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Solvent and excitation wavelength effects on photocleavage of *N*-(9-anthroyloxy)-9-fluorenylideneamine as a precursor of 9-anthroyloxyl radicals. A mechanistic study

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Abstract

Photocleavage of the N–O bond of *N*-(9-anthroyloxy)-9-fluorenylideneamine takes place efficiently in acetonitrile in the excited singlet state attributed to the fluorenylidene moiety. This made it possible for the first time to directly observe 9-anthroyloxyl radicals. However, the efficiency decreases remarkably in benzene in which the lowest excited singlet state is attributed to the anthroate moiety. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Diaroyl peroxides are useful precursors of aroyloxyl radicals and have been used for studies on various kinds of benzoyloxyl and naphthoyloxyl radicals.[1–10] Anthroyloxyl radicals are attractive species to study, since they have a more expanded conjugated ring system and the carbonyloxyl moiety suffers varying extents of steric hindrance depending on its attached ring position. Among some anthroate esters of aromatic and aliphatic ketoximes employed as precursors, only fluorenone oxime esters have been found to produce the anthroyloxyl radicals efficiently in polar solvents. According to the previously proposed triplet mechanism,[11–13] fluorenone oxime esters should be less reactive than acetophenone and benzophenone oxime esters. Firstly, we have undertaken to clarify the mechanism of photocleavage of the radical precursors in polar solvents and herein describe the results as studied from the viewpoints of solvent and excitation wavelength effects.

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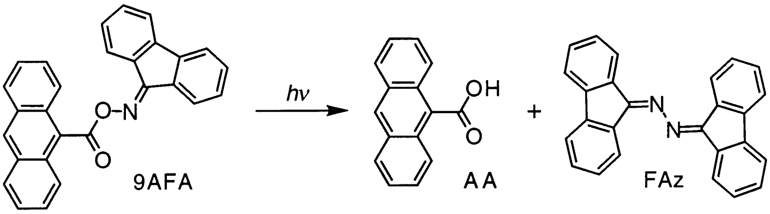
2. Photocleavage of the oxime ester

N-(9-Anthroyloxy)-9-fluorenylideneamine (9AFA, Scheme 1) exhibits absorption bands around 300 and 365 nm due to the fluorenylidene and anthroate moieties, respectively (Fig. 1). 9AFA was photolyzed with 366 nm stationary light in a low concentration (1×10^{-3} mol dm^{-3}) in acetonitrile under argon at ambient temperature to give 9-anthroic acid (AA; 0.92 mol/mol oxime ester) and fluorenone azine (FAz; 0.42) as products. Similar irradiation of 9AFA at 300 nm gave almost the same results. The formation of FAz indicates intermediacy of 9-fluorenylideneaminyl radicals,[11] which must be generated together with 9-anthroyloxyl radicals (9-AnthCO$_2$•) via homolysis of the N–O bond of 9AFA. The quantum yields for photocleavage of 9AFA ($1–3\times10^{-4}$ mol dm^{-3}) were determined to be 0.10 with 302 or 365 nm light in acetonitrile, and 0.04 and 0.01 with 302 and 365 nm light, respectively, in benzene. It is noticeable that the quantum yield is dependent on the solvents and excitation wavelengths. In the above concentration range the quantum yields were not affected.



Scheme 1.

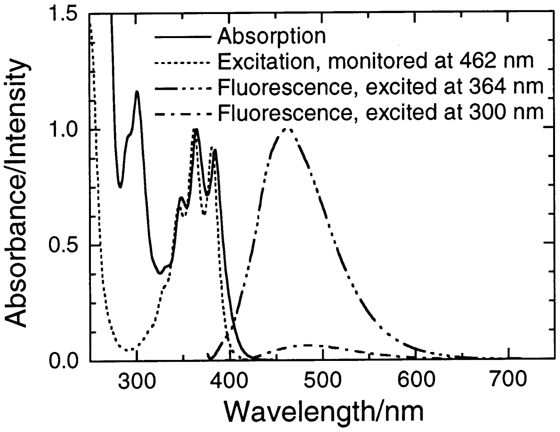


Figure 1. Absorption, fluorescence and fluorescence excitation spectra of 9AFA in acetonitrile. The spectra were normalized at a band maximum except for the fluorescence spectrum measured on 300 nm excitation; this spectrum was depicted relative to the fluorescence spectrum measured on 364 nm excitation

