Fluorescence Quenching of Naphthalene and Its Derivatives by Acetyl Chloride

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The fluorescence of naphthalene and its methyl or methoxy derivatives has been found to be quenched by acetyl chloride. The quenching constants, determined by the Stern-Volmer treatment of the emission intensity and lifetime have been found to be in good agreement within experimental error. The quenching rate constants have been correlated with the energy terms of electron-donating forces in the excited states of these naphthalenes. The results suggest that the quenching mechanism involves a charge-transfer stabilized complex, in which the excited naphthyl compounds act as donors. Exciplex formation has been supported by oxygen quenching experiments.

The fluorescence quenching of aromatic molecules by carbonyl compounds is a current topic of research, a special interest of which is that some quenchings occur through non-classical energy transfer to a variety of acids, aldehydes, or ketones, which are of higher singlet excitation energy than those of the fluorescers.[1-3] Although these quenching systems reveal no exciplex emission, studies of the linear-free-energy relationship of the quenching efficiency indicate the validity of an exciplex, formed from excited aromatic compounds (electron donor) and electrophilic carbonyl groups (electron acceptor). This has been related to the anthracene–benzoyl chloride system, which is an example of the Friedel-Crafts-type photoreaction.[4] In addition to the Hammett correlation of the quenching ability of substituted benzoyl chloride, the complete interruption of the photoreaction by oxygen indicated that the exciplex is involved in the fluorescence quenching of anthracene and successive photochemical processes.

This paper reports the fluorescence quenching behavior of naphthalenes by acetyl chloride, based on the Stern-Volmer treatment of the fluorescence intensity and lifetime, and on oxygen quenching experiments, which are method for demonstrating the presence of a non-fluorescent exciplex.[5]

Experimental

All naphthyl compounds examined were purified by recrystallization from benzene or successive vacuum distillation. Distilled acetyl chloride was carefully kept from atmospheric moisture. Acetonitrile was dried and purified by fractional distillation over phosphorus pentoxide.

The fluorescence spectra measurements were made using a Hitachi MPF-2A spectrofluorometer at 21 °C. Samples were prepared in 1 cm square quartz cells with a 5 cm-length cylindrical neck which could be stoppered. The quencher concentrations employed were 0.02—0.4 M and the concentration of naphthalenes was 10^{-5} M. The excitation wavelength was 310 nm, where the absorption of the quencher was negligible. The emission spectra were generally the same both in the absence and presence of quencher and consequently the relative fluorescence intensity was determined by measurements of the height of the peak maxima. The experimental errors were 10%. Unless otherwise reported, the oxygen dissolved in the sample solution was purged by flushing with argon prior to measurement. A time of 10 min was required for complete elimination of oxygen-induced quenching under the conditions.

The fluorescence lifetime measurements were conducted using an ORTEC SP-3 nanosecond spectrometer at 25 °C, the sample preparation being the same as described above. The excitation was made by the 313 nm light and with this instrument, the fluorescence lifetime of quinine sulfate (10^{-5} M) has been estimated to be 20 ns (lit,[6] 19.2 ns).

Results and Discussion

In table 1 the results of the Stern-Volmer treatment for the fluorescence quenching of naphthalene and its methyl and methoxy derivatives by acetyl chloride are listed. The values of K_{SV} have been estimated from the initial slopes of the Stern-Volmer plots, which exhibited upward curvature above 0.1 M. The quenching rate constant, k_q, has been calculated by using the fluorescence lifetime observed.

It appears unlikely that static quenching is important since no new absorption band could be detected for the mixed solutions of naphthalenes and acetyl chloride. This is further supported by the quenching experiments of the fluorescence lifetime. The formation of a non-emissive complex prior to photoexcitation would enable the quenching to affect the fluorescence intensity, but not the fluorescence lifetime. However, this is not the case. As is shown in Table 1, the values of K_{SV} derived from the lifetime measurements are in good agreement with those of the intensity measurements within experimental error. The Stern-Volmer plots found here indicate the formation of the ground-state complex in high quencher concentrations[7] and consequently the dynamic property may be strictly pertinent to the quenching behaviors in low quencher concentrations.

The first excited states of carboxylic acids and derivatives are known to be n-π^* transitions, which are of higher energy than the corresponding transitions of aldehydes and ketones.[8] The singlet n-π^* transition energy of acetyl chloride is 121 kcal/mol (log ε 1.7),[9] which is higher than that of the naphthyl compounds (<92 kcal/mol). Thus, there is no region of spectral overlap between the donor fluorescence and the quencher absorption indicating the impossibility of triavial or resonance energy transfer. The quenching data listed in Table 1 reveals that k_q decreases with increase in the excitation energy of the fluorescers, and so endothermic energy transfer through collisional exchanges[10] can be excluded.

