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

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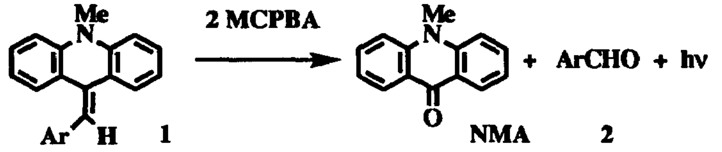
Abstract: *Reaction of 9-arylmethylene-10-methyl-9,10-dihydroacridine (1) with more than two equivalents of m-choloroperoxybenzoic acid in CH_2Cl_2 affords intermediary β-hydroxy-tertiary-alkyl peroxyester (5) decomposing to N-methylacridone and aromatic aldehyde with chemiluminescence by a CIEEL mechanism.*

Applications of chemiluminescence (CL) and bioluminescence in analytical chemistry have attracted considerable interest in recent years.[1] We have recently found CL during the epoxidation of 9-arylmethylene-10-methyl-9,10-dihydroacridine (1)[2] with m-chloroperoxybenzoic acid (MCPBA), dimethyldioxirane, and hydroperoxides. As far as we know, CL in the reaction of olefin with peroxides is unprecedented. We report here about a novel CL from the reaction of 1 with MCPBA, and suggest its plausible mechanism.

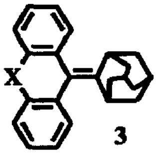
During the study on 1,2-dioxetanes having arene-moiety and N-methylacridan-ring, we attempted the epoxidation of 1 with MCPBA in CH_2Cl_2 at 25°C in order to obtain the corresponding epoxide. The oxidation of 1 with more than two equivalents of MCPBA gave quantitatively corresponding aromatic aldehyde (2) and N-methylacridone (NMA), but no epoxide, as shown in eq. 1. Moreover, the reaction was confirmed to be chemiluminescent by means of a Mitchell-Hastings photometer.[3]



(1)

a: Ar = Phenyl, b: Ar = 1-Naphthyl, c: Ar = 2-Naphthyl

Similarly, 9-(10-methyl-9,10-dihydroacridinylidene)adamantane (3a) shows light emission on the reaction with two equivalents of MCPBA in CH_2Cl_2 at 25°C, but several related adamantylidene derivatives, i.e. 9-xanthenylideneadamantane (3b), 9-thioxanthenylideneadamantane (3c), 9-fluorenylideneadamantane (3d) and 9-(9,10-dihydroanthrylidene)adamantane (3e),[4] give no light emission under similar conditions. Therefore, the 9-(10-methyl-9,10-dihydroacridinylidene) moiety is required for the CL reaction with MCPBA. Molecular oxygen is not responsible for the CL,[2b] as CL under oxygen atomosphere shows no difference from that under argon.



3 **a: X= -NMe- b: X= -O- c: X= Bond d: X= -S- e: X= -CH_2-**

On the reaction of **1c** with equimolar MCPBA under argon atomosphere, a half amount of **1c** is consumed to give 2-naphthaldehyde (**2c**) and NMA with light emission. Hence the CL reaction needs two equivalents of MCPBA. Moreover, it is apparent that the reaction of a second molecule of MCPBA is much faster than the reaction of the first molecule of MCPBA with **1**.

The kinetics for the reaction of **1c** with 20 to 100 equivalents of MCPBA in CH_2Cl_2 are carried out by following the UV absorbance of the reaction mixture.[5] The rate for consumption of **1c** is of the first order both on MCPBA and on **1c**. The second order rate constant of the reaction of **1c** with MCPBA is 8.8 $M^{-1}s^{-1}$ at 25°C, and the activation parameters are $\Delta G^{\ddagger}_{298}$ = 67.6±4.6 kJ/mol, $\Delta H^{\ddagger}$ = 50.2±3.3 kJ/mol, $\Delta S^{\ddagger}$ = -59±11 J/K•mol. These values are comparable to those of the reaction of electron-rich tri-substituted olefin with MCPBA.[6] These CL reactions with MCPBA show the initial fast increase and the following slower first-order decay of the light intensities. The decay of light emission from the reaction of **1c** with MCPBA is followed by a Mitchell-Hastings photometer.[3] The first order rate constant of the slower part of the CL is 0.078 s^{-1} at [MCPBA] = 4.3×10^{-2} M. Hence the emission curve indicates the initial fast accumulation and the following slower decomposition of a chemiluminescent intermediate.