3. Direct observation of the radical species

Pulsed laser photolysis of 9AFA (5×10^{-4} mol dm^{-3}) at 308 nm under argon in acetonitrile at ambient temperature exhibited transient absorption bands at 400–500 and 500–800 nm, as shown in Fig. 2. Similar laser photolysis of 9AFA at 360 nm gave almost the same spectrum. The longer-wavelength band exerted essentially identical decay time constants of 6–7 μs at 580, 630 and 720 nm, and can be reasonably assigned to 9-AnthCO$_2$• in comparison with the spectra of 2,6-dimethylbenzoyloxyl and other aroyloxyl radicals.[2–8] For this band, molecular oxygen neither reduced spectral intensity nor affected spectral and decay profiles. These facts not only support the above assignment of the oxygen-centered radicals, but also indicate that excited triplet states are not involved in the radical formation.

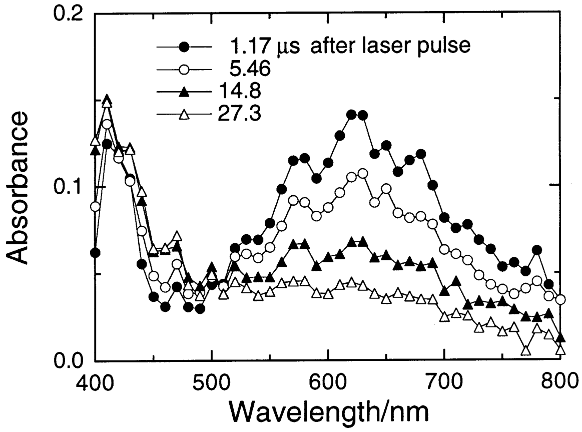


Figure 2. Transient absorption spectra observed on 308 nm pulsed laser excitation of 9AFA in acetonitrile under argon

The shorter-wavelength band may be ascribed to a plural species, such as 9AFA triplets and a long-lived intermediate which is formed concurrently with the disappearance of 9-AnthCO$_2$•. Biacetyl-sensitized excitation of 9AFA (5×10^{-4} mol dm^{-3}) with 444 nm laser pulses in acetonitrile exhibited an absorption band around 430 nm (lifetime (τ_T) 7.8 μs), which was assigned to T–T absorption of the anthroate moiety (E_T 177 kJ mol^{-1}).[14] However, no bands assignable to the radicals were detected in the 500–800 nm region. These observations also indicate that the 9AFA triplets are not responsible for the N–O bond cleavage. This is in contrast to the photocleavage of some acetates and benzoates of aromatic ketoximes, which proceeds in the triplet state.[11–13] The anthroate triplet energy may be insufficient for the bond cleavage.[13] Behavior of 9-AnthCO$_2$• and detailed analysis of the shorter-wavelength band will be reported elsewhere.

Laser photolysis of 9AFA (5×10^{-4} mol dm^{-3}) at 308 nm in benzene also exhibited two bands, one attributable to 9-AnthCO$_2$• at 500–800 nm and the other mainly due to 9AFA triplets around 430 nm; the latter was much stronger in intensity than the former.

4. Roles of excited singlet states played in the photocleavage

The fluorescence spectra of 9AFA (1×10^{-4} mol dm^{-3}) are structureless and very similar to those of methyl 9-anthroate (M9A, 1×10^{-4} mol dm^{-3}) in acetonitrile (Fig. 1) and benzene, respectively, on excitation at 364 nm. The fluorescence quantum yield (ϕ_f) and lifetime (τ_f) of 9AFA were, however, much lower and shorter, respectively, than those of M9A, as determined in acetonitrile (in benzene) to be ϕ_f=0.31 (0.69) and 0.01 (0.05) and τ_f=8.3 (12.0) and 0.60 (7.7) ns for M9A and 9AFA, respectively. The results were not affected up to a substrate concentration of 1×10^{-4} mol dm^{-3}. These results indicate that the anthroate singlet is efficiently quenched by the fluorenylidene moiety. The interaction between the two chromophores was confirmed by quenching of the M9A fluorescence by *N*-methoxy-9-fluorenylideneamine (MFA); linear Stern–Volmer plots of fluorescence lifetimes gave quenching rate constants (k_q) of 1.5×10^{10} and 8.3×10^{9} mol^{-1} dm^{3} s^{-1} in acetonitrile and benzene, respectively. The Stern–Volmer plots of fluorescence intensities provided much larger values of the quenching rates, suggesting a possibility of static interaction in the ground state.

