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Solid Surface Enhancement Effects on Chemiluminescence. I. Diaryloxalate and Filters as Media Solids

Tetsutaro YOSHINAGA,* Michihiko MORITA, Ken-ichi WADA, Teijiro ICHIMURA,† and Hiroshi HIRATSUKA††
Department of Chemistry, Faculty of Engineering, Kyushu Institute of Technology, Sensuicho Tobata-ku, Kitakyushu 804
† Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, Ookayama Meguro-ku, Tokyo 152
†† Department of Chemistry, Faculty of Engineering, Gunma University, Tenjincho Kiryu, Gunma 376

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Solid-surface enhancement effects on chemiluminescence were observed using diaryloxalate bis[3,4,6-trichloro-2-(pentyloxycarbonyl)phenyl] oxalate, fluorophore[1-chloro-9,10-bis(phenylethynyl)anthracene], hydrogen peroxide and solids (filters) as media. An especially strong emission was observed when glass fiber filters were used. It is suggested that both the chemical composition and the surface physical properties of the solids affect luminescence. The effects of humidity and temperature on chemiluminescence were also examined. A relative humidity of 50% (at 30°C) gave the highest luminescent intensity. A power functional relation of one hundredth lifetime ($t_{1/100}$) and the temperature(T) was obtained.

Chemiluminescence is a very useful light source in the case of natural disasters and under severe conditions where no electricity or batteries are availale, and the use of heat is not permitted. Recently, chemiluminescence has been extensively applied to analytical chemistry,[1—8] since the chemiluminescence technique has a high sensitivity and very low background luminescence. Regarding chemiluminescence, itself, there have been many basic investigations in view of its experimental and theoretical aspects.[9—22] However, there have been only a few reports[4,20] concerning the effect of a solid surface on chemiluminescence. Therefore, the effects of solid surfaces on the luminescence were investigated for organic chemiluminescent reagents in this study. Chemiluminescence enhancement was ovserved for several kinds of materials, such as filters, inorganic compounds and organic compounds. In the present paper only the results concerning filters are reported.

Experimental

Reagents: **(a) Humidity Regulators.** Saturated aqueous solutions of KOH, $LiCl \cdot H_2O$, $CaCl_2 \cdot 6H_2O$, $K_2CO_3 \cdot 2H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, NaCl, and $K_2Cr_2O_7$ were prepared in order to maintain the humidity of a sample box at 5.0, 10.2, 31.0, 42.8, 52.9, 75.4, and 98.1%, respectively. Each constant-humidity solution was put into a closed vessel (box) made of acrylic resin plates (3 mm/in thickness). All of the reagents used were of reagent grade and were commercially obtained from Wako Chemical Company.

b) Chemiluminescent Reagent. Sticks of a chemiluminescent (CL) reagent having the same composition as Cyalume (American Cyanamid Company) were commercially obtained from Nippon Kagaku Hakko Company. The constituents of CL reagent in the stick comprised A and B solutions. The A-solution (packed in a polyethylene capsule (outer tube sealed)) was a mixture of reagents (1), (2), and (3) as follows: (1) The basic chemiluminescent reagent was bis(3, 4, 6-trichloro-2-(pentyloxycarbonyl)phenyl) oxalate (0.14—0.17 ($\mathrm{mol\,dm^{-3}}$)); (2) the fluorescent reagent was 1-chloro-9, 10-bis(phenylethynyl)anthracene (7×10^{-3} ($\mathrm{mol\,dm^{-3}}$)); and (3) the solvent was dibutyl phthalate. The B-solution (in a glass tube sealed (inner tube)) was a mixture of reagents (4), (5), and (6): (4) The oxidizing reagent was H_2O_2 (ca. 4%); (5) the activator was *t*-butyl alcohol; and (6) the catalyst was sodium salicylate.

The CL stick was a polyethylene tube containing the A-solution and an inner glass tube containing the B-solution. 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.

Filters: *Qualitative filter papers*; Toyo No. 1 (0.2 mm, 6 μm capturing particle size), No. 131 (0.25 mm, 3 μm).

Quantitative filter papers; Toyo No. 5A (0.22 mm, 7 μm), No. 5C (0.23 mm, 1 μm).

Silica fiber filter papers; QR-80 (0.40 mm, containing inorganic binder), QR-100 (0.35 mm, no binder).

Glass fiber filter papers; GS-25 (0.25 mm, 0.6 μm, containing organic binder), GC-50 (0.2 mm, no binder).

Active carbon filter paper; CP-20 (2.00 mm, active carbon 50%)

Membrane filters;(nitrocellulose type) A010 (0.110 mm, 0.10 μm, porosity 65%), A080 (0.155mm, 0.80 μm, porosity 80%), poly(tetrafluoroethylene) [abbreviated as PTFE hereafter] type; polyflon PF0-020 (0.55 mm, 2.0 μm), PF0-060 (0.50 mm, 6.0 μm).

All of the filters were commercially obtained from Toyo Filter Company.