A weak CL from some epoxides was reported on heating to 50-70 °C.[7] As phenyl oxirane gave phenylethanal on heating, it was suggested that the CL reaction of epoxide would be explained by the NIH shift of a polarized epoxide to give excited states of a carbonyl compound. However, as the reaction of **1** with MCPBA gives the carbonyl compounds cleaved at the carbon-carbon double bond, the present CL reaction with MCPBA is different from the reported CL. The epoxidation of enol ethers with excess peroxyacid is known to give carbonyl products which were cleaved at the carbon-carbon double bond by way of intermediary unstable epoxides and β-hydroxyalkyl peroxyesters.[8] Hence, the light-emitting species will be not intermediary epoxides (**4**) but β-hydroxyalkyl peroxyesters (**5**) formed by the reaction of **4** with MCPBA, as shown in Scheme 1.

The decomposition of secondary-alkyl peroxyesters has been reported to give light emission by a few modes of processes.[9] On the other hand, a tertiary-alkyl perester was reported to be inefficient in emitting light.[8c] As the intermediary β-hydroxyalkyl peroxyesters **5** are tertiary-alkyl derivatives, the mechanism for their decomposition would be different from those of reported one. The successive addition of triethylamine (NEt_3)[10] and trifluoroacetic acid to the reaction mixture, as shown in Table 1, indicates the important role of the lone pair of N in acridan-ring on CL. The similar off /on switching by successive addition of acetic acid and NEt_3 was reported in the CL from the decomposition of 1,2-dioxetanes derived from 9-alkylidene-10-methyl-9,10-dihydroacridines.[11] The mechanism was proposed to involve an intramolecular electron transfer (N to peroxide bond). Hence, a similar mechanism would operate in the present CL from **5**.

The activation parameters for CL of **1c** with MCPBA in CH_2Cl_2 are determined as follows: $\Delta G^{\ddagger}_{298}$ = 79.3±1.4 kJ/mol, $\Delta H^{\ddagger}$ = 20.0±1.0 kJ/mol, $\Delta S^{\ddagger}$ = -199±3 J/K•mol. The large negative activation entropy and the small activation enthalpy of CL suggest a bimolecular catalysis for the decompositon of **5**. The addition of NEt_3 (0.22mmol) after 40 s of reaction to the reaction mixture of olefin **1c** (0.010mmol) with MCPBA (0.20mmol) in 4.5mL CH_2Cl_2 at 25°C leads to the decrease of first order rate constant of CL decay, i.e. 0.019 s^{-1}, which is slower by a factor of ca. 4. A strong increase in intensity of light emission and a decrease in the rate of CL decay by the addition of NEt_3 to the reaction mixture[12] indicate that the main pathway is the non-chemiluminescent decomposition of intermediate **5** catalyzed by m-chlorobenzoic acid (MCBA), formed from

Table 1. Successive Addition of NEt_3 and CF_3CO_2H to Reaction Mixture of **1c** and MCPBA in CH_2Cl_2 at 25°C[a]

