate ion, together with many other inorganic and organic trace constituents, solutes and impurities [5,6]. According to European statutes, the nitrate concentration in drinking water must not exceed 50 mg dm^{-3} (the nitrite limit is much smaller, 0.1 mg dm^{-3}). It has been established previously [4,7] that, at a fluence (monochromatic 254 nm radiation) of 400 J m^{-2}, which is required for adequate disinfection, i.e. when overirradiation is avoided, hygienically relevant nitrite concentrations are not attained even if the nitrate content is at the legally allowed limit.

The UV absorption spectrum of nitrate ion in aqueous solution (Fig. 1) shows a weak band with a maximum at 302 nm ($\epsilon = 7.2$ dm^3 mol^{-1} cm^{-1}) and a stronger band with a maximum near 200 nm ($\epsilon = 9900$ dm^3 mol^{-1} cm^{-1}) [8]. At 254 nm, $\epsilon = 4$ dm^3 mol^{-1} cm^{-1}. The possibility of the nitrate-induced photo-oxidation of trace organic chemicals by sunlight in natural waters has been recognized [9–11]. The photolysis of nitrate has attracted considerable interest (aqueous solutions [12–22]; crystalline alkali metal nitrates [23–26]; argon matrix [27,28]). The reaction system is complex, even in the absence of additives. Nitrite ion is always produced; in the absence of an oxidizable additive, its material-balance counterpart is O_2. The mechanism of the formation of O_2 has, to date, never been satisfactorily explained. Only during the course of the present study has the implication of the nitric oxide peroxyl radical been recognized [29] (see below). In the presence of primary or secondary alcohols, no oxygen is produced [16], but aldehydes or ketones are formed instead. The pH has a pronounced effect on the photolysis: maximum nitrite quantum yields (generally of the order of 0.1) are found in the alkaline region, whereas below about pH 6 in the absence of an oxidizable additive the quantum yields of nitrite are much lower (see Fig. 2). It must be borne in mind, however, that the traditional colorimetric nitrite assay in these systems does not always produce the "true" value, but one that may be higher, reflecting the generation of additional nitrite from the decomposition (see below) of the photolysis product peroxynitrite which is formed under alkaline conditions [12,16,17,23–26]. Furthermore, the concentrations of nitrate and the additives, the wavelength, light intensity and temperature all influence the course of photolysis.

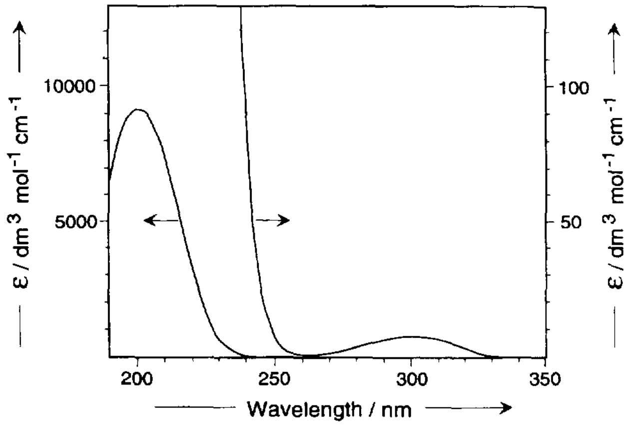
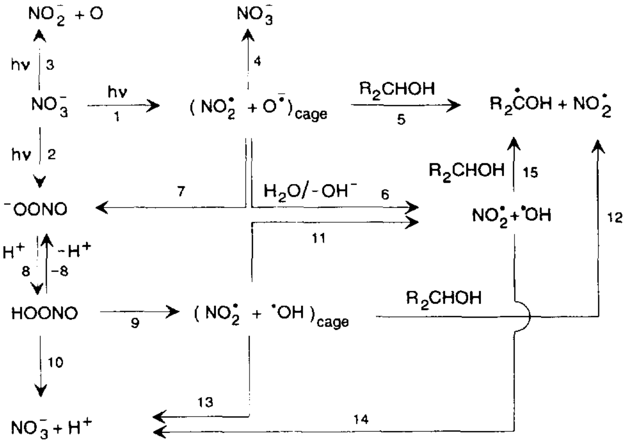


Fig. 1. UV absorption spectrum of aqueous magnesium nitrate.

Three primary processes have been discussed in the literature (reactions (1)–(3), see Scheme 1; the subsequent reactions in Scheme 1 will be discussed later). The energetics of reactions (1) and (3), leading to products in various electronic states, have been explored theoretically. It has been deduced that the pathway reflecting reaction (1) is connected with the lowest bond dissociation energy [30]. A clear picture of the relative importance of reactions (1)–(3) has not yet emerged. It appears certain, however, that $^{\cdot}NO_2$ is formed in a primary (photolytic) process (reaction (1)). For instance, nitroaromatic products are observed when the photolysis (315 nm) is carried out in the presence of phenolic compounds [31]. (It is shown below that, in the presence of oxidizable additives, reaction (1) constitutes the only pathway to nitrogen dioxide.) Apparently, such products are formed via free radical routes.

The $^{\cdot}OH$ radical holds a position of central importance in the photolysis of aqueous nitrate, as the primary fragment $O^{\cdot -}$ is protonated to yield the $^{\cdot}OH$ radical (reaction (6), Scheme 1). Since $pK(^{\cdot}OH) = 11.9$ [32], this reaction is quite fast ($k_6 = 1.8 \times 10^6$ dm^3 mol^{-1} s^{-1} [32]), implying a pseudo-first-order rate constant of 10^8 s^{-1}; therefore any other reaction of $O^{\cdot -}$ in dilute solution below pH 10–11 will be precluded. Both the $^{\cdot}OH$ and $O^{\cdot -}$ radicals are very reactive species and may effect hydrogen atom abstraction (*cf.* reactions (5), (12) and (15) in Scheme 1) [32] in the presence of organic material. Reaction (16) is an obvious pathway to nitrite, although other routes through free radical precursors exist, as will become apparent later

$$2\,^{\cdot}NO_2 + H_2O \rightarrow NO_2^- + NO_3^- + 2H^+ \qquad (16)$$



Scheme 1. Primary photoprocesses and subsequent reactions involving the $^{\cdot}OH$ radical. Reactions of $^{\cdot}OH$ with any final products are not shown.

No distinction has been made to date between reaction (2) and the possibility that peroxynitrite $ONOO^-$ is not strictly a primary photoproduct, but rather formed by recombination of $^{\cdot}NO_2$ and $O^{\cdot -}$ in the solvent cage (reaction (7), Scheme 1). On the other hand, on the basis of results obtained during the photolysis of crystalline KNO_3, it has been suggested recently that reaction (2) is indeed the dominant primary process [25].

In reaction (3), 254 nm radiation may produce oxygen atoms in the singlet (high-energy) or triplet (low-energy) state. The singlet oxygen atom is known to insert rapidly into the water molecule, forming H_2O_2 [33,34]. However, H_2O_2 has not been detected among the products [14,16,17], which leaves the possibility of triplet oxygen atom formation. Inconsistently, this has been believed to be the main primary process [17], ruled out altogether [14] or given a share of about 10% (90% $^{\cdot}OH$ radical formation) [20] on the basis of the reaction of $O(^3P)$ with cyclopentene (this gives rise to ethylene [35] which is then measured).

The photochemistry changes on going from acidic/neutral to alkaline solutions [13,14,17] (see Fig. 2). This cannot be due to the influence of pH on the primary processes; instead, it must be linked to the consecutive chemistry of short-lived intermediates formed in the primary processes. This follows from the observation that a change in the nitrite quantum yield is observed at a pH value as low as pH 8, corresponding to an OH^- concentration of 10^{-6} mol dm^{-3}. With regard to the excited state of the nitrate ion, we estimate a half-life of the order of 10^{-4} s for the quenching process by OH^- ions, assuming a maximum rate constant of 10^{10} dm^3 mol^{-1} s^{-1} for the quenching; this is certainly too long for the lifetime of an excited state under such conditions. In addition, the interaction with OH^- is ruled out on the basis of experiments, since on flash photolysis it has been observed that peroxynitrite formation follows first-order kinetics (half-time, 15 ms), independent of the pH [15]. The only intermediate resulting from the primary processes which is likely to display a pronounced pH-dependent chemistry is peroxynitrous acid whose pK_a value has been reported to be 6.7 [36], 6.8 [37] or 6.5 [38].

Other attempts have been made in the past to explain the pH behaviour. The pH dependence has been linked to the hypothetical formation of peroxynitric acid and its subsequent decay into O_2 and HNO_2, the sigmoidal curve reflecting the pK_a value of $HOONO_2$ [13], or to the reaction of peroxynitrous acid with the substrate NO_3^- and the product NO_2^-, depending on its state of dissociation [14]. Competing reactions of $O^{\cdot -}$, e.g. the formation of O and NO_2^- from $O^{\cdot -}$ and $^{\cdot}NO_2$, have also been held responsible [18]. However, this seems impossible in view of the fast protonation of $O^{\cdot -}$ (reaction (6), Scheme 1), at least below pH 11.

