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CHEMILUMINESCENCE OF 9-METHYLENEACRIDANS IN MICELLAR AND MEMBRANOUS SYSTEMS

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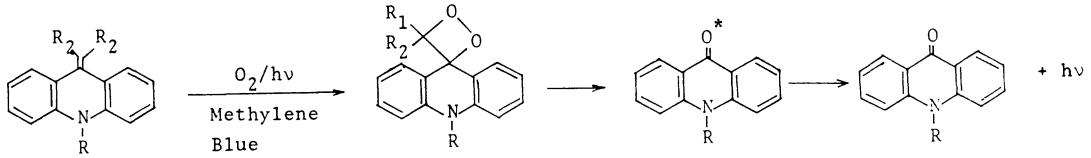
Chemiluminescence of a 1,2-dioxetane derived from 9-methylene-10-dodecylacridan was not detected in aqueous solution but was detected in micellar and membranous systems. The quantum yield and the rate of the chemiluminescence decay in the membranous ($2C_{16}15G$ and $2C_{16}30G$) system were affected by the chain melting transition. The results indicate that the chemiluminescence is sensitively affected by the microenvironmental effect.

Recently, chemically initiated electron exchange luminescence(CIEEL) was proposed as a general mechanism of chemi- and bioluminescence of 1,2-dioxetanes and related compounds.[1-3] One of the most widely investigated molecules is a dioxetane family derived from 9-alkylidene-10-methylacridans.[4-6] Decompositions by the CIEEL mechanism of the dioxetanes are characterized by the high yields of the excited singlet state of 10-methylacridone which is principally associated with the luminescent phenomenon.



In contrast to the versatility of the fluorescent phenomenon as a probe to estimate microscopic reaction environments, almost nothing is known as to the influence of environments on the luminescent phenomenon. To our knowledge, only one example — chemiluminescence of luciferin in a micellar system — has been reported by Goto and Fukatsu.[7] In order to test whether the microenvironmental effect might be responsible for the quantum yield, we measured the chemiluminescence of 1,2-dioxetanes derived from 9-methylene-10-methylacridan (MMA: R = Me, $R_1 = R_2 = H$) and 9-methylene-10-dodecylacridan (MDA: $R = C_{12}H_{25}$, $R_1 = R_2 = H$) in the micellar and membranous systems.

9-Methyl-10-methylacridinium methosulfate (or 9-methyl-10-dodecylacridinium

iodide: 1.0×10^{-3} M) in 2 ml of dry DMF was mixed with potassium t-butoxide (5.0×10^{-4} M) in 4 ml of dry DMF. After 30 min at room temperature, an O_2-stream was introduced into the solution for 10 min. After mixing with Methylene Blue (1.2×10^{-5} M) in 2 ml of dry DMF, the photooxygenation was carried out by irradiating the solution through a 530 nm shorter-wavelength cutoff filter with a 200 W tungsten lamp. An aliquot was withdrawn from the solution and rapidly mixed with the reaction solution in a measurement cuvette. The quantum yields of light emission were determined by comparing the areas under the chemiluminescent decays with similar curves obtained from the standardized luminol-hemin-H_2O_2 reaction run[8] in exactly the same geometry and were corrected for the yield of the acridones determined by fluorescence spectroscopy after the reactions.[9]

Prior to the investigation on the chemiluminescence, we measured fluorescence spectra of 10-dodecylacridone in various media. The relative intensity(R.I.) of the emission maximum (419 nm in DMF, 434 nm in water, and 428 nm in aqueous surfactants) is plotted as a function of the medium temperature in Fig. 1. The R.I. values in water (4.8 ± 0.1 at 22～48°C: data not shown in Fig. 1) were much smaller than those in DMF (73.9～42.5 at 15～52°C). Figure 1 shows that R.I. in DMF and aqueous micelle (Brij-35) changed linearly with temperature, whereas that in the presence of membranous surfactants ($2C_{16}15G$ and $2C_{16}30G$: the structures are illustrated below Table 1) resulted in break points at 39°C and 27°C, respectively. The break point at 39°C

Table 1. Quantum yield of MMA and MDA in DMF and aqueous solutions[a]

