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INTRAMOLECULAR FLUORESCENCE QUENCHING AND PHOTOLYSIS OF 1-NAPHTHYLACETIC ACID DERIVATIVES

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Intramolecular fluorescence quenching of 1-naphthylacetic acid derivatives has been interpreted in terms of electron transfer from the excited state of the naphthyl ring to the acyl group. Remarkable fluorescence quenching of the acyl chloride is attributable to successive deactivation of the excitation energy through the photocleavage of the C-Cl bond.

Although photochemistry of carboxylic acid derivatives has been widely investigated, little has been reported about the photoreaction involving acyl halides.$^{1)}$ Recently, some carboxylic acids and acyl chlorides have been found to quench the fluorescence of aromatic compounds intermolecularly via exciplexes.$^{2-4)}$ Electron transfer from excited aromatics to electrophilic acyl compounds is primarily responsible for these bimolecular interactions. Aromatics-acyl chloride systems are of special interest because they involve exciplexes which decay mainly through chemical transformation to give rise to the Friedel-Crafts-type photoproducts.$^{4a)}$ It appears reasonable that the related electron transfer mechanism is operating in the intramolecular fluorescence quenching of ω-arylalkanoic acid derivatives.$^{2)}$ This letter reports a study on the fluorescence measurements and the photolysis of 1-naphthylacetic acid (NAA) derivatives.

The absorption spectra of NAA and its chloride (NAC) are shown in Fig. 1. The spectrum of the methyl ester (NAM) was quite similar to that of NAA. General shapes of these spectra resemble to the shape of the parent substance, 1-methylnaphthalene (MN), with the exception of NAC which reveals a slight broadening of the absorption bands. The situation is different in phenylacetic acid (PAA) derivatives, in which fundamental dissimilarities of the absorption spectra were observed between toluene and PAA derivatives.$^{5)}$ The deformation of the spectra in the latter case is deduced to strong inductive effect and CT interaction of the acyl moiety attached to benzene ring through a methylene group.$^{5c)}$ Slight broadening of NAC absorption bands may be ascribable to such intramolecular interactions, yet it can be noted that the naphthyl and carbonyl moieties of NAA derivatives are electronically independent in the ground state.

The emission spectra of the NAA derivatives and MN were almost the same both in peak positions and general shapes. The quantum yield, φ_f and the lifetime, τ_f of these compounds are listed in Table 1 together with the relative emission yield in methylcyclohexane at 77 K.$^{6)}$ The results for MN are also listed for comparison.

Both the yield and the lifetime of fluorescence in NAA derivatives are smaller than in MN. The fluorescence quenching becomes more remarkable in the order, COOH ≃ CO_2CH_3 ≪ COCl, which is consistent with the sequence of the electrophilicity of the carbonyl groups. The quenching was confirmed to be independent on the solute concentration over the range of 10^{-5} - 10^{-3} $mol \cdot dm^{-3}$, indicating that it occurs intramolecularly.

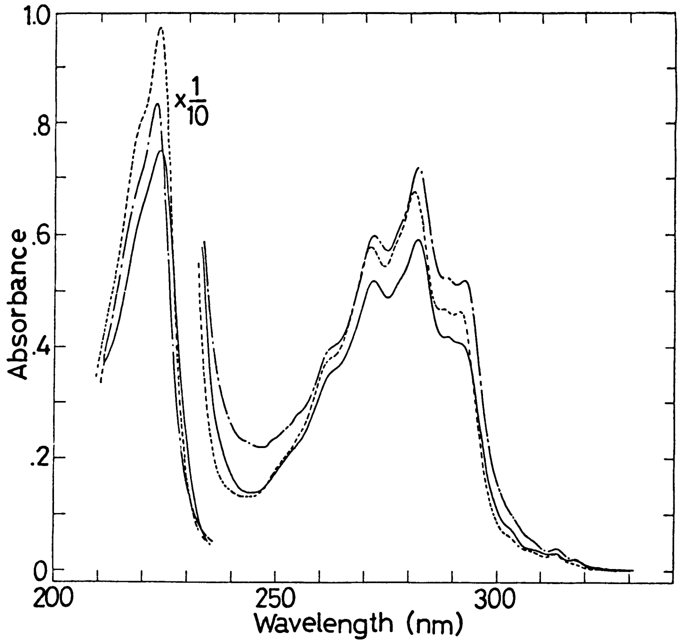

Fig. 1. Absorption spectra of 1-methylnaphthalene (——), 1-naphthylacetic acid (---), and its chloride (-·-) in acetonitrile (10^{-4} $mol \cdot dm^{-3}$).

