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Photooxidation of Organic and Inorganic Substrates during UV Photolysis of Nitrite Anion in Aqueous Solution

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Abstract: The UV photolysis (360 nm) of nitrite anion has been investigated in aqueous solution in the presence of organic and inorganic substrates: alcohols, 1,4-dioxane, sodium ascorbate, Me_2CO, Me_2SO, HCOONa, NaSCN, NaN_3, Na_2S, and Na_2SO_3. The hydroxyl radical, the primary photodissociation product of NO_2^-, was observed by electron spin resonance (EPR) using the spin trap 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO). With nitromethane (NM) in alkaline solution as a spin trapping agent, we observed $NO_2^{\bullet}$ which is a product of $HO^{\bullet}$ self-scavenging by nitrite. In the presence of organic/inorganic substrates, the $HO^{\bullet}$ radical gives rise to secondary radicals which we trapped and identified as DMPO or NM adducts; the respective EPR spectra are presented. Secondary carbon radicals react with oxygen in solution increasing the yield of oxygen consumption 10–1000 times over the control level. The quantum yield of O_2 consumption increases with increasing molar ratio of the substrate/NO_2^-, usually following the plot of oxygen solubility in solution. Besides $HO^{\bullet}$ radicals, nitrogen oxides and inorganic nitrogen peroxides may also contribute to oxidation by nitrite. We also detected weak singlet oxygen phosphorescence during UV irradiation of NO_2^- in deuterium oxide.

Introduction

UV excitation of nitrite anions in anaerobic aqueous solution leads to $NO^{\bullet}$ and $HO^{\bullet}$ radicals[1–3] (eq 1). The hydroxyl radical may recombine with $NO^{\bullet}$ giving HNO_2 (eq 2) or be scavenged by nitrite anions at a diffusion-controlled rate to yield OH^- and $NO_2^{\bullet}$ (eq 3). $NO^{\bullet}$ and $NO_2^{\bullet}$ may react to give N_2O_3 (eq 4) which hydrolyzes to regenerate nitrite[4] (eq 5). Thus no apparent chemical change is observed during anaerobic photolysis. However, in air saturated solution, $NO^{\bullet}$ may be competitively oxidized by oxygen which leads to oxygen depletion[5] and the formation of nitrate (eq 6).

$$(NO_2^-)^* + H_2O \rightarrow HO^{\bullet} + NO^{\bullet} + OH^- \tag{1}$$

$$HO^{\bullet} + NO^{\bullet} \rightarrow HNO_2 \tag{2}$$

$$HO^{\bullet} + NO_2^- \rightarrow NO_2^{\bullet} + OH^- \tag{3}$$

$$NO^{\bullet} + NO_2^{\bullet} \rightarrow N_2O_3 \tag{4}$$

$$N_2O_3 + H_2O \rightarrow 2HNO_2 \tag{5}$$

$$NO^{\bullet} + NO_2^{\bullet} + O_2 + H_2O \rightarrow 2HNO_3 \tag{6}$$

The most chemically reactive intermediate of nitrite photolysis is the $HO^{\bullet}$ radical. This radical is also the most aggressive oxidant in the natural environment where photochemical processes may be responsible for its formation.[6–12] Photolytic processes have been postulated to be especially significant in water deficient of iron[13] where the $HO^{\bullet}$ radical cannot be formed by the Fe^{2+}-catalyzed reduction of peroxides (Fenton reaction). An important source of $HO^{\bullet}$ radicals in water is the photolysis of peroxides, nitrite, and nitrate ions. The $HO^{\bullet}$ radical formed during nitrite/nitrate photolysis has been found to contribute to oxidation processes in marine waters.[14]

Because nitrogen oxides, which are formed during nitrite photolysis, are less reactive species than the $HO^{\bullet}$ radical, they may be more selective in their reactions. It has been reported that $NO_2^{\bullet}$, which is also an important environmental pollutant, possesses strong oxidative power. It can add to double bonds to initiate oxidation of unsaturated fatty acids,[15,16] abstract hydrogen atoms from alkenes,[15–17] and oxidize thiols to disulfides.[18] The non-acidic oxide $NO^{\bullet}$ is more stable, but it can be easily oxidized by oxygen to nitrogen dioxide. Thus, $NO_2^{\bullet}$ seems to be the next most important transient of nitrite UV photolysis after $HO^{\bullet}$.

UV photodissociation of nitrite alone has been investigated previously,[1–3] and the quantum yield of $HO^{\bullet}$ formation has been measured.[19,20] Some radicals produced during irradiation of concentrated nitrite solution and organic substrates in NaOH solution have been identified by direct EPR.[21] However, to our knowledge, neither the $HO^{\bullet}$ nor the $NO_2^{\bullet}$ radical has been detected by the EPR spin trapping technique. The purpose of our study was to examine the oxidation started by irradiation of NO_2^- in the presence of various substrates in aqueous solution. EPR spectra of spin adducts of hydroxyl and nitrogen dioxide radicals derived from the nitrite photolysis are reported; the formation of the latter is confirmed by using labeled (^{15}N) nitrite ion. EPR spectra of spin adducts of DMPO and nitromethane with radicals derived from organic and inorganic substrates are also reported. In addition we have measured the overall quantum yield of oxygen consumption for some organic substrates. The solubility of oxygen in several mixtures of organic solvents and water, necessary to calculate the respective quantum yields of oxygen consumption,

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has been determined. Our results suggest that NO_2^- photolysis may significantly contribute to the oxidative decay of natural organic matter and pollutants present in the environment.

Experimental Section

The quantum yield of oxygen consumption during irradiation of nitrite aqueous solutions has been measured as described previously.[5] The samples were saturated with air or oxygen and their temperature carefully controlled. Oxygen solubility in mixtures of water and 1,4-dioxane, formaldehyde, and acetone was assayed chemically employing the self-oxidation of the reduced sodium salt of anthraquinone-2-sulfonic acid.[22] Oxygen solubilities in water/methanol mixtures were taken from published data.[23]

EPR spin trapping of the radicals occurring during nitrite photolysis was performed using a Varian E-109 spectrometer equipped with a TM_{110} cavity. The sample contained in a quartz aqueous sample cell was excited in the EPR cavity using monochromatic radiation (Kratos Instrument Co., Westwood, NJ) from a 1000-W Xenon lamp and the signal was recorded during the photolysis as a first derivative. In most experiments the excitation wavelength was 360 nm (fluence rate 7.2 W/m^2). Where indicated, a 305-nm-cutoff filter (Oriel Corp., Stratford, CT) or window glass (340-nm cutoff) was used. The samples were deoxygenated by bubbling with argon or nitrogen (all 99.9%) for 5 min or saturated with air/oxygen in the same manner, if not indicated otherwise. All EPR experiments were carried out at room temperature.

The g factor was evaluated using Fremy's salt as an internal standard (g = 2.0055) as described previously.[24]

The maximum absorption of DMPO is 227 nm so it did not overlap with that of nitrite, which was the only other light-absorbing compound in our system. Similarly, nitromethane did not absorb at the 360-nm wavelength which we used in experiments with this spin trapping agent. None of the substrates we used absorbed at the wavelengths employed for irradiation.

The formation of the DMPO adduct during the Fenton reaction (oxidation of Fe^{2+} by H_2O_2) was monitored as follows: to a solution of DMPO (0.03 M) and Fe^{2+}/EDTA complex (0.001 M) in an appropriate buffer (pH from 6 to 9, 0.05 M) we added H_2O_2 (0.001 M). The growth of the DMPO/$^{\bullet}$OH signal was monitored during subsequent scanning, and the signal amplitude was compared after the same incubation time.

Singlet oxygen luminescence was detected using equipment previously described.[25] Oxygen-saturated solutions of nitrite in D_2O or D_2O-wet organic solvents were irradiated through a 305-nm-cutoff filter (Oriel Corp., Stratford, CT) in a 0.5-cm quartz fluorescence cell.

Formation of acidic photoproducts was assayed by standard titration with NaOH solution after prolonged irradiation performed with continuous O_2 gassing. The same procedure was applied to the reference sample which was not irradiated. Acetone formed during photooxidation of 2-propanol by nitrite was assayed by gas chromatography (GC).

