J. Phys. Chem. A **2002,** *106,* 5989−5998 **5989**

Electron Transfer from Triethylamine to the Triplet State of Dinitronaphthalenes, 4,4′-Dinitrobiphenyl and 2,7-Dinitrofluorenone: Time Resolved UV−Vis Spectroscopic and Conductometric Study in Polar Solvents†

Helmut Görner

Max-Planck-Institut für Strahlenchemie, D-45413 Mülheim an der Ruhr, Germany

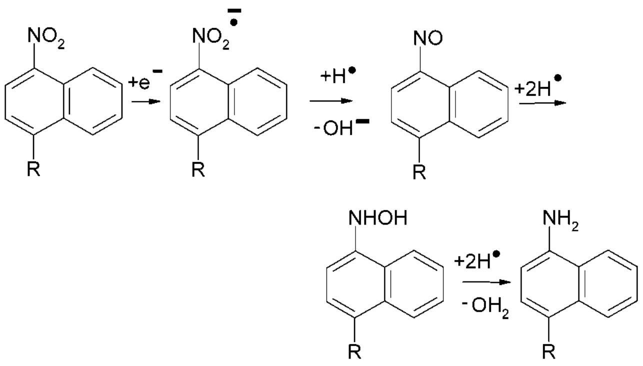
Received: October 10, 2001; In Final Form: March 20, 2002

The photoreduction of 1,3-, 1,4-, 1,5-, 1,8-, and 2,3-dinitronaphthalene (DNN) as well as of 4,4′-dinitrobiphenyl and 2,7-dinitrofluorenone by 1,4-diazabicyclo[2.2.2]octane (DABCO), triethylamine (TEA), and diethylamine (DEA) in argon-saturated acetonitrile and mixtures with water was studied by spectroscopic and conductometric means after nanosecond 354 nm pulses. The rate constant for quenching of the triplet state of the dinitroarenes by TEA is $k_q \approx 1.6 \times 10^{10}$ M^{-1} s^{-1} in acetonitrile and markedly smaller on an addition of water. The secondary transients with maxima at 380−550 nm in the presence of TEA or DEA at concentrations of <1 mM and of DABCO are ascribed to radical anions of the dinitroarenes, formed via photoinduced electron transfer to the triplet state. With TEA at higher concentrations, in addition a delayed radical formation, involving the α-aminoethyl radical as precursor, was observed throughout. The radicals subsequently undergo a termination reaction yielding the corresponding nitroso compounds as major primary products; the process is substantially slowed in the presence of water (≤5 M). For 1,4-DNN a longer lived intermediate is formed. It is attributed to the dianion, which is also observable in alkaline 2-propanol. The two photoinduced reduction reactions of the dinitroarenes by TEA and the subsequent radical disproportionation are supported by time-resolved conductometric measurements. The conductivity signals have generally a much longer half-life than the absorbing intermediates. The mechanism and the effects of substitution and concentrations of TEA, oxygen, and water are discussed.

Introduction

The photoreduction of aromatic compounds by aliphatic amines has been intensively investigated.[1−10] Considerable emphasis has been placed on the photoreduction of nitroaromatic compounds.[11−24] The photochemistry of 1-methoxy-4-nitronaphthalene depends on the amine and the amount of water in acetonitrile.[18] A related topic is the photoreduction of nitronaphthalenes in the presence of alcohols.[11,13] The major photoproduct of 1,5-dinitronaphthalene (1,5-DNN) in alkaline methanol−water (95:5) is 1-amino-5-nitronaphthalene.[17] For the photoinduced electron transfer from triethylamine (TEA) and diethylamine (DEA) to the triplet state of *N*-phenyl-naphthalimides, two reduction steps, a primary and a secondary electron transfer have been reported.[10] Nitroaromatic compounds, especially (di)-nitronaphthalenes, are potential candidates for studying the delayed radical formation with TEA or DEA. In fact, a similar reaction mechanism has recently been reported for nitronaphthalenes.[21] From the electrochemistry it is known that transfer steps of H-atoms lead from the radical anion of a nitro compound via a nitroso to the amino compound.[25]

Most photochemical information is available for nitrobenzene, where, however, the reactive state is not well defined and the overall quantum yield and reactivity are rather small.[11,12,22] Nitronaphthalenes have been better characterized. They exhibit a sufficiently long triplet lifetime (τ_T) and a high quantum yield of intersystem crossing (Φ_{isc}), whereas the fluorescence is negligible.[21−23,26] 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 biological active substrates, e.g., in proteins.[27] Nitrosobenzene is a postulated intermediate in this photoreaction. Nitronaphthalenes could replace nitrobenzene derivatives. It seemed therefore desirable to get a deeper insight into the photoinduced reduction of nitroarenes.



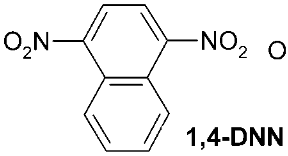
1,4-Dinitronaphthalene (1,4-DNN), several other dinitronaphthalenes (1,3-, 1,5-, 1,8-, and 2,3-DNN) as well as 4,4′-dinitrobiphenyl (DNB) and 2,7-dinitrofluorenone (DNF) were chosen for this work. Triplet quenching by TEA, DEA, and DABCO in polar media yields the radical anion of the dinitroarenes. The electron transfer and eventual consequences of secondary reactions in the presence of the aliphatic amines were studied by time-resolved UV−vis spectroscopic and conductometric measurements in neat and wet acetonitrile

---

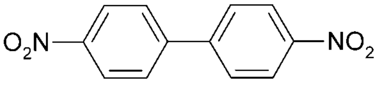
[†] Dedicated to Professor Karl E. Wieghardt on the occasion of his 60th birthday.

10.1021/jp013754o CCC: $22.00

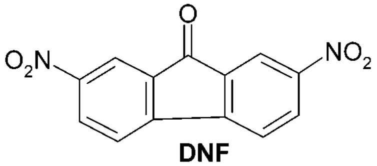
solutions. Thermal reactions (and secondary photolysis) may lead to further products.



1,4-DNN



DNB



DNF

Experimental Section

The nitroarenes (Merck, Aldrich, K&K) and 1,4-diazabicyclo-[2.2.2]octane (DABCO) were used as supplied. 1,3- and 1,8-DNN were recrystallized from methanol. The purity of all dinitroarenes was checked by GC and/or HPLC to be >99%, except for 1,8-DNN; since 1,5-DNN as impurity (20%) in 1,8-DNN could not be separated, only a few data are presented. TEA and DEA were purified by distillation. The solvents, e.g., acetonitrile (Merck Uvasol) or 2-propanol, were of the purest spectroscopic quality. Water was from a Milli Q system. The molar absorption coefficient at the maximum is $\epsilon_{342} = 6 \times 10^3$, $\epsilon_{328} = 6.6 \times 10^3$, $\epsilon_{319} = 7.0 \times 10^3$, and $\epsilon_{342} = 2.6 \times 10^4$ $M^{-1}cm^{-1}$ for 1,4-, 1,5-, 1,8-DNN, and DNF, respectively. The absorbance of neat TEA has no effect on the excitation of the compounds at 354 nm. The absorption spectra were monitored on a diode array spectrophotometer (HP, 8453).

A Nd laser (J. K. Lasers, pulse width: 15 ns and energy: <30 mJ) (unless otherwise indicated) was used for excitation at 354 nm. In one case an excimer laser (Lambda Physik, EMG 200, pulse width of 20 ns and energy <100 mJ) with $\lambda_{exc} = 308$ nm was used. The absorption signals were measured with two digitizers (Tektronix 7912AD and 390AD).[8,28] Typically, absorbances of 1−2 were used for λ_{exc}, corresponding to concentrations of 0.1−0.3 mM. The increase in absorbance of the triplet state at the end of the pulse and of the absorption of the radicals at the maximum, detected at appropriate times, are almost linear with the incident laser intensity. The relative triplet yield ($\Delta A_T/\Delta A_T^{max}$) was obtained with respect to DNF. The fast (0.05−10 μs) and slow (5 μs−10 s) conductivity signals were measured by DC and AC bridges as reported elsewhere.[28] The first half-life ($t_{1/2}$) in both absorption and conductivity signals was found to depend strongly on the amount of oxygen and the presented values refer to those after vigorous bubbling by argon (unless otherwise indicated). For photoconversion the 366 nm line of a 200 W Hg lamp combined with an interference filter were used. The dinitroarene concentration was adjusted such that the absorbance (in a 1 cm cell) was 1−3 at λ_{irr}. The conversion was carried out after vigorous bubbling by argon prior to and during irradiation. For HPLC analyses a 125 × 4.6 mm Inertsil ODS-3 5 μm column was used and MeOH−water 2:1 as eluent for all dinitroarenes.[21] The quantum yield of decomposition (Φ_d) was determined using the aberchrome 540 actinometer.[29] The quantum yield of formation of singlet oxygen (Φ_Δ) was determined as described previously.[30] All measurements refer to 24 ± 2 °C.

