CYCLIC PEROXIDES. 11. CHEMILUMINESCENT REACTION MECHANISM OF N-METHYL-9-(DICARBOALKOXYMETHYL)ACRIDANES

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A new chemiluminescent system (**1**) which has a $-\overset{|}{C}H-\overset{O}{\overset{\|}{C}}-$ function in it and gives a very effective fluorescent product, N-methylacridone (**2**), was found to give chemiluminescence light emission under basic oxidative conditions. One mole of **1** could be oxidized twice (first at **i** and then at **ii**). Hence, it could give two photons a mole. The mechanistic investigation was performed.

N-Methyl-9-(dicarboalkoxymethyl)acridanes (**1**: R = Me, Et, t-Bu, and Ph: 0.5×10^{-2}M) gave long-lasting chemiluminescence ($\tau_{\frac{1}{2}} \sim 40$ h) with moderate intensity (Φ_{CL}: $10^{-4} \sim 10^{-5}$ *einstein/mole*) at 60°C in a basic dimethyl sulfoxide (DMSO) solution upon oxidized by molecular oxygen.

The final product was **2**, which was proved to be the emitting species (emitter) after a first strong flash. t-Butyl formate (**3**), which was formed by $t\text{-BuO}^-$-anion-induced transesterification of methyl, ethyl, and phenyl formates originally generated from the CL reactions under the conditions, was isolated as the product. Evolution of CO_2 was detected also.

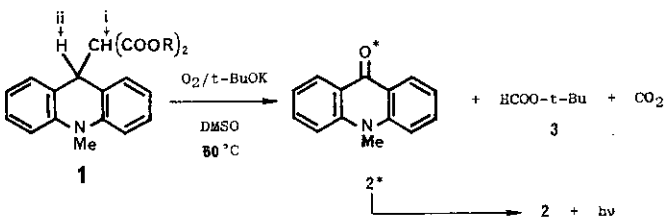

Table 1. Chemiluminescence of **1a-d** and Fluorescence of **2** at 60°C in DMSO

Substrate[a]	Temp. (°C)	CL[b] λ_{max}(nm)	FL[c] of 1 $\lambda_{max}(O_2)$(nm)	FL[c] of 1 λ_{max}(Ar)(nm)	$\Phi_{CL} \times 10^5$[d] (einstein/mol)	Product (%)[e] (2)
1a	60	430	435	411	8.20	50.4
1b	60	430	435	359	7.26	18.0
1c	60	430	435	465	1.27	5.3
	43	---[f]	---	---	0.33	---
1d	60	---	---	---	0.58	---
2	60	—	430[b] 435[c]	---	—	—

a) Initial concentrations: [1] = 5.0×10^{-3} M; [t-BuOK] = 1.0×10^{-1} M. b) Slit-width: 45 nm. c) Slit-width: 24 nm. d) Relative to the Hasting's standard (ref. **4**). e) Isolated yields. f) ---: no data.