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Transients in the photoreduction of dinitroarenes by triethylamine and *N*,*N*-dialkylanilines in benzene

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Abstract

The photochemistry of dinitronaphthalenes (1,3-, 1,4-, 1,5-DNN), 4,4′-dinitrobiphenyl (DNB) and 2,7-dinitrofluorenone (DNF) in benzene at room temperature was studied by time-resolved UV-Vis spectroscopy after ns laser pulses at 354 nm. The triplet states of the five dinitro compounds, $3^*O_2NArNO_2$, react with *N*,*N*-dimethylaniline (DMA) and *N*,*N*-diethylaniline (DEA), the rate constant of quenching of the triplets is close to the diffusion-controlled limit. An intermediate with peak at 340 nm is attributed to the $PhN(R)^{\bullet}CHR'$ radical ($R = CH_3, R' = H$ or $R = C_2H_5, R' = CH_3$, respectively). On the other hand, quenching of the triplet state of dinitroarenes by triethylamine (TEA) leads to $O_2NAr^{\bullet}NO_2H$, the conjugate acid of the radical anion, which is suggested to yield nitrosoarenes by termination within a few ms. For DNB an H-atom transfer from the α-aminoethyl radical to the $O_2NAr^{\bullet}NO_2H$ radical, thereby forming *N*,*N*-diethylvinylamine and a quinonoid structure prior to 4-nitroso-4′-nitrobiphenyl, is proposed. Decay of the $PhN(R)^{\bullet}CHR'$ radical, thereby converting the dinitroarenes into nitrosonitroarenes and dealkylation of the dialkylanilines, is faster than that of the $O_2NAr^{\bullet}NO_2H$ radical. The mechanisms of demethylation and the reduction reactions in benzene under conditions where no free radical ions are formed, are discussed.

Keywords: Dinitroarenes; *N*-demethylation; Photoreduction; Triplet state; Radicals

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1. Introduction

The photoreduction of aromatic compounds, either at various electron accepting functional groups [1–3] or involving the skeleton of electron poor hetarenes as a whole [4], by aliphatic or mixed aliphatic/aromatic amines has been and still is the subject of intensive investigations. Among these, photoreduction of nitroarenes by amines has been studied with emphasis on both the fate of the nitro function and α-oxidative and α-dealkylating processes of the amines used [5–9]. The photoreactions and also photophysical processes of various nitrobenzenes [10–17] and nitronaphthalenes [18–22] have been studied in the presence of various electron donors. In comparison to nitrobenzenes, nitronaphthalenes have the advantage of high quantum yields of intersystem crossing, Φ_{isc}, to the lowest excited triplet states and show appropriate redox properties [20,21]. In acetonitrile rate constants for triplet quenching, k_q, of mononitronaphthalenes [20] and dinitronaphthalenes [22] by triethylamine (TEA), diethylamine, and 1,4-diazabicyclo[2.2.2]octane (DABCO) are close to the diffusion-controlled limit. Involvement of the α-aminoethyl radical, derived from TEA by a net α-hydrogen atom abstraction, in the reductive processes has been discussed [3,20–22]. While the photochemistry of aromatic nitro compounds has been repeatedly reviewed [23–25], the specific role of aliphatic and mixed aliphatic/aromatic amines still awaits adequate treatment and clarification.

In polar solvents following photoinduced electron transfer, the radical anion of the nitroarene and the radical cation derived from the amine involved are to be regarded as distinct entities. For the photoreduction of naphthalimides by aliphatic amines in acetonitrile, a two-step mechanism involving free radical ions has been established by Demeter et al. [3]. In less polar media, also in neat triethylamine and diethylamine [8], the situation is different, the formation of separated radical ions cannot be expected. Still, efficient *N*-dealkylation of *N*,*N*-dimethylaniline (DMA) or *N*,*N*-diethylaniline (DEA) by photoexcited nitroarenes is observed [9–14].

For 1- and 2-nitronaphthalene and 1-methoxy-4-nitronaphthalene the major transient upon H-atom transfer from

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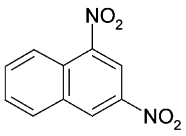
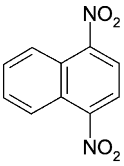
DMA or DEA to the nitroarene triplet state has been attributed to the PhN(R)$^•$CHR$'$ radical [21]. Two related but special cases are (i) the photomonodemethylation of *N*,*N*-dimethyl-4-nitroaniline, which may occur both by action of an external photoexcited nitroarene and by a novel “self-dealkylation” upon irradiation in methanol containing sodium methoxide [12], and (ii) the photoreduction of 4-nitrobenzylidene malononitrile by TEA, which is accompanied by the replacement of one cyano group by the 1-diethylaminoethyl moiety [13]. This is another example of incorporation of amine fragments into stable photoproducts, which had also been observed earlier [8]. It should be noted that the 4-nitroaniline/DMA/benzene system has recently been reported to produce a photopolymer [26,27], and in the thioxanthone/DMA/benzene system the α-aminomethyl radical PhN(CH$_3$)$^•$CH$_2$ initiates a polymerization as well [28].

