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Copper halide chemiluminescence in O_2 discharge flows containing Cl_2

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Abstract

Chemiluminescence of copper monohalides (CuX; X≡Br, I) in oxygen discharge flows was observed in the range 400–800 nm when heated CuX vapour was injected into the oxygen glow produced by a microwave discharge. When chlorine was added to the flow, the blue emission of the CuBr $A^1\Pi \rightarrow X^1\Sigma$ and $B^1\Pi \rightarrow X^1\Sigma$ transitions and of the CuI $A^1\Pi \rightarrow X^1\Sigma$ transition changed to that of the CuCl $B^1\Pi \rightarrow X^1\Sigma$ transition. With an increasing amount of chlorine, the intensity of the CuCl bands in the 400–550 nm region decreased and the $CuCl_2$ emission appeared in the 600–750 nm region. These observations suggest that a halogen substitution reaction of CuX with Cl_2 occurs to produce CuCl and finally $CuCl_2$.

Keywords: Chemiluminescence; $CuCl_2$; Copper monohalide; Oxygen discharged flow; Chlorine addition

1. Introduction

Discharge flow systems have been widely used for measuring the chemiluminescence of metal compounds [1,2]. Recently the intense red emission of $CuCl_2$ in a flow of singlet oxygen, $O_2(^1\Delta)$, produced by chemical reaction of chlorine and H_2O_2 has attracted much attention in relation to the development of a visible chemical laser [3–5]. Since chlorine highly enhances the red emission of $CuCl_2$, the role of molecular chlorine, which remains as an impurity in the chemically produced singlet oxygen flow, is important in the red emission process [4–9]. However, the dependence of the chemiluminescence on the amount of Cl_2 in the chemical system has not been measured accurately, because it is difficult to control the amount of unreacted chlorine residue in the chemical production of $O_2(^1\Delta)$.

In the present paper we utilize an oxygen discharge flow containing $O_2(^1\Delta)$ for studying the copper halide chemiluminescence, because it enables examination of the effect of chlorine addition on the copper halide chemiluminescent process. Copper monohalide (CuX; X≡Br, I) vapour was injected into the oxygen plasma atmosphere and the copper halide chemiluminescence spectra were measured by varying the amounts of chlorine.

2. Experimental details

A microwave discharge produces substantial concentrations of $O_2(^1\Delta)$ and atomic oxygen [10,11]. In the present work we employed a microwave discharge flow of oxygen for generation of the oxygen metastable states in order to study the chemiluminescent reaction of gaseous CuX with $O_2(^1\Delta)$. Fig. 1 shows the discharge flow system equipped with a microwave generator (500 W, 2450 MHz) and an injector of metal halide vapour. The oxygen gas was excited in the upstream of the reaction tube equipped with a CuX vapour injector. The purities of oxygen and CuX were as follows: oxygen, 99.9%, Toyo Sanso; CuBr, 99%, Nakarai; CuI, 99%, Nakarai. The injector was composed of a powder cell and its cap, made of a Pyrex glass tube of 10 mm diameter. The cell was surrounded by a Nichrome wire heater and coated with ceramics. The vapour of copper halide was injected through a pore of 1 mm diameter. The cell was placed in the upstream of the outlet of active oxygen flow to the reaction tube, 70 mm in diameter. CuX powder was placed in the cell prior to the experiment. The amount of copper halide vapour was controlled by the heater temperature; the powder was vaporized by heating the injector cell at 500 °C.

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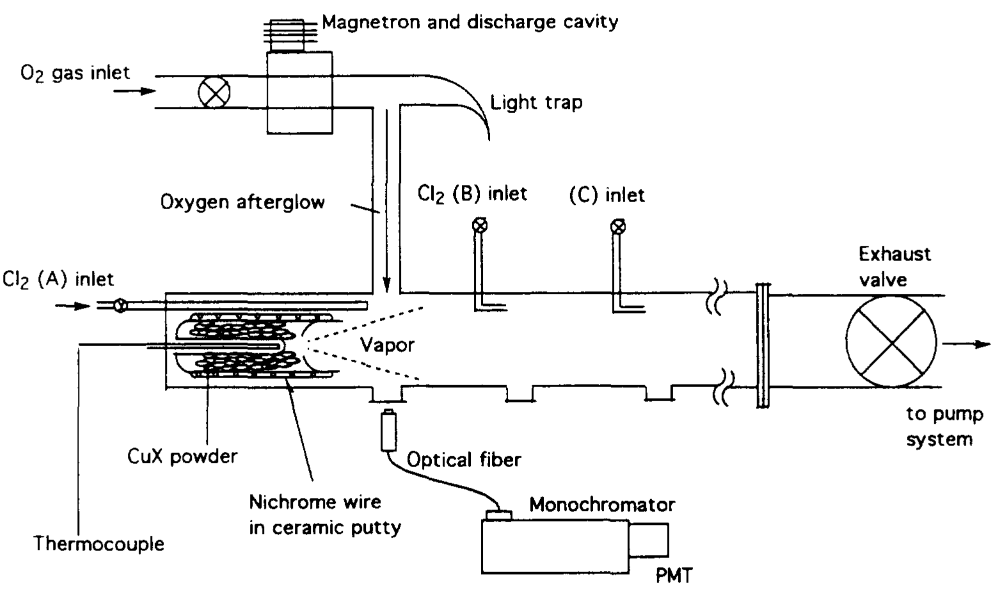