Apparatus: The intensity of the chemiluminescence was measured with a Sanwa Model SLP-40000 light power and multitester. The light sensor of the power meter was made from a silicon photodiode and its light-sensitive range was 660—800 nm. We therefore used the 660 nm range as the shortest wavelength limit of the sensor, because the diaryloxalate chemiluminescent reagent used had a luminescence maximum wavelength of ca. 526 nm. The luminescent intensity could be measured in the range from $-60\ \mathrm{dB_m}$(10 nW) to $+10\ \mathrm{dB_m}$(10 mW). When the luminescence intensity was measured in mW units, it was converted to $\mathrm{dB_m}$ using the following formula (definition):

$$N(\mathrm{dB}_m) = 10\log_{10}(E/\mathrm{mW})\ (= 4.34\log_e(E/\mathrm{mW})). \quad (1)$$

The chemiluminescent temperature was regulated using a Taitec CL-80 accurate digital thermostat.

In a practical experiment using filters the water content varied with the humidity. Filter paper (No. 5A) was dried and kept in a decicator prior to use; it was then put into a constant-humidity box (at ca. 30°C) for 5 h until equilibration. The filter was then taken out and weighed as soon as possible. It was dried for 3 h (at 110°C), which was a sufficient time to remove the water; the weight was then measeured. The relative humidity was measured using a Yamato Humidex YL-12 degital hygrometer (0—100%).

Immediately after the inner tube of the CL stick was broken, mixing took place using a Yamato MT-51 touch mixer.

Procedures. The detector of the light power meter and the position of the sample are illustrated in Fig. 1a. A sample filter is put on the slide glass, and the CL tube which is maintained at constant temperature prior to the experiment is broken at 2 points using radio pliers (Fig. 1b). It is then immediately shaken for 10 s; 100 μl (or desired quantity) of the CL mixture is sampled out using a microinjector and then dropped at the center of the filter. The chemiluminescence is measured 30 s after injection. The luminescent intensity is measured at appropriate intervals until the intensity is reduced to less than −50 dB_m. Blank samples are measured for a comparison; i.e., a CL mixture was dropped directly on the glass slide having a round concave part in the center.

To examine the temperature effects the following procedure was used. The distance of the photosensor and the base (aluminumplate) on which two pieces of slide glass were placed was fixed at 1 cm; wooden frames were then fitted on to the slide in order to fix the CL stick rigidly. For the temperature region higher than 40°C, a block heater made of aluminum was used. For the temperature region less than 40°C, an accurate digital thermostat was used. For 25°C heatings, measurement was carried out at room temperature. In practical experiments, a CL stick was placed into one of the thermostats and heated for one hour. It was removed using a pair of tweezers. Immediately after removal, the glass tube in the stick was broken and shaking took place for 10 s. The stick was then swiftly put into the sample base in the thermostat and the chemiluminescence was measured 20 s after shaking.

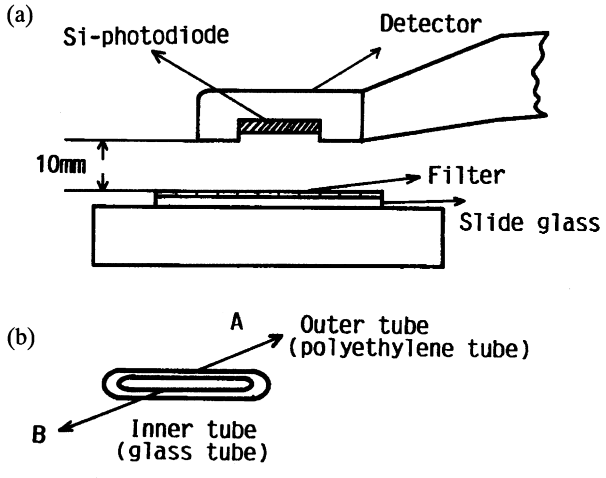
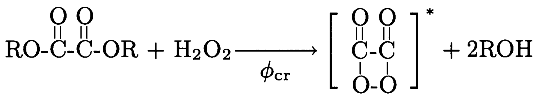
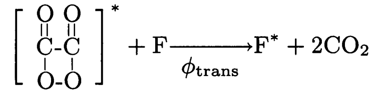


Fig. 1. (a) Schematic figure of the device used for the measurement of chemiluminescence. (b) CL stick comprising a polyethylene tube (A) in which the chemiluminescent reagent is contained, and an inner tube (B) in which the oxidizing reagent is contained.

