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Oxygen uptake after electron transfer from donors to the triplet state of nitronaphthalenes and dinitroaromatic compounds

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Abstract

The effects of oxygen in the photolysis of nitroaromatic compounds, such as 1-nitronaphthalene (1NN), 1,4-dinitronaphthalene, 4,4′-dinitrobiphenyl and mono- or di-nitrofluorenone, were studied in air-saturated aqueous acetonitrile solution in the presence of donors, such as aliphatic amines, e.g. triethylamine (TEA), aromatic amino acids or ascorbic acid. The overall reaction is conversion of oxygen via the $HO_2^{\bullet}/O_2^{\bullet-}$ radical into hydrogen peroxide. The quantum yield of oxygen uptake ($\Phi_{\text{-}O_2}$) increases with the donor concentration. The maximum values are $\Phi_{\text{-}O_2} = 0.3$, e.g. for 1NN and 3–30 mM ascorbic acid or TEA. The photoinduced formation of H_2O_2 is initiated by triplet quenching and subsequent reaction of the donor and acceptor radicals with oxygen. The rate constant of scavenging of the nitroaromatic radical anion by oxygen is $(0.6–1) \times 10^7\ M^{-1}\ s^{-1}$. Some specific properties of oxygen and nitroarene compounds, including the radicals involved and the pH and donor concentration dependences, were discussed.

Keywords: Nitroaromates; Photooxidation; Photoreduction; Electron transfer; Radicals

1. Introduction

Photoreduction of nitroaromatic compounds is the subject of various studies [1–18]. Parent nitrobenzene is not a good candidate for photoreduction since its quantum yield upon direct excitation is as low as 0.012 and the deactivation is extremely fast [1–5]. The quantum yield of photodecomposition of 4-nitrotoluene and 4-nitroanisol by triethylamine (TEA) increases with the amine concentration and the maximum values for [TEA] = 0.1 M in argon-saturated acetonitrile are 0.007 and 0.03, respectively [17]. The quantum yield of intersystem crossing (Φ_{isc}) is also rather small for substituted nitrobenzenes and *p*-nitroacetophenone (*p*NAP) [5]. In contrast, Φ_{isc} and the quantum yield of molecular singlet oxygen formation (Φ_{Δ}) of 1- and 2-nitronaphthalene (1NN, 2NN) are substantial [14]. Nitronaphthalenes and 2-nitrofluorenone (NF) [6–10] are appropriate for photoreduction studies because the triplet state is spectroscopically accessible and Φ_{isc} is sufficiently high [13,14].

Another important photoreaction of nitroaromatic compounds is photoconversion into nitroso derivatives, which can take place intramolecularly, when the nitro group is located in *o*-position to an appropriate H-donor substituent, e.g. CH_3 or CHO groups [19–22]. Intramolecular nitro group assisted proton transfer in photoirradiated 2-(2′,4′-dinitrobenzyl)pyridine has been reported [21]. Recently, the effects of the 4,5-dimethoxy groups on the conversion of 2-nitrobenzyl alcohols and 2-nitrobenzaldehyde into nitroso derivatives were studied [22]. The mechanisms of the photoinduced nitro to nitroso reaction and applications of photoremovable protecting groups have been reviewed [19]. Some nitroarenes, e.g. *p*NAP, are suitable as radiosensitizers [5,23].

Dinitro compounds, such as 1,4-dinitronaphthalene (DNN), 4,4′-dinitrobiphenyl (DNB) and 2,7-dinitrofluorenone (DNF) (see Scheme 1), constitute another group which is suitable for photoreduction. Their triplet state is the major intermediate as supported by $\Phi_{\Delta} = 0.4–0.6$ [15]. In these cases the efficiency of photoreduction can be enhanced by TEA and in polar solvents electron transfer takes place to the lowest triplet state [14,15]. Subsequently, the radical anion ($ArNO_2^{\bullet-}$) and the radical cation ($Et_3N^{\bullet+}$) are formed. A second nitroaromatic radical is formed since the α-aminoalkyl radical, formed by deprotonation, reacts with the substrate via H-atom transfer. If oxygen is excluded, these two radicals undergo a slow termination reaction

