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Green chemiluminescence of $SnBr_2$ vapor in nitrogen discharge flow

Takaomi Kobayashi, Eiji Ikehara, Masashi Tsukada, Nobuyuki Fujii *

Department of Chemistry, Nagaoka University of Technology, Kamitomioka, Nagaoka, 940-21, Japan

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Abstract

Green chemiluminescence peaking at 505 nm is observed when heated $SnBr_2$ vapor is mixed with an activated nitrogen flow produced by microwave discharge. The dependence of the chemiluminescence on the vapor injector temperature suggests that the green chemiluminescence emitter is vaporized $SnBr_2$. Evidence is presented which indicates that the excitation of $SnBr_2$ occurs by energy transfer from the $N_2(A^3\Sigma_u^+)$ state in the nitrogen glow.

Keywords: Chemiluminescence; Nitrogen discharge flow; $SnBr_2$ Vapor

1. Introduction

Although the chemiluminescence process and spectroscopy of Sn and tin monohalide compounds have been widely investigated, the spectroscopic data for tin dihalides are poor. The chemiluminescence process of tin dihalides, such as $SnCl_2$ and $SnBr_2$, has previously been reported by Rosano and Parson [1,2]. The chemiluminescence reaction of tin with Cl_2 or Br_2 at high temperature was examined using a molecular beam apparatus. As a result of the reaction, a broad emission spectrum, which may be due to dihalide formation, was observed. Since then, few emission measurements of tin bromide metastable states have been performed.

In this report, we found the characteristic green chemiluminescence of tin dibromide ($SnBr_2$) vapor in a plasma afterglow of nitrogen. In order to study the chemiluminescence process in the nitrogen glow, the nature of the emission in the glow was examined under various discharge conditions.

2. Experimental procedure

The experimental flow system, equipped with a microwave generator (500 W, 2450 MHz) and a vapor injector, is shown schematically in Fig. 1. The vapor injector device for $SnBr_2$ was made as follows [3]. The injector cell (diameter, 10 mm) and cap were made of Pyrex glass. The cell was surrounded by a Nichrome wire heater and coated with ceramics. The $SnBr_2$ vapor was injected through the cap pore (diameter, approximately 1 mm). The cell injector was placed upstream of the inlet of the N_2 glow in the reaction tube (diameter, 70 mm). $SnBr_2$ powder (Nakarai, 99% purity) was placed in the cell prior to the experiment. The total pressure in the flow was measured by a Baratron pressure gauge (MKS 122A) and was controlled in the range 0.1–1 Torr (1 Torr = 133 Pa).

The visible glow downstream of the injector outlet was observed through the window of the reaction tube and the emission spectra were measured as follows. The emission was collected by a silica optical fiber, which was connected to the entrance aperture of a spectrometer (Ritu MC-25NI, 30 cm, 300 grooves mm^{-1}) equipped with a spectral multichannel analyzer (Princeton Instruments, IRY-512/R/par type). A diode-array detector with 512 pixel elements was connected to the multichannel analyzer.

In order to estimate the amount of nitrogen atoms in the nitrogen glow, NO titration was carried out according to the literature [4–8]. The NO_2* emission intensity was measured at 515 nm with a monochromator (Nihon Bunko CT-50) and a photomultiplier (Hamamatsu R-446).

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* Corresponding author.