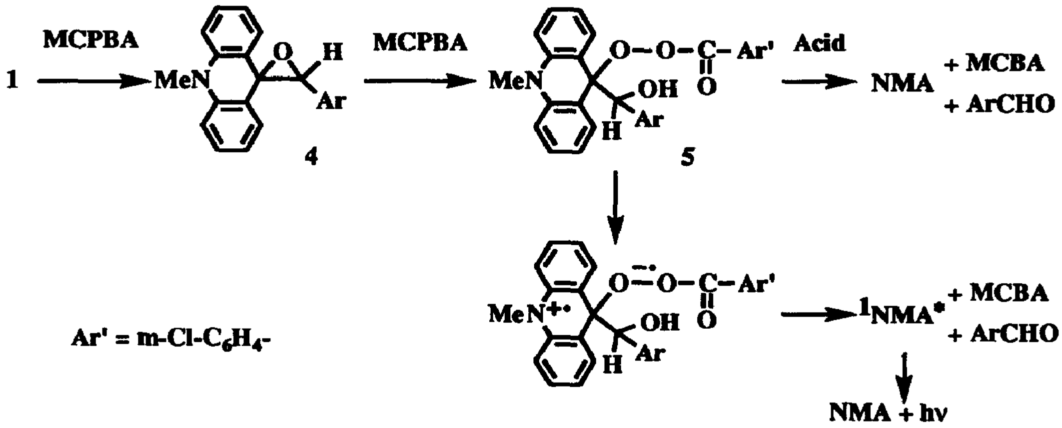
Additive(molar ratio to olefin) and Addition Time	Maximum Intensity of Emission[b]
(initial reaction mixture)	20690
NEt_3 (11) after 77 s	1241000
CF_3CO_2H (20) after 137 s	208
NEt_3 (11) after 175 s	814510

a) In 4.5 mL CH_2Cl_2, [olefin] = 2.1×10^{-3} M, [MCPBA] = 4.2×10^{-2} M. b) Arbitrary unit.

MCPBA upon epoxidation, and that the minor non-catalyzed decomposition of **5** gives the excited product.

The addition of NEt_3 (0.22mmol) to the reaction mixture after 40 s changes the activaton parameters for CL of **1c** as follows; $\Delta G^{\ddagger}_{298} = 83\pm9$ kJ/mol, $\Delta H^{\ddagger} = 72\pm6$ kJ/mol, $\Delta S^{\ddagger} = -35\pm22$ J/K•mol. These values are very different from those without addition of NEt_3, but similar to those for CL from the 1,2-dioxetane derived from the phenyl-substituted olefin **1a**; i.e. $\Delta G^{\ddagger}_{298} = 83.2\pm1.3$ kJ/mol, $\Delta H^{\ddagger} = 63.9\pm0.9$ kJ/mol, $\Delta S^{\ddagger} = -62\pm3$ J/K•mol.[11] These activation parameters and the off/on switching described above suggest that **5** will decompose to give the singlet excited state of NMA by the mechanism similar to that of the phenyl-substituted 1,2-dioxetane,[11] i.e. chemically initiated electron exchange luminescence (CIEEL) mechanism, as shown in scheme 1.

In conclusion, we have shown that a novel CL reaction from **1** and MCPBA proceeds probably via β-hydroxy-tertiary-alkyl peroxyesters **5** and that the addition of NEt_3 makes the decomposition of **5** by CIEEL mechanism the main pathway.



Scheme 1

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1 a) McGown, L. B.; Warner, I. M. *Anal. Chem.* **1990**, *62*, 255R. b) Imai, K. *Bunseki* **1991**, 892; *Chem. Abstr.* **1992**, *116*, 147122p. c) Kricka, L. J. *Anal. Chem.* **1993**, *65*, 460R.

