PHOTODEGRADATION OF COUMARIN LASER DYES: AN UNEXPECTED SINGLET SELF-QUENCHING MECHANISM

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(Received January 3, 1984; in revised form March 26, 1984)

Summary

The photolysis of a series of aminocoumarin laser dyes, including 7-diethylamino-4-methylcoumarin (1), has been investigated. Dealkylation of groups at the 7-dialkylamino functionality, reduction of the lactone moiety and overall photodecomposition of the dyes have been observed. Concentration quenching of dye fluorescence is important at concentrations above 0.01 M. The concentration dependence of photoreduction is shown to be consistent with a singlet self-quenching mechanism. Dye photodegradation is not quenched on addition of *trans*-stilbene, although the latter is an effective quencher of the triplet of 1. Intersystem crossing yields for the coumarin dyes are very low. A mechanism for dye photodegradation is proposed involving singlet self-quenching and net hydrogen atom transfer between dye molecules, followed by disproportionation and coupling of radicals.

Aminocoumarins are widely used in dye lasers for the blue—green region [1] despite problems of photodegradation [2, 3] which reduce service life and lasing efficiency. A number of reports have recently appeared involving the characteristics of dye solutions under conditions of flash-lamp pumping [4] and the effects of additives which inhibit photodegradation [5, 6]. We have investigated the mechanism of dye photodecomposition and wish to report here a number of unusual characteristics for three representative dyes (for previous papers in this series, see refs. 7 and 8). In particular, the self-quenching of dye fluorescence is measurable at moderate dye concentrations, despite the typically short singlet lifetimes (shorter than 5 ns). In addition, triplet photochemistry appears to be relatively unimportant for direct photolysis of the coumarins (for an example of rhodamine laser dye photochemistry involving bimolecular triplet reaction, see ref. 9), and a well-known electron transfer path involving tertiary amine moieties, which might have served as a model for photodecomposition, is likewise unsuitable.

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Lengthy irradiation of coumarins **1** (R ≡ CH$_3$), **2** (R ≡ CF$_3$) and **3** (mercury lamps; Pyrex filter; argon-purged solutions) results in loss of dye which can be followed spectrophotometrically:

1, 2   **3**
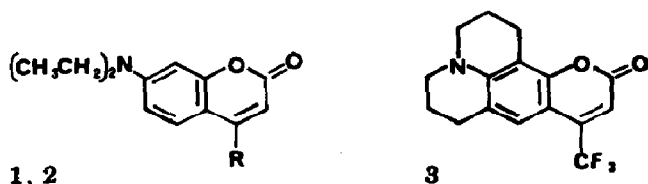
The filmy deposit which results is not readily characterized: nuclear magnetic resonance analysis of the progress of photolysis simply shows dye disappearance. For structures **1** and **2**, gas chromatograms (2 m 10% OV-101 column; 200 °C) reveal small amounts of at least two products which grow to very modest levels (generally less than 1%) and finally disappear. The monodealkylated coumarins **4** (R ≡ CH$_3$) [2] and **5** (R ≡ CF$_3$) as well as products of bis dealkylation could be identified by comparison with authentic samples:

4, 5
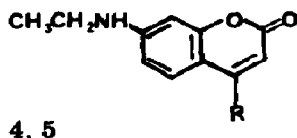
Another product originating from **1** could not be isolated but was identified by combined gas—liquid chromatography and mass spectrometry analysis as the reduced species **6**:
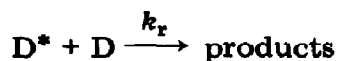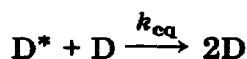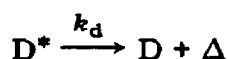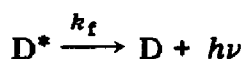

6
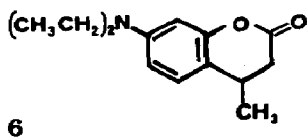
Major peaks for **6** were as follows: $m/e = 233$ (molecular ion); $m/e = 218$ (—CH$_3$); $m/e = 190$ (—CH$_3$, —CO or —C$_2$H$_4$); $m/e = 148$ (190 — CH$_2$CO). A product having $m/e = 205$ (molecular ion) corresponding to hydrogenated **4** was also observed in trace amounts. The formation of trace products as determined by gas—liquid chromatography analysis displayed erratic behavior at longer irradiation times. At the shortest times suitable for product detection, **6** was favored over **4** in the ratio of about 5:1 whereas this ratio was nearly reversed at intermediate irradiation periods. Photodecomposition, including formation of **4** and **5**, was observed in a variety of solvents including acetonitrile, toluene, chloroform and cyclohexane. Comparable efficiencies were generally observed; degradation was somewhat enhanced in chloroform but retarded in alcohols.

