Photoreduction of nitronaphthalenes in benzene by *N*,*N*-dialkylanilines and triethylamine: a time-resolved UV–vis spectroscopic study

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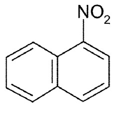
The triplet state of 1-methoxy-4-nitronaphthalene and 1- and 2-nitronaphthalene in benzene at room temperature was studied by time-resolved UV–vis spectroscopy with ns laser pulses at 354 nm. The triplet state reacts with *N*,*N*-dimethylaniline and *N*,*N*-diethylaniline; the rate constant is close to the diffusion-controlled limit. A transient with a peak at 340 nm is attributed to the α-aminoalkyl radical, $PhN(R)^{\bullet}CHR'$, being formed by H-atom transfer from the dialkylaniline. Decay of this radical takes place within a few µs, as observed by bleaching in the 340–410 nm range. Thereby, a nitronaphthalene is eventually converted into stable products, such as nitrosonaphthalene, and dealkylation of the dialkylaniline occurs. Triplet quenching by triethylamine yields the radical anion, $ArNO_2^{\bullet-}$, as an intermediate in acetonitrile and the conjugate acid, $Ar^{\bullet}NO_2H$, in benzene. These radicals are suggested to ultimately yield nitrosonaphthalenes by slow termination in the ms time range. Decomposition of the three nitronaphthalenes in benzene takes place in the presence of the three amines with maximum quantum yields of 0.1–0.3. The mechanisms of photodemethylation of the dialkylanilines and the photoreduction reactions of the nitronaphthalenes are discussed.

Introduction

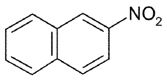
The photoreactions of nitroaromatic compounds, such as nitrobenzene, are the subject of various investigations.[1–11] In particular, the photoinduced electron transfer from amines to nitrobenzenes[1–4] and nitronaphthalenes[5–10] has been studied. Nitronaphthalenes exhibit efficient electron transfer from tertiary amines and the rate constant for triplet quenching (k_q) by triethylamine (TEA) or 1,4-diazabicyclo[2.2.2]octane in acetonitrile is close to the diffusion-controlled limit.[9,10] Recently, nitrobenzene derivatives have become important as photoreactive *caged* probes since the irreversible photoredox reaction of the protecting group can be used to trigger the release of appropriate biochemical or biologically active substrates, *e.g.* in proteins.[12] Nitrosobenzene is a postulated intermediate in this photoreaction. Nitronaphthalenes are characterized by a high quantum yield of intersystem crossing (Φ_{isc}) and can thus replace nitrobenzene derivatives.

The photoreduction in polar solvents involves the radical anion of the nitronaphthalenes ($ArNO_2^{\bullet-}$) and the radical cation of the amine and nitrosonaphthalenes are the major products. The intermediacy of the α-aminoethyl radical, which originates from the radical cation, $NEt_3^{\bullet+}$,[13] opens a second path for reduction of $ArNO_2$.[10–12] On the other hand, for nitroaromatic compounds in benzene photoinduced dealkylation of *N*,*N*-dimethylaniline (DMA) or *N*,*N*-diethylaniline (DEA) takes place.[14–16] A special case is the photomonodealkylation of 4-nitro-*N*,*N*-dimethylaniline, where the major photoproduct is 4-nitroso-*N*,*N*-dimethylaniline.[17–19] 4-Nitroaniline in ethyl acetate in the presence of DMA was used as a photopolymerization initiator.[20] A related case is the thioxanthone–DMA–benzene system, where the aminomethyl radical, $PhN(Me)^{\bullet}CH_2$, initiates the polymerization.[21] It is therefore of interest to obtain a deeper insight into the dealkylation of the *N*,*N*-dialkylanilines upon excitation of suitable nitroarenes.

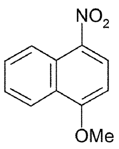
Here, the photoreactions of 1- or 2-nitronaphthalene (1-NN and 2-NN, respectively) and 1-methoxy-4-nitronaphthalene (MNN) in benzene were studied by time-resolved UV–vis spectroscopy and continuous UV irradiation. The observed secondary intermediates, produced by quenching of the triplet state, $^{3*}ArNO_2$, are attributed to α-aminoalkyl radicals and $Ar^{\bullet}NO_2H$ radicals in the presence of *N*,*N*-dialkylanilines and TEA, respectively. The possible reactions that give the photoproducts, several concentration dependences and the effects of oxygen are described.