2 a) **1b** and **1c** were prepared by a Wittig-Horner reaction of 10-methoxyphosphinyl-9-methyl-9,10-dihydro-9-azoniaanthracene with aromatic aldehyde; see, Ishikawa, K.; Akiba, K.; Inamoto, N., *Bull. Chem. Soc.*

Jpn. **1978**, *51*, 2684. **1b**: m.p. 95 - 96 °C; ^1H nmr ($CDCl_3$, 60MHz) δ 3.52(N-Me), 6.47-8.14; $\{^1H\}^{13}C$ nmr ($CDCl_3$, 15 MHz) δ 33.59(N-Me), 112.39, 112.80, 119.80, 120.33, 121.14, 122.17, 123.84, 124.96, 125.57, 125.72, 125.99, 126.36, 126.74, 128.13, 128.37, 128.76, 132.22, 133.28, 133.83, 136.23, 141.20, 142.50; gc/ms (70eV) m/z (r.i.) 334(26). 333(M^+, 100), 332(57), 318(30), 166(20), 159(13), etc. **1c**: m.p. 195.7-196.5 °C; ^1H nmr ($CDCl_3$, 60MHz) δ 3.51(N-Me), 6.68-7.91; $\{^1H\}^{13}C$ nmr ($CDCl_3$, 15 MHz) δ 33.54(N-Me), 112.34, 113.05, 119.87, 121.21, 122.11, 122.24, 123.38, 125.33, 125.77, 126.60, 126.82, 127.13, 127.25, 127.50, 127.60, 127.91, 128.52, 128.86, 131.88, 132.18, 133.63, 136.05, 141.09, 142.92; gc/ms(70eV) m/z (r.i.) 334(27), 333(M^+, 100), 332(54), 318(28), 166(18), 159(11), etc. b) As the sensitive photometer can detect weak light emission from **1** exposed to room light, **1** was carefully prepared and purified by low-temperature column chromatography in the dark or under a red lamp.

3 a) Mitchell, G. W.; Hastings, J. W. *Anal. Biochem.* **1971**, *39*, 243. b) The photometer was modified by use of a photon-counting unit (Hamamatsu C1230) and a photomultiplier tube (Hamamatsu R928) cooled by circulating -35 °C ethanol, and connected with a microcomputer for data-processing.

4 Adamantylidene derivatives **3** were prepared by p-toluenesulfonic acid-catalyzed dehydration of the corresponding alcohol derived from adamantanone and the organolithium of heterocyclic aromatics and identified by proton and carbon-NMR spectra.

5 a) Pseudo-first order rate constants are estimated from UV absorbance of the reaction mixture at 420 nm by use of nonlinear least squares treatment. b) See for the correlation of UV absorbance of reaction mixture with concentrations: Frost, A. A.; Pearson, R. G. "Kinetics and Mechanism", second ed. Wiley Internat., Tokyo, **1961**, p.28. c) See for nonlinear least squares program: Yamaoka, K.; Tanigawara, Y.; Nakagawa, T.; Uno, T. *J. Pharm. Dyn.* **1981**, *4*, 879.

6 Lynch, B. M.; Pausacker, K. H. *J. Chem. Soc.* **1955**, 1525. For example, in the reaction of trans-stilbene with peroxybenzoic acid in benzene: $\Delta G^{\ddagger}_{298} = 92.0$ kJ/mol, $\Delta H^{\ddagger} = 63.6$ kJ/mol, $\Delta S^{\ddagger} = -95.4$ J/K•mol.

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10 Initial addition of NEt_3 to the reaction mixture caused instantaneous decomposition of MCPBA, which was confirmed by peroxide test (NaI on silica gel plate).

11 Lee, C.; Singer, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 3823.

12 a) The chemiluminescence quantum yield (ϕ_{cl}) from the reaction of **1a** and MCPBA at 25°C and ϕ_{cl} on the addition of NEt_3 to the reaction mixture were estimated to be 7×10^{-9} and 4×10^{-7} Einstein mol^{-1}, respectively, by use of the luminol aqueous light standard. b) See for the luminol light standard: Lee, J.; Wesley, A. S.; Ferguson, III, J. F.; Seliger, H. H. "Biolumin. in Progr.", ed. by Johnson, F. H.; Haneda, Y. Princeton Univ. Press, Princeton, **1966**, pp. 35-43 and Lee, J.; Seliger, H. H. *Photochem. Photobiol.* **1972**, *15*, 227.

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