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New Analytical Chemiluminescence System Using Peroxymonosulfate as Oxidant

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Transition metal ion- and ketone-catalyzed decompositions of peroxymonosulfate ion were found to produce light emission. The luminous decompositions permitted flow chemiluminescent determinations of cobalt(II), iron(II) and vanadium(IV) ions and fluorescent organic compounds.

Peroxymonosulfate(PMS) $KHSO_5$, in the form of a triple salt $2KHSO_5\cdot KHSO_4\cdot K_2SO_4$, catalytically decomposes to generate dioxygen in the presence of transition metal ions(M^{n+})1) or organic substrates such as ketones(R_2CO),2)

$$2HSO_5^- \xrightarrow{M^{n+}\text{ or }R_2CO} 2HSO_4^- + O_2.$$

The ketone-catalyzed decomposition proceeds via the formation of an intermediate, dioxirane(DOR) $R_2\underbrace{C{-}O{-}O}$ which is a powerful oxidant, in high energetic state.3) We recognized for the first time that some of these decompositions were accompanied by light emission. Judging from the above reaction scheme, the luminescence comes likely from the dioxygen in the excited state, singlet oxygen($^1O_2$). It is expected that the decompositions of PMS yielding the active species($^1O_2$ and DOR) offer new analytical chemiluminescent(CL) systems capable of detecting transition metal ions and organic compounds. Such analytical CL methods are based on the measurement of the light emission from singlet oxygen and excited products formed by the interaction with PMS or the active species. The objective of this study is to explore the possibility of the development of new analytical CL systems using PMS.

Experiments were conducted by means of both batch and flow methods using a Lumicounter 1000(NITI-ON) and a LUMIFLOW LF-800(NITI-ON), respectively. First, various transition metal ions were examined for the luminous decomposition of PMS in buffer solutions by the batch method. As a result, Co^{2+}, Fe^{2+} and VO^{2+} were found to provide strong CL in a phosphate buffer solution, an unbuffered solution and a bicarbonate buffer solution, respectively. From the CL profiles obtained, it was found that the light emission occurred with rather high speed and reached the maximum intensity within several seconds. This prompted us to make flow determinations of these metal ions. Thus each metal ion was subjected to the flow experiments using a system shown in Fig. 1. Among the metal ions causing

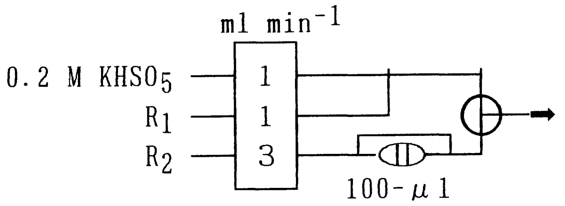


Fig. 1. Schematic diagram of the flow CL system (for key, see text).

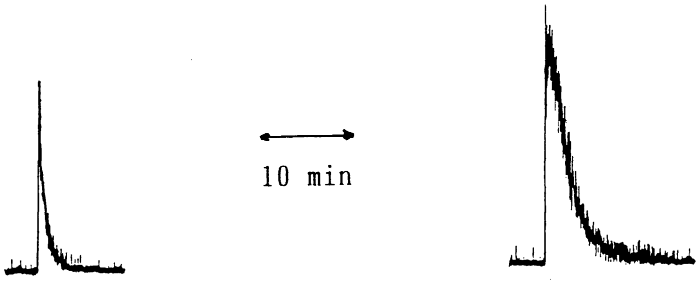
the catalytic decomposition, Co^{2+} was the most effective CL-inducer when R_1 and R_2 were 0.3 M (1 M=1 mol dm^{-3}) Na_2HPO_4 and H_2O (Co^{2+} mode, pH 7.1), respectively. Under unbuffered conditions of H_2O for R_1 and R_2 (Fe^{2+} mode, pH 2.1), Fe^{2+} induced the most intense CL. On the other hand, VO^{2+}-induced CL was the strongest when R_1 and R_2 were 0.01 M $NaHCO_3$ and H_2O (VO^{2+} mode, pH 2.3), respectively. The detection limits (S/N=3) in each mode were 1×10^{-8} M for Co^{2+}, 2×10^{-7} M for Fe^{2+} and 6×10^{-7} M for VO^{2+}. The Co^{2+} and Fe^{2+} modes were fairly selective. With the Co^{2+} mode VO^{2+}, Fe^{2+}, Ni^{2+} and S^{2-} provided CL signals 0.1, 0.02, 0.01 and 0.01% of that for Co^{2+}, respectively; with the Fe^{2+} mode VO^{2+}, Co^{2+}, Fe^{3+}, Ni^{2+} and S^{2-} did those 4, 2, 0.1, 0.02 and 0.01% of that for Fe^{2+}, respectively. The VO^{2+} mode, however, exhibited poor selectivity, Co^{2+} and Fe^{2+} giving CL signals 155 and 51% of that for VO^{2+}. In these modes, the following transition metal ions were found not to induce CL: Cu^{2+}, Mn^{2+}, Zn^{2+}, Pb^{2+}, Al^{3+}, Cr^{3+}, CrO_4^{2-}, VO_3^-, $Mo_7O_{24}^{6-}$, WO_4^{2-} and Ag^+. The above results indicate that by changing the buffer solution, the luminous decomposition of PMS may be used for selective flow CL determinations of Co^{2+} and Fe^{2+}, and also VO^{2+} when the interferences from Co^{2+} and Fe^{2+} can be avoided.