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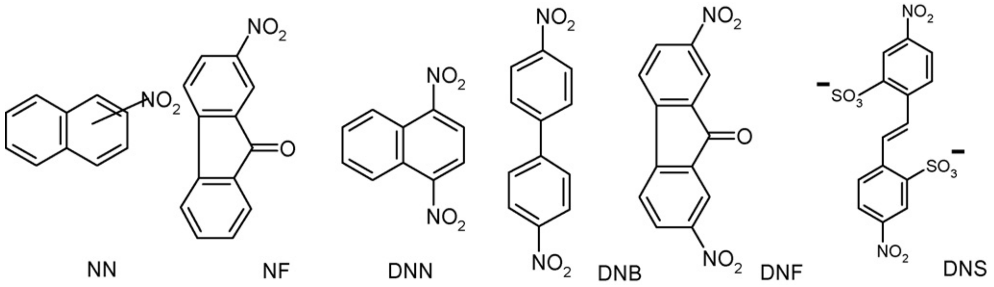


Scheme 1.

yielding the nitroso compounds in most cases as labile products and finally essentially naphthylhydroxylamines [13–16]. The specificity of the substitution pattern indicates three different major pathways via termination. For DNN the corresponding *aci*-nitro dianion is observable as longer lived intermediate [15]. The chemistry of the nitroaromatic radicals has been investigated [23–25] and reviewed [26].

Generally, the admission of oxygen suppresses photoreduction of aromatic compounds and molecular singlet oxygen is the second short-lived intermediate [27,28]. This is photodamage of Type I (energy transfer), but no permanent product is expected in the absence of macromolecules (e.g. vesicles). For example, the reactivity of the triplet state of aromatic nitrones with singlet oxygen is low even when they are present in a mM amount [29]. However, when the donor concentration is appropriate, photodamage of Type II (electron transfer) takes place. Oxygen is thereby converted via hydroperoxyl or superoxide ion radicals ($HO_2^{\bullet}/O_2^{\bullet-}$) into H_2O_2. This gives rise to photoinduced oxygen uptake.

In this work the oxygen consumption was measured for mono- and di-nitroaromatic compounds, 1NN, 2NN, NF, DNN, DNB and DNF in aqueous acetonitrile solution in the presence of amines, e.g. *N*,*N*-diethylhydroxylamine (DHA), ethylenediaminetetraacetate (EDTA) or TEA, aromatic amino acid derivatives, e.g. *N*-acetyltyrosine (*N*aTyr) and *N*-acetyltryptophan (*N*aTrp), and ascorbic acid. In addition, *trans*-4,4′-dinitrostilbene-2,2′-disulfonate (*trans*-DNS), a water-soluble nitrostilbene was studied, see Scheme 1. Most of the relevant photochemical properties of *trans*-4-nitrostilbenes are well known [30–37]. The quantum yield of oxygen uptake ($\Phi_{\text{-O}_2}$) increases for the seven nitroaromatic compounds with the concentration of a given donor in a characteristic manner and $\Phi_{\text{-O}_2}$ is up to 0.3. Moreover, termination of the nitroaromatic radicals was examined in argon-saturated acetonitrile–water.

2. Experimental details

trans-DNS and the mono- and other di-nitroaromatic compounds were as commercially available (EGA) and the same as previously used [13–15,30]. The donors, e.g. ascorbic acid, DHA, EDTA, TEA, *N*aTyr and *N*aTrp were as previously [38–40]. The oxygen concentration prior to (0.27 mM) and upon photolysis was determined by a Clark electrode (Hansatech). The relative yield of oxygen consumption was determined from the slope of [O_2] versus irradiation time [38]. Photoconversion was achieved by a 1000 W Xe–Hg lamp and a monochromator for irradiation at 313 and 366 nm and aberchrome-540 was applied as actinometer, cf. Refs. [38–40]. The experimental error in the quantum yield determination is ±25%. Excimer lasers (Lambda Physik, pulse width of 20 ns and energy <100 mJ) were used for excitation at 308 and 248 nm (EMG 200, EMG 210 MSC). For the sake of simplicity the presented steady-state and time-resolved data refer to $\lambda_{\text{irr}} = 313$ nm and $\lambda_{\text{exc}} = 308$ nm, respectively. The absorption signals were measured with two digitizers (Tektronix 7912AD and 390AD) and an Archimedes 440 computer for data handling. The measurements were performed in air-saturated acetonitrile–water (1:5 and 1:1) for oxygen uptake and transient absorption, respectively. No buffers were added and the typical pH was 3, 6–8 and 12–13 for ascorbic acid, amino acids and amines, respectively. The samples were freshly dissolved and measured at 24 °C.