The foremost reason for the mechanistic complexity of the nitrate system is that the protonated form of the initial product peroxynitrite $ONOO^-$ (reaction (8), Scheme 1), peroxynitrous acid ONOOH (see Refs. [16,18,36,39,40]), isomerizes to nitric acid. This may occur directly [37] (reaction (10)), but also by way of cleavage into $^{\cdot}NO_2$ and $^{\cdot}OH$ radicals (reaction (9), Scheme 1) followed by bulk (reaction (14)) and cage (reaction (13)) recombination [36,40–42], with a rate constant for the decay of the order of a few reciprocal seconds [16,18,36,39,40,43] (most recent values: 1.4 ± 0.4 s^{-1} [36]; 1.3 s^{-1} at 25 °C [37]; 1.0 s^{-1} at 20 °C [38]), while the anion itself is thermally stable for minutes [39] or even several days [16,36] (for a recent review, see Ref. [44]). It has been proposed that the probability that $^{\cdot}OH$ radicals become manifest in this decomposition (i.e. do not eventually lead to the formation of nitrate in a solution of ONOOH) may be approximately 30%–40% [36,41]. Recently, the peroxynitrous acid molecule in its "trans" conformation has been implicated in hydroxyl-radical-like reactions [37,45–47].

It is shown below that the gross features of the pH dependence of the nitrite and oxygen quantum yields in the absence of oxidizable additives must be explained on the basis of these facts, and that in the presence of oxidizable additives the reaction mechanism changes drastically. Methanol, propan-2-ol and cyclopentane were chosen as model compounds for the natural polysaccharide trace constituents and hydrocarbon impurities in surface waters.

2. Experimental details

Aqueous solutions of magnesium nitrate (Merck, p.a.; 10^{-3}–10^{-1} mol dm^{-3}; for solutions of pH < 11, this salt was chosen because it handles better than alkali nitrates) or potassium nitrate (Merck, p.a.; dried at 105 °C and stored over dry silica gel), in the presence or absence of an oxidizable additive, were photolysed using light from a low-pressure mercury arc (Heraeus Sterisol NN30/89, fluence rates H(254 nm) = 0.5–10 J m^{-2} s^{-1}, which could be varied by changing the distance between the lamp and sample; or Graentzel (Karlsruhe) UV irradiator 185–254 nm, Vycor-filtered, H(254 nm) = 200 J m^{-2} s^{-1}). The higher nitrate concentrations (where the rates of product formation are higher) were usually chosen when the assay of a product was relatively insensitive (whereas the nitrite assay is very sensitive).

The optical cells were Suprasil QS (Hellma) (size, 4 cm × 1 cm (face) × 1 cm (depth)) or were made from rectangular quartz tubing type HSQ-300 (Heraeus Quarzschmelze, Hanau) (size, 15 cm × 3 cm (face) × 0.5 cm (depth)). Oxygenation of the solutions was achieved by passing a stream of oxygen gas through the sample for 5 min. When solutions were required to be oxygen free, the samples were purged with a stream of argon for about 20 min (the cell assembly used in such cases has been described elsewhere [48]).

The fluence rate of the incident UV light was determined by ferrioxalate actinometry [49] (the visible part of the lamp light was taken into account by shutting out the UV part with a glass plate) or by using a peroxidisulphate/tert-butanol/O_2 actinometer [50] (which registers only the 254 nm line).

The fluence rate absorbed by the nitrate solutions was calculated according to Beer's law.

Millipore Milli-Q purified water was used. The highest possible purity is desirable for experiments to be performed without organic additives. Even small traces of such material modify the course of photolysis (see below). Irradiations were also performed in the presence of additives (oxygen, methanol, propan-2-ol and cyclopentane). Methanol and propan-2-ol concentrations were in the range 10^{-4}–18 and 0.1–10 mol dm^{-3} respectively; that of cyclopentane was 2×10^{-3} mol dm^{-3} (saturation concentration).

Nitrite was determined spectrophotometrically by its red azo dye formed from sulphanilamide and *N*-(1-naphthyl)ethylenediamine [51] (see also German Standard Methods, determination of nitrite in water, DIN 38505). Peroxynitrite is produced together with nitrite when the photolysis is carried out in basic solution. Its presence interferes with the nitrite assay, in which it is decomposed via (in part) free radical pathways, giving rise to further nitrite as well as nitrate (see below). The nitrite assay involves the presence of an oxidizable organic compound in a solution of low pH.

The presence of $NO^{\bullet}$ as an intermediate in nitrate photolysis was unequivocally established by electron spin resonance (ESR) spectroscopy: a stream of Ar (20 ml min^{-1}) was passed through 3 ml of a 1 mol dm^{-3} potassium nitrate solution under continuous 254 nm photolysis (Rayonet photoreactor) for 1 h, and the volatile products were transferred into a 4 mm quartz ESR tube containing a 10^{-3} mol dm^{-3} hexane solution of the $NO^{\bullet}$ spin trap 7,7,8,8-tetramethyl-*o*-quinodimethane (NOCT-1) at −30 °C [52,53]. ESR spectra were recorded at 20 °C on a Bruker ER-420 X-band spectrometer.

Peroxynitrite ion in alkaline samples [39] was determined spectrophotometrically by measuring the optical absorption at 302 nm (ϵ(302 nm) = 1670 dm^3 mol^{-1} s^{-1} [54]) after photolysis.

Organic products from the cyclopentane system (cyclopentanol, cyclopentanone, cyclopentene, nitrocyclopentane, cyclopentyl nitrate) were analysed by gas chromatography (GC) and identified with the help of reference material [55] and/or mass spectrometrically. Formaldehyde was determined by the acetylacetone method [56] and acetone by high performance liquid chromatography (HPLC) as dinitrophenylhydrazone (column, Nucleosil 5C18; eluent, 70% acetonitrile/H_2O) [57]. In some experiments, the OH^- production was determined by titration or by measurement of the pH after photolysis. The evolution of O_2 was followed during the course of irradiation with an oxygen-sensitive electrode (Wissenschaftlich-Technische Werkstätten, Weilheim, Germany); because of its round shape, the quartz vessel (Heraeus Hanau, HSQ-300) that accommodates the electrode is not suitable for quantum yield measurements. Nitrite was measured in parallel with each oxygen determination, and the ratio of the oxygen and nitrite yields permits an estimate to be made of $\Phi(O_2)$ since, for reasons of stoichiometry, $2\Phi(NO_2^-) = \Phi(O_2)$. It is noted that the plastic casing of the electrode slowly releases small amounts of organic material into the solution. This is manifested by an increase in the optical absorbance of the solution, especially in the wavelength range below 250 nm, on standing in the dark. This may influence the oxygen readings, since free radical reactions during the course of photolysis cause oxygen consumption (see below). The chemical identity of this material is not known.

Key products indicating the importance of reaction (3) are sought from the reaction of singlet O atoms with water molecules (key product, H_2O_2) [33] and from the reaction of triplet O atoms with cyclopentene (key product, C_2H_4) [35]. Irradiated, argon-purged, 0.1 mol dm^{-3} nitrate solutions of pH 5 were tested for H_2O_2 using the iodide method (Allen's reagent) [58], observing the I_3^- absorbance at 350 nm. The ethylene produced on irradiation of cyclopentene-containing (5×10^{-3} mol dm^{-3}) deoxygenated nitrate solutions (10^{-2} mol dm^{-3}) was determined by gas chromatography (see Ref. [48]).

Together with formaldehyde, formate was found in irradiated, oxygenated, alkaline, ethanol-containing nitrate solutions. It was determined by ion chromatography (Dionex 2000i; column, HPIC AS4; eluent, 5×10^{-4} mol dm^{-3} $NaHCO_3$; retention time, 2.5 min).

In order to examine the thermal decomposition pathway of peroxynitrous acid, solutions of peroxynitrite were prepared from nitrous acid and H_2O_2 [12,39], or by photolysis of an alkaline nitrate solution (0.2 mol dm^{-3}, pH 13) at a high intensity, whereby peroxynitrite concentrations of up to 3×10^{-4} mol dm^{-3} could be achieved. The reactivity of superoxide $O_2^{\bullet -}$ towards NO_3^- was studied by subjecting a neutral dilute nitrate solution (10^{-3} mol dm^{-3}) containing 0.1 mol dm^{-3} formate, saturated with a 4 : 1 (v/v) mixture of N_2O and O_2, to ^{60}Co γ radiolysis, whereby $O_2^{\bullet -}$ is generated [59] (for an introduction into the field of radiation chemistry, see Refs. [60–62]).

3. Results

The experiments described here were performed using 254 nm radiation from a low-pressure mercury arc, i.e. with the 185 nm line shut out, whereby only the 254 nm line and a very small component at 313 nm remain. The spectrum of the nitrate anion overlaps with both lines, but the extinction coefficients are small for both (Fig. 1). In the present case, the effect of excitation of the longer wavelength band is neglected as the emission of the Hg low-pressure arc is small in this wavelength region; in addition, the effectiveness of the production of nitrite ions may be lower by a factor of roughly one order of magnitude at this wavelength [17,20]. Thus we are dealing with a relatively simple situation: practically monochromatic excitation of the nitrate ion at 254 nm.

The quantum yields of nitrate photolysis products, especially nitrite, were determined under different conditions: no oxidizable additive/(Ar or O_2); methanol/O_2; propan-2-ol/O_2; cyclopentane/Ar. The results are presented in this order.