1-NN



2-NN



MNN

Materials and methods

The nitronaphthalenes were the same as those used previously,[10] the three anilines were purified by distillation and the solvents (benzene, acetonitrile: Uvasol) were used as received. The absorption spectra were monitored on a UV–vis spectrophotometer (HP, 8453). The molar absorption coefficients of 1- and 2-NN at 354 nm are $\varepsilon_{354} = 3 \times 10^3$ and 2×10^3 M^{-1} cm^{-1}, respectively. Photoconversion was carried out after vigorous bubbling by argon prior to and during irradiation at 366 nm using a 200 W Hg lamp combined with an interference filter. The quantum yield of decomposition (Φ_d) was determined using the Aberchrome 540 actinometer.[22] HPLC analyses were carried out on a 125 × 4.6 mm Inertsil ODS-3 5 µm column with MeOH–water 5 : 1 as eluent.

For time-resolved measurements we used a Nd laser (J.K. Lasers, pulse width 15 ns and energy <30 mJ at 354 nm) and digitizers (Tektronix 7912AD and 390AD). Typically, absorbances of 1–2 were used for λ_{exc}, corresponding to concentrations of 0.3–1.0 mM. In order to observe transients below 400 nm, lower concentrations were used ($A_{354} = 0.2$–0.8). A second-order component in the decay kinetics was deduced from the (more

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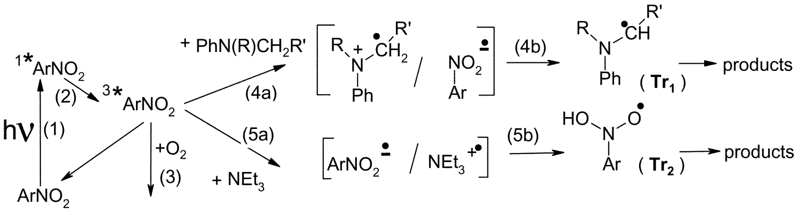
Table 1 Absorption maximum, lifetime and relative yield of the triplet state[a] and quantum yield of formation of singlet molecular oxygen for nitronaphthalenes

Compound	Solvent	λ_{TT}/nm	$\tau_T{}^b$/μs	$\Delta A_T/\Delta A_T{}^{max}$	Φ_Δ
1-NN	Benzene	545	8	0.7	0.35 (0.40)[c]
	Acetonitrile	400, 560	10	0.7	0.42 (0.45)
2-NN	Benzene	480	3	0.9	0.33 (0.38)
	Acetonitrile	480	8	1.0	0.42 (0.45)
MNN	Benzene	420, 630	5	0.9	0.34 (0.40)
	Acetonitrile	650	10	0.8	0.32 (0.36)

[a] In argon-saturated solution. [b] At low pulse intensity. [c] In air-saturated solution; values in parentheses refer to oxygen saturation.



Scheme 1

than twofold) increase of the first half-life, when the intensity was varied, typically by factors of 2–4. The results refer to 24 ± 2 °C and deoxygenated solutions, unless otherwise indicated. Phosphorescence of singlet molecular oxygen at 1269 nm was detected as described elsewhere.[19] The quantum yield (Φ_Δ) was obtained using optically matched solutions (A_{354} = 0.8) and acridine (Φ_Δ = 0.7) as reference.[23]

Results

Triplet state properties

The transient absorption spectrum of 1-NN in argon-saturated benzene at room temperature has two maxima (λ_{TT}) at 400 and 630 nm. The species, which is present during the pulse and quenched by oxygen, is assigned to the $^{3*}ArNO_2$ state. The T–T absorption spectrum of MNN is similar and that of 2-NN has λ_{TT} = 480 nm and a broad long-wavelength tail extending to 700 nm, consistent with reports in the literature.[7–10] The T–T absorption spectra just after the pulse are generally not changed by the presence of a donor at low enough concentration. The rate constant for triplet quenching by oxygen of MNN, 1- and 2-NN using argon-, air- and oxygen-saturated benzene is $k_{ox} = (1.2\text{–}1.4) \times 10^9$ M^{-1} s^{-1}.

The observed relative strength of T–T absorption ($\Delta A_T{}^{rel}$) of the three nitronaphthalenes in benzene and acetonitrile is substantial and comparable. At low pulse intensity the decay follows a first-order law. For diluted samples with A_{354} = 0.2–0.8, a bleaching in the 340–410 nm range was also observed; its grow-in kinetics are the same as the T–T absorption decay kinetics at 450–600 nm. As a minimum measure of Φ_{isc} the quantum yield of formation of singlet molecular oxygen was determined. The values of ΔA_T, Φ_Δ and the triplet lifetime (τ_T) in benzene and acetonitrile at room temperature are compiled in Table 1. Φ_Δ is substantial and rather independent of the kind of nitronaphthalene and the solvent polarity. The small increase of Φ_Δ in air- *vs.* oxygen-saturated solution is due to insufficient quenching (90–98% in air). The UV spectra at the end of the pulse did not show any fluorescence originating from one of the three nitronaphthalenes. This is consistent with a quantum yield of fluorescence of less than 10^{-3}, at least in benzene and in the absence of any donor.