3. Results and discussion

3.1. Transients and reaction mechanism

For the mono- and di-nitroaromatic compounds in acetonitrile and mixtures with water fluorescence is negligible and the first transient in the ns–μs time range is the lowest triplet state ($^{3*}ArNO_2$). This triplet is produced by population of the excited singlet state ($^{1*}ArNO_2$) via isc (1) and decays via isc step (2) or via quenching by oxygen, reaction (3). The rate constant, using an oxygen concentration of 0.3 mM in air-saturated acetonitrile–water 1:1, is $k_3 = (1.7–3) \times 10^9\ M^{-1}\ s^{-1}$ (Table 1). A literature value for 1-methoxy-4-nitronaphthalene in acetonitrile is $2 \times 10^9\ M^{-1}\ s^{-1}$ [7]. The triplet lifetime (τ_T) in argon- and air-saturated solution is in the 10 μs range and below 1.8 μs, respectively. The T–T absorption spectra are rather broad and the maxima (λ_T) range from 470 to 600 nm.

$$^{1*}ArNO_2 \rightarrow {}^{3*}ArNO_2 \qquad (1)$$

$$^{3*}ArNO_2 \rightarrow ArNO_2 \qquad (2)$$

$$^{3*}ArNO_2 + O_2 \rightarrow ArNO_2 + O_2 \qquad (3)$$

$$^{3*}ArNO_2 + DH_2 \rightarrow ArNO_2^{\bullet-} + DH_2^{\bullet+} \qquad (4)$$

The reactive intermediate of all nitroaromatic compounds examined is the triplet state which is quenched on addition of a donor. For 1NN in acetonitrile–water (1:1, v/v) the rate constant for this quenching step, obtained from linear

Table 1
Triplet lifetime, rate constant for quenching ($10^9\ M^{-1}\ s^{-1}$) by oxygen and radical peak[a]

Compound	Argon: τ_T (μs)	Air: τ_T (μs)	k_3 ($10^9\ M^{-1}\ s^{-1}$)	λ_T (nm)	λ_{rad} (nm)	k_6[b] ($10^7\ M^{-1}\ s^{-1}$)
1NN	≥8	1.8	1.7 (1.4)[c]	560	390	0.8
2NN	≥8	1.8	1.7 (1.3)	600	390	0.7
NF	12	1.1	2.7	470	370	0.6
DNN	10	1.2	3 (1.2)	550	545	0.9
DNB	2	0.8	3.6	510	440	1
DNF	8	0.9	3 (0.8)	500	470	1
trans-DNS[d]	0.06	0.05		450	450	

[a] In acetonitrile–water (1:1, v/v), $\lambda_{exc} = 308$ nm.
[b] Using TEA.
[c] In parentheses: acetonitrile.
[d] Values in neat water.

Table 2
Rate constant k_4 for quenching ($10^9\ M^{-1}\ s^{-1}$) by donors[a]

Compound	TEA	DHA	*N*aTrp	Ascorbic acid
1NN	1.3			1.0
2NN	1.4	1 0.5[b]	0.2	1.1
NF	1.0			1.5
DNN	1.5			1.5
DNB	2.1	0.6	0.2	2.5
DNF	2.6			1.0
trans-DNS	0.6			1

[a] In acetonitrile–water (1:1, v/v), $\lambda_{exc} = 308$ nm.
[b] For EDTA.

plots of $1/\tau_T$ versus the ascorbic acid and TEA concentration, is $k_4 = 1.0 \times 10^9$ and $1.3 \times 10^9\ M^{-1}\ s^{-1}$, respectively. For 1-methoxy-4-nitronaphthalene/TEA in acetonitrile–water 3:1 and 1:1 $k_4 = 0.8 \times 10^9$ and $0.4 \times 10^9\ M^{-1}\ s^{-1}$, respectively [7]. Similar kinetics were observed for DNN, DNF and DNB in argon-saturated acetonitrile–water (1:1, v/v). The values are $k_4 = (1–2.5) \times 10^9\ M^{-1}\ s^{-1}$ for ascorbic acid and TEA (Table 2), i.e. they are lower than in neat acetonitrile [15]. The transient absorption spectra of 2NN in the presence of TEA and ascorbic acid are shown in Fig. 1a and b, respectively. Other examples of time-resolved absorption spectra in the presence of TEA are shown in Figs. 2 and 3 for DNN, DNB and DNF.