Table 1. Fluorescence quenching of naphthyl compounds by acetyl chloride in acetonitrile[a]

	Donor	^1E_D[b] (eV)	IP_D[c] (eV)	τ^0 (ns)	Lifetime meas. K_{sv} (M^{-1})	Lifetime meas. $k_q\times10^{-7}$ ($M^{-1}s^{-1}$)	Intensity meas. K_{sv} (M^{-1})	Intensity meas. $k_q\times10^{-7}$ ($M^{-1}s^{-1}$)
1	Naphthalene	3.99	8.07	87	1.0	1.2	1.1	1.3
2	2-Methylnaphthalene	3.89	7.90	51	1.2	2.4	1.1	2.2
3	2,3-Dimethylnaphthalene	3.87	7.85	79	2.0	2.5	1.6	2.0
4	1-Methylnaphthalene	3.91	7.88	71	1.6	2.3	1.7	2.4
5	2,6-Dimethylnaphthalene	3.83	7.74	43	4.6	11	3.1	7.2
6	1,2-Dimethylnaphthalene	3.86	7.74	40	4.5	11	3.8	9.5
7	1,5-Dimethylnaphthalene	3.86	7.74	62	4.5	7.3	3.1	5.0
8	1,4-Dimethylnaphthalene	3.86	7.72	47	6.0	13	5.0	11
9	Acenaphthene	3.86	7.66	49	22	45	18	37
10	2-Methoxynaphthalene	3.78	8.06[d]	16	7.2	45	5.0	31
11	1-Methoxynaphthalene	3.87	7.85[d]	18	34	189	28	156

a) Measured under deoxygenated conditions. b) Determined from the absorption and fluorescence spectra. c) Obtained from Ref. 16. d) Calculated[17] from the polarographic potential.[18]

These cosiderations suggest that the fluorescence quenching is due to exciplex formation, as in the case of the anthracene–benzoyl chloride system.[4] If an exciplex is formed, in which the excited molecules act as the electron donor with the same electron acceptor, the values of $\ln k_q$ should correlate with the energy terms of the electron-donating force, $IP_D - {}^1E_D$,[11] where IP_D and ${}^1E_D$ represent the ionization potential and the singlet excitation energy of the donor, respectively. Figure 1 shows the plots of $\ln k_q$ *vs.* $IP_D - {}^1E_D$, calculated for the naphthalenes examined. The linearity of the plots is remarkable, except for Compounds **10** and **11**. The electron transfer in the excited state is then primarily responsible for the fluorescence quenching.

Therefore, the quenching results can be accounted for by the following equations,

$$N \xrightarrow{h\nu} {}^1N^*, \qquad (1)$$

$${}^1N^* \xrightarrow{k_f} N + h\nu', \qquad (2)$$

$${}^1N^* \xrightarrow{k_{isc}} {}^3N^*, \qquad (3)$$

$${}^1N^* \xrightarrow{k_{ic}} N, \qquad (3')$$

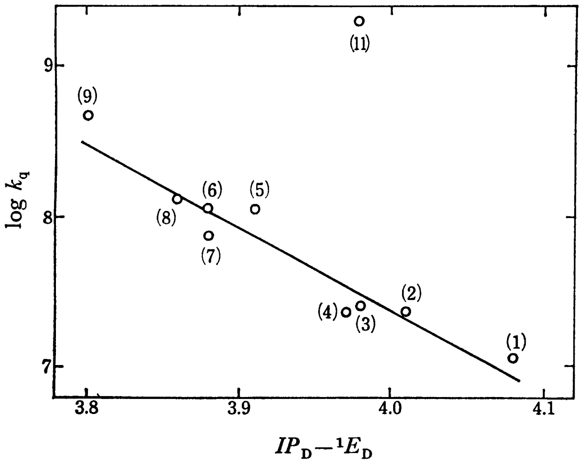

Fig. 1. Plots of log k_q as a function of $IP_D - {}^1E_D$. The values of k_q from the lifetime measurements were used. The numbers in parentheses refer to those in Table 1.

$${}^1N^* + A \underset{k_{-e}}{\overset{k_e}{\rightleftharpoons}} [N\cdots A]^* \xrightarrow{k_{de}} N + A \text{ or products,} \qquad (4)$$

where N and A represent the naphthyl compounds and acetyl chloride, respectively, $[N\cdots A]^*$ represents an exciplex, and k_q refers to $k_e k_{de}/(k_{-e}+k_{de})$.

