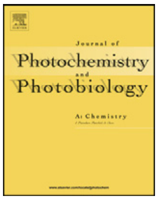
Journal of Photochemistry and Photobiology A: Chemistry 222 (2011) 34–39

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Photoreactions of *n*-alkyl-3-nitrophenyl ethers with aromatic amines in SDS micelles: A laser flash photolysis study

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ARTICLE INFO

Article history:
Received 1 September 2010
Received in revised form 15 April 2011
Accepted 24 April 2011
Available online 8 May 2011

Keywords:
Photosubstitution reactions
Amines
Meisenheimer complex
Triplet state
n-Alkyl 3-nitrophenyl ether

ABSTRACT

The quenching of the triplet state of three *n*-alkyl 3-nitrophenyl ethers: 3-nitroanisol (3-NA), *n*-butyl 3-nitrophenyl ether (3-NB) and *n*-decyl 3-nitrophenyl ether (3-ND) by four aniline derivatives: aniline (AN), *N*,*N*-dimethylaniline (DMA), 2,4,6-trimethylaniline (TMA), and 4-tetradecylaniline (TDA), was investigated in aqueous micellar SDS solutions by laser flash photolysis. The transient absorption spectra for 3-NA and 3-NB reveal the formation of long-lived intermediate species in the presence of all four quenchers, while for 3-ND no amine-induced intermediates are observed. Comparison of the transient absorption spectra of the probe 3-NA in the presence of DMA in aqueous and micellar solutions shows that the intermediate species are favored by the SDS micelles. With DMA and TMA as quenchers the intermediates are suggested to be the ion radicals generated by single electron transfer from the amine to the probe in the triplet excited state. For the quenchers AN and TDA, the intermediates may be σ-complexes. The relative quenching efficiencies generally decrease as the affinity of the quencher for the micellar phase (AN < DMA < TMA < TDA) increases and the mobility of the excited probe (3-NA > 2-NB) decreases.

1. Introduction

Nitrophenyl ethers are potential biological photoreagents [1–3]. In recent years, the photoreactions of nitrophenyl ethers in the presence of amines have received special attention since several successful examples of their use as biochemical photoprobes were reported [1]. The mechanism of nucleophilic aromatic photosubstitution reactions (S_N2Ar^*) of nitroaromatics assumes a bimolecular attack of the nucleophile on the lowest triplet excited state, producing an intermediate sigma or Meisenheimer complex [4–7]. The latter may decompose to substitution products when the lowest triplet state of the nitroaromatic has π,π^* character and the rate of nucleophilic attack is higher than that of the competitive electron transfer from the potential nucleophile to the excited nitroaromatic compound [8,9].

The photoreactions of nitrophenyl ethers in the presence of amines show a complex mechanistic variety [10]. In homogeneous media, several studies of the photosubstitution reactions of nitrophenyl ethers in the presence of amines have emphasized the importance of the nucleophile on the orientation of the reaction [11–14]. Cantos et al. [11] showed that *meta*-regioselectivity is preferred for amines with high ionization potentials and *para*-selectivity for amines with low ionization potentials. When those reactions were investigated in the presence of hydroxide ions, only *meta* orientation relative to the nitro group was reported [7,14,15]. However, there is still a lack of information concerning the effects of tertiary, secondary and primary amines on the photosubstitution reactions of nitrophenyl ethers.

Several studies of the photosubstitution reactions of nitrophenyl ethers in micellar media have been reported [5,8,16–18]. Tedesco et al. [8] evaluated the effect of sodium dodecyl sulfate (SDS) micelles on the alkaline photohydrolysis of *n*-alkyl 3-nitrophenyl ethers and showed that the affinity of the triplet state of 3-nitrophenyl ethers for SDS micelles is about an order of magnitude smaller than that of the ground state. Bonilha et al. [16] investigated the alkaline photohydrolysis of the triplet state of 3,5-dinitroanisol (3,5-DNA) in cationic tetradecyl trimethylammonium chloride (TTAC) micelles and observed a decrease of the photoproduct quantum yield in TTAC micelles.