Mechanism and Quantum Yield of the Chemiluminescence

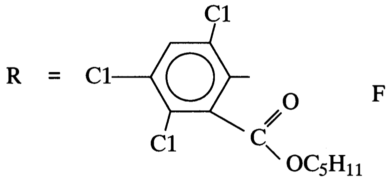

(2)

$$\mathrm{RO\text{-}\overset{\overset{O}{\|}}{C}\text{-}\overset{\overset{O}{\|}}{C}\text{-}OR} + H_2O_2 \xrightarrow[\phi_{cr}]{} \left[\begin{array}{c} \mathrm{O\ \ O} \\ \|\ \ \| \\ \mathrm{C\text{-}C} \\ |\ \ | \\ \mathrm{O\text{-}O} \end{array}\right]^* + 2ROH \qquad (2)$$


(3)

$$\left[\begin{array}{c} \mathrm{O\ \ O} \\ \|\ \ \| \\ \mathrm{C\text{-}C} \\ |\ \ | \\ \mathrm{O\text{-}O} \end{array}\right]^* + F \xrightarrow[\phi_{trans}]{} F^* + 2CO_2 \qquad (3)$$

$$F^* \xrightarrow[\phi_f]{} F + h\nu \quad \text{(Luminescence)} \qquad (4)$$


F= Fluorophore (5)

The mechanism of diaryloxalate chemiluminescence is conventionally described as previously shown.[22] The quantum yield of chemiluminescence is given as follows:

$\phi_{CL} = \phi_{cr}\phi_{trans}\phi_f$

ϕ_{CL}=chemiluminescence quantum yield

ϕ_{cr}=yield of activated intermediate by chemical reaction

ϕ_{trans}=efficiency of energy transfer from the products to the excited states of the fluorophore.

ϕ_f=fluorescent quantum yield of the excited molecule (or excited fluorophore)

ϕ_{cr} is usually affected by the reaction conditions (solvent, pH, temperature, catalyst, etc.)

Results and Discussion

Effect of CL Reagent Volume on the Chemiluminescence. The luminous intensity depends on the CL reagent volume. The relationship between the volume and the luminous intensity was examined using filter paper (No. 5A). The results are shown in Fig. 2. This figure shows the relationship of the luminous intensity vs. time at respective constant volumes of the CL reagent. The CL intensity increases with an increase in the CL reagent volume over the region 40 to 70 μl, while the intensity becomes nearly constant in the region greater than 70 μl. This is interpreted as follows. Since the wet area (i.e., emitting area) increases with an increase in the CL reagent volume, the light intensity at the sensor part also increases if the luminous intensity at a unit surface is nearly constant. However, since the diameter of the sensor is 8.5 mm, it can not detect the total emission. The luminous intensity remained constant for a CL reagent volume of over 70 μl. From a reproducibility point of view, 100 μl was chosen as the standard sample volume.

Effect of Filter Materials on the Chemiluminescence. Figure 3a shows the time profile of the luminous intensity for cellulose-type filters (qualitative,

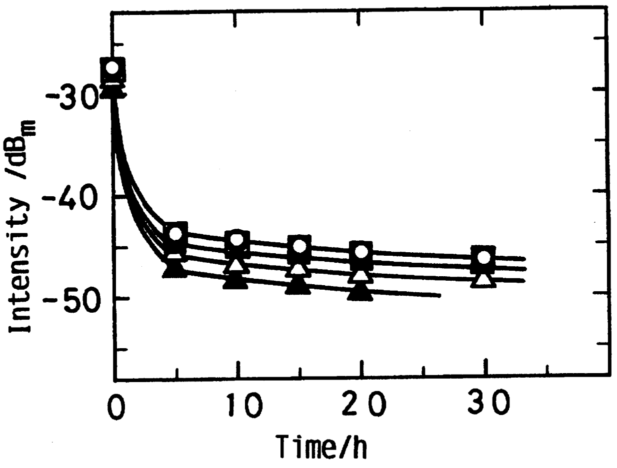


Fig. 2. Volume effect of CL reagent on the chemiluminescence at room temperature (30°C). ▲: 40 μl, △: 50 μl, ■: 60 μl, □: 70 μl, ●: 80 μl, ○: 90 μl. (R.H.=50%). Filter paper used: No. 5A.

quantitative, and active carbon filter paper). The initial intensities for all filters are higher than that of the blank, except for the active carbon filter. However, the chemiluminescent lifetime (the time at which the intensity becomes −50 dB$_m$) for quantitative filter papers was shorter than those for qualitative filter papers. As for the chemical composition, there was no explicit difference between the qualitative and quantitative papers. These small differences in the lifetime may be due to differences in the surface properties, that is, the fiber diameters, porosities, etc. For the active-carbon filter (CP-20), the intensity and luminous lifetime are very weak and short (6 to 8 min). This filter contains 50% of the active carbon other than cellulose and has a strong absorption and adsorption ability. Thus, the oxygen fully sorbed in the filter paper might quench the chemiluminescence. Furthermore, active carbon is a kind of blackbody; such a body can absorb radiation. Two kinds of black sheets and active carbon filters were examined to test the idea of using a light-emitting diode (LED: $\lambda_{\max}$=567 nm); a sheet of black plastic, a sheet of black paper and CP-20 were compared with a sheet of white paper. For those samples, the relative intensities were reduced to ca. 1/10—1/2, compared with that of white paper. The CL reagent permeates and passes through the two sheets of cellulose filter and remain on the filter surface as a thin liquid film. In the case of carbon filters, however, almost all of the CL reagent was absorbed into the filter. This may be another reason for the weak luminescence. After cutting the carbon filter into two parts, weak emission from inside the filter was observed in the dark.