The following chemicals were used as received: $NaNO_2$ and l-ascorbic acid sodium salt (Sigma Chem. Co., St. Louis, MO); $Na^{15}NO_2$ 99% ^{15}N (Cambridge Isotope Laboratories); KSCN, NaN_3, Na_2S, $FeSO_4{\cdot}7H_2O$, D_2O, formic acid sodium salt, ethylenediaminetetraacetic acid tetrasodium salt, ethanol, and 1,4-dioxane (Aldrich Chem. Co., Inc., WI); NaOH and methanol (J.T. Baker Inc., Phillipsburg, NJ); $MeNO_2$, Na_2SO_3, and 3% H_2O_2, (Fisher Sci. Co., Fairlawn, NJ); formamide, 1-propanol, 2-propanol, 1-butanol, 2-methyl-2-propanol, propionaldehyde, tetrahydrofuran, ethylene glycol, and phenol (Fluka, Switzerland); potassium phosphate dibasic, sodium phosphate monobasic, sodium bicarbonate, and acetone (Mallinckrodt, Inc., Paris, KY); formaldehyde (POCH-Gliwice).

5,5-Dimethyl-1-pyrroline N-oxide (DMPO, purchased from Aldrich Chem. Co., Inc., WI) was vacuum distilled and stored in a freezer. Stock solution of nitromethane (90 mM) was prepared just before experiments. All solutions were prepared using deionized water.

Results and Discussion

1. Oxygen Consumption. The addition of organic substrates during aerobic nitrite photolysis in aqueous solution caused considerable increases in the quantum yield (ϕ) of oxygen consumption (Table I and Figures 1 and 2). The quantum yield varied from about 0.04 to 0.08 for the examined compounds and is about two orders of magnitude higher than that for nitrite alone. When nitrite anions are irradiated in the absence of any organic substances, O_2 consumption is low because NO$^{\bullet}$ reacts with molecular oxygen[5] (eq 6). Organic substrates added to the irradiated samples efficiently scavenge the primary HO$^{\bullet}$ radicals to produce carbon radicals (vide infra), which by reacting with O_2 may be responsible for the enhanced O_2 depletion (Table I).

Table I. The Quantum Yield of Oxygen Consumption during Irradiation of $NaNO_2$ in Aqueous Solution Containing Organic Substrates[a]

substrate/concn, M	quantum yield	substrate/concn, M	quantum yield
none[b]	0.0007	1-butanol/1	0.055
phenol[c]/0.7	0.031	1-propanol/1	0.056
ethylene glycol/1	0.038	ethanol/1	0.057
2-propanol/1	0.045	tetrahydrofuran/1	0.065
2-methyl-2-propanol/1	0.052	propionaldehyde/0.5	0.066

[a] The samples contained 50 mM $NaNO_2$ and were irradiated through a UG11 filter at 20 °C. [b] Data from ref 5. [c] Solution was brown after irradiation.

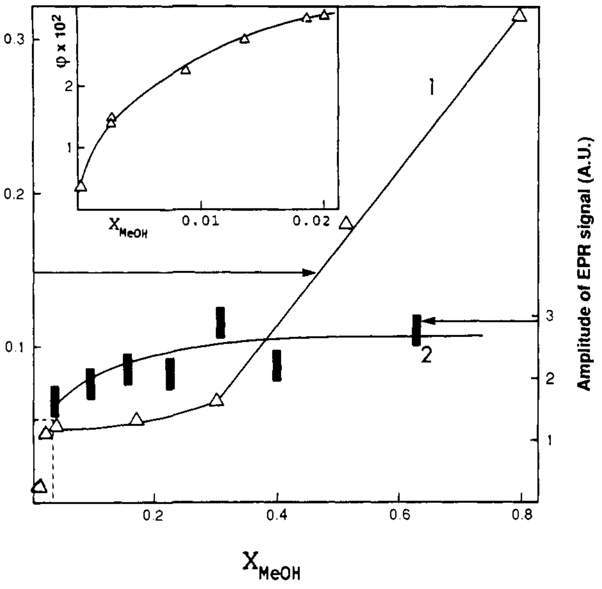

Figure 1. Plots of the quantum yield of oxygen consumption in air saturated solution (plot 1) and the EPR amplitude of DMPO/$^{\bullet}CH_2OH$ adduct in anaerobic solution (plot 2) as a function of methanol molecular fraction (x_{MeOH}). The insert shows the quantum yield of oxygen consumption for low x_{MeOH} values. Solutions contained 0.05 M $NaNO_2$. For quantum yield measurements, the samples were irradiated through a UG11 filter at 20 °C as described previously.[5] The EPR measurements, irradiation was carried out in an EPR cell using 360-nm radiation; solutions with different x_{MeOH} contained 0.3 M DMPO and the signal amplitude of the low field peak was measured after 6 min of irradiation at room temperature.

We chose methanol as a model compound to examine how oxygen photoconsumption changes with the molar fraction (x_{MeOH}) of organic substrate (Figure 1). The quantum yield (ϕ) of oxygen consumption increased initially with increasing MeOH mole fraction and saturated in a range ca. 0.05–0.3 mol fraction. When the methanol concentration was raised further, the quantum yield increased again almost linearly (Figure 1). The character of the $\phi = f(x_{MeOH})$ plot, for $x_{MeOH} > 0.05$, closely resembled the plot of oxygen solubility in water/methanol mixtures.[23,26] Similarly, the quantum yield of O_2 consumption in the mixtures of water with 1,4-dioxane (Figure 2A) and acetone (Figure 2B) resembled

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[26] Oxygen solubility hardly changes up to about 50% volume of alcohol in water ($0.3x_{MeOH}$ in Figure 1) but increases steeply for mixtures containing more alcohol.[23] Such behavior suggests that solvent properties which determine O_2 solubility in water/methanol solutions may initially be similar to those of water but that as more methanol is added the solvent structure is significantly altered. This in turn may affect NO_2^- solvation and any subsequent photochemical processes.

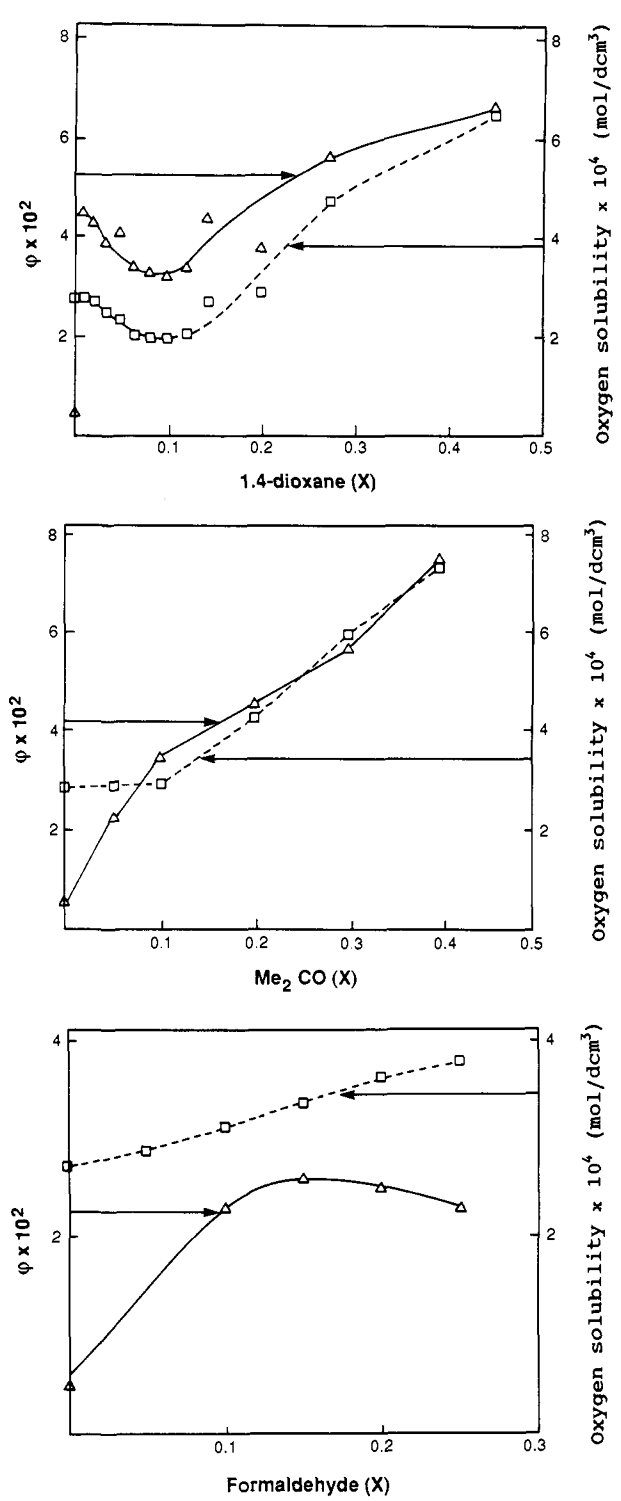

Figure 2. Plots of the quantum yield of oxygen consumption (left scale) and oxygen solubility (right scale) as a function of molecular fraction of organic solvent in water at 20 °C: (A, top) 1,4-dioxane; (B, middle) acetone; (C, bottom) formaldehyde. Solutions were air saturated at atmospheric pressure and contained 0.05 M $NaNO_2$ for irradiation.