Secondary transients in the presence of anilines

The observed photoreactions of the mononitronaphthalenes occur from the triplet state as illustrated in Scheme 1. On addition of DMA the triplet decay of MNN in argon-saturated benzene becomes faster and the first-order decay rate constant (k_{obs}) shows a linear dependence on the amine concentration. The rate constants for triplet quenching of MNN by DMA and DEA, taken at 550–650 nm from the slope of the plots, are $k_q \approx 8 \times 10^9$ and 9×10^9 M^{-1} s^{-1}, respectively. A 50% triplet quenching is achieved at rather low DMA concentrations. $[DMA]_{½}$ = 20 μM, taking τ_T = 5 μs and $k_q = 9 \times 10^9$ M^{-1} s^{-1}. Analogous reactions and comparable k_q values (Table 2) were observed for 1- and 2-NN.

A secondary transient (Tr_1) with a maximum at λ_{max} = 340 nm appears for MNN in benzene in the presence of DEA (Fig. 1) or DMA (Table 2). The triplet state is concluded to be the precursor of Tr_1 from the similarity of the T–T absorption decay kinetics at 500–600 nm and the grow-in kinetics at 340 nm, as well as from their dependence on the DMA concentration. The decay of Tr_1 occurs essentially by second-order kinetics with a first half-life of $t_{½}$ = 3–10 μs under our conditions and a permanent bleaching in the 340–410 nm range was also observed. Tr_1 with a major maximum at 340 nm also appears with 1- and 2-NN in benzene and the decay is likewise accompanied by a bleaching at 340–410 nm (Figs. 2 and 3, respectively), especially in the presence of DEA. The changes in the time-resolved spectra are in agreement with the conversion of 1- or 2-NN into photoproducts (*e.g.* nitrosonaphthalene) using λ_{irr} = 366 nm. The similarity of the triplet decay and grow-in kinetics clearly shows that the triplet state is the precursor

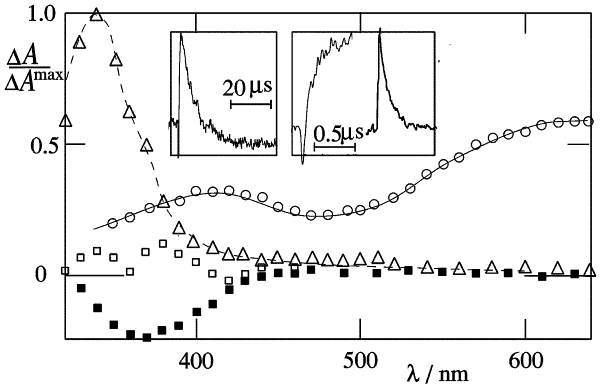


Fig. 1 Transient absorption spectra of MNN in argon-saturated benzene in the presence of DEA (0.4 mM) at 20 ns (○), 1 μs (△), 10 μs (□) and 0.1 ms (■) after the 354 nm pulse; insets: kinetics for decay at 360, 340 and 600 nm (left to right).

Table 2 Rate constant for triplet quenching of nitronaphthalenes by amines, absorption maxima and half-lives of the radicals and quantum yields of decomposition[a]

Compound	Amine	$k_q/10^9\ M^{-1}\ s^{-1}$	$\lambda_{max}(Tr_1)$/nm	$\lambda_{max}(Tr_2)$/nm	$t_{1/2}(Tr_1)$/μs	$t_{1/2}(Tr_2)$/μs	Φ_d[b]
1-NN	DMA	8	340		≤5		0.1
	DEA	9	345	380	≤5	>100	0.20 (0.03)[c]
	TEA	2.8		≤330, 375[d]		>100	0.12 (<0.002)
2-NN	DMA	9	340		≤9		0.15
	DEA	8	340	380	≤8	>100	0.16 (0.02)
	TEA	2.4		≤330, 385[d]		>100	0.10 (<0.002)
MNN	DMA	8	340		≤9		0.25
	DEA	6	340	380	≤8	>100	0.28 (0.05)
	TEA	0.9		395[d]		>300	0.18 (<0.002)

[a] In argon-saturated benzene using [amine] = 0.1–10 mM. [b] Using HPLC, [amine] = 10 mM. [c] In parentheses: air saturation. [d] Effect of [TEA], see text.