The fluorescence excitation spectrum of 9AFA monitored at 462 nm shows no clear peak around 300 nm in acetonitrile, though the absorption spectrum exhibits the band due to fluorenylidene moiety in this region (Fig. 1). A very weak fluorescence spectrum observed on 300 nm excitation in acetonitrile was more than 20 nm shifted to the longer wavelengths compared to that observed on 364 nm excitation, and can be ascribed to the fluorenylidene moiety. Actually, MFA exhibited a weak fluorescence in a similar region on 300 and 361 nm excitation. In benzene, however, the excitation spectrum of 9AFA exhibited a weak but clear band around 300 nm, and the excitation at 300 nm gave the same fluorescence spectrum as did the 364 nm excitation.

These facts indicate that the relative singlet energy levels of the two chromophores in 9AFA change with the polarity of solvents; the lowest excited singlet of the fluorenylidene moiety (S_2(F)) is higher in energy than, or similar to, that of the anthroate moiety (S_1(A)) in benzene (Fig. 3). In acetonitrile, however, the lowest excited singlet of the fluorenylidene moiety (S_1(F)) is clearly lower than that of the anthroate moiety (S_2(A)) and may be responsible for the N–O cleavage. This order of the singlets is consistent with other spectral behavior; the fluorescence excitation spectrum is slightly shifted in the 350–400-nm region to the shorter wavelengths compared to the absorption spectrum (Fig. 1). This can be interpreted in terms of location of a weak absorption band due to the fluorenylidene moiety extending to slightly longer wavelengths than that of the anthroate moiety, coupled with the low emission efficiency of S_1(F). Inspection of absorption and fluorescence spectra of M9A and MFA indicates that the difference in the singlet energy between M9A and MFA is larger in acetonitrile than in benzene though the singlet level of M9A is higher than that of MFA in both solvents.

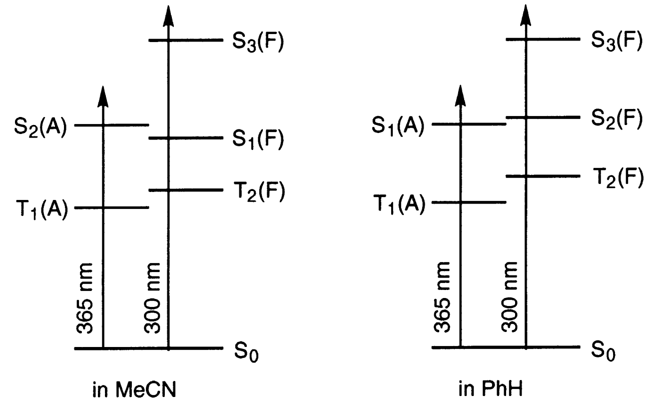


Figure 3. Schematic energy diagrams of 9AFA in polar and nonpolar solvents

Thus, the irradiation of 9AFA at 300 nm (ca. 400 kJ mol^{-1}) in acetonitrile results in the production of a higher excited singlet state of the fluorenylidene moiety (probably S_3(F); Fig. 3) followed by its internal conversion to the lowest excited singlet state, S_1(F) (E_S ca. 290 kJ mol^{-1}, as estimated from absorption and fluorescence spectra), which undergoes N–O bond cleavage to give the radicals. The weak fluorescence results predominantly from S_1(F). On the contrary, the irradiation at 365 nm produces the S_2(A) state (ca. 300 kJ mol^{-1} from absorption and fluorescence spectra), which undergoes fluorescence emission or energy transfer to the fluorenylidene moiety to give S_1(F), leading to the N–O bond cleavage. In benzene, however, the S_2(F) state produced by 300 nm irradiation followed by internal conversion undergoes predominantly energy transfer to the anthroate moiety to produce S_1(A), which undergoes fluorescence emission or intersystem crossing to give eventually the T_1(A) state; thus the N–O cleavage is less efficient.

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