the plots of oxygen solubility in these mixed solvents (Figure 2, A and B). However, the yield of oxygen consumption did not follow closely the oxygen solubility in solutions containing formaldehyde (Figure 2C). It may be that polmerization of formaldehyde in aqueous solution changes the concentration and the nature of the species that react with the products of nitrite photolysis.

The influence of temperature on the quantum yield of O_2 consumption during nitrite photolysis is different in the presence of methanol from that observed in its absence.[5] For nitrite irradiated alone in aqueous solution, the rate of oxygen consumption (k) increased linearly with increasing temperature,[5] giving an activation energy $E_a = 11 \pm 1$ kJ/mol which is the same as that reported for NO• oxidation by oxygen in solution, $E_a = 11 \pm 0.6$ kJ/mol.[27] However, in the presence of methanol, a minimum in the plot of $\ln k = f(T^{-1})$ occurs at 12 °C (Figure 3), which suggests a more complex mechanism of oxygen photoconsumption for temperatures below 12 °C. It is possible that the increase in ϕ is caused by an accumulation of product(s) which are more stable at the lower temperatures.

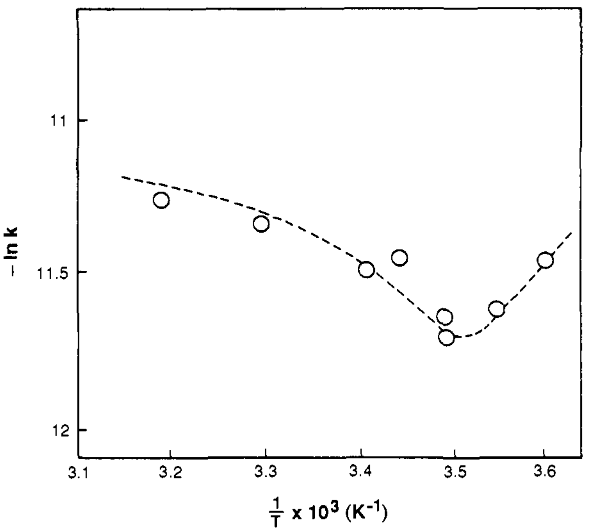

Figure 3. Arrhenius plot of oxygen consumption during irradiation of nitrite solution (0.05 M) containing 0.15 M MeOH.

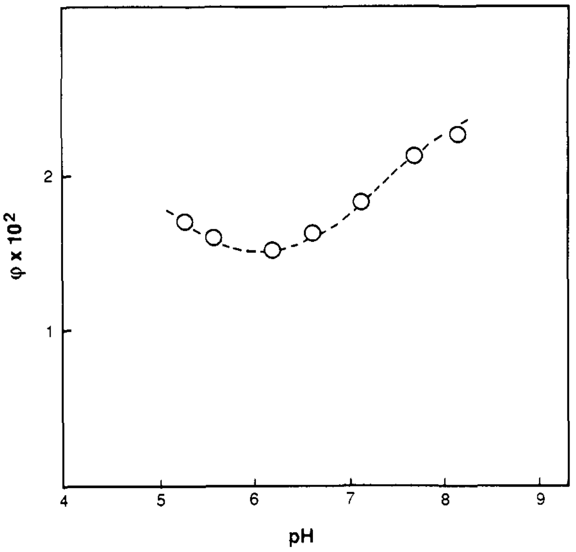

Figure 4. Quantum yield of oxygen consumption of nitrite solutions (0.05 M) containing MeOH (0.15 M) as a function of pH.

When the rate of oxygen consumption of a nitrite solution containing MeOH was measured as a function of pH, a shallow minimum occurred near pH 6 (Figure 4). The reason for this pH dependence is not clear since the quantum yield of primary HO• radicals was reported to be independent of pH over the range $6 \le pH \le 9$ and to increase only slightly below pH 6.[20] HNO_2 does decompose in acidic solution[28] but at a much lower pH than the minimum seen in Figure 4. It may be that nitrogen oxides derived from nitrite photolysis, or unknown secondary reactions with methanol, are involved in the change of oxygen consumption with pH.

2. Generation of HO• Radicals. The HO• radical, which is the primary product of NO_2^- photodissociation, was identified in

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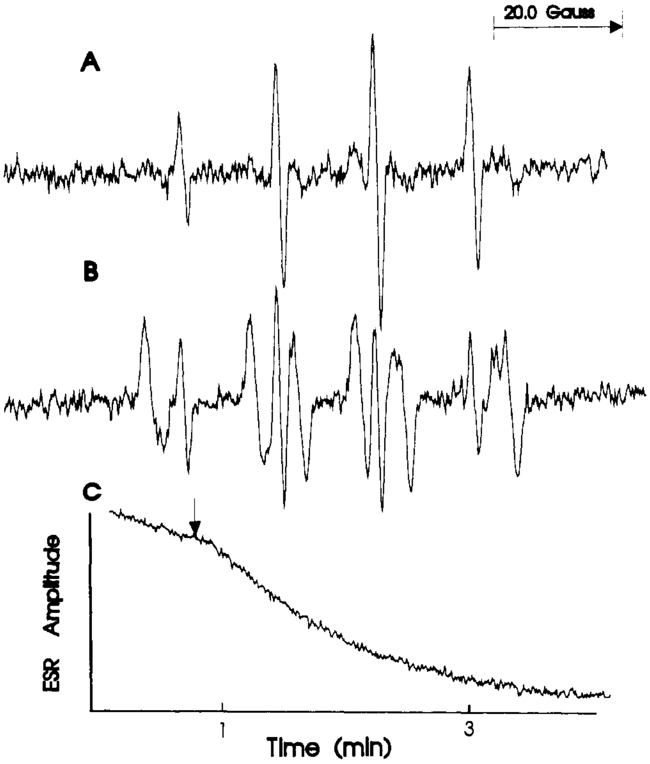
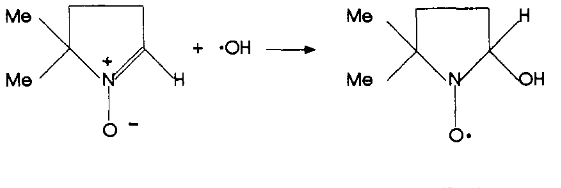


Figure 5. (A) EPR spectrum of DMPO/OH$^•$ adduct recorded during irradiation of nitrite solution (0.05 M) containing DMPO (0.3 M); one scan. Instrumental settings: microwave power, 10 mW; modulation amplitude, 0.33 G; gain, 5 × 10^4; time constant, 0.25 s; scan rate, 4 min. (B) Spectrum of sample A after 30 min of irradiation; instrumental settings as in A. (C) Amplitude of DMPO/OH$^•$ EPR signal (arbitrary units) as a function of time. The adduct was produced using H_2O_2 photolysis and then nitrite (0.05 M) was added and the sample was irradiated at the time marked by an arrow. Instrumental settings: microwave power, 20 mW; modulation amplitude, 0.5 G; gain, 2 × 10^4; time constant, 0.25 s; scan rate, 4 min.

