Solid Surface Enhancement Effects on Chemiluminescence: Effects of Number of Cationic Species in Solid Media

Tetsutaro Yoshinaga,* Shigekazu Akimoto, Teijiro Ichimura,† Hiroshi Hiratsuka,††
Miki Hasegawa,††† Michio Kobayashi,††† and Toshihiko Hoshi†††
Department of Applied Chemistry, Faculty of Engineering, Kyushu Institute of Technology,
Sensuicho, Tobata, Kitakyushu 804-8550
†*Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, Ookayama, Meguro, Tokyo 152-8551*
††*Department of Chemistry, Faculty of Engineering, Gunma University, Tenjincho, Kiryu, Gunma 376-8515*
†††*Department of Chemistry and Biological Science, College of Science and Engineering, Aoyama-Gakuin University,*
Fuchinobe, Sagamihara, Kanagawa, Tokyo 229-8558

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Solid surface enhancement effects on chemiluminescence (CL) have been studied using alkaline metal salts as solid media. Effects of number of cationic species (alkali metal ions: Na^+ and K^+ ions) on chemiluminescence of diaryl oxalate type CL reagent were investigated. It was found that sodium and potassium ions are the most active CL enhancers among alkaline metal ions, and the more sodium ions (or potassium ions) are included in the solid medium, the stronger the CL intensity.

Chemiluminescence has been used in many fields[1–5] although most of them are biased towards analytical applications. Especially flow-injection chemiluminescence for the sensitive determination of living organism relatives has been extensively investigated using the enhancement phenomena of luminol.[6–8] However, most of these experiments have been carried out in liquid phases. We have studied chemiluminescent characteristics[9–12] on solid surfaces using diaryl oxalate (as a representative of chemiluminescent reagents) and many kinds of solid media expected to be used as solid surface enhancers, since there are few studies on the relationship between chemiluminescence and solid surfaces. Only very recently, Lu et al. reported[13] that peroxinitrous acid (ONOOH) was produced by the on-line mixing of acidified H_2O_2 with nitrite in a flow system, and a strong CL emission was observed when ONOOH reacted with carbonate without any special CL reagents. Furthermore, they described that when cotton was present in the CL cell, the CL emission was enhanced significantly. However, we have already reported the effect of cellulose (filter paper and cellulose powder) as solid media on CL (peroxalate + H_2O_2 system), and have shown that the relative CL intensity to blank was about 2 times and not so strong.[9,10] These results suggest that solid surface enhancement effects on CL might depend on the kind of CL system.

Thus far, we have used many solid substances as activated solid media that were water or solvent insoluble, since the CL enhancement occurs after CL reagent is dropped onto the center of active solid media. But in real experiments, we have found that even if the active solid media are solvent soluble, some media worked as excellent CL enhancers without any difficulty as long as the sample (CL reagent) quantities are small enough. These findings enlarged the selection scope of possible compounds as solid enhancers. Moreover, in the previous work,[12] we have shown that metal salicylates used as solid media that are solvent soluble greatly affected CL intensities, and sodium (and potassium) gave the highest intensities as CL enhancers as reported. To raise the reliability of the previous work at first, we have used carbonates and chlorides as additional experiments in this work. As is shown in Figure 1, CL intensity dependence patterns on cationic species were nearly the same irrespective of type of solid media especially for alkaline metal ions, although

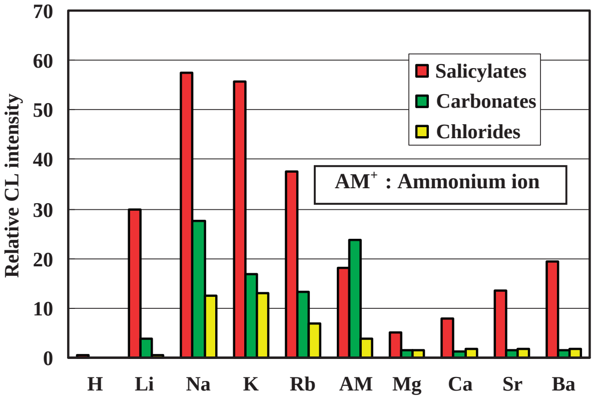

Figure 1. Effect of cationic species in solid compounds on solid surface chemiluminescence.

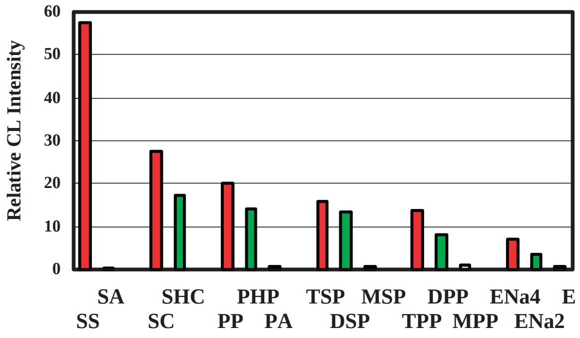

Figure 2. Effect of number of cationic species (Na^+ or K^+) on solid surface chemiluminescence. SS: Sodium salicylate, SA: Salicylic acid, SC: Sodium carbonate, SHC: Sodium hydrogen carbonate, PP: Potassium phthalate, PHP: Potassium hydrogen phthalate, PA: Phthalic acid, TSP: Trisodium phosphate, DSP: Disodium hydrogen phosphate, MSP: Sodium dihydrogen phosphate, TPP: Tripotassium phosphate, DPP: Dipotassium hydrogen phosphate, MPP: Potassium dihydrogen phosphate, ENa4: Ethylenediaminetetraacetic acid 4Na, ENa2: Ethylenediaminetetraacetic acid 2Na, E: Ethylenediaminetetraacetic acid.

small differences were recognized in other cationic species (alkaline earth metal ions). Considering these results, we have investigated the effect of number of cations (especially sodium or potassium ion) in the present work.