The aim of this work is to contribute to an understanding of the photoreactions involving nitrophenyl ethers and amines in an ionic micellar medium. Thus, the dynamics of the triplet state of three *n*-alkyl 3-nitrophenyl ethers: 3-nitroanisol (3-NA), *n*-butyl 3-nitrophenyl ether (3-NB) and *n*-decyl 3-nitrophenyl ether (3-ND) (Scheme 1) were investigated in SDS micelles by laser flash

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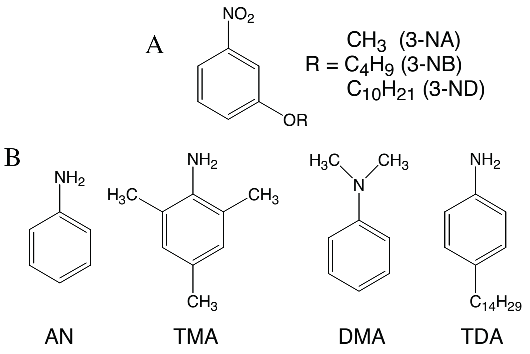
doi:10.1016/j.jphotochem.2011.04.023



Scheme 1. Structures of the *n*-alkyl 3-nitrophenyl ether probes (A), and aniline quenchers (B).

photolysis. The triplet state of the probes was quenched with four aniline derivatives: aniline (AN), *N*,*N*-dimethylaniline (DMA), 2,4,6-trimethylaniline (TMA), and 4-tetradecylaniline (TDA) (Scheme 1). The transient absorption spectra reveal the formation of long-lived intermediates in a manner dependent on the structures of the probe and the aniline derivative and their ability to exit from the micelle.

2. Experimental

2.1. Materials

Aniline, AN (98%, Synth), *N*,*N*-dimethylaniline, DMA (98%, Riedel-de Haën), and 2,4,6-trimethylaniline, TMA (98%, Aldrich) were refluxed over metallic Zn (Merck) for one hour and distilled under reduced pressure. The distilled aniline was stored in an amber flask under nitrogen atmosphere. 4-Tetradecylaniline, TDA (97%, Aldrich) was purified by sublimation. SDS (99.5%, Polysciences), and pyrene (99%, Aldrich) were purified by several recrystallizations from ethanol, adding activated charcoal (PA, Acros Organics) in the case of pyrene. The purity of SDS was checked by surface tension measurements of the cmc employing the Wilhelmy plate method. 3-Nitroanisole (3-NA), *n*-butyl 3-nitrophenyl ether (3-NB) and *n*-decyl 3-nitrophenyl ether (3-ND) were prepared and purified by literature procedures [5,18]. Methanol, ethanol, acetone (spectroscopic grade, Aldrich), hydrochloric acid, sodium tetraborate decahydrate (PA, Merck) and benzene (PA, Synth) were used as received. All solutions were prepared using ultrapure water from a Millipore system.

Borate buffer (pH 9.0) was prepared from 50 mL of 0.025 mol/L sodium tetraborate decahydrate (PA, Merck), and 4.2 mL of 0.1 mol/L hydrochloric acid (PA, Merck). The pH was adjusted using an Analion PM-600 pHmeter with a Micronal glass combination electrode.

2.2. Methods

2.2.1. Laser flash photolysis measurements

Aqueous solutions of the probes (1.0×10^{-4} mol/L 3-NA, 3-NB or 3-ND) in the presence and absence of 40 mmol/L of SDS were prepared. The ground state UV–Vis absorbance at 355 nm, measured on a Hitachi U-3000 spectrometer, was kept in the range of 0.20–0.25. Aliquots of a 0.1 mol/L stock solution of the quenchers (AN, DMA, TMA, and TDA) in methanol were added to the probe solutions with the aid of a Hamilton microsyringe. In some experiments, the solutions of the quenchers DMA and TDA were prepared directly in pH 9.0 borate buffer solution.

