to Johnson Matthey, Inc., and Engelhard Industries for generous loans of palladium chloride.

**Registry No.** 1, 87993-70-2; 2, 90414-23-6; 3, 31666-74-7; 4, 90414-24-7; 5, 33111-55-6; 6 (isomer I), 90414-25-8; 6 (isomer II), 90527-94-9; 7 (isomer I), 41529-00-4; 7 (isomer II), 41529-00-4; 9, 90414-26-9; 10, 31886-52-9; 11, 87993-71-3; 12, 12112-73-1; 13, 90414-27-0; 14, 90414-28-1; $C_6H_5HgCl$, 100-56-1; $CH_3O_2CHgCl$, 17261-26-6; $CH_3HgCl$, 115-09-3; $CH_3CH_2HgCl$, 107-27-7; $H_2C{=}CHCH_2CH{=}CH_2$, 591-93-5; *trans*-$H_2C{=}CHCH_2CH{=}CHCH_3$, 7319-00-8; $H_2C{=}CHCH_2C(CH_3){=}CH_2$, 763-30-4; $H_2C{=}CHCH(CH_3)CH{=}CH_2$, 1115-08-8; $H_2C{=}C(CH_3)CH_2C(CH_3){=}CH_2$, 4161-65-3; $H_2C{=}CH(CH_2)_2CH{=}CH_2$, 592-42-7; $H_2C{=}CH(CH_2)_3CH{=}CH_2$, 3070-53-9; $H_2C{=}CH(CH_2)_4CH{=}CH_2$, 3710-30-3; $Li_2PdCl_4$, 15525-45-8; *trans*-1-phenyl-1,5-hexadiene, 56644-04-3; 1,4-cyclohexadiene, 628-41-1.

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# Electron Donor-Acceptor Quenching and Photoinduced Electron Transfer for Coumarin Dyes

Guilford Jones, II,* Susan F. Griffin, Chol-yoo Choi, and William R. Bergmark[1]

*Department of Chemistry, Boston University, Boston, Massachusetts 02215*

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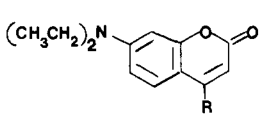
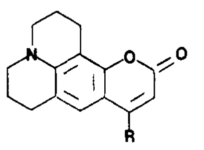
The fluorescence of 7-aminocoumarins is quenched by a variety of organic electron donors or acceptors in acetonitrile. In general, donors with half-wave oxidation potentials less positive than 1.0 V vs. SCE and acceptors with reduction potentials less negative than −1.5 V vs. SCE are candidates for diffusion limited quenching of coumarin singlet states. Profiles of quenching rates are consistent with calculated free energies for electron transfer between excited coumarins and donors or acceptors. In flash photolysis experiments electron transfer for several dyes and quenchers (e.g., methyl viologen) is demonstrated. Relatively low yields of net electron transfer are consistently obtained due to inefficient ionic photodissociation via singlet quenching or a low yield of more photoactive coumarin triplets. Electrochemical properties of the coumarins have been investigated by cyclic voltammetry with the indications of reversible oxidation and irreversible reduction as important processes.

The 7-aminocoumarins (e.g., 1–5) constitute an important class of organic dyes which lase[2] and which in some circumstances may act as photosensitizers.[3,4] These structures are also related to the furocoumarins which have received much attention due to their photobiological properties.[5] In previous papers in this series, photophysical and photochemical properties for coumarin dyes have been reported with particular attention given to the pronounced medium dependences of spectral properties and emission yields associated with the highly polar coumarin excited states (nominally depicted by 6).[6] Other recent investigations have been directed to the mechanism of coumarin photodegradation,[7] the behavior of coumarin dyes in water and in aqueous detergent media,[8] and the effects of medium and additives on photostability and emission yield under lasing conditions.[9-11]