earlier work by scavenging using Br^- or SCN^- anions.[19,20] Hydroxylation of benzene or benzene derivatives has also been used for HO$^•$ identification in photochemical systems.[29] We employed the spin trapping technique to detect HO$^•$ radicals. DMPO was used as a trapping agent because it efficiently scavenges HO$^•$ [30] (eq 7), $k_7 = 2.7 \times 10^9$ M^{-1} s^{-1}, to produce the DMPO/$^•$OH adduct, which has a characteristic EPR spectrum.[31]



(7)

DMPO DMPO/OH

The quantum yield, ϕ(OH), of HO$^•$ formation from NO_2^- photolysis was reported to be 0.046 ± 0.003 for 351-nm excitation at pH 8 and 298 K,[20] therefore a slow but steady buildup of the DMPO/$^•$OH adduct was anticipated. However, the intensity of the DMPO/$^•$OH signal during NO_2^- (0.05 M) photolysis in the presence of DMPO (0.08 M) was low and it could not be increased either by prolonged exposure to light or by using a higher nitrite concentration. A stronger EPR signal from the DMPO/$^•$OH adduct was observed (Figure 5A) when a significantly higher concentration of DMPO (0.3 M) was used. When the sample was further exposed to UV, a second signal appeared (Figure 5B) with hyperfine splittings $a_N = 16.08$ and $a_H{}^\beta = 22.8$ G. This signal was assigned to the DMPO adduct of an unidentified carbon-centered radical originating from DMPO oxidation.

Table II. Hyperfine Splitting Constants (G) from EPR Spectra of DMPO and Nitromethane Adducts with Organic and Inorganic Radicals Produced during NO_2^- Photolysis in Aqueous Solution

DMPO adducts	a_N	$a_H{}^\beta$	comments
HO$^•$	14.9	14.9	H_2O
$CH_3C^•HOH$	16.07	23.35	EtOH
$CH_3CH_2O^•$	13.50	7.4	EtOH, $a_H{}^\gamma = 1.7$
$CH_3^•$	16.56	23.73	H_2O
$CO_2^{•-}$	15.70	18.71	H_2O
$^•CONH_2$	15.45	20.52	H_2O
$SO_3^{•-}$	14.49	15.97	H_2O
$S^{•-}$	16.09	16.19	H_2O
nitromethane adducts	**a_N**	**a_H**	**comments**
$^{14}NO_2^•$	9.6 (2 ^{14}N)	4.10 (1 H)	0.5 M NaOH
$^{15}NO_2^•$	9.6 (^{14}N) 13.43 (^{15}N)	4.11 (1 H)	0.5 M NaOH
NO$^•$	11.49 (NO_2) 6.43 (NO)	2.82 (1 H)	chemical production in 0.5 M NaOH
$CO_2^{•-}$	24.5	8.415 (2 H)	0.5 M NaOH
$SO_3^{•-}$	22.19	7.5 (2 H)	0.5 M NaOH
$S^{•-}$	24.36	6.64 (2 H)	0.5 M NaOH
reduced NM $CH_3NO_2^-$	26.35	12.35 (3 H)	H_2O, pH = 9.5

The weakness of the DMPO/$^•$OH signal and the DMPO oxidation were contrary to what might be expected on the basis of the known literature data. Inefficient DMPO/$^•$OH production may have at least two causes. First is the fast rate of HO$^•$ self-scavenging by nitrite anion, $k_3[NO_2^-] = 0.5 \times 10^9$ s^{-1} ($k_3 = 1 \times 10^{10}$ M^{-1} s^{-1}).[32] This could be compensated to a certain degree by increasing the DMPO concentration. For DMPO concentrations of 0.08 and 0.3 M, the product of k_7[DMPO] is 0.08 × 10^9 and 0.3 × 10^9 s^{-1}, respectively. Thus even at high DMPO concentrations self-scavenging may prevail. Second, the DMPO/$^•$OH adduct already formed may undergo destruction by other photoproducts.

To test the latter hypothesis we studied the effect of UV irradiation of the NO_2^- anion on the EPR signal of the DMPO/$^•$OH radical generated independently by the UV photolysis of H_2O_2 in the presence of DMPO. Then an aliquot of the NO_2^- stock solution was added to a final concentration of 50 mM and the sample was deaerated with N_2 for 2 min. Dark decay of the EPR signal of DMPO/$^•$OH adduct was accelerated by NO_2^- photolysis at 360 nm (Figure 5C). The DMPO/$^•$OH adduct was also weaker and decayed even faster when a more concentrated $NaNO_2$ solution was used or when the process was carried out in an air-saturated sample (not shown). We conclude that a buildup of other oxidative transients of nitrite photolysis, like nitrogen oxides and the peroxynitric anion, or oxygen derived species in aerobic solutions, must be responsible for destruction of the DMPO/$^•$OH adduct in this photochemical system. The intensity of the DMPO/$^•$OH adduct EPR signal depended on pH with optimum detection when nitrite was irradiated at neutral pH (either with or without phosphate buffer). On decreasing or increasing the pH (6–9), the DMPO/$^•$OH spectrum became weaker, which was not a peculiarity of the photochemical $^•$OH generation since the DMPO/$^•$OH radical produced using the Fenton reaction showed the same dependence on pH (data not presented).

3. Identification of $NO_2^•$ Radicals. Nitrogen dioxide is another radical product of nitrite photolysis that is formed during the scavenging of HO$^•$ radicals by NO_2^- (eq 2).[1-3] However, either the $NO_2^•$ does not add readily to DMPO or the resulting adduct is not stable enough under our conditions for detection because no EPR signal from DMPO/$NO_2^•$ was observed. We attempted to trap the $NO_2^•$ radical using nitromethane (NM) in 0.5 M NaOH solution.[33,34] In earlier reports NM was successfully used

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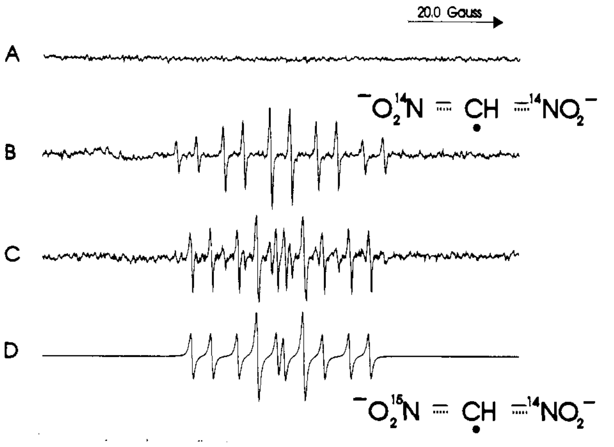

Figure 6. EPR spectra of $NM/NO_2{}^{\bullet}$ adduct in alkaline solution (0.5 M NaOH) recorded during irradiation of nitrite solutions containing NM: (A) nitrite omitted (control); (B) nitrite present (0.1 M), NM, 0.018 M; (C) Nitrite labeled with ^{15}N present (0.4 M), NM, 0.009 M; (D) simulation of EPR spectrum of $NM/^{15}NO_2{}^{\bullet}$ adduct using parameters from Table II. Instrumental settings: same as in Figure 5C except for gain 2.5×10^4 (A, B) or 3.2×10^4 (C).

to trap this radical generated by chemical or radiolytical means.[33,34] In strong alkaline solution NM exists in the aci form, $CH_2{=}NO_2{}^-$, and a radical $R^{\bullet}$ may add to the double bond of the NM anion forming a spin adduct, $R^{\bullet}CH_2NO_2{}^-$. Figure 6 shows the EPR spectrum observed when $NO_2{}^-$ (100 mM) and NM (10 mM) were irradiated in deaerated 0.5 M NaOH solution. The spectrum originates from interaction of an unpaired electron with 2 equivalent nitrogens and one hydrogen atom. In the $NM/NO_2{}^{\bullet}$ adduct, one of the methylene hydrogen atoms dissociates in strong alkaline solution forming the symmetrical $^-O_2NC^{\bullet}HNO_2{}^-$ radical. The hyperfine splittings are shown in Table II, and they are similar to those reported by others.[33,34]

In control experiments, we found that NM (40 mM) itself produced an $NM/NO_2{}^{\bullet}$ adduct similar to that in Figure 6B upon irradiation through a 340-nm-cutoff filter (window glass) in NaOH aqueous solution. Therefore, we used low $MeNO_2$ concentrations and excited $NO_2{}^-$ at 360 nm to prevent NM photodecomposition. Nonetheless, this observation raised the question about the origin of the $NO_2{}^{\bullet}$ radical. To clarify this situation, we employed ^{15}N-labeled sodium nitrite which should produce a different EPR spectrum due to the difference in the nuclear spins of ^{15}N and ^{14}N atoms, 1 and $^1/_2$, respectively. When ^{15}N-labeled nitrite was used, the EPR spectrum shown in Figure 6C was observed. It consists of triplets from ^{14}N and two sets of doublets from hydrogen and ^{15}N atoms (see Table II for hf splittings). This confirms that trapped nitrogen dioxide originated predominantly from nitrite photolysis. The spectrum in Figure 6C contains, however, weaker lines from a $^{14}NO_2$ adduct, which may come only from sensitized destruction of NM since direct photolysis of this spin trap alone at this wavelength did not produce any signal (Figure 6A).