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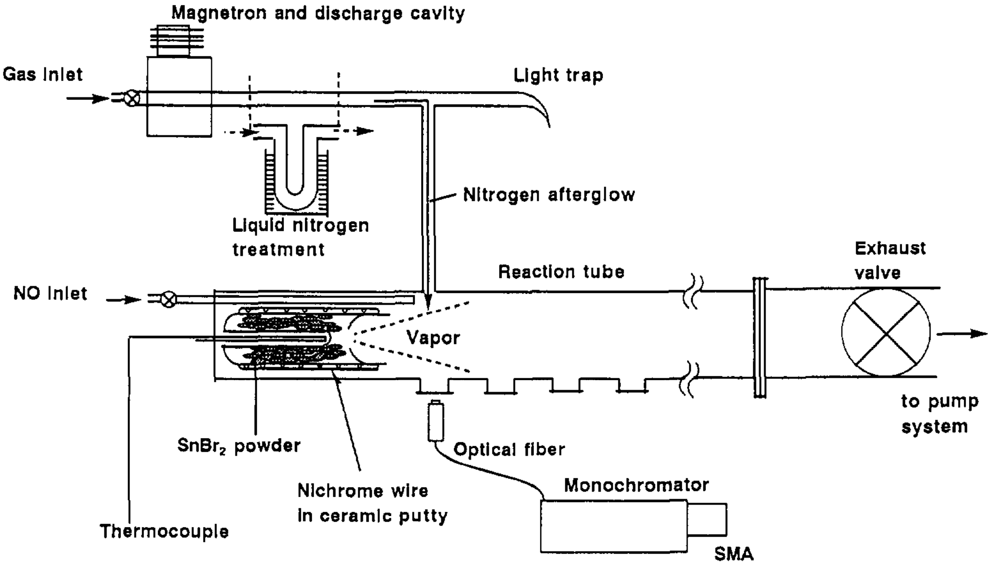

Fig. 1. Schematic diagram of the present flow system made up of a reaction tube, injector and microwave discharge region.

3. Results and discussion

3.1. Emission spectrum of $SnBr_2$ vapor in nitrogen after glow

As the active nitrogen flow is mixed with gaseous $SnBr_2$, an intense green glow fills the downstream area of the reaction tube. Reproducible spectral data for the glow over a wide range of wavelengths were obtained. Fig. 2 shows the emission spectra of the glow observed at various downstream positions. The spectra contain a structureless broad band in the 440–550 nm region and many bands in the 375–390 nm region. On moving the observation position from the injector outlet downstream along the reaction tube, we observed that the emission intensity of the broad band increased and attained a maximum at 10–15 cm downstream. On moving the observation position further downstream, the emission intensity gradually decreased. At 40 cm downstream, the emission of the glow was not detected.

From the emission data of tin halide reported previously [9], the emission bands for the SnBr $B^2\Sigma$–$X^2\Pi$ and $A^2\Delta$–$X^2\Pi$ transitions were in the 300–340 nm and 390–420 nm regions respectively. However, we cannot assign the bands in the 370–390 nm region to the SnBr $A^2\Delta$–$X^2\Pi$ transition, because the most intense band of the SnBr $^2\Delta$–$^2\Pi$ state (0,0) at 407 nm was not detected in the present spectra.

Rosano and Parson [1] reported that the chemiluminescence reaction of Sn with a halogen molecule results in a broad emission band peaking at 470 nm. They concluded that the emitter responsible for the chemiluminescence is $SnBr_2$, by analogy with the low-lying electronic state of SnF_2 for the $^3B_1$–$^1A_1$ transition. However, these spectroscopic data are not helpful for the identification of the present chemiluminescence.