3.1. No oxidizable additive

In general accordance with the literature [13,14], in the absence of an oxidizable additive we find a sigmoidal pH dependence of the nitrite quantum yield as shown in Fig. 2, with $\Phi(NO_2^-)$ increasing from approximately 0.01 in the acidic pH range to about 0.1 at pH 10 and above. Here, the significance of $\Phi(NO_2^-)$ is not straightforward, especially because the product peroxynitrite (which accumulates in the photolysed samples at sufficiently alkaline pH) contributes to the NO_2^- reading, since it partly decomposes into nitrite (see below) during the course of the nitrite assay.

Similar to earlier reports [13,19], we observe that, with the exception of the alkaline pH range, the NO_2^- yield vs. dose plots are noticeably curved downwards (Fig. 3). This implies that the quantum yield $\Phi(NO_2^-)$ in this system is dose dependent. The photolysis undertaken with a certain amount of nitrite initially added to the sample shows the same time course as the photolysis of an initially nitrite-free sample when the same amount of nitrite has accumulated (Fig. 3). The major cause of this is the partial re-oxidation of nitrite (reaction (17)) as shown below.

$$^{\cdot}OH + NO_2^- \rightarrow {}^{\cdot}NO_2 + OH^- \qquad (17)$$

By definition, the instantaneous or differential quantum yield is expressed as $\phi = dN/dD$ and the integral quantum yield as $\Phi_{int} = N/D$, where N and D are the number of molecules of the product and the number of quanta expended to produce them respectively. Φ_{int} is identical with ϕ only if the yield vs. dose function is linear, otherwise both quantities are dose dependent. The quantity plotted in Fig. 2 is neither. It is the apparent quantum yield, which reflects the integral quantum yield but which, while coinciding with the integral quantum yield in the acidic and neutral range, in the alkaline range contains an additional term due to the unavoidable "artefact" of peroxynitrite decomposition under the conditions of the nitrite assay that furnishes additional nitrite. The data shown were obtained at fluence rates in the range 6–10 W m^{-2} and fluences of up to about 30 kJ m^{-2}. When widely differing fluence rates are applied, it becomes apparent that the rate of nitrite formation decreases on going from low to high fluence rates. This effect is shown in Fig. 4. It has been established that, with regard to the behaviour shown in Fig. 4, there is no discernible difference between argon-purged and oxygenated ($[O_2] = 1.3 \times 10^{-3}$ mol dm^{-3}) solutions.

In accordance with literature reports [12,16], at pH > 10, we observe the formation of peroxynitrite anion, the buildup of which tends towards a steady state (Fig. 5). It is seen that the steady state concentration is lower and is reached sooner at lower pH values. The initial slopes are similar, and initial peroxynitrite quantum yields of about 0.07 are estimated. In the presence of propan-2-ol, the quantum yield of peroxynitrite reaches about 0.1 at propan-2-ol concentrations below

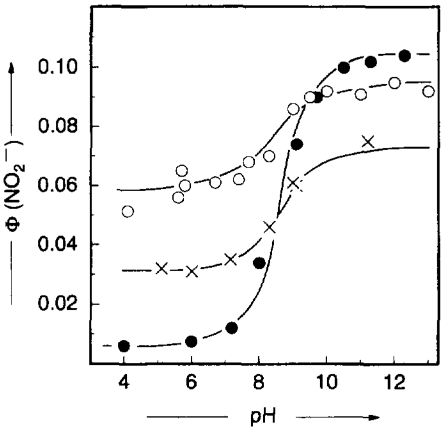


Fig. 2. Integral nitrite quantum yields from the photolysis (254 nm) of aqueous NO_3^- solutions (0.01 mol dm^{-3}, at different pH values), without organic additive (●) and at small OH radical scavenger concentrations: ○, 0.01 mol dm^{-3} methanol, air saturated; ×, 2×10^{-3} mol dm^{-3} cyclopentane, argon saturated. Fluence rate, 0.5 W m^{-2}. Data not corrected for additional nitrite formed from peroxynitrite under the conditions of the nitrite assay (see text).

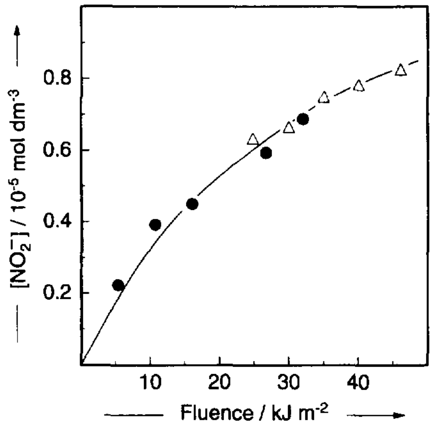


Fig. 3. Formation of nitrite at pH 6 (argon saturated): $[NO_2^-]$ vs. fluence. Fluence rate, 0.5 W m^{-2}. Without additive (●) and with 6×10^{-6} mol dm^{-3} NO_2^- added before photolysis (△); sequence of △ symbols shifted to the right to match the sequence of ● symbols.

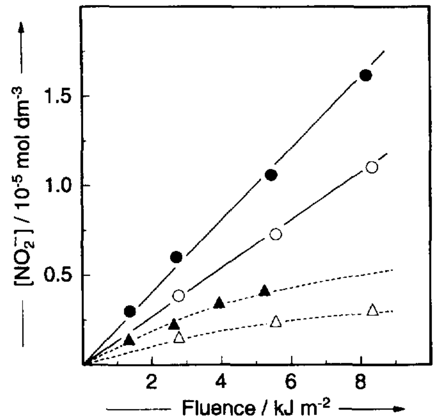


Fig. 4. Nitrite yield vs. fluence at different pH values (circles, pH 11; triangles, pH 5) and different fluence rates (open symbols, 10 W m^{-2}; filled symbols, 0.5 W m^{-2}) in argon-saturated nitrate solutions (0.01 mol dm^{-3}). No oxidizable additive.

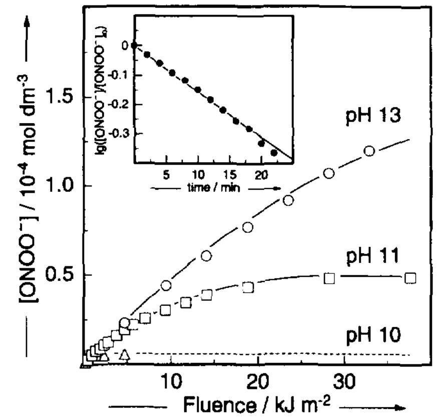


Fig. 5. Peroxynitrite buildup during the photolysis of alkaline aqueous NO_3^- (0.1 mol dm^{-3}) at different alkaline pH values without oxidizable additive. Fluence rate, 0.5 W m^{-2}. Peroxynitrite concentration vs. dose. Inset: post-irradiation decay of peroxynitrite at pH 11: $t_{1/2} \approx 30$ min.

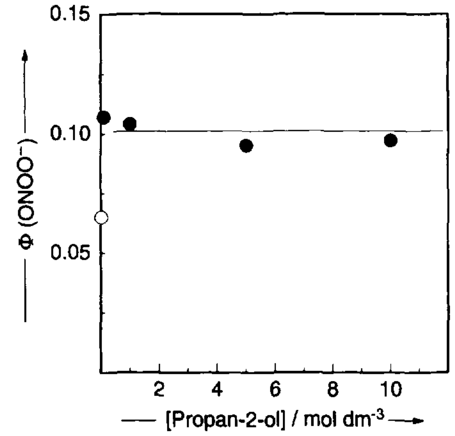


Fig. 6. Peroxynitrite quantum yield vs. propan-2-ol concentration during the photolysis of oxygenated nitrate solutions (NO_3^- = 0.1 mol dm^{-3}) containing up to 10 mol dm^{-3} propan-2-ol at pH 13 (○, without propan-2-ol). Fluence rate, 0.5 W m^{-2}.

0.1 mol dm^{-3}, and stays roughly at this level when higher concentrations of the alcohol, up to approximately 10 mol dm^{-3}, are used, as shown by the data in Fig. 6. (With regard to the degree of alkalinity in the case of solutions with supramolar alcohol concentrations, "pH 13" signifies that the solution is 0.1 mol dm^{-3} in sodium hydroxide.)

The pH trend of the oxygen yields parallels that of nitrite (data not shown). However, the O_2 quantum yields are somewhat lower than one-half of the nitrite quantum yields (on the basis of stoichiometry, we expect them to be exactly one-half). In the alkaline pH range, this is ascribed to an "artefact", namely the effect of the product peroxynitrite, which under the acidic conditions of the NO_2^- assay gives rise to additional nitrite [25,36].

The oxygen deficit is relatively larger in the acidic pH range (O_2 reading practically zero) where the NO_2^- quantum yield (and therefore also the expected oxygen quantum yield) is small compared with its value at pH 13. (It is argued below that the zero oxygen reading is a consequence of the oxygen electrode casing being made of plastic.)

Hydrogen peroxide (a possible indicator product of the occurrence of reaction (3)) is not observed. Its quantum yield must be less than 7×10^{-4} (argon saturated, 0.1 mol dm^{-3} nitrate, pH 5). Ethylene, a product from the ^3O atom assay [35], is another indicator product of the occurrence of reaction (3). Its quantum yield is 3×10^{-4} (10^{-2} mol dm^{-3} nitrate, 5×10^{-3} mol dm^{-3} cyclopentene, argon saturated, pH 7).

