

MEDIUM EFFECTS ON THE FLUORENONE FLUORESCENCE

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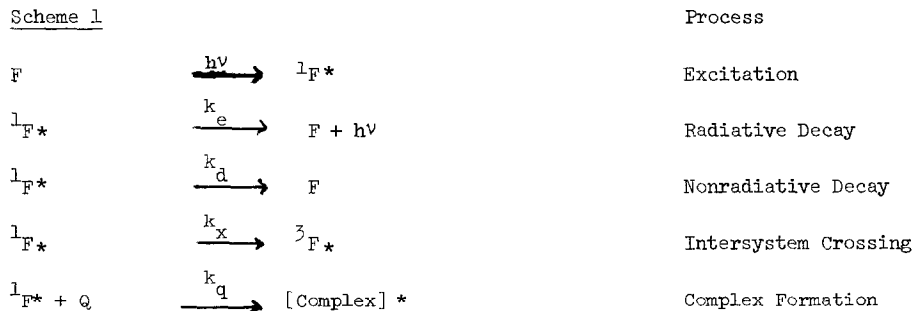
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(Received in USA 6 January 1969; received in UK for publication 6 February 1969)

Our recent observation that the fluorenone fluorescence (1) is quenched by di-t-butyl-nitroxide (DTBN) and dimethyl-N-(cyclohexyl)ketenimine (2) led us into a study of medium effects on this emission.

The quenching of the fluorenone emission by the ketenimine cannot be due to classical singlet-singlet energy transfer because of the unfavorable disposition of the energy levels in the potential donor and acceptor which would make this transfer highly endothermic (3). Instead, we proposed deactivation of the fluorenone singlet via complex formation as shown in Scheme 1. (2) Similar explanations have been offered to explain the fluorescence quenching of aromatic hydrocarbons by dienes (4) and perylene by amines (5).

Scheme 1



Triethylamine also efficiently quenches the fluorenone emission but pyridine is inactive. Table 1 contains some of our recent data which are presented as the slope of a Stern-Volmer plot of the ratio of the quantum yield of emission in the absence and presence of a given amount of quencher (Φ_0/Φ) against quencher concentration such that for Scheme 1

$$\Phi_0/\Phi = 1 + k_q(Q)/[k_e + k_d + k_x].$$

Table 1. Quenching of the Fluorenone Emission by Various Quenchers.^a

Quencher	Solvent	$k_q/k_1's^b$
Et ₃ N	Cyclohexane	6.0 M ⁻¹
DTBN	Benzene	64.5
Et ₃ N	Benzene	22.4
Me ₂ C=C=NC ₆ H ₁₁	Benzene	13.0
Pyridine	Benzene	0.0
DTBN	Acetonitrile	305
Et ₃ N	Acetonitrile	141
Pyridine		0.0

^aMeasured in degassed and sealed, 1 cm sq. standard bore Pyrex cells containing fluorenone at ca 10⁻² M. Exciting light was a narrow band centered at 400 mμ, emission was monitored at 500 mμ. ^b $k_1's = [k_e + k_d + k_x]$.
Limit of error ± 10%.

Table 2. Quantum Yields for Fluorenone Emission in Various Solvents.^a

Solvent	Φ_E^b	$\Phi_{Relative}$
DMF ^c	0.043	3.28
Acetonitrile	0.029	2.21
Benzene	0.013	1.00
2-Propanol	0.0027	0.21
Cyclohexane	0.0005	0.045

^aAt room temperature in degassed and sealed, 1 cm sq., standard bore Pyrex cells containing fluorenone at ca 2 x 10⁻⁵ M. Excitation at 340 mμ with a band of 6.5 mμ.

^bBy reference to quinine sulfate in 0.10 N sulfuric acid (6) using solutions of the same optical density.

^cDimethylformamide.

From Table 1 it is seen that the quenching efficiency of triethylamine depends on the medium such that acetonitrile > benzene > cyclohexane. While this trend, in part, may reflect an increase in k_q with increasing polarity of the medium if the complex has charge transfer character, we believe the medium influences another important parameter as well (7).