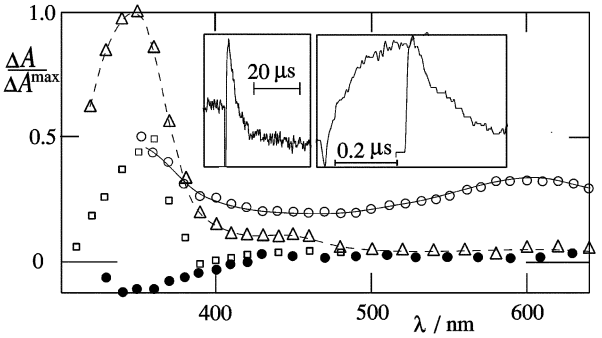


Fig. 2 Transient absorption spectra of 1-NN in argon-saturated benzene in the presence of DEA (0.5 mM) at 20 ns (○), 1 μs (△), 10 μs (□) and 10 ms (●) after the 354 nm pulse; insets: kinetics at 390, 350 and 600 nm (left to right).

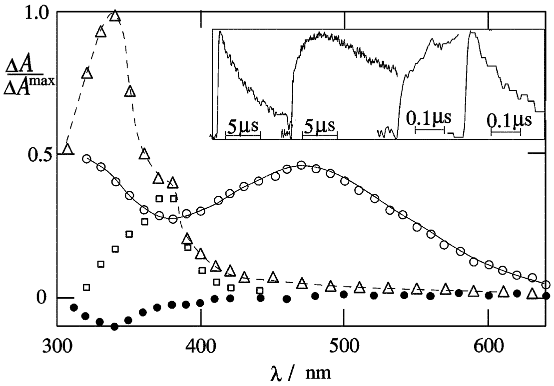


Fig. 3 Transient absorption spectra of 2-NN in argon-saturated benzene in the presence of DEA (0.5 mM) at 20 ns (○), 1 μs (△), 10 μs (□) and 10 ms (●) after the 354 nm pulse; insets: kinetics for grow-in and decay at 340, 410, 340 and 600 nm (left to right).

of Tr_1 which is assigned to the α-aminoalkyl, PhN(R)$^{\bullet}$CHR′, radical of the *N*,*N*-dialkylanilines (see Discussion).

At low DMA concentrations (0.1 mM) Tr_1 does not appear as the triplet state is quenched by oxygen. At larger aniline concentrations, however, when this quenching cannot compete with the formation of radicals, the decay of Tr_1 is quenched by oxygen (see below). A further, weaker absorbing transient (Tr_2) with a maximum at λ_{max} = 380 nm was observed with DEA, but not with DMA on a longer time scale (Table 2). In contrast, in acetonitrile the only secondary transient (Tr_3) for the nitronaphthalene–dialkylaniline system has a peak at λ_{max} = 400–410 nm (Fig. 4). Tr_3 is assigned to the radical anion, $ArNO_2^{\bullet-}$, and Tr_2 to its conjugate acid, $Ar^{\bullet}NO_2H$.

Secondary transients in the presence of TEA

The decay of the triplet state of a nitronaphthalene in benzene is also accelerated by addition of TEA. The rate constant for triplet quenching, using the dependence of k_{obs} *vs.* the TEA concentration, is k_q = (1–3) × $10^9\ M^{-1}\ s^{-1}$ (Table 2). Transient Tr_2 with a maximum at λ_{max} = 395 nm appears for MNN in the presence of TEA (0.05–1 mM) by quenching of the triplet state (Fig. 5). A 50% triplet quenching is achieved at $[TEA]_{1/2}$ = 0.07–0.2 mM, taking k_q = (1–3) × $10^9\ M^{-1}\ s^{-1}$. Decay of Tr_2 under argon occurs by mixed first- and second-order kinetics with a first half-life in the 0.1–0.5 ms range under our conditions. A permanent bleaching component remains at 340–410 nm. The radical nature is supported by quenching with oxygen. Corresponding results were obtained for 1- and 2-NN (Table 2). For 1-NN (Fig. 6) and 2-NN, however, conversion of Tr_2 with maximum at 375 nm into a second longer-lived intermediate ($Tr_{2'}$) with a maximum at 395 nm was observed. This effect is smallest for MNN and becomes better resolved for 1- and 2-NN at a high TEA concentrations of 0.05–0.5 M (inset of Fig. 6), where the half-life of decay of $Tr_{2'}$ (if vigorously purged