Fig. 1. Schematic diagram of the flow system composed of reaction, injector and microwave discharge parts.

Emission spectra in the visible region, which appeared in the downstream of the injector outlet, were measured as follows. The emission was gathered with a silica optical fibre on to the entrance aperture of a monochromator (CT-50, Nihon Bunko, 30 cm, 300 grooves mm^{-1}) and detected with a photomultiplier (Hamamatsu R-446).

The generation of $O_2(^1\Delta)$ in the oxygen flow was confirmed by measuring the near-IR emission intensity at 1270 nm with a Ge detector as reported previously [5,9]. Atomic oxygen was identified by nitric oxide titration for a trace of NO_2^* chemiluminescence [1]. The total pressure in the flow was measured with a Baratron pressure gauge (MKS 122A) and controlled in the range 0.1–0.9 Torr (1 Torr = 133 Pa).

3. Results and discussion

Prior to the chemiluminescence experiments on copper halides, it was confirmed that $O_2(^1\Delta)$ and atomic oxygen were present in the oxygen glow produced. When the oxygen afterglow containing the oxygen metastable states was allowed to flow into the reaction tube with gaseous CuX flow, a definitive blue chemiluminescence appeared downstream of the reaction tube. Fig. 2 shows the emission spectra for CuBr vapour with various chlorine additions. Without Cl_2 addition the resulting emission spectrum was that of excited CuBr. The assignment of the transitions was made on the basis of reported spectroscopic data [12–15]. The major peaks in the 500 nm region are due to the CuBr $A^1\Pi \rightarrow X^1\Sigma$ sequences and the minor peaks at about 450 nm are due to the $B^1\Pi \rightarrow X^1\Sigma$, $\Delta v = -1, 0, 1, 2$, sequences. With a slight addition of chlorine from inlet (A), the spectral shape of the CuBr $A^1\Pi \rightarrow X^1\Sigma$ transition changed to that of the CuCl $B^1\Pi \rightarrow X^1\Sigma$ transition, though the CuBr $A^1\Pi \rightarrow X^1\Sigma$ bands remained faintly in the emission spectrum (b).

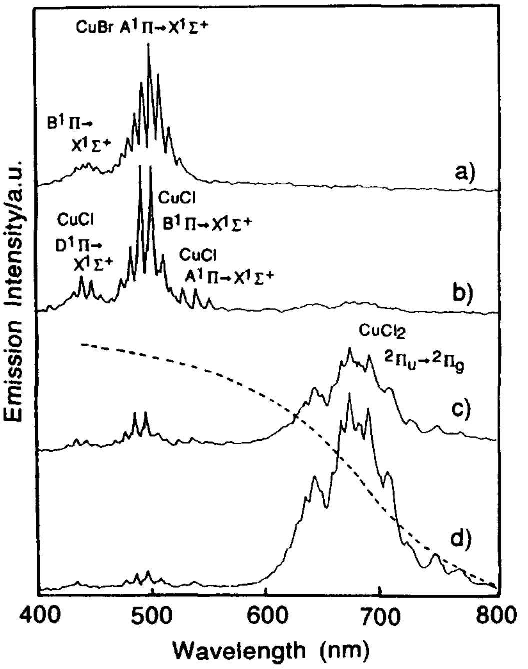

Fig. 2. Emission spectra in the oxygen discharge flow containing CuBr vapour with various chlorine additions: (a) no addition; (b) Cl_2 flow rate of 0.3 mmol min^{-1}; (c) 2.2 mmol min^{-1}; (d) 6.5 mmol min^{-1} (vapour injector temperature 500 °C, O_2 flow rate 19 mmol min^{-1}, pressure 0.27–0.3 Torr). Broken curve shows detector sensitivity.