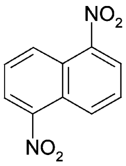
We became interested in the dealkylation of DMA and DEA upon excitation of dinitroarenes in benzene. 1,3-, 1,4- and 1,5-dinitronaphthalene (1,3-, 1,4-, 1,5-DNN, respectively), 4,4$'$-dinitrobiphenyl (DNB) and 2,7-dinitrofluorenone (DNF) were chosen as suitable acceptors (see structures shown below). The photoreactions were studied by time-resolved UV-Vis spectroscopy. The observed secondary intermediates in benzene are induced by quenching of the nitroarene triplet state and possible reactions to the final photoproducts are described.



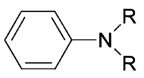
1,3-DNN



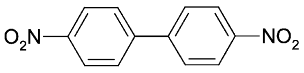
1,4-DNN



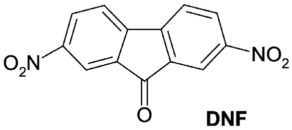
1,5-DNN



R = Me: DMA
Et: DEA



DNB



DNF

2. Experimental

2-Nitrofluorene (NF) and the other nitrocompounds [22] and benzene (Uvasol) were used as received or purified by distillation (amines). The absorption spectra were monitored on a UV-Vis spectrophotometer (HP, 8453). For photoconversion, the 366 nm line of a 200 W Hg lamp combined with an interference filter was used. The conversion was carried out after vigorous bubbling by argon prior and during irradiation. For HPLC analyses, a 125 mm × 4.6 mm Inertsil ODS-3 5 μm column was used and MeOH:water 5:1 as eluent. The quantum yield of decomposition, Φ_d, was determined using the Aberchrome 540 actinometer [29]. A Nd laser (J.K. Lasers, pulse width 15 ns, energy <30 mJ) was applied for excitation at 354 nm. The absorption signals were measured with two digitizers (Tektronix 7912AD and 390AD). Typically, absorbances of 1–2 (1 cm pathlength) were used for λ_{exc}, corresponding to concentrations of 0.5–1 mM. The inner filter effect plays no role for absorbances of 2 since in our perpendicular set-up only a penetration depth of ca. 0.1 cm just after the entrance window of the cuvette is focused via the slit of the monochromator to the photomultiplier. Non-linear effects do not occur due to substantial triplet yields and relatively low laser intensities of <1 MW cm^{-2}. The $\Delta A_T/\Delta A_T^{max}$ and $\Delta A_{rad}/\Delta A_T^{max}$ values for optically matched solutions are relative measures of the triplet yield and the product of extinction coefficient and radical yield, respectively. Phosphorescence of singlet molecular oxygen at 1269 nm was detected as described previously [12,21]. The quantum yield of formation of $O_2(^1\Delta_g)$ was obtained using optically matched solutions ($A_{354} = 0.8$) and acridine as reference $\Phi_\Delta^{ref} = 0.7$. All measurements refer to deoxygenated solution, unless otherwise indicated, and 24 ± 2 °C.

3. Results and discussion

3.1. Continuous irradiation

Continuous UV irradiation at 366 nm of 1,4-DNN, 1,3-DNN and DNF in argon-saturated benzene in the presence of DEA (0.05–1 mM) leads to an absorption increase in the visible region (not shown). No bleaching region at 340–390 nm exists in contrast to the case of mononitronaphthalenes [21]. Comparable spectra were recorded in the presence of DMA, as well as for 1,5-DNN and DNB. Photodecomposition of the substrate was also followed by HPLC, where *N*-ethylaniline was identified as major photoproduct from DEA absorbing above 280 nm. This is in agreement with the literature on photodealkylation of *N*,*N*-dialkylanilines by mononitronaphthalenes [9–11]. The quantum yield of decomposition of 1,4-DNN in argon-saturated benzene increases with increasing DEA concentration, approaching a maximum value of $\Phi_d = 0.16$ at [DEA] = 10 mM. The Φ_d values under these conditions are compiled in Table 1. With DEA Φ_d is also substantial in air-saturated benzene, in contrast to the results in the presence of TEA. The spectra prior to and after irradiation

Table 1
Quantum yields Φ_d of decomposition of dinitroarenes in the presence of amines[a]

Compound	DEA	DMA	TEA
1,3-DNN	0.15 (0.1)[b]	0.14	0.16 (<0.01)
1,4-DNN	0.16	0.15	0.15 (<0.001)
1,5-DNN	0.08	0.1	0.13
DNB	0.04	0.04	0.02
DNF	0.15	0.18	0.2

[a] In argon-saturated benzene using $\lambda_{irr} = 366$ nm and HPLC, [amine] = 1–2 mM.

