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

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Solid surface enhancement effects on chemiluminescence (CL) have been studied using metal salicylates as solid media. Interesting CL characteristics depending on kinds of cationic species (alkaline metal ions, alkaline earth metal ions etc.) on chemiluminescence of diaryloxalate were found.

Chemiluminescence has been used in many fields[1–5] such as food industries, forensic, biological, agricultural and medical fields etc. In recent years, more practical applications such as road signs and lighting at night, night fishing, interior lighting and so forth have become common. We have studied chemiluminescent characteristics[6–8] on solid surfaces, using diaryloxalate[9] (as a representative of chemiluminescent reagents) and many kinds of solid media expected to be used as solid surface enhancers for detectors of instrumental analyses or controllers of CL characteristics (intensities and/or life time etc.), because there are few studies on the relationship between chemiluminescence and solid surface, although there are extensive studies on solids and fluorescence or phosphorescence.[10] We have so far found interesting solid surface enhancement phenomena.[6–8] Certain kinds of glass fiber filters,[6] several organic polymers,[7] and inorganic compounds,[8] gave very high intensity enhancement effects on solid surfaces.

In the present work, the main focus of our investigations was the influences of cationic species in organic compounds (salicylates) as a solid media, and interesting tendencies were found as reported.

First, the relationship between relative chemiluminescent (CL) intensities and particle sizes of slide glass ground or silica gel (large granular [white: 4 ± 1 mm]) ground were investigated. Relative intensities of chemiluminescence on solid media were measured by the same method as that previously reported.[6–8] As shown in Figure 1, when slide glass (used for blank test) is ground to fine particle sizes, the relative CL intensity increases exponentially, and relative initial intensity (*RI*) became around 21 when final particle size was 2.77 µm (average in diameter). When silica gel used for drying is ground to fine particles, the relative initial intensities are almost constant ($RI \fallingdotseq 1$), except at the small particle size region (less than 50 µm, and $RI \fallingdotseq 1.7$ [at 26 µm]).

As CL intensity reflects the rate of chemiluminescence reactions, we expected that, the smaller the particle sizes of media solid, the higher the CL intensities, and the larger the specific surface, the larger the CL intensity. The glass gave the expected results but the silica gel gave unexpected ones. The difference between these two kinds of materials examined is unexpectedly

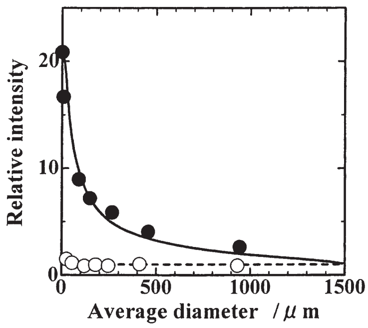

Figure 1. Relationship between relative initial intensities and particle sizes of solid media. Materials used: (○) silica gel, (●) slide glass. Temperature: 25 °C, R.H.: 53%, Blank intensity was set at 1.00, since the value is reference.

too large, despite the fact that the silica gel in general has specific surface of ca. 500 m^2/g, while glass particle has specific surface of ca. 0.4–1 m^2/g. Therefore, we assumed that the main reason for this interesting result is due to the difference in constituents. The slide glass is mainly composed of six oxides as follows; SiO_2(72%), Al_2O_3(2%), CaO(8%), MgO(4%), Na_2O(13%) and K_2O(1%).[11]

For respective compound(oxide) as a solid medium, relative CL intensity and other parameters were measured. These values were obtained using CL intensity-time profiles as reported elsewhere.[7,8] Measured values of CL parameters[8] such as relative maximum or initial CL intensity, relative lifetime, and relative CL energy were shown in Table 1. Table shows that aluminum oxide, sodium oxide (hydroxide), and potassium oxide (hydroxide) give considerably high relative initial CL intensities compared to that of silica. The results suggest that the influence of cationic species in solid media is great. Thus, alkaline metal series and alkaline earth metal series in periodic groups were chosen as representatives of cationic species. On the other hand, sodium salicylate has been used as a catalyst of peroxyoxalate chemiluminescent reagent such as Cyalume which is obtained commercially. Here, we have investigated the dependence of cationic species in metal salicylates on CL intensities using salicylates as solid media.[12] The results are shown in Figure 2.