Results and Discussion

Triplet State Properties. The T-T absorption spectra of the dinitroarenes show one or two broad bands with absorption maxima (λ_{TT}) in the visible region. Formation of the triplet state occurs within the pulse width, the decay is essentially first-order (if the pulse intensity is low enough), and the lifetime in argon-saturated acetonitrile is typically in the 10 μs range. Only for 2,3-DNN and DNB the lifetime is much smaller, $\tau_T = 80$ and 140 ns, respectively. The observed triplet state is quenched by oxygen, the rate constant for quenching is $k_{ox} = (1-2) \times 10^9$ M^{-1} s^{-1}. Some properties of the triplet state of mono- and dinitronaphthalenes have been reported.[22,26] The triplet energy ranges from $E_T = 190$ kJ mol^{-1} for DNF to 210 kJ mol^{-1} for 1,4-DNN and further to 240 kJ mol^{-1} for DNB.[16,22] The quantum yield of triplet formation of the dinitroarenes is substantial in solution at room temperature, $\Phi_{isc} = 0.6-0.8$ for 1,3- and 1,4-DNN, and in glassy media at −196 °C.[16,23] The quantum yield of singlet oxygen formation (Φ_Δ) as lower limit of Φ_{isc} and further triplet state characteristics are compiled in Table 1. $\Phi_{isc} = 0.7$ for DNB in methanol has been concluded from results of photoreduction in the presence of MeO^-.[17]

TABLE 1: T-T Absorption Maxima, Lifetime, and Relative Triplet Yield,[a] Rate Constant for Quenching by Oxygen and Quantum Yield of Singlet Oxygen

compound	λ_{TT}[b] (nm)	τ_T[c] (μs)	k_{ox} ($\times 10^9$ M^{-1} s^{-1})	$\Delta A_T/\Delta A_T^{max}$	Φ_Δ[d]
1,3-DNN	*430*,550	7	1.1	0.8	0.6 (0.65)
1,4-DNN	410,*550*	10	1.2	0.9	0.6 (0.68)
1,5-DNN	410,*540*	10	1.2	0.6	0.4 (0.47)
1,8-DNN	400,540	8	1.2		
2,3-DNN	470	0.08	<2	0.8	
DNB	510	0.14	<2	0.8	
DNF	510	10	0.8	1.0	0.6 (0.65)

[a] In argon-saturated acetonitrile. [b] Main band (italics). [c] At low pulse intensity. [d] Using air- and (in parentheses) oxygen-saturated solution.

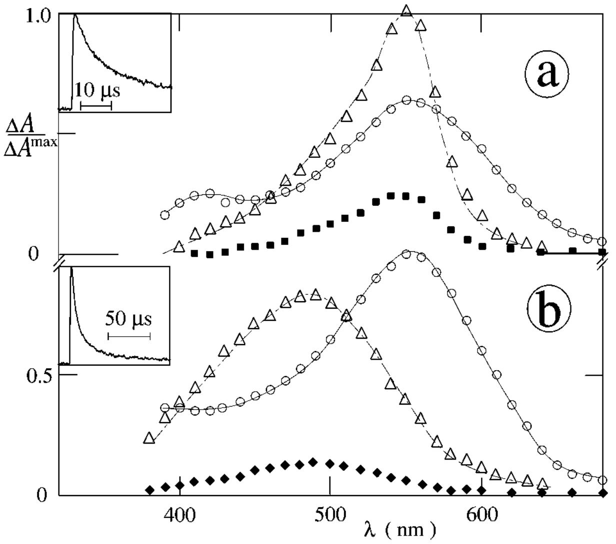


Figure 1. Transient absorption spectra of (a) 1,4-DNN and (b) 1,5-DNN in argon-saturated acetonitrile in the presence of DABCO (0.03 M) at <30 ns (○), 1 μs (△), 50 μs (♦), and 80 μs (■) after the pulse; insets: decay kinetics at (a) 540 nm and (b) 480 nm.

Quenching of the Triplet State of Dinitroarenes by DABCO. The T−T absorption spectrum of 1,4-DNN in acetonitrile shows a broad band with $\lambda_{TT} = 550$ nm and levels off at 700 nm. The triplet state is formed concomitant to the pulse with or without DABCO at low concentration (<0.1 mM). On addition of DABCO the initial spectrum remains unchanged (see circles in Figure 1a), but the triplet lifetime is shorter. The first-order rate constant (k_{obs}), taken at ca. 600 nm, shows a linear dependence on the DABCO concentration. The rate

TABLE 2: Maximum of the Radical Anion and Rate Constants for Triplet Quenching of Dinitroarenes by Electron Donors[a]

		k_q (10^9 M^{-1} s^{-1})			k_q (10^5 M^{-1} s^{-1})[c]
compound	λ_{rad}[b] (nm)	DABCO	TEA	DEA	2-propanol
1,3-DNN	420	16	14 (4)[d]		0.3
1,4-DNN	545	18	15 (4)	14	1
1,5-DNN	480	18	14 (3)		0.1
1,8-DNN	430	16	14 (4)		
DNB	440	>15	>12		
DNF	380,540	18	14 (4)	15	3

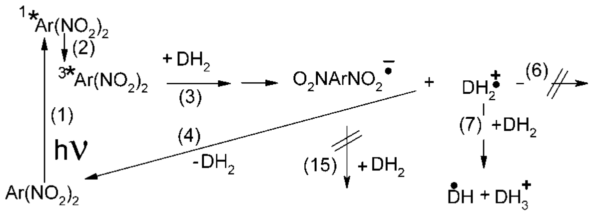
[a] In argon-saturated acetonitrile. [b] Using [DABCO] = 1−30 mM. [c] In a mixture of acetonitrile, 2-propanol, and 5 M water at pH > 12. [d] Values in parentheses refer to the presence of water (5 M).

TABLE 3: Properties of the Resulting Radicals Obtained from Spectroscopy of Dinitroarenes[a]

compound	λ_{rad}[b](nm)	k_{rad} ($\times$ 10^8 M^{-1} s^{-1})[c]	$t_{1/2}$ (ms)
1,3-DNN	420 [550][d]	3 (1)[e]	1 (10)[e]
1,4-DNN	540 [440] 540[f]	4 (1.5)	1−10 (0.1−0.2)[e]
1,5-DNN	480	4 (1)	<0.5
1,8-DNN	430 [540]	5 (1)	
2,3-DNN	400	6	<0.5
DNB	435	2	<0.3 (10)
DNF	390, 540	2	2 (≥10)

[a] In argon-saturated acetonitrile, using [TEA] = 2−30 mM. [b] Maximum of the radical anion. [c] See text. [d] Values in brackets refer to a subsequently formed transient. [e] Values in parentheses refer to the presence of water (5 M). [f] For DEA.

SCHEME 1



constant, i.e., slope of this plot, is $k_q \approx 1.8 \times 10^{10}$ M^{-1} s^{-1} (Table 2). A transient with larger absorbance at the maximum λ_{rad} = 545 nm and lower absorbance than the triplet state above 580 nm (Figure 1a), which decays by second-order kinetics, is assigned to the radical anion ($O_2NArNO_2^{\bullet-}$). Linear dependences on [DABCO] (at appropriate wavelengths), similar k_q values, and second-order decay kinetics (Figure 1b) with a half-life of $t_{1/2}$ = 10−30 μs (depending on the laser intensity) were also observed for the other dinitronaphthalenes, DNB, and DNF (Tables 2 and 3).

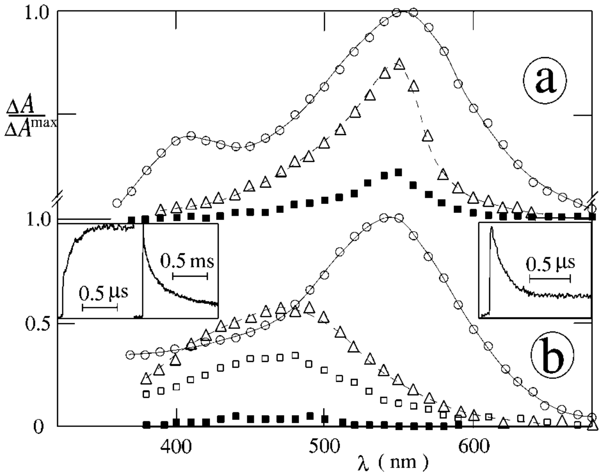


Figure 2. Transient absorption spectra in the presence TEA of (a) 1,4-DNN ([TEA] = 0.2 mM) and (b) 1,5-DNN ([TEA] = 2 mM) in argon-saturated acetonitrile at <30 ns (○), 0.1 μs (□), 1 μs (△), and 1 ms (■) after the pulse; insets: kinetics at 480 nm (left) and 560 nm (right).