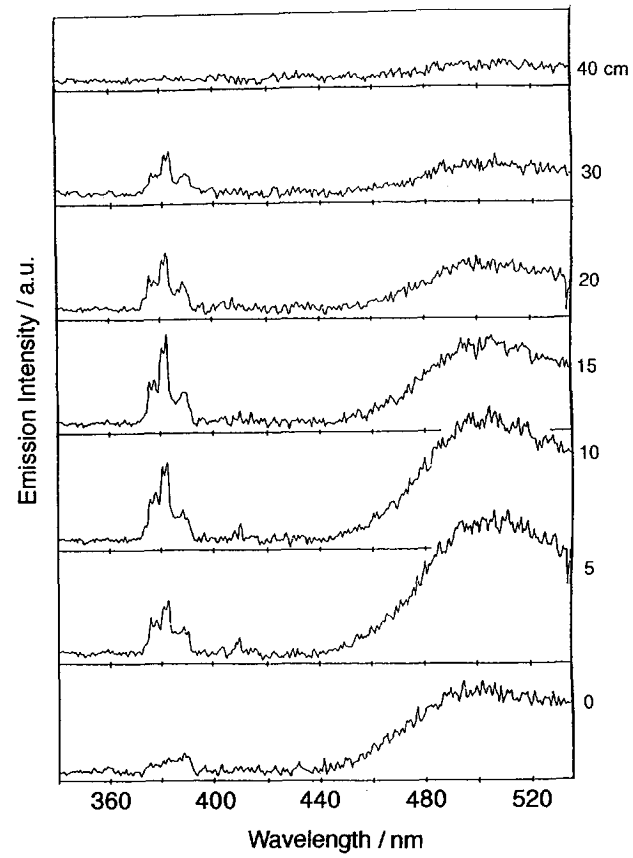

Fig. 2. Emission spectra observed in the visible region for $SnBr_2$ vapor (injector temperature, 593 K; flow pressure, 0.8 Torr). The right ordinate indicates the distance of the observation point from the injector outlet.

In order to determine the identification of the emitting source for the broad band, the dependence of the chemiluminescence on the injector temperature was examined. Fig. 3 shows plots of the chemiluminescence

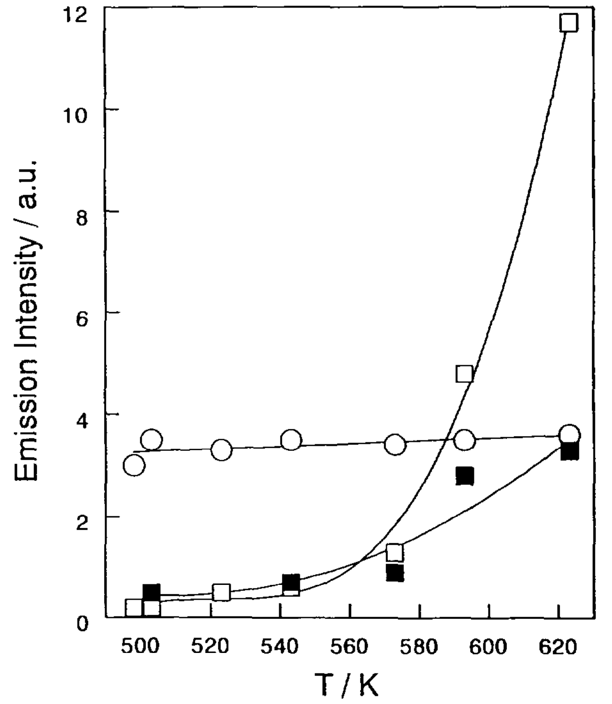

Fig. 3. Plots of the emission intensity vs. injector temperature for the N_2(B–A) band at 580 nm (○) and for the bands appearing at 505 nm (□) and 375 nm (■). The pressure is 0.8 Torr.

intensities monitored at 375, 505 and 580 nm vs. the injector temperature. The band at 580 nm is typical of the N_2(B–A) transition ($\Delta v = 5$, $v' = 11$) [9,10], observed in the present nitrogen glow containing $SnBr_2$ vapor. The emission intensity from the $N_2(B^3\Pi_u^+)$ state is constant over the experimental temperature range, implying that stable discharge of nitrogen takes place regardless of the change in the injector temperature.

In the temperature range below 540 K, the green glow was not detected. As the injector temperature was increased in the range 543–623 K, the emission intensities at 375 nm and 505 nm gradually increased. This suggests that the vaporization of $SnBr_2$ is due to the heat from the injector temperature in this range. Plots of the emission intensity vs. injector temperature have different slopes for the bands at 375 nm and 505 nm. This suggests that different emitters are responsible for the emission bands at 375 and 505 nm.

Maya [11] and Oldershow and Robinson [12] reported that tin dibromide vapor shows absorption bands at 365, 285 and 245 nm for the $SnBr(X^2\Pi)$ ground state and 200 nm for the SnBr(A′) state. They indicated the dissociation of $SnBr_2$ to SnBr and $Br(^2P_2)$ in the vapor. In the present work, in order to examine whether $SnBr_2$ dissociates in the injector, X-ray diffraction spectra of the $SnBr_2$ residue in the injector and of the powder stuck to the reaction tube wall were measured. From the spectra, we found that the heating of $SnBr_2$ to yield vaporization does not give rise to the dissociation of $SnBr_2$. In other words, the present injector device only generates $SnBr_2$ vapor. Accordingly, it seems reasonable to assume that $SnBr_2$ is responsible for the broad band downstream from the injector, as shown in Fig. 2.