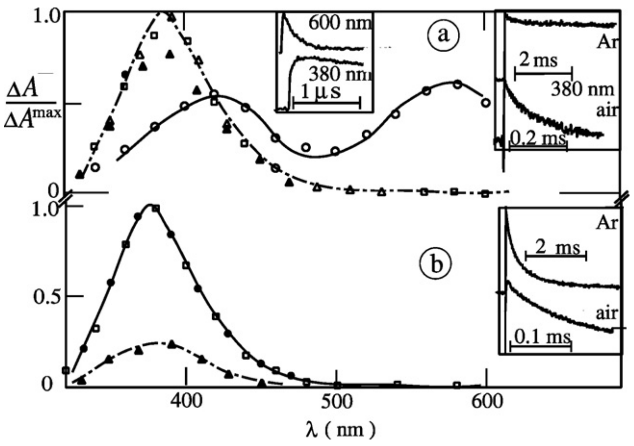


Fig. 1. Transient absorption spectra of 2NN in argon-saturated acetonitrile–water (1:1, v/v) in the presence of (a) 3 mM TEA and (b) 3 mM ascorbic acid at 20 ns (○), 1 μs (△), 10 μs (□), 0.1 ms (●) and 1 ms (▲) after the 308 nm pulse; insets: kinetics under argon and air as indicated.

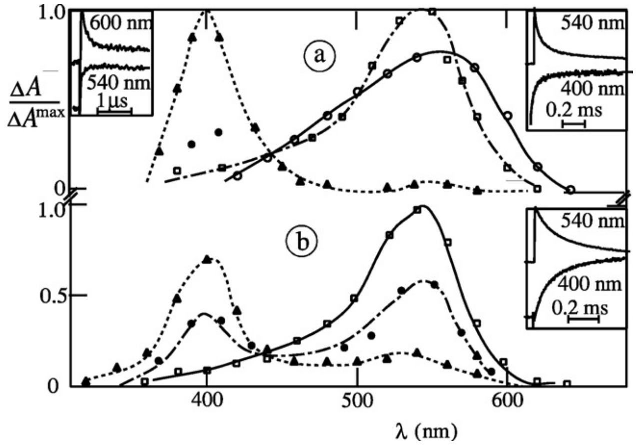


Fig. 2. Transient absorption spectra of DNN in the presence of 10 mM TEA in (a) in argon- and (b) air-saturated acetonitrile–water (1:1, v/v) at 20 ns (○), 10 μs (□), 0.1 ms (●) and 1 ms (▲) after the 308 nm pulse; insets: kinetics as indicated.

The triplet state as first transient is in all cases observable unless the donor concentration is too large. The absorption spectra of the secondary species depend on the acceptor structure

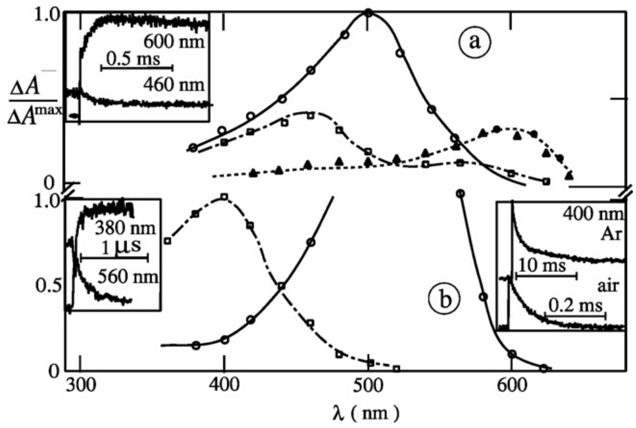


Fig. 3. Transient absorption spectra of (a) DNF and (b) DNB in argon-saturated acetonitrile–water (1:1, v/v) in the presence of 10 mM TEA at 20 ns (○), 10 μs (□), 0.1 ms (●) and 1 ms (▲) after the 308 nm pulse; insets: kinetics under argon and air as indicated.

[15]. The secondary transient with maxima at $\lambda_{rad} = 390$ nm for 1NN or 2NN is practically only due to the radical of the nitroaromatic compounds since the radical cations of the donors have a low ε value [18]. The half-life of the nitroaromatic radical anion is rather long-lived in argon-saturated solution [9,15]. In air-saturated acetonitrile–water the decay follows a first-order law and the lifetime of the short-lived radicals is in the 30–120 μs range, an example is shown in Fig. 2b.