4. Radicals from Organic Substrates. We wished to identify the secondary radicals produced by $HO^{\bullet}$ and/or $NO_2{}^{\bullet}$ from organic substrates added to the irradiated solution of nitrite. The hydroxyl radical reacts with organic substrates forming secondary radical species that are more stable and can be trapped by DMPO. Consequently, the EPR spectrum of the $DMPO/^{\bullet}OH$ radical can be replaced by the spectrum of a DMPO adduct from a scavenger-derived radical.[31,35] In our experiments the following substrates were used: methyl and ethyl alcohols, DMSO, formate, and formamide. Upon UV irradiation of deaerated aqueous solutions of $NO_2{}^-$ (50 mM) and DMPO (80 mM) in the presence of the above substrates, EPR spectra of the DMPO adducts of carbon-centered radicals were observed. They were identified as $^{\bullet}CH_2OH$, $CH_3C^{\bullet}HOH$, $CH_3{}^{\bullet}$, $CO_2{}^{\bullet-}$, and $^{\bullet}CONH_2$ radicals, respectively. Figure 7 shows the spectra of DMPO adducts with $CO_2{}^{\bullet-}$ (A) and $CH_3C^{\bullet}HOH$ and $CH_3CH_2O^{\bullet}$ (B) radicals. Table II summarizes the observed hf splitting constants. The EPR signals of the carbon-centered radicals appeared immediately upon irradiation and were about 10 times stronger than that observed during prolonged DMPO (0.3 M) irradiation (Figure 5B). For methanol, the intensity of the $DMPO/^{\bullet}CH_2OH$ signal increased initially with increasing concentration of methanol and saturated above 0.1 mol fraction (Figure 1, line 2).

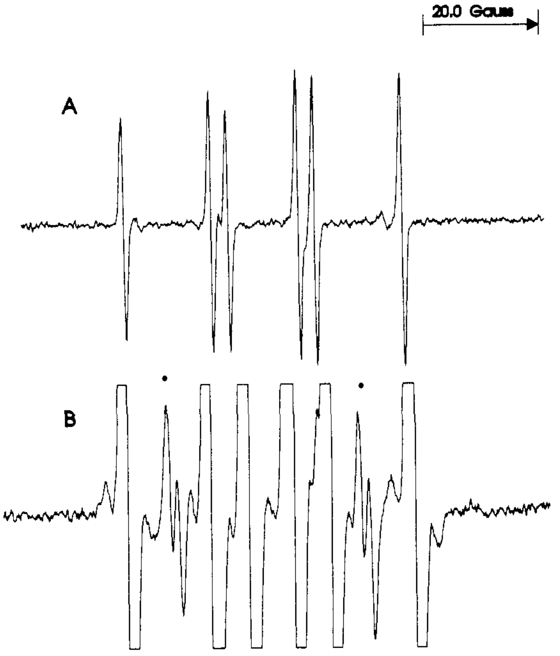

Figure 7. (A) EPR spectrum of $DMPO/CO_2{}^{\bullet-}$ adduct recorded during irradiation (second scan) of nitrite solution (0.05 M) containing HCOONa (0.2 M) and DMPO (0.08 M). (B) Composite spectrum of $DMPO/CH_3C^{\bullet}HOH$ and $DMPO/CH_3CH_2O^{\bullet}$ (marked with asterisk) adducts obtained during irradiation of ethanol saturated with sodium nitrite (second scan). Instrumental settings: same as in Figure 5C except gain 1.6×10^3 (A) or 2×10^4 (B) and modulation amplitude 0.33 G (A, B).

The yield of $^{\bullet}CH_2OH$ radical formation in the presence of high methanol concentration must be determined by the yield of initially photoproduced $HO^{\bullet}$ radicals. If it is assumed that $^{\bullet}CH_2OH$ radicals are scavenged by DMPO (0.3 M), then the intensity of the $DMPO/^{\bullet}CH_2OH$ adduct should be proportional to the yield of $^{\bullet}OH$ production. If methanol becomes a component of a solvent cage for nitrite photodissociation,[26] it would scavenge primary $HO^{\bullet}$ radicals prior to cage recombination with NO; this would increase the EPR signal of the $DMPO/^{\bullet}CH_2OH$ adduct in anaerobic solution. However, saturation of this signal in the region where oxygen consumption (Figure 1, line 2, above $0.2x_{MeOH}$) and solubility[23] increase steeply indicates that the higher O_2 consumption is not caused by an increase in $HO^{\bullet}$ yield due to a change in solvent properties. Therefore, the increased O_2 consumption in aerated $MeOH/H_2O$ solution (Figure 1, line 1) is caused mainly by dissolved oxygen which adds to carbon-centered radicals.

Photolysis of $NO_2{}^-$ in deaerated ethanol (nitrite-saturated solution) in the presence of DMPO yielded adducts of the hydroxyethyl ($CH_3C^{\bullet}HOH$) and ethoxyl ($CH_3CH_2O^{\bullet}$) radicals (Figure 7B, see Table II for hf splittings). The latter species could be produced by abstraction of hydrogen from the hydroxy group of alcohol. The resulting ethoxyl radicals are very unstable in aqueous solutions and rearrange rapidly to carbon-centered radicals, although they can be observed more readily in ethanol.[36]

Nitrite photolysis may provide an oxidative environment that even facilitates the direct detection of a radical product under steady-state conditions without resorting to spin trapping. For example when $NO_2{}^-$ (250 mM) was irradiated through a 305-

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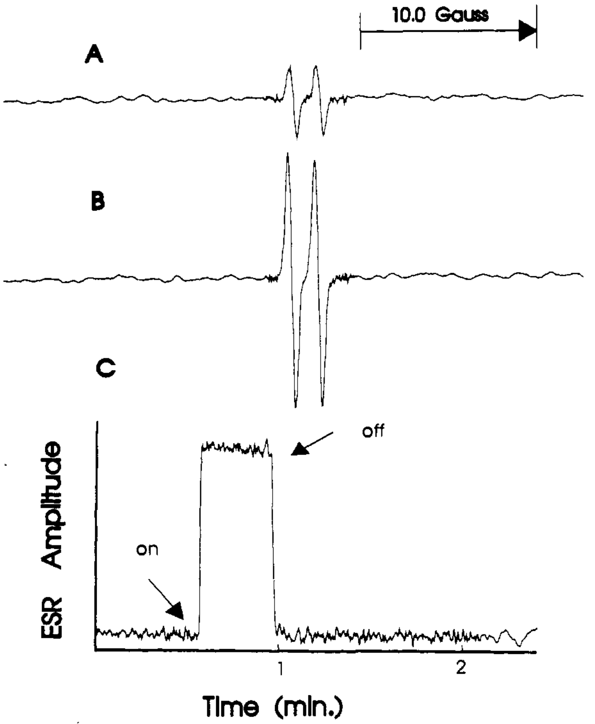

Figure 8. Formation of ascorbyl radical during irradiation (305-nm-cutoff filter) of nitrite solution (0.25 M) containing sodium ascorbate (0.01 M): (A) in the dark; (B) during irradiation. (C) Plot showing the kinetics of formation and decay of ascorbyl radical when light was turned on and off (marked with arrows). Instrumental settings: microwave power, 5 mW; modulation amplitude 0.33 G; gain, 10^4 (A, B) or 2×10^4 (C); time constant, 0.25 s; scan time, 8 min (A, B) or 4 min (C).