The photoinduced electron transfer from an amine as electron donor (DH_2) to the triplet state of the acceptor ($^{3*}O_2NArNO_2$) occurs via reactions 1−3, where $DH_2^{\bullet+}$ is the radical cation of the amine (Scheme 1). $DABCO^{\bullet+}$ has the absorption maximum at 450 nm and the ϵ value[31] is much smaller than those of the triplet precursor and the radical anion. A transient with a broad absorption band, a characteristic maximum, and no absorption on the millisecond time scale was observed for all compounds examined (Table 2). It is assigned to the radical anion of the dinitroarene, formed by electron transfer from DABCO to the triplet state. $DH_2^{\bullet+}$ and $O_2NArNO_2^{\bullet-}$ are long-lived species. Back electron transfer 4 accounts for the observed second-order decay kinetics without further absorbance. The spectra of the radical anion in the presence of water (5 M), too, extend over the vis range with similar λ_{rad} values. In principle, the radical anion could be converted into $O_2NAr^{\bullet}NO_2H$, the conjugate acid.

$$O_2NArNO_2^{\bullet-} + H_2O \rightleftharpoons O_2NAr^{\bullet}NO_2H + OH^- \qquad (5)$$

For the (di)nitroarenes, however, this protonation has to be excluded in acetonitrile and in mixtures with water (pH > 9). From pulse radiolysis studies of nitrobenzene in aqueous solution, the pK_a value of 3.2 is known for equilibrium 5.[32]

Quenching of the Triplet State of Dinitroarenes by TEA and DEA. In the presence of TEA at low concentration (<1 mM) the T-T absorption spectrum of 1,4-DNN in acetonitrile is also unchanged (see circles in Figure 2a). For all dinitroarenes addition of TEA gives rise to secondary transients after triplet quenching. The k_{obs} value (measured at appropriate wavelengths) depends linearly on [TEA], the rate constant varies from k_q = 1.4×10^{10} to 1.8×10^{10} M^{-1} s^{-1}. An example of the transient absorption spectra in the presence of TEA at relatively low concentrations is shown in Figure 2a. The species after the triplet state should be assigned (at least the major part) to the radical anion on the basis of the comparison with DABCO and the second-order decay kinetics (Scheme 1). For most dinitroarenes 50% triplet quenching is achieved for rather low donor concentrations, $[amine]_{1/2}$ = 10 μM, taking τ_T = 10 μs. Only for 2,3-DNN and DNB, where τ_T < 0.15 μs, the $[amine]_{1/2}$ values are ca. 1 mM.

On addition of TEA in higher concentrations, however, significant changes were registered concomitant with the laser pulse and at later times (see Figures 3−7). The triplet precursor can be detected by ns time resolution only when [TEA] is below ca. 3 mM. To further test for the nature of the longer lived transient and the permanent component, TEA was replaced by DEA. The kinetics and spectra are virtually identical to those using TEA (Tables 1 and 2). On the other hand, in water−acetonitrile mixtures the k_q values with TEA are generally much lower than in neat acetonitrile and the spectra reveal slight changes in their maxima (Figures 3−7). Markedly lower k_q values on addition of water to acetonitrile have also been reported for azaarenes,[8] 1-, 2-nitronaphthalene, and 1-methoxy-4-nitronaphthalene.[18,21] The reason may be due to hydrogen bonding between water and the amine lone pair, making the latter less oxidizable.

The rate constant for triplet quenching by TEA in dry acetonitrile is close to the diffusion-controlled limit (Table 2),

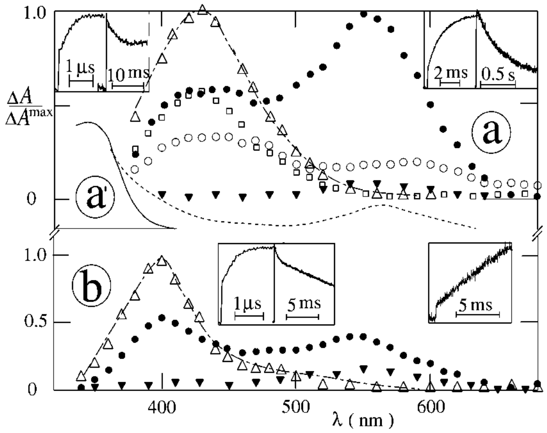


Figure 3. Transient absorption spectra of 1,3-DNN ([TEA] = 5 mM) in (a) argon-saturated acetonitrile at <30 ns (○, [TEA] = 0.1 mM) and (b) acetonitrile−water (9:1) at 0.1 μs (□), 1 μs (△), 10 ms (●), and 1 s (▼) after the pulse; insets: kinetics at 420 nm (left) and 540 nm (right); (a′) ground state (prior to and after conversion with λ_{irr} = 366 nm, full and broken lines, respectively).

i.e., the electron transfer is strongly favored by the electron-accepting power of the nitro group. This is in agreement with the free energy changes using the Rehm−Weller relationship.[33]

$$\Delta G = E_{ox} - E_{red} - E_T - E_c$$

Here, E_{ox} is the oxidation potential of the amine, E_{red} the reduction potential of the nitroarene, E_T the triplet energy, and E_c (0.06 V) the Coulombic term accounting for ion pairing. The $-E_{red}$ values of 1,4-, 1,5-, 1,8-DNN, and DNB in acetonitrile were reported to be 0.4, 0.6, 0.69, and 0.74 V, respectively.[16,23] Using the E_{red} and E_T values and the oxidation potential of TEA, E_{ox} = 0.78 V (vs SCE in acetonitrile),[34] it follows that the ΔG value is negative (−0.3 to −1.2 V) for the dinitroarenes examined. For the case of DABCO with E_{ox} = 0.57 V[34] the ΔG values are more negative and the k_q values are likewise close to the diffusion-controlled limit.

Secondary Electron Transfer in the Presence of TEA. At higher TEA concentrations (1−100 mM) the transient absorption of all dinitroarenes examined shows two essentially identical spectra, one is formed directly via triplet quenching and the second in a delayed build-up, increasing within a few microseconds by a factor of 1−2. Examples of the kinetics and spectra are presented in Figures 3−7. For DNF (Figure 5a) it is shown that the absorption spectra of both parts are the same, having λ_{rad} = 390 and 540 nm. The transient absorption signal of DNB (Figure 4b) and DNF (Figure 5b) in the presence of 5 M water (and an appropriate TEA concentration) consists also of two subsequently formed components, but the maxima in wet acetonitrile are blue-shifted with respect to dry acetonitrile. Even stronger spectral changes were registered for 1,3- and 1,8-DNN. The transient absorption spectra of 1,3-DNN in acetonitrile after triplet decay contain two subsequently formed parts which have maxima at 420 and 550 nm (Figure 3a); the latter is similar in the presence of 5 M water (Figure 3b). The transient absorption spectra of the 1,8-DNN/TEA system are comparable; that with λ_{rad} = 430 nm is converted into one with maximum at 540 nm in dry and at 520 nm in wet acetonitrile. Generally, the decay extends into the second time range.

For the 9-chloroanthracene/TEA system in acetonitrile a second-order decay of the radical anion of the acceptor has been reported but no back electron transfer.[5] For the 1,4-naphthoquinone/TEA system in aqueous acetonitrile electron transfer to the triplet state has been observed.[7] This is also the case for 3,5,6-triphenyl-1,2,4,-triazine, 3-phenyl-1,2,4-benzotriazine, and 3-phenylphenanthro[9,10-*e*]-1,2,4-triazine in several solvents in

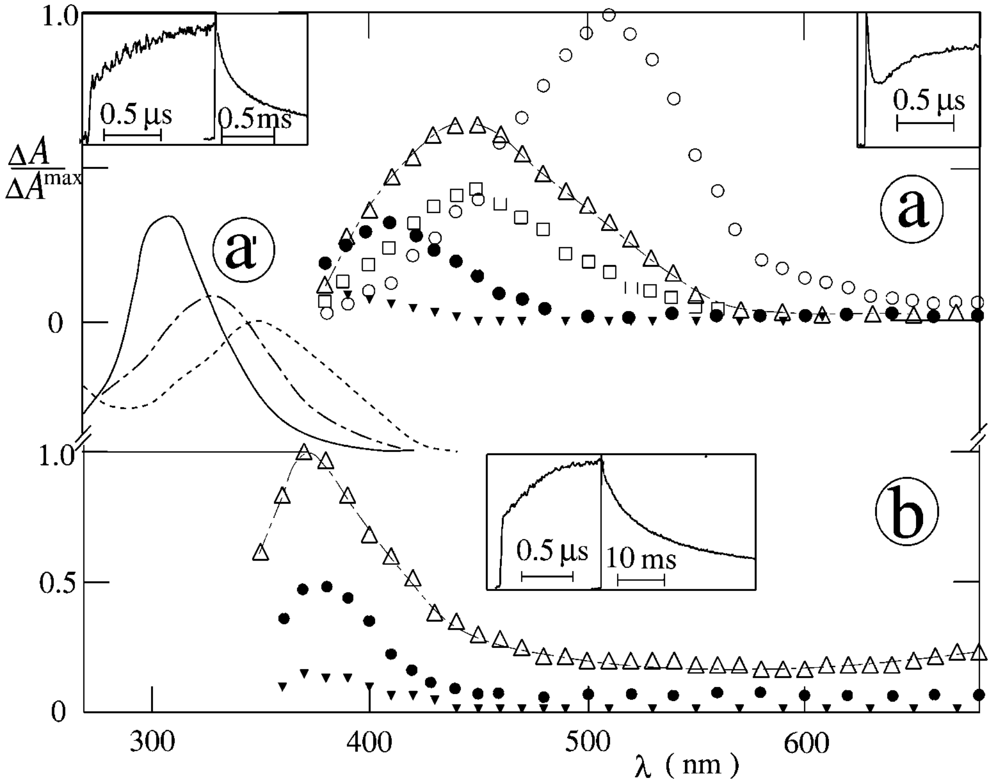


Figure 4. Transient absorption spectra of DNB ([TEA] = 10 mM) in argon-saturated (a) acetonitrile and (b) acetonitrile−water (9:1) at <30 ns (○, [TEA] = 0.1 mM), 0.1 μs (□), 1 μs (△), 10 ms (●), and 1 s (▼) after the pulse; insets: kinetics at (a) 450 nm (left) and 510 nm (right) and (b) 390 nm; (a′) ground state prior to (full) and after conversion with λ_{irr} = 366 nm (dotted); the dot−dashed curve was obtained after purging the photoproduct with oxygen.

