

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

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A new chemiluminescent system (1) which has a $-\text{CH}(\text{H})-\text{C}(=\text{O})-$ 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: $0.5 \times 10^{-2}\text{M}$) gave long-lasting chemiluminescence ($\tau_{\frac{1}{2}} \sim 40\text{ h}$) 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-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 CO₂ was detected also.

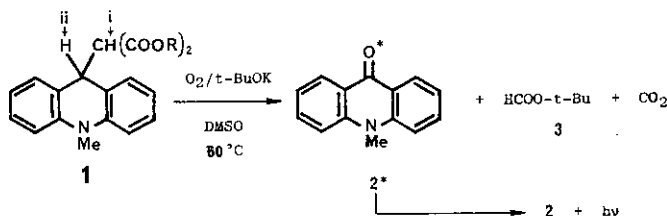


Table 1. Chemiluminescence of 1a-d and Fluorescence of 2 at 60°C in DMSO

Substrate ^{a)}	Temp. ($^\circ\text{C}$)	CL ^{b)} λ_{max} (nm)	FL ^{c)} of 1			$\phi_{\text{CL}} \times 10^5$ ^{d)} (einstein/mol)	Product (%) ^{e)} (2)
			$\lambda_{\text{max}}(\text{O}_2)$ (nm)	$\lambda_{\text{max}}(\text{Ar})$ (nm)			
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] = $5.0 \times 10^{-3}\text{ M}$; [t-BuOK] = $1.0 \times 10^{-1}\text{ M}$. 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.