Quenching of Aromatic Hydrocarbon Fluorescence by Alkylpyridinium Halides

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Summary Aromatic hydrocarbon fluorescence is quenched efficiently by simple alkylpyridinium halides most likely *via* an electron transfer mechanism.

We recently reported that very low (sub-micellar) concentrations of cationic detergents were effective at influencing the fluorescence of 1-dimethylamino-5-naphthylsulphonylglycine (dansylglycine).[1] In particular, we were intrigued to find that the fluorescence of dansylglycine was unexpectedly quenched upon interaction with cetylpyridinium bromide (CPB). We now report the results of several experiments which show that the fluorescence of aromatic hydrocarbons in general is effectively quenched upon interaction with alkylpyridinium halides.

The hydrocarbons pyrene, anthracene, or perylene were warmed with aqueous solutions of purified CPB, cetyltrimethylammonium bromide (CTB), or sodium dodecyl sulphate (SDS). After cooling, the solutions were filtered and the concentration of micelle-dissolved hydrocarbon was determined spectrally by u.v.-visible absorbance. Fluorescence spectra were taken using an Aminco–Bowman spectrofluorimeter with the following results: pyrene, $1{\cdot}58 \times 10^{-3}$M and $1{\cdot}09 \times 10^{-3}$M in 0·05M CTB and 0·1M SDS, respectively, displayed both monomeric and dimeric (eximer) emission.[2] Essentially similar results have previously been described by Förster[3] using cetyldimethylbenzylammonium chloride, and by Hauser[4] using SDS. By contrast, however, we have found that $1{\cdot}59 \times 10^{-3}$M pyrene displays no observable fluorescence in 0·05M CPB.† Similarly, perylene at concentrations of $2{\cdot}7 \times 10^{-5}$M in $1{\cdot}04 \times 10^{-1}$M SDS or $6{\cdot}4 \times 10^{-5}$M in $8{\cdot}3 \times 10^{-2}$M CTB, displays intense normal fluorescence; however $3{\cdot}6 \times 10^{-4}$M perylene in $7{\cdot}8 \times 10^{-2}$M CPB shows less than 1% of the fluorescence intensity seen in CTB solution. Similarly, $2{\cdot}81 \times 10^{-4}$M anthracene in $7{\cdot}8 \times 10^{-2}$ CPB displays only 4% of the fluorescence intensity of a $2{\cdot}33 \times 10^{-4}$M solution in $8{\cdot}3 \times 10^{-2}$M CTB. Irradiations in these experiments were done at 350, 398, and 340 nm for pyrene, perylene, and anthracene, respectively. No light was absorbed by the detergents in any case.

The potassium salt of 1-pyrenebutyric acid (PBA^-K^+) was irradiated at 350 nm in water solution. At $4{\cdot}4 \times 10^{-3}$M two emission maxima of comparable intensity were observed at 395 and 480 nm. Upon dilution to $1{\cdot}1 \times 10^{-3}$M, the intensity ratio of short to long λ emission increased to 3:1; at $8{\cdot}8 \times 10^{-5}$M, no long λ peak was observed. We suggest monomeric and eximer emission[2] to account for these results. Addition of as little as $8{\cdot}6 \times 10^{-5}$M CPB to an $8{\cdot}8 \times 10^{-5}$M PBA^-K^+ solution completely quenched the emission of the latter. Formation of a 1:1 complex between these salts is implied by this result. By contrast, addition of $13{\cdot}8 \times 10^{-5}$M CTB to an $8{\cdot}8 \times 10^{-5}$M PBA^-K^+ solution results in complete conversion of the monomeric emission into apparent eximer emission at 480 nm.

We have also looked into the quenching ability of a non-detergent pyridinium salt. It was found that the fluorescence of an $8{\cdot}8 \times 10^{-5}$M solution of PBA^-K^+ in water was very efficiently quenched by *N*-ethylpyridinium bromide. A Stern–Volmer slope of 685^{-1} was found. PBA^-K^+ has a reported lifetime (τ) of 100 ns. in oxygen equilibrated solution.[5] Since the Stern–Volmer slope may be identified with the quantity of $k_q\tau$, we may compute a quenching constant, k_q, of $6{\cdot}85 \times 10^9$ l mol^{-1} s^{-1}, indicating an essentially diffusion controlled quenching process.

We irradiated $1{\cdot}36 \times 10^{-4}$M perylene in absolute alcohol in the presence of 0·135M *N*-ethylpyridinium bromide, and

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† We estimate that the limit of detection of our experiment is 0·1% of the fluorescence intensity seen in CTB solution.

found that the salt was an effective quencher of the perylene excited singlet state. Emission intensity is decreased by 90% under these conditions.

These experiments clearly demonstrate that the pyridinium nucleus is an effective quenching function for singlet excited states of aromatic hydrocarbons. We suggest an electron-transfer mechanism as the most reasonable to explain these results. Kosower[6] has thoroughly described the photoinduced transfer of an electron from iodide ion to an *N*-alkylpyridinium nucleus. The photoexcited aromatic hydrocarbons described here may similarly be serving as electron donors with transient formation of the radical–cation of the hydrocarbon and the neutralized pyridinium radical. Low ionization potentials of 7·6 and 7·7 eV for anthracene and pyrene, respectively, have been reported,[7] thus lending further credence to this mechanism. Electron transfers from amines of low ionization potential to photoexcited aromatic hydrocarbons[8] as well as to the singlet[9] and triplet[10] excited states of aromatic ketones, have been subjected to considerable study. The data presented here would seem to implicate pyridinium salts as the opposite counterpart of amines with respect to photochemical electron transfer.

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