FLUORENONE FLUORESCENCE

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It has been previously noted that polar solvents enhance the lifetime[1] and quantum yield[2] of fluorenone fluorescence. The Stern-Volmer slopes for quenching of fluorenone fluorescence with amines[1-4], di-t-butyl nitroxide[2], and phosphines[4] increase greatly in polar solvents. Since this value is the product of quenching rate (K_q) and singlet lifetime (τ_o), variation of either or both of these quantities can lead to the observed change.

We have measured the fluorescence lifetime of fluorenone in a variety of solvents and find that it is highly solvent dependent. A study of fluorescence quenching shows that the rate at which oxygen quenches fluorenone fluorescence is an order of magnitude lower than the corresponding rate for aromatic hydrocarbon fluorescence, and that water, ethanol, and conjugated dienes quench fluorenone fluorescence.

Fluorescence lifetimes in the range 1-20 nsec were measured to $\pm$ 5% by phase shift. Samples were excited by the 442 nm output of a Spectra-Physics Model 185 helium-cadmium laser modulated at 9.86 MHz by an Isomet Model TFM-502 beam modulator. Because of the relatively low rate of oxygen quenching, it was unnecessary to degas except for measurement of K_{O_2}.

The fluorescence lifetime shows a large solvent dependence which, except for alcohols, correlates roughly with solvent dielectric constant.

Table I

Fluorenone Fluorescence Lifetime[a]

Solvent	Lifetime (nsec)	Solvent	Lifetime (nsec)
Dimethylformamide	19.5	Isopropyl Alcohol	3.5
Acetonitrile[b]	18.5	Tetrahydrofuran	3.0
Acetone[b,c]	10.8	Ethanol	1.8
Ethyl acetate	4.4	Cyclohexane	1.8
Benzene[c]	4.1	Methanol	1.1

[a] 0.05 M fluorenone; room temperature; not degassed. [b] In degassed solution: acetonitrile, 19.3 nsec; acetone, 11.3. [c] Literature: acetone, 9 ± 1.5 nsec; benzene 3 ± 1; cyclohexane, 0 ± 1 (Ref. 1).

The K_q's for triethylamine quenching in various solvents can be calculated from these lifetimes and the Stern-Volmer slopes reported by Singer[2].

Table II

Quenching of Fluorenone Fluorescence by Triethylamine

Quencher	Solvent	$\tau_o K_q$ (l/mole)[a]	K_q ($\times 10^9 l$/mole sec)
Et$_3$N	cyclohexane	6.0	3.3
Et$_3$N	benzene	22.4	5.5
Et$_3$N	acetonitrile	141	7.3

[a] Reference 2.

Singer[2] suggested that the large change in slope might be due to a change in τ_o and pointed out that, if the change in K_q reflected only the effect of solvent viscosity on diffusion-controlled rate, the relative values would be acetonitrile:benzene:cyclohexane = 1.7:1:0.6. Since the observed ratio of K_q's is 1.3:1:0.6, there is little if any solvent effect on K_q. Similar observations have been reported for the anthracene-diethylamine system[5].

From these lifetimes and the fluorescence quantum yields reported by Singer[2] fluorescence rates (K_f) in 4 solvents can be calculated: acetonitrile, $1.5 \times 10^6 \text{sec}^{-1}$; benzene, $3.2 \times 10^6 \text{sec}^{-1}$; 2-propanol, $8 \times 10^5 \text{sec}^{-1}$, and cyclohexane, $3 \times 10^5 \text{sec}^{-1}$.

Little change in τ_o or fluorescence intensity was observed on degassing. The K_q for oxygen was determined from comparison of both τ_o and fluorescence intensity of degassed samples with those under atmosphere of oxygen.

Table III
Quenching of Fluorenone Fluorescence

Quencher	Solvent	K_q (l/mole sec)
O_2	acetone	$1.2 \pm 0.2 \times 10^9$
O_2	acetonitrile	$1.7 \pm 0.2 \times 10^9$
H_2O	acetonitrile	$7.7 \pm 0.6 \times 10^7$
D_2O	acetonitrile	$4.6 \pm 0.4 \times 10^7$
Ethanol	acetonitrile	$7.6 \pm 0.6 \times 10^7$
2,5-Dimethyl-2,4-hexadiene	benzene	$3.4 \pm 0.3 \times 10^9$
1,3-Cyclohexadiene	benzene	$3 \pm 1 \times 10^8$

Since the solubility of O_2 in acetonitrile has not been reported, the K_{O_2} for tetracene was measured under the same conditions and found to be 17 times greater. If it is assumed that O_2 quenches tetracene fluorescence at the diffusion-controlled rate, $2.9 \times 10^{10} l$/ mole sec, a K_q of 1.7×10^9 is calculated[6]. Even lower K_q's were measured for oxygen quenching of the fluorescence of the α-diketones camphorquinone and 2,3-butanedione ($\sim 3 \times 10^8 l$/mole sec). Since these rates are one and two orders of magnitude less than the corresponding rates for aromatic hydrocarbons, quenching interaction between oxygen and ketones may be either much weaker and/or different than that between oxygen and aromatic hydrocarbons.

The anomously short τ_o's measured in alcohols are due to quenching by OH containing compounds. Quenching by water, D_2O, and ethanol was measured over the range 0-4% in acetonitrile. A K_D/K_H of 0.60 was found. (Table III).

Conjugated dienes, which quench the fluorescence of a wide variety of molecules, also quench fluorenone fluorescence[8] (Table III). On prolonged irradiation of fluorenone in 2,5-dimethyl-2,4-hexadiene, the yellow color of fluorenone disappeared indicating that a photoproduct probably was formed. This diene adds to naphthalene photochemically[9].

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