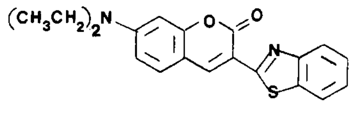
1, R = $CH_3$

2, R = $CF_3$

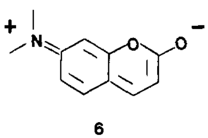


3, R = $CH_3$

4, R = $CF_3$



5



6

Table I. Absorption and Emission Properties of Coumarin Dyes in Acetonitrile

| | $\lambda_a$[a] | $\lambda_f$[a] | $\tau_f$,[b] ns |
|---|---|---|---|
| 1 | 367 | 434 | 2.8 |
| 2 | 396 | 501 | 0.60 |
| 3 | 380 | 451 | 2.8 |
| 4 | 418 | 521 | 4.6 |
| 5 | 454 | 501 | (3.1)[c] |

[a] Absorption ($\lambda_a$) and emission ($\lambda_f$) maxima in nm. [b] Fluorescence lifetimes reported for $N_2$- or Ar-purged solutions (ref 6) corrected for fluorescence quenching by $O_2$ in air-saturated solutions (ref 6c). [c] Obtained from dimethylaniline quenching results (see text).

The coumarin dyes give rise to strong, broad absorption bands extending into the visible accompanied by solvent dependent red shifts in emission indicative of an emissive state having a large dipole moment (i.e., 6). The interaction of such excited species with added quenchers has not been studied in detail although coumarin singlet[6c,12]

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[1] On sabbatical leave from Ithaca College, Ithaca, NY.

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**Table II. Redox Potentials for Coumarin Dyes from Cyclic Voltammetry**

| | $E_{ox}$ (V vs. SCE)[a] | $E_{red}$ (V vs. SCE)[b] |
|---|---|---|
| **1** | 1.09 | −2.2 |
| **2** | 1.20 | −1.8 |
| **3** | 0.72 | <−2.3 |
| **4** | 0.89 | −1.8 |
| **5** | 1.02 | −1.5 |

[a] Oxidation potentials from reversible waves calculated as $[E_p(\mathrm{ox}) + E_p(\mathrm{red})]/2$ ($CH_3CN$ solvent). [b] Reduction (peak) potentials from irreversible waves ($CH_3CN$).

**Table III. Electron Donor or Acceptor Quenchers[a]**

| electron donor | $E_{ox}$ | electron acceptor | $E_{red}$ |
|---|---|---|---|
| diethylamine (DEA) | 2.2 | dimethyl maleate (DMM) | −1.6 |
| triethylamine (TEA) | 1.1 | *p*-dicyanobenzene (DCB) | −1.7 |
| dimethylaniline (DMA) | 0.73 | fumaronitrile (FUM) | −1.3 |
| | | methyl viologen (MV) | −0.69 |

[a] Redox potentials = half-wave potentials from polarography or cyclic voltammetry of quenchers in acetonitrile (ref 17). Potentials in V vs. SCE.

and triplet[13] quenching by oxygen have been reported. Our expectation was that the internal combination of donor and acceptor groups for the aminocoumarins would activate the intramolecular charge-transfer state toward quenching by both reducing and oxidizing agents. This feature would in turn dictate to a significant degree the bimolecular photochemistry displayed by coumarin dyes and also prescribe the types of reagents that might be suitable as additives to dye solutions (agents that might insure photostability). We report here the behavior of representative aminocoumarins toward electron-transfer agents in acetonitrile, the detection of products resulting from photoinduced electron transfer, and related electrochemistry for the dyes.

## Results and Discussion

**Coumarin Dye Properties: Cyclic Voltammetry.** Absorption and fluorescence emission data for dyes **1–5** are shown in Table I along with fluorescence lifetimes appropriate for air-saturated acetonitrile solutions at room temperature. In Table II are included values for oxidation and reduction potentials for the dyes obtained by cyclic voltammetry[14] for acetonitrile solutions. The electrochemical oxidations were characterized by relatively clean forward and return waves with 60–100 mV peak to peak separation consistent with quasi-reversible behavior.[15] The dyes were somewhat more difficultly reduced (a peak potential could not be measured for **3**) and reduction return waves were not observed. Due to the irreversibility of reduction of the dyes in acetonitrile, peak potentials which varied somewhat according to scan rate (100–500 mV/s) represent rough approximations to the thermodynamic reduction potentials.

