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A Novel Chemiluminescence from the Reaction of 9-Arylmethylene-10-methyl-9,10-dihydroacridines and Dimethyldioxirane.

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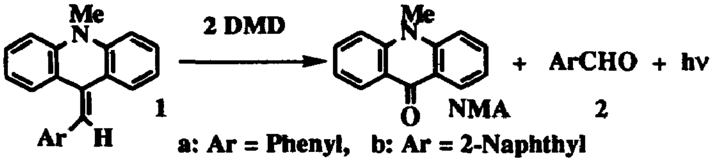
Abstract: *Reaction of 9-arylmethylene-10-methyl-9,10-dihydroacridine (1) with isolated dimethyldioxirane affords cleavage products with chemiluminescence via a 1,2,4-trioxane (5) which will be formed by the reaction of an intermediary epoxide (3) with dimethyldioxirane as a nucleophile.*

Dimethyldioxirane (DMD) is a novel oxidant which has an efficient ability to transfer oxygen atoms to a variety of organic substrates in high selectivity.[1] We have observed chemiluminescence (CL) in the reaction of 9-arylmethylene-10-methyl-9,10-dihydroacridine (1) in CH_2Cl_2 with solutions of isolated DMD in acetone.[2] As far as we know, CL in the reaction of an olefin with DMD is unprecedented. Thus, we report here about novel CL from the reaction of 1 with DMD, and suggest its plausible mechanism.

During the study of 1,2-dioxetane, we have found CL in the reaction of 1 with m-chloroperoxybenzoic acid[3] (MCPBA), DMD and hydroperoxides. The reaction of 1 with more than two equivalents of DMD gave quantitatively corresponding aromatic aldehyde (2) and N-methylacridone (NMA) with light emission,[4] as shown in eq. 1. On the reaction of **1b** with equimolar DMD, a half amount of **1b** is consumed to give 2-naphthaldehyde (**2b**) and NMA with light emission. Hence the CL reaction needs two equivalents of DMD. Also, the reaction of a second molecule of DMD with the oxidized product of **1**, probably an epoxide, has proved to be much faster than the reaction of the first molecule of DMD with **1**.



1 NMA 2 (1)

a: Ar = Phenyl, b: Ar = 2-Naphthyl

The kinetics of the reaction of **1b** in CH_2Cl_2 with 5 to 30 equivalents of isolated DMD in acetone are carried out by following the UV absorbance of the reaction mixture at 420 nm.[5] The rate for the consumption of **1b** is of the first order both on DMD and on **1b**, and hence the rate determining step may be the epoxidation of **1** with DMD. The activation parameters for the consumption of **1** on the reaction with DMD are given in Table 1. The larger negative activation entropies for the reaction of olefin with DMD compared to those for the reaction with MCPBA indicate more steric hindrance in the transition state. These are compatible with the steric effects on the reaction of alkenes with DMD[7] and the suggestion by the molecular orbital calculations.[8] The relative reactivities in the reaction with DMD are mainly reflected in the activation enthalpies.

The CL from the reaction of **1** with DMD shows the initial fast increase and the following slower first-order decay of the light intensities. The rate constants for the first-order decay of CL are independent of the concentration of **1b** and DMD. The time profiles of emission may be explained by the initial faster second-

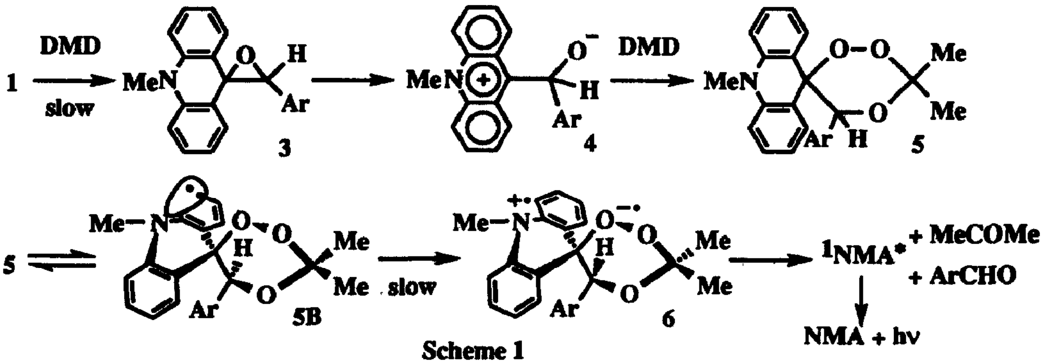
Table 1. The Activation Parameters for the Consumption of 1

