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CHEMILUMINESCENCE OF 10-METHYLACRIDINIUM SALTS FOLLOWING BASE CATALYSED OXYGENATION IN DIMETHYL SULFOXIDE

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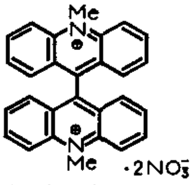
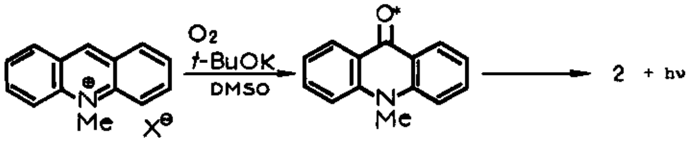
Abstract — When oxidized with ground state oxygen in the presence of t-BuOK in DMSO, 10-methylacridinium methosulfates (1a) gave strong light emission owing to the fluorescence of 10-methylacridone (2) excited to the S_1 state.



Lucigenin

In the course of the studies on chemiluminescence (CL) of 9,10-substituted acridanes,1) we found a new chemiluminescent reaction of 10-methylacridinium salts (1) when oxidized by molecular oxygen under basic conditions. The appearant structure resembles to the powerful chemiluminescent compound, lucigenin2,3) (Φ_{CL} 3.0 x 10^{-3}),4) but the reaction mechanism of 1 seems to differ from the lucigenin's. We describe here the bright blue chemiluminescent reactions of 10-methylacridinium methosulfate (1a) owing to the fluorescence of 10-methylacridone (2) excited to the S_1 state, when oxidized with ground state oxygen in the presence of t-BuOK in dimethyl sulfoxide (DMSO) (scheme 1). Happ et al. reported a weak CL of 10-methylacridinium chloride (1b) catalysed by excess KCN, instead of t-BuOK, in DMSO/H_2O (9:1). Under the similar conditions, 1a yielded reduced amounts of CL (less than 1/3 of that by t-BuOK).



(1)

1a: X = OSO_3Me
1b. X = Cl

2*

Each solution (2 ml) of 1a6) - b7) (1 mmol/1) in DMSO (dried over and distilled from CaH_2 and saturated by O_2 before use) was treated with DMSO solution (2 ml) of t-BuOK (Merck, 10 mmol/1) or KCN (Wako, 10 mmol/1) at room temperature. The mixture was flushed by O_2 gas for 10 min before and during the oxygenation reaction. Fast light emission was observed.8) After neutralization of the resulted mixture with dry ice, solvents were evaporated in vacuo and the residue was extracted with ether, from which the final product 2 10) was characterized by IR, NMR, and mp and identified on GLC11) and TLC11) with the authentic sample. The results are shown in Table 1.

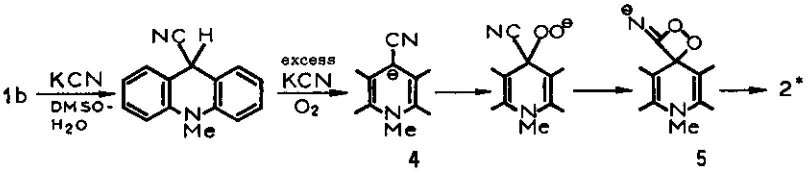
CL spectrum of 1 was identical with fluorescence (FL) spectrum of 2 (420 and 435 nm) under the similar basic conditions (t-BuOK/DMSO/O_2 or KCN/DMSO-H_2O/O_2). These results suggest that the emitter in the CL reactions is the ketone (2) generated quantitatively. When treated first with the base in the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

Table 1. Chemiluminescence of the Acridinium Compounds 1.[8)]

	[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	—	—

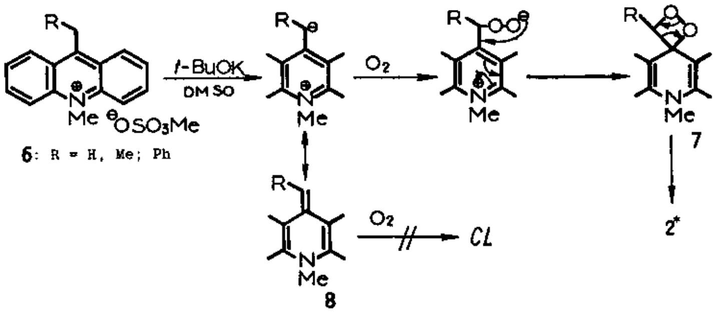
a) Standard: luminol in aqueous solution (ref. 9).

The behaviors of **1a** in the present reactions show that the reaction path way is different from that of the Happ's[5)] (scheme 2) and that for the 9-substituted compounds shown below (scheme 3).[12)] Happ et al. had suggested the reaction mechanism for **1b** with KCN as shown scheme 2.[5)]



(2)

Kamiya and Sugimoto[12)] have investigated the similar chemiluminescent systems, 9-alkyl- and 9-benzyl-10-methylacridinium methosulfates (**6**) in the presence of t-BuOK and O_2 in DMSO solution (Φ_{CL} $10^{-2} \sim 10^{-4}$) and suggested the reaction mechanism as shown below (scheme 3). The emitter is probably the anhydrobase **8** excited by the ketones **2** primarily produced as the excited state(s).



