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Base-induced Oxygenation and Chemiluminescence of 10-Methylacridinium and 1-Methylquinolinium Salts in Dimethyl Sulfoxide[1)]

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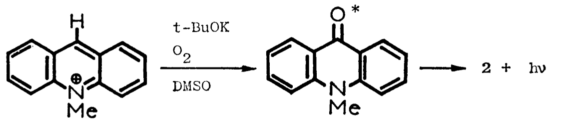
10-Methylacridinium methyl sulfate and the 1-methylquinolinium salt gave strong light emission, when oxidized with ground state oxygen in the presence of *t*-BuOK in DMSO, owing to the fluorescence of 10-methyl-9(10*H*)-acridinone and 1-methyl-1(4*H*)-quinolinone excited to their S_1 state.

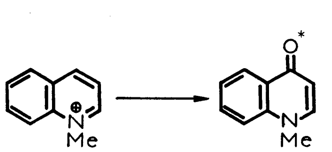
Lucigenin[2)] is one of the most powerful chemiluminescent compound (quantum yield of CL: Φ_{CL} 3.0×10^{-3})[3)] and has the most complex mechanism known so far, for the chemiluminescence reactions.[4)]

In the course of the studies on chemiluminescence (CL) of 9,10-substituted acridine compounds,[5)] a new chemiluminescent reaction of 10-methylacridinium salts (**1**), which resembles to lucigenin apparently, was found when oxidized by molecular oxygen under basic conditions. We describe here the bright blue chemiluminescent reactions of 10-methylacridinium methyl sulfate (**1a**) owing to the fluorescence of 10-methyl-9(10*H*)-acridinone (**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). The similar CL reaction of 1-quinolinum methyl sulfate (**3**) is also described. Happ *et al.* reported a weak CL of a similar chemiluminescent system, 10-methylacridinium chloride (**1b**) *via* addition of $^{-}$CN anion to 9-carbon, catalyzed by excess KCN, instead of *t*-BuOK, in DMSO/H_2O (9:1).[6)] Under the similar conditions, **1a** yielded reduced amounts of CL (less than 1/3 of that by *t*-BuOK).



(1)

1a: X=OSO$_3$Me
1b: X=Cl
2*



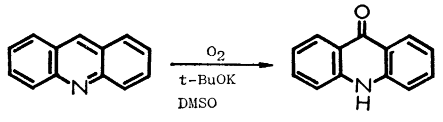
(2)

3 $^{-}$OSO$_3$Me **4***

CL spectrum of **1** was identical with the 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 during the reactions quantitatively. When treated first by the base *in vacuo* (freeze-thaw cycle: 10^{-4} mmHg** $\times$ 3 times)[7)] and then by oxygen, **1a** also gave CL. The compound **3** showed the similar behavior under the similar conditions above.

The behavior of **1a** in the present reactions shows that the reaction pathway is different both from that of the Happ's[6)] and also that for the 9-substituted compounds shown by Kamiya and Sugimoto.[8)]

Contamination of **1** with acridine (**5**) or its *N*-protonated salt was suspected to be responsible for the strong CL emission. In fact, acridine itself showed CL, although it was very weak, to give 9(10*H*)-acridinone under the similar conditions (scheme 3).



(3)

5 **6**

Rosenthal and Bercovici[9)] found that the final product, **2**, gave CL in DMSO when treated with KO_2. The CL spectrum exhibits a broad emission band with three peaks, maxima at 470, 494, and 532 nm of the relative intensities 3:5:2, respectively, owing to the fluorescence of radical anion of **2**. The comparison of CL spectra shows that the present CL reactions do not result from the Rosenthal's mechanism (scheme 4).

$$\begin{aligned} 2 + O_2^{\bar{\cdot}} &\longrightarrow (2^{\bar{\cdot}})^* + O_2 \\ &\qquad \longrightarrow 2^{\bar{\cdot}} + h\nu \end{aligned} \qquad (4)^{9)}$$

The degradation energy of 67.3 kcal/mol***, at least, is required for exciting **2** to the lowest singlet excited state.[5)] (i) If one O_2 molecule oxidizes one molecule of **1** to give one molecule of **2** and 1/2 molecule of H_2O_2,[6,10)] the balance of the heat of reaction (ΔH) would be $\Delta H = +5.6$ kcal/mol (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, which is sufficient for exciting **2** to its S_1 state (scheme 6) (Table 2). Thus, we prefer the latter mechanism (scheme 6) for the explanation of the present effective chemiluminescent reaction of **1a**.

