

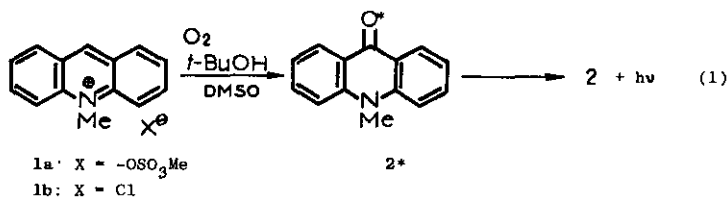
CHEMILUMINESCENCE OF 10-METHYLACRIDINIUM METHOSULFATE

Nobutaka Suzuki,* Yoshihiko Kazui, Masahiro Kato, and Yasuji Izawa

Department of Industrial Chemistry, Faculty of Engineering,

Mie University, Tsu, Mie 514, Japan

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/H₂O (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).



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/O₂ or KCN/DMSO-H₂O/O₂). 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)	[<i>t</i> -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.