The production of a volatile nitrogen-containing compound [17] in the absence of an oxidizable additive has been confirmed. Purging the solution during photolysis with an inert carrier gas leads to its partial removal, as demonstrated by the formation of nitrite and nitrate in the trapping solution, while the pH of the photolysed solution is shifted towards the alkaline region. When the purging gas stream is passed into a hexane solution of the cheletropic spin trap NOCT-1 [52,53], strong ESR signals of the corresponding NO adduct 1,1,3,3-tetramethyl-isoindolin-2-oxyl (NOCT-1NO) are detected, together with weak signals of the corresponding NO_2 adduct (NOCT-1NO_2) (Fig. 7). The formation of the corresponding nitroxide radical NOCT-1NO unambiguously proves that free nitric oxide is produced during the course of photolysis.

Using the photochemical pathway to prepare peroxynitrite in solution, alkaline nitrate solutions (0.2 mol dm^{-3}, pH 13) were irradiated at high light intensity; the concentration of the peroxynitrite formed was determined spectrophotometrically. Aliquots of this solution were stirred into oxygenated solutions of methanol (5 mol dm^{-3}) and adjusted to pH 4. This results in the protonation of the peroxynitrite and the formation of $^{\cdot}OH$ radicals (reaction (9)) (or another strongly oxidizing species, see above). Formaldehyde was formed in a yield corresponding to approximately 20%–30% of the peroxynitrite originally present.

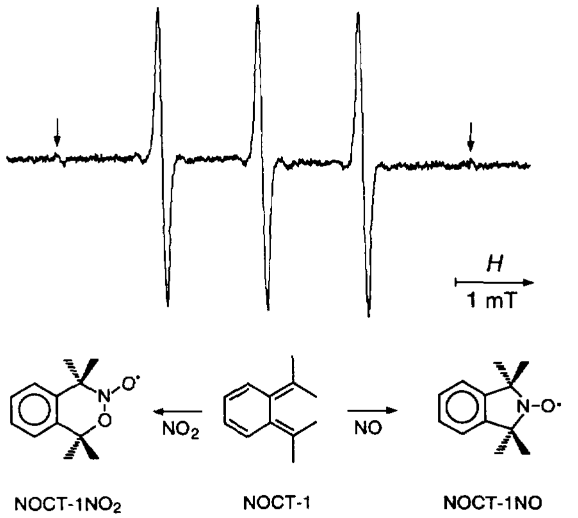


Fig. 7. ESR spectrum of the cyclic nitroxide radicals obtained by reaction of $NO^{\cdot}$ (NOCT-1NO; intense triplet) and $^{\cdot}NO_2$ (NOCT-1NO_2; weak triplet, central line masked) with tetramethyl-*o*-quinodimethane in cyclohexane at 20 °C. $NO^{\cdot}$ and $^{\cdot}NO_2$ stripped from a potassium nitrate solution (1 mol dm^{-3}) under 254 nm irradiation.

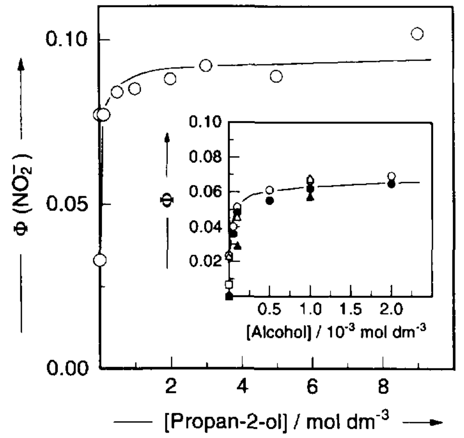


Fig. 8. Dependence of the nitrite quantum yield on the propan-2-ol concentration at pH 5 (0.01 mol dm^{-3} nitrate, up to 10 mol dm^{-3} propan-2-ol, oxygen saturated). Fluence rate, 0.5 W m^{-2}. Inset: photolysis of oxygen-saturated nitrate solutions (10^{-2} mol dm^{-3}; pH 5) in the presence of propan-2-ol (circles) or methanol (triangles) at concentrations up to 0.01 mol dm^{-3}. Nitrite (○, △), acetone (●) and formaldehyde (▲) quantum yields as a function of the alcohol concentration; □, nitrite yield in the absence of any oxidizable additive.

3.2. Alcoholic additives and oxygen

Oxygen-saturated nitrate solutions (0.01 mol dm^{-3}) containing varying amounts of methanol or propan-2-ol were irradiated at pH 5, and the nitrite quantum yield was determined as a function of the alcohol concentration (Fig. 8). The salient point here is that, after a steep rise to a value of about 0.06 within the centimolar alcohol concentration range (inset), the curve then bends into a section with a much smaller upward slope that finally brings $\Phi(NO_2^-)$ up to 0.1. The inset in Fig. 8 shows the dependence of the nitrite and formaldehyde quantum yields in the case of methanol, and the nitrite and acetone quantum yields in the case of propan-2-ol, on the concentration of the alcohol additive in the millimolar range at pH 5 ($[NO_3^-]=10^{-3}$ mol dm^{-3}). The picture is basically the same for both alcohols, and represents an expanded view of the steep rise section of the main graph of Fig. 8. It is seen in the inset that there is an increase in the nitrite quantum yield, which "plateaus out" at about 0.06 beyond an alcohol concentration of 2×10^{-3} mol dm^{-3}. It is also seen that, at this pH, $\Phi(NO_2^-)$ matches Φ(carbonyl compound). This "plateau" is taken to reflect the chemistry of the system (Scheme 1) when the additive concentration is still low enough so as not to interfere with the cage reactions.

It is perhaps useful to emphasize that the sharp rise over the region of the very lowest alcohol concentration (inset of Fig. 8) reflects the competition for the ${}^{\cdot}$OH radical between the alcohol and the product nitrite and, as explained earlier, is a consequence of the fact that the diagram represents the integral quantum yield and not the differential quantum yield at the limit of zero photolysis time.

The quantum yields of nitrite and formaldehyde as a function of pH are shown in Fig. 9 (methanol concentration, 10^{-2} mol dm^{-3}). In the acidic range, the quantum yields (about 0.06) are equal within experimental error, as expected from the stoichiometry represented by relation (18)

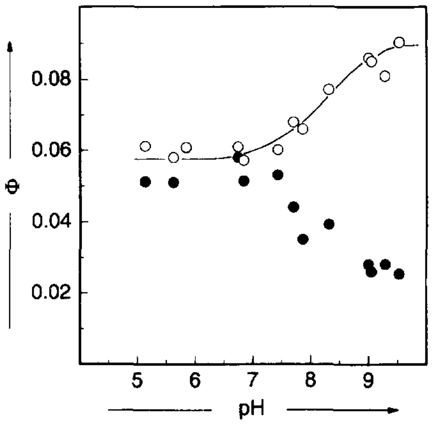


Fig. 9. Photolysis of oxygen-saturated nitrate solutions (10^{-2} mol dm^{-3}) in the presence of methanol (10^{-2} mol dm^{-3}). Fluence rate, 0.5 W m^{-2}. Nitrite (○) and formaldehyde (●) quantum yields as a function of pH. Buffer: phosphate, borate.

$$NO_3^- + CH_3OH \rightarrow NO_2^- + CH_2O + H_2O \qquad (18)$$

In the alkaline region, the "plateau" (see inset, Fig. 8) yields of nitrite and formaldehyde diverge (Fig. 9). The trend of NO_2^- production with pH (Fig. 2) is in agreement with earlier findings in the presence of alcohols [18,20]. It has also been reported that aldehyde or ketone will be formed when the additive is a primary or secondary alcohol respectively [18]. Keeping in mind that the nitrite readings in alkaline solution are boosted by post-photolytically formed nitrite from the decomposition of peroxynitrite in the nitrite assay, we would expect the formaldehyde yield to be lower than the apparent nitrite yield, but not to decline below its acidic pH range level. In fact, the decline is roughly balanced by the appearance of formate whose yield increases with increasing pH. The production of formate is apparently due to a thermal reaction, and we confirmed in a separate series of experiments that peroxynitrite prepared from nitrite and H_2O_2 [12] does indeed oxidize formaldehyde to formate at pH 10.

Peroxynitrite has also been measured in alkaline propan-2-ol solutions above pH 10. In the propan-2-ol system, the peroxynitrite ion is not reduced in a post-photolysis thermal reaction since it is unreactive towards acetone. Its initial quantum yield is close to 0.1, i.e. higher than the value in additive-free nitrate solution by about a factor of 1.5. The curves (similar to those in Fig. 5, data not shown) bend towards a steady state concentration which increases with pH, as it does in the absence of an oxidizable additive (Fig. 5).

3.3. Cyclopentane solutions

In water at 20 °C, cyclopentane is soluble to a concentration of 2×10^{-3} mol dm^{-3}. Any free radical attack on cyclopentane will yield only one type of radical, namely cyclopentyl. Fig. 2 shows the pH dependence of the quantum yield of

Table 1
Photolysis of nitrate (10^{-2} mol dm^{-3}) in the presence of cyclopentane (2×10^{-3} mol dm^{-3}) in weakly acidic and weakly basic oxygen-free aqueous solution. Quantum yields of organic nitrogen compounds in comparison with the nitrite quantum yield

Product	pH 5	pH 9
Nitrocyclopentane	0.02	$<10^{-3}$
Cyclopentylnitrate	$<10^{-3}$	0.01
Nitrite	0.03	0.07

nitrite in the absence of oxygen. Together with nitrite, cyclopentyl nitrate (its formation shows a brief induction period), nitrocyclopentane and cyclopentene are observed (Table 1). We detect a change in pH in the alkaline direction which is most conspicuous when the initial pH is about neutral. Small amounts of cyclopentanone and cyclopentanol are also observed. In oxygenated solutions, the formation of cyclopentyl nitrate and nitrocyclopentane is suppressed, while the contents of cyclopentanone and cyclopentanol increase as peroxyl radical reactions take over (see Refs. [63,64]).