Kamiya and Sugimoto[8)] have investigated the similar chemiluminescent systems, 9-alkyl- and 9-benzyl-10-methyl-acridinium methyl sulfates (**7**) in the presence of *t*-BuOK and O_2 in DMSO solution (Φ_{CL} 10^{-2}—10^{-4}) and suggested the reaction mechanism initiating from a deprotonation reaction of the alkyl side chain of **7**. The emitter is probably the anhydrobase excited by the ketones **2*** produced primarily as the excited state(s). After mixing with *t*-BuOK in the

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** 1 mmHg $\approx$ 133.322 Pa.

*** 1 kcal $\approx 4.184\times10^3$ J.

Table 1. Chemiluminescence of the acridinium compounds

	[Substrate] mmol/l	[t-BuOK] mmol/l	[KCN] mmol/l	Yield of **2**/%	Φ_{CL}/(einstein/mol×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	—	+	0.014
	1.00	—	10	—[b]	—[b]
5	1.00	10	—	44	0.015
	1.00	—	10	—[b]	—[b]

a) Standard: luminol in aqueous solution (Ref. 11). b) Not detected.

Table 2. Balance sheets of bond energy[a,b]

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

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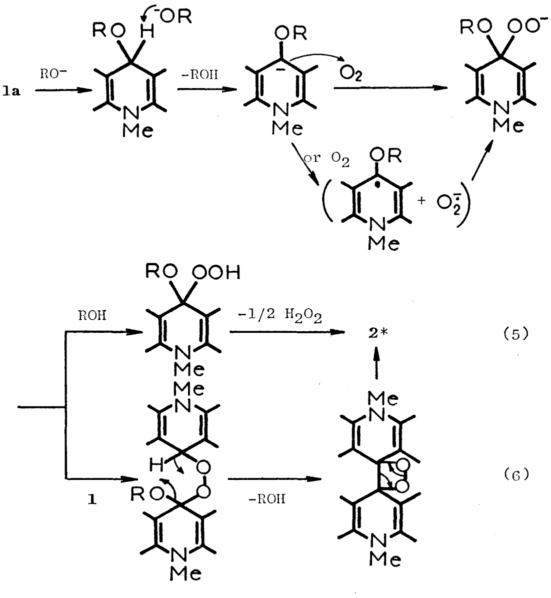

absence of O_2, the solution of **7** did not give CL on exposure to O_2 gas. The mechanism seems to be similar to the CL of lucigenin.[3)]

Experimental

Instrumentation. All mps were uncorrected. Following spectrophotometers were used for spectral measurements: IR: JASCO IR-G and A-100; UV: Hitachi 220S Spectrophotometer; NMR: JEOL JNM-MH-100 (100 MHz) and FX-100 (99 MHz for ^1H and 25.05 MHz for ^{13}C); MS: JEOL JMS-D-100; Fluorescence: Hitachi MPF-2A. The spectral data are presented as follovs: IR in cm^{-1}; UV: λ_{max} in nm (ε given in parentheses); NMR: δ in ppm from int. TMS and J in Hz (accuracy±0.5 Hz); MS in m/z; fluorescence; λ_{max} in nm. GLC were carried out by Yanagimoto Yanaco G-1800F. GLC Conditions: Yanagimoto Yanaco G-1800F (FID); 10% Silicone GE-SE-30 on Diasolid L in $0.93\times\phi$ 4 mm stainless steel column; col. temperature 240 °C, inj. temperature 280 °C, carrier gas (N_2) 42.0 ml/min. TLC Conditions: Silica gel 60 PF_{254}-gipshaltig (Merck, ♯7749), thickness: 0.25 mm, $CHCl_3$.