The substituent influences for dye reduction and oxidation are readily apparent in terms of the lactone moiety and other groups such as $CF_3$ providing a retarding influence on oxidation (relative to dialkylanilines for which $E_{ox}$ = ca. 0.7 V vs. SCE[17]). Alkyl substitution at the aniline ring provides for greater ease of oxidation whereas the series is less readily reduced due to these electron-donating influences (relative to unsubstituted coumarin for which $E_{red} = -1.4$ V vs. SCE[16]).

**Table IV. Fluorescence Quenching Data for Coumarins and Electron Donors**

| dye | quencher | $k_q\tau$, $M^{-1}$ | $k_q$ ($\times 10^{-9}$ $M^{-1}$ $s^{-1}$) | $\Delta G_{et}$[a] |
|---|---|---|---|---|
| **1** | DMA | 27 | 9.7 | −4.6 |
| **2** | DEA | <0.10 | <0.17 | 28 |
| | TEA | 1.5 | 2.5 | 4.0 |
| | DMA | 11 | 18 | −5.7 |
| **3** | DMA | 6.7 | 2.4 | >−1.2 |
| **4** | DMA | 50 | 11 | −4.6 |
| **5** | DMA | 31 | (10) | −8.3 |

[a] Free energy change for electron transfer (kcal/mol) calculated by using the Weller equation (see text).

**Table V. Fluorescence Quenching Data for Coumarins and Electron Acceptors**

| dye | quencher | $k_q\tau$, $M^{-1}$ | $k_q$ ($\times 10^{-9}$ $M^{-1}$ $s^{-1}$) | $\Delta G_{et}$[a] |
|---|---|---|---|---|
| **1** | FUM | 29 | 8.7 | −17 |
| | MV[b] | 81 | 29 | −31 |
| **2** | FUM | 3.5 | 5.8 | −6.8 |
| **3** | FUM | 66 | 24 | −23 |
| **4** | FUM | 25 | 5.4 | −11 |
| **5** | DCB | <0.2 | <0.06 | 2.2 |
| | DMM | 0.6 | 0.2 | 0.8 |
| | FUM | 31 | 9.7 | −6.8 |

[a] Free energy change for electron transfer (kcal/mol) calculated by using the Weller equations (see text). [b] Quenching results for 85% $CH_3CN/H_2O$, assuming $\tau_f(1) = 2.8$ ns, the value for $CH_3CN$ (Table I).

**Singlet Quenching by Electron Donors and Acceptors.** The selection of potential quenchers of dye fluorescence is shown in Table III along with the appropriate electrochemical data which reflect their relative strengths as oxidizing or reducing agents in acetonitrile. The results of Stern–Volmer analysis of steady-state emission quenching by the electron donor amines are assembled in Table IV. DMA is sufficiently potent to quench the fluorescent state of three of the dyes (**1**, **2**, and **4**) at rates which approach the diffusion controlled limit (ca. 2–3 × $10^{10}$ $M^{-1}$ $s^{-1}$).[18] The exception involves the least readily reduced dye, **3**, for which a diminished rate is observed. Consistent with this indication of dominant donor–acceptor influence is the trend established for quenching **2** fluorescence in which rate constants fall in a regular fashion according to amine oxidation potential. If a near diffusion limited value for $k_q$ is supplied for DMA quenching of **5**, a quite reasonable value for the lifetime of emission for this dye (not presently available from photon counting measurements) is obtained (Table I).

A similar series of quenching data involving various electron acceptors is reproduced in Table V. Again, one common quencher, FUM, is successful in sequestering coumarin singlets at a high rate. A more potent acceptor, the 1,1′-dimethyl-4,4′-bipyridinium dication (methyl viologen, MV), which required for solubility considerations a mixed aqueous medium, is somewhat more successful in quenching **1** fluorescence (reaching the diffusion limited rate). When less effective oxidizing quenchers are inspected for **5**, fall off of the quenching constants is again observed, consistent with a diminished quencher reduction potential.

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(18) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker, Inc.: New York, 1973; p 55.