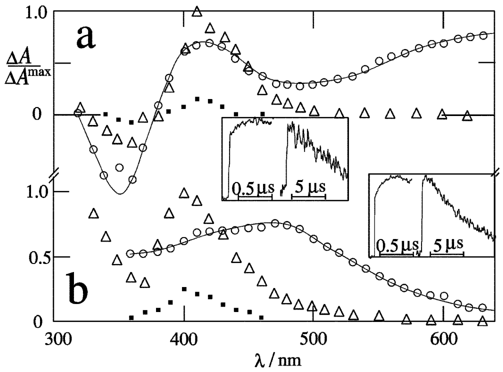


Fig. 4 Transient absorption spectra of (a) MNN and (b) 2-NN in argon-saturated acetonitrile in the presence of DEA (0.2 mM) at 20 ns (○), 1 μs (△) and 10 μs (■) after the 354 nm pulse; insets: kinetics for grow-in and decay at 410 nm (both).

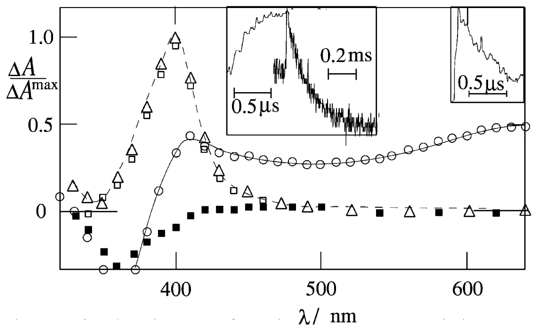


Fig. 5 Transient absorption spectra of MNN in argon-saturated benzene in the presence of TEA (2 mM) at 20 ns (○), 1 μs (△), 10 μs (□) and 1 ms (■) after the 354 nm pulse; insets: kinetics at 410 nm (left) and 600 nm (right).

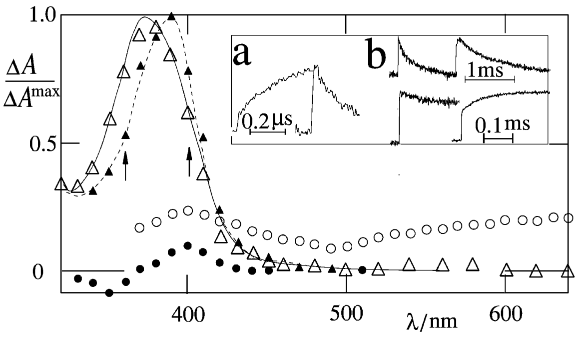


Fig. 6 Transient absorption spectra of 1-NN in argon-saturated benzene in the presence of TEA (1 mM) at 20 ns (○), 1 µs (△), 100 µs (▲) and 10 ms (●) after the 354 nm pulse; insets: kinetics (a) at 380 nm (left) and 600 nm (right) and (b) at 360 nm (left) and 400 nm (right) for [TEA] = 1 mM (upper) and 0.2 M (lower).

by argon) is in the 20–50 ms range. Note that the spectra of the radical anion and the conjugate acid of the three nitronaphthalenes with λ_{max} = 390 nm are virtually the same in acetonitrile[10] and benzene.

Continuous irradiation

Continuous irradiation at 366 nm of MNN in argon-saturated benzene in the presence of DEA (10 mM) leads to a decrease in absorption at 340–410 nm and no development of colour (Fig. 7a). The decomposition of the substrate was also measured by HPLC, where *N*-ethylaniline was identified as the major photoproduct absorbing above 280 nm. This is in agreement with the literature on photodealkylation of dialkylanilines in the presence of nitroarenes.[14–19] The decrease of the concentration of MNN with irradiation time is shown in Fig. 7. The quantum yield of decomposition (Φ_d) increases with increasing DEA concentration, approaching a maximum value of $\Phi_d = 0.3$ at [DEA] = 1 mM. The Φ_d values of 1- and 2-NN are slightly smaller (Table 2). The spectra of MNN in the presence of TEA show isosbestic points at 340 and 415 nm (Fig. 7b). In air-saturated benzene the Φ_d values are lower than those with dialkylanilines. The latter indicates a photodecomposition process involving oxygen.