[b] Values in parentheses: air saturation.

Table 2
Absorption maximum, triplet lifetime, relative triplet yield and quantum yield of formation of singlet molecular oxygen[a]

Compound	λ_{TT} (mm)[b]	τ_T (μs)[c]	k_{ox} ($\times 10^9$) ($M^{-1}\,s^{-1}$)[d]	$\Delta A_T/\Delta A_T^{max}$	Φ_Δ
1,3-DNN	$\underline{430}$, 550	4	1.4	1.0	0.4 (0.55)[e]
1,4-DNN	410, 550	4	1.4	1.0	0.4 (0.45)
1,5-DNN	400, $\underline{540}$	5	1.1	1.0	0.3 (0.4)
DNB	510	0.2	<2	0.9	0.02 (0.12)
DNF	510	5	1.3	0.9	0.45 (0.55)
NF[f]	450	6	1		

[a] In argon-saturated benzene.
[b] Largest peak underlined.
[c] At low pulse intensity.
[d] Rate constant for triplet quenching by oxygen using argon-, air- and oxygen-saturated solution.
[e] Air saturation; values in parentheses refer to oxygen saturation.
[f] 2-Nitrofluorene.

are very similar to those for 1-methoxy-4-nitronaphthalene [21].

3.2. Triplet state properties

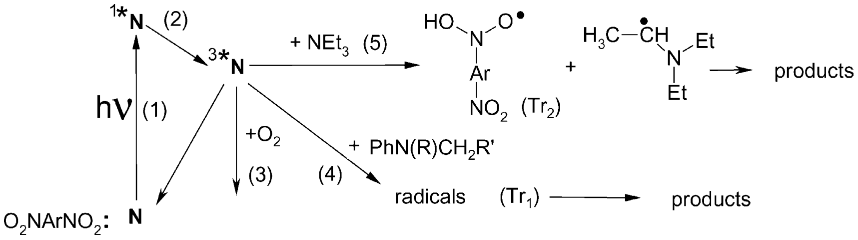
The transient absorption spectrum of 1,4-DNN in argon-saturated benzene, $\lambda_{exc} = 354$ nm, has a maximum, λ_{TT}, at 560 nm. This species, which is present during the pulse and quenched by oxygen, is assigned to the triplet state, $3^*O_2NArNO_2$. The T–T absorption spectra of the other dinitrohydrocarbons have a broad long-wavelength tail extending to 700 nm. The data are consistent with literature reports [16,22]. The rate constant for triplet quenching by oxygen of dinitroarenes in benzene is $k_{ox} = (1–2) \times 10^9\,M^{-1}\,s^{-1}$. The observed strength of T–T absorption, ΔA_T, in acetonitrile [22] and benzene is substantial for the nitroarenes under examination. No bleaching in the 330–380 nm range was observed when the concentration of a dinitroarene was low enough. This being in contrast to the mononitronaphthalenes, where the amount of bleaching increases with increasing ground state absorbance as long as A_{354} is smaller than 0.8 [21]. The decay kinetics follow a first-order law when the intensity is low enough. 2-Nitrofluorene exhibits similar triplet properties (Table 2). Some properties of the triplet state of nitronaphthalenes have already been reported [18–25].

Phosphorescence of singlet molecular oxygen was observed in acetonitrile [22] and benzene at room temperature. The ΔA_T values under optically matched conditions ($\Delta A_T/\Delta A_T^{max}$), the quantum yield of formation of singlet molecular oxygen and the triplet lifetime, τ_T, are compiled in Table 2. In oxygen-saturated benzene a significantly larger Φ_Δ value with respect to air saturation was obtained for DNB, where τ_T is smallest. In the other cases, τ_T is sufficiently long and a higher oxygen concentration has virtually no enhancing effect on Φ_Δ. The relative ΔA_T values change by less than 20% (Table 2), indicating that the product $\varepsilon_{TT} \times \Phi_{isc}$ does not markedly depend on the type of dinitroarene. Φ_Δ is a minimum measure of Φ_{isc}, is rather large for DNF and any DNN, but low for DNB, where the triplet lifetime is extremely short and quenching by oxygen cannot be the major pathway.