Experimental procedure is simply described as follows: Sticks of CL reagent (Cyalume) were commercially obtained from Lumica Co. Ltd., Japan. The constituents of CL reagent in the stick comprised A and B solutions. The A solution (packed in PE capusule: outer tube sealed) was a mixture of (1) aryl oxalate (bis(3,4,6-trichloro-2-(pentyloxycarbonyl)phenyl) oxalate) and (2) fluorescent reagent (1-chloro-9,10-bis(phenylethynyl)-anthracene, and (3) the solvent (dibutyl phthalate: DBP). The B solution (packed in glass tube sealed: inner tube) was a mixture of (4) oxidizing reagent (H_2O_2), (5) the solvent (*t*-butyl alcohol + dimethyl phthalate) and (6) the catalyst (sodium salicylate). Upon use, the stick was bent and the inner glass tube was broken up to mix up the A and B solutions in which the CL reaction took place. After shaking up for 10 s, 100-µL CL reagent was sampled out using a micropipet and dropped at the center of the solid media sample. CL intensities are measured at appropriate intervals using digital power meter. For more details, see Refs 10 and 11.

The effect of a number of cationic species (restricted to sodium and potassium ions here) on chemiluminescence were examined, and the results are shown in Figure 2. As the figure shows, for every compound, we can conclude that the more sodium ions (or potassium ions) are included in the compound (solid medium), the stronger the CL intensity. There seems to be no exception in this experimental rule. For more detailed discussion, we have obtained parameters such as relative CL lifetime, relative CL energy, including relative CL intensity for these solids, and all the data is shown in Table 1. These values were obtained by CL intensity–time profiles using first order approximation as reported elsewhere.[10,11] The table shows that there seems to be no explicit relation between number of alkaline ions in solid media and relative lifetime (or relative CL energy) but for relative CL intensity. As for CL intensity, sodium ions in solid media might work as a strong catalyst. Concerning the relative CL energy, phthalate gave the highest energy (about 2 times to blank).This is a very interesting phenomenon, and apparently, the electronic structure is related to the results, although clear explanation is difficult at the present stage.[11,12]

Table 1. Parameters on CL characteristics for alkaline metals containing compounds

Compounds (Solid media)	Relative CL Intensity (I_r)[a]	Relative CL lifetime (τ_r)[a]	Relative CL energy (E_r)[a]
Blank (glass plate)	1.00	1.00	1.00
Sodium salicylate	57.5	7.29×10^{-4}	4.20×10^{-2}
Salicylic acid	0.300	4.03×10^{-1}	1.19×10^{-1}
Sodium carbonate	27.6	7.76×10^{-3}	2.14×10^{-1}
Sodium hydrogen carbonate	17.2	2.86×10^{-4}	4.90×10^{-2}
Dipotassium phthalate	20.1	1.04×10^{-1}	2.09×10^{0}
Potassium hydrogen phthalate	14.2	8.01×10^{-2}	1.27×10^{0}
Phthalic acid	0.630	2.02×10^{0}	1.27×10^{0}
Trisodium phosphate	16.0	3.43×10^{-4}	5.49×10^{-3}
Disodium hydrogen phosphate	13.5	1.50×10^{-2}	2.03×10^{-1}
Sodium dihydrogen phosphate	0.760	4.49×10^{-1}	3.41×10^{-1}
Tripotassium phosphate	13.7	1.56×10^{-3}	2.14×10^{-2}
Dipotassium hydrogen phosphate	8.20	2.31×10^{-4}	1.89×10^{-3}
Potassiun dihydrogen phosphate	1.21	2.83×10^{-1}	3.42×10^{-1}
Ethylenediaminetetraacetic acid (4Na)	26.9	1.91×10^{-2}	5.14×10^{-1}
Ethylenediaminetetraacetic acid (2Na)	19.2	1.13×10^{-1}	2.17×10^{0}
Ethylenediaminetetraacetic acid	2.09	2.26×10^{-3}	4.72×10^{-3}

[a] $I_\mathrm{r} = I/I_0$ (blank), I = initial intensity [$\log_{10} I_0 \fallingdotseq -2.86$; $\tau_\mathrm{r} = \tau/\tau_0$ (blank) [$\tau_0 \fallingdotseq 3.21 \times 10^3$ (s)]; $E_\mathrm{r} = E/E_0$ (blank) $= I_\mathrm{r}\tau_\mathrm{r}$ ($E = I\tau$)

In conclusion, it was found that sodium and potassium ions are the most active CL enhancers among alkaline metal ions, and the more sodium ions (or potassium ions) are included in the solid medium, the stronger the CL intensity.

We have now been studying the influence of anionic species on solid surface chemiluminescence systematically, and those results will be reported in the following works. This work was partly supported by a Grant-in-Aid for Scientific Research (C) (No.15550074) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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14 In almost all cases, maximum intensities (I_max) are the same as the initial CL intensities (I_0) in this experimental work, but only rarely, CL max (peak) appears after the measurement of the initial intensity. In that case, I_max was used instead of initial intensity (I_0). All these data were obtained using first approximation, that is, CL intensity (I(t)) vs time profile has a linear relation. For more detail, see Refs 10 and 11.

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