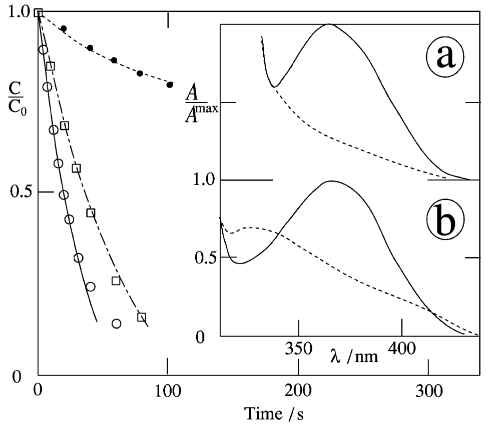


Fig. 7 Decomposition of MNN in argon-saturated benzene; concentration of MNN *vs.* irradiation time for DEA (○; air-saturated: ●) and TEA (□); absorption spectra in the presence of (a) DEA (10 mM) and (b) TEA (10 mM) prior to (full) and after irradiation (dotted) at 366 nm.

Discussion

Reactions of the triplet state

Some properties of the triplet state of nitronaphthalenes in solution have already been reported.[5–10] The ΔA_T values of the three nitronaphthalenes in benzene and acetonitrile change by <30% (Table 1), indicating that the product $\varepsilon_{TT} \times \Phi_{isc}$ does not markedly depend on the polarity of the solvent. Triplet quenching by oxygen yields singlet molecular oxygen [reaction (3)].

$$^{3*}ArNO_2 + {}^3O_2 \longrightarrow ArNO_2 + {}^1O_2 \text{ (and } {}^3O_2) \qquad (3)$$

The quantum yield of formation of $O_2(^1\Delta_g)$, which is a lower limit of Φ_{isc}, is sufficiently large (Table 1).

The photoinduced conversion of the dialkylanilines into PhNHMe or PhNHEt involves electron transfer.[14,15] A singlet reaction is unlikely, as indicated by the absence of any fluorescence. For amine concentrations of 0.1–10 mM the Φ_d values reflect that 30–60% of the populated triplet state leads to decomposition (Table 2). Triplet quenching of the nitronaphthalenes in benzene by dialkylanilines [reaction (4)], and by TEA [reaction (5)] yields intermediates Tr_1, $PhN(R)^{\bullet}CHR'$, and Tr_2, $Ar^{\bullet}NO_2H$, respectively (Scheme 1).

Secondary reactions of nitronaphthalenes with TEA

The proposed photoinduced process (Scheme 2) is electron transfer from TEA to the nitronaphthalene triplet state *via* reaction (5a) followed by internal proton transfer [reaction (5b)], whereby a cage reaction is consistent with the low [TEA] of 0.1–1 mM required for efficient radical formation.

$$^{3*}ArNO_2 + NEt_3 \longrightarrow (ArNO_2^{\bullet -}/NEt_3^{\bullet +}) \qquad (5a)$$

$$(ArNO_2^{\bullet -}/NEt_3^{\bullet +}) \longrightarrow Ar^{\bullet}NO_2H + Et_2N\text{–}^{\bullet}CHMe \qquad (5b)$$

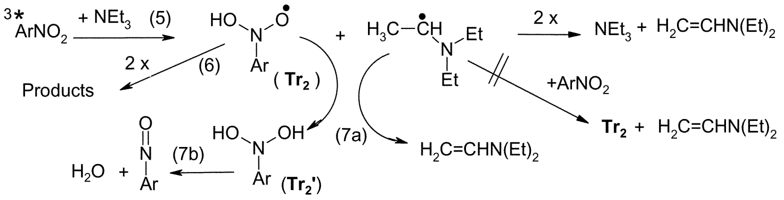
The radical ion pair escapes observation. Generally, proton transfer in benzene is faster than our 10 ns time resolution.[24,25] The remaining transient of MNN (Tr_2) absorbs with a maximum at 395 nm (Fig. 5). The rate constants of the grow-in and the triplet decay are the same, *i.e.* Tr_2 is formed by triplet quenching. Tr_2, which also gives rise to a subsequent transient and a permanent bleaching at 340–410 nm, is assigned to the conjugate acid of the radical anion. The spectra are similar to those in acetonitrile,[10] apart from a small hypsochromic shift of λ_{max} in benzene.

For decay of the observed species at relatively low TEA concentrations radical disproportionation [reaction (6)] is suggested (Scheme 2).