3.2. Effects of nitrogen metastable states on the chemiluminescence

The triplet states of the nitrogen molecule, such as $N_2(B^3\Pi_g$ and $C^3\Pi_u)$, were detected immediately after the discharge position. However, both emission intensities gradually decreased and at the injector position, 40 cm downstream from the discharge position, the triplet nitrogen observed was almost limited to $N_2(B^3\Sigma_g)$ states. Here, the observed nitrogen glow is considered to be due to the recombination of nitrogen atoms following energy transfer [13,14]

$$N(^4S)+N(^2D) \longrightarrow N_2(C^3\Pi_u) \longrightarrow N_2(B^3\Pi_g)+h\nu$$

The spectral shape of the N_2(B–A) band changes with pressure as shown in Fig. 4(a). With an increase in the nitrogen glow pressure, the emission intensity of the N_2(B–A) band at 580 nm ($\Delta v = 5$, $v' = 11$) increases. Fig. 4(b) shows the chemiluminescence spectra

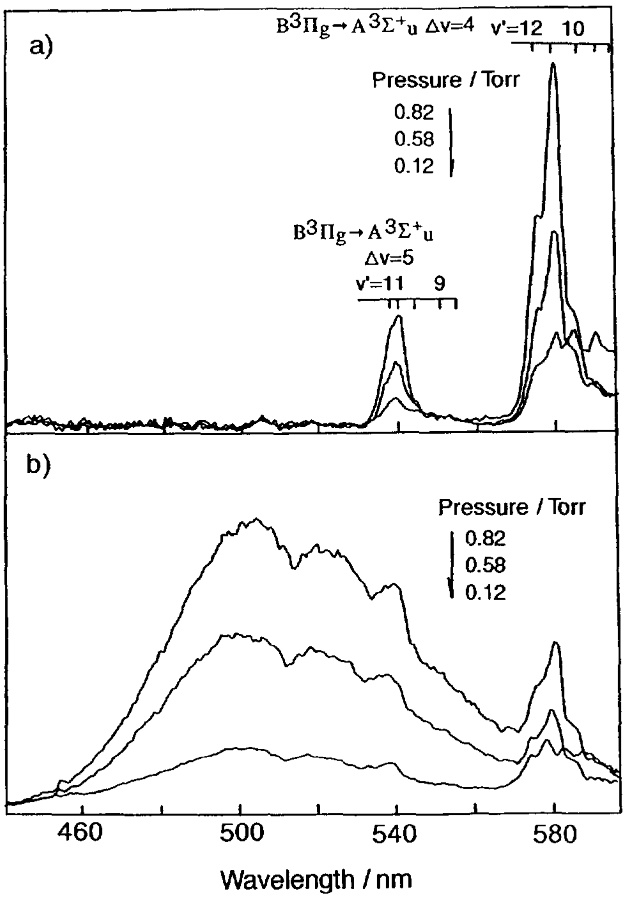

Fig. 4. Emission spectra of: (a) nitrogen glow at various pressures and (b) in the presence of $SnBr_2$ vapor.

of the glow with $SnBr_2$ vapor at various pressures. In the same manner, the emission intensity of the broad band peaking at 505 nm increases as the pressure increases.

NO titration was carried out downstream of the injector position. Fig. 5 shows the intensity of the NO_2^* chemiluminescence for various amounts of NO added to the nitrogen glow. When the amount of NO added was increased in the range 0.1–8 mmol min^{-1}, the NO_2^* chemiluminescence intensity at 515 nm increased. The figure also shows that the NO_2^* intensity increases as the flow velocity increases. Because the intensity of the NO_2^* emission is proportional to $[N]^2$, the results of the titration indicate that the N atom concentration increases as the flow velocity increases.