Next, various organic compounds were examined for CL emission using three flow systems, a PMS system (R_1: 0.3 M Na_2HPO_4, R_2: H_2O), a PMS/acetone system (R_1: 0.3 M Na_2HPO_4, R_2: 30% acetone) where dimethyldioxirane was formed in situ, and a PMS/M^{2+}(M=Co,Fe,VO) system (R_1: 1×10^{-3} M M^{2+}, R_2: H_2O). In the former two systems, some fluorescent compounds chemiluminesce intensely as shown in Table 1; with the PMS/acetone system, especially, rhodamine B and pyranine give 25 times higher CL signals than those with the PMS system. This is in contrast to other compounds including luminol which gives rise to strong CL, showing CL signal ratios ((B)/(A)) less than 2. The difference appears to lie in the involvement of the energy transfer to the fluorescent compounds from the dimethyldioxirane in high energetic state (ca. 80 kcal/mol), enough to electronically excite rhodamine B and pyranine, as it is well documented for 1,2-dioxetanes. However, this is in conflict with the fact that the CL spectrum of rhodamine B exhibits an emission maximum at ca. 510 nm, shorter wavelength than that (573 nm) of its fluorescence. Therefore, it is reasonable to consider that the CL is emitted through the destructive oxidation of rhodamine B with the dioxirane. In order for the energy transfer to occur, fluorescent compounds will be necessary to resist the destruction by the DOR, a much more powerful oxidant than the dioxetanes. On the other hand, the PMS/M^{2+} system allows many fluorescent compounds to luminesce when M is cobalt (Table 1). This implies that the system may be used for the detection of these fluorescent compounds. In the unbuffered solution, the Co^{2+}-catalyzed decomposition of PMS does not cause appreciable CL per se, unlike in

Table 1. CL Signal for Fluorescent Organic Compounds

Compound (10^{-6} M)	CL signal (signal-to-noise ratio)			
system=	PMS[a] (A)	PMS/acetone[a] (B)	(B)/(A)	PMS/Co^{2+}[b]
Rhodamine B	28	780	28	21
Methylene Blue	44	21	0.5	618
Pyronine Y	8	16	2	27
Rose Bengal	6	13	2	6
Uranine	ND	5		7
Eosin Y	17	7	0.4	9
Brilliant sulfoflavine	2	2	1	49
Anthracene	ND	ND		7
1-Aminoanthracene	ND	55		44
Pyrene	ND	ND		29
1-Aminopyrene	55	7	0.1	67
9,10-Diphenylanthracene	ND	ND		13
Fluorene	ND	ND		66
Pyranine	4	100	25	11
4-Amino-3-hydroxy-1-naphthalenesulfonate	4	3	0.8	10
DNS-alanine	ND	ND		73
Alanine[c]	ND	ND		ND
Phenylalanine[d]	ND	ND		8
Tyrosine[d]	ND	ND		19
Tryptophan	2	2	1	2
7-Hydroxycoumarin	ND	ND		125
Luminol	380	760	2	19

a) 0.2 M $KHSO_5$, b) 0.02 M $KHSO_5$, c) not fluorescent, d) 10^{-4} M.



(A) (B)

Fig. 2. Effect of the isotope (D_2O) on the CL signal for VO^{2+} by the batch method Solvent: (A) H_2O, (B) 99% D_2O. Each 50-μl solution of 2×10^{-3} M $KHSO_5$ and 1×10^{-4} M VO^{2+} was injected into a reaction cell.

the phosphate buffer solution. This leads to low background and hence is of great advantage from the analytical point of view. The Co^{2+} catalyst can not be replaced by Fe^{2+} or VO^{2+} since they are less active for the present CL emission.

It seems likely that $^1O_2$ participates in the above mentioned CL reactions because the decomposition of PMS is considered to yield $^1O_2$ as stated above. This was confirmed by means of (i) the evolution of O_2 gas from the reaction mixtures at high concentration levels, (ii) the quenching of $^1O_2$ due to 10^{-7}-10^{-3} M sodium azide and 1,4-diazabicyclo[2,2,2]octane (DABCO) and (iii) the isotope effect in D_2O. The isotope effect on the CL signal for VO^{2+} is shown in Fig. 2. The lifetime of $^1O_2$ depends greatly on the solvent used, 20-30 times longer in D_2O than in H_2O.[4] The result exhibits a marked increase in the CL quantum yield due to a reduction in the interaction between $^1O_2$ and D_2O. It is known that the M^{n+}-catalyzed decomposition is pH-dependent; in acidic solution,[5]

$$HSO_5^- + M^{n+} \longrightarrow SO_4^{-\cdot} + OH^- + M^{n+1}.$$

It should be noted that in the acidic solution Co^{2+} does not induce so strong CL as Fe^{2+} does. This might closely be related with the fact that the PMS/Co^{2+} system makes many fluorescent compounds CL-emissive. It is conceivable that the trivalent metal ion formed plays a key role in the CL reactions.

In conclusion, we have found that the PMS decompositions yield the active species causing the CL emission which is usable for new analytical CL systems. In particular, it is worthwhile proposing the CL system for the detection of fluorescent compounds since oxalate diester CL is an only system for it. Further study including the improvement of the CL characteristics by use of molecular assemblies and/or sensitizers[6] will offer promising analytical CL methods.

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