Quenching data may be analyzed using the Weller equation,[19]

$$\Delta G_{\text{et}} = E_{\text{ox}} - E_{\text{red}} - E_{00} - C$$

with which the free energy change for an encounter pair undergoing electron transfer is computed by using redox potentials (converted to energies), the excitation energy of the excited state participating in quenching ($E_{00}$, for coumarin singlets, computed from absorption and emission curves), and a coulombic term, $C$, usually assumed to value ca. 0.1 eV for acetonitrile solvent.

Computed free energies are provided in Tables IV and V. The "rule of thumb"[19] which suggests that near diffusion limited quenching behavior is observed in bimolecular quenching via electron transfer when $\Delta G_{\text{et}} \leq -5.0$ kcal/mol is again valid for the coumarin quenching data. The pattern of free energy dependence shown by the data for **2** and **5** reflects a diminution in quenching constant of about one order of magnitude for each reduction in electron-transfer exothermicity of 5–10 kcal/mol. A similar dependence for organic donors and acceptors in excited-state quenching has been found in a variety of other systems.[20,21]

**Triplet Quenching. Flash Photolysis.** The coumarins in combination with several quenchers were subjected to flash irradiation with conventional equipment (Xenon flash lamp, 35 μs fwhm). Under conditions where quencher concentrations dictated that coumarin singlets were substantially quenched (from Stern–Volmer analyses, vide supra), transients were not generally observed in the 450–700 nm range (100 μs/100 ms regime). Such combinations included **1** and **2** with DMA and FUM. Spectra for coumarin radical–ions have not yet been reported, but transients such as $DMA^+$ ($\lambda_{\max}$ 500 nm)[22] are readily observed. The failure of singlet quenching in providing even moderate yields of radical–ions in bulk solution is consistent with a number of recent findings which show that the fate of singlet radical–ion pairs resulting from exothermic electron-transfer quenching is predominantly in-cage recombination.[23,24]

The search for electron-transfer products from quenching was combined with the detection of triplet–triplet absorption for two of the dyes. For **1** alone in acetonitrile or in 85% acetonitrile/water, a transient with $\lambda_{\max}$ at 600–625 nm was observed and assigned to the coumarin triplet which has been detected previously.[7,13,25] The triplet of **1**, which showed a first-order decay and a lifetime of 120–180 μs (several runs) in acetonitrile could be completely quenched by 1.0 mM FUM (where singlet quenching is not important). In this experiment the 600-nm transient is not replaced by another absorbing species in the 400–700 nm region (the FUM radical–anion absorbs at 350 nm,[26] an area obscured by dye bleaching and recovery). DMA (1.0 mM), on the other hand, is not successful in intercepting triplet **1**. Both of these results are consistent with electron-transfer quenching by FUM, but not by DMA, if the energetics of Tables IV and V are modified by reducing the exothermicity of electron transfer by ca. 10 kcal/mol, the estimated difference in singlet and triplet energies for similar dyes as shown by recent spectroscopic measurements.[3,27]

**Table VI. Transient Absorption on Flash Photolysis of 1 and 5 with MV**[a]

| | [MV], mM | $A_{600}$ | $\tau_{1/2}$, ms | assignment |
|---|---|---|---|---|
| **1** | | 0.28 | 0.16 | triplet **1** |
| | 0.02 | 0.25 | 1.3 | MV radical–ion |
| | 4.0 | 0.57 | 4.8 | MV radical–ion |
| | 10.0 | 0.67 | 1.3 | MV radical–ion |
| **5** | | 0.02 | 0.3 | triplet **5** |
| | 0.04 | 0.65 | 1.4 | MV radical–ion |

[a] Absorbances recorded at 600 nm, 100 μs after flash (argon-purged 85% v/v $CH_3CH/H_2O$).

Exceptions to the general pattern of negligible reactivity (net electron transfer) were encountered for the acceptor quencher, MV.[28] Flash photolysis of **1** and **5** was examined in some detail under conditions appropriate for quenching by MV of dye singlets or triplets. A transient similar to triplet **1** was observed on flash irradiation in the presence of MV (Table VI). The absorption maximum was again at about 600 nm, consistent with formation of the reduced species $MV^+$.[28] (The other well characterized absorption of $MV^+$ at 395 nm is obscured by strong absorption by the dye in that region.) That this transient observed with added MV is clearly a species other than the dye triplet is indicated by the extended decay time (millisecond range) which is more consistent with the appearance of a radical–ion. Decay data for the presumed $MV^+$ intermediate (reduced MV) did not uniformly obey first- or second-order kinetics and decay times (reported as half-lives, Table VI) varied somewhat from run to run and were sensitive to sample preparation (Ar purging).

The dependence of yield of electron transfer was inspected for **1** as a function of MV concentration in acetonitrile/water. A moderate increase in maximum absorbances (Table VI) recorded at about 100 μs following the lamp flash (prior to the onset of significant decay) is noted for increased concentrations of MV. Absolute values for electron-transfer yield were not determined but were clearly quite low, as suggested by data for viologen quenching in other well characterized systems.[28,29] The relative yields reported here are consistent with an inefficient photoinduced electron transfer for coumarin singlet quenching (vide supra). A more robust reaction is apparent for the coumarin triplet whose yield in the absence of quencher (via intersystem crossing) is known to be very low (<1% for **1** in acetonitrile).[8] Concentrations of MV = 4.0 and 10.0 mM correspond to 20% and 40% singlet quenching, respectively.

Electron transfer involving **5** and methyl viologen appears also to be important (Table VI). Yields of electron transfer for **1** and **5** appear similar but the comparison is complicated since triplet yields (or triplet extinction

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[24] We cannot exclude the appearance of transients which are short-lived (<100 μs), have small extinction coefficients, or have overlapping absorption with native dye.

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[27] Quenching of triplets of **1** by energy transfer to FUM cannot be ruled out. The FUM triplet energy has been placed at 59 kcal/mol; a value similar to that expected[3] for **1**: Weng, P. G. *Can. J. Chem.* **1982**, *60*, 339.

[28] For a review of data concerning electron transfer to MV, see: Kalyanasundaram, *Coord. Chem. Rev.* **1982**, 159.

[29] In a crude comparison (where absorbances cannot be exactly matched) the well characterized system, ruthenium(II) trisbipyridyl and MV in $H_2O$, $\phi_{\text{et}} = 0.2$–$0.3$,[28] produces on flash photolysis the viologen radical in a yield at least 10-fold greater than the system **1**/MV in acetonitrile/water.

coefficients) for both dyes are not known.[30,31]

In summary, the quenching of the fluorescence of coumarin laser dyes by a variety of electron donors and acceptors has been observed. Net electron transfer is not a dominant path for donor-acceptor quenching, although the photoreduction of methyl viologen on quenching of dye singlets or triplets is confirmed by flash photolysis results. The ranges of oxidation and reduction potential for additives which will diminish the fluorescence of several representative coumarin dyes have been established.

## Experimental Section

**Materials.** Dyes **1**–**5** were laser grade materials obtained from Eastman Kodak Co. (coumarins 1, 35, 102, 153, and 6, respectively). The dyes were checked for purity by TLC (silica, ethyl acetate/hexane) and in most cases used as received. Several of the commercial samples were recrystallized from heptane or methanol/water. The amine quenchers and DMM were distilled prior to use; DMA was dried by addition of lithium aluminum hydride under nitrogen prior to distillation under reduced pressure (20 torr). FUM was recrystallized three times from hexane/chloroform and DCB and MV (chloride salt) were recrystallized twice from methanol. Solvents employed were spectroquality acetonitrile used as received and triply distilled water.

**Fluorescence Quenching.** Dye emission was recorded on a Perkin-Elmer MPF-44A fluorimeter equipped with a spectrum correction unit and quartz cells. Solutions of $10^{-5}$ M dye were excited at the absorption maximum and the fluorescence intensity (at $\lambda_{max}$) recorded as a function of added quencher (samples were air saturated). No changes were recorded in the emission maximum or in the dye absorption profile as the result of addition of quencher. Intensity changes were plotted vs. quencher concentration by using the Stern-Volmer equation, $I_0/I = 1 + k_q\tau$ [Q]. Linear regression analysis ($r = \geq 0.98$) provided slopes ($k_q\tau$ values) and intercepts (typically 1.00 ± 0.02).

**Triplet Quenching. Flash Photolysis.** Flash photolysis apparatus which consisted of a Xenon flash lamp with ca. 35 μs duration (fwhm) and a 22-cm Pyrex cell has been described previously.[31] Argon-purged solutions of ca. $10^{-5}$ M dye were employed. Photographs of oscilloscope traces were obtained to record percent transmission values which were converted to transient absorbance. For measurement of relative yield of transients, absorbance values were recorded at their maximum at the shortest practical times following lamp discharge (usually 100 μs following the flash).

**Cyclic Voltammetry.** Current-voltage curves were obtained for 10 mM dye in reagent grade (wet) acetonitrile with 0.1 M tetraethylammonium perchlorate (TEAP) or 0.1 M $LiClO_4$ supporting electrolyte with a Bioanalytical Systems potentiostat. Other conditions included working electrode (Au or Pt), reference electrode (Ag, $AgNO_3$ (0.01 M)), auxiliary electrode (Pt), and operating temperature (22 °C).

**Acknowledgment.** This work was supported by the Office of Naval Research. We thank also Drs. W. R. Jackson and S. Kanoktanaporn for technical assistance, and Professors M. Z. Hoffman and M. F. Delaney for the loan of equipment.

**Registry No.** **1**, 91-44-1; **2**, 41934-47-8; **3**, 41267-76-9; **4**, 53518-18-6; **5**, 38215-36-0; DEA, 109-89-7; TEA, 121-44-8; DMA, 121-69-7; DMM, 624-48-6; DCB, 623-26-7; FUM, 764-42-1; MV, 1910-42-5.

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[30] Dempster el al.[25] report $\epsilon$ = 19 000 ± 2000 $M^{-1}$ $cm^{-1}$ for triplet **1** in ethanol, also to be compared with a value of 14 000 $M^{-1}$ $cm^{-1}$ for MV in water. A weak transient ($\lambda_{max}$ ~500 nm) can be observed on quenching **5** with DMA in acetonitrile. This absorption is much like that of the DMA radical-cation.[22]

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# Rauwolfia Alkaloid Synthesis Approach Employing the Zwitterionic Amino-Claisen Rearrangement. Improvements in the Efficiency for Yohimbane Ring Construction and Unambiguous DE-Ring-Fusion Stereochemical Assignments

Shouchung Chao, Fen-Ann Kunng, Jia-Ming Gu, Herman L. Ammon, and Patrick S. Mariano*

*Department of Chemistry, University of Maryland, College Park, Maryland 20742*

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A high yielding method for inducing amino-Claisen rearrangement of the *tert*-butyl propiolate *N*-tryptophylisoquinuclidene **1** system to form the *N*-tryptophylisoquinoline **6** has been found. Accordingly, reaction of **1** with the acetylene ester in refluxing $CH_3CN$ generates **6** in a 65% yield in contrast to earlier results which had suggested that the above reaction fails; causes for the variable success are proposed. Isoquinoline **6** is smoothly (75%) transformed to the C-3 epimeric yohimbanes **8** and **9**. Spectroscopic and X-ray crystallographic data are presented to support the assignments of stereochemistry to **8** and **9** and conformational preferences as **8A** and **9A**.

In a recent publication,[1] we have described the results of our investigations of a new version of the amino-Claisen rearrangement of *N*-vinylisoquinuclidene systems.[2] In particular, we have pointed out how reactions of *N*-tryptophylisoquinuclidenes **1** and **2** with propiolate esters proceed to generate the *N*-tryptophylhydroisoquinolines **4** and **5** via zwitterionic intermediates **3**. Further studies with the hydroisoquinoline **4** have demonstrated that the base-induced, Wenkert[3] cyclization process, e.g., **4** → **7**, can be used to generate substances (H-3 α and β) possessing pentacyclic yohimbane skeletons. Lastly, this exploration has provided results which authenticate the viability of

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