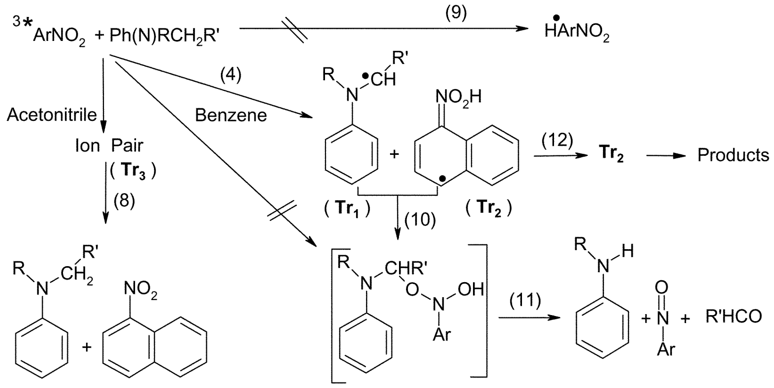
$$2 \times Ar^{\bullet}NO_2H \longrightarrow ArNO_2 + ArNO + H_2O \qquad (6)$$

The possibility that Tr_2 is due to the radical anion and $Tr_{2'}$ (Fig. 6) to its conjugate acid can be excluded because in benzene overall H-atom transfer is favoured with respect to ion stabilization. One could argue that radical ions are not detectable in argon-saturated benzene. For the benzil–TEA–benzene system, however, the rate constant of this conversion is postulated to be 1.5×10^6 s^{-1}.[26] Thus under these conditions the free ions are rather short-lived and the conversion of $ArNO_2^{\bullet -}$ into $Ar^{\bullet}NO_2H$ is incompatible with the observed half-life of 0.1 ms or longer. The lifetime of the radical ion pair of the benzophenone–DABCO–benzene system is 50 ns.[27]

The fate of the spectroscopically unobservable α-aminoethyl radical remains open, although termination could be considered. Electron back transfer in competition with reaction (5b) accounts for the result $\Phi_d < \Phi_\Delta$ (Tables 1 and 2). The reaction of 1-NN (Fig. 6), 2-NN or MNN to give products, observed at higher TEA concentrations, is ascribed to a secondary H-atom transfer [reaction (7a)] yielding *N*,*N*-diethylvinylamine and the hydrate of 1-nitrosonaphthalene, followed



Scheme 2



Scheme 3

by water elimination [reaction (7b)]. Thus $Tr_{2'}$ is tentatively assigned to $ArN(OH)_2$. The termination of α-aminoethyl radicals is probably slowed down at TEA concentrations larger than 0.1 mM, thereby enhancing the route *via* reaction (7a). In contrast to acetonitrile,[10] no indication for a second path towards $Ar^{\bullet}NO_2H$ *via* reaction with the substrate was found in benzene.

Secondary reactions of nitronaphthalenes with *N*,*N*-dialkylanilines

The spectral and kinetic properties of the nitronaphthalenes in acetonitrile (Fig. 4) reveal that triplet quenching by the dialkylanilines yields intermediate $ArNO_2^{\bullet -}$ (Tr_3) rather than its conjugate acid (Tr_1). The proposed photoinduced process in acetonitrile is electron transfer from the dialkylaniline to the triplet state via reaction (4′a).

$$^{3*}ArNO_2 + PhN(R)CH_2R' \longrightarrow ArNO_2^{\bullet -} + PhN^{\bullet +}(R)CHR' \quad (4'a)$$

Apparently, separation of the radical ions is faster than a few ns. The major absorbing species with $\lambda_{max} = 390$ nm is the nitronaphthalene radical anion, whereas the radical cation of the amine is masked by spectral overlap. The literature values are $\varepsilon_{470} = (4–5) \times 10^3\ M^{-1}\ cm^{-1}$ for $PhN^{\bullet +}(CH_3)_2$.[28] The decay of the radical ions within a few μs under our conditions is due to electron back transfer.

$$ArNO_2^{\bullet -} + PhN^{\bullet +}(R)CHR' \longrightarrow ArNO_2 + PhN(R)CH_2R' \quad (8)$$

In benzene, however as mentioned above, triplet quenching by the dialkylanilines yields essentially intermediate Tr_1 (Figs. 1–3) for which several species are considered. An exciplex ($^{3*}ArNO_2^{\delta -}/PhN^{\delta +}RCH_2R'$) or the radical ion pair have to be excluded. The radical ions in benzene are probably in close vicinity and would decay in the ps range;[24] a half-life of 1 μs for proton transfer[26] is therefore too large. The lifetime of the radical ion pair of the benzophenone–*N*-methylacridan–benzene system is 0.50 ns.[25] Moreover, for nitroarenes the formation of a C-centered radical *via* reaction (9) (Scheme 3) can also be excluded.[7,8] Also a detectable addition product, formed *via* reaction (10), has to be excluded since no rapid quenching by oxygen is expected for this non-radical species. A radical complex, $Ar^{\bullet}NO_2^{\delta -}H/PhN^{\delta +}(R)^{\bullet}CR'$, formed after triplet quenching but prior to separation, also seems unlikely.