Acridan	Solvent	Surfactant	$\Phi \times 10^7$		
			20.5°C	25.3°C	48.7°C
MMA	DMF		5.9 ± 1.0	5.6 ± 0.9	4.8 ± 0.8
MMA	Water		～0		
MMA	Water	Brij-35(10 mM)	～0		
MDA	DMF		5.3 ± 0.9	5.9 ± 1.0[b]	7.2 ± 1.2
MDA	Water		～0		
MDA	Water	Brij-35(10 mM)	0.39 ± 0.07	0.41 ± 0.07	0.24 ± 0.04
MDA	Water	CTAC(10 mM)	0.11 ± 0.03		
MDA	Water	SDS(10 mM)	0.19 ± 0.09		
MDA	Water	$2C_{16}30G$(1 mM)	2.3 ± 0.3[c]	1.7 ± 0.3	0.39 ± 0.06
MDA	Water	$2C_{16}15G$(1 mM)		0.04 ± 0.01[d]	0.04 ± 0.01
MDA	Water	$2C_{14}N2C$(1 mM)	ca. 0.02[e]	ca. 0.01[d]	

a) [MDA] = [MMA] = 2.50×10^{-5} M. b) 31.0°C. c) 15.1°C. d) 29.0°C. e) 12.2°C.
$2C_nxG$: $[CH_3(CH_2)_{n-1}OCH_2]_2CHO(CH_2CH_2O)_xH$. $2C_{14}N2C$: $[CH_3(CH_2)_{13}]_2N^+(CH_3)_2Br^-$.

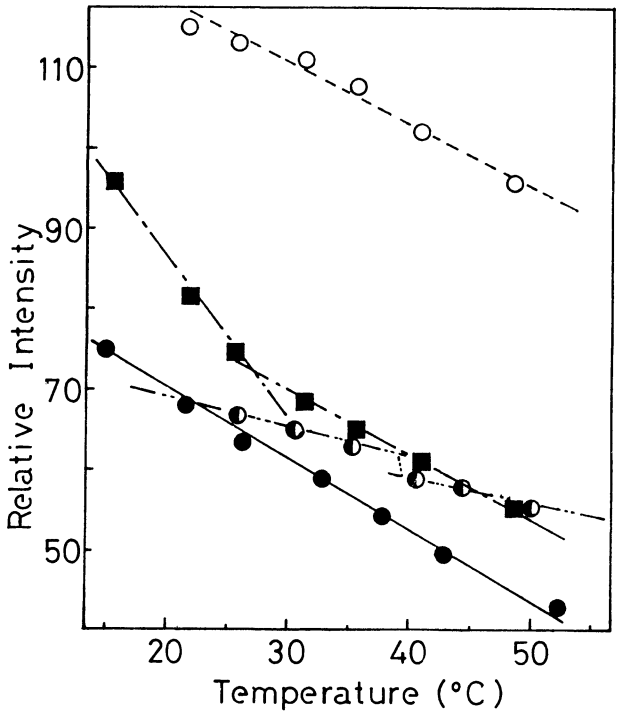


Fig. 1. Fluorescence intensity of 10-dodecylacridone (2.50×10^{-6} M). ● DMF; ○ Briji-35(10 mM); ■ $2C_{16}30G$ (1 mM); ◐ $2C_{16}15G$(1 mM).

