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THE QUENCHING OF FLUORENONE FLUORESCENCE BY TRIETHYLAMINE. MEDIUM EFFECTS ON THE SINGLET LIFETIME.

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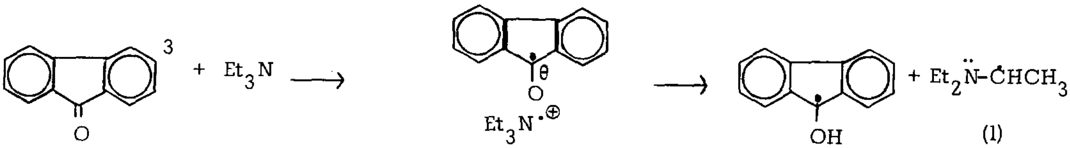
There has been much recent interest in the photoreduction of carbonyl compounds by amines (1,2,3). The reaction is thought to take the course of electron transfer from the amine to a ketone n-π^* triplet state, followed by proton transfer to give a pair of neutral radicals. Equation (1) illustrates this for fluorenone and triethylamine.



(1)

Recently, Cohen (3) has reported solvent effects on this particular reaction, including the remarkable observation that high concentrations (>0.2M) of triethylamine quench the reduction in cyclohexane. We have carried out experiments which permit the following conclusions: (1) the quenching is due to the quenching of fluorenone singlets and (2) there is a remarkable solvent effect on the singlet lifetime, ie. the intersystem crossing rate decreases markedly with increasing solvent polarity.

The fluorescence of fluorenone is well known (4,5), and it has been suggested (4) as originating from a π - π^* singlet. We have carried out quantitative studies of the fluorescence in three different ways. Measurement of the relative quantum yields of emission was done in various solvents in a rectangular Pyrex cell with right angle geometry (Cary 15 spectrophotometer, 1P28 photomultiplier, results uncorrected for spectral response). Measurement of the quenching of fluorescence by triethylamine (purified by spinning-band distillation) was performed similarly. Finally, the lifetimes in the various solvents were measured directly via nanosecond flash spectroscopy using a Q-switched, frequency-doubled ruby laser. Some experiments were performed with carefully purified benzene or acetone; these results were completely consistent with other experiments in which commercial solvents (AR or spectro grade) were used as received. Samples generally were not outgassed; the short lifetimes made it unnecessary. Kearns (4) observed that the fluorescence is unaffected by outgassing (however, see note a to Table I).

It is clear from inspection of Table I that triethylamine is a quencher of fluorescence (i.e, of fluorenone singlets) in all solvents studied. No fluorescence could be detected in neat triethylamine; the observation of Cohen (3) that fluorenone disappears with less than 10% quantum efficiency in neat triethylamine then must mean that at most 10% of the interactions of triethylamine with fluorenone singlets lead to photoreduction products. This stands in marked contrast to the interaction with fluorenone triplets, where the corresponding number is high in cyclohexane (3). A tempting speculation is that the quenching is in both cases electron transfer in nature, but that the ion-pair resulting has a "spin memory." The singlet pair may relax rapidly _via_ electron transfer in the reverse sense to generate ground-state reactants. This process would be spin-forbidden for a triplet pair, and a slower proton transfer to give the two neutral radicals might then compete.

We calculate values of k_Q for the singlet as $10 \pm 2 \times 10^9 M^{-1} sec^{-1}$ in acetone and $7 \pm 2 \times 10^9 M^{-1} sec^{-1}$ in benzene, in excellent agreement with the hypothesis that triethylamine quenches fluorenone singlets at a diffusion-controlled rate.

The singlet lifetimes themselves are of interest. They are orders of magnitude larger than that estimated for typical aromatic ketones, e.g. benzophenone at 10^{-11} sec (6). Intersystem crossing in fluorenone is known to occur with >90% efficiency in cyclohexane (3) and benzene (7), and should surely be the dominant competing process in acetone as well. The lifetimes thus to a good approximation represent the inverse of the rate constants for intersystem crossing. All three measures of the relative lifetimes in benzene and acetone give consistent results, with the lifetime being longer by a factor of 2.4 to 3 in acetone. All three measures point to a much shorter lifetime in cyclohexane, but give different values. The assumption that the radiative lifetime is solvent independent leads to the conclusion that the lifetime in cyclohexane is 0.15 nanoseconds; the assumption of diffusion-controlled quenching by triethylamine gives 0.6 nanoseconds. We prefer the former, since the high concentrations of triethylamine used in cyclohexane (0.2-1M) might give rise to "static" quenching and therefore incorrect lifetimes calculated from the Stern-Volmer plot.

We believe these lifetimes are dominated by the interaction of S_1, presumably $\pi-\pi^*$ or at least with but slight $n-\pi^*$ character, with T_2, presumably mostly $n-\pi^*$ and rather close in energy to S_1. Intersystem crossing between singlets and triplets of _different_ electronic origin (i.e., $\pi-\pi^*$ and $n-\pi^*$) is expected to dominate when the two states are close to one another

TABLE I

Solvent (λ max)	$\tau \times 10^9$, sec.	$k_Q\tau$, M^{-1}	ϕ_F (relative)
Acetone (503)	9 ± 1.5^a	$93 \pm 4^{a,b,c}$	$2.3 \pm .1^{a,d}$
Benzene (498)	3 ± 1	$21 \pm 1^{b,c}$	$(1.00)^d$
Cyclohexane (479)	0 ± 1	2.3 ± 0.4^b	$.050 \pm .004^d$

(a) It was calculated that outgassing would have increased each of the acetone numbers by 15% or so. This was confirmed for ϕ_F.

(b) Stern-Volmer plots were linear except for cyclohexane. In this case, the complication may be the extreme case of photoreduction. Deviation is less than 40% from linearity in any event.

(c) Independent of concentration in the range .002M-.02M and identical at 3660Å and 4358Å excitation. Cyclohexane was studied only at 3660Å and over a much narrower concentration range owing to the weakness of the emission.

(d) Independent of concentration and identical for 3660Å and 4045Å excitation.

(6,8). In the present case, the shift to more polar solvents should push the $\pi - \pi^*$ singlet S_1 down in energy and the $n - \pi^*$ triplet T_2 up. It would not be surprising if this resulted in an increased lifetime for S_1, as we observe. More work of both a kinetic and spectroscopic nature is needed before the details of the intersystem crossing mechanism can be completely worked out.

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