Furthermore, the reaction tube was filled with a red glow when an excess of Cl_2 was added. As shown in the spectra (c) and (d) of Fig. 2, the CuCl band disappeared and a broad band appeared in the 600–750 nm region. The spectrum (d) in Fig. 2 is basically identical with that of $CuCl_2$ reported by Yoshida et al. [3] and Tokuda and coworkers [5,9]. The concavity at 650 nm was found to be due to the monochromator.

Fig. 3 shows the spectral change in the glow intensity for the CuI vapour. The addition of chlorine to the flow with a blue emission due to the CuI $A^1\Pi \rightarrow X^1\Sigma$ transition caused the appearance of the emission due to the CuCl $B^1\Pi \rightarrow X^1\Sigma$ transition. When a small amount of chlorine was added, the spectrum was a mixture of the CuCl $B^1\Pi \rightarrow X^1\Sigma$ and CuI $A^1\Pi \rightarrow X^1\Sigma$ transitions. The blue emission was quenched with an increasing amount of chlorine and the spectrum was dominated by the red emission of the $CuCl_2$ transition.

These observations suggest that halogen substitution of CuX by chlorine occurs in the active oxygen atmosphere. Furthermore, when an excess of chlorine is added, the substitution proceeds further to form $CuCl_2$, as evidenced by the red $CuCl_2$ emission:

$$\text{CuX }(\text{X} \equiv \text{Br, I}) \xrightarrow{\text{oxygen glow}} \text{CuX*} \xrightarrow{\text{Cl}_2}$$

$$\text{CuCl* }(A^1\Pi, B^1\Pi, C^1\Pi) \xrightarrow{\text{Cl}_2} \text{CuCl}_2\text{*} \quad (1)$$

where CuX*, CuCl* and $CuCl_2$* denote electronically excited states.

In order to study this chlorine substitution by observation of the emission, we also attempted to observe the chemiluminescence of CuCl vapour. When gaseous CuCl, vaporized at 500 °C in the injector, was mixed with the oxygen glow, the emission peaks of the resulting blue glow were assignable to CuCl ($A^1\Pi \rightarrow X^1\Sigma$, $B^1\Pi \rightarrow X^1\Sigma$, $C^1\Pi \rightarrow X^1\Sigma$, $D^1\Pi \rightarrow X^1\Sigma$) transitions. The addition of chlorine to this blue glow caused the quenching of the CuCl excited states. With an excess addition of chlorine, the red glow filled the downstream of the reaction tube. In this CuCl chemiluminescent process the following reaction occurs:

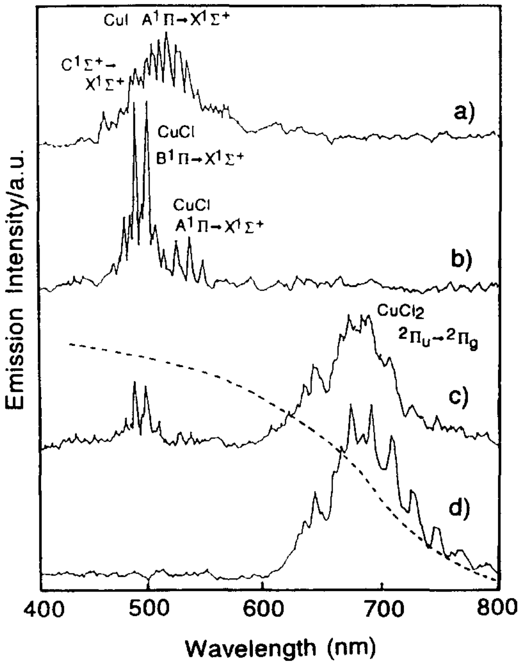

Fig. 3. Emission spectra in the oxygen discharge flow containing CuI vapour with various chlorine additions: (a) no addition; (b) Cl_2 flow rate of 0.1 mmol min^{-1}; (c) 1.0 mmol min^{-1}; (d) 3.0 mmol min^{-1} (vapour injector temperature 500 °C, O_2 flow rate 19 mmol min^{-1}, pressure 0.27–0.3 Torr). Broken curve shows detector sensitivity.

$$\text{CuCl} \xrightarrow{\text{oxygen glow}}$$

$$\text{CuCl* }(A^1\Pi, B^1\Pi, C^1\Pi) \xrightarrow{\text{Cl}_2} \text{CuCl}_2\text{*} \quad (2)$$

Table 1 summarizes the emission species observed for CuCl, CuBr and CuI addition, where no CuO_2 and CuO species were detectable [15]. This indicates that oxidation of the gaseous CuX with the active oxygen does not occur. In addition, no Cu chemiluminescence was detectable; namely, there is no dissociation to Cu and X under the present experimental conditions.