For glass fiber and silica fiber filters the results are shown in Fig. 3b. The figure shows that the glass fiber filter had a very short luminescence lifetime (5 min to 10 min), but produced very strong initial intensities, especially for GS-25 (contains organic binder) and GC-

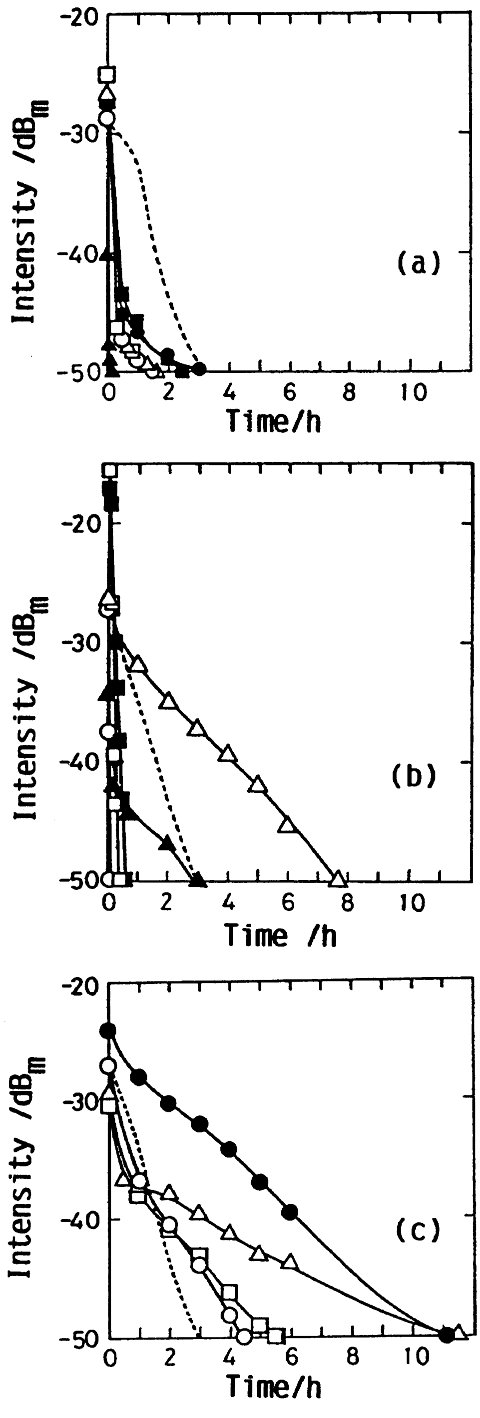


Fig. 3. Effect of the filter material on the chemiluminescence at 30°C. (a): filters used (cellulose papers) ○: No. 5A, □: No. 5B, △: No. 5C, ●: No. 2, ■: No. 131, ▲: CP-20 (active carbon filter). (b): filters used (glass fiber filters [G series] & silica fiber filters [Q series]). ▲ : QR-80 (contain inorganic binder), △: QR-100, ■: GS-25 (contain organic binder), □: GC-50, ○: GA-100. (c): filters used (membrane filters), ○: A020 (nitrocellulose type), □: A300 (nitrocellulose type), △: C020 (acetylcellulose type), ●: PF060 (PTFE type; polyflon filter), - - -(broken line): blank (CL reagent only).

50 (no binder). For example, GC-50 gave an initial intensity of 15-times (or more) greater than that of the blank, although more than a factor of several times above the initial intensity may be expected if it is possible to make observations at an earlier time. In this case, the effect of an organic binder (type of acrylic ester resin) is small. The reason why the glass fiber filter produce a higher enhancement effect on the chemiluminescence is not clear, although it is apparent that the origin involved both the chemical compositions and surface physical properties. One possible reason may be pointed out that, in part, the initial increase in the intensity might be caused by light reflection by the filter materials, as was discussed in regarding room-temperature phosphorescence and fluorescence.[4] This contribution, however, seems to be small considering the experimental conditions, since no excitation radiation in used in the CL experiment. In order to confirm the statement mentioned above the following experiments were carried out. First, the LED (light-emitting diode; $\lambda_{\max}=567$ nm)was set below the sensor (1 cm apart). Several kinds of sheets (filter papers, membrane filters, black paper, aluminum foil, glass and mirror etc.) were then placed under the LED (5 mm apart). Second,the sum of the light energy of the LED and the reflected light on the surface was measured using the same sensor. The measured values showed that there was no significant differences among them, except for a slide glass, a sheet of black paper and a sheet of black plastic, as mentioned above.