If an exciplex is non-fluorescent and its formation is reversible, the oxygen quenching method is convenient for demonstrating the presence of the exciplex.[5] When oxygen is allowed into the sample solutions, both the excited monomer and exciplex are appreciably intercepted with a rate which is diffusion-controlled.

$${}^1N^* + O_2 \xrightarrow{k_{qm}} N + O_2, \qquad (5)$$

$$[N\cdots A]^* + O_2 \xrightarrow{k_{qe}} N + A + O_2. \qquad (6)$$

From Eqs. 1—6, the Stern-Volmer equation is derived.

$$\phi_f^\circ/\phi_f = 1 + k_{qm}\tau^\circ[O_2] + k_e p\tau^\circ[A],$$

$$p = (k_{de}+k_{qe}[O_2])/(k_{-e}+k_{de}+k_{qe}[O_2]),$$

where $\phi_f^\circ = k_f/(k_f+k_{isc}+k_{ic}) = k_f\tau^\circ$, ϕ_f represents the fluorescence quantum yield in the presence of the quencher and oxygen, and p is the fraction of the exciplex which does not regenerate an excited monomer. The Stern-Volmer relation of the fluorescence lifetime is the same as that of the fluorescence intensity. If the exciplex formation were irreversible, *i.e.*, $k_{-e} \ll k_{de}$, then the product $k_e p$ approximates to k_q. The oxygen-induced quenching would be strictly competitive with quenching by A and the Stern-Volmer slopes as a function of [A] would be identical, irrespective of oxygen. If the exciplex is reversibly formed, the value of p may increase in the presence of oxygen, resulting in an increase of slope. As shown in Fig. 2, the fluorescence quenching of naphthalene by acetyl chloride is apparently enhanced by dissolved oxygen, strongly supporting the presence of a reversibly formed exciplex. As shown in Table 2, the quenching enhancement decreases with increase in the electron-donating ability of the excited naphthyl compound and consequently the reversibility of exciplex formation becomes less important with electron-rich aromatics.

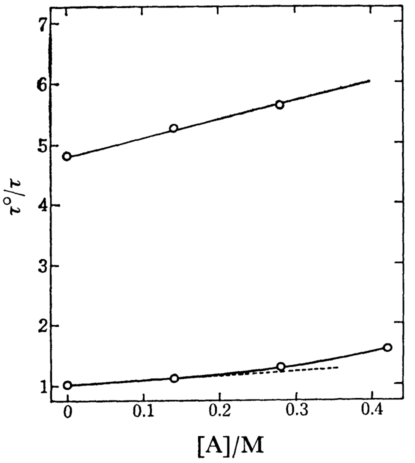

Fig. 2. Fluorescence quenching of naphthalene by acetyl chloride: lower, deoxygenated; upper, aerated.

Table 2. Results of the oxygen quenching experiments

Donor	K_{sv} a) (M^{-1})	K_{sv} b) (M^{-1})	$k_e p/k_q$
Naphthalene	3.0	3.2	3.0
2-Methylnaphthalene	2.3	1.8	1.8
1-Methylnaphthalene	2.0	2.1	1.2
Acenaphthene	—	21	1.1

a) Determined from lifetime measurements. b) Determined from intensity measurements.

Irradiation of the mixture of naphthalenes and acetyl chloride in benzene with 313 nm light produced an appreciable loss of the starting materials, indicating that the exciplex decays mainly through chemical transformations analogous to the photoreaction of anthracene with benzoyl chloride.[4] Attempts to isolate characterizable products by TLC were, however, unsuccessful. The large k_q values obtained for methoxynaphthalenes are thought due to the increased rates of such chemical changes. Preliminary experiments, in fact, showed that the initial rate of acetyl chloride loss monitored by the iron(III) hydroximate method[12] was larger than that for the methylnaphthalenes, although no precise evaluation of the quantum yield could be made because of the appearance of new intense absorption bands near the excitation wavelength.

Quenching behavior is of interest in view of structure-reactivity relationships. In contrast with the quenching of the excited aromatic hydrocarbons by aromatic ketones or aldehydes,[3] systems involving acyl chlorides as quencher do not necessarily require the assertion that the quencher should have a conjugated system capable of frontier orbital overlap with the aromatic fluorescer. It appears certain that in addition to the electron-withdrawing properties of the carbonyl group of acyl chlorides the chemical reactivity of activated acyl C–Cl bonds play an important role in the quenching processes. This may recall the concept concerned with bimolecular interactions between electron-rich aromatics and chlorinated compounds as the quenching center, *e.g.*, indole–methyl chloroacetate,[13] 1,4-dimethoxybenzene–benzyl chloride,[14] and methoxynaphthalenes–chloroacetonitrile systems.[15] These studies have emphasized that the rate of exciplex decay to chemical transformation is dominant in limiting an overall quenching rate. The CT interaction is of importance, however, giving rise to the association of an exciplex. The quenching mechanism in the present work is related to these instances.

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