The transient spectra and kinetics of the triplet state decays of the probes (at 410 nm) in the absence and presence of quenchers were determined with an Edinburgh Analytical Instruments LP900S1 laser flash photolysis system, exciting with the third harmonic (355 nm) of a Continuum SURELITE I-10 Nd-YAG laser. The transient spectra were taken from 260 to 650 nm with a 10 nm step and an average of three laser shots at each wavelength. For each of the three probes, at least two transient spectra were registered in the absence and presence of quenchers. All solutions were air equilibrated and the temperature of all experiments was 24 °C.

Table 1
Rate constants for the intramicellar quenching (k_q) of pyrene (2.0 μmol/L) fluorescence by AN, DMA, and TDA in SDS micelles (20–80 mmol/L) and for micellar exit of the quencher (k_-) in borate buffer (pH 9.0), at 25.0 ± 0.2 °C.

	k_q ($s^{-1} \times 10^{-7}$)	k_- (s^{-1})
(0.44–1.32) mmol/L AN	2.6 ± 0.2	$(13 \pm 1) \times 10^6$
(0.08–0.24) mmol/L DMA	5.8 ± 0.8	$(0.10 \pm 3) \times 10^6$
(0.28–0.84) mmol/L TDA	3.0 ± 0.1	$(0.15 \pm 0.2) \times 10^6$

2.2.2. Mobility of the quenchers

Aliquots of a pyrene stock solution (2.0 mmol/L) in methanol were added to SDS solutions (20, 40, and 80 mmol/L) to obtain a final concentration of pyrene of ca. of 2 μmol/L. Quencher stock solutions (0.1 mol/L AN, DMA, or TDA) were prepared in methanol. Pyrene fluorescence decay curves were obtained by the single photon-counting technique, using an Edinburgh Analytical Instruments Model FL-900 Lifetime Spectrometer (H_2 flashlamp gas, $\lambda_{exc.} = 337$ nm; $\lambda_{em.} = 390$ nm). The pyrene fluorescence decay curves in the absence and presence of quenchers were analyzed, respectively, with the standard routine for exponential decay and with the micelle quenching module of the Level 2 analysis software from Edinburgh Analytical Instruments. The Level 2 module fits the Infelta-Tachiya model for micellar quenching kinetics [19–21] to the decay curve.

3. Results and discussion

3.1. Dynamics of the quenchers in anionic micellar solution

The mobility of the aniline derivatives in SDS micelles was evaluated from the rate constants for intramicellar quenching (k_q) of excited pyrene by a single quencher and for quencher exit (k_-) from the micelle. These values were obtained from an analysis of time-resolved fluorescence measurements of the quenching of pyrene fluorescence by the anilines [19–22] in borate buffer, pH 9.0, to avoid the protonation of aniline ($pK_a = 4.63$) [23]. The rate constants for intramicellar quenching (k_q) of pyrene by AN, DMA and TDA (Table 1) are fairly insensitive to the SDS or quencher concentrations. The value of k_q obtained for DMA (5.8×10^7 s^{-1}) was about two-fold higher than that for AN or TDA (2.6×10^7 and 3.0×10^7 s^{-1}, respectively). These values are typical of diffusion-controlled encounter within a SDS micelle. The rate constant for quencher exit from the micelle (k_-) is highest for AN (13×10^6 s^{-1}), followed by DMA and TDA (1×10^6 and 0.15×10^6 s^{-1}, respectively). The most hydrophilic quencher, AN, rapidly partitions between the aqueous and micellar phases, while TDA remains within the micelle for at least several microseconds

3.2. Nanosecond laser flash photolysis studies

Laser flash photolysis experiments were performed to investigate the interaction between the triplet state of the nitrophenyl ethers and the aniline derivatives in aqueous solution in the presence and absence of micellar SDS with excitation at 355 nm. Care was taken to adjust the laser power in order to guarantee mono-exponential decays in the absence and presence of quencher. All transient spectra in the absence of quencher display a maximum at