The triplet of **1** can be observed as an absorbing transient by flash photolysis [10]. Addition of *trans*-stilbene (0.06 M) serves to quench this triplet effectively but does not inhibit the photodecomposition of **1** to **4** and

6. The triplet was observed (xenon flash-lamp; pulse duration, approximately 30 μs full width at half-maximum; argon purge; λ_{max} = 625 nm [10]) to undergo first-order decay in acetonitrile which is dependent on [1]. The triplet self-quenching data revealed a unimolecular decay constant of 2.4 × 10^3 s^{-1} and a concentration quenching constant k = 1.3 × 10^8 M^{-1} s^{-1}, similar to the behavior of the triplet state of Michler's ketone (k = 1.25 × 10^8 M^{-1} s^{-1} in benzene [11]). In a polar medium the yield of triplet 1 is clearly low [10]. Using 1,3-cyclohexadiene as a triplet counter [12] we obtain values for triplet formation of 0.006 for 1 (ethanol) and less than 0.001 for 2 and 3 (for a discussion of coumarin triplet yields, see also ref. 13).

Anticipating a bimolecular singlet reaction, fluorescence quantum yields were measured as a function of dye concentration using the front-face illumination technique. Emission quenching was indeed readily observed in a relatively high concentration range (0.01 - 0.25 M) and analyzed according to the following model:

$$D \xrightarrow{h\nu} D^*$$

$$D^* \xrightarrow{k_f} D + h\nu$$

$$D^* \xrightarrow{k_d} D + \Delta$$

$$D^* + D \xrightarrow{k_{cq}} 2D$$

$$D^* + D \xrightarrow{k_r} \text{products}$$
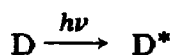
$$\frac{1}{\phi_f} = \frac{k_f + k_d}{k_f} + \frac{k_{cq} + k_r}{k_f}[D]$$

$$\frac{1}{\phi_r} = \frac{k_r + k_{cq}}{k_r} + \frac{k_d + k_f}{k_r}\frac{1}{[D]}$$

The relationships between the fluorescence yield ϕ_f, the photoreaction yield ϕ_r and the dye concentration are readily derived. Values for the sum of the self-quenching constants k_{cq} and k_r were calculated from the slopes of reciprocal quantum yield−concentration plots and are shown in Table 1 along with fluorescence yield and lifetime data obtained for very dilute dye solutions (less than or equal to 10^{-4} M) [7]. The trends in the rate of total self-quenching ($k_{cq} + k_r$) are modest but suggest a more favorable interaction between ground and excited state for dyes which support a larger dipole moment (2 and 3 over 1).

The photodegradation mechanism involving singlet self-quenching was fortified by measurement of the profile of quantum yield for conversion 1 → 6 as a function of [1] measured at very low conversion (less than or equal to 0.01%). A double-reciprocal plot provided an alternative source for the sum $k_{cq} + k_r$ = 7.8 × 10^8 M^{-1} s^{-1}, a value in reasonable agreement with

TABLE 1

Photophysical properties and singlet self-quenching rate data for coumarin dyes[a]

| Dye	Solvent	λ_f (nm)	ϕ_f	τ_f[b] (ns)	$k_{cq} + k_r$ ($\times 10^9$ M^{-1} s^{-1})
1	CHCl$_3$	421	1.01	(3.1)	1.1
	CH$_3$CN	434	1.03	3.4	2.9
	CH$_3$CH$_2$OH	451	0.73	3.1	4.5
2	CHCl$_3$	466	0.92	(4.6)	5.3
	CH$_3$CN	501	0.064	0.6	3.3
	CH$_3$CH$_2$OH	509	0.078	0.8	14.7
3	CHCl$_3$	483	0.80	(5.4)	3.5
	CH$_3$CN	521	0.56	5.6	17.0
	CH$_3$CH$_2$OH	531	0.38	3.4	6.9

[a] Fluorescence yield and lifetime data for acetonitrile and ethanol were taken from refs. 7 and 8.
[b] Lifetimes in chloroform were assumed to be similar to values measured for ethyl acetate solvent [7, 8].

the value obtained for fluorescence quenching in acetonitrile (Table 1). The limiting quantum yield $k_r/(k_r + k_{cq})$ for formation of 6 was 3×10^{-4}, indicating that the dominant result of self-quenching is return to ground state dye.