Reaction	$\Delta G^{\ddagger}_{298}$/kJ/mol	$\Delta H^{\ddagger}$/kJ/mol	$\Delta S^{\ddagger}$/J/K•mol	k^{rel}_{298} [d]	Temp Range/°C
1a + DMD [a]	63.1 ± 4.9	22.0 ± 3.4	-138 ± 12	1 [e]	9.4 — 34.4
1b + DMD [a]	62.1 ± 3.5	21.3 ± 2.5	-137 ± 8	1.47	7.3 — 35.0
1b + MCPBA [b]	67.6 ± 4.6	50.2 ± 3.3	-59 ± 11	0.16	13.0 — 37.5
Cinnamate+DMD [c]	89.9 ± 12.1	55.8 ± 8.5	-115 ± 29	0.00002	10.0 — 30.0

a) Ten equivalents of DMD in acetone (10μL) were added to the olefin in 4.0 mL CH_2Cl_2; [1] = 2.7×10^{-5} M. b) In CH_2Cl_2, reported in the previous paper.[3] c) *(E)*-PhCH=$CHCO_2Et$+ DMD in acetone, calculated from the data of ref. 6. d) Relative rate at 25°C. e) Second order rate constant is 55.3 $M^{-1}s^{-1}$.

order accumulation and the following slower first-order decomposition of a chemiluminescent intermediate. This chemiluminescent intermediate should be formed by the reaction of a second molecule of DMD with the initial oxidized product, probably an epoxide. The epoxidation of enamines by DMD was reported to afford 1,4-dioxanes by dimerization of intermediary enamine epoxides via the corresponding 1,3-dipoles.[9] In the reaction of 1 with DMD, the intermediary epoxide (3) will form the 1,3-dipole, which will be stabilized as a 9,10-dihydroacridinyl cation (4), as shown in Scheme 1. The reactions involving peroxides as nucleophiles give peroxidic adducts,[10] and hence the reaction of an electron-deficient moiety of 4 with DMD as a nucleophile should form the product containing O-O bond, i.e. the 1,2,4-trioxane (5) as a chemiluminescent intermediate.[11, 12]

The emitting species on the reaction of 1b with DMD is the singlet excited state of NMA (^{1}NMA*), because the emission spectra of CL are the same as those of the luminescence of the photo-excited NMA and the CL from the 1,2-dioxetane of 1b. The off/on switching on CL by successive addition of trifluoroacetic acid and triethylamine, as shown in Fig. 1, indicates the important role of the lone pair of nitrogen in acridan-ring on CL.[3,13] As the acridan-ring system is conformationally flexible,[13] in the boat conformation (5B) the lone pair of nitrogen can approach the O-O bond and transfer one electron to the antibonding σ orbital of the O-O bond. The electron transfer should be the rate determining step for CL and form the dipolar intermediate (6), which will afford ^{1}NMA* on the decomposition, as shown in Scheme 1. The activation parameters for the CL from 1a or 1b with DMD are similar to those of the corresponding 1,2-dioxetane and β-hydroxy-alkyl