To identify more clearly the blue and red emission processes with various chlorine additions, a nitrogen discharge flow was applied to the chemiluminescence study of the CuBr vapour system. In the active nitrogen glow the blue emission for the CuBr $A^1\Pi \rightarrow X^1\Sigma$ and $B^1\Pi \rightarrow X^1\Sigma$ transitions was observed in a similar manner to the corresponding oxygen glow system. However, various excited species in the discharge flow may further complicate the identification of the energy source for the CuX excitation. In fact, NO gas titration [1] in the present study suggests the presence of O atoms in the oxygen flow; namely, NO_2* chemiluminescence was observed clearly in the present discharge flow when NO was added to the oxygen glow and nitrogen glow from outlet (A). It is known that gaseous metal halide is excited by a three-body reaction when N atoms are recombined in the nitrogen discharge flow [16,17]. A similar excitation process in the O atom recombination was reported in the oxygen discharge flow [18,19]. Therefore our observation of the CuX blue emission in both oxygen and nitrogen glows suggests that the

Table 1
Summary of chemiluminescence spectra observed in active oxygen flow

Emitting species	Electronic transition	Wavelength region (nm)	Energy (cm^{-1})
CuCl	$A^1\Pi \rightarrow X^1\Sigma^+$	520–550	18997
	$B^1\Pi \rightarrow X^1\Sigma^+$	470–530	20476
	$C^1\Sigma^+ \rightarrow X^1\Sigma^+$	460–520	20622
	$D^1\Pi \rightarrow X^1\Sigma^+$	445–455	22958
CuBr	$A^1\Pi \rightarrow X^1\Sigma^+$	455–540	20489
	$B^1\Pi \rightarrow X^1\Sigma^+$	420–435	23029
CuI	$A^1\Pi \rightarrow X^1\Sigma^+$	485–540	19708
	$C^1\Sigma^+ \rightarrow X^1\Sigma^+$	455–470	21849
	$D^1\Sigma^+ – X^1\Sigma^+$	435–450	22932
	Unknown	470–490	

blue chemiluminescent process occurs by a three-body reaction.

We further examined the dependence of the CuBr emission on Cl_2 addition in the nitrogen glow. The emission of CuBr in the glow changed upon addition of Cl_2. With a slight addition of Cl_2 to the CuBr blue glow, the CuCl transition was detected; this indicates that halogen substitution takes place in the nitrogen glow system. Although an excess of chlorine was added to the glow system, the emission spectrum did not change to that for $CuCl_2$*. The blue glow was only quenched by the chlorine addition.

Consequently, our present observations suggest that a halogen substitution reaction of CuX occurs by the Cl_2 addition and produces CuCl and finally $CuCl_2$ and the resulting $CuCl_2$ is excited by $O_2(^1\Delta)$. A comparison of the emission processes in oxygen and nitrogen glow systems shows that halogen substitution takes place regardless of the presence of $O_2(^1\Delta)$. As a result of the reaction of CuX with Cl_2, the emitter, $CuCl_2$, in the red glow is finally produced only in the presence of $O_2(^1\Delta)$. This information provides a clue for interpretation of the emission process.

Fig. 4 shows the emission intensities of the CuCl B–X (0,0) band measured at 488 nm with various amounts of chlorine added to the CuBr glow in the reaction tube from the three inlets shown in Fig. 1: (A) upstream of the vapour injector and (B) 10 cm and (C) 20 cm downstream from the injector vapour outlet. The emission intensity of the CuCl $B^1\Pi \rightarrow X^1\Sigma$ band appearing upon Cl_2 addition decreased with increasing amount of Cl_2. The CuCl emission observed upon Cl_2 addition from outlet (A) was the most intense. As shown in Fig. 5, the red glow intensity at 691 nm was enhanced when a large amount of chlorine was added. This implies that the formation of $CuCl_2$ increases with excess chlorine. Further, the addition of chlorine from outlet (A) enhanced the red glow intensity relative to that from outlets (B) and (C). Figs. 4 and 5 show that the halogen substitution reaction forming the emitting CuCl and $CuCl_2$ is favoured in the upstream near the heated injector.