nm-cutoff filter in the presence of sodium ascorbate (10 mM), the EPR spectrum of ascorbyl radical was enhanced. The ascorbate anion may be oxidized by either $HO^\bullet$ or $NO_2^\bullet$ radicals[17,37,38] (eqs 8 and 9). At the nitrite concentration used in our

$$\mathrm{AH^- + HO^\bullet \rightarrow A^{\bullet-} + H_2O}\ (k_8 = \simeq 10^9\ \mathrm{M^{-1}\ s^{-1}})\text{[37]} \qquad (8)$$

$$\mathrm{AH^- + NO_2^\bullet \rightarrow A^{\bullet-} + HNO_2}\ (k_9 = 1.8 \times 10^7\ \mathrm{M^{-1}\ s^{-1}})\text{[17]} \qquad (9)$$

experiments, the $HO^\bullet$ radical will react predominantly with nitrite, yielding $NO_2^\bullet$. Therefore the ascorbate anion is less likely to be oxidized by the hydroxyl radical than by the nitrogen dioxide. Figure 8 shows the dark (A) and photoinduced signals (B) as well as the kinetics of their generation and decay (C).

5. Radicals from Inorganic Substrates. We examined the oxidation of sodium sulfide, sodium sulfite, sodium azide, and potassium thiocyanate during nitrite photolysis. DMPO and NM were used as spin traps. When NO_2^- (50 mM), Na_2SO_3 (0.018 M), and DMPO (0.08 M) were irradiated in deaerated aqueous solution, the EPR spectrum shown in Figure 9A was observed. It was assigned to $DMPO/SO_3^{\bullet-}$ radical (g factor is 2.0057 and hf splittings are listed in Table II). These parameters are similar to those reported for the same radical produced photochemically or enzymatically.[39,40]

Figure 9B shows the EPR spectrum observed when NO_2^- was photolyzed in the presence of sodium sulfide (0.1 M) and DMPO (0.08 M) in deaerated solution. This spectrum has a g factor of 2.0061 and it is tentatively assigned to a $DMPO/S^{\bullet-}$ radical, although the formation of a polysulfide radical (e.g. S_2^-) and its corresponding DMPO adduct in our system cannot be ruled out (Table II shows the hf splitting constants). The pattern of this spectrum resembles that of DMPO/glutathionyl$^\bullet$ adduct[41] but its lines are much narrower. This is the first time that the EPR spectrum of such a DMPO adduct has been observed.

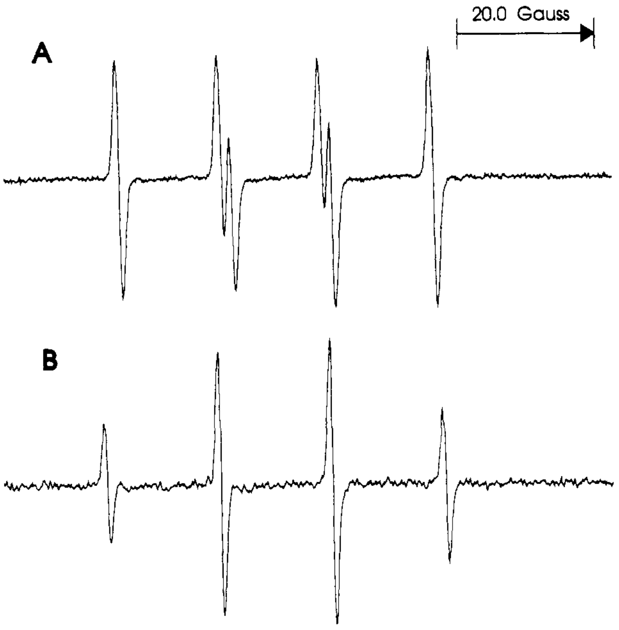

Figure 9. Spectra of DMPO adducts obtained during irradiation of nitrite solution (0.05 M) containing DMPO (0.08 M) and (A) Na_2SO_3 (0.018 M) or (B) Na_2S (0.1 M). No signal was observed without irradiation. Instrumental settings: same as in Figure 5C but gain 10^4 (A) or 2.5×10^4 (B). Recording started after 4 min of irradiation.

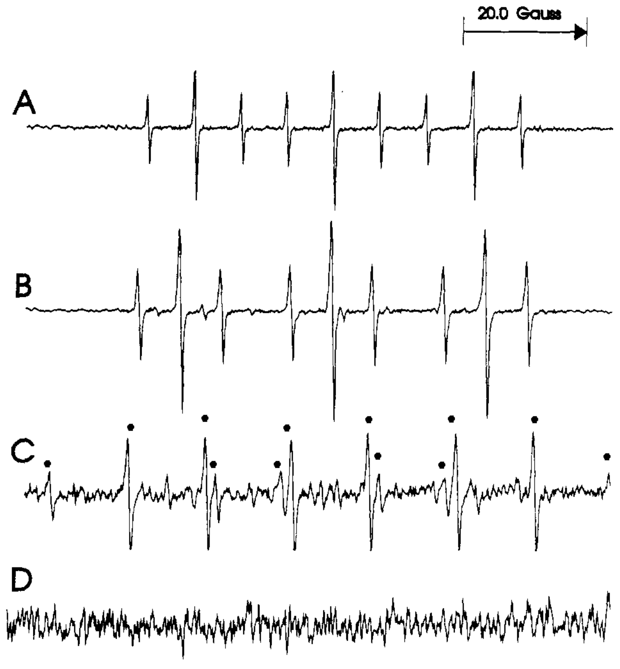

Figure 10. Spectra of NM adducts (A and B) obtained during irradiation of nitrite solution (0.1 M) in NaOH (0.5 M) containing NM (0.009 M) and (A) Na_2SO_3 (0.2 M) or (B) Na_2S (0.2 M). No signal was observed without irradiation. Instrumental settings: same as in Figure 9, but gain 1.6×10^4 (A, B); modulation amplitude, 0.5 G; microwave power, 20 mW; second scan. Spectrum of reduced nitromethane (C) observed during irradiation of nitrite solution (0.2 M) in bicarbonate buffer (pH = 9.5) containing NM (0.009 M) and Na_2S (0.2 M) and (D) control without Na_2S. Instrumental settings: gain, 3.2×10^4; modulation amplitude, 0.5 G; microwave power, 20 mW; second scan.

We further examined the oxidation of sulfur compounds using NM in alkaline solution. It was essential to use high pH (vide supra) to observe the sulfur adducts of NM. When the photolysis was carried out at pH 9.5 in the presence of Na_2S, the spectrum of reduced nitromethane appeared (Figure 10C). A similar spectrum of $MeNO_2^{\bullet-}$ appeared when Na_2S was replaced by

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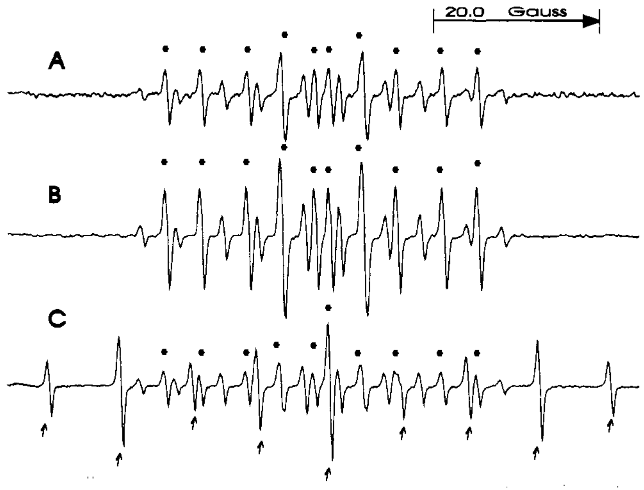