Scheme 1

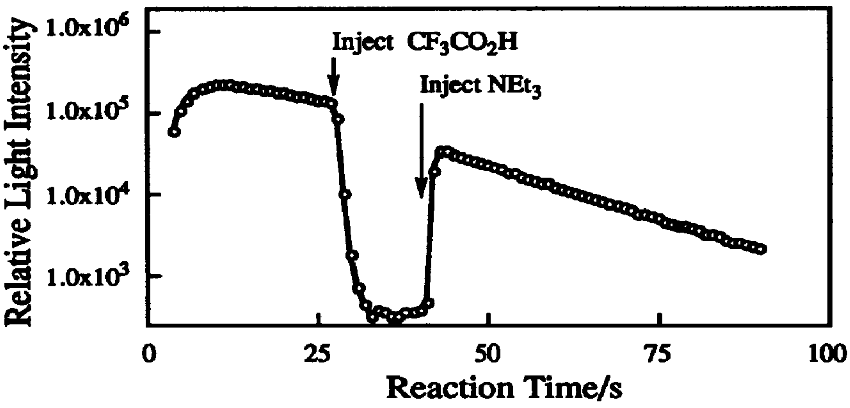


Figure 1. Time profile on the successive addition of CF_3CO_2H (0.2 mmol) and NEt_3 (0.5 mmol) to the reaction mixture of **1b** (9.3 μmol) with DMD (97 μmol) at 25°C

perester, as shown in Table 2. The above results indicate that the decomposition of 1,2,4-trioxane **5** will proceed by a chemically initiated electron exchange luminescence (CIEEL) mechanism, in a similar manner to the decomposition of analogous 1,2-dioxetane[13] and β-hydroxy-tertiary-alkyl perester.[3]

The hitherto known 1,2,4-trioxanes are thermally stable.[14] The related compounds such as amino-substituted 1,2,4-trioxanes[15, 16a] and 1,2,4,5-trioxazines[16b] also are stable, but their lone pair of nitrogen will not approch their O-O bond in view of their X-ray structures.[14a,15,16] The difference on the thermal stabilities between 1,2,4-trioxanes will depend on the availability of the favourable conformation for the electron transfer from lone pair of nitrogen to the O-O bond.

In conclusion, we have shown that the reaction of **1** with DMD affords CL which will be responsible for the decomposition of intermediary 1,2,4-trioxane **5** by a CIEEL mechanism. We have also suggested that the

Table 2. The Activation Parameters for the Chemiluminescence of the reaction of **1**.

Reaction	$\Delta G^{\ddagger}_{298}$/kJ/mol	$\Delta H^{\ddagger}$/kJ/mol	$\Delta S^{\ddagger}$/J/K•mol	k^{rel}_{298} [e]	Temp Range/°C
1a + DMD [a]	82.9 ± 3.6	52.5 ± 2.5	-102 ± 9	1 [f]	5.0—25.0
1b + DMD [a]	81.7 ± 9.5	68.5 ± 6.6	-44 ± 23	1.7	-5.0—30.0
1b + MCPBA [b]	82.7 ± 9.2	72.2 ± 6.4	-35 ± 22	1.0	10.0—25.0
1a + $^1O_2$ [c]	83.2 ± 1.3	63.9 ± 0.9	-65 ± 3	0.85	0.0—25.0
1b + $^1O_2$ [d]	85.2 ± 5.9	61.0 ± 4.1	-81 ± 14	0.37	5.0—25.0

a) CL from the 1,2,4-trioxane intermediates **5**. Olefin-CH_2Cl_2 solution was added to 10 equivalents of DMD solution. Final composition of the solvent was 5:1 CH_2Cl_2-acetone. b) CL from the perester intermediate, prepared by the reaction of **1b** with excess of MCPBA and determined after addition of excess of NEt_3.[3] c) CL from the 1,2-dioxetane of **1a** in CH_2Cl_2, calculated from the data of ref. 12. d) CL from the 1,2-dioxetane of **1b**, prepared by Methylene Blue-sensitized photooxygenation of **1b** at -78°C in CH_2Cl_2 by use of 940W Sodium lamp and yellow filters. e) Relative rate at 25°C. f) First order rate constant is $1.873 \times 10^{-2}\ s^{-1}$.

intermediary 1,2,4-trioxane 5 may be formed by the reaction of the 1,3-dipole 4 with DMD as a nucleophile.

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