As is seen from Figure 2, salicylic acid itself does not show any enhancement effect as solid media, or rather less than blank CL intensity [$RI = 0.4 < 1$]. However, *RI* of cationic species corresponding to alkaline metal ions rapidly increases with an increase in atomic numbers until it reaches the maximum CL intensity at sodium [$RI \fallingdotseq 57$], and gradually decreases from potassium to rubidium. Ammonium salt was also examined from

Table 1. Parameters on chemiluminescence characteristics for glass constituents

Compounds	Maximum CL intensities[a] (RMI[c])	CL life time[b]	CL energies[b]
SiO_2[d]	1.79	5.40×10^{-1}	1.23×10^{0}
Al_2O_3[e]	11.2	1.21×10^{-2}	4.60×10^{-1}
CaO	1.83	7.87×10^{-2}	2.00×10^{-1}
MgO	4.69	1.84×10^{-1}	8.54×10^{-1}
K_2O[f]	12.6	3.16×10^{-4}	1.02×10^{-2}
Na_2O[f]	17.3	8.50×10^{-4}	3.25×10^{-2}
Blank*	1.00	1.00×10^{0}	1.00×10^{0}

[a]: In almost all cases, maximum CL intensities (I_{max}) were the same as the initial CL intensities (I_0) in this experimental work but only rarely, I_{max} (peaks) appeared after the measurements of the initial intensities. [b]: CL life time and CL energies were obtained in the same manner as the one already reported.[8] [c]: RMI is relative maximum intensity to that of blank data. RMI = (I_{max}(sample)/I_{max}(blank))~(I_0(sample)/I_0(blank)), I_0 to be initial intensity. [d]: Reagent grade SiO_2(99.9%) (Wako Pure Chemicals) was used and values change according to the properties of SiO_2. [e]: AX-25 (25 μm) was used as shown in reference 8. [f]: For Na_2O and K_2O, NaOH and KOH were used instead. *Blank data is obtained when slide glass is used as a solid medium.

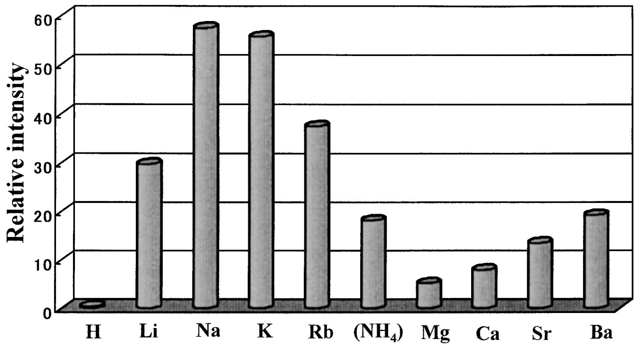

Figure 2. The relationship between relative CL intensities and cationic species in salicylates as solid media.

an ionic size point of view. For alkaline earth metal ions, a similar but slightly different phenomenon was found, that is, CL intensity increases linearly with an increase in atomic numbers.

Is there any reason why the sodium atom in alkaline metal series gave the highest CL intensity? We have examined several factors, such as atomic or ionic radius, ionization potential, electron affinity, electronegativity, specific density, specific conductivity, specific thermalconductivity, pK_a, and so on. However, no appropriate factors or combined factors that explain the above tendency were found. Salicylic acid itself did not work as catalyst, and this suggests that those elements which tend to have highly ionic character in the media affects some effects on enhancement phenomena, although related properties such as ionic potential, electron affinity, or electronegativity did not allow explanation of the results. Probably kinetic properties are more important than thermodynamical ones (or equilibrium theory).

In conclusion, it was found that alkaline metal ions in salicylates as solid media showed very interesting phenomena on solid surface chemiluminescence with sodium ions as the highest enhancer.

The influence of cationic species on CL intensities using solid media has been investigated for other compounds, and we have obtained interesting results. Those results will be reported in future research papers.

References and Notes

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9 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) aryloxalate (bis(3,4,6-trichloro-2-(pentyloxycarbonyl)phenyl)anthracene) 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 (*tert*-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 micropipet and dropped at the center of the solid media sample. CL intensities were measured at appropriate intervals using digital power meter. For more details see references 6 to 8.

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11 These slide glasses were commercially obtained from Matsunami glass industries, Ltd., and the data for the constituents of the glasses were also given by the company.

12 Sodium salicylate was commercially obtained, and other salicylates were prepared by mixing of salicylic acid and the desired metal carbonate in hot water. These newly prepared salicylates were refined by repeated recrystallization using appropriate solvents.