The absence of any fluorescence for the dinitroarenes in benzene and acetonitrile is consistent with the conclusion that the observed photoreactions occur from the triplet state. After triplet population via steps (1) and (2), the quenching reaction (3) yields singlet molecular oxygen (Scheme 1). Triplet quenching of mononitronaphthalenes [21] and dinitroarenes by the dialkylanilines in deoxygenated benzene, reaction (4), yields a major intermediate, denoted as Tr_1, which is assigned to the α-aminoalkyl radical, $PhN(R)^\bullet CHR'$. Intermediate Tr_2, observed after triplet quenching by TEA, differs from Tr_1 by spectrum and decay kinetics and is assigned to the $O_2NAr^\bullet NO_2H$ radical; for the identities of Tr_1 and Tr_2 see later.

3.3. Secondary transients from dinitroarenes in the presence of TEA

On addition of TEA, the triplet decay of the dinitroarenes in argon-saturated benzene is accelerated. The first-order decay rate constant, k_{obs}, taken at 460–650 nm, shows a



Scheme 1.

Table 3
Rate constants for triplet quenching by DEA and TEA, absorption maxima and half-life of the radicals[a]

Compound	Amine	k_q ($\times 10^{10}$) ($M^{-1}\,s^{-1}$)	λ_{rad} (nm)	$\Delta A_{rad}/\Delta A_T^{max}$	$t_{1/2}$ (ms)
1,3-DNN	DEA	1	<350 (340)[b]	1.8	<0.2
	TEA	0.6	390		0.5
1,4-DNN	DEA	1.5	400	0.2	0.1/>5
	TEA	0.5	400, 520	0.6	0.1
1,5-DNN	DEA	1.2	340	0.9	0.1/1
	TEA	0.5	400	1.2	0.2
DNB	DEA	>0.8	340	1.1	0.03
	TEA	0.5	380/500[c]	1.0/1.3	10^{-3}/2[c]
DNF	DEA	1.8	340	0.5	0.03/>2
	TEA	0.9	355, 430[d]	0.9	0.1
NF	DEA	1	335		0.15

[a] In argon-saturated benzene using [amine] = 0.1–10 mM.
[b] Value in parentheses refers to DMA.
[c] Second (left) and third (right) transients.
[d] Minor maximum.

linear dependence on the TEA concentration. The rate constant for triplet quenching, obtained from the slope of these plots, is $k_q = (5–9) \times 10^9\ M^{-1}\,s^{-1}$ (Table 3). For 1,4-DNN, transient Tr_2 with maxima at 400 and 520 nm persists after quenching (Fig. 1b). Corresponding spectra with maxima at <400 nm were recorded for DNF (Fig. 2b) and 1,3- and 1,5-DNN. Decay of Tr_2 under argon occurs by second-order kinetics with a first half-life in the 0.2–2 ms range under our conditions. A weak quasi-permanent component remains in the 360–420 nm range, this being in accord with the steady-state spectrum of a given photoproduct. Addition of oxygen strongly accelerates the decay of Tr_2, indicating the radical nature of this intermediate.

Triplet quenching of all dinitroarenes in benzene by TEA occurs via reaction (5), see Scheme 1. The remaining transient of 1,4-DNN (Tr_2) absorbs at 400 and 520 nm (Fig. 1b). In general, the $O_2NAr^{\bullet}NO_2H$ radical is expected as intermediate after triplet quenching (Scheme 2). The assignment of Tr_2 to the conjugate acid of the radical anion also in the cases of 1- and 2-nitronaphthalene and 1-methoxy-4-nitronaphthalene in benzene is based on similar spectra and kinetics in acetonitrile [20]. For 1,3- and 1,5-DNN (Table 3) and DNF in benzene (Fig. 2b) the spectral and kinetic properties are partly similar to those in acetonitrile [22]. Reaction (6, Scheme 2) of the conjugate acid of the radical anion accounts for the second-order decay of Tr_2 within a few ms. This is a two-step process the first and rate-determining of which is disproportionation by H-atom transfer and the second of which is dehydration yielding a nitrosonitroarene. Termination of the α-aminoethyl radical, $Et_2N^{\bullet}CHCH_3$, occurs via reaction (7). Another a priori