The complete absence of cyclopentyl nitrite from the products is remarkable. Authentic material has been synthesized [55] and its GC retention time established. If it had been formed photolytically, it would certainly have been detected, since there was no interference by other GC peaks. Also, when a trace amount of cyclopentylnitrite was added to the solution prior to photolysis, it was seen to remain unaffected by radiation.

4. Discussion

4.1. No oxidizable additives

Nitrate photolysis in the absence of an oxidizable additive yields nitrite, oxygen and peroxynitrite; the first two are found in a molar ratio somewhat in excess of two (pH 13). The excess nitrite stems from the decomposition of peroxynitrite under the acidic conditions of the nitrite assay, with its partial conversion to nitrite [25,36]. O_2 must be formed as a consequence of the primary reactions (1) and (2), but not of reaction (3), since any important contribution of the latter to the photolysis can be ruled out: a value of $\Phi(H_2O_2) < 10^{-3}$ demonstrates the lack of importance of the primary formation of the singlet oxygen atom [33,34]. The low yield of ethylene, $\Phi(C_2H_4) = 3\times10^{-4}$, when the irradiation is carried out in the presence of cyclopentene (this is a reagent for the triplet oxygen atom [20,35,65]) indicates that $\Phi(^3O)$ does not exceed 10^{-3}.

The oxygen deficit in the acidic pH range (O_2 reading practically zero) is ascribed to the fact that small amounts of oxidizable material from the plastic casing of the O_2-sensitive electrode are constantly being liberated into the solution. During irradiation, this material may undergo free radical formation and so may be consuming the oxygen (see below) that, at acidic pH, is produced at a relatively low rate (see NO_2^- yield vs. pH, Fig. 2).

There are several already acknowledged intermediate and product species in this system ($^{\cdot}OH$, NO_2^-, $NO^{\cdot}$, $^{\cdot}NO_2$, $ONOO^-$, ONOOH) that are mutually reactive, together with the probable species $ONOO^{\cdot}$ (see below); therefore the reaction scheme is expected to be complicated. Nevertheless, it is possible to gain an understanding of the pH dependence and, at the same time, of the hitherto unsatisfactorily explained manner in which O_2 is formed.

Our hypothesis is that, in the absence of an oxidizable additive, the main influencing factor regarding the pH behaviour of the nitrite quantum yield involves the oxidation of peroxynitrite by the $^{\cdot}OH$ radical to give the nitric oxide peroxyl radical $ONOO^{\cdot}$ (reactions (19) and (20)), in competition with the isomerization of peroxynitrite into nitrate via the protonated form (reactions (10) and (13), Scheme 1). A similar process involving $^{\cdot}NO_2$ instead of $^{\cdot}OH$ as the oxidizing agent (reaction (21)) has been estimated to be exothermic by about 13 kcal mol^{-1} [37] and therefore cannot be ruled out.

$$^{\cdot}OH + ONOO^- \rightarrow ONOO^{\cdot} + OH^- \tag{19}$$

$$^{\cdot}OH + ONOOH \rightarrow ONOO^{\cdot} + H_2O \tag{20}$$

$$^{\cdot}NO_2 + ONOO^- \rightarrow ONOO^{\cdot} + NO_2^- \tag{21}$$

The effect of the decay of ONOOH is not only reflected in the pH dependence of the NO_2^- quantum yield (Fig. 2), but by the data shown in Fig. 5: the photolytic steady-state concentration of $ONOO^-$ decreases as the tendency to form the peroxynitrous acid molecule from its anion increases with decreasing pH.

We propose [29] that oxygen O_2 is released from $ONOO^{\cdot}$ mainly through reaction (22), its occurrence being strongly supported by the discovery of $NO^{\cdot}$ which behaves as a reactive intermediate in this system, but can be purged from the solution under photolysis. The second-order reaction (23) offers a further possibility for an oxygen-forming process involving $ONOO^{\cdot}$

$$ONOO^{\cdot} \rightleftharpoons O_2 + NO^{\cdot} \tag{22,-22}$$

$$2ONOO^{\cdot} \rightarrow 2\,^{\cdot}NO_2 + O_2 \tag{23}$$

These reactions are in accordance with the fact that both oxygen atoms in the product O_2 stem from the nitrate [17]. Moreover, the sequence of reactions (9), (11), (19) and (22), (23) provides an explanation for the observation [25,66] that the decomposition of peroxynitrite in neutral solution in the absence of organic compounds gives rise to some nitrite, and by implication, to O_2, in addition to isomerization to NO_3^-. The involvement of the nitric oxide peroxyl radical in this photolysis has hitherto not been suspected. (This species has been considered to be the probable intermediate in the oxidation of $NO^{\cdot}$ by dioxygen to $^{\cdot}NO_2$ in the gas phase [67,68], and to nitrous acid in aqueous solution [69–71], and has been observed in an argon matrix isolation infrared spectroscopic study of the reaction of $NO^{\cdot}$ with O_2 [72].) Under our experimental conditions, i.e. in the presence of up to 1.3×10^{-3} mol dm^{-3} (saturation at atmospheric pressure) oxygen, and relatively small $NO^{\cdot}$ steady-state concentrations, reaction (−22) does not yet seem to play a significant role as indicated by the fact that oxygen-free and oxygenated samples of additive-free nitrate solutions behave in the same way (not shown) within the limits of experimental error. Regarding the question of the stability of $ONOO^{\cdot}$, it is noteworthy that, according to quantum chemical estimates, this species is endothermic by up to 11.5 kcal mol^{-1} relative to its constituents $NO^{\cdot}$ and O_2 [73,74]. Below approximately pH 10, owing to the isomerization of peroxynitrous acid (reactions (10) and (13)), we expect a steady state concentration of peroxynitrite to be reached fairly soon after the onset of photolysis (see Fig. 5). The recombination of $NO^{\cdot}$ and $^{\cdot}NO_2$ represents a further pathway to nitrite (reaction (24)), together with reaction (16)

$$NO^{\cdot} + {}^{\cdot}NO_2 + H_2O \rightarrow 2NO_2^- + 2H^+ \tag{24}$$

Apart from the pH dependence, a concentration dependence and a fluence rate dependence are, in principle, also expected for this photolysis. The energy deposition density, and therefore the radical density, increases with $[NO_3^-]$; thus several of the elementary reactions involved in the reaction mechanism must be second order in radical concentration.

The fact that, in the absence of an oxidizable additive, the nitrite quantum yield falls with increasing fluence rate (see Fig. 4) indicates that second-order reactions, ultimately resulting in the full restitution of nitrate, play a part. Reaction (25) accounts for this feature.

$$^{\cdot}NO_2 + ONOO^{\cdot} + H_2O \rightarrow 2NO_3^- + 2H^+ \tag{25}$$

Both the products nitrite and peroxynitrite are subject to attack by the $^{\cdot}OH$ radical (reactions (17) and (19)); it may be said that nitrite protects peroxynitrite and vice versa.

To sum up, the product peroxynitrite to some extent protects the product nitrite against re-oxidation by $^{\cdot}OH$ through reaction (19) to O_2 and the nitrate precursor $^{\cdot}NO_2$ (reaction (16)), the protective effect being greatest in the alkaline range where the $ONOO^-$ steady-state concentration is highest. At the same time, peroxynitrite contributes to nitrite production on account of reactions (22) and (24). The protective effect is locked in as the resulting nitric oxide peroxyl radical is transformed into molecular oxygen (reactions (22) and (23)) (which is inert under these conditions) and into the nitrite precursor $NO^{\cdot}$.

Regarding the situation in the more strongly alkaline pH range, a question remains as to whether photolytic destruction of $ONOO^-$ (ϵ(254 nm) ≈ 360 dm^3 mol^{-1} cm^{-1}, estimated on the basis of ϵ(302 nm) = 1670 dm^3 mol^{-1} cm^{-1}) may contribute to some extent to nitrite formation [44], e.g. via $ONOO^- + h\nu \rightarrow O_2^{\cdot -} + NO^{\cdot}$. Both $NO^{\cdot}$ and $O_2^{\cdot -}$ (see below) in effect reduce $^{\cdot}NO_2$ to nitrite. Their recombination [37,75–77] is probably unimportant under the present conditions. Apparently, the effect of any peroxynitrite photolysis is quite small since, in strongly alkaline solutions, where the compound is thermally stable, the peroxynitrite yield vs. dose plot is only very slightly curved downwards (Fig. 5).