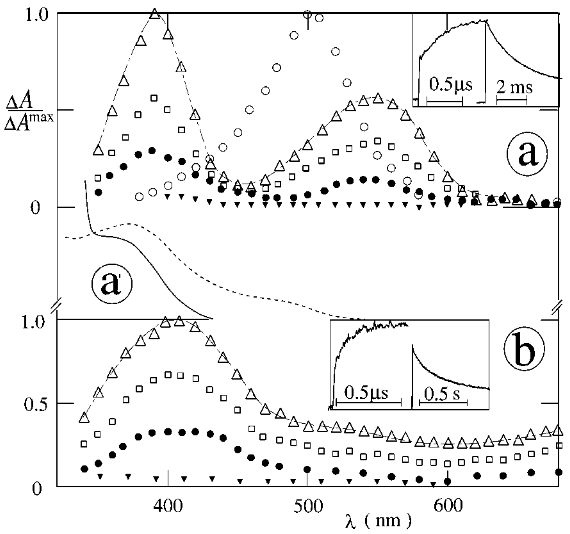


Figure 5. Transient absorption spectra of DNF ([TEA] = 10 mM) in argon-saturated (a) acetonitrile at <30 ns (○, [TEA] = 0.1 mM), and (b) acetonitrile−water (9:1) at 0.1 μs (□), 1 μs (△), 10 ms (●), and 1 s (▼) after the pulse, insets: kinetics at 390 nm; (a′) ground state (prior to and after conversion with λ_{irr} = 366 nm, full and broken lines, respectively).

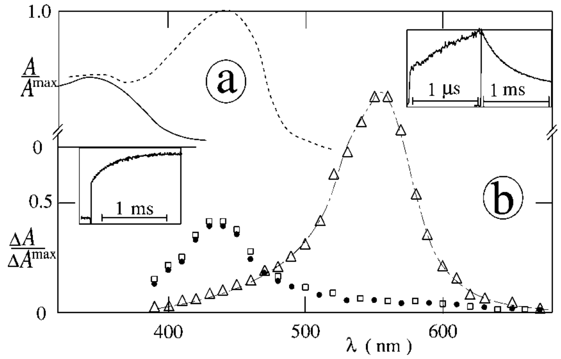


Figure 6. (b) Transient absorption spectra of 1,4-DNN in the presence of TEA (2 mM) in argon-saturated acetonitrile at <2 μs (△), 10 ms (●), and 1 s (□) after the pulse; insets: kinetics at 440 nm (left) and 540 nm (right), and (a) ground state (prior to and after conversion with λ_{irr} = 366 nm, full and broken lines, respectively).

the presence of TEA and DEA.[8] The longer lived and quasi-permanent species in the photoreduction of the electron-deficient azaarenes by TEA or DEA are the H-adduct radicals and dihydro derivatives, respectively.[8] For the dinitroarenes examined in the presence of TEA at low concentration (10−30 μM) the radical anion essentially disappears via back electron transfer 4. $\mathrm{Et_3N^{\bullet+}}$ in aqueous solution was reported to have a lifetime of 3 μs.[3] In contrast, when [TEA] is larger than 1 mM, longer lived intermediates appear which could also be due to a reaction with the TEA-derived radicals. The following secondary reactions with alkylamines are considered (Scheme 2). The lifetime of the radical cation of TEA is limited by the back reaction 4, proton transfer 6, equilibrium 7, or deprotonation. For (di)-nitroarenes proton transfer 6 is considered to be unlikely because at higher [TEA] forward reaction with a second TEA molecule to form the cation ($\mathrm{DH_3^+}$) and the α-aminoethyl radical ($\mathrm{D^{\bullet}H}$ in Scheme 1) in equilibrium 7 dominates.

$$\mathrm{Et_3N^{\bullet+} + O_2NArNO_2^{\bullet-} \rightarrow O_2NAr^{\bullet}NO_2H + Et_2N{-}^{\bullet}CHMe} \qquad (6)$$

$$\mathrm{Et_3N^{\bullet+} + Et_3N \rightleftharpoons Et_2N{-}^{\bullet}CHMe + Et_3NH^+} \qquad (7)$$

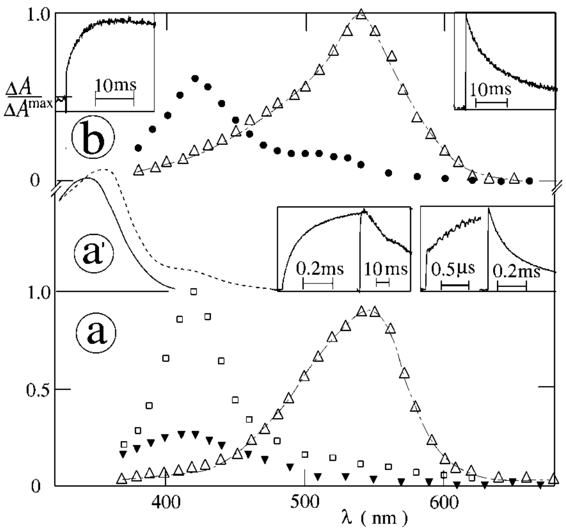
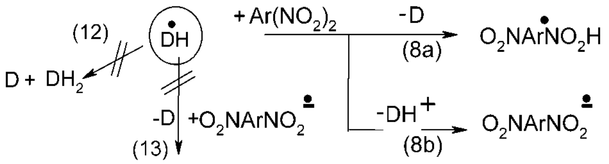


Figure 7. Transient absorption spectra of 1,4-DNN in the presence of TEA (2 mM) in argon-saturated mixtures of 5 M water in (a) acetonitrile at <2 μs (△), 1 ms (□), and 0.1 s (▼) and (b) 2-propanol at <2 μs (△) and 10 ms (●) after the pulse; insets: kinetics at 420 nm (left) and 540 nm (right) and (a′) ground state in acetonitrile−water (9:1) (prior to and after conversion with λ_{irr} = 366 nm, full and broken lines, respectively).

SCHEME 2



Upon photoinduced electron transfer from TEA to the 1,8 and 2,3 derivatives of *N*-phenylnaphthalimide, step 7 was found to occur with $k_7 = 5.7 \times 10^9$ and 1.9×10^9 $\mathrm{M^{-1}\ s^{-1}}$, respectively.[10] This is consistent with the finding that the ratio of rate constants of forward to backward reactions k_7/k_{-7} is ca. 100,[6] i.e., the α-aminoethyl radical will not react back, Reactions 4 and 6 are excluded under the applied conditions of [TEA] = 1−100 mM, because formation of the α-aminoethyl radical dominates. In fact, closer inspections of the two-step formation of the longer lived intermediates shows that the absorption spectra are very similar or identical and that the build-up kinetics depend on the TEA concentration. Several examples of the kinetics and spectra are presented (Figures 2b, 3, 4, 5a, 6a, and 7a). The half-life of the build-up kinetics decreases with the TEA concentration, from typically 2−5 μs at [TEA] = 1 mM in neat acetonitrile to 100 ns at 20 mM. Roughly, rate constants of $k_{\mathrm{rad}} = (2{-}6) \times 10^8$ $\mathrm{M^{-1}\ s^{-1}}$ and significantly smaller values in wet acetonitrile have been estimated (Table 3).

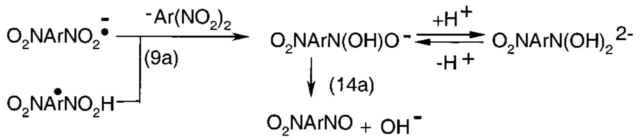
Formation of secondary radicals derived from dinitroarenes can be ascribed to reactions 8a and 8b.

$$\mathrm{Et_2N{-}^{\bullet}CHMe + O_2NArNO_2 \rightarrow O_2NAr^{\bullet}NO_2H + Et_2NCH{=}CH_2} \qquad (8a)$$

$$\mathrm{Et_2N{-}^{\bullet}CHMe + O_2NArNO_2 \rightarrow O_2NArNO_2^{\bullet-} + Et_2N^+{=}CHMe} \qquad (8b)$$

Forward reaction 5, which could lead to the H-adduct radical in other systems, is excluded for nitroarenes.[11,32] On the other hand, backward reaction 5 may be hindered in neat acetonitrile (see below). A reaction forming an $\mathrm{Et_2NCH(Me){-}O{-}(NO^{\bullet})}$-

SCHEME 3



Ar type product seems unlikely since the absorption spectrum of the amine adduct radical is expected to differ from that of the radical anion. For the case of DEA, $Et_2N-{}^{\bullet}CHMe$ has to be replaced by the $EtHN-{}^{\bullet}CHMe$ radical and diethylvinylamine by *N*-ethyliminoethane. It is worth mentioning that with DEA the same k_7 value as with TEA was found with the *N*-phenyl-1,8-naphthalimide system.[10] For the reaction of α-aminoalkyl radicals with benzil in di-*tert*-butyl peroxide, rate constants of 1.8×10^9 and 3.3×10^9 M^{-1} s^{-1} have been reported for TEA and DEA, respectively.[4]