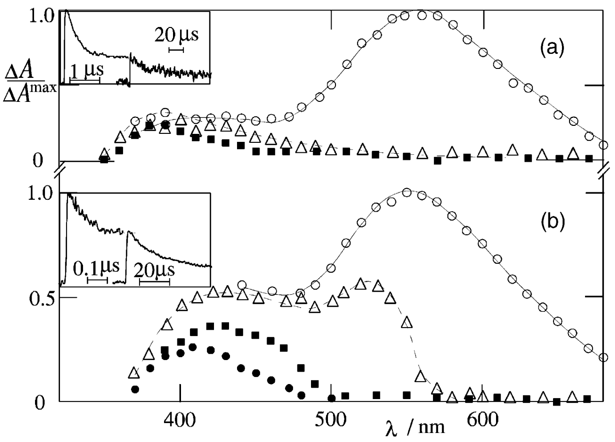


Fig. 1. Transient absorption spectra of 1,4-DNN in argon-saturated benzene in the presence of (a) DEA (3 mM) and (b) TEA (10 mM) at 20 ns (○), 1 µs (△), 100 µs (■) and 10 ms (●) after the 354 nm pulse. Insets: kinetics at 450 nm.

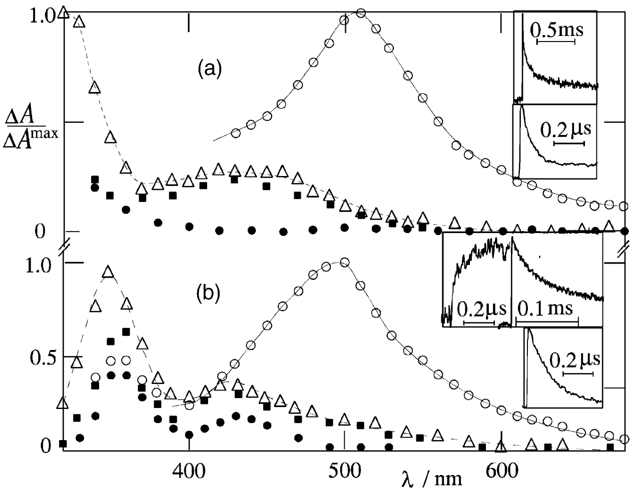
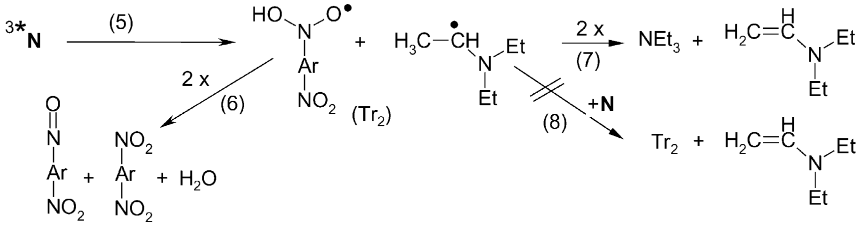


Fig. 2. Transient absorption spectra of DNF in argon-saturated benzene in the presence of (a) DEA (2 mM) and (b) TEA (0.5 mM) at 20 ns (○), 1 µs (△), 100 µs (■) and 10 ms (●) after the 354 nm pulse. Insets: kinetics at 350 nm (upper) and 500 nm (lower).



Scheme 2.

possible reaction (8) can be excluded since the yield of Tr_2 was not markedly changed, when the substrate concentration was varied.

The time resolved spectra for DNB in the presence of TEA are more complex (Fig. 3). Two further intermediates (Tr_2 and Tr_3) were observed prior to the formation of the product, $ONArNO_2$. The order of intermediates of the special case of DNB in the presence of TEA is triplet state, Tr_2 and Tr_3. Tr_3 strongly absorbs at 500 nm, appears within 0.3 μs, i.e. not directly by quenching of the triplet state, and decays with $t_{1/2} = 10$ μs. It is assigned to a quinonoid structure, formed prior to 4-nitroso-4′-nitrobiphenyl as the final product (Scheme 3). The proposed conversion of Tr_2 into Tr_3 is reaction (9a) with the "invisible" α-aminoethyl radical, thereby forming *N*,*N*-diethylvinylamine.

A quinonoid structure can in principle be proposed also for intermediates arising from 1,4-DNN and DNF. The question arises as to why this sequence is observed only for the photoreduction of DNB? Since formation of a quinonoid structure clearly requires co-planarity of the six-membered ring and the N(O)OH fragment, this can well be reached for Tr_3 from DNB, but not for a corresponding transient from 1,4- or 1,5-DNN, where the peri-hydrogen atoms obstruct co-planarity.

For the lack of any Tr_3-like intermediate from DNF, there is no obvious explanation. Since the main difference between DNF and DNB is the carbonyl "clamping" the two benzenoid rings, it may be surmised that this clamping renders any quinonoid structure unfavorable.