The silica fiber filter contained silica of greater than 99% and the glass fiber filter contained SiO_2 (62%), B_2O_3 (11%), Na_2O (10%), Al_2O_3 (6%), BaO (5%), K_2O (3%), and CaO (3%). This composition difference might have caused the intensity difference. Another possibility to explain the enhancement phenomena is that these filters may cause a slight wavelength shift (red shift) in the maximum emission wavelength. However, this was disproved by a measurement of the fluorescence spectra; no spectral shift was observed in the surface luminescence. On the other hand, for silica fiber filters, the effect of an inorganic binder (a kind of aluminium oxide) seems to be significant. QR-80, which contains an inorganic binder, gave a lower initial intensity and a shorter lifetime compared with those of QR-100, which contained no binder. Although QR-100 gave nearly the same initial intensity as that of the blank CL reagent, the lifetime was about 2.5-times greater than that of the blank CL reagent. Considering the fact that the lifetime of the blank CL reagent in a tube was about 8 h at room temperature, and about 2.5-times greater than that of the blank CL reagent in open air, quenching by oxygen would be inhibited on a QR-100 silica filter.

The results for membrane filters (nitrocellulose, cellulose acetate, and PTFE type) are shown in Fig. 3c. The initial intensities for these filters,except for polyflon (PTFE), are nearly the same as that (around -28 dB_m) of the blank CL reagent; the lifetime, however, was greater by about 1.5 to 4 times. Especially the polyflon filter gave larger values for both the initial intensity (-24 dB_m) and lifetime (7.8 h). In this case, the wettability of the polyflon filter was very low and the CL reagent became an oblate sphere (ca. 3 mm high) with the apparent wet surface becoming very small. Accordingly, the quenching effect by oxygen was remarkably reduced.

We now consider that this chemiluminescence reaction was a first-order reaction; the CL intensity can then be expressed by $I(t)=I_0\exp(-kt)$. In this calculation the intensities are expressed in units of decibels, as defined in Section of Apparatus. Since $E(t)=\text{const}\cdot I(t)$, $N(\text{dB}_\text{m})=4.34\log_e[\text{const}\cdot I(t)]=N_0-4.34kt+\text{const}$; that is, the relationship between $N(\text{dB}_\text{m})$ versus the reaction time should be linear. Indeed, this linearity can be observed in Fig. 3. However, the first-order reaction holds only for the initial stage. The deviation from linearity may be explained by interference of the chemical reaction to the yield products.

It has been shown that appropriate aqueous micellar solutions can amplify the chemiluminescence.[23—27] It is reported that CL enhancements have been rationalized in terms of the miscellar catalysis of the CL reaction and/or an improved excitation efficiency due to the unique microenvironment provided by the miscellar assembly.[27] These interpretations seem to be applicable for our solid-state media. In the present work, the CL enhancement phenomenon can be caused by the following reasons: an increase in the quantum yield (due to the unique microenvironment effect of the solid), and/or an increase in the reaction rate (catalytic effect). The contribution, or role of the solids (media) in the mechanism of chemiluminescence in the present work seems to affect mainly the first step of the CL reaction shown in Section of Mechanism (cf. ϕ_{cr}).

Relationship between the CL Reagent Volume and the Wet Area. As already stated regarding the wet area, the luminating area, seems to affect the CL intensity. The relationship between the added CL reagent volume and the wet area of filter was examined after a constant elapsed times of 30 and 60 min. The results are shown in Fig. 4. The wet area was observed by placing filter paper on a glass plate onto which the CL reagent was dropped using a microsyringe. The following power functional relation was obtained regarding the wet area (S/cm^2) and the CL reagent volume (v/μl) for the quantitative-type filter paper (No. 5A).

$$\begin{aligned}&S(t=\text{const},v)=kv^p \quad (k,p=\text{constant});\\&\text{e.g. } S(30,v)=0.80\times v^{0.714},\ S(60,v)=0.98\times v^{0.697},\\&\text{temp.}=25.4^\circ\text{C},\quad \text{R.H.}=46.6\%. \qquad (6)\end{aligned}$$

(The apparent thickness of dried filter paper (No. 5A) was 0.2 mm; the thickness after wetting was 0.22 mm.

The apparent thickness of the CL reagent liquid film after wetting was ca. 0.015 mm, which was calculated using the CL sample volume (100 μl) and the wet area (diameter=ca. 9 cm). This means that the CL reagent volume occupied only one tenth of the inner space of the filter paper.)