Since the NAA derivatives and MN have closely related oscillator strengths and 0-0 transition frequencies, they are expected to possess similar radiative rate constant, $k_f = \varphi_f/\tau_f$. This is correct in non-polar solvents like cyclohexane, but apparent decrease of k_f is seen in a polar solvent like acetonitrile. Although the reason for the inconsistency is unclear at this stage of the investigation, it appears likely that a rapid and radiationless decay route is involved in the non-relaxed state immidiately after the photoexcitation. If it is correct, the ratio of φ_f/τ_f would correspond to γk_f in place of k_f, where γ is the fraction of the "thermalized" species which converts into the fluorescent equilibrium state. The fraction, $1 - \gamma$, should be responsible for the depletion of the fluorescence intensity.

The intramolecular fluorescence quenching for PAA derivatives has been investigated in details by Tournon and coworkers.$^{5)}$ Based on the observations for CT absorption bands and for high yield ratio of phosphorescence/fluorescence, they concluded that the fluorescence quenching was brought about by the enhancement of the intersystem crossing rate which was induced by an intramolecular CT interaction between the phenyl and the carbonyl groups. Different quenching mechanism should be proposed in this study because no evidence was obtained for CT interaction in the

Table 1. Emission data of 1-naphthylacetic acid derivatives

	In cyclohexane			In acetonitrile			at 77 K	
Compounds	φ_f	τ_f (ns)	φ_f/τ_f (10^6/s)	φ_f	τ_f (ns)	φ_f/τ_f (10^6/s)	φ_f (Relative)	φ_p
1-Methylnaphthalene (MN)	0.25	83	3.0	0.23	80	2.9	1.0	1.0
1-Naphthylacetic acid (NAA)	0.17	53	3.2	0.14	63	2.2	0.40	0.35
Methyl ester (NAM)	0.17	54	3.1	0.13	63	2.1	0.54	0.58
Chloride (NAC)	0.01	<5	>2	0.01	14	0.7	0.43	3.7

ground state and for the enhancement of phosphorescence yield in the cases of NAA and NAM. An attractive alternative has arisen from an analogy of intermolecular fluorescence quenching for indole by aliphatic acids[2)] and for naphthalene by acetyl chloride,[4b)] for which dynamic interaction is important. It appears probable that electron transfer in the excited equilibrium state is mainly responsible for the intramolecular fluorescence quenching of the NAA derivatives, although the ground-state CT interaction leading to high phosphorescence yield is also important in the case of NAC which has a strong electrophilic group in the quenching center. The rapid radiationless decay in acetonitrile may involve fast electron transfer and/or intersystem crossing from the non-relaxed excited state.[7)] The assertion of this viewpoint, however, should be sustained with further studies on photophysical behavior of these compounds in polar solvents.

The quenching of the fluorescence is much more remarkable in NAC than in the other derivatives. This implies the consumption of the excitaiton energy through chemical transformation subsequent to electron transfer to the side group. It is well known that NAA, the salt form of which is effective for the regulation of plant growth, undergoes decarboxylation upon irradiation.[8)]

The photolyses of the NAA derivatives were carried out in benzene or in acetonitrile (6×10^{-2} mol·dm^{-3}) under a nitrogen atmosphere at room temperature. Irradiation was carried out using a medium pressure mercury lamp equipped with a filter combination of a Corning 7-54 and an 0.2% K_2CrO_4 solution which permits only 313 nm light.[9)] Under the conditions, all compounds examined were confirmed to undergo photolyses, but the reaction rates for the acid and the ester were smaller than that for the chloride, presumably reflecting the relative strength of (O=)C-hetero atom bonds. This trend of the photosensitivity is in line with the ability of the fluorescence quenching of these compounds.