To consider the chemiluminescence process of $SnBr_2$ in the nitrogen glow, the emission intensities for N_2^*, $SnBr_2^*$ and NO_2^* are plotted against the flow pressure in Fig. 6. The plot of the green emission for $SnBr_2^*$ shows a positive slope, i.e. an increase in pressure favors excitation of $SnBr_2$ vapor in the nitrogen glow. For the N_2(B–A) transition, the emission intensity increases with pressure, whereas for the N_2(C–B) transition, the emission intensity decreases with pressure. Furthermore, the plot of the NO_2^* emission intensity vs. pressure has a positive slope. Consequently, the pressure dependence of the $SnBr_2$ emission corresponds well to that of the intensities of the NO_2^* and N_2(B–A) emissions. However, it is difficult to identify the excitation source of the nitrogen atoms or the excited nitrogen molecules from the present data.

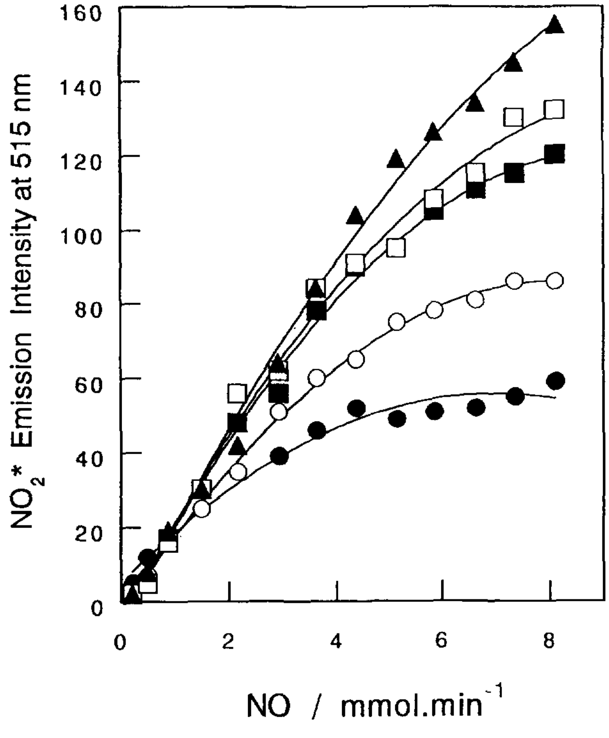

Fig. 5. Plots of NO_2^* chemiluminescence intensity vs. NO added; nitrogen discharge flow velocities are (●) 11.7, (○) 20.5, (■) 31.6, (□) 50.8 and (▲) 69.0 mmol min^{-1}.

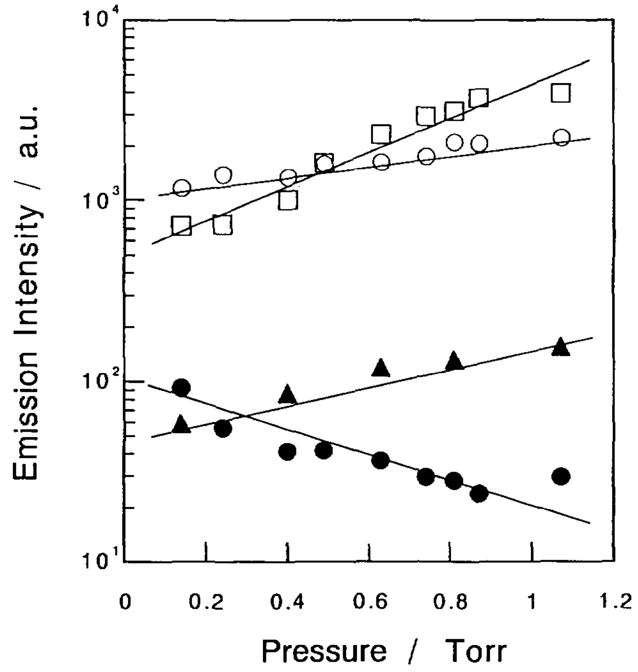

Fig. 6. Glow pressure dependence of the emission intensities for (●) N_2(C–B) at 337 nm, (○) N_2(B–A) at 580 nm, (□) green band at 505 nm and (▲) NO_2^* chemiluminescence.