We are now left to assign Tr_1 to the α-aminoalkyl radical of the *N*,*N*-dialkylanilines. The decay of Tr_1 is mainly due to the sequence (10) and (11). This accounts for the above findings (Figs. 1, 2 and 3) and is in agreement with the efficient *N*-dealkylation process of dialkylanilines upon irradiation of 1- and 2-NN.[14,15] Variation of the MNN concentration (corresponding to $A_{354} = 0.4–2$) has no significant effect, *i.e.* the α-aminoalkyl radical does not react with the substrate.

Pulse radiolysis of DMA yields the cyclohexadienyl radical with two maxima at 330 and 455 nm which absorb almost equally.[28] If the α-aminoalkyl radical had a low molar absorption coefficient at 330 nm (as its cation), then it could not be assigned to Tr_1. However, Scaiano has shown that the UV-band of $PhN(Me)^{\bullet}CH_2$ in di-*tert*-butyl peroxide exhibits a rather high ε value.[29] For the thioxanthone–DMA–benzene system Yates and Schuster have reported that the aminomethyl radical takes part in the photoreduction, but is not observable (above 400 nm); they have postulated the involvement of an exciplex with only partial charge transfer.[21] The observation of the $Ar^{\bullet}NO_2H$ radical after decay of the α-aminoethyl radical in the presence of DEA indicates radical separation [reaction (12)] in competition with combination reaction (10). The possibility of a further H-atom transfer analogous to reaction (7a) may also be considered; a hint for this is the conversion of Tr_1 into the longer lived transient, shown in the inset of Fig. 3. The pathway to the products is impeded by electron back transfer, thereby reducing Φ_d with respect to the maximum value of Φ_{isc}, as for TEA. Nevertheless, the Φ_d values for nitronaphthalenes (Table 2) are significantly larger than for nitrobenzenes,[15] where the Φ_{isc} values are probably smaller.[1–4]

Effects of oxygen

The above measurements refer to deoxygenated solution, unless otherwise indicated. For nitronaphthalenes in the presence of either dialkylanilines or TEA, due to the high k_q values, reactions (4) and (5) could compete successfully with triplet quenching by oxygen [reaction (3)], *e.g.* for amine concentrations of 1 mM or more in air-saturated benzene. The important quenching reactions, however, involve the relevant radicals.

Apparently the aromatic α-aminoalkyl radicals are quenched by oxygen, probably involving peroxyl radicals.

$$PhN(R)^{\bullet}CHR' + O_2 \longrightarrow PhN(R)CHR'O_2^{\bullet} \quad (13)$$

To account for the result that for the anilines decomposition of the nitronaphthalenes is detectable even in air-saturated benzene (Table 2), a reaction with oxygen is proposed that does not fully restore the substrate. The other possibility for quenching radicals by oxygen is reaction (14).[30]

$$Ar^{\bullet}NO_2H + O_2 \longrightarrow ArNO_2 + HO_2^{\bullet} \quad (14)$$

Therefore, when oxygen is present in the case of H-atom transfer from TEA, Φ_d is close to zero (Table 2). Moreover oxygen reacts with the α-aminoethyl radicals.[31] From the observed lifetimes of Tr_2 and Tr_1 in air-saturated benzene (not shown) it follows that the rate constant for reaction (14), $k_{14} = (1\text{–}3) \times 10^7\ M^{-1}\ s^{-1}$, is significantly smaller than for reaction (13), $k_{13} \approx 1 \times 10^9\ M^{-1}\ s^{-1}$.

Conclusion

The spectral and kinetic properties of the triplet states of the three nitronaphthalenes in benzene and acetonitrile are very similar, but the observed secondary reactions are different. H-atom transfer from TEA, thereby forming the $Ar^{\bullet}NO_2H$ radical, occurs in benzene, while electron transfer, radical ion pair formation and electron back transfer are favoured in acetonitrile. Concomitant with triplet quenching in benzene by DEA or DMA, transients were observed with different spectral and kinetic properties to the $Ar^{\bullet}NO_2H$ radical. They are assigned to α-aminoalkyl radicals and their decay in the μs range leads to substrate decomposition and dealkylation of the dialkylanilines in substantial yield. Detection of the α-aminoalkyl radical with a maximum at 340 nm is often masked, *e.g.* in the cases of ketones,[21,29] by ground state and ketyl radical absorption.

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