3.4. Secondary transients from dinitroarenes in the presence of anilines

The triplet decay of the dinitroarenes is also accelerated on addition of *N*,*N*-dialkylanilines and the rate constant for triplet quenching of 1,4-DNN is $k_q \approx 1.4 \times 10^{10}\ M^{-1}\ s^{-1}$.

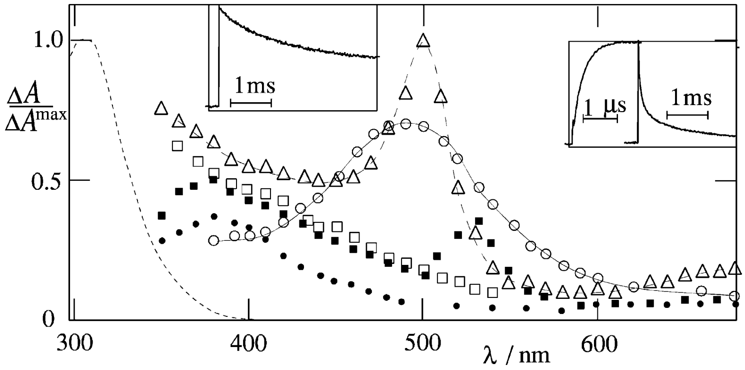
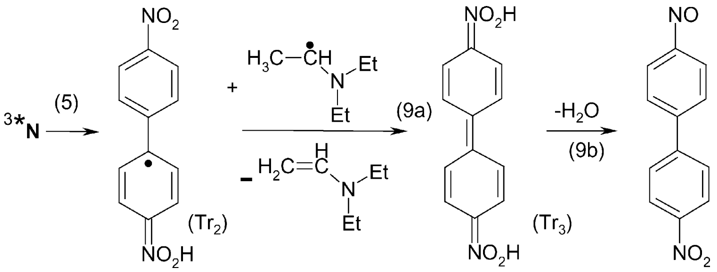


Fig. 3. Transient absorption spectra of DNB in argon-saturated benzene in the presence of TEA (5 mM) at 20 ns (○), 0.1 μs (□), 1 μs (△), 100 μs (■) and 10 ms (●) after the 354 nm pulse. Insets: kinetics for grow-in and decay at 400 nm (left) and 500 nm (right); absorption spectrum prior to irradiation (dotted).



Scheme 3.

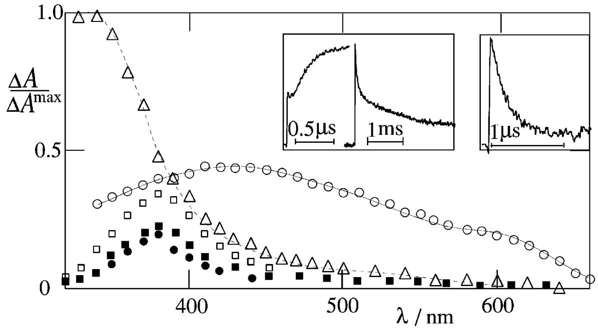


Fig. 4. Transient absorption spectra of 1,3-DNN in argon-saturated benzene in the presence of DEA (1 mM) at 20 ns (○), 0.1 µs (□), 1 µs (△), 100 µs (■) and 10 ms (●) after the 354 nm pulse. Insets: kinetics for grow-in and decay at 370 nm (left) and 500 nm (right).

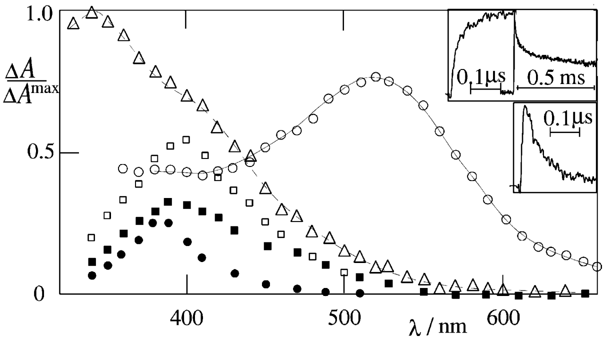


Fig. 5. Transient absorption spectra of 1,5-DNN in argon-saturated benzene in the presence of DEA (1 mM) at 20 ns (○), 0.1 µs (□), 1 µs (△), 100 µs (■) and 10 ms (●) after the 354 nm pulse. Insets: kinetics for grow-in and decay at 390 nm (upper) and 500 nm (lower).

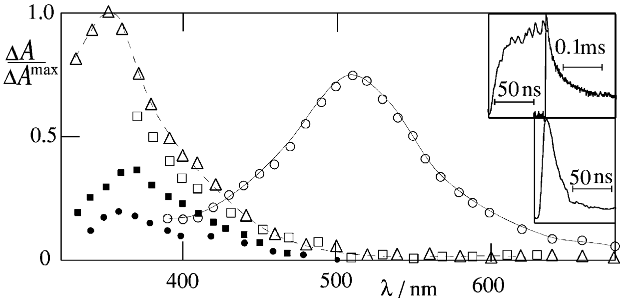


Fig. 6. Transient absorption spectra of DNB in argon-saturated benzene in the presence of DEA (3 mM) at 20 ns (○), 0.1 µs (□), 1 µs (△), 100 µs (■) and 10 ms (●) after the 354 nm pulse. Insets: kinetics for grow-in and decay at 370 nm (upper) and 500 nm (lower).

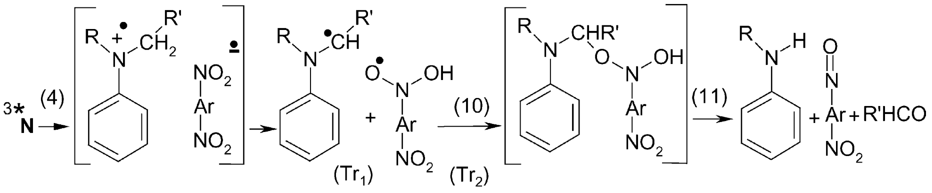
A 50% triplet quenching is achieved at the rather low concentration of $[DMA]_{1/2} = 30\,\mu M$, taking $\tau_T = 3\,\mu s$. Analogous effects were observed for 1,3-, 1,4- or 1,5-DNN, DNB and DNF, where the rate constants are $k_q = (0.8–1.6) \times 10^{10}\,M^{-1}\,s^{-1}$ (Table 3). The transient absorption spectra for 1,4-, 1,3-, 1,5-DNN, DNB and DNF in the presence of DEA (0.05–1 mM) are shown in Figs. 1a, 4-6, 2a, respectively. For NF and the dinitroarenes transient Tr_1 with maximum, λ_{rad}, in the UV originates from the triplet state and is a radical since its decay is accelerated by oxygen. The decay under argon occurs by second-order kinetics with a first half-life of $t_{1/2} = 0.03–1$ ms under our conditions, taking into account the presence of a weak longer lived or permanent component. The half-lives for mononitronaphthalenes ($t_{1/2} < 9\,\mu s$) [21] are shorter. The $\Delta A_{rad}/\Delta A_T^{max}$ values show large changes between DNNs, indicating that the yield of Tr_1 is largest for 1,3-DNN and smallest for 1,4-DNN.

For mononitronaphthalenes, it has been shown that the photoinduced conversion of $PhNMe_2$ into PhNHMe involves electron transfer [21]. This proposed initial step occurs intermolecularly from the amine to the triplet state, but the radical ions are not detectable in argon-saturated benzene [2,28]. To account for the presence of the aminoalkyl radical, $PhN(R)^{\bullet}CHR'$ (Figs. 1a, 2a, 4–6) as major absorbing species, reaction (4) and proton transfer are proposed (Scheme 4). The nitro-derived radical seems to be too weakly absorbing for separate detection. For decay of the aminoalkyl radical, reactions (10) and (11) of the two radicals into a quasi-stable product are considered. A dealkylation via (11) has not been studied for the dinitroarenes.

3.5. Effects of oxygen

The above measurements refer to deoxygenated solutions, unless otherwise indicated. For nitrohydrocarbons in the presence of TEA, DEA or DMA, due to the high k_q values, reactions (4) and (5) could compete successfully with triplet quenching by oxygen (3), e.g. for amine concentrations of >0.1 M in air-saturated benzene. The important quenching reactions, however, involve the relevant radicals. The proposed reaction of oxygen in the case of H-atom transfer to nitroarenes is trapping of the $O_2NAr^{\bullet}NO_2H$ radical. The proposed quenching reaction in the case of H-atom transfer from TEA is reaction (12).

$$O_2NAr^{\bullet}NO_2H + O_2 \rightarrow O_2NArNO_2 + HO_2^{\bullet} \qquad (12)$$



Scheme 4.

Therefore, when oxygen is present, Φ_d is much lower (Table 1) and the half-life in the decay kinetics of the observed $O_2NAr^{\bullet}NO_2H$ radical (Tr_2) is very short. Oxygen reacts also with the α-aminoethyl radicals [30] and the α-aminoalkyl radicals [21] in the cases of TEA and *N*,*N*-dialkylanilines, respectively.