As shown in Figs. 3 and 4(b), the N_2(B–A) transition is observed, as well as the broad band for $SnBr_2^*$. Thus the $N_2(B^3\Pi_g)$ state is not quenched in the presence of $SnBr_2$ vapor, indicating that $N_2(B^3\Pi_g)$ is not the excitation source of $SnBr_2$. However, this strongly suggests that the $N_2(A^3\Sigma_u^+)$ state is generated in the nitrogen glow. Since the $N_2(A^3\Sigma_u^+)$ state is a long-lived reservoir for excitation transfer, it may be the energy source for $SnBr_2$ excitation. However, the so-called Vegard Kaplane bands [9,13,14] for the transition $A^3\Sigma_u^+ \rightarrow X^1\Sigma_u^+$ is absent in the present spectra observed at the injector position.

In order to determine the chemiluminescence process of $SnBr_2$, a liquid nitrogen trap was set behind the discharge position in the flow line, as shown schematically in Fig. 1. This method eliminates N atoms from the discharge flow [15,16]. We attempted to measure the broad emission peaking at 505 nm with and without liquid nitrogen treatment. The green emission was observed regardless of the treatment. In contrast, the NO_2^* emission was significantly reduced by liquid nitrogen treatment, indicating that N atoms are deactivated by immersing the flow line in the liquid nitrogen vessel. In particular, at 0.1 Torr, the NO_2^* emission was not detected with the liquid nitrogen trap in place. This suggests that the N atom recombination reaction is not responsible for the excitation of $SnBr_2$. As well as the NO_2^* emission, the N_2(B–A) emission intensity decreases with liquid nitrogen treatment, but does not completely disappear. The reduction of the $N_2(B–A)$ emission intensity may be due to the decrease in the N atom recombination process, because N atoms effectively deactivate at 77 K.

In the present flow system, the nitrogen glow generated by the discharge reaches downstream of the injector after about 20 ms. Since $N_2(A^3\Sigma_u^+)$ has a long radiation time, this state may be present without deactivation. Thus it is considered that the $SnBr_2$ emitter must be generated by energy transfer from the $N_2(A^3\Sigma_u^+)$ state.

4. Conclusions

We found green chemiluminescence in a nitrogen afterglow containing $SnBr_2$ vapor. The green chemiluminescence exhibits a broad band in the 500–550 nm region. The dependence of the chemiluminescence on the $SnBr_2$ injector temperature suggests that the emitter responsible for the broad band is vaporized $SnBr_2$. Evidence is shown that the $N_2(A^3\Sigma_u^+)$ state is the energy source for the $SnBr_2$ emission.

References

[1] W.J. Rosano and J.M. Parson, *J. Chem. Phys., 84* (1986) 6250.
[2] W.J. Rosano and J.M. Parson, *J. Chem. Phys., 85* (1986) 2644.
[3] T. Tokuda and N. Fujii, *J. Phys. Chem., 96* (1992) 6504.
[4] R.L. Brown, *J. Chem. Phys., 52* (1970) 4604.
[5] J.E. Morgan and H.L. Schiff, *Can. J. Chem., 41* (1963) 903.
[6] M.F. Gole, A.E. Roche and F. Kaufman, *J. Chem. Phys., 59* (1973) 3953.
[7] M.L. Spealman and W.H. Podebush, *J. Am. Chem. Soc., 57* (1935) 1474.
[8] A. Fontajin, C.B. Heger and H.I. Schiff, *J. Chem Phys., 40* (1964) 64.
[9] R.W.B. Pearse and A.G. Gaydon, *The Identification of Molecular Spectra*, Chapman & Hall, London, 1950, p. 227.
[10] U.V. Ivanov, A.M. Pravilov, L.G. Smirnova and A.F. Vilosov, *J. Photochem. Photobiol. A: Chem., 54* (1990) 139.
[11] J. Maya, *J. Chem. Phys., 67* (1977) 4976.
[12] G.A. Oldershow and K. Robinson, *Trans. Faraday Soc., 64* (1968) 616.
[13] J. Kaplane, *Phys. Rev., 45* (1934) 675.
[14] O.J. Dunn and R.A. Young, *Int. J. Chem. Kinet., 8* (1976) 161.
[15] O. Dressanx, *J. Chim. Phys., 67* (1970) 1137.
[16] W. Hark and W. Langel, *J. Phys. Chem., 87* (1983) 3462.