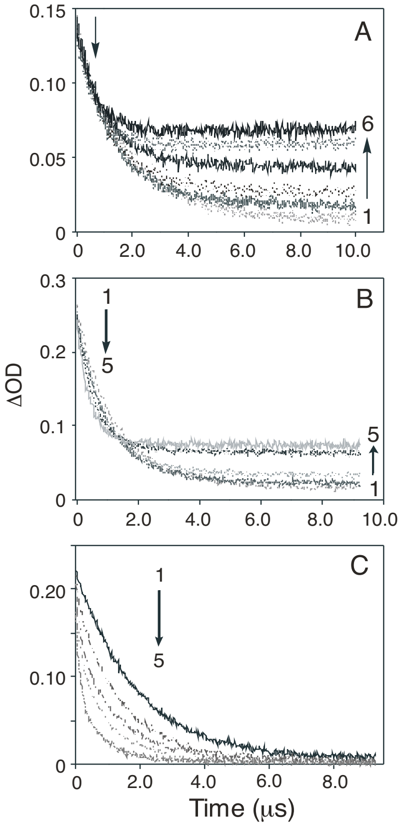


Fig. 1. Decay at 410 nm of 1.0×10^{-4} mol/L: (A) 3-NA, (B) 3-NB, and (C) 3-ND in SDS (40 mmol/L) in the presence of: (A) (1) 0; (2) 0.04; (3) 0.06; (4) 0.12; (5) 0.24, and (6) 0.36 mmol/L AN; (B) (1) 0; (2) 0.06; (3) 0.12; (4) 0.24, and (5) 0.36 mmol/L AN; and: (C) (1) 0; (2) 0.12; (3) 0.24; (4) 0.36, and (5) 0.48 mmol/L TMA.

410 nm due to the probe triplet state [5,8,18,24] that decays monoexponentially without formation of other observable transients. In addition, there is an absorption band between 550 and 660 nm, ascribed to the solvated electron [25]. Fig. 1 shows representative decay curves at 410 nm for the probes 3-NA, 3-NB and 3-ND in the absence and presence of quenchers, in which the formation of a much longer-lived species is evident for 3-NA and 3-NB. In contrast, no long-lived species were observed for 3-ND with any of the quenchers employed in this work (*vide infra*). Stern-Volmer plots of the lifetime ratio of the probes at 410 nm in the absence (τ^0) and presence (τ) of quencher, τ^0/τ, versus total added quencher concentration (Q_T) furnished the apparent Stern-Volmer constants (K'_{SV}) shown in Table 2 (see Fig. S1 of the Supporting Information for a representative plot). These K'_{SV} values merely provide an indication of the relative accessibility of the quencher to the excited triplet state and mirror the relative order of mobility of the aniline in and out of the SDS micelle and, to a large extent, the relative mobility of the excited probe.

Table 2
Apparent Stern-Volmer constants (K'_{SV}) (L/mol) for quenching of the probe triplet state (3-NA, 3-NB, and 3-ND) (1.0×10^{-4} mol/L) in aqueous SDS solution (40 mmol/L) at 24 °C.

Quencher (mmol/L)	K'_{SV} (L/mol)		
	3-NA	3-NB	3-ND
AN	6820 ± 880	4430 ± 390	8460 ± 1500
DMA	6200 ± 200	4300 ± 250	3780 ± 210
TMA	1720 ± 150	2640 ± 180	1500 ± 100
TDA	1580 ± 150	1570 ± 160	670 ± 230

Fig. 2 shows the comparison between the transient absorption spectra of 3-NA in the absence and presence of quenchers (AN, TMA, DMA, and TDA) in micellar SDS (the full spectral range for 3-NA and the transient absorption spectra of 3-NB and 3-ND with these quenchers are provided as Figs. S2–S4, respectively, of the Supporting Information). In the presence of the quenchers, the transient spectra of 3-NA and 3-NB show rather similar behavior that is clearly different from that of the triplet state of the probe at longer times.