Change in the Wet Area upon Standing. The size of the wet area (i.e., luminating area) could affect the luminous intensity. Figure 5a shows the time profiles of the wet area for filters No. 5A and 5C at relative humidities (R.H.) of 52 to 60%. Although the relative difference in these time profiles was small, a relatively large difference was found between one sheet of filter and two sheets of filters. The reason for this was that 40% of the CL reagent was transfered to the bottom filter, and the luminescence from the CL reagent in the bottom filter was masked by the upper filter. This experiment was performed at relative humidities (R.H.) of 52 to 60%. In another experiment using filters dried at 110°C for 2hrs, a power function relation was observed between the wet area (S/cm^2) and the reaction time (t/min); that is, $S(t,v=\text{const})=k't^q$; e.g., $S(t,v=100\ \mu\text{l})=10\times t^{0.235}$, temp.=29—30°C, R.H.=52—60%. Considering these results, we can formulate a general relationship among the wet area (S/cm^2), the reaction time (t/min) and the CL reagent volume (v/μl) for the No. 5A filter:

$$S(t,v)=kv^pt^q\ (k,p,q=\text{const.};\text{Temp.\&R.H.}=\text{const.}). \quad (7)$$

The glass fiber filters, silica fiber filters, and membrane filters gave different time-profile patterns of the wetting area compared to that of the cellulose-type filter papers,

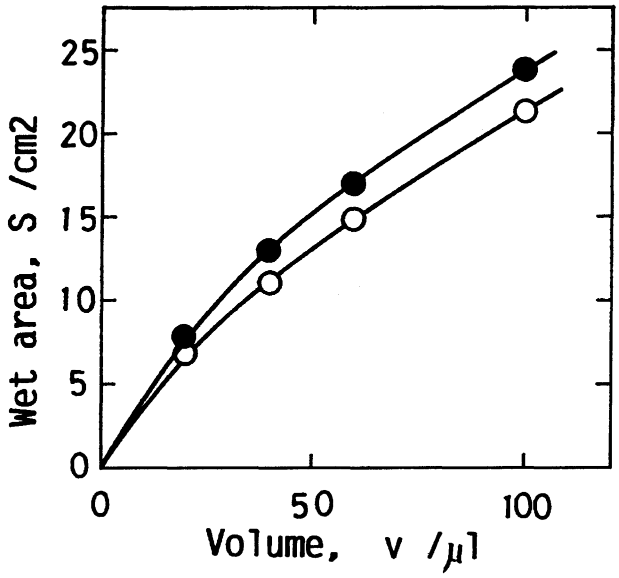


Fig. 4. Relationship between the dropped volume of the CL reagent and the wet area of the filter paper (No. 5A). Measured time; 30 min. or 60 min. after beginning (at 25.4°C, R.H.=46.6%). ○: 30 min. ●: 60 min.

as shown in Fig. 5b. All of these filters except tor the celluloseacetate-type membrane filter (C020), showed a simple time profile of the wetting area: the wet area increased rather rapidly during the early stage after the CL reagent addition (5 to 10 min), and then reached a plateau value. The celluloseacetate-type membrane filter gave a similar wetting pattern to that of the cellulose quantitative-filter paper.

Influence of the Humidity on Chemiluminescence. The influence of the humidity was numerically examined, since it has been found that the humidity has some effects on chemiluminescence. At first, the influence of the relative humidity (R.H.) on the blank CL reagent was studied as a reference. The R.H. value was adjusted so as to be constant by using saturated salt solutions. The experimental results are shown in Fig. 6. In this figure the luminous intensity of the blank CL reagent at 50% R.H. (at 30°C) is at the maximum value. To the best of our knowledge this is the first report that there is an optimum humidity for maximum chemiluminescence. The reason for this is not clear at present, but the phenomenon suggests that water in moist air reacts with the CL reagent to give rise to hydrolysis and/or to

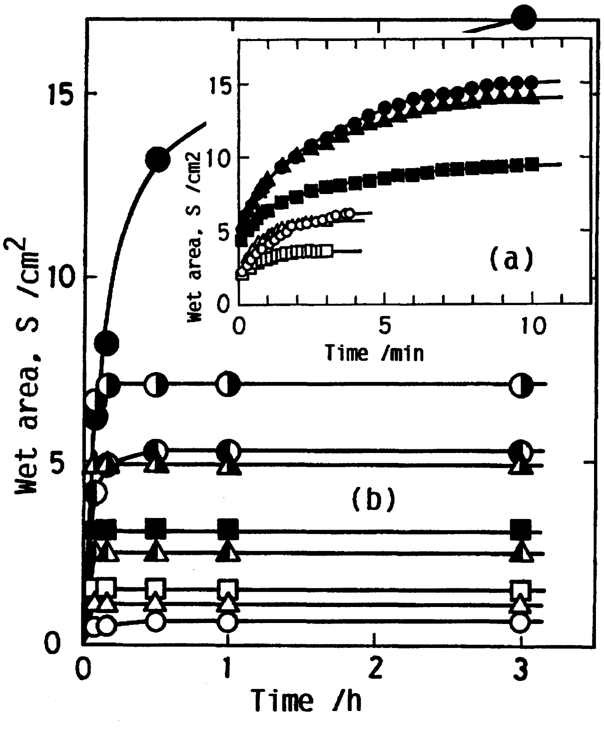


Fig. 5. Relationship between the wet surface area of the filter papers and the time course elapsed at room temperature (29—30°C). [R.H.=52—60%]. (a): △: No. 5A (1 piece), □: No. 5A (2 pieces overlapped), ○: No. 5A (1 piece; after 110°C & 2 h dry). CL reagent used: 50 μl. ▲: No. 5A (1 piece), ■: No. 5A (2 pieces overlapped), ●: No. 5C (1 piece). CL reagent used: 100 μl. (b): ●: C020, ◑: A300, ◐: A020, ▲: GC-50, ◭: GS-25, □: QR-80 & QR-100, △: GA-100, ○: PF060. CL reagent used: 100 μl.

react with the reaction products of CL reagent–H_2O_2 to give a luminescent compound. In other words, there are some simultaneous reactions that have opposite effects, that is, accelerating and preventing reactions that induce luminescence.