The photolysis of NAC was further studied. The initial quantum yield of the loss of NAC[10)] in benzene was ca. 0.1, with or without oxygen. Addition of acetophenone (0.1 mol·dm^{-3}) showed no sensitization of the photoreaction. The photolysis products obtained were identified by GC-MS spectrometry to be 1-(chloromethyl)naphthalene (84% of NAC consumed), 1,2-dinaphthylethane (9%), and 1(2*H*)-acenaphthylenone (4%). In the experiment in oxygen stream, 1-naphthylaldehyde was a sole major product. Consequently, the photolysis of NAC conforms to the following reaction scheme, which is comparable to the reported mechanism for the photolysis of 1-naphthylacetate.[8)]

$$\begin{array}{lcl}
\mathrm{NAC^*} & \longrightarrow & \mathrm{Naph\text{-}CH_2CO\cdot + Cl\cdot} \\
 & \longrightarrow & \mathrm{Naph\text{-}CH_2\cdot + COCl\cdot} \\
\mathrm{Naph\text{-}CH_2CO\cdot} & \longrightarrow & \mathrm{Naph\text{-}CH_2\cdot + CO\cdot} \\
 & \longrightarrow & \text{cyclization} \\
\mathrm{COCl\cdot} & \longrightarrow & \mathrm{CO\cdot + Cl\cdot} \\
\mathrm{Naph\text{-}CH_2\cdot + Cl\cdot} & \longrightarrow & \mathrm{Naph\text{-}CH_2Cl} \\
\mathrm{2\ Naph\text{-}CH_2\cdot} & \longrightarrow & \text{dimerization}
\end{array}$$

where Naph- represents a naphthyl group. The radical intermediates well explain the predominant formation of 1-naphthylaldehyde. Since the quantum yield is much lower than unity, radical chain reaction can be excluded. The formation of a definite amount of 1(2*H*)-acenaphthylenone suggests the sequence of bond cleavage, i.e. the α cleavage of relatively weak C-Cl bond at first, followed by the fragmentation of carbon monoxide. From the fact that oxygen and acetophenone had no influence on the efficiency of the photolysis, it is evident that the excited singlet state is responsible for the photoreaction. The first excited state of acetyl chloride is known to be n-π* state at 506 kJ mol^{-1}.11) The energy is so high that the excitation radiation (313 nm) is insufficient to generate the excited state of the side group of NAC. It is also difficult to take into account spontaneous energy transfer from the excited state of the naphthyl ring (377 kJ mol^{-1}). Electron transfer is valid in accounting for the reaction mechanism, since it is favorable for the formation of the radical products.

References and Notes

1) J. D. Coyle, Chem. Revs., 78, 97 (1978).
2) R. W. Ricci and J. M. Nesta, J. Phys. Chem., 80, 974 (1976).
3) N. H. C. Cooke and B. S. Solomon, J. Phys. Chem., 76, 3563 (1972).
4) a) T. Tamaki, Bull. Chem. Soc. Jpn., 51, 1145 (1978). b) T. Tamaki, ibid., 52, 1031 (1979).
5) a) J. Tournon and M. A. El-Bayoumi, J. Am. Chem. Soc., 93, 6369 (1971). b) J. Tournon, E. Kuntz, and M. A. El-Bayoumi, Photochem. Photobiol., 16, 425 (1972). c) J. Tournon and M. A. El-Bayoumi, J. Chem. Phys., 56, 5128 (1972).
6) The fluorescence measurements were made in an argon atmosphere at room temperature according to the analogous method described in preceding papers.4) The solute concentrations employed were ca. 3×10^{-4} $mol \cdot dm^{-3}$ and the excitation wavelength was 313 nm. Quantum yields were based on the value of 0.25 for 1-mathylnaphthalene in cyclohexane (L. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., p. 332 (1971)) and the values in acetonitrile were corrected for the refractive index of the solvent.
7) E. M. Kosower and H. Dodiuk, Chem. Phys. Lett., 26, 545 (1974).
8) D. G. Crosby and C-S. Tang, J. Agr. Food Chem., 17, 1291 (1969).
9) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York, p. 104 (1973).
10) The conversion of the starting material was followed by the method of iron(III) hydroxamate. The intensities of the incident and transmitted lights were measured by an Eppley thermopile calibrated against the radiant energy of a standard tungsten-filament lamp.
11) H. Baba, Nippon Kagaku Zasshi, 72, 341 (1951).

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