For the donor–acceptor systems under investigation, $ArNO_2^{\bullet-}$ and donor$^{\bullet+}$ are formed by electron transfer. The electron transfer from TEA to the triplet state of 1NN, 2NN, NF, DNN, DNB and DNF takes place with $k_4 = 1 \times 10^{10}\,M^{-1}\,s^{-1}$ in argon-saturated benzene, but the radicals are non-ionic and the products different [16] with respect to acetonitrile [14,15]. Photoreactions with TEA result from two longer lived radicals (anion and the conjugate acid or two radical anions in neat and wet acetonitrile, respectively) and their conversion into the nitroso compound [15]. For aliphatic amines deprotonation of the radical cation leads to the α-aminoalkyl radical, reaction (5). $ArNO_2^{\bullet-}$ reacts with oxygen, reaction (6), as does the $DH^{\bullet}$ radical, reaction (7). Finally, the superoxide ion radical is converted into H_2O_2, reaction (8), completing the oxygen uptake [38–44]. An electron back transfer to the amine radical cation, step (9), is an important reaction competing with step (6) of superoxide ion radical formation. The rate constant of scavenging of the nitroaromatic radical anion by oxygen is $k_6 = (0.6–1) \times 10^7\,M^{-1}\,s^{-1}$ (Table 1), i.e. three orders of magnitude smaller than the diffusion controlled limit [26]. For comparison, for several ketones k_6 is close to this limit [38]. This large k_6 value is expected for C-centered radicals, whereas a lower reactivity towards oxygen is known for N-centered radicals [43,44].

$$DH_2^{\bullet+} \rightarrow DH^{\bullet} + H^+ \tag{5}$$

$$ArNO_2^{\bullet-} + O_2 \rightarrow ArNO_2 + O_2^{\bullet-} \tag{6}$$

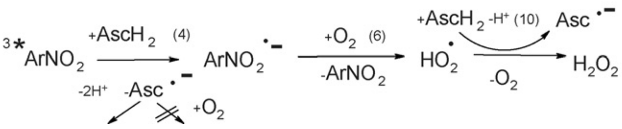
$$DH^{\bullet} + O_2 \rightarrow D + H^+ + O_2^{\bullet-} \tag{7}$$

$$2 \times (O_2^{\bullet-} + H^+) \rightarrow O_2 + H_2O_2 \tag{8}$$

$$ArNO_2^{\bullet-} + DH_2^{\bullet+} \rightarrow ArNO_2 + DH_2 \tag{9}$$

If oxygen is excluded, a second nitroaromatic radical is formed since the α-aminoalkyl radical (formed by deprotonation of $Et_3N^{\bullet+}$) reacts with the substrate via H-atom transfer [9]. These two radicals undergo a slow termination reaction yielding the nitroso compounds in most cases as labile products and finally essentially naphthylhydroxylamines [9,13–16]. The radical cation of an amino acid also deprotonates in water at pH 7 (5) and the radical ($DH^{\bullet}$) can be the subject of another reduction step.

In the case of ascorbic acid ($AscH_2/AscH^-$) a ground state equilibrium has to be considered [38–40]. The $Asc^{\bullet-}$ radical is not quenched by oxygen, in contrast to the other donors. However, reaction (10) of scavenging of the $HO_2^{\bullet}/O_2^{\bullet-}$ radical takes place (Scheme 2). While in principle two $HO_2^{\bullet}/O_2^{\bullet-}$ radicals are formed per triplet population, the donor radical does not contribute to oxygen uptake for $AscH_2$. However, reaction (10) converts each oxygen radical into H_2O_2, in contrast to the amine and amino acid cases.



Scheme 2.

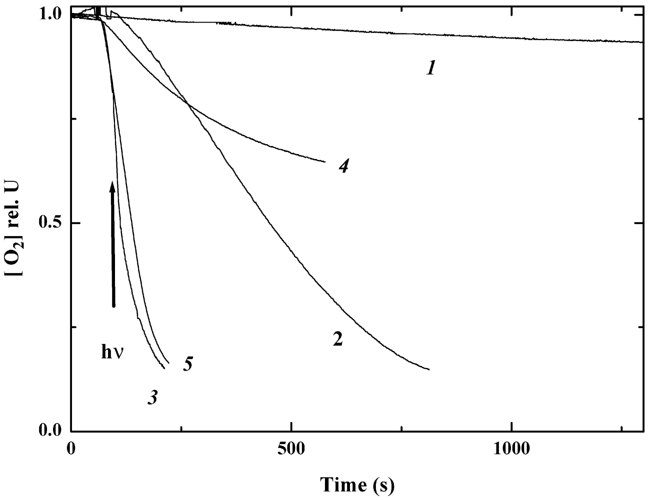


Fig. 4. Plots of the O_2 concentration *vs.* irradiation time, $\lambda_{irr} = 313$ nm, for 1NN in air-saturated acetonitrile–water (1:5, v/v) (1) and in the presence of 0.2 mM (2) and 10 mM (3) ascorbic acid and 0.2 and 10 mM TEA (4 and 5).