With AN as the quencher and 3-NA as the probe (Fig. 2A), the transient spectrum exhibits absorption bands at 360 and 380 nm, respectively, at 0.08 and 0.70 μs after the laser pulse. With DMA as the quencher, Fig. 2B, there is a transient absorption band with a maximum at ca. 380 nm with a shoulder at ca. 450–460 nm at intermediate times that converts to a broad band with a maximum at 450–460 nm at longer times. With TMA as quencher (Fig. 2C), the transient absorption spectrum shows a new absorption band at ca. 380 nm at intermediate times and a broad band with a maximum around 420 nm, similar to that with TDA as quencher, at long times.

Although the triplet state of 3-NB is more hydrophobic than that of 3-NA, the transient spectra of 3-NB also show the formation of very similar longer-lived intermediate species in the presence of quenchers, particularly with AN and DMA (Figs. S3A and S3B of the Supporting Information). In contrast to the other two probes, the transient spectra of the hydrophobic probe 3-ND (Fig. S4 of the Supporting Information) do not show the presence of any long-lived intermediates in the presence of any of the four quenchers (AN, TMA, DMA or TDA).

3.3. *Nature of the transients formed in the presence of the quenchers*

Several studies have been reported of the photoreactions of nitrophenyl ethers in the presence of amines [10–12,14,15,13,26]. Although several different products can be formed, there is a consensus relative to the earliest steps of the reaction in the excited state. Several studies [7,11–15] have shown that encounters between nitro aromatics in the triplet state and amines can lead to electron transfer, generating the geminate radical ion pair consisting of the radical anion of the nitroaromatic compound and the radical cation of the amine. When primary or secondary amines are used as quenchers, single electron transfer can be followed by proton transfer from the α-carbon or the nitrogen of the amine, depending on their relative acidities. For aliphatic tertiary amines, the electron transfer can be followed by proton transfer from the α-carbon. For example, Mir et al. [14] showed that nitroveratrole can give either photoreduction or photosubstitution products, depending on the amine used. With *n*-hexylamine, piperidine and triethylamine in aqueous solutions, only photosubstitution products were observed. The amount of photoreduction products was higher when primary amines like 1-phenylethylamine were employed.

In the present work, longer-lived species are formed upon laser flash photolysis of 3-NA and 3-NB in the presence of all of the anilines. In principle, these intermediate species could be: (a) the radical ions formed by electron transfer from the amine to the excited probe; (b) neutral radicals formed by subsequent proton transfer from the amine radical cation or other proton donor to the radical anion or from the radical cation to an appropriate proton acceptor; or (c) an amine-probe adduct (via radical pair coupling). These potential processes in the aqueous and micellar phases are illustrated in Scheme 2.

In this regard, the simplest quencher appears to be the tertiary amine DMA (Fig. 2B). This transient can be readily identified as the DMA radical cation, given the similarity of the spectrum to that reported [27–29] in aqueous solution (460–470 nm) for this