Table 2 contains the quantum yields for fluorescence from fluorenone in various solvents. In the aprotic solvents, the emission efficiency increases with increasing polarity of the medium. This trend cannot be explained by an enhanced k_e in the polar media since the absorption spectra of fluorenone in cyclohexane, benzene, acetonitrile (Figure 1) and dimethylformamide are very similar and the radiative lifetime (τ_0) of an emitting state can be estimated from the absorption spectrum by $\tau_0 \approx 10^{-4}/\epsilon_{max}$ (9).

We believe the polarity of the medium influences the splitting between the lowest lying $\pi - \pi^*$ and a slightly higher $n - \pi^*$ singlet state (10). As the polarity of the medium is increased, the $\pi - \pi^*$ state drops and the $n - \pi^*$ state rises in energy leading to increased splitting as shown in Figure 2. According to Lower and El-Sayed (11), intersystem crossing in aromatic ketones

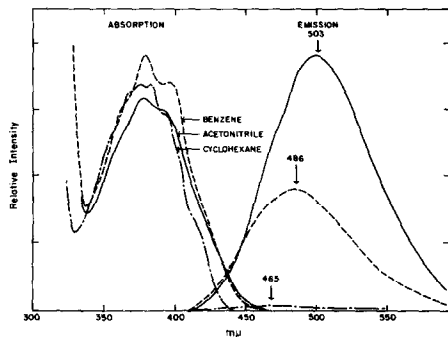


Fig. 1 Spectroscopic data for fluorenone. Absorption spectra recorded on solutions containing 20×10^{-3} M fluorenone. Emission spectra recorded on solutions of same optical density at wavelength of excitation, 340 mμ.

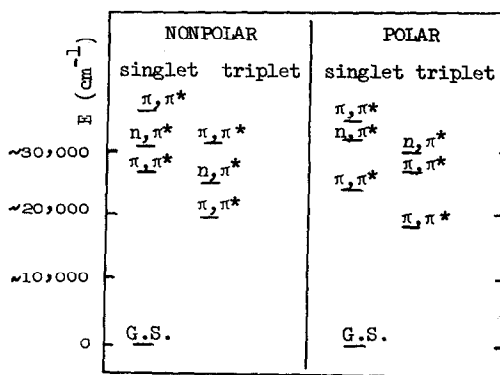


Fig. 2 Effect of Medium on Excited Electronic States of fluorenone.

is most efficient when it is between states of different electronic configuration so that it is faster for $n-\pi^* \leftrightarrow \pi-\pi^*$ than for $\pi-\pi^* \leftrightarrow \pi-\pi^*$ or $n-\pi^* \leftrightarrow n-\pi^*$. If the polarity of the medium leads to an ordering of the states along the lines indicated in Figure 2, we would expect intersystem crossing to be faster in cyclohexane than in acetonitrile. Thus, the observed quenching efficiency of triethylamine in acetonitrile relative to cyclohexane (24:1) could be due, in large part, to a change in k_x in going from one solvent to the other. Such variations in k_x between allowed and disallowed intersystem crossings, according to the El-Sayed selection rules, range up to 10^3 (11). Recently, Cohen and Guttenplan (12) reported that fluorenone is photoreduced by amines and that with triethylamine (i) a 10-fold increase in the quantum yield occurs upon diluting neat triethylamine (7.23 M) down to 0.10 M with cyclohexane but (ii) a retardation of the reaction occurs upon dilution with 2-propanol or acetonitrile. We believe (i) and (ii) reflect the importance of the singlet quenching process at high triethylamine concentration as well as the medium effect on k_x as discussed above.

Further work on these effects is in progress.

Acknowledgement. We thank the Petroleum Research Fund, administered by the American Chemical Society for a grant in support of this work.

References

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- (9) ibid, p. 174
- (10) Yoshihara and Kearns (reference 1) suggest that the lowest lying singlet state in fluorenone is of $\pi-\pi^*$ character. The shift of the emission to the red with increasing polarity of the medium (Figure 1) supports this assignment.
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