3.2. Oxygen uptake

The oxygen concentration decreases with time of irradiation at 313 or 366 nm. Examples are shown in Figs. 4 and 5. The quantum yields of oxygen uptake are compiled in Table 3. For a given compound ascorbic acid, *N*aTrp or the three amines behave

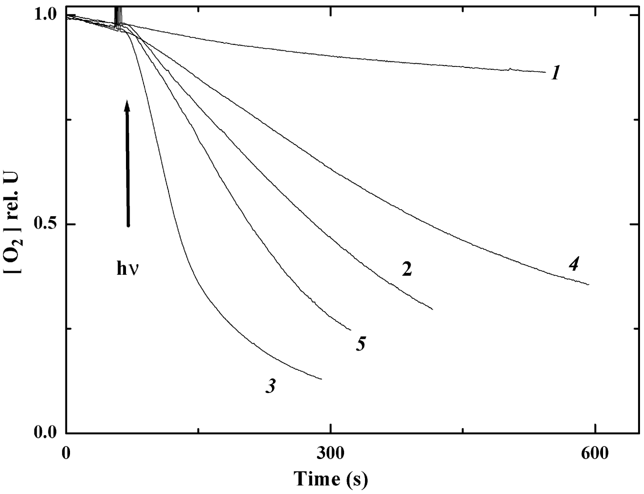


Fig. 5. Plots of the O_2 concentration *vs.* irradiation time, $\lambda_{irr} = 313$ nm, for *trans*-DNS in air-saturated aqueous solution in the presence of TEA 1, 10 and 80 mM (1–3) and 5 and 20 mM (4 and 5) ascorbic acid.

Table 3
Quantum yield of oxygen uptake ($\Phi_{\text{-}O_2}$) in the presence of donors[a]

Compound	None	TEA	EDTA	*N*aTrp	Ascorbic acid
1NN	0.01	0.28 (0.2)[b]	0.25	0.1	0.32
2NN	0.01	0.2			0.3
NF	<0.01	0.2	0.06	0.2	0.1
DNN	<0.01	0.2	0.2	0.1 [0.08][c]	0.07
DNB	<0.01	0.23 (0.2)	0.14	0.1	0.18
DNF	<0.01	0.1	0.18		0.2
trans-DNS	0.01	0.17			0.2

[a] In air-saturated acetonitrile–water (1:5, v/v), $\lambda_{irr} = 313$ nm, 5 mM ascorbic acid and 30 mM other donors.

[b] Values in parentheses refer to DHA.

[c] Using *N*aTyr.

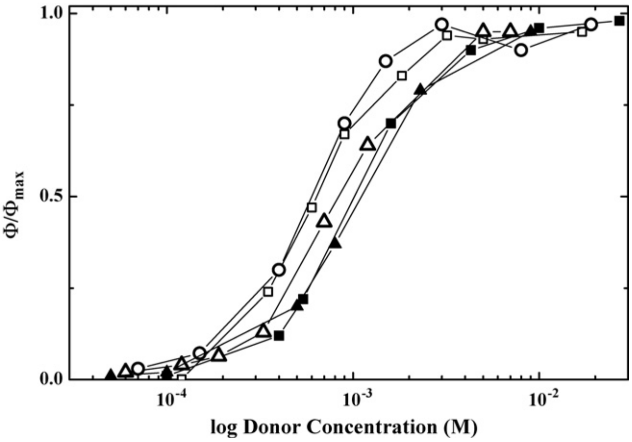


Fig. 6. Semilogarithmic plots of the quantum yield $\Phi_{\text{-}O_2}$ ($\lambda_{irr} = 313$ nm) as a function of the donor concentration for 1NN (circles), DNN (triangles), and DNB (squares) in air-saturated acetonitrile–water (1:5, v/v) using TEA (open) ascorbic acid (full).

similarly. For all cases presented $\Phi_{\text{-}O_2} = 0.1$–0.3 in the presence of 10 mM donor and the values are lower at smaller donor concentrations. This is visualized by semilogarithmic plots of $\Phi_{\text{-}O_2}$ as a function of the ascorbic acid or TEA concentration (Fig. 6). The donor half-concentration was determined for 50% of the maximum $\Phi_{\text{-}O_2}$ value. The [donor]$_{1/2}$ values are 0.4–1 mM for 1NN, DNN, DNB, and DNF with ascorbic acid or TEA (Table 4). $[\text{Donor}]_{1/2} = (1/\tau_T) \times k_4$ defines conditions, where triplet quenching by oxygen and the donor are each 50%. Both the experimental and calculated [donor]$_{1/2}$ values are in reasonable agreement.