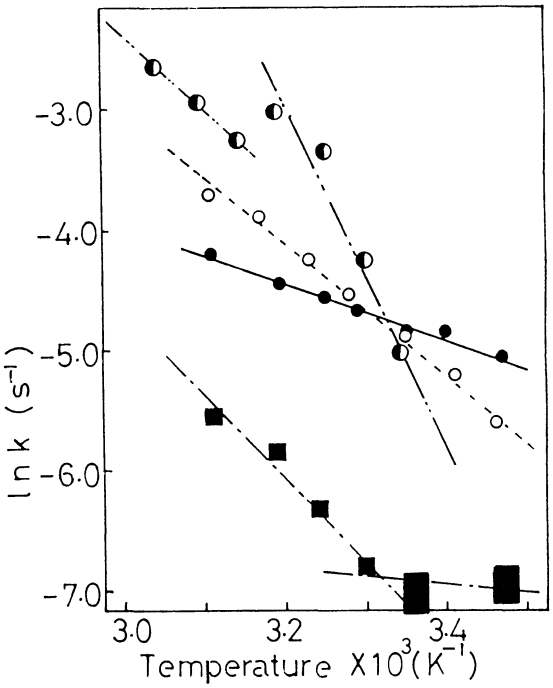


Fig. 2. Chemiluminescence decay of MDA (2.50×10^{-5} M). ● DMF; ○ Brij-35 (10 mM); ■ $2C_{16}30G$(1 mM); ◐ $2C_{16}15G$ (1 mM).

for $2C_{16}15G$ is approximately in accord with the T_c value (41°C),[10] indicating the R.I. value being affected by the fluidity of the membrane phase. Although the clear DSC peak was not observed for $2C_{16}30G$ ($\Delta H < 0.1$ kcal mol^{-1}),[10] the break point at 27°C would reflect the change in some physical property of the membrane.

The chemiluminescence of MMA and MDA in DMF afforded the emission maximum at 430 nm which is comparable with the fluorescence maximum of 10-dodecylacridone in DMF (419 nm), and the quantum yields were $(4.8\text{-}7.2) \times 10^{-7}$. The addition of water or methanol to the DMF solution efficiently suppressed the quantum yield, and light emission from MMA (or MDA) was not detected at all in an aqueous solution (Table 1). The results show that the formation of the excited singlet state is efficiently quenched in protic media.

In the presence of aqueous Brij-35(10 mM) micelle, light emission from MMA was not detected again, whereas that from more hydrophobic MDA was observable (emission maximum, 435 nm). The quantum yield was smaller by about one order of magnitude than that in DMF. Cationic micelle(CTAC) and anionic micelle(SDS) were also effective, and nonionic micelle(Brij-35) gave a quantum yield greater than other ionic micelles. Hence, one can conclude that the formation of the exited singlet acridone from the 1,2-dioxetane is facilitated by the micellar environment. The result of the solvent effect suggests that the partial dehydration of MDA molecule, which occurs owing to the binding to the hydrophobic region of the micelles, would lead to the formation of the excited singlet state.

Light emission from aqueous MDA was also observable in the presence of membranous

surfactants, $2C_{16}15G$, $2C_{16}30G$, and $2C_{14}N2C$ (Table 1). In particular, relatively high quantum yields were obtained in the presence of $2C_{16}30G$. The chemiluminescence decays in DMF and Brij-35 showed first-order behavior to at least 3 half-lives and the Arrhenius plots gave good straight lines at 15-49°C (Fig. 2). The chemiluminescence decays in $2C_{16}15G$ and $2C_{16}30G$ were also first-order above 42°C and 30°C, respectively, but became biphasic below these temperatures: an initial fast decay which was completed in several seconds, followed by a relatively slow, first-order decay. Apparently, the initial fast decay component disappeared at high temperature region. These transition temperatures are comparable with the break point temperatures observed in fluorescent emission (Fig. 1). The Arrhenius plots of $2C_{16}15G$ and $2C_{16}30G$ made for the slow decay process again gave the break points at 42°C and 30°C, respectively (Fig. 2). These results suggest that the kinetic abnormality may be related to the membrane fluidity. At present, we consider that the initial fast decay reflects a metastable binding of the 1,2-dioxetane molecule to the rigid membrane at low temperature region and this process disappears when it is bound to the fluid membrane at high temperature region.[11)]

The foregoing results indicate that the chemiluminescence from MMA and MDA is sensitively affected by the (microscopic) solvent effect. It is also clear that the membrane fluidity is significantly associated with the chemiluminescence phenomenon. At present, however, it seems difficult to further specify the fluidity effect, because the change in the membrane fluidity induces many changes influencing the quantum yield: e.g., partition of 1,2-dioxetane molecules between bulk phase and aggregate phase, R.I. value, rate of chemiluminescence decay, etc.

A further study is currently under way in these laboratories.

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