4.2. Oxidizable additives

In the presence of $^{\cdot}OH$ radical scavengers, such as alcohols or hydrocarbons, there is a pronounced change in mechanism. This is the obvious consequence of the rapid and, at sufficiently high additive concentrations, practically exclusive reaction of $^{\cdot}OH$ radicals with the additive. A possible reaction of the photoexcited nitrate ion with these compounds can be ruled out [15]. Looking at the situation in the alkaline range, we see that the alcohol protects the products nitrite and peroxynitrite. In the neutral and acidic pH range, it protects the nitrite and ONOOH, the latter being present in a relatively low steady state concentration. The fact that the peroxynitrite quantum yield is greater in the presence of $^{\cdot}OH$ radical scavengers than in their absence lends strong support to the existence of reaction (19). The hydroxyalkyl radicals which result from reaction (26) ($k_{26} = 9.7 \times 10^8$ dm^3 mol^{-1} s^{-1} [32]) are rapidly converted in the presence of oxygen to the corresponding peroxyl radicals (reaction (27); $k_{27} = 4 \times 10^9$ dm^3 mol^{-1} s^{-1} [78]). The latter further decays into the carbonyl compound and superoxide radicals [79]. It can be shown that the bimolecular self-reaction of these peroxyl radicals, which in the case of $HOCH_2OO^{\cdot}$ gives rise to formic acid [80], must be insignificant above pH 5 at the light intensities applied (for a review of the reactions of peroxyl radicals in aqueous solution, see Ref. [64]). The superoxide elimination has a slow spontaneous component (reaction (28); $k_{28} < 10$ s^{-1}) and an OH^--catalysed component (reaction (29); $k_{29} = 1.5 \times 10^{10}$ dm^3 mol^{-1} s^{-1}) [79], i.e. at pH ≈ 6 ($[OH^-] \approx 10^{-8}$ mol dm^{-3}), the OH^--induced reaction is already quite fast ($k \approx 100$ s^{-1}), despite the fact that $[OH^-]$ is low at this pH. Thus $O_2^{\cdot -}/HO_2^{\cdot}$ is a major radical in this system [81].

$$^{\cdot}OH + CH_3OH \rightarrow {}^{\cdot}CH_2OH + H_2O \tag{26}$$

$$^{\cdot}CH_2OH + O_2 \rightarrow HOCH_2O_2^{\cdot} \tag{27}$$

$$HOCH_2O_2^{\cdot} \rightarrow CH_2O + HO_2^{\cdot} \tag{28}$$

$$HOCH_2O_2^{\cdot} + OH^- \rightarrow CH_2O + O_2^{\cdot -} + H_2O \tag{29}$$

$$HO_2^{\cdot} \rightleftharpoons O_2^{\cdot -} + H^+ \quad (pK_a = 4.8) \tag{30}$$

At lower pH, where the hydroxyalkylperoxyl radicals are increasingly long-lived as the pathway (29) becomes barred, we expect the reaction of $^{\cdot}NO_2$ with the hydroxyalkylperoxyl radicals to play a role (reaction (31) [82]). The hydroxyalkylperoxynitrate thus formed is expected to undergo hydrolysis (reaction (32)), releasing formaldehyde and peroxynitric acid. The latter is known to decompose into oxygen and nitrite [83,84] (reaction (33)).

$$HOCH_2O_2^{\cdot} + {}^{\cdot}NO_2 \rightarrow HOCH_2OONO_2 \quad (31)$$

$$HOCH_2OONO_2 + H_2O \rightarrow CH_2O + O_2NOO^- + H^+ \quad (32)$$

$$O_2NOO^- \rightarrow O_2 + NO_2^- \quad (33)$$

Here, the question as to the fate of the superoxide radical must be posed; in particular, whether the increase in $\Phi(NO_2^-)$ with increasing pH may perhaps be partially due to the reduction of NO_3^- by $O_2^{\cdot -}$. Since the lifetime of superoxide increases with increasing pH, this reaction may potentially have more scope. However, such a process can be ruled out on the basis of radiation chemical experiments where superoxide radicals were generated in the presence of nitrate but were ineffective in giving rise to nitrite. Instead, $O_2^{\cdot -}$ is expected to be involved in a radical termination reaction with ${}^{\cdot}NO_2$. It is seen (Fig. 2) that $\Phi(NO_2^-)$, in the presence of oxidizable additives as well as in their absence, begins to increase near pH 7 from a lower value in the acidic range. However, this is much higher in the presence than in the absence of the additive methanol: about 0.06 instead of less than 0.01. The probable reason for this is that $O_2^{\cdot -}$ reduces ${}^{\cdot}NO_2$ to nitrite (reaction (34); $k_{34} = 2 \times 10^8$ dm^3 mol^{-1} s^{-1} [83]), apparently via the short-lived peroxynitrate O_2NOO^- ($t_{1/2} \sim 0.7$ s [84]).

$$O_2^{\cdot -} + {}^{\cdot}NO_2 \rightarrow O_2 + NO_2^- \quad (34)$$

Thus at pH < 7, the sequence of reactions (1), (16), (15), (27), (28), (30) and (34) results in the stoichiometric relation (18). The ${}^{\cdot}NO_2$ radical is not sufficiently reactive [85] to abstract H atoms from methanol (even with formaldehyde where the C–H bond strength is somewhat less than in methanol, $k({}^{\cdot}NO_2 + CH_2O)$ is only 4×10^{-4} dm^3 mol^{-1} s^{-1} at room temperature [86]). In contrast, the hydroxymethyl radical can react with ${}^{\cdot}NO_2$ at a diffusion-controlled rate [87,88], but will effectively do so only in the absence of oxygen. Under anoxic conditions, ${}^{\cdot}CH_2OH$ may act as a reducing agent towards various nitrogen-containing intermediates (also to some extent dropping out of such an interaction by dimerization [89]). Separate experiments (data not shown) have indicated that the nitrite quantum yields are slightly lower in oxygen-free than in oxygenated solutions.

In the alkaline methanol/O_2 case, there are obviously secondary reactions occurring which transform the primary product formaldehyde into formic acid. As this happens only in the alkaline pH region, we propose that the peroxynitrite anion is involved (reaction (35)). It is known that peroxynitrite anion can act as a potent oxidant towards certain compounds, e.g. thiols [37,90] and methionine residues in proteins [91]. We found it to be practically unreactive towards NO_2^-: in solutions of pH 13, the rate of decay of $ONOO^-$ ($t_{1/2} \approx 3$ h), monitored at 302 nm, is not noticeably accelerated on addition of nitrite at nitrite concentrations up to 10^{-2} mol dm^{-3}. The reaction of formaldehyde with nitrogen dioxide, if it leads to formic acid, is much too slow [86]. Equally, reaction (36) [80] cannot provide an explanation since, under alkaline conditions, the OH^--catalysed decay reaction (29) of the $HOCH_2OO^{\cdot}$ radicals [79] must completely eclipse reaction (36) [80]. The alkali-catalysed Cannizzaro disproportionation of formaldehyde into formic acid and methanol was ruled out on the basis of a control experiment.

$$CH_2O + ONOO^- \rightarrow HCO_2^- + H^+ + NO_2^- \quad (35)$$

$$2HOCH_2OO^{\cdot} \rightarrow 2HCO_2H + H_2O_2 \quad (36)$$

It has been shown recently that the peroxynitrite anion does indeed react with formaldehyde, $k_{35} = 1.4 \times 10^3$ dm^3 mol^{-1} s^{-1} [36]. Apparently, it also reacts with formate, although more slowly, $k = 2$ dm^3 mol^{-1} s^{-1} [77]. A control experiment has shown that, in alkaline solution, peroxynitrite does not react with methanol on the timescale of our experiments.

The fall-off (Fig. 6) in the nitrite integral quantum yield at very small methanol concentrations is probably due to increasing competition of nitrite and peroxynitrite with methanol for the ${}^{\cdot}OH$ radical as photolysis proceeds. This indicates an experimental difficulty encountered in the study of the additive-free (below neutral) nitrate photolysis. If the water used is not very pure with respect to oxidizable solutes, initial nitrite quantum yields will be relatively high before they settle down to their "real" values after the impurity has been completely oxidized. At basic pH, the effect of such an impurity will be less conspicuous (see Fig. 2).

With the additive cyclopentane, only a single type of radical, cyclopentyl, will be generated by ${}^{\cdot}OH$ radical attack. Fig. 2 shows the pH dependence of the quantum yield of nitrite in the presence of cyclopentane and in the absence of O_2. Apart from nitrite and peroxynitrite, cyclopentyl nitrate (its formation showing a brief induction period) and nitrocyclopentane were found (Table 1). There is also a change in pH in the alkaline direction which is most conspicuous when the initial pH is about neutral. The reason for this is that, due to the formation of the organic nitrogen compounds (cf. nitrocyclopentane in reaction (37)), the nitrogen-based anion is removed and the negative charge must come to reside elsewhere, i.e. hydroxide ion is liberated

$$C_5H_9^{\cdot} + {}^{\cdot}NO_2 \rightarrow C_5H_9NO_2 \quad (37)$$

This also explains why the nitrite yields should be lower than in the methanol/O_2 case. Moreover, since the photolysis chemistry itself is pH dependent, it is important to buffer the solution or to keep conversions very small in the neutral region so that the pH changes as little as possible during the course of photolysis. An increase in pH in the additive-free nitrate photolysis has been observed previously [17], and impurities were suspected as the cause of this. Not every kind of organic impurity will readily act in this way, as certain types of radicals, such as α-hydroxyalkyl radicals (which are oxidized (reaction (38)) to the carbonyl compound, accompanied by the formation of nitrite [92]), may not give rise to non-hydrolysing organic nitrogen compounds

$${}^{\cdot}CH_2OH + NO_2^{\cdot} \rightarrow CH_2O + NO_2^- + H^+ \quad (38)$$

Table 2
Photolysis of aqueous nitrate in the absence and presence of propan-2-ol. Some product quantum yields under limiting conditions of additive concentration and pH (see also Figs. 2, 6 and 8)

Product	No additive		Approximately 10 mol dm^{-3} propan-2-ol (O_2 saturated)	
	pH 5[a]	pH 13[a]	pH 5[a]	pH 13[b]
NO_2^-	0.006	0.1[c]	0.1	–
O_2	–	0.03	(0)	(0)
$ONOO^-$	0	0.06	0	0.1

[a] $[NO_3^-]=0.01$ mol dm^{-3}.
[b] $[NO_3^-]=0.1$ mol dm^{-3}.
[c] Includes nitrite produced from peroxynitrite under the conditions of the nitrite assay.