Table 4
Donor half-concentrations (mM)[a]

Compound	$[\text{TEA}]_{1/2}$	$[\text{Ascorbic acid}]_{1/2}$
1NN	06 (0.4)[b]	1 (0.6)
DNN	1(0.6)	0.8 (0.6)
DNB	07 (0.6)	1 (0.5)
DNF	05 (0.7)	1 (0.9)
trans-DNS	35 (30)	25 (20)

[a] For 50% of the maximum $\Phi_{\text{-}O_2}$ values, conditions as in Table 3.

[b] Values in parentheses refer to calculation.

3.3. Nitronaphthalenes

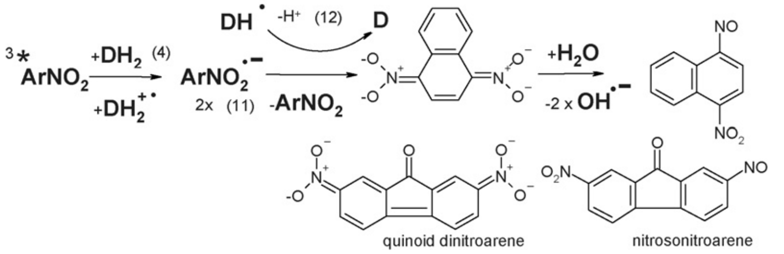
The features of the nitronaphthalenes are: $\tau_T \approx 10$ µs under argon, $k_3 = 1.4 \times 10^9\ \text{M}^{-1}\,\text{s}^{-1}$ and $\Phi_\Delta = 0.60$ and 0.68 in air- and oxygen-saturated acetonitrile, respectively [14]. The rate constant for electron transfer from *N*aTyr and *N*aTrp are lower than those from amines and ascorbic acid (Table 2). To check for quenching via H-atom transfer [38] formate and alcohols were applied as additives to 1NN. A reaction with 2-propanol is not effective at all, $k_5 \leq 1 \times 10^5\ \text{M}^{-1}\,\text{s}^{-1}$. This is in support of the low value of 0.01 for the quantum yield of photodecomposition of 1NN in neat 2-propanol [2]. Formate could be used for H-atom transfer; $k_5 = 1 \times 10^5\ \text{M}^{-1}\,\text{s}^{-1}$. For 1NN in the presence of 0.5 M formate $\Phi_{\text{-}O_2} = 0.02$ was found. For the two nitronaphthalenes in the presence of 10 mM ascorbic acid or TEA $\Phi_{\text{-}O_2} = 0.3$ and lower at smaller donor concentrations. Electron transfer (4) and steps (6) + (7) yield up to two superoxide radicals per triplet and thus $\Phi_{\text{-}O_2}$ could be up to 1. The experimental values in Table 3, however, are much lower, indicating that electron back transfer (9) is operative as major step.

The spectroscopic and kinetic properties of NF are essentially similar to those of the nitronaphthalenes (Tables 1 and 2). Likewise the $\Phi_{\text{-}O_2}$ values are comparable (Table 3).

3.4. 1,4-Dinitronaphthalene and 2,7-dinitrofluorenone

For DNN $\tau_T = 1.2$ and 10 µs under air and argon, $\Phi_\Delta = 0.60$ and 0.68 in air- and oxygen-saturated acetonitrile, respectively [15]. The overall reaction of dinitronaphthalenes with TEA is likewise proposed to lead partly to nitroso compounds as result of the two steps of radical formation and their termination reactions. Photolysis of DNN in argon-saturated acetonitrile in the presence of TEA at >0.1 mM involves the lowest triplet state, the radical anion/conjugate acid pair with $\lambda_{rad} = 545$ nm and then a species with a maximum at 440 nm. This long-lived transient has been assigned to an *aci*-nitro dianion with a non-radical quinoid valence structure [15], as illustrated in Scheme 3. With increasing the amount of water in the mixture, the absorption maximum is blue-shifted (Fig. 2a) and the yield increases. The *aci*-nitroarene is formed via radical termination, either self-coupling (11) or cross-coupling (12). It is tentatively converted into 1-nitroso-4-nitronaphthalene which has a similar spectrum. At first glance it seems unusual that the nitroaromatic radical anion is partly converted into the *aci*-nitro dianion even under air atmosphere (Fig. 2b). However, as the radical half-life is ca. 0.1 ms and $k_6 = 9 \times 10^6\ \text{M}^{-1}\,\text{s}^{-1}$, competition of reactions (6) and (11/12) takes place.