Radical Termination Reactions. To account for radical−radical termination, reactions 9a−13 are considered (Scheme 3).

$$O_2NArNO_2^{\bullet -} + O_2NAr^{\bullet}NO_2H \rightarrow O_2NArNO_2 + O_2NArN(OH)O^- \quad (9a)$$

$$O_2NArNO_2^{\bullet -} + O_2NAr^{\bullet}NO_2H + H_2O \rightarrow (O_2NArNO_2H)_2 + OH^- \quad (9b)$$

$$2O_2NAr^{\bullet}NO_2H \rightarrow O_2NArNO_2 + O_2NArNO + H_2O \quad (10a)$$

$$2O_2NAr^{\bullet}NO_2H \rightarrow (O_2NArNO_2H)_2 \quad (10b)$$

$$2O_2NAr^{\bullet}NO_2H \rightarrow O_2NArNO_2 + O_2NH_2ArNO_2 \quad (10c)$$

$$2O_2NArNO_2^{\bullet -} \rightarrow O_2NArNO_2 + O_2NArNO_2^{2-} \quad (11)$$

$$2Et_2N-{}^{\bullet}CHMe \rightarrow Et_3N + Et_2NCH{=}CH_2 \quad (12)$$

$$Et_2N-{}^{\bullet}CHMe + O_2NArNO_2^{\bullet -} \rightarrow O_2NArN(OH)O^- + Et_2NCH{=}CH_2 \quad (13)$$

$$O_2NArN(OH)O^- \rightarrow O_2NArNO + OH^- \quad (14a)$$

$$O_2NArNO_2^{2-} + H_2O \rightarrow O_2NArNO + 2OH^- \quad (14b)$$

$$O_2NArN(OH)O^- + OH^- \rightleftharpoons O_2NArNO_2^{2-} + H_2O \quad (14c)$$

Reaction 12, which competes with reactions 8 and 13 and would also lead to diethylvinylamine (D in Scheme 2), is not accessible by our spectroscopic analysis. Photodimers via 9b and 10b could be detected for other systems,[1] but no indication for dimers was found for the cases of nitroarenes and disproportionation competes probably successfully. Reaction 10c yielding a dihydro derivative[8,9] is unlikely for nitroarenes. A self-termination reaction 11 of two radical anions is very slow, based on pulse radiolysis studies of nitrobenzene in aqueous solution.[32] The nitroso compound could be generated via 10a, 9a plus 14a, or 11 plus 14b. Reaction 13 describes formation of the anion, which would also lead to the nitroso compound. However, photolytic results in neat or wet acetonitrile reveal delayed formation of radicals of the nitroarenes (Figures 2b−7), indicating that amine radicals are not present any more at ca. 0.01 ms after the pulse. Thus, reactions 12 and 13 cannot play a significant role. In principle, the decay kinetics of $O_2NArNO_2^{\bullet -}$ could also follow a first-order law by reaction 15 with the amine itself.

TABLE 4: Properties of the Resulting Radicals Obtained from Conductometry of Dinitroarenes[a]

compound	donor	$\Delta\kappa/\Delta\kappa^{\max\,b}$	$t_{1/2}$ (ms)
1,3-DNN	TEA	0.7	>30 (>50)[c]
1,4-DNN	TEA	0.7(0.7)	2−10 (5−20)
	DABCO	0.6	0.01−0.03
	DEA	0.6	(>10)
1,5-DNN	TEA	0.6	0.3−1 (>20)
1,8-DNN	TEA	0.6	>30 (>30)
2,3-DNN	TEA	0.6	10 (>30)
DNB	TEA	0.8	0.1−0.3 (>20)
DNF	TEA	1.0 (0.9)	3−10 (>10)
	DABCO	0.7	0.01−0.03

[a] In argon-saturated acetonitrile, using [amine] = 5−10 mM. [b] Under normalized conditions. [c] Values in parentheses refer to the presence of water (5 M).

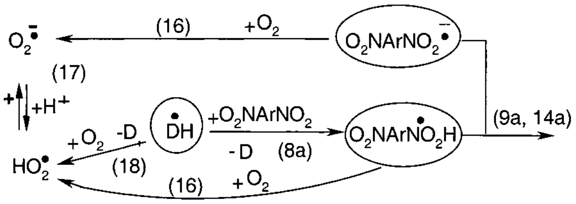
$$O_2NArNO_2^{\bullet -} + Et_3N \rightarrow O_2NArN(OH)O^- + Et_2N-{}^{\bullet}CHMe \quad (15)$$

However, for most cases with alkylamines at higher concentrations (up to 0.5 M) in neat or wet acetonitrile solution, there is no clear indication for this reaction.

Thus, the nature of the intermediates derived from the dinitroarene/TEA (<1 mM/1−100 mM) systems per one event is suggested to be first the triplet, then two longer lived radicals (anion and the conjugate acid or two radical anions in neat and wet acetonitrile, respectively), and eventually the nitroso compound (Scheme 3). A corresponding sequence from the radical anion (electron adduct) into the nitroso compound has been established by pulse radiolysis of nitrobenzene in aqueous solution.[32] Whether or not the anion appears as a separate intermediate prior to formation of the nitroso compound via step 14 is difficult to reveal and may depend on the (di)nitro compound.

Triplet quenching by oxygen and amines compete (Scheme 1), but under conditions of triplet quenching via 3 ([TEA] >1 mM), oxygen strongly quenches the longer lived dinitroarene radicals (16 in Scheme 4). This should be ascribed to formation of $O_2^{\bullet -}$ by quenching of the radical anion and the conjugate acid.[35] Note that for equilibrium 17 in aqueous solution the pK_a = 4.7.

SCHEME 4



$$Et_2N-{}^{\bullet}CHMe + O_2 \rightarrow Et_2NCH{=}CH_2 + O_2^{\bullet -} + H^+ \quad (18)$$

The α-aminoethyl radical should react with oxygen. Reaction 18 is only one of several quenching possibilities.

Charge Separation in the Presence of Amines. In the presence of TEA (>1 mM) a conductivity increase (Δκ: positive for increasing signal within the 1 μs range) was observed for all dinitroarenes in argon-saturated neat acetonitrile (Table 4). The time dependences of representative cases are given for 1,4- and 1,5-DNN (Figure 8), DNB, and DNF (Figure 9), 1,3- and 1,8-DNN (Figure 10). The rate constant of the fast increase

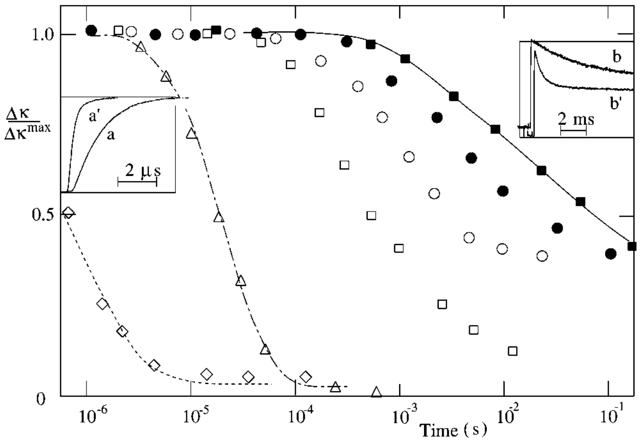


Figure 8. Pulse-induced conductivity signals as a function of time of 1,5-DNN (squares) and 1,4-DNN (other symbols) in the presence of TEA (2 mM, except for Δ: DABCO, 1 mM) in argon-saturated acetonitrile (open, except for ◇: oxygen-saturated) and acetonitrile−water (9:1, full); insets for 1,4-DNN: increase (a: [TEA] = 0.1 mM and a′: 1 mM), decay (b: [TEA] = 1 mM and b′: 30 mM).

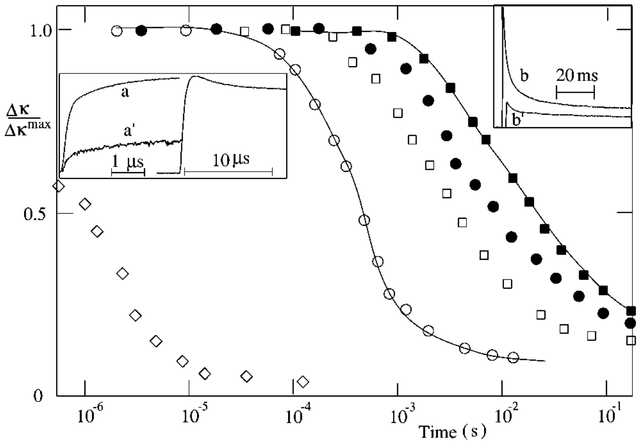


Figure 9. Conductivity signals as a function of time of DNB (circles), DNF (other symbols) in the presence of TEA (2 mM) in argon-saturated acetonitrile (open, except ◇: oxygen-saturated) and acetonitrile−water (9:1, full); insets for DNF: (a) increase and (b) decay; a′ and b′ refer to 1/4 pulse intensity.

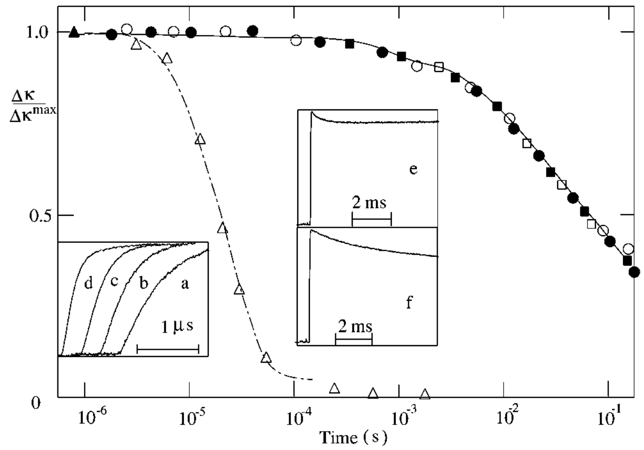
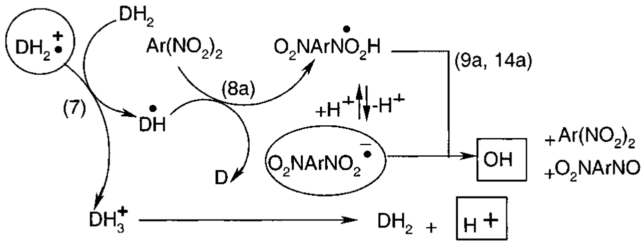


Figure 10. Conductivity signals as a function of time of 1,8-DNN (squares) and 1,3-DNN (other symbols) in the presence of TEA (2 mM, except △: DABCO, 1 mM) in argon-saturated acetonitrile (open) and acetonitrile-water (9:1, full); insets: for 1,3-DNN: (a−d) increase for [TEA] = 0.1, 0.3, 0.6, and 1 mM, respectively, and decay (e, f [H_2O] = 0 and 5 M, respectively).

SCHEME 5



depends linearly on the TEA concentration and the signal approaches a maximum at [TEA] > [TEA]$_{1/2}$ (inset (a) in Figure 10). These findings are in full agreement with reactions 1−3 of photoinduced electron transfer and the back electron transfer 4 for [TEA] < 1 mM. A delayed formation of the conductivity signal was not registered in most cases even at higher TEA concentrations of 3−10 mM or when TEA was replaced by DEA, e.g., for 1,4-DNN. Only for DNF in wet acetonitrile a minor further increase could be detected (Figure 9, inset (a)). The positive signal in aqueous acetonitrile (5 M water) reaches a plateau and increases again in the 0.1−1 μs range only very slightly (inset a′ in Figure 9).

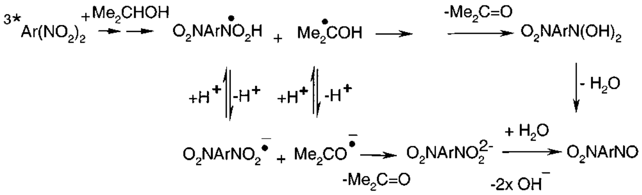
The nature of the second longer lived radical in wet acetonitrile (anion or neutral radical) can now be specified as H-adduct radical (Scheme 5) since H-atom transfer 8a should not result in a conductivity change. This holds for all compounds except for 1,4-DNN where a modification is proposed (see below). The conductivity signal in argon-saturated neat acetonitrile in the presence of TEA (>1 mM) decays by second-order kinetics, at least as major part. After subtracting of a (minor) remaining part, it was shown that the half-lives (in the 3−30 ms range) increase by a factor of ca. 5−8 when the laser intensity was 10-fold decreased. This also holds in the presence of 5 M water, where, however, the half-lives are typically one or 2 orders of magnitude longer (Table 4). This is consistent with termination process 9a and OH$^-$ release via eq 14. Exceptions were found for 1,3-DNN (Figure 10) and 1,8-DNN, where $t_{1/2}$ is longer than 30 ms and addition of water has virtually no effect. For 1,4-DNN the TEA concentration has also some influence on the decay (insets b and b′ in Figure 8).

The photoinduced electron transfer from DABCO (1−10 mM) to the triplet state of the dinitroarenes occurs, like in the case of TEA at low concentrations, where the back reaction 4 operates (triangles in Figures 8 and 10), with $t_{1/2} = 10-30$ μs (Table 4). For all amines the signal decreases in the 10^{-5}−0.1 s range to a value which is still larger than the initial one and levels off within seconds, i.e., finally, released OH$^-$ and H$^+$ result in neutralization (Scheme 5). If a proton would be released prior to OH$^-$ elimination, a strong negative signal is expected in alkaline solution due to the removal of bulk OH$^-$. On the other hand, OH$^-$ elimination without rapid neutralization would increase the signal markedly due to its larger equivalent conductivity of OH$^-$ ($\Lambda = 180$ cm^2 Ω^{1-} mol^{-1}) with respect to that of an organic anion ($\Lambda \leq 50$ cm^2 Ω^{-1} mol^{-1}). Positive and comparable signals (but partly differing half-lives) were obtained when TEA was replaced by DEA. Under normalized conditions ($A_{354} = 2$, [TEA] = 10 mM, constant intensity) the relative amplitude at 10 μs, $\Delta\kappa/\Delta\kappa^{max}$, is largest for DNF in dry and wet acetonitrile and comparable or smaller (up to 40%) in the other cases (Table 4).

The presence of oxygen has no marked effect on the initial conductivity signal under conditions of sufficient triplet quenching ([TEA] > 1 mM), but the decay in the 0.1−10 ms range is significantly decreased (diamonds in Figures 8 and 9). The quenching should be ascribed to reactions 16 and 18 of oxygen with the relevant radicals. Nevertheless, a small component remains in the 0.1−10 ms range in oxygen-saturated acetonitrile, this being significantly higher in the presence of 5 M water. It should be mentioned that comparable time-resolved conductivity changes were reported for nitrostilbenes and nitronaphthalenes.[20,21]

Photoreduction of Dinitroarenes in the Presence of 2-Propanol. The major photoproduct of 1,5-DNN in alkaline methanol is 1-amino-5-nitronaphthalene.[17] Concerning the photoreduction of nitronaphthalenes in the presence of alcohols, only a few time-resolved UV−vis spectroscopic measurements have been reported. It is now proven that the triplet state of the dinitroarenes in 2-propanol is formed upon excitation by 354 nm pulses. The rate constant for 1,5-DNN triplet quenching by 2-propanol in the neat alcohol or a mixture with water (10:1, pH < 9) is estimated to be smaller than 1×10^4 M^{-1} s^{-1}. For DNF in argon-saturated acetonitrile and 5 M water at pH 12−13, where the k_q value is larger (3×10^5 M^{-1} s^{-1}) and k_{obs} (measured at 480 nm) was shown to depend linearly on [2-propanol]. For other cases even at pH 12−13 k_q is smaller (Table 2). Although triplet quenching is generally inefficient, the radical anion of dinitroarenes can be detected, an example for the 1,4-DNN/2-propanol system is shown in Figure 7b.

SCHEME 6



The eventual consequences of secondary reactions in the presence of 2-propanol are illustrated in Scheme 6. The proposed reaction involves electron transfer to the ^{3*}O$_2$NArNO$_2$ state, followed by proton transfer. The increasing triplet quenching by 2-propanol at pH >12 is ascribed to the better reactivity of the radical toward the dinitroarenes and a lower termination reactivity of the Me$_2$CO$^{\bullet -}$ radicals themselves.[37]

Photoconversion upon Continuous Irradiation. The pattern of the photoproducts, which were observed by absorption above 280 nm followed by HPLC, is complex and not a major part of this work. Nevertheless, we aimed at revealing the primary photoproducts of the dinitroarenes, thereby avoiding further irradiation (which is not possible for all cases, e.g., for DNB with $\lambda_{irr} = 366$ nm). Continuous UV irradiation of 1- or 2-nitronaphthalene and 1-methoxy-4-nitronaphthalene in argon-saturated acetonitrile and TEA (1−10 mM) leads to decomposition and no absorption in the visible range.[21] On the other hand, irradiation at 366 nm of 1,5-, 2,3-DNN, DNB, and DNF in the presence of TEA yields new bands with absorption maxima at 360−440 nm (Table 5). With DEA the spectra are the same or only slightly different. Moreover, for 1,3-DNN (Figure 3a) or 1,8-DNN the new absorption with TEA (0.03 M) extends up to 600 nm with maximum at 550 nm. These products were not formed in the presence of water, albeit an intermediate appears with a similar spectrum (Figure 3b).

The quantum yields of educt decomposition (Φ_d) in the presence of TEA are compiled in Table 5. A maximum value in most cases was achieved under careful exclusion of oxygen and when [TEA] is larger than 1 mM. The largest coloration effect was found for the photoreduction of 1,4-DNN by TEA in argon-saturated acetonitrile. A strong band with absorption maximum at 450 nm (Figure 6a) overlaps with educt decomposition using HPLC.

TABLE 5: Absorption Properties and Quantum Yields of Decomposition of Dinitroarenes[a]

compound	[TEA] (mM)	λ_i[b] (nm)	λ_{prod} (nm)	Φ_d[c]
1,3-DNN	10	370	550	0.09
1,4-DNN	1		450	0.16
	10			(0.03)[d]
	10[e]		460	0.02
	10[f]		450	0.09
1,5-DNN	1	308,365	385,440sh	0.1 (<0.003)
1,8-DNN	1	305,365	550	0.08
2,3-DNN	10	350,380		0.06
DNB	10	280,330	345	0.1
DNF	1	348	370,430sh	0.14

[a] In argon-saturated acetonitrile, $\lambda_{irr} = 366$ nm. [b] Isosbestic points. [c] Obtained by absorption and/or HPLC. [d] In parentheses: air-saturated acetonitrile solution. [e] Plus water (5 M). [f] Using DEA.

For the TEA (0.01 M) dinitroarene systems in aqueous acetonitrile, nitroso compounds are proposed as major photoproduct, e.g., 1-nitroso-5-nitronaphthalene for 1,5-DNN (Figure 2b). This is consistent with the photoreduction of 1,5-DNN in methanol−water (95:5) in the presence of NaOH (0.03 M).[17] Nitrosoarenes are postulated as labile intermediates in the photoreduction of nitrobenzenes by alcohols, but thermal reactions lead to phenylhydroxylamine (ArNHOH) and further products, such as azoxybenzenes.[11,12,22,23] An intermediate prior to phenylhydroxylamine could be the nitrophenylnitroxide radical (O$_2$NArNOH$^\bullet$) which may be present in basic solution as nitronitrosobenzene radical anion (O$_2$NArNO$^{\bullet -}$).[36] In the photoreduction of nitrobenzylidene malonic derivatives by TEA the nitroso compounds are postulated, but the stable photoproducts are due to secondary excitation.[24] Upon UV irradiation of 1-methoxy-4-nitronaphthalene in argon-saturated acetonitrile in the presence of TEA, formation of the naphthylhydroxylamine may become important.[21] Once a considerable amount of nitrosonaphthalene is formed, a further reaction competing with 8a and yielding the naphthylhydroxylamine via the naphthylnitroxide radical has to be considered.

$$\mathrm{Et_2N{-}^{\bullet}CHMe + O_2NArNO \rightarrow Et_2NCH{=}CH_2 + O_2NArNOH^{\bullet}} \qquad (19)$$

$$\mathrm{2O_2NArNOH^{\bullet} \rightarrow O_2NArNO + O_2NArNHOH} \qquad (20)$$

With continuous UV irradiation at 366 nm, in contrast to the pulsed excitation, where the conversion is low and reactions 19 and 20 may be neglected, formation of the naphthylhydroxylamines cannot be ignored. This is supported by the finding that addition of oxygen to the photoproduct of 1-methoxy-4-nitronaphthalene leads to a spectrum with red-shifted maximum.[21] Since the oxygen effect is not reversible,[8] it is tentatively attributed to reaction 21.

$$\mathrm{O_2NArNHOH + {}^{1}/{}_{2}O_2 \rightarrow O_2NArNO + H_2O} \qquad (21)$$

An example for a different spectrum on addition of oxygen to the photoproduct of DNB is shown in Figure 4a′ (dot−dashed curve), where the nitroso compound as product in the absence of oxygen has to be excluded. Nevertheless, significant spectral changes on addition of oxygen after photoconversion were not observed for most of the other dinitroarenes. The previously studied electron-deficient azaarenes reveal a different behavior; they are photochemically converted into dihydro derivatives and react reversibly back upon addition of oxygen.[8] Also for phenazine/TEA the labile photoproduct is assigned to 5,10-dihydrophenazine.[9]

Once arylhydroxylamines are present, they could react with nitrosoarenes into azoxyarenes.

$$O_2NArNHOH + O_2NArNO \rightarrow O_2NAr\text{-}N(O){=}NArNO_2 + H_2O \quad (22)$$

Note that several reports on photoproducts[11−17,22−24] may refer to secondary excitation or the involvement of oxygen which was aimed to be avoided in this work. In the cases of DNB and DNF, where the product was irradiated at 366 nm already at low conversion, pulsed excitation at 308 nm with little product irradiation gave comparable results (not shown).

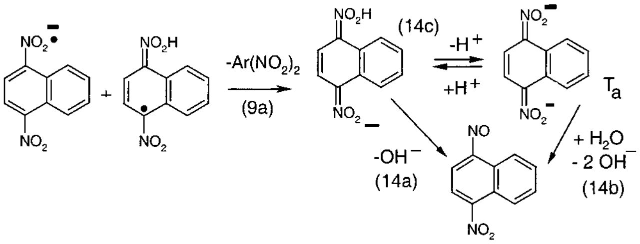
Mechanistic Consequences. For dinitroarenes in air-saturated acetonitrile and rather high donor concentrations of [TEA] >1 mM, reaction 3 can compete successfully with triplet quenching by oxygen. The important reactions, however, are formation of the rather unreactive $O_2^{\bullet-}$ by quenching of the $O_2NArNO_2^{\bullet-}$ and $Et_2N-{}^{\bullet}CHMe$ radicals (Scheme 4). Therefore, Φ_d is very low for all dinitroarenes, when oxygen is present, except for 1,4-DNN. This is in agreement with much shorter half-lives in the decay kinetics of the optical and conductometric signals in the presence of oxygen.

For the photoreduction of aromatic compounds by aliphatic amines in the absence of oxygen, a common pattern is proposed. The transient absorption spectra and conductivity signals in the presence of DABCO are in agreement with electron transfer to the lowest triplet state and back electron transfer without any permanent changes. The photoinduced electron transfer from TEA or DEA to nitroarenes is efficient in all cases examined, but the net conversion into stable products is generally rather low. The proposed key step at higher [TEA] is forward reaction 7 of $Et_3N^{\bullet+}$ with a second TEA molecule to form Et_3NH^+ and the α-aminoethyl radical, which gives rise to a variety of substrate-dependent disproportionation reactions; the proposed sequence is 9a and 14a. An H-atom transfer via reaction 13 is excluded because of a different reaction of the precursor (see above). The relatively long conservation of the two charges under conditions of pulsed excitation, which is longest in acetonitrile−water (9:1), i.e., much longer than the half-life of most absorbing intermediates, appears to be due to released OH^- (from the nitroarene) and H^+ (from the amine) and their neutralization (Scheme 5).

Mononitronaphthalenes. The spectra and kinetics of 1-methoxy-4-nitronaphthalene and 1- or 2-nitronaphthalene in the presence of TEA reveal also two-step radical formation and slow radical disproportionation in the 0.1−1 ms range.[21] The conductivity signal remains positive for 1−10 ms, indicating even slower release of OH^- and neutralization. The photoproducts should be nitrosonaphthalenes, but for continuous irradiation with substantial conversion the involvement of the naphthylhydroxylamine has been considered.[21] Concerning the structural changes, mono- and dinitronaphthalenes as well as the two other dinitroarenes behave similarly. The primary photoproducts should be of the type ArNO, and further products may result from thermal steps.

Dinitronaphthalenes. The overall reaction of dinitronaphthalenes with TEA is proposed to lead partly to nitroso compounds as result of the two steps of radical formation and their termination reactions. A rough classification indicates that the properties of 1,5- and 2,3-DNN are similar and differ from 1,4-DNN on one hand (see below) and 1,3- and 1,8-DNN on the other. For 1,5-DNN (Figure 2b) and 2,3-DNN the longer lived radicals (anion and the conjugate acid or two radical anions in neat and wet acetonitrile, respectively) and their conversion into the nitroso compounds (yellow photoproducts) were observed. The transient absorption spectra of the 1,3- and 1,8-DNN/TEA systems in acetonitrile after triplet decay contain essentially the radical anion/conjugate acid pair. The 550 nm intermediate, which appears by radical termination in the ms range (Figure 3), is tentatively assigned to the dianion.

SCHEME 7



1,4-Dinitronaphthalene. A special case was found for 1,4-DNN insofar that the major product is strongly yellow (Figure 6a). Photolysis of 1,4-DNN in neat 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 transient (T_a) with a maximum at 440 nm. T_a is subsequently converted into one with similar spectrum (Figure 6b). The latter species, owing to its quasi constant amplitude (extending to >1 s), is assigned to 1-nitroso-4-nitronaphthalene. T_a, the precursor of the nitrosoarene, is assigned to the dianion of 1,4-DNN with a nonradical valence structure (Scheme 7), formed via reaction 9a or 11.

In wet acetonitrile, apart from a smaller k_q value for triplet quenching (see above), a much faster termination of the radicals and a markedly higher yield of intermediate T_a were observed in the presence of TEA (Figure 7a) and DEA. The conductivity signal remains positive for 1−10 ms range (Figure 8), indicating slower release of OH^- prior to neutralization in the presence than in the absence of water. Moreover, the permanent component, i.e., the absorption above 380 nm, is consistent with the steady-state spectra (Figures 6a and 7a). Even for high TEA concentrations (>0.1 M), when precursors could only partly be observed (on a 100 ns time scale), the spectra of the two observable components are essentially the same as at lower concentrations. The higher yield of T_a and the faster formation in the presence of water could be due to equilibrium 14c. For 1,4-DNN and TEA(1−10 mM) in air-saturated acetonitrile, where colored products with maximum at 440 nm are formed, Φ_d is ca. 3 times smaller than in the absence of oxygen. To account for the observation of the radical (which is partly present in air-saturated acetonitrile) and the possibility to generate a yellow product of 1,4-DNN even in the presence of air (Table 5), it appears that a back reaction may be involved in step 16. It is interesting to note that T_a type intermediates were not observed for the other dinitronaphthalenes.