4. Concluding remarks

The photoreaction of dinitronaphthalenes, 4,4′-dinitrobiphenyl and 2,7-dinitrofluorenone in benzene is initiated by photoinduced electron transfer from an amine to the lowest triplet state of the dinitroarene. Nitroso compounds are the photoproducts which are detectable in the UV-Vis. $O_2NAr^{\bullet}NO_2H$ radicals, observed as intermediates after triplet quenching by TEA, differ by spectrum and decay kinetics from $PhN(R)^{\bullet}CHR'$ radicals, the intermediates in the presence of *N*,*N*-dialkylanilines. A mechanism of photodealkylation of DMA and DEA in benzene as solvent is proposed.

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References

[1] S.G. Cohen, A. Parola, G.H. Parsons Jr., Chem. Rev. 73 (1973) 141.
[2] J.C. Scaiano, J. Phys. Chem. 85 (1981) 2851.
[3] A. Demeter, L. Biczók, T. Bérces, V. Wintgens, P. Valat, J. Kossanyi, J. Phys. Chem. 97 (1993) 3217.
[4] H. Görner, D. Döpp, A. Dittmann, J. Chem. Soc., Perkin Trans. 2 (2000) 1723.
[5] H. Görner, Chem. Phys. Phys. Chem. 4 (2002) 482.
[6] J.A. Barltrop, N.J. Bunce, J. Chem. Soc. (C) (1968) 1467.
[7] M. Takami, T. Matsuura, I. Saito, Tetrahedron Lett. 8 (1974) 661.
[8] D. Döpp, D. Müller, Recl. Trav. Chim. Pays-Bas 98 (1979) 297.
[9] D. Döpp, J. Heufer, Tetrahedron Lett. 23 (1982) 1553.
[10] D. Döpp, B. Gerding, J. Heufer, J. Photochem. 17 (1981) 107.
[11] J. Lin, Ph.D. Thesis, University of Duisburg, 1994.
[12] H. Görner, D. Döpp, Photochem. Photobiol. Sci. 1 (2002) 270.
[13] F.M. Abd El Latif, M.A. Barsy, E.A. Rady, M.E. Hassan, M.A. El Maghraby, J. Photochem. Photobiol. A: Chem. 121 (1999) 111.
[14] M. Fawi, A. El Latif, J. Photochem. Photobiol., A: Chem. 141 (2001) 241.
[15] R. Hurley, A.C. Testa, J. Am. Chem. Soc. 90 (1968) 1949.
[16] A.N. Frolov, N.A. Kuznetsova, V.A. El'tsov, N.I. Rtishchev, Z. Org. Khim. 9 (1973) 963.
[17] C. Paradisi, G. Scorrano, Acc. Chem. Res. 32 (1999) 958.
[18] E. Havinga, J. Cornelisse, Pure Appl. Chem. 47 (1976) 1.
[19] N.J. Bunce, S.R. Cater, J.C. Scaiano, L.J. Johnston, J. Org. Chem. 52 (1987) 4214.
[20] H. Görner, D. Döpp, J. Chem. Soc., Perkin Trans. 2 (2002) 120.
[21] H. Görner, J. Chem. Soc., Perkin Trans. 2 (2002) 1778.
[22] H. Görner, J. Phys. Chem. A 106 (2002) 5989.
[23] D. Döpp, Top. Curr. Chem. 55 (1975) 51.
[24] D. Döpp, in: W.M. Horspool, P.-S. Song (Eds.), CRC Handbook of Photochemistry and Photobiology, CRC Press, Boca Raton, 1995, p. 1019, and references cited therein.
[25] T.-I. Ho, Y.L. Chow, in: S. Patai (Ed.) The Chemistry of Amino, Nitroso, Nitro and Related Groups, Wiley, Chichester, 1996, p. 747.
[26] A. Costela, I. García-Moreno, J. Dabrio, R. Sastre, J. Photochem. Photobiol. A 109 (1997) 77.
[27] A. Costela, I. García-Moreno, O. Garcia, R. Sastre, J. Photochem. Photobiol. A 131 (2000) 133.
[28] S.F. Yates, G.B. Schuster, J. Org. Chem. 49 (1984) 3349.
[29] H.G. Heller, J.R. Langan, J. Chem. Soc., Perkin Trans. 2 (1981) 341.
[30] R.F. Anderson, W.A. Denny, W. Li, J.E. Packer, M. Tercel, W.R. Wilson, J. Phys. Chem. 101 (1997) 9704.