It is interesting to note that the radical with $\lambda_{rad} = 460$ nm, observed for DNF/TEA, is converted into a long-lived species with maximum at 600 nm (Fig. 3a). This species is attributed to the *aci*-nitro dianion with quinoid structure (Scheme 3). The mechanism via radical termination, reactions (11) or (12) is suggested to be the same as for DNN. Radical formation for the DNF/TEA system in acetonitrile-d_3 has been studied by photo-CIDNP [9].



Scheme 3.

3.5. 4,4′-Dinitrobiphenyl and trans-4,4′-dinitrostilbene

For DNB $\lambda_{rad}=440$ nm, $\tau_T=0.2$ µs and $\Phi_\Delta=0.1$ and 0.3 in air- and oxygen-saturated acetonitrile, respectively [15]. Also in the mixture with water is the triplet shorter-lived than for the other arenes (Table 1). The $[\text{donor}]_{1/2}$, however, is not markedly different, because the smaller τ_T under air is compensated by a larger k_4 (Tables 2 and 4). A quinoid dinitroarene structure has first been reported for the photoreaction of DNB in benzene with TEA, in contrast to DNN and DNF [16].

trans-DNS has been the subject of a laser-induced optoacoustic study, where the structural volume changes upon photoisomerization were determined [37]. Photoreduction of *trans*-DNS and other *trans*-nitrostilbenes takes place by electron transfer from the donor, e.g. DABCO, diethylamine or TEA, to the *trans* configuration of the lowest triplet state [30]. Different to the other cases without flexible double bond, the triplet lifetime of *trans*-nitrostilbenes, due to *trans–cis* isomerization, is below 0.1 µs. The photoisomerization behaviour of *cis*- and *trans*-nitrostilbenes has been reviewed [31]. Moreover, the first excited singlet state of *trans*-nitrostilbenes has been characterized by picosecond transient absorption spectroscopy [34,35]. A special case is *trans*-DNS in so far as that the maxima of T–T and radical absorption coincide at 460 nm [32].

The oxygen uptake in the presence of TEA and ascorbic acid is shown in Fig. 5. The oxygen concentration for *trans*-DNS/donor in air-saturated aqueous solution decreases with time of irradiation at 313 or 366 nm. The maximum is $\Phi_{\text{-}O_2}=0.2$ and may be compared with 0.01 in the absence of a donor. $[\text{TEA}]_{1/2}$ and $[\text{ascorbic acid}]_{1/2}=0.02$ and 0.04 M, respectively. This is in agreement with $\tau_T=60$ ns [30] and $k_3=0.6\times10^9$ and $1\times10^9\ \text{M}^{-1}\,\text{s}^{-1}$, respectively. Competition kinetics account for the intermediacy of the $HO_2^\bullet/O_2^{\bullet-}$ radical also for *trans*-DNS and the donors.

4. Conclusion

The photoinduced oxygen uptake of seven nitroaromatic compounds in air-saturated acetonitrile–water is initiated by isc, followed by electron transfer from the donor to the triplet state. Oxygen is converted into H_2O_2 via $HO_2^\bullet/O_2^{\bullet-}$ radicals, whereby their nitroaromatic radicals are spectroscopically and kinetically observable in contrast to the donor counter partners. Competition kinetics excludes formation of molecular singlet oxygen. Electron back transfer limits the quantum yields which are up to $\Phi_{\text{-}O_2}=0.2$–0.3 for all nitro compounds examined. The half-life of nitroaromatic radicals in air-saturated acetonitrile–water is around 0.1 ms and much longer, depending on the kind of donor, under argon. For 1,4-dinitronaphthalene and 2,7-dinitrofluorenone *aci*-nitro dianions were observable as intermediate species in the absence of oxygen, arising from disproportionation of the radical anions.

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