A reasonable mechanism which follows for dealkylation in polar media finds analogy in the bimolecular photochemistry of tertiary amine functions [14, 15]. The steps would include for the present dyes electron transfer self-quenching and proton transfer leading to free α-aminoalkyl radicals (e.g. 1) which lose a second electron, followed by hydrolysis of a resulting iminium or enamine function. The data for 1 and 2 do not support such a mechanistic route for amine fragmentation. Added water does not alter significantly the course of photolysis in acetonitrile (indeed, dealkylation occurs in all media), and acetaldehyde (expected from iminium hydrolysis [14]) was not observed as a byproduct. (Added acetaldehyde survived irradiation and did not quench dye photolysis.) Dealkylation is in fact inhibited with added methyl viologen (MV^{2+}; 3.0 mM), a well-known electron transfer quencher [16], even though flash photolysis of 1 (0.02 mM) and MV^{2+} in argon-purged water results in formation of the reduced viologen radical (λ_{max} = 395 nm and λ_{max} = 600 nm; half-life, a few milliseconds). In addition, electro-oxidation of 1 - 3 is reversible in acetonitrile, suggesting that successive electron and proton transfer processes which irreversibly destroy the dyes are unimportant. Oxidation in acetonitrile gave half-wave potentials of 1.09, 1.20 and 0.89 V with respect to a saturated calomel electrode (all quasi-reversible waves) from cyclic voltammetry. Reduction values were -2.2, -1.7 and -1.8 V (peak potentials; waves irreversible). Using singlet energies of 72 kcal mol^{-1}, 64 kcal mol^{-1} and 61 kcal mol^{-1} for 1, 2 and 3 respectively, the free-energy change for dye self-quenching via electron transfer can be calculated ($\Delta G = 0$ - 5 kcal mol^{-1}).

We favor a mechanism involving radicals 7 and 8 (R $\equiv$ CH$_3$ or CF$_3$) as suggested by von Trebra and Koch [5]:

7   8
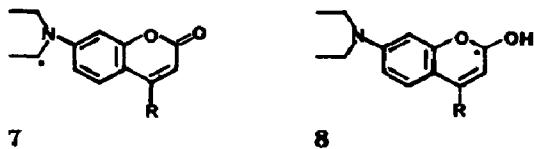
The origin of these species is a relatively slow and inefficient hydrogen atom transfer step (from the energetics above, in-cage successive electron–proton transfer leading to 7 and 8 cannot be ruled out), occurring within a singlet excimer intermediate obtained on dye self-quenching. Reduction product 6 results from disproportionation of 8, while 7 is permitted to participate in dealkylation or the induction of polymerization. Free radicals are not readily observed because of fast in-cage reaction of singlet radical pairs (most returning to native dye) which may include coupling to form aminol derivatives capable of rearrangement finally leading to dealkylation and other products. A role for radicals which reach bulk solution is clearly indicated by the inhibition of photolysis by thiols or sulfides (including incorporation of an isotopic label in the dye) [5] and the amine, 1,4-diazabicyclo[2.2.2]octane [6]. However, since monomeric or even dimeric products do not accumulate appreciably, the exact course of secondary steps is difficult to determine. An aminol coupling product has been proposed for the decomposition of Michler's ketone, by itself [17] and on reaction with benzophenone [18], and appearance of the requisite radicals is indicated in flash photolysis results [11, 18]. Suppan [19] has reported a concentration dependence for Michler's ketone analogous to the coumarins (bimolecular decomposition at higher concentrations) although the ketone triplet state is responsible for degradation in this case.

The relevance of our results to the problem of coumarin photodegradation *under lasing conditions* is not yet established. Wavelength and intensity dependences associated with pumping are entirely possible and, in fact, documented in part by Fletcher's measurements [4]. The photoproducts identified in the present study are not obviously deleterious (except as competitive absorbers of pump energy), but the continued implication of radical intermediates, which are most likely responsible for fragmentation, polymerization etc., merits further attention.

Acknowledgments

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