The relation of the water content of the filter and R.H. at constant temperature is shown in Fig. 7. With an increase in R.H. from 3% to 40%, the water content ($100\times w[H_2O]/w[\text{dry filter}]$) increased approximately linearly; the water content increased exponentially in the region of more than 50% (e.g. 5.1% (R.H. 50%); 12% (R.H. 80%)).

Effect of Humidity on Solid (filter)–Surface Chemiluminescence. The relationship between chemiluminescence and R.H. was investigated using a cellulose filter (No. 5A). Figure 8 shows that even in the case of using filter paper (cellulose), the dependence of the humidity on the chemiluminescence was similar to that of the blank chemiluminescence, even though the lifetime of the luminescence was reduced to ca. 1/5 compared with that of the blank CL reagent. Why does 50% relative humidity (at 30°C) give the maximum luminescent value, except for the initial intensity? It is probably the same as that for the CL blank experiment. One possible reason is that although most of the CL reagent is absorbed into the filter, a small amount of the CL reagent exist on the filter surface as a thin liquid film.

Temperature Dependence on the Chemiluminescence. The effect of the temperature on the chemiluminescence of the blank CL reagent was investigated. The relationship between the chemiluminescence intensity and the temperature is shown in Fig. 9. As expected, the results are that the higher is the temperature, the higher the intensity becomes and the shorter is the lifetime. In the region lower than 10°C, the lifetime of the luminescence was very long (at ca. −40°C, more than one month). The half-lifetime is very short at higher temperature; it is therefore difficult to obtain good reproducibility. We adopted a one-hundredth lifetime ($t_{1/100}$) instead of the half-lifetime ($t_{1/2}$). Figure 10 illustrates the Arrhenius plots. From the slope in Fig. 10, in which rate constants used are the inverse of $t_{1/100}$, the apparent activation energy (ΔE^*) was obtained to be 10.5 kcal mol^{-1} (T=80—30°C). The dif-

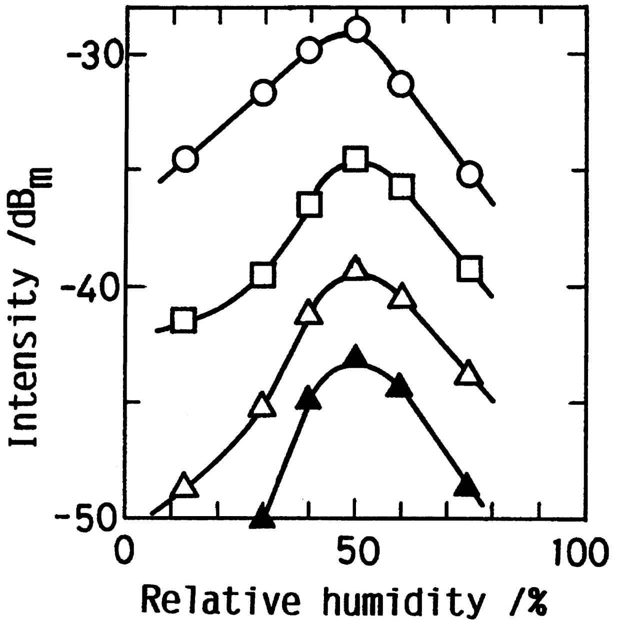


Fig. 6. Effect of the humidity on chemiluminescence at 30°C. [blank condition; CL reagent used: 100 μl]. ○: 30 min., □: 60 min., △: 90 min., ▲: 120 min. after beginning.

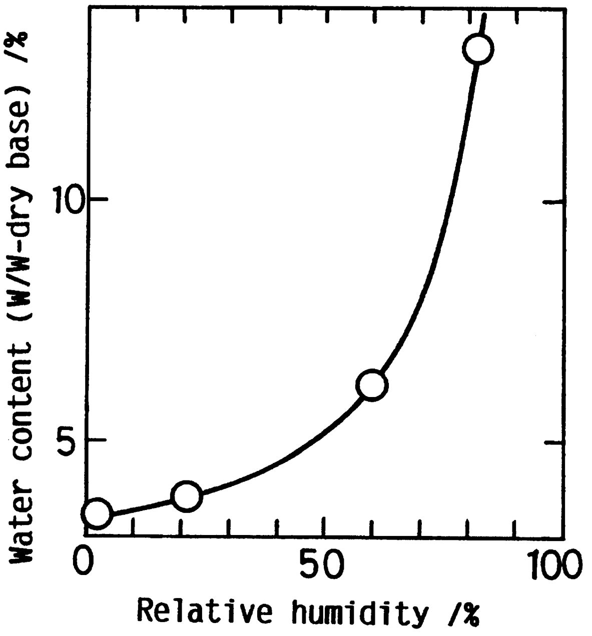


Fig. 7. Relationship between the water content of the filter paper and the relative humidity at room temperature (29—30°C). Filter paper used: No. 5A.

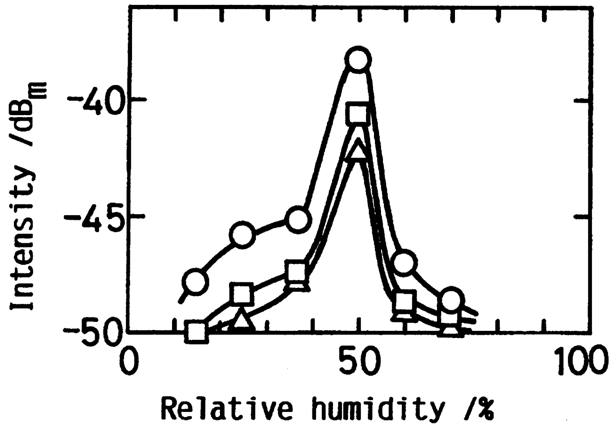


Fig. 8. Effect of the humidity on chemiluminescence at room temperature (29—30°C). CL reagent used: 100 μl. Filter paper used: No. 5A. ○: 5 min., □: 10 min., △: 15 min. after beginning.

ferential method, however, gave an apparent activation energy of 9.3 kcal mol^{-1}. The magnitude of the activation energy (ca. 10 kcal mol^{-1}) suggests that the CL reaction may be susceptible to the effects of both the physical and chemical properties. That is, in the blank CL reaction both of the rate-determining steps of diffusion though boundary film and chemical reaction seem to be equally important, since the CL reaction is a heterogeneous-type reaction.

In a future report, the results for other kinds of solids, correction methods for intensity, etc. will be discussed.

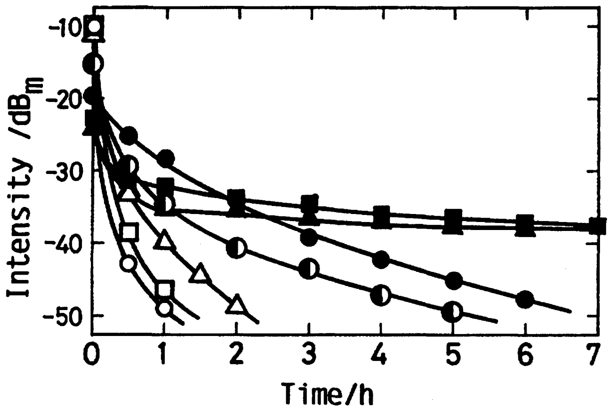


Fig. 9. Temperature effect on chemiluminescence. ○: 100°C, □: 80°C, △: 60°C, ◐: 40°C, ●: 25°C, ■: 10°C, ▲: 0°C. CL reagent used: in stick state.

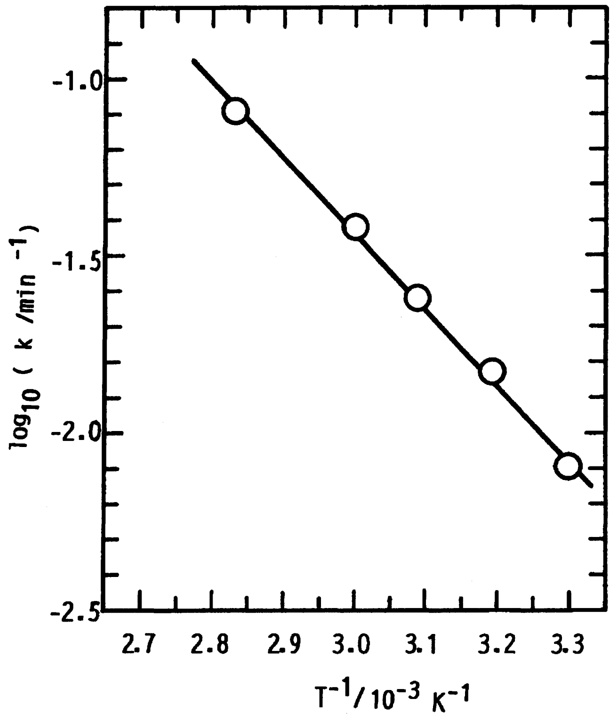


Fig. 10. Arrhenius plot for the blank CL reagent in the tube; logarithm of the rate constant (inverse of one hundredth life time ($t_{1/100}$)) against the inverse of temperature.

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