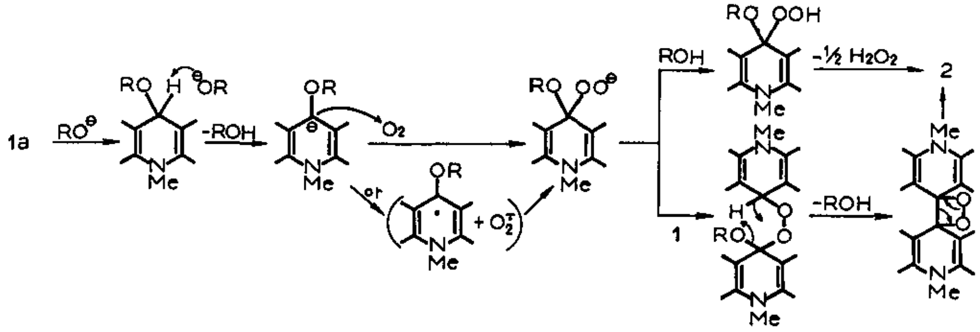
(3)[12)]

$$2^* + 8 \longrightarrow 2 + 8^* \quad ; \quad 8^* \longrightarrow 8 + h\nu$$

After mixing with t-BuOK in the absence of O_2, the solution of **6** did not give CL on exposure to O_2 gas. The mechanism seems to be similar to the CL of lucigenin.[3)]

Rosenthal and Bercovici[13)] had found that **2** in DMSO gave CL when treated with KO_2. The CL exhibited a broad emission band with three peaks, maxima at 470, 494, and 532 nm of the relative intensities 3:5:2, respectively. The wave length of CL shows that the present CL reactions do not result from the Rosenthal's mechanism (scheme 4).

$$2 + O_2^{\overline{\cdot}} \longrightarrow (2^{\overline{\cdot}})^* + O_2 \longrightarrow 2^{\overline{\cdot}} + h\nu \qquad (4)^{13)}$$



(5)

(6)

The degradation energy of 67.3 kcal/mol, at least, is required for exciting 2 to the lowest singlet excited state.1) (i) If one O_2 molecule oxidized one molecule of 1 to give one molecule of 2 and 1/2 molecule of H_2O_2,5,14) the balance of the heat of reaction (ΔH) would be $\Delta H = +5.6$ kcal/mol15) (scheme 5), which is not sufficient to excite 2. (ii) If one O_2 molecule oxidizes two molecules of 1 to give two molecules of 2 and H-OR, ΔH would be -113.5 kcal/mol,15) which is sufficient for exciting 2 to its S_1 state (scheme 6). Thus, we prefer the latter mechanism (scheme 6) for explaining the present effective chemiluminescent reaction of 1a.

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5) J. W. Happ, E. G. Janzen, and B. C. Rudy, J. Org. Chem., 1970, **35**, 3382; J. W. Happ and E. G. Janzen, ibid., 1970, **35**, 96. There was no description on the quantum yield of CL.
6) Yellow granules: mp >300 °C; Anal. found, C, 59.28; H, 5.15%. Calcd. for $C_{15}H_{15}NO_4S$: C, 59.00; H,4.95%. MS (m/z) 194 (cation part); IR (KBr) 3000, 1390, 1220, 1170 cm^{-1}.
7) mp 170-185 °C dec. [lit. mp 183 °C dec. ; A. Albert, "The Acridines", St. Martin's Press, New York, N. Y., 1966, p. 343.]
8) Photometric determinations were made by measuring the output of R106 photomultiplier-photometers (Hitachi MPF-2A Fluorescence/Phosphorescence Photometer) exposed to the reacting solution. The values obtained were corrected for phototube spectral response. Quantum yields (Φ_{CL}) are relative to luminol.9)
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11) *GLC Conditions:* Yanagimoto Yanaco G-1800F (FID); 10% Silicone GE-SE-30 on Diasolid L in 0.93 m x ϕ 4 mm stainless steel column; col. temp. 240°, inj. temp. 280°, carrier gas (N_2) 42.0 ml/min.

TLC Conditions: Silica gel 60 PF_{254}-gipshaltig (Merck, # 7749), thickness: 0.25 mm, $CHCl_3$.

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14) E. G. Janzen, J. B. Pickett, J. W. Happ, and W. deAngelis, *J. Org. Chem.*, 1970, **35**, 88.

15) From bond energies,[a,b]

	Energy spent (kcal/mol)		Energy gained (kcal/mol)		Balance (kcal/mol)		Energy spent (kcal/mol)		Energy gained (kcal/mol)		Balance (kcal/mol)
(i)	C-H	98.7	C=O	181		(ii)	2C-H	197.4	2C=O	362	
	C=C	145.8	C-C	83			2C=C	291.6	2C-C	166	
	O=O	119.1	arom	43			O=O	119.1	2H-OR	221.2	
			1/2HOOH	51[c]					2arom	86	
		363.6		358	ΔH=+5.6			608.1/2		835.2/2	ΔH=-113.5

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b) See T. Wilson and A. P. Schaap, *J. Am. Chem. Soc.*, 1971, **93**, 4126.

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