The complete absence of cyclopentyl nitrite C_5H_9ONO among the products is remarkable. If it had been formed photolytically, it would have been detected since there was no interference by other GC peaks. Also, when a trace amount of authentic cyclopentyl nitrite was added prior to photolysis, it was seen to remain unaffected on photolysis. Small amounts of cyclopentanone and cyclopentanol were also observed. An induction period for cyclopentyl nitrate formation was observed. This would be expected if reactions (39)–(42) were to occur, since the rate of reaction (39) increases from zero as the photolysis proceeds. Moreover, cyclopentyl nitrate formation should be favoured at alkaline pH, as is in fact the case (see Table 1).

$$R^{\cdot}+ONOO^{-}\rightarrow RON(OO^{-})^{\cdot} \quad (39)$$

$$RON(OO^{-})^{\cdot}+H^{+}\rightarrow RON(OOH)^{\cdot} \quad (40)$$

$$RON(OOH)^{\cdot}+NO_2^{\cdot}\rightarrow {}^{+}N(OO^{-})OR+NO_2^{-}+H^{+} \quad (41)$$

$${}^{+}N(OO^{-})OR\rightarrow O_2NOR \quad (42)$$

In oxygenated solutions, the formation of cyclopentyl nitrate and nitrocyclopentane is suppressed, while cyclopentanone and cyclopentanol increase in concentration. This is as expected since, in the presence of O_2, the cyclopentyl radical is converted into the corresponding peroxyl radical whose termination products are cyclopentanol and cyclopentanone. (For details of the cyclopentylperoxyl radical chemistry in aqueous solution, see Ref. [63].)

4.3. The importance of photoreactions (1)–(3)

On the basis of the results discussed above, whose salient points are collected in Table 2, the question of the relative importance of the photoreactions (1)–(3) (see Scheme 1, where the possibility of solvent cage effects is taken into consideration) can now be addressed.

First, reaction (3), in which a nitrite ion is formed together with an oxygen atom, seems to be of minor importance [14] compared with the sum of reactions (1) and (2) for the following reasons.

1. Its frequency is thought to be at most 10% of that of reaction (1) [20].
2. The presence of ^1O atoms and any reaction with the substrate can be ruled out because they would react very efficiently with water to produce H_2O_2: $^1O+H_2O\rightarrow H_2O_2$ [33,34]; however, H_2O_2 was not detected by us or others [14,16]; $\Phi(H_2O_2)$ must be smaller than 10^{-3}.
3. When determining the presence of $O(^3P)$ atoms in aqueous solution according to the method of Brown and Hart [35], we found a quantum yield of less than 10^{-3}, i.e. less than about 1% of the maximum nitrite content. It has been proposed that the triplet oxygen atom may react with the nitrate ion via the formation of the peroxynitrate ion O_2NOO^- [13]. This would give rise to NO_2^- and O_2 in a thermal decomposition reaction [83,84], i.e. to the same products as generated in the reactions subsequent to the primary reactions (1) and (2); thus it would be impossible to judge the importance of reaction (3) solely by looking at the photolysis products. However, the reactivity of the triplet oxygen atom with NO_3^- should be smaller than that with cyclopentene by about two orders of magnitude (see Ref. [93] in conjunction with Ref. [65]). Therefore, under the conditions of the ^3O assay [35], essentially all of the ^3O generated should have reacted with cyclopentene.

This leaves reactions (1) and (2) as the major primary processes. Peroxynitrite may be formed directly by reaction (2), but also from $^{\cdot}NO_2$ and $O^{\cdot -}$ in the solvent cage (reaction (7)). If the cage recombination reaction (7) is important, the $ONOO^-$ yield should be depressed in the presence of high concentrations of a scavenger such as propan-2-ol, which removes $O^{\cdot -}$ via reaction (5). This seems to be the case to a slight extent only (Φ(reaction 7) ≈ 0.01) as the data in Fig. 6, obtained at pH 13, indicate. It is therefore concluded that reaction (2) is the main pathway to peroxynitrite, formed with a quantum yield of 0.1. Solutions of pH 13 have been employed, since the peroxynitrite anion is sufficiently stable at this pH on the timescale of these experiments [16,39].

The importance of reaction (2) relative to reaction (1) cannot be directly inferred from the NO_2^- yields because of the complications introduced by the secondary reactions of the product peroxynitrite. Nevertheless, an estimate can be made on the basis of the O_2 yield measured at pH 13 ($\Phi(O_2)=0.03$), or on the basis of the difference between the peroxynitrite yields at this pH in the presence of propan-2-ol ($\Phi(ONOO^-)_{8\,M\,i\text{-}PrOH}=\Phi(\text{reaction 2})=0.1$) and in its absence ($\Phi(ONOO^-)_{\text{no additive}}=0.06$–$0.07$, see Fig. 6); this difference should be equal to $\Phi(O_2)$ (see above). It has been noted above that propan-2-ol, which scavenges $^{\cdot}OH$ and $O^{\cdot -}$ radicals, protects peroxynitrite against $^{\cdot}OH$ radical attack. At pH 13, where $ONOO^-$ is stable, the only source for the $^{\cdot}OH/O^{\cdot -}$ radical is reaction (1). Each $ONOO^-$ ion oxidized by $^{\cdot}OH$ produces one molecule of O_2 if reaction (19) is followed by reaction (22), but only a half-equivalent of O_2 if followed by reaction (23). The value of $\Phi(O_2)=0.03$ is in fair agreement with the value for $\Phi(ONOO^-)_{8\,M\,i\text{-}PrOH}-\Phi(ONOO^-)_{\text{no additive}}=\Delta\Phi(ONOO^-)=0.04$ (see Fig. 6), which may be taken as an indication that reaction (23) is of minor importance compared with reaction (22). $\Phi(O_2)$, or $\Delta\Phi(ONOO^-)$, represents the lower limits to $\Phi(\text{reaction 1})$ since, in the absence of propan-2-ol, the $^{\cdot}OH$ radicals generated in reaction (1) do not only react with $ONOO^-$, but are partitioned between the products $ONOO^-$ and NO_2^-. Allowing for a conceivable nitrate-forming cage reaction (4) and assigning a value of 0.03 to it (see also below), the $^{\cdot}OH$ radical partitioning finds its expression in Eq. (43)

$$\frac{\Phi(O_2)}{\Phi(^{\cdot}OH)}=\frac{\Phi(O_2)}{\Phi(\text{reaction 1})-\Phi(\text{reaction 4})-\Phi(\text{reaction 7})}=\frac{k_{19}[ONOO^-]}{k_{19}[ONOO^-]+k_{17}[NO_2^-]} \qquad (43)$$

With Φ_0 as the sum of $\Phi(\text{reaction 1})$ and $\Phi(\text{reaction 2})$, Eq. (43) is equivalent to Eq. (44)

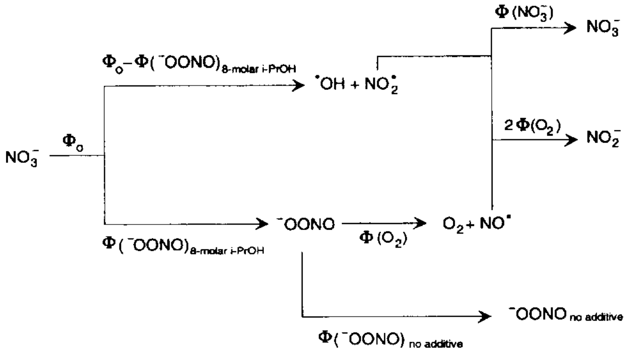
$$\frac{2k_{17}\Phi(O_2)}{k_{19}\Phi(ONOO^-)_{\text{no additive}}}+1=\frac{\Phi_0-\Phi(ONOO^-)_{8\,M\,i\text{-}PrOH}-0.04}{\Phi(O_2)} \qquad (44)$$

since $\Phi(\text{reaction 1})=\Phi_0-\Phi(ONOO^-)_{8\,M\,i\text{-}PrOH}$ and $[NO_2^-]/[ONOO^-]=\Phi(NO_2^-)/\Phi(ONOO^-)_{\text{no additive}}=2\Phi(O_2)/\Phi(ONOO^-)_{\text{no additive}}$. With the assumption that $k_{17}\approx k_{19}$, on insertion we obtain $\Phi_0\approx 0.19$.