Figure 11. EPR spectra obtained when $Na^{15}NO_2$ (0.1 M) was irradiated in 0.5 M NaOH solution containing NM (0.009 M) and KSCN (0.1 M) or HCOONa (0.2 M): (A) $NM/^{15}NO_2^\bullet$ adduct (asterisk) and $NM/NO_2^\bullet$ adduct (unmarked); receiver gain, 2.5×10^4; modulation amplitude, 0.5 G; microwave power, 20 mW; time constant, 0.25 s; scan, 4 min; (B) same as A but in the presence of KSCN (0.33 M); gain, 1.6×10^4; (C) same as A but in the presence of HCOONa (0.33 M); new adduct $^-CO_2CH_2NO_2^-$ is marked with arrows; receiver gain, 6.3×10^3; modulation amplitude, 0.5 G; time constant, 0.25 s; scan, 4 min. Solutions were deoxygenated (N_2, 8 min). No signal was observed in the dark; second scan.

sodium formate at pH 9.5[42] (not shown). Irradiation of Na_2S and Na_2SO_3 (both 0.2 M) in 0.5 M NaOH solution containing $NaNO_2$ (0.1 M) and $MeNO_2$ (10 mM) produced the spectra of the NM adduct of $^-SCH_2NO_2^{\bullet-}$ and $^-SO_3CH_2NO_2^{\bullet-}$ (Figure 10). The hf splitting constants of all observed spectra are listed in Table II. The hf values agree with those reported for the same species generated chemically or radiolytically.[33,34,44]

6. Reactions of NO_2^- with Secondary Radicals. Some radicals produced from inorganic/organic substrates by the primary $HO^\bullet$ can subsequently react with NO_2^- anions. The reaction of $HO^\bullet$ with NaN_3, KSCN, and $HCOO^-$ is very fast (rate constants of order 10^9 M^{-1} s^{-1}) and they are excellent sources of azidyl ($N_3^\bullet$), thiocyanyl ($SCN^\bullet$), and formyl ($CO_2^{\bullet-}$) radicals.[45-47] Reported redox potentials for these radicals are the following: $E°(N_3^\bullet/N_3^-) = 1.3$ V,[48] $E°(SCN^\bullet/SCN^-) = 1.66$ V,[49] and $E°(CO_2^{\bullet-}/CO_2^{2-}) = -1.9$ V.[50] Since the NO_2^-/NO_2 couple has a redox potential $E°(NO_2^\bullet/NO_2^-) = 1.03$ V,[48] it is likely that the oxidizing radicals $N_3^\bullet$ and $SCN^\bullet$ might react with NO_2^- forming $NO_2^\bullet$ radicals. We wished to examine this hypothesis and for comparison we used strongly reducing $CO_2^{\bullet-}$ radicals.

Photolysis of nitrite in the presence of NaN_3 did not produce either DMPO or NM adducts of $N_3^\bullet$ radicals, although such adducts are readily formed by other $HO^\bullet$ sources.[33,34,47,51] Similarly, we could not observe the DMPO and NM adducts with $SCN^\bullet$ radicals. What was observed instead was a marked increase in the formation of $NM/NO_2^\bullet$ adduct, and we used the ^{15}N labeled nitrite to identify the origin of the $NO_2^\bullet$ radicals. The EPR signal of the $NM/^{15}NO_2^\bullet$ adduct increased about threefold when NaSCN (0.25 M) was added to an irradiated $Na^{15}NO_2$ solution (0.05 M) containing $MeNO_2$ (0.01 M) (Figure 11B). A similar result was obtained in the presence of NaN_3 in NaOH solution (not shown). These observations, together with the values of redox potentials, can be explained assuming that the nitrite anion is oxidized by inorganic $N_3^\bullet$ and $SCN^\bullet$ radicals (eq 10).

$$N_3^\bullet/SCN^\bullet + NO_2^- \rightarrow N_3^-/SCN^- + NO_2^\bullet \qquad (10)$$

In contrast the formyl radical, $CO_2^{\bullet-}$, was observed during NO_2^- photolysis using both DMPO and NM traps (Figures 6 and 11). However, $HCOO^-$ also enhanced production of $NO_2^\bullet$ radicals. When $^{15}NO_2^-$ (0.1 M), NM (10 mM), and $HCOO^-$ (0.2 M) were photolyzed in deaerated NaOH (0.5 M) an EPR spectrum shown in Figure 11C was observed. It contains components from three species. One species was not present in Figure 11, A or B, and was identified as $NM/CO_2^{\bullet-}$ adduct (arrows). The second species was $NM/NO_2^{\bullet-}$ originating from NM. The third species was identified as the $^{-15}NO_2CHNO_2^{\bullet-}$ radical (marked with asterisks in Figure 11C). The intensity of this latter component was markedly higher in comparison to the sample where the formate was omitted. To explain the enhanced formation of $NM/^{15}NO_2^\bullet$ adduct in the presence of HCOONa, we suggest that the $CO_2^{\bullet-}$ radical reacts with NO_2^- to give the $NO_2^{\bullet 2-}$ radical. This reaction has been proposed before.[52] The NO_2^{2-} may be trapped by NM, and the resulting $NM/NO_2^{\bullet 2-}$ adduct may be oxidized yielding the symmetrical $NM/NO_2^\bullet$ radical adduct (eq 11). Probably a mild oxidizer, like $NO^\bullet$ present in our system, is responsible for this oxidation.[53]

$$NO_2^{\bullet 2-} + CH_2NO_2^- \rightarrow ({}^{2-}O_2NCH_2NO_2^-)^\bullet \xrightarrow{-H^-} {}^-O_2NC^\bullet HNO_2^- \qquad (11)$$

Thus the $NO_2^\bullet/NM$ adduct may be detected in the presence of either oxidative or strongly reducing intermediates. Nevertheless, we could not observe accumulation of this adduct when sodium sulfite or sodium sulfide were examined (Figure 10). A possible explanation may involve efficient $HO^\bullet$ scavenging by SH^-/S^{2-} and SO_3^{2-} which competes with reaction 3 and/or reduction of $NO_2^\bullet$ radical back to NO_2^- by the sulfur anions. The oxidation of thiol –SH groups by $NO_2^\bullet$ has been reported,[18] and the oxidation of SO_3^- to SO_4^{2-} by nitrogen dioxide has also been proposed.[38]

The reduction of $SCN^\bullet$ radicals by nitrite could lead to the lowering of $(SCN)_2^-$ absorption and consequently to an underestimation of the quantum yield of $HO^\bullet$ production from nitrite, where sodium thiocyanate was used as a $HO^\bullet$ scavenger.[19,20] The back reduction of substrate-derived radicals by NO_2^- may also maintain some steady-state concentration of $NO_2^\bullet$. Thus, $NO_2^\bullet$ might react with $HO^\bullet$ ($k = 1.2 \times 10^{10}$ M^{-1} s^{-1}) yielding peroxynitrous acid.[32] This reaction seems unlikely to be important considering low steady-state concentration of $HO^\bullet$ and $NO_2^\bullet$ transients. However, the peroxynitrous anion is a long-lived oxidizer (half-life about 1 s at 37 °C, pH = 7.5[54]), so it may accumulate and possibly account somewhat for oxidation.

7. Singlet Oxygen Production. In a previous flash photolysis study of nitrite, singlet oxygen has tentatively been suggested as a possible transient.[3] We attempted to examine this suggestion by monitoring $^1O_2$ phosphorescence. Irradiation of a 0.15 M

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[42] At pH 9.5, NM is mostly present in a non-ionized form ($pK = 10.3$)[43] which cannot act efficiently as a spin trap, but can act as an electron acceptor. Yet, the mechanism of $MeNO_2^{\bullet-}$ formation is not obvious in our system. The $MeNO_2^{\bullet-}$ signal was light-dependent but did not appear without Na_2S, which excludes the simple electron transfer sensitization by nitrite. Rather the transients of S^{2-} photo-oxidation are capable of donating an electron to nitromethane while S^{2-} itself cannot. This may suggest that nitrite photolysis carried out in the presence of a suitable electron donor (S^{2-}, $HCOO^-$) can generate a reducing environment for NM.

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[53] NO, which is produced in reaction 1, is a non-acidic nitrogen oxide that can accumulate in aqueous solution. It possesses oxidative properties, e.g. can oxidize thiols[18] and CO_2^-.[52] Bubbling an alkaline solution of NM with NO, we found that NO can add to nitromethane anion forming an adduct whose spectrum differs from that of NO_2 adduct (spectrum not shown but splitting parameters are listed in Table II).