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.[11)]

Materials. Acridine, quinoline, and 9(10*H*)-acridinone (**6**) were purchased. 10-Methylacridinium chloride (**1b**),[12)] 10-methyl-9(10*H*)-acridinone (**2**),[13)] and 1-methyl-1(4*H*)-quinolinone (**4**)[14)] were prepared according to literatures.

1b: mp 180—187 °C (decomp) [lit,[12)] mp 183 °C (decomp)]; ν_{max} (KBr) 1620, 1230, 1010, 730 cm^{-1}; δ (DMSO-d_6) 3.40 (4H, br), 4.80 (3H, s), 7.9—8.9 (8H, m), 10.30 (1H, s).

2: mp 207—209 °C (lit,[13)] 203.5 °C); ν_{max} (KBr) 1630, 1590, 1490, 1180 cm^{-1}; δ ($CDCl_3$) 3.82 (3H, s), 7.46 (6H, m), 8.52 (2H, d).

4: mp 143—151 °C (lit,[14)] 152 °C); ν_{max} (KBr) 1620 cm^{-1}; δ ($CDCl_3$) 3.80 (3H, s), 6.20 (1H, m), 7.50 (4H, m), 8.40 (1H, m).

*10-Methylacridinium Methyl Sulfate (**1a**):* A solution of acridine (Nakarai Chem. Co) (5 g; 27.9 mmol) and dimethyl sulfate (bp 189 °C) (2.9 ml; 30.5 mmol) in benzene (50 ml) was stirred at 30—40 °C overnight with excluding moisture. Resulted precipitates were filtered and washed with ether. Into the mother liquor was added 1 ml of dimethyl sulfate. After strring, resulted ppt was collected with filtration. Yellow granules, mp >300 °C. Yields 7.14 g (23.4 mmol; 83%). Found C, 59.28; H, 5.15%. Calcd for $C_{15}H_{15}NO_4S$: C, 59.00; H, 4.952%; m/z 194 (cation part) ν_{max}

(KBr) 3000, 1390, 1220, 1170 cm^{-1}; δ (DMSO-d_6) 3.40 (3H, s), 4.88 (3H, s), 8.04 (2H, m), 8.60 (4H, m), 10.20 (1H, br, s).

*1-Methylquinolinium Methyl Sulfate (**3**)*: A solution of quinoline (TCI) (3.0 ml: 3.27 g; 25.3 mmol) and dimethyl sulfate (10 ml: 13.3 g; 105 mmol) in benzene (30 ml) was stirred at 30—40 °C for 20 h and, then, cooled in an ice bath. Resulted precipitate was filtered and crystallized from acetone. Colorless needles, mp 98.0—99.0 °C (lit,[15] 100 °C), yields 5.04 g (19.7 mmol; 77.9%); $\nu_{\max}$ (KBr) 1620, 1210, 1020, 760 cm^{-1}; δ (DMSO-d_6) 3.40 (3H, s), 4.64 (3H, s), 8.42 (2H, m), 9.35 (2H, m).

*Chemiluminescent Reaction of **1** and **3***: Each solution (2 ml) of **1a**, **1b**,[15] and **3** (1 mmol/l) 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/l) or KCN (Wako, 10 mmol/l) 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.[11] 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**[13] and **4** were characterized by IR, NMR, and mp and identified on GLC and TLC with the authentic samples. The results are shown in Table 1. CL spectra were recorded and compared with their fluorescence spectra measured under the similar conditions.

*Base Catalyzed Oxygenation of **5***. The CL reactions of **5** (1.00 mmol/l) were observed under the similar conditions and the spectra and products were analysed as described above (Table 1). Products were also determined by UV spectra.

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