In view of the partitioning of $^{\cdot}OH$ radicals, a balance regarding the products may be drawn up (Scheme 2). We may write Eq. (45), where $\Phi(NO_3^-)$ refers to the out-of-cage NO_3^- restitution yield due to the partial re-oxidation of the product nitrite and $\Phi(\text{reaction 4})$ stands for the in-cage nitrate formation as above, both of which are invisible

$$\Phi_0=\Phi(ONOO^-)_{\text{no additive}}+\Phi(NO_2^-)+\Phi(NO_3^-)+\Phi(\text{reaction 4}) \qquad (45)$$

Here, $\Phi(NO_2^-)$ represents the intrinsic quantum yield (which is smaller than the corresponding experimental value, the apparent quantum yield, because of the nitrite-forming reactions of peroxynitrite during the nitrite assay as mentioned above). Insertion of the known quantities in Eq. (45) yields a value of 0.03 for $\Phi(NO_3^-)$.



Scheme 2. Illustration of the material balance regarding the products from the photolysis of aqueous nitrate ion at pH 13. $\Phi_0=0.19$, $\Phi(ONOO^-)_{8\,M\,i\text{-}PrOH}=0.1$, $\Phi(ONOO^-)_{\text{no additive}}=0.07$, $\Phi(O_2)=0.03$, $\Phi(NO_3^-)=0.03$.

Let us now consider the acidic case. In agreement with the findings reported in the literature [36], we observe a substoichiometric oxidation of an oxidizable substrate, namely methanol, by acidified peroxynitrite. Nitrate solutions (0.1 mol dm^{-3}, pH 13) were irradiated at a high light intensity. Aliquots of this solution were stirred into oxygenated solutions of methanol (5 mol dm^{-3}) and adjusted to pH 4. Formaldehyde was produced in a yield corresponding to approximately 20%–30% of the peroxynitrite present; this does not contradict the assumption that a decomposition reaction of the peroxynitrous acid molecule into the $^{\cdot}OH$ radical and nitrogen dioxide exists (reaction (9)) [26,36,94,95]. This reaction has been disputed [45–47] on thermochemical grounds [37]; however, it is difficult to see how the peroxynitrous acid molecule itself can oxidize the alcohol in a manner that would mimic the action of the $^{\cdot}OH$ radical, since the alcohol is an aliphatic compound lacking a π system and therefore the ability to undergo complexation with this oxidant molecule prior to reaction. Some form of complexation would appear to be necessary to facilitate HO–ONO bond cleavage which must precede the manifestation of any $^{\cdot}OH$ radical-like reactivity of this molecule. These questions certainly deserve further study. If we choose to follow the $^{\cdot}OH$ radical hypothesis, reaction (9) in the absence of $^{\cdot}OH$ radical scavengers represents the first step of another isomerization pathway to nitrate (reactions (13) and (14)), together with a direct isomerization reaction (reaction (10)). At sufficiently high concentrations (see Fig. 8), the $^{\cdot}OH$ radical scavenger should interfere via reaction (12) with the cage reactions and therefore suppress any cage reaction part of the isomerization to NO_3^-. Isomerization would then only occur via reactions (13) and (11) followed by (14), i.e. by the radical-mediated pathway (Scheme 1). During photolysis at pH 5 and at high scavenger concentrations, the apparent nitrite quantum yield is equal to the intrinsic quantum yield, since there is no post-irradiation peroxynitrite to interfere with the nitrite assay. It thus should be represented by the sum of $\Phi(\text{reaction 1})$ and $\Phi(\text{reaction 9})$

Table 3
Photolysis of aqueous nitrate (10^{-2} or 0.1 mol dm^{-3}). Quantum yields of some reactions (see Scheme 1) as estimated on the basis of material balancing

Reaction	Φ(reaction)
1	~0.09
2	~0.1
3	<0.001
4	~0.03
5	<0.001
7	~0.01
9	~0.01
10	~0.09

$$\Phi(\mathrm{NO_2^-})_{10\ \mathrm{M\ i-PrOH}} = \Phi(^{\cdot}\mathrm{OH})_{\mathrm{total,\ pH\ 5}} = \Phi(\text{reaction 1}) + \Phi(\text{reaction 9}) \qquad (46)$$

Fig. 8 shows the results of a series of experiments performed at pH 5 with moderate to high concentrations of propan-2-ol as the additive. It can be seen that the measured nitrite quantum yield (which at this pH exclusively represents nitrite produced during photolysis since no peroxynitrite persists once the irradiation is terminated) reaches a value of approximately 0.1 at a propan-2-ol concentration of about 10 mol dm^{-3}. (Fig. 8 further suggests that the importance of cage reactions may be of the order of 0.04.) The value of 0.1 for $\Phi(\mathrm{NO_2^-})_{10\ \mathrm{M\ i\text{-}PrOH}}$ (Fig. 8) represents $\Phi(^{\cdot}\mathrm{OH})_{\mathrm{total,\ pH\ 5}}$. Together with Φ(reaction 1) ~0.09, estimated on the basis of the results obtained at pH 13, Eq. (46) implies that Φ(reaction 9) is about 0.01, i.e. approximately 10% of Φ(reaction 2). Most (approximately 90%) of the peroxynitrous acid produced thus isomerizes directly to nitric acid (reaction (10)). This proportion is somewhat higher than the 60% reported in the literature [34] and the 70%–80% estimated on the basis of the formaldehyde yield found in the methanol oxidation experiment mentioned earlier. However, the value of 90% is considered to be less reliable in view of the uncertainties that are propagated in the exercise of material balancing. The quantum yields estimated for some of the steps which have been discussed and are displayed in Scheme 1 are collected in Table 3.

5. Conclusions

The 254 nm photolysis of aqueous nitrate solutions has been studied without oxidizable additive, with methanol or propan-2-ol (dilute and molar to supramolar, oxygen saturated) and with cyclopentane (oxygen free). The primary species are $^{\cdot}\mathrm{NO_2}$ and $\mathrm{O^{\cdot -}}$, and the peroxynitrite anion $\mathrm{ONOO^-}$. Three primary reactions (1)–(3) have been discussed and their quantum yields estimated: $\Phi(1) \approx 0.09$, $\Phi(2) \approx 0.1$, $\Phi(3) < 0.001$. There is a marked sigmoidal pH dependence of the observed nitrite quantum yield which, near pH 8, rises from a lower level in the acidic pH range to a level in the vicinity of 0.1 in the alkaline pH range. Part of this rise is not a true quantum yield increase, but is due to the partial conversion of peroxynitrite into nitrite under the conditions of the nitrite assay.

In the additive-free system, the quantum yield increase occurs because the peroxynitrite anion, which is thermally quite stable in alkaline solutions, protects the product nitrite from re-oxidation by $^{\cdot}\mathrm{OH}$ (or $\mathrm{O^{\cdot -}}$) radicals. This protective effect of $\mathrm{ONOO^-}$ is locked in through the formation of $\mathrm{O_2}$, as a consequence of the reaction of the $^{\cdot}\mathrm{OH}$ radical with $\mathrm{ONOO^-}$, which gives rise to the nitric oxide peroxyl radical $\mathrm{ONOO^{\cdot}}$, the precursor of $\mathrm{O_2}$. The formation of dioxygen is accompanied by the release of $\mathrm{NO^{\cdot}}$. The anion $\mathrm{ONOO^-}$ corresponds to the weak acid ONOOH which rearranges into nitric acid within a matter of seconds. Thus, under acidic conditions, the protective effect of $\mathrm{ONOO^-}$ with respect to nitrite production largely falls away. The stoichiometry with respect to nitrite formation is given by the equation $2\mathrm{NO_3^-} \rightarrow 2\mathrm{NO_2^-} + \mathrm{O_2}$. The peroxynitrite anion exhibits no detectable reactivity towards the nitrite anion.

Oxidizable additives protect the products nitrite and peroxynitrite from destruction by the $^{\cdot}\mathrm{OH}$ radical. In the presence of methanol (or propan-2-ol) and $\mathrm{O_2}$, the chemistry with respect to nitrite formation is described by the stoichiometric equation $\mathrm{NO_3^-} + \mathrm{CH_3OH} \rightarrow \mathrm{NO_2^-} + \mathrm{CH_2O} + \mathrm{H_2O}$. The α-hydroxyalkylperoxyl radical, e.g. $\mathrm{HOCH_2OO^{\cdot}}$, and superoxide $\mathrm{O_2^{\cdot -}}$ are essential intermediates. The apparent rise of the nitrite quantum yield at alkaline pH is mainly due to partial nitrite formation from peroxynitrite during the nitrite assay.

Cyclopentane, similar to the alcohols, acts as a protector of nitrite. In the absence of $\mathrm{O_2}$, however, some of the cyclopentyl radicals combine with the intermediate $^{\cdot}\mathrm{NO_2}$ to form organic nitrogen compounds, such as nitrocyclopentane, thus leading to a decrease in the nitrite quantum yield compared with the alcohol case. Again, the rise of the nitrite quantum yield in alkaline solution is believed to be at least partially due to the decomposition of peroxynitrite.

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Note added in proof

While this paper went to press, an extensive review on the chemistry of peroxynitrous acid had been published [96]. A study on the kinetics of the reaction of nitric oxide with oxygen has come out recently which postulates the intermediacy of $ONOO^{\cdot}$ [97]. Some features of the present work have been presented under the heading "Aspects of nitric oxide chemistry and biochemistry" at the NATO workshop, *Free Radicals in Biology and the Environment, June 21–26, 1996, Bordolino, Italy* [98].