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# Effects of Metal Ions on Delayed Chemiluminescence Reaction of Luminol Catalyzed by Copper(II)

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**Synopsis.** The delay time and chemiluminescence (CL) intensity in delayed-luminol CL catalyzed by copper(II) were remarkably affected by the presence of such metal ions as Cr(III), Mn(II), Co(II), and Ni(II). The variation of the delay time could be explained in terms of the effects of the metal ions on the oxidation rate of cysteamine by Cu(II). Meanwhile, all of the metal ions reduced the CL intensity compared with that by Cu(II) alone. This result could be ascribable to a deactivation of Cu(II) by the metal ions for the decomposition of hydrogen peroxide, thus decreasing the CL emission due to the peroxidation of luminol.

Mutual metal interference has been observed in a chemiluminescence (CL) reaction of luminol with alkaline hydrogen peroxide ($H_2O_2$) catalyzed by metal ions, since many metal ions serve as catalysts for the luminol CL reaction. Thus, the conventional luminol CL is subject to limited routine use due to a lack of specificity.[1—4)]

We previously applied a luminol CL-delay method to the determination of Cu(II) by measuring the delay time or CL intensities.[5)] The selectivity for Cu(II) in the luminol CL-delay method was superior to that in the conventional luminol CL method. Iron(III) and some metal ions were tolerable in greater amounts than those in the conventional luminol CL method. However, serious interference from Cr(III), Mn(II), Co(II), and Ni(II) remains, even at a level equal to that of Cu(II). The aim of this work was to elucidate the effects of these metal ions on the delay time and CL intensities in the delayed-luminol CL.

## Experimental

**Reagents.** All of the chemicals used were of guaranteed-grade reagents and were used without further purification. Standard solutions of Cu(II), luminol, and cysteamine ($H_2NCH_2CH_2SH$) were prepared as previously described.[5)]

**Standard Procedure.** A 0.5 $cm^3$ portion of a $1.0\times10^{-5}$ M (1 M=1 mol $dm^{-3}$) Cu(II) solution was added into a glass cuvette. The solution was saturated with oxygen by bubbling. Next, a 1 $cm^3$ portion of a $2.5\times10^{-3}$ M luminol solution and a 1 $cm^3$ portion of a $1.0\times10^{-3}$ M cysteamine solution were simultaneously injected into the cuvette. The CL reaction was initiated, and the CL emission was detected by a photomultiplier. Bubbling of oxygen at a rate of 50 $cm^3\,min^{-1}$ was continued during the reaction. All of the CL measurements were made at room temperature. The maximum light emission was referred to as the CL intensity. The time period from the reaction initiation to a CL flash was defined as being the delay time. Information concerning the CL instrumental system has been previously described.[5)]

**Analytical Procedure for Cysteamine and $H_2O_2$.** The determination of cysteamine consumed and $H_2O_2$ formed during cysteamine oxidation was carried out spectrophotometrically according to a previously described procedure, in which a $1.0\times10^{-5}$ M Cu(II) solution, a $1.0\times10^{-3}$ M cysteamine solution and a 0.1 M NaOH solution were used.[5)]

## Results and Discussion

The CL measurement was carried out according to the standard procedure. A luminol CL-delay response curve is shown in Fig. 1 {curve(1)}. A sharp CL flash suddenly appeared after a dark period of about 8.5 min from the start of the reaction. The appearance of the delay time was previously interpreted as follows.[5)] Dur-

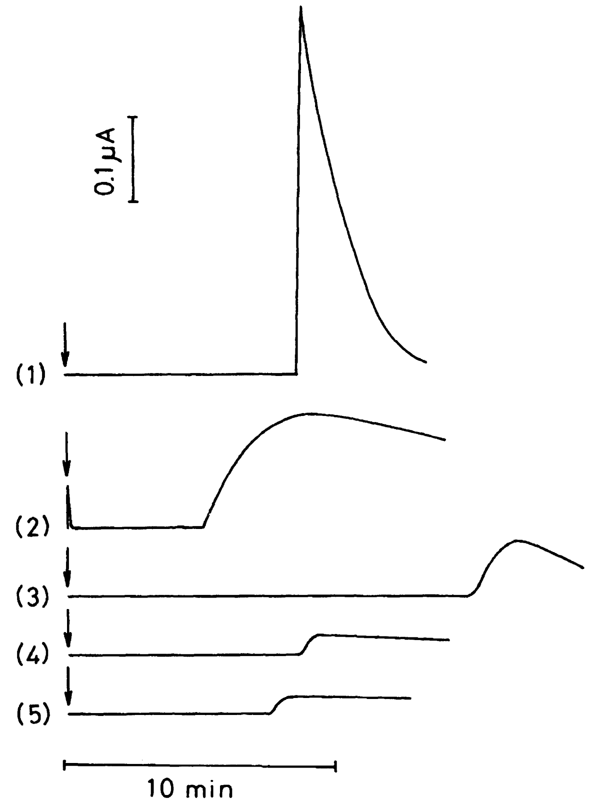

Fig. 1. Typical chemiluminescence responce curves. (1) Cu(II) only, (2) Cu(II)+Co(II), (3) Cu(II)+Mn(II), (4) Cu(II)+Ni(II), (5) Cu(II)+Cr(III). Conditions: $1.0\times10^{-5}$ M Cu(II), $1.0\times10^{-4}$ M foreign metal ion, $1.0\times10^{-3}$ M cysteamine, $2.5\times10^{-3}$ M luminol. At the arrow, luminol and cysteamine were injected.

ing cysteamine oxidation, Cu(II) is strongly complexed with cysteamine, thereby being inactivated for the luminol CL reaction. After complete oxidation of cysteamine, the Cu(II)-catalyzed luminol CL reaction subsequently commences using the accumlated $H_2O_2$. Thus, a delay time from the reaction initiation to a sharp flash of CL is observed. This delayed CL of luminol was applied to the determination of Cu(II) by measuring the delay time or CL intensities.[5] However, the delay time and CL intensity were remarkably affected by the presence of Cr(III), Mn(II), Co(II), and Ni(II).

In order to elucidate the interference from metal ions, CL measurements were carried out according to the procedure, except that a mixture of Cu(II) and a specified metal ion was added into the cuvette. The concentration of the metal ion added was 10-times greater than that of Cu(II). Typical CL response curves are shown in Fig. 1 {curve (2)—(5)}, which are highly dependent upon the metal ions added. When Co(II) was added, two peaks appeared in the response curve, as shown in Fig. 1 {curve (2)}. CL emission occurred instantaneously just after the initiation of the reaction, and then began to decay rapidly. A CL flash occurred again after about 5 min. The first peak was probably due to a CL reaction of luminol catalyzed by Co(II) with oxygen molecules. Meanwhile, when Cr(III), Ni(II), and Mn(II) were added, a delay CL was observed, as shown in Fig. 1 {curve (3)—(5)}.

The delay time in the presence of Ni(II) was about the same as that in Cu(II) alone. Manganese(II) gave a longer delay time than did Cu(II) alