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The Effect of "Chemiluminescence Quenching" on the Chemiluminescence Quantum Yields from 9-Benzylacridine and 9-Benzyl-10-methylacridinium Iodide

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Synopsis. A visible chemiluminescence (CL) has been found from the air oxidation of 9-benzyl-10-methylacridinium iodide, in contrast to the case of 9-benzylacridine, from which only a feeble CL could be detected. The difference in the CL quantum yields from the acridinium salt and acridine is interpreted in terms of a "CL quenching" of the chemiexcited species by benzaldehyde generated simultaneously in a solvent cage.

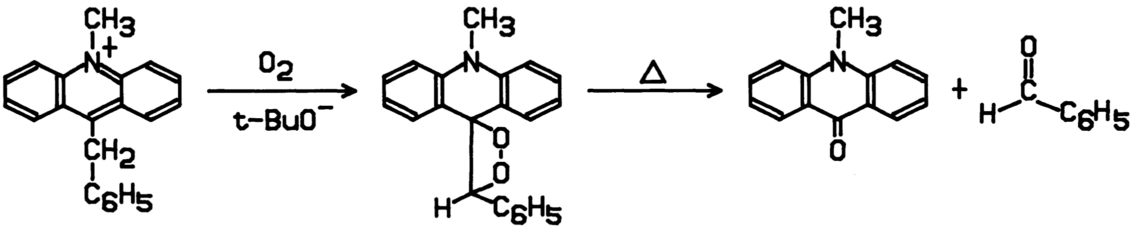
We have found a visible chemiluminescence (CL) of 9-benzyl-10-methylacridinium iodide¹⁾ (**1**) upon base-catalyzed air oxidation: a solution of potassium *t*-butoxide (*t*-BuOK) in *t*-butyl alcohol (*t*-BuOH) (2×10^{-2} mol dm^{-3}, 0.2 cm^3) was added to an aerated solution of **1** in *N*,*N*-dimethylformamide (DMF) (1.0×10^{-4} mol dm^{-3}, 2.0 cm^3) at 313 K. The CL emission with a peak at 415 nm showed the same spectral distribution as that of the fluorescence of 10-methylacridone (**3**) and the spent reaction mixture. Benzaldehyde was detected as one of the reaction products by gas chromatography. The overall CL quantum yield was determined to be 2.5×10^{-3}. The reaction pathway involving the cleavage of 10-methyl-4′-phenylspiro[acridine-9(10*H*),3′-[1,2]-dioxetane] **2** shown in Scheme 1 seems most probable for the CL of **1**, since **2** is known to give singlet, excited 10-methylacridone (**3***), together with benzaldehyde, on decomposition.²⁾ In a previous paper,³⁾ a similar reaction pathway via the cleavage of a dioxetane intermediate **5** to give excited singlet acridone anion (**6***), shown as Scheme 2, was presented as the mechanism⁴⁾ for the CL of 9-alkylacridines. Among these, 9-methylacridine (**4c**) produced the excited product **6*** in a relatively high CL quantum yield (6.3×10^{-3}), while 9-benzylacridine (**4a**) and 9-(diphenylmethyl)acridine (**4b**) produced **6*** in extremely low yields (1.5×10^{-6} and 1.1×10^{-5} respectively), in spite of the high yield of unexcited acridone anion (**6**). Thence, there remained the problem of why the CL quantum yields from **4a** and **4b** are far lower than those from **4c** and **1**.

Recently, Perkizas and Nikokavouras⁵⁾ have proposed a "CL quenching" process of an excited moiety by the simultaneously produced leaving moiety in a solvent cage: an efficient quenching would arise through molecular collision inside the solvent cage if the quenching probability per collision were great. This paper will present some experimental results giving support to the idea that the low CL quantum yields from **4a** and **4b** are due to a CL quenching.

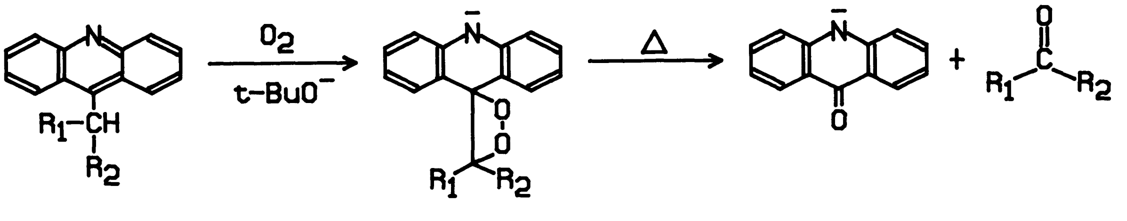
When the CL quenching arises through the collision of two moieties produced inside a solvent cage, the apparent CL quantum yield (Φ) is given approximately by the following equation:

$$\Phi = \Phi^\circ k_{-\mathrm{d}}/(k_{-\mathrm{d}} + k_{\mathrm{e}})$$

where Φ° is the proper CL quantum yield, obtained as the product of the yield of the excited product from the substrate and the fluorescence quantum yield of the



Scheme 1.



Scheme 2.

excited product, k_{-d} is the rate constant of the moieties to get out of the cage, and k_e is the rate constant for energy transfer by collision.

The Stern–Volmer constant (K_{sv}) for the quenching is given by the following convenient equation:

$$K_{sv} = (I_0/I - 1)/[\mathrm{Q}] = k_q \tau$$

where I_0 and I are the fluorescence intensities of an excited species in the absence and in the presence of a quencher Q at a given concentration [Q], k_q is the quenching rate constant, and τ is the lifetime of the excited species in the absence of Q. When the quenching arises via a diffusion controlled encounter in a solvent cage, k_q is given approximately by the following equation:

$$k_q = k_d k_e/(k_e + k_{-d}) = k_d p$$

where k_d is the rate constant for the molecular diffusion in the fluid solution and p is the quenching probability per encounter. Thus, Φ is given by:

$$\Phi = \Phi^\circ(1 - k_q/k_d) = \Phi^\circ(1 - p)$$

If the two CL systems, I and II, are assumed to posses similar k_d and Φ°, the following relation is established:

$$\Phi(\mathrm{I})/\{1 - p(\mathrm{I})\} = \Phi(\mathrm{II})/\{1 - p(\mathrm{II})\} = \Phi^\circ$$

Thus, the effect of the CL quenching on the CL quantum yield can be interpreted by taking account of the value of p ($=k_q/k_d$) obtained from the Stern–Volmer analysis.

The plot of $I_0/I-1$ versus [Q] for the quenching of **3*** and **6*** by benzaldehyde and of **6*** by benzophenone in DMF solutions containing *t*-BuOK and *t*-BuOH at 313 K were determined; the slopes of the lines gave the values of $K_{sv}(\mathbf{1})=10.3$, $K_{sv}(\mathbf{4a})=145$, and $K_{sv}(\mathbf{4b})=144$ $\mathrm{dm^3\,mol^{-1}}$.[6] From the values of K_{sv} and τ (7.6×10^{-9} s)[7,8], $k_q(\mathbf{1})$, $k_q(\mathbf{4a})$, and $k_q(\mathbf{4b})$ were calculated to be 1.4×10^9, 1.9×10^{10} and 1.9×10^{10} $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ respectively.

These experimental values give the following relation:

$$\begin{aligned}1.5\times10^{-6}/\{1 - p(\mathbf{4a})\} &= 1.1\times10^{-5}/\{1 - p(\mathbf{4b})\}\\ &= 2.5\times10^{-3}/\{1 - p(\mathbf{1})\} = \Phi^\circ\end{aligned}$$

Since $\Phi^\circ \geqq 2.5\times10^{-3}$, the values of $1-p(\mathbf{4a})$ and $1-p(\mathbf{4b})$ might be very small, indicating that $k_d \sim k_q(\mathbf{4a}) \sim k_q(\mathbf{4b}) \sim 1.9\times10^{10}$ $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$, though the value is somewhat larger than that calculated by the use of $k_d=8RT/3\eta$.[9] Taking $k_d=1.90\times10^{10}$ $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$, a large value of $1-p(\mathbf{1})$ is obtained by the following calculation:

$$1 - p(\mathbf{1}) = 1 - 1.4\times10^9/1.9\times10^{10} = 0.93$$

It is, therefore, reasonable to conclude that an efficient CL quenching arises in the CL system of **4a** and **4b** because of the extremely low value of $1-k_q/k_d$ whereas no remarkable CL quenching occurs in the CL of **1** because of the large value of $1-k_q/k_d$.

No appreciable quenching of **6*** by formaldehyde[10] was observed. Thence, the much higher CL quantum yield from **4c** than from the analogues seems to be attributable to the absence of "CL quenching".

Experimental

Materials. The 10-methyl-9(10*H*)-acridone (Aldrich) and 9(10*H*)-acridone (Tokyo Kasei) were chromatographically pure. The luminol was recrystallized from dilute hydrochloric acid prior to use. The benzaldehyde and benzophenone were purified by distillation prior to use.

Measurement of CL and Fluorescence. The intensity and spectrum of CL were measured on a Opelecs CLS-1 chemiluminescence spectrophotometer equipped with a R446 photomultiplier and 1200/mm grating. The overall CL quantum yield, defined as (total light per unit volume)/(the initial concentration of the substrate), was determined from the ratio of the total light emitted from the CL of the substrate to that from a standard luminol solution in the same way as has been described previously.[3] The fluorescence spectrum was measured on a Hitachi MPF-2A fluorescence spectrophotometer.

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3) I. Kamiya, T. Sugimoto, and K. Yamabe, *Bull. Chem. Soc. Jpn.*, **57**, 1735 (1984).

4) An analogous mechanism was proposed by E. H. White and M. J. Harding in *Photochem. Photobiol.*, **4**, 1129 (1965).

5) G. Perkizas and J. Nikokavouras, *Monatsh. Chem.*, **117**, 89 (1986).

6) For the quenching of **3*** by benzaldehyde, we use the symbol $K_{sv}(\mathbf{1})$, since **3*** and benzaldehyde are produced from **1**. Similarly, $K_{sv}(\mathbf{4a})$ and $K_{sv}(\mathbf{4b})$ are used to symbolize the quenching of **6*** by benzaldehyde and benzophenone respectively.

7) Since the values of τ of **3*** and **6***, as determined on a nano-second fluorimeter equipped with a Lomonics TE-type XeCl Laser (excited at 308 nm), were both ca. 1×10^{-8} s, the value (7.6×10^{-9} s) in the literature[8] was employed for the calculation of k_q.

8) K. D. Legg and D. M. Hercules, *J. Am. Chem. Soc.*, **91**, 1902 (1969).

9) The viscosity of DMF containing *t*-BuOK and *t*-BuOH was determined to be 6.6×10^{-4} $\mathrm{kg\,m^{-1}\,s^{-1}}$ at 313 K. Using the value, k_d was calculated to be 1.1×10^{10} $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$.

10) A solution of formaldehyde in DMF (ca. 0.5 $\mathrm{mol\,dm^{-3}}$, 0.2 $\mathrm{cm^3}$), prepared by dissolving gaseous formaldehyde (*Org. Synth.*, Coll. Vol. 1, p. 80), was added to 2.0 $\mathrm{cm^3}$ of a solution of acridone anion or 10-methylacridone in DMF containing *t*-BuOK.