4,4′-Dinitrobiphenyl and 2,7-Dinitrofluorenone. The spectra and kinetics of UV-excited DNB (Figure 4) and DNF (Figure 5) with TEA likewise 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. An aci-anion is spectroscopically difficult to separate. The conductivity signals of DNB and DNF show a specific effect of water (Figure 9), due to the slower release of OH^- in the presence of water. The major photoproducts are proposed to be the nitrosoarenes.

Conclusions

The photoreduction of 4,4′-dinitrobiphenyl and 2,7-dinitrofluorenone and several dinitronaphthalenes in dry and wet acetonitrile by TEA (even in relatively low concentration) involves electron transfer to the lowest triplet state, formation of the radical anion and, via H-atom transfer from the α-aminoalkyl radical to the substrate, formation of a second nitroarene radical. If oxygen is carefully excluded, these two radicals subsequently undergo a slow termination reaction yielding the nitroso compounds in most cases as labile products and finally essentially naphthylhydroxylamines. The specificity of the substitution pattern indicates three different major pathways via termination. For 1,4-dinitronaphthalene the corresponding aci-dianion is observable as longer lived intermediate.

Acknowledgment. The author thanks Professor Wolfgang Lubitz for his support, Professor Dietrich Döpp for discussions, and Mr. Leslie J. Currell and Horst Selbach for technical assistance.

References and Notes

(1) Cohen, S. G.; Parola, A.; Parsons, G. H., Jr. *Chem. Rev.* **1973**, *73*, 141.

(2) Chanon, M.; Eberson, L. In *Photoinduced Electron Transfer*; Fox, M. A., Ed.; Chanon, M. part A, Elsevier: Amsterdam, 1988; p 409. Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 1048. Hamanoue, K.; Nakayama, T.; Ikenaga, K.; Ibuki, K. *J. Phys. Chem.* **1992**, *96*, 10297. Aspari, J. P.; Ghoneim, N.; Haselbach, E.; v. Raumer, M.; Suppan, P.; Vauthey, E. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1689. Gonzales-Blanco, R.; Bourdelande, J. L.; Marquet, J. *J. Org. Chem.* **1997**, *62*, 6903.

(3) Goez, M.; Zubarev. V.; Eckert, G. *J. Am. Chem. Soc.* **1998**, *120*, 5347.

(4) Scaiano, J. C. *J. Phys. Chem.* **1981**, *85*, 2851.

(5) Marquet, J.; Moreno-Maòas, M.; Vallribera, A.; Virgili, A.; Bertran, J.; Gonzales-Lafont, A.; Lluch, J. M.*Tetrahedron* **1987**, *43*, 351.

(6) Goez, M.; Sartorius, I. *J. Am. Chem. Soc.* **1993**, *113*, 11123.

(7) Amada, I.; Yamaji, M.; Tsunoda, S.; Shizuka, H. J. *Photochem. Photobiol., A: Chem*. **1996**, *95*, 27.

(8) Görner, H.; Döpp, D.; Dittmann, A. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1723.

(9) Davis, G. A.; Gresser, J. D.; Carapellucci, P. A. *J. Am. Chem. Soc.* **1971**, *93*, 2179.

(10) Demeter, A.; Biczók, L.; Bérces, T.; Wintgens, V.; Valat, P.; Kossanyi, J. *J. Phys. Chem.* **1993**, *97*, 3217.

(11) Barltrop, J. A.; Bunce, N. J. *J. Chem. Soc. (C)* **1968**, 1467.

(12) Hurley, R.; Testa, A. C. *J. Am. Chem. Soc.* **1968**, *90*, 1949. Trotter, W.; Testa, A. C. *J. Am. Chem. Soc.* **1968**, *90*, 7044. Wubbels, G. G.; Jordan, J. W.; Mills, N. S. *J. Am. Chem. Soc.* **1973**, *95*, 1281. Levy, N.; Cohen, M. D. *J. Chem. Soc., Perkin Trans. 2* **1979**, 553. Döpp, D.; Müller, D. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 297. Wan, P.; Yates, K. *J. Chem. Soc. Chem. Commun.* **1981**, 1023. Fukuzumi, S.; Tokuda, Y. *Chem. Soc. Jpn.* **1992**, *65*, 831. Paradisi, C.; Scorrano, G. *Acc. Chem. Res.* **1999**, *32*, 958.

(13) Letsinger, R. L.; Hautala, R. R.*Tetrahedron Lett.* **1969**, *48*, 4205.

(14) Lammers, J. G.; Cornelisse, J. *Isr. J. Chem.* **1977**, *16*, 299. Havinga, E.; Cornelisse, J. *Pure Appl. Chem.* **1976**, *47*, 1. Lin, J. Ph.D. Thesis, University of Duisburg, 1994.

(15) Obi, K.; Bottenheim, J. W.; Tanaka, I. *Bull Chem. Soc. Jpn*. **1973**, *46*, 1060.

(16) Frolov, A. N.; El'tsov, V. A.; Sosonkin, I. M.; Kuznetsova, N. A. *Z. Org. Khim.* **1973**, *9*, 973, Engl. transl. in *Z. Org. Chem.* **1973**, *9*, 999.

(17) Frolov, A. N.; Kuznetsova, N. A.; El'tsov, V. A.; Rtishchev, N. I. *Z. Org. Khim.* **1973**, *9*, 963, Engl. transl. in *Z. Org. Chem.* **1973**, *9*, 988.

(18) Bunce, N. J.; Cater, S. R.; Scaiano, J. C.; Johnston, L. J. *J. Org. Chem.* **1987**, *52*, 4214.

(19) Martins, L. J. A.; Mendes M.; Fernandes, M. M.; Kemp, T. J.; Formosinho, S. J.; Branco, J. S. *J. Chem. Soc. Faraday Trans.* **1991**, *87*, 3617.

(20) Görner, H. *Phys. Chem. Chem. Phys.* **2002**, *4*, 482.

(21) Görner, H.; Döpp, D. *J. Chem. Soc., Perkin Trans. 2* **2002**, 120.

(22) Döpp, D. *Top. Curr. Chem.* **1975**, *55*, 51. Ho, T.-I.; Chow, Y. L. In *The Chemistry of Amino, Nitroso, Nitro and Related Groups;* Patai, S., Ed.; Wiley: Chichester, 1996; p 747.

(23) Döpp, D. In *Photochemical Reactivity of the Nitro Group, CRC Handbook of Photochemistry and Photobiology*; Horspool, W. M., Song, P.-S., Eds.; CRC Press: Boca Raton, 1995; p 1019 and references cited therein.

(24) Abd El Latif, F. M.; Barsy, M. A.; Rady, E. A.; Hassan, M. E.; El Maghraby, M. A. *J. Photochem. Photobiol., A: Chem.* **1999**, *121*, 111.

(25) Lund, H. In: *Organic Electrochemistry*; Lund, H., Baizer, M. M., Eds.; Dekker: New York, 1991; p 401. Zuman, P.; Fijalek, Z. *J. Electroanal. Chem*. **1990**, *296*, 583.

(26) Capellos, C.; Suryanarayanan, K. *Int. J. Chem. Kinet*. **1976**, *8*, 529 and 541; ibid. **1977**, *9*, 399. Fournier, T.; Tavender, S. M.; Parker, A. W.; Scholes, G. D.; Phillips, D. *J. Phys. Chem. A* **1997**, *101*, 5320.

(27) McCray, J. A.; Trentham, D. R. *Annu. Rev. Biophys. Biophys. Chem.* **1989**, *18*, 239. DiMagna, T. J.; Stowell, M. H. B.; Chan, S. I. *J. Phys. Chem*. **1995**, *99*, 13038. Park, C.-H.; Givens, R. S. *J. Am. Chem. Soc.* **1997**, *119*, 2453.

(28) Görner, G.; Kuhn, H. J. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2671. Görner, G.; Warzecha, K.-D.; Demuth, M. *J. Phys. Chem. A* **1997**, *101*, 9964.

(29) Heller, H. G.; Langan, J. R. *J. Chem. Soc, Perkin Trans. 1* **1981**, 341.

(30) Görner, H. *Chem. Phys. Lett.* **1998**, *282*, 381.

(31) Peters, K. S.; Freilich, S. C.; Schaeffer, C. G. *J. Am. Chem. Soc.* **1987**, *102*, 5701.

(32) Asmus, K.-D.; Wigger, A.; Henglein, A. *Ber. Bunsen-Ges. Phys. Chem*. **1966**, *70*, 862.

(33) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259; Rehm, D.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 834.

(34) Nelsen, S. F.; Hinz, P. J. *J. Am. Chem. Soc.* **1972**, *94*, 7114.

(35) Anderson, R. F.; Denny, W. A.; Li, W.; Packer, J. E.; Tercel, M.; Wilson, W. R. *J. Phys. Chem. A* **1997**, *101*, 9704.

(36) Ogata, Y.; Tsuchida, M.; Tagaki, Y. *J. Am. Chem. Soc.* **1957**, *79*, 3397. Ogata, Y.; Sawaki, Y.; Mibae, J.; Morimoto, T. *J. Am. Chem. Soc.* **1964**, *86*, 3854. Russell, G. A.; Knaupp, G. *J. Am. Chem. Soc.* **1967**, *89*, 3821.

(37) Görner, H. *J. Photochem. Photobiol. A: Chem.* **1995**, *89*, 147.