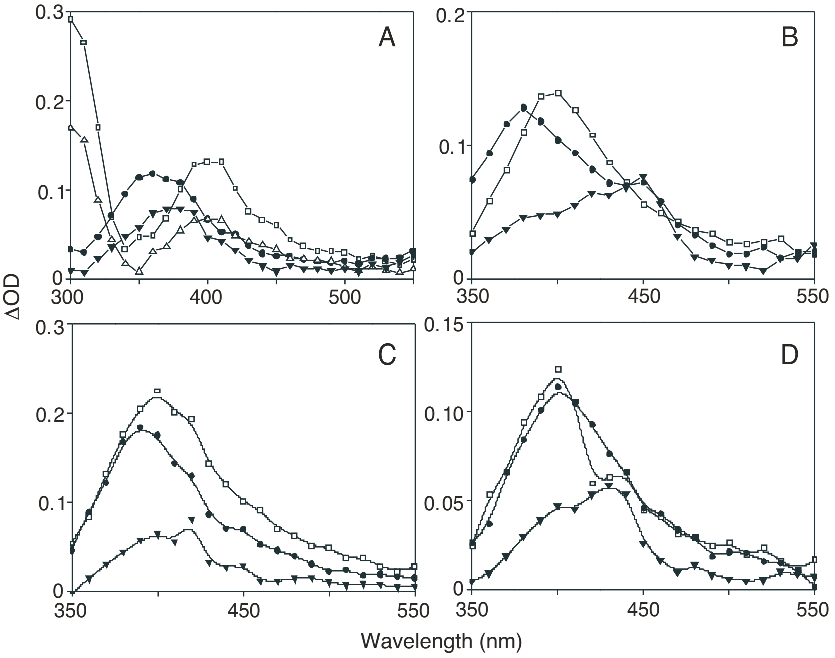
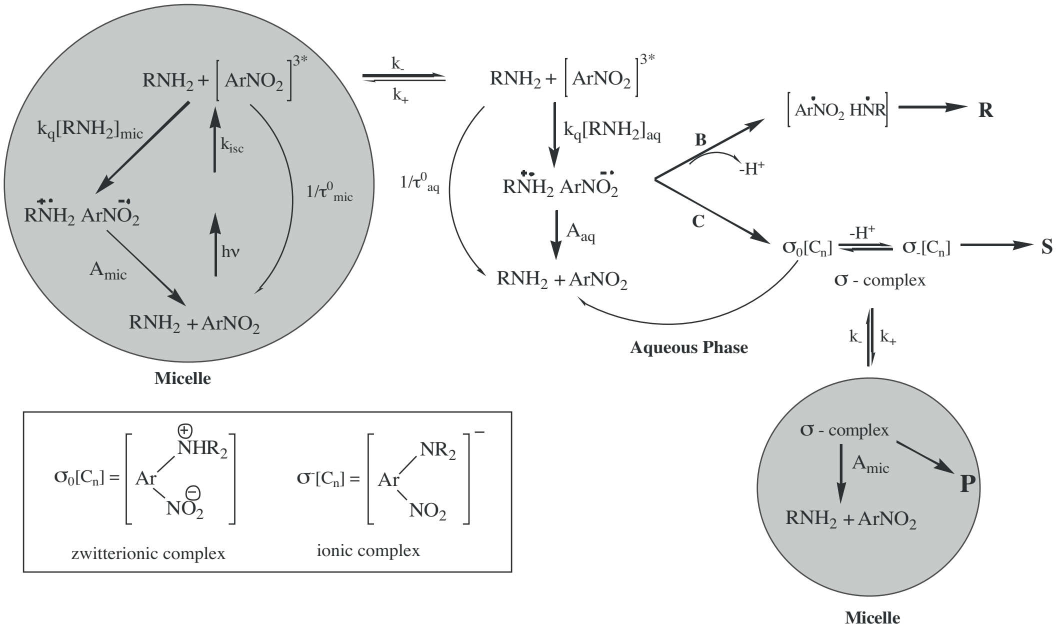


Fig. 2. Transient absorption spectra of 3-NA (1.0×10^{-4} mol/L) in aqueous SDS solution (40 mmol/L) in the absence (open symbols) and presence (closed symbols) of quenchers: (A) □ 0.08, △ 0.94 μs no quencher; ● 0.08, ▼ 0.70 μs with 0.36 mmol/L AN; (B) □ 0.28 μs no quencher; ● 0.28, ▼ 1.4 μs with 0.12 mmol/L DMA; (C) □ 0.08 μs no quencher; ● 0.2, ▼ 2.3 μs with 0.24 mmol/L TMA; and (D) □ 0.04 μs no quencher; ● 0.03, ▼ 1.3 μs with 0.40 mmol/L TDA.