When chlorine is added from outlet (A) near the injector, there is a possibility that it penetrates into the heated injector, thereby causing halogen substitution in the heated device. Therefore an X-ray differential (XRD) spectrum of the CuBr residue in the injector was measured after the chemiluminescence experiments. This XRD analysis showed that the CuBr residue contained no CuCl and $CuCl_2$, indicating no chlorine substitution of CuBr in the injector. As a consequence, halogen substitution of the CuX proceeds in the gas phase. In particular, the data of Figs. 4 and 5 suggest that the substitution reaction is enhanced in the CuBr vaporized immediately from the heated injector. Subsequently, the excitation of CuX may occur by oxygen recombination in the glow.

At present, little is known about the energy source for the energy transfer reaction in the chemiluminescent process responsible for O atoms and $O_2(^1\Delta_g)$. However, our present results suggest that the $CuCl_2$ producing the red emission is formed by the halogen substitution reaction through a CuCl intermediate in either an excited state or the ground state.

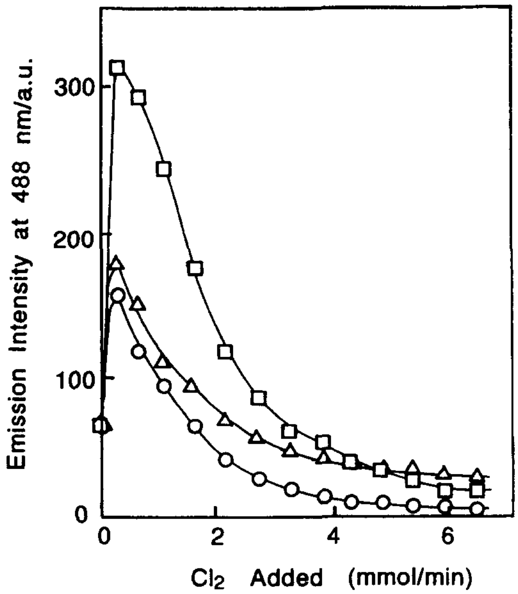

Fig. 4. Intensities of the blue emission at 488 nm in the oxygen discharge flow containing CuBr vapour with various amounts of chlorine. Chlorine gas was added from outlets (A) (□), (B) (△) and (C) (○) (vapour injector temperature 500 °C).

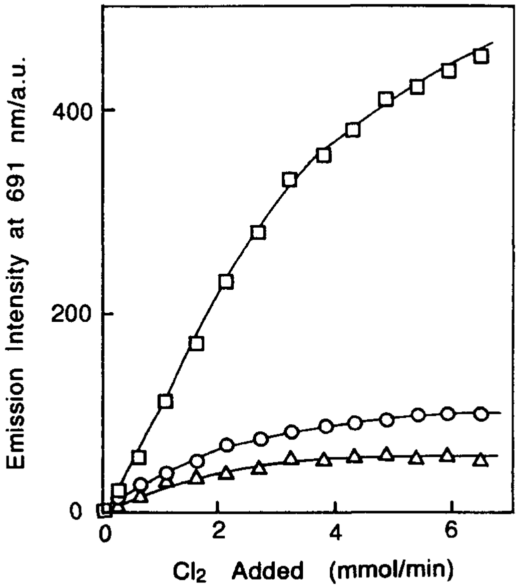

Fig. 5. Intensities of the red emission at 691 nm in the oxygen discharge flow containing CuBr vapour with various amounts of chlorine. Chlorine gas was added from outlets (A) (□), (B) (△) and (C) (○) (vapour injector temperature 500 °C).

4. Conclusions

The chemiluminescence of CuX ($X \equiv Br,I$) and $CuCl_2$ in an oxygen glow produced by a microwave discharge was observed with various amounts of chlorine added. The chlorine addition resulted in substitution of the halogen atom X in gaseous CuX, as evidenced by the observed change in the emission spectrum from that of CuX to those of CuCl and $CuCl_2$ due to the addition of chlorine. The substitution reaction is enhanced in the hot gaseous CuX. Our results demonstrate that the halogen substitution of CuX proceeds as far as $CuCl_2$ through the excited or ground state of CuCl. The $CuCl_2$ emitting the red glow must be excited by $O_2(^1\Delta_g)$ in the active oxygen flow.

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