CHEMILUMINESCENCE OF 10-METHYLACRIDINIUM METHOSULFATE

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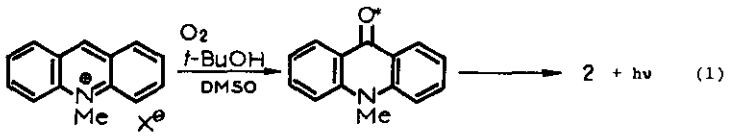
A bright blue chemiluminescence (CL) of a new chemiluminescent system, 10-methylacridinium methosulfate (**1a**) owing to the fluorescence of 10-methylacridone (**2**) excited to the S_1 state, is described, when oxidized with ground state oxygen in the presence of t-BuOK in dimethyl sulfoxide (DMSO) (scheme 1). Addition of excess KCN solution in DMSO/H_2O (9:1) to the solution of **1a** instead of addition of t-BuOK, as similarly as described in the literature of Happ et al on the weak CL of 10-methylacridinium chloride (**1b**), resulted in a depressed amount of CL (less than 1/10 of that by t-BuOK).



1a: X = $-OSO_3Me$ **2***
1b: X = Cl

After neutralization of the resulted CL mixture with dry ice, solvents were evaporated in vacuo and the residue was extracted with ether, from which the final product **2** was characterized by IR, NMR, and mp and determined on GLC and TLC comparing with the authentic sample. The results are shown in Table 1.

CL spectra of **1** showed the same value of λ_{max} of fluorescence (FL) spectrum of **2** (420 and 435 nm) under the similar basic conditions (t-BuOK/DMSO/O_2 or KCN/DMSO-H_2O/O_2). These results suggest that the emitter in the CL reactions is the ketone (**2**) generated quantitatively. When treated with the base in the vacuum first (freeze-thaw cycle: 10^{-4} mmHg x 3 times), and then treated by oxygen, **1a** also gave CL. The free base of **1**, acridine (**3**) itself, also gave weak CL under the similar conditions to yield 9-acridone.

Table 1. Chemiluminescence of the Acridinium Compounds **1**.

	[**1**] (mmol/l)	[t-BuOK] (mmol/l)	[KCN] (mmol/l)	Yield of **2** (%)	Φ_{CL} (einstein/mol x 10^3)[a]
1a	1.01	10	—	97%	0.69
	1.01	—	10	99	0.20
1b	1.00	10	—	93	0.56
	1.00	—	10	39	0.063
3	1.00	10	—	—	0.015
	1.00	—	10	—	——

a) Relative to luminol in aqueous solution.

From the considerations as above and on the other acridinium CL systems and the degradation energies, a reaction mechanism is proposed for the present CL reaction.