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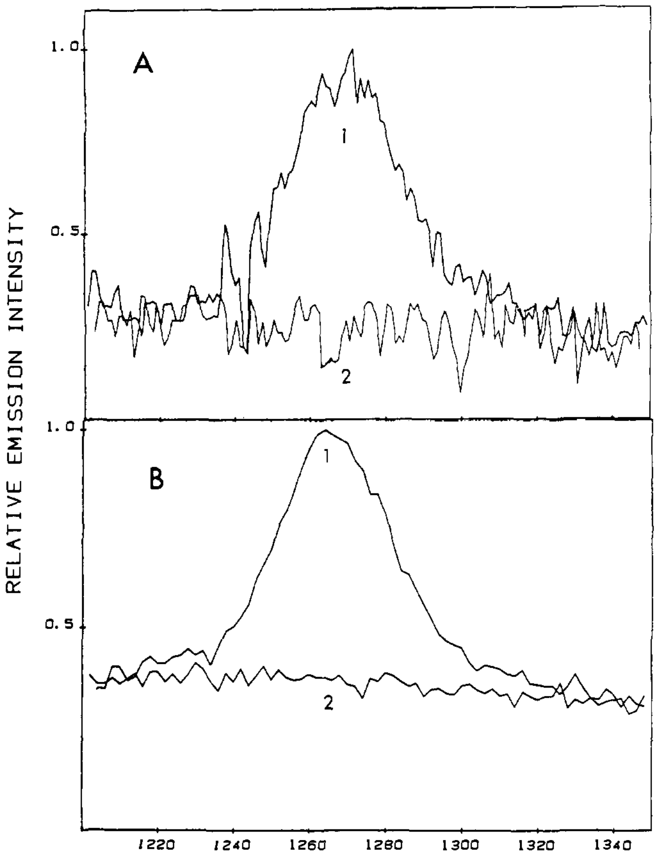

Figure 12. Spectra showing singlet oxygen phosphorescence observed when sodium nitrite (0.15 M) was irradiated (305-nm-cutoff filter) in oxygen-saturated D_2O (line 1); the phosphoresence was quenched by NaN_3 (0.01 M) (line 2): (A) single scan spectrum; (B) average of 10 scans with random noise filtered out.

solution of sodium nitrite in D_2O through a 305-nm-cutoff filter (one scan) produced weak and noisy $^1O_2$ phosphorescence (Figure 12A, line 1). The $^1O_2$ phosphorescence was distinct when an average of 10 scans was accumulated and the noise was filtered out (Figure 12B). This weak signal was probably attenuated by $^1O_2$ self-quenching by nitrite, since singlet oxygen reacts with NO_2^- during photosensitization by eosine or rose bengal ($k_q = 5.4 \times 10^4$ M^{-1} s^{-1}).[55] The $^1O_2$ phosphorescence was abolished by the efficient $^1O_2$ quencher, sodium azide, 10 mM (Figure 12A, line 2).

When nitrite was irradiated in wet acetone or 1,4-dioxane, the $^1O_2$ signal was reduced more than half (data not shown). In both acetone and dioxane, the lifetime of $^1O_2$ is close to that in D_2O.[56] While the $^1O_2$ radiative rate constant in these solvents is unknown, recent studies have shown that it is solvent-dependent.[57] Thus $^1O_2$ emission in D_2O cannot be correlated quantitatively with that in organic solvents. The mechanism of $^1O_2$ production is unknown and may involve the triplet state of NO_2^- and excited fragments from photodissociation or decomposition/recombination of peroxides in solution.[58] Peroxides are a less likely source of $^1O_2$ because photolysis of nitrite in 1,4-dioxane or acetone appeared to produce much less $^1O_2$, despite strong O_2 consumption in these solvents that must proceed via peroxides. Singlet oxygen production seems to be a less important oxidative pathway during the UV photolysis of nitrite anion, although many substrates we used, e.g. ascorbate and sulfide, are known to react efficiently with singlet oxygen.

8. Chemical Consequence of Nitrite Photolysis. The importance of the chemical reactions initiated by NO_2^- photooxidation is supported by efficient oxygen consumption suggesting the formation of many oxidation products. Indeed, we found that acetone was the main GC product when nitrite was irradiated in the presence of 2-propanol; acetone was also the major product (87%) observed during nitrate photolysis.[29,59] Our sample containing 2-propanol did not become acidic during photooxidation, which was in contrast to the samples containing methanol, and especially 1,4-dioxane (both 9:1 v/v mixture with water). The quantum yield of acid formation was 1.1×10^{-3} for methanol and 3.1×10^{-2} for dioxane. The enhanced O_2 consumption in the presence of organic substrates is consistent with detection of carbon-centered radicals, which are known to react readily with O_2.[60] The resulting peroxyl radicals are unstable and may promote further oxidation reactions. We could not trap peroxyl radicals, however, due to their low reactivity with DMPO and the instability of their DMPO adducts in water. However, the final oxidation products must be determined by the chemistry of appropriate peroxides, which was not studied here. Besides oxygen-consuming reactions, the products of radical recombination are also expected, and formation of nitroso and nitro products during nitrite photolysis is currently under investigation.

Conclusions

In this work we used the EPR spin trapping technique to demonstrate the potential of nitrite to photogenerate radical products. The absorption maximum of nitrite in aqueous solution is 360 nm, as compared to less than 300 nm for H_2O_2, which is often used as an efficient photochemical source of radicals ($HO^\bullet$).[61] Thus a broader selection of substrates whose absorption overlaps with that of H_2O_2 but not with the absorption of NO_2^- may be used in such photochemical investigations. However, one should be aware that, besides $HO^\bullet$ radical, nitrite photolysis produces other reactive radical species.

We have shown that nitrite/UV photooxidation of organic and inorganic substrates proceeds by radical reactions. Using the EPR spin trapping technique, we have provided spectroscopic evidence for the formation of $HO^\bullet$ and $NO_2^\bullet$ radicals and characterized for the first time some organic and inorganic radicals occurring during this photolysis. Although the $HO^\bullet$ radical is the most reactive oxidant formed during nitrite photolysis, other transients like nitrogen oxides, singlet oxygen, or nitrogen peroxy anions occur during photolysis and may participate in oxidation processes. The high rate of oxygen consumption by organic substrates emphasizes the potential importance of photooxidation initiated by nitrite in the destruction of organic environmental pollutants from both natural and industrial sources.

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Registry No. $NaNO_2$, 7632-00-0; $HO^\bullet$, 3352-57-6; $CH_3C^\bullet HOH$, 2348-46-1; $CH_3CH_2O^\bullet$, 2154-50-9; $CH_3^\bullet$, 2229-07-4; $^\bullet CONH_2$, 2858-51-7; $^{14}NO_2^\bullet$, 10102-44-0; $^{15}NO_2^\bullet$, 137496-65-2; $NO^\bullet$, 10102-43-9; $CO_2^{\bullet-}$, 14485-07-5; $SO_3^{\bullet-}$, 12210-38-7; $S^{\bullet-}$, 14337-03-2; $CH_3NO_2^-$, 18137-96-7; MeOH, 67-56-1; HCOONa, 141-53-7; Na_2SO_3, 7757-83-7; Na_2S, 1313-82-2; KSCN, 333-20-0; NaN_3, 26628-22-8; $^-O_2{}^{14}N\text{-}C^\bullet H\text{-}{}^{14}NO_2^-$, 16454-26-5; $^-O_2{}^{15}N\text{-}C^\bullet H\text{-}{}^{14}NO_2^-$, 137496-66-3; Me_2SO, 67-68-5; NaSCN, 540-72-7; DMPO/OH, 55482-03-6; phenol, 108-95-2; ethylene glycol, 107-21-1; 2-propanol, 67-63-0; 2-methyl-2-propanol, 75-65-0; 1-butanol, 71-36-3; 1-propanol, 71-23-8; ethanol, 64-17-5; tetrahydrofuran, 109-99-9; propionaldehyde, 123-38-6; formaldehyde, 50-00-0; acetone, 67-64-1; 1,4-dioxane, 123-91-1; sodium ascorbate, 134-03-2.

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