species. This same species is formed with the probes 3-NA and 3-NB and in both the presence and absence of SDS. For 3-NA in the presence of DMA, there is a substantial difference in the time at which this species become dominant in the spectrum in the absence (ca. 3.5 μs) and presence (1.8 μs) of SDS micelles, indicating that it is favored by SDS micelles, presumably due to electrostatic attraction of the radical cation to the anionic micelle. In several cases where they have been determined, the transient spectrum of the nitrophenyl ether triplet state and of the corresponding radical anion are qualitatively similar [7,10,30], which leads us to identify the initial species absorbing at ca. 380 nm in the spectrum of 3-NA in the presence of DMA as the radical anion of 3-NA. Since the



Scheme 2. Proposed reactions of *n*-alkyl-3-nitrophenyl ether probes with aromatic amines in the presence of SDS micelles. In the bulk aqueous phase, the triplet excited state $[ArNO_2]^{3^*}$ can decay non-radiatively back to the ground state, (predominantly by quenching by the molecular oxygen present in the non-degassed solution) or undergo electron transfer quenching by the amine, forming the radical ion pair. Back electron transfer in the pair can regenerate the initial reagents (step A_{aq}), while proton transfer (step B) would lead preferentially to photoreduction products (R) and radical coupling (step C) to intermediate zwitterionic or ionic sigma complexes that could decompose to substitution products, S. The same photochemical events that take place in aqueous solution can occur with the excited triplet state of the probe in the micellar phase. The nitrophenyl ether ground state and triplet state, the sigma complexes, and the amines can potentially partition between the aqueous and micellar pseudophases.

solutions were not degassed, the single electron transfer reaction of the radical anion with dissolved molecular oxygen to give the superoxide anion and regenerate the parent nitrophenyl ether is presumably the major decay pathway of the radical anion [31]. The formation of the radical anion also appears to occur as an initial intermediate in the quenching of 3-NA (Fig. 2C) and 3-NB (Fig. S3C) by TMA. Although the radical cation of TMA can potentially undergo proton transfer reactions with the radical anion of the probe, it is also sterically hindered, which should prevent any subsequent radical coupling. At longer times, the transient spectrum is compatible with that expected for the radical cation of TMA [27].

In contrast, the transient spectra with AN and TDA as quenchers, both of which have a primary amine group, fail to give clear indications of the formation of either the probe radical anion or the quencher radical cation, suggesting formation of radical coupling products or sigma complexes. The clear differences in the spectra may reflect the fact that, with AN, product formation occurs predominantly in the aqueous phase followed by migration to the micelle, while, for the more hydrophobic analog TDA, product formation presumably occurs at or near the micelle surface. Finally, in the case of the hydrophobic probe 3-ND, which is essentially totally incorporated into the micelle, the observation that the probe triplet state is quenched without the formation of any intermediates can be attributed to highly efficient geminate recombination of the radical ion pair produced in the quenching act, leading back to the ground state of the starting materials.

4. Conclusions

Photoreactions between nitrophenyl ethers and amines in SDS micellar medium point to preferential formation of long-lived intermediates in the aqueous phase. Thus, the probes 3-NA (hydrophilic) and 3-NB (moderately hydrophobic) form long-lived intermediates in the presence of all quenchers used, while no amine-induced intermediate species were observed with the micelle-localized probe 3-ND. The relative efficiencies of quenching by the amines depend on the rates of exit of the excited triplet probe and of the amines from the micelle (3-NA > 3-NB and AN > DMA > TMA > TDA). Photoreactions of the probe 3-NA with DMA (tertiary amine) and TMA (sterically hindered primary amine) show a similar behavior, suggesting that the reactive intermediates are the radical ions generated by single electron transfer from the amine to the probe in the triplet excited state. With AN and TDA as quenchers, the intermediates are suggested to be σ-complexes.

Acknowledgements

The authors thank Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP), and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for financial support. I.C.R. acknowledges FAPESP graduate fellowship. F.H.Q is affiliated with the National Institute for Catalysis in Molecular and Nanostructured Systems (INCT-Catalysis) and thanks the CNPq for a senior research fellowship.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2011.04.023.

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