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Novel Adsorption and Desorption Chemiluminescence of 10,10′-Disubstituted 9,9′(10*H*,10′*H*)-Biacridinylidenes in Alumina Slurries

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10,10′-Disubstituted 9,9′(10*H*,10′*H*)-biacridinylidene (**1**) has a novel chemiluminescence (CL) in an alumina slurry. The CL is yellowish green emissions I and II from the excited singlet state of adsorbed **1** onto alumina, $^1\mathbf{1}^*$(ads), and blue emission III from the excited singlet state of 10-substituted 9(10*H*)-acridinone (**2**), $^1\mathbf{2}^*$. In this study the effects of alumina activity and solvent polarity on the generation of those emitters were investigated and the mechanism was clarified: 1) $^1\mathbf{1}^*$(ads) is generated by two-step electron transfers, the first electron transfer from **1** to O_2 gives $\mathbf{1}^{+\bullet}$(ads) accompanied by adsorption of **1** and the following electron transfer from –OH and/or $-O^-$ on alumina to $\mathbf{1}^{+\bullet}$(ads) gives $^1\mathbf{1}^*$(ads), and 2) $^1\mathbf{2}^*$ is generated from the reaction of $\mathbf{1}^{2+}$ and $O_2^{-\bullet}$, both of which are formed during the reaction of emissions I and II. The two key compounds, $\mathbf{1}^{2+}$ and $O_2^{-\bullet}$, were detected spectroscopically. $O_2^{-\bullet}$ in a slurry of **1**, benzene, and highly activated alumina was found to be extremely stable and to generate $^1\mathbf{2}^*$ upon the addition of alcohol to the slurry. Then terms "adsorption chemiluminescence" for emissions I and II, and "desorption chemiluminescence" for emission III are proposed.

10,10′-Dimethyl-9,9′(10*H*,10′*H*)-biacridinylidene (**1a**) in a solution has been known to give a blue chemiluminescence (CL) from the excited singlet state of 10-methyl-9(10*H*)-acridinone (**2a**), $^1\mathbf{2}^*$, which is formed from the reaction of **1a** and active oxygen ($^1O_2$[1,2] or O_3[3,4]) via a 1,2-dioxetane intermediate. In a certain case[2,5] the blue CL is accompanied by green CL from the excited singlet state of **1a**, $^1\mathbf{1a}^*$, which is formed by energy transfer from the primary emitter $^1\mathbf{2a}^*$. The two kinds of CL appear at almost the same time and can be distinguished by spectroscopy. However, we[6] found that two similar kinds of CL are generated at completely separate times in a slurry involving alumina, but not requiring such active forms of oxygen as $^1O_2$ and O_3. Upon preparation of a slurry composed of 10,10′-disubstituted 9,9′(10*H*,10′*H*)-biacridinylidene (**1**), a nonpolar solvent, and alumina, yellowish green CL (emissions I and II from $^1\mathbf{1}^*$) is generated in the presence of air. Upon addition of a polar solvent to the slurry, blue CL (emission III from $^1\mathbf{2}^*$) is generated. Since the order of the appearance of these CL is never reversed from this, the formation of $^1\mathbf{1}^*$ by energy transfer as in solution CL[2] can be ruled out. In addition the findings that $^1\mathbf{1}^*$ is adsorbed onto alumina in a slurry and $^1\mathbf{2}^*$ is produced from the alumina part of the slurry have suggested the strong participation of alumina in the occurrence of these CL. We have proposed a mechanism for generation of the sequence of these CL, shown in Scheme 1. It has been supposed that in the processes of electron exchange to form $^1\mathbf{1}^*$, O_2 acts as an electron acceptor and $-O^-$ and/or –OH on alumina acts as an electron donor and in the following blue CL, $^1\mathbf{2}^*$ is formed by the reaction of $O_2^{-\bullet}$ and $\mathbf{1}^{2+}$, both of which are produced in the reaction of yellowish green CL. To confirm the above mechanism, in this work we investigated several factors (alumina, solvent, O_2, etc) for generation of these CL. The relationship between adsorption of substrates onto alumina/desorption of adsorbates from alumina and the occurrence of these CL and effects of alumina activity or solvent polarity on these CL were studied. In addition the electron donor and acceptor in emissions I and II and the two reactants in emission III were identified. Especially the formation and reaction of $O_2^{-\bullet}$ were shown by ESR sepctroscopy. Furthermore we applied the CL reactions to various metal oxides to clarify the role of alumina in forming a slurry for the novel CL more definitely. In this work 10,10′-diallyl-9,9′(10*H*,10′*H*)-biacridinylidene (**1b**) was used as a substrate.

Results and Discussion

Yellowish Green CL. **(1) Adsorption of 1b onto Alumina.** While the yellowish green CL was being generated, **1b** was adsorbed onto alumina from benzene in a slurry. Figure 1 shows the change of the amount of adsorbed **1b** with time. Under the same

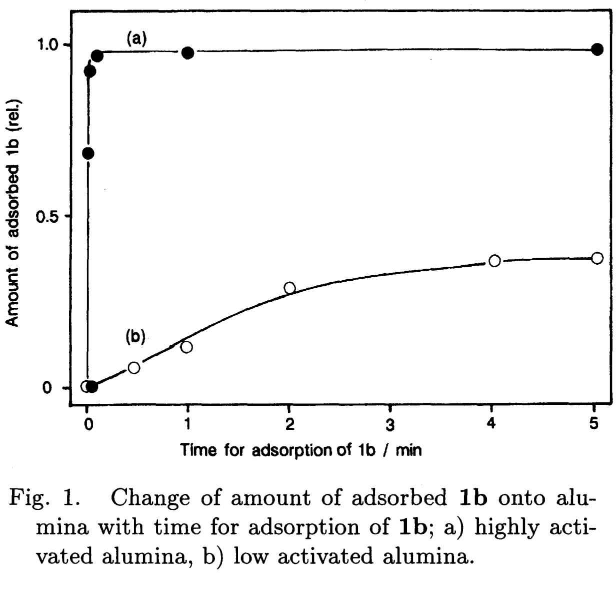
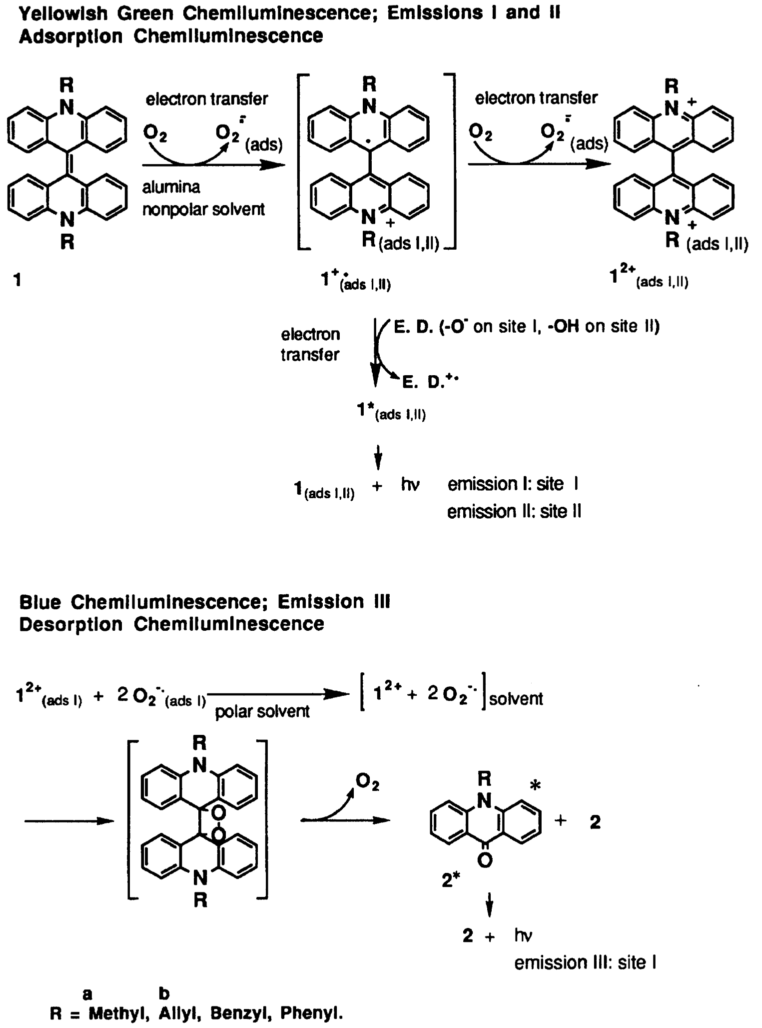


Fig. 1. Change of amount of adsorbed **1b** onto alumina with time for adsorption of **1b**; a) highly activated alumina, b) low activated alumina.



Scheme 1.

conditions the change of the CL intensity with time is shown in Fig. 2. It is obvious from Figs. 1 and 2 that the adsorption of **1b** and the generation of the CL occurred simultaneously. Furthermore a linear relationship between the integrated CL intensity and the amount of adsorved **1b**, which depended on the concentration of **1b** in benzene solutions was observed (Fig. 3). Here we propose a term "adsorption CL" for this yellowish green CL.

(2) Effects of Alumina Activity on Generation of the CL; the Presence of Two Adsorption Sites, I and II, and the Occurrence of Emissions I and II. As reported previously,[6] adsorption CL generated on highly activated alumina (Brockmann's activity grade I) is composed of emissions I (λ_{max} 520 nm) and II (λ_{max} 507 nm), but that on low activated alumina (Brockmann's activity grade III) is composed of emission II only. Despite the different emission maxima the emitter of both of emissions I and II is identified with ^{1}**1b*** adsorbed onto alumina. The difference of the emission maximum between emissions I and II led us to suppose the presence of two adsorption sites on

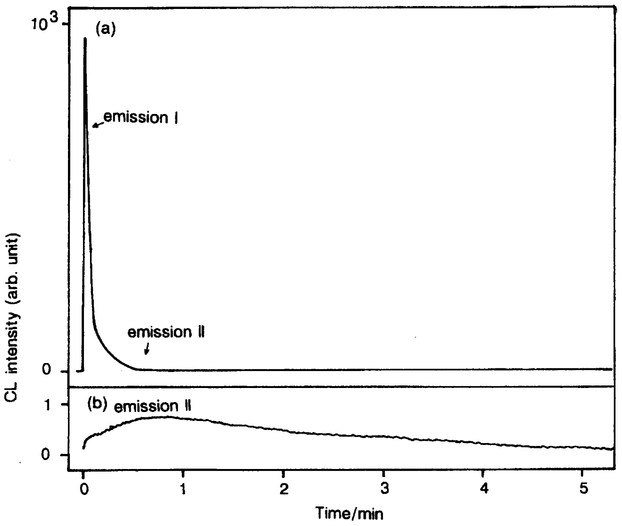


Fig. 2. Change of CL intensity of yellowish green CL generated from a slurry composed of **1b**, benzene, and alumina with time; a) highly activated alumina, b) low activated alumina.

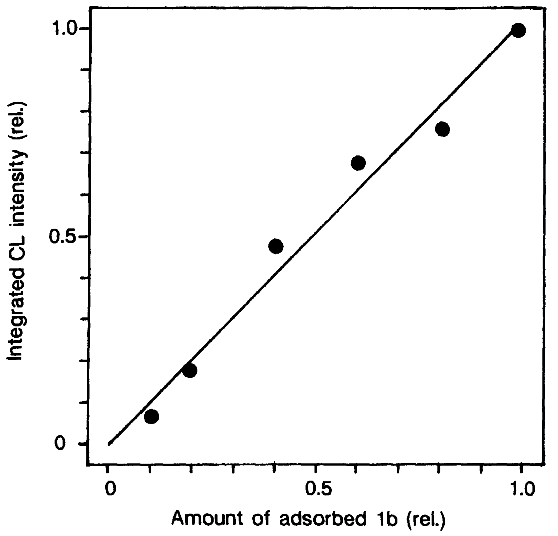


Fig. 3. Plots of integrated CL intensity of yellowish green CL for 20 min vs. amount of adsorbed **1b** onto alumina.

alumina; site I, a dehydrated site, for emission I and site II, a hydrated site, for emission II. IR spectra of the surface of highly and low activated aluminas showed an OH stretching band at around 3500 cm^{-1} (Fig. 4). The intensity of the band of highly activated alumina is weaker than that of low activated alumina, but the intensity of the former increased to become identical to that of the latter upon exposure of the former alumina to humid air. The increase in amounts of OH groups on alumina directly caused a decrease in the CL intensity of emission I. The facts indicated that emission I is generated on dehydrated site I only. Furthermore referring to Flockhart and Salem's report[7] that the presence of two adsorption sites on alumina results in the two kinds of adsorption strength of an adsorbate onto alumina, we concluded that $^{1}\mathbf{1b}^{*}$ is adsorbed tenaciously onto site I and loosely onto site II to lead to emissions with the different emission maxima; emission I with 520 nm and emission II with 507 nm (Chart 1).

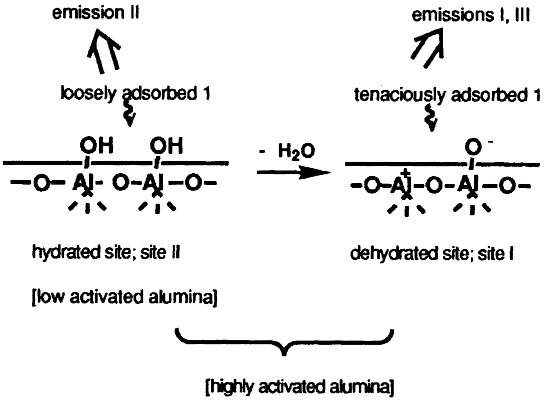


Chart 1.

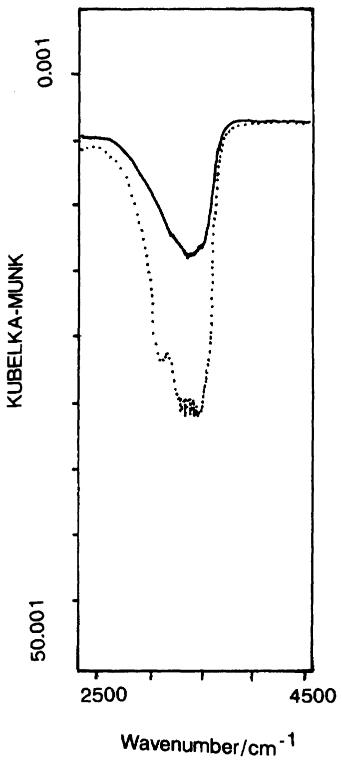


Fig. 4. FT-IR spectra of alumina surfaces; a) —— : highly activated alumina, b) ···· : low activated alumina.

(3) Electronic Oxidation of 1b to $\mathbf{1b}^{2+}$ and the Roles of Alumina and Molecular Oxygen. The formation of $\mathbf{1b}^{2+}$ has been clarified in the reaction of emission II using low activated alumina.[6] However, it has not been clarified in the reaction of emission I, because addition of a polar solvent such as ethanol to extract adsorbates from highly activated alumina causes the subsequent reaction of blue CL (emission III). Therefore UV spectra of highly and low activated alumina surfaces were directly observed after the reaction of adsorption CL. Both of them showed a broad band at around 372 nm, characteristic of $\mathbf{1b}^{2+}$ adsorbed onto alumina. It showed that **1b** is electronically oxidized to give $\mathbf{1b}^{2+}$ on highly activated alumina as well as on low activated alumina. Accordingly, the cation radical of **1b**, $\mathbf{1b}^{+\bullet}$ is present as an intermediate in the oxidation step of **1b** to $\mathbf{1b}^{2+}$ on site I as on site II.[6] In the oxidation step, O_2 was identified as the electron acceptor and the role of alumina was considered to be as a catalyst, because the oxidation never occurred in an anaerobic slurry or proceeded very slowly in a aerobic solution without alumina. After accepting an electron, O_2 can convert to superoxide ($O_2^{-\bullet}$), which was now proved by ESR spectroscopy. The details are described in blue CL section.

(4) Formation of $^{1}\mathbf{1b}^{*}$ from $\mathbf{1b}^{+\bullet}$ and Another Role of Alumina as Electron Donor. We have proposed that $\mathbf{1b}^{+\bullet}$ accepts an electron from the electron donor parts of alumina (–O$^-$ on site I and –OH on site II). When fluorided alumina,[8] the surface of which is composed neither of –O$^-$ nor of –OH, was used in the reaction of the adsorption CL, no CL was generated, though **1b**$^{2+}$ was given from **1b** as a product. This finding strongly supported the idea that –O$^-$ and/or –OH acts as an electron donor for generation of the CL. Hence the mechanism for adsorption CL was established as shown in Scheme 1.

(5) Solvent Effects on Generation of the CL. The generation of the CL depended on the kind of solvent, which were classified into 3 groups; A) Non or less polar solvents with small donor number (DN) such as benzene (0.1) and carbon tetrachloride, B) polar solvents with medium DN such as ethanol (20) and acetonitrile (14.1), and C) polar solvents with large DN such as pyridine (33.1) and *N*,*N*-dimethylformamide (DMF) (26.6). The CL was generated strongly in the A group and very weakly in the B group, but it was never generated in the C group. In A group **1b** was adsorbed onto alumina accompanied with electronic oxidation of **1b** to **1b**$^{2+}$. In the B group **1b** was almost not adsorbed at all, but easily oxidized even in the absence of alumina. In the C group neither adsorption nor oxidation of **1b** occurred. Pyridine and DMF apparently inhibited the CL reaction due to their polarity and electron donating ability. Figures 5 and 6 show the effects of pyridine and DMF upon the amount of adsorbed **1b** and upon integrated CL intensity. In both of Figs. 5 and 6 the corresponding two-couple slopes are in a close parallel, which points out that most important factor for generation of the CL is oxidation of **1b** accompanied by adsorption of **1b**.

(6) The CL Reactions Using Other Metal Oxides; Effects of Metal Oxides on Generation of the CL. When various metal oxides, CaO, MgO, ZnO, Y_2O_3, ZrO_2, TiO_2 (anatase, rutile), SiO_2, and SiO_2–Al_2O_3 (SAH-1, SAL-2) were used for preparation of slurries instead of alumina, all of the slurries had CL similar to the slurry of alumina, though the CL intensities, duration time, and other appearance patterns varied. Figure 7 shows plots of integrated CL intensity observed with each of the metal oxides including alumina vs. electronegativity (χ_i) of metal ions in metal oxides proposed by Tanaka and Ozaki.[9] χ_i is used as an index for the activity of oxidation occurring on the metal oxides, besides as the index of acidity and basicity of metal oxides. The plots show a maximum at alumina of medium χ_i among the metal oxides, but neither at CaO of maximum χ_i nor at SAL-2 of minimum χ_i.[11] On the other hand the order of electron donor activities parallels the order of basic strength of metal oxides.[9] Accordingly, it is explained that alumina takes a balance in electronic oxidation and reduction to be most effective

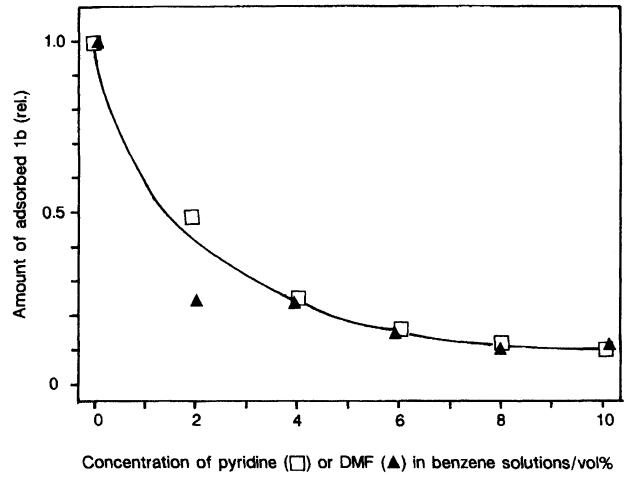


Fig. 5. Plots of amount of adsorbed **1b** onto highly activated alumina vs. concentration of pyridine (☐) or DMF(▲) in benzene solutions.

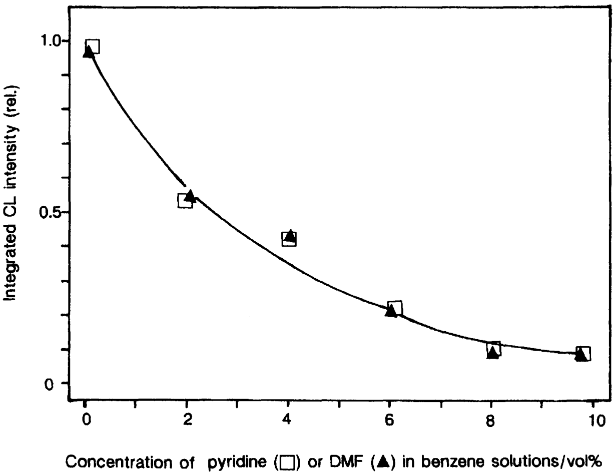


Fig. 6. Plots of integrated CL intensity observed from highly activated alumina slurries vs. concentration of pyridine (☐) or DMF (▲) in benzene solutions.

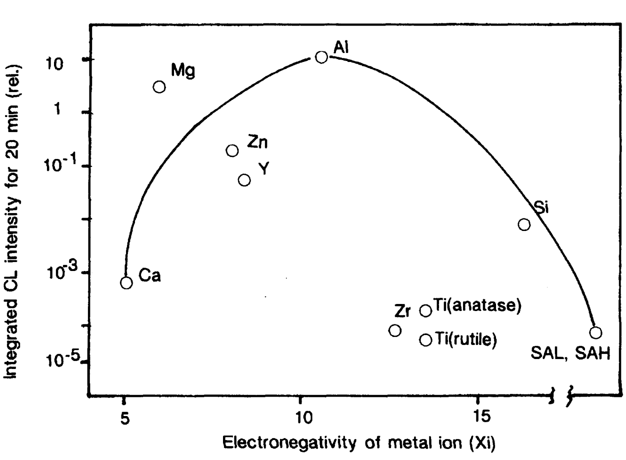


Fig. 7. Plots of integrated CL intensity of adsorption CL generated in metal oxide slurries vs. electronegativity (χ_i) of metal ion in metal oxides.

in the generation of the CL. This finding intensively supports the idea that electronic properties of metal oxides affect both of the electron transfer processes; oxidation, **1b**$\xrightarrow{-e}$**1b**$^{+\cdot}$ and reduction, **1b**$^{+\cdot}$$\xrightarrow{+e}$^{1}**1b***.

Blue CL. (1) Detection of Superoxide by ESR Spectroscopy—A Reactant for Generation of the CL. For formation of ^{1}**2b*** to give Blue CL (emission III), one reactant, **1b**$^{2+}$, has already been discussed in the preceding yellowish green CL section, while the other reactant, $O_2^{-\bullet}$, was studied by ESR spectroscopy in this section. A slurry of highly activated alumina generating adsorption CL gave a strong anisotropic signal (g values 2.040, 2.017, and 2.001; Fig. 8), which was characteristic of $O_2^{-\bullet}$ adsorbed on alumina.[12)] The decay of the signal was extremely slow even under atmospheric pressure at room temperature; for instance, when a slurry was kept without shaking or stirring, the signal intensity decreased by about 40% in a month. Whenever the signal was observed, addition of ethanol to the slurry led to generation of blue CL. This is important evidence for $O_2^{-\bullet}$ as a reactant for generation of blue CL. Therefore ethanol added to the reaction mixture of blue CL is concluded to act as a solvent desorbing $O_2^{-\bullet}$ and **1b**$^{2+}$ from alumina. Moreover a correlation between the amount of **2b** produced in the reaction of blue CL and the adsorption time of **1b** is observed as shown in Fig. 9. Then blue CL is given the term "desorption CL" in contrast to "adsorption CL".

(2) Why Does the CL Appear in a Slurry of Highly Activated Alumina Only? Unlike a slurry of highly activated alumina, a slurry of low activated alumina never gave an $O_2^{-\bullet}$ signal. This seemed to indicate that $O_2^{-\bullet}$ is formed on site I only, though $O_2^{-\bullet}$ should be formed not only on site I but also on site II in the oxidation step of **1b** to **1b**$^{2+}$. It was considered to be due to the unstability of $O_2^{-\bullet}$ in a hydrophilic medium. Since site II was covered with surface hydroxyl groups, $O_2^{-\bullet}$ formed on site II was too unstable either to be observed by ESR spectroscopy or to remain until the reaction of desorption CL. As a result the CL appears on site I, that is, in a slurry of highly activated alumina only.

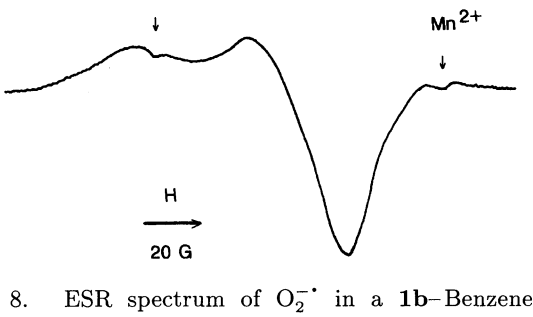


Fig. 8. ESR spectrum of $O_2^{-\bullet}$ in a **1b**–Benzene–highly activated alumina–molecular oxygen system; g=2.040, 2.017, 2.001.

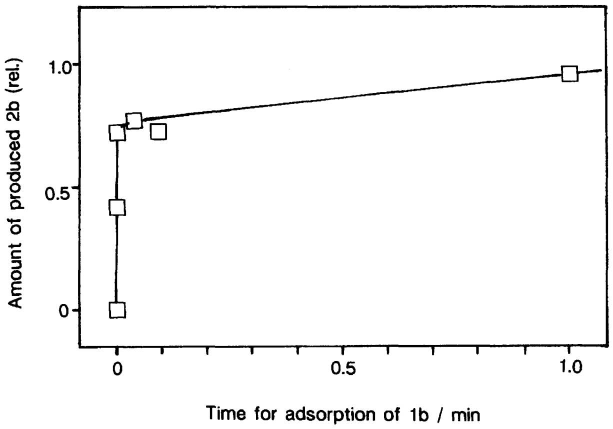


Fig. 9. Plots of amount of **2b** produced in the reaction of desorption CL vs. time for adsorption of **1b** in the preceding adsorption CL reaction.

Inhibition of Desorption CL with Acetic Acid. In general $O_2^{-\bullet}$ is easily protonated at pK_a 4.7 like this:

$$O_2^{-\bullet} + H^+ \rightarrow \cdot O_2H.$$

When acetic acid (pK_a 4.7) was used as a polar solvent for desorption CL the integrated CL intensity was about 5% of that in the case of ethanol. With acetic acid **1b**$^{2+}$ was mainly desorbed and **2b** in a trace. Acetic acid as expected inhibited the reaction of desorption CL, which strongly supported the idea that $O_2^{-\bullet}$ is a reactant for desorption CL to afford **2b** as a product. This result absolutely excludes the mechanism of energy transfer from ^{1}**2b*** for generation of ^{1}**1b*** in adsorption CL as reported in solution CL.[2,9)] Consequently, the mechanism for the adsorption and desorption CL of **1** in slurries was established as shown in Scheme 1. To our knowledge, it is the first example that very stable $O_2^{-\bullet}$ was readily formed and observed under atmospheric pressure at room temperature without any special treatments such as γ- and UV-irradiation of alumina.[12,13)] This finding indicates that **1b** and O_2 are a good pair of electron donor and acceptor on highly activated alumina and a slurry contributes to maintain such stable $O_2^{-\bullet}$ and to make the occurrence of desorption CL possible. Here we would like to emphasize that this novel CL is brought out with the direct and indirect participation of alumina. In addition we have tried to apply this CL reaction to several compounds and found that some derivatives of 2,4,5-triphenylimidazole showed both adsorption and desorption CL, though those CL were very faint.

Experimental

Materials. 10,10′-Diallyl-9,9′(10*H*,10′*H*)-biacridinylidene (**1b**) was prepared from 9(10*H*)-acridinone via 10-allyl-9(10*H*)-acridinone (**2b**) by the method of Amiet.[14)] Alumina purchased from Wako (for chromatography, 300 mesh) was used as low activated alumina without further activation and as highly activated alumina with further activation (heated at 700 °C for 4 h in air and cooled to room temperature over P_4O_{10} in a vacuum). Fluorided alumina was prepared by the method of Flockhart et al.[8] SiO_2–Al_2O_3 (JRC-SAH-1; alumina content 28.61%, JRC-SAL-2; 13.75%) and other metal oxides (Wako) were used with activation like alumina.

Generation of Yellowish Green CL (Adsorption CL). When a benzene solution of **1b** (1.00×10^{-3} mol dm^{-3}) was added to highly activated alumina, or the alumina was added to the benzene solution in a ratio of 1 : 1 ml/g, yellowish green CL (emissions I, II/highly activated alumina; emission II/low activated alumina) was observed on the alumina surfaces in the slurry.

Generation of Blue CL (Desorption CL). After yellowish green CL on highly activated alumina in a slurry of **1b**, alumina, and benzene disappeared, an appropriate amount of ethanol was added to the slurry and blue CL simultaneously was observed.

Estimation of Amount of 1b Adsorbed onto Highly or Low Activated Alumina. Slurries were prepared of a benzene solution of **1b** (0.5 ml) and highly or low activated alumina (0.5 g) in volumetric flasks and left for various periods. After each adsorption period, benzene was added to the slurry to make the total volume up to 10 ml. The alumina in the slurry was filtered out and the absorption spectrum of the filtrate was measured. On the basis of the absorbance at 420 nm due to **1b** remaining in the liquid phase the amount of **1b** adsorbed onto alumina was estimated.

Estimation of Amount of 2b, a Product of the Reaction of Blue CL. Slurries (benzene solution of **1b** (0.5 ml) and highly activated alumina (0.5 g)) were left for various periods. In each adsorption period ethanol was added to the slurry and made the total volume up to 10 ml to desorb the adsorbed species of **1b**, **1b**$^{2+}$. Simultaneously the reaction of blue CL occurred and **2b** was produced in the liquid phase of the resulting slurry. After the alumina was filtered out from the slurry, the absorption spectrum of the filtrate was measured. The amount of **2b** was estimated based on the absorbance at 368 nm due to **2b**.

Instruments. The UV-vis spectra of solutions and adsorbates on alumina were recorded on a Shimadzu UV-240 spectrophotometer and on a Hitachi 340 spectrophotometer, respectively. The IR spectra of alumina surfaces were measured on a JASCO FT-IR-7000 spectrometer. The CL intensities (400—650 nm) were monitored and integrated with a NITI-ON lumicounter type 1000. ESR spectra of slurries were recorded on a JEOL JES-FE2XG spectrometer.

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References

1) F. McCapra and R. A. Hann, *J. Chem. Soc., Chem. Commun.*, **1969**, 442.

2) K-W. Lee, L. A. Singer, and K. D. Legg, *J. Org. Chem.*, **41**, 2685 (1976).

3) E. G. Janzen, I. G. Lopp, and J. W. Happ, *J. Chem. Soc. D*, **1970**, 1140.

4) J. Nikokavouras, A. Vavayannis, and G. Vassilopoulos, *J. Prakt. Chem.*, **320**, 43 (1978).

5) K. D. Legg and D. M. Hercules, *J. Am. Chem. Soc.*, **91**, 1902 (1969).

6) K. Maeda and S. Yamada, "Chemiluminescence Properties of Adsorbed Biacridylidenes," in "Photochemistry on Solid Surfaces," ed by M. Anpo and T. Matsuura, Elsevier Sci. Pub. B. V., Amsterdam (1989), pp. 184—195.

7) B. D. Flockhart and M. A. Salem, *J. Colloid Interface Sci.*, **103**, 76 (1985), and references cited therein.

8) B. D. Flockhart, K. Y. Liew, and R. C. Pink, *J. Chem. Soc., Faraday Trans. 1*, **76**, 2026 (1980).

9) K. Tanaka and A. Ozaki, *J. Catal.*, **8**, 1 (1967).

10) χ_i of SAL-2 is speculated to be a minimum based on the acidity, which is in the order of SAL$-$2>SAH$-$1>SiO_2.

11) D. Cordischi and V. Indovina, *J. Chem. Soc., Faraday Trans. 1*, **72**, 2341 (1976).

12) L. D. Bruce, *J. Catal.*, **50**, 545 (1977), and references cited therein.

13) D. Cordischi, V. Indovina, and M. J. Occhiuzzi, *J. Chem. Soc., Faraday Trans. 1*, **74**, 883 (1978).

14) R. G. Amiet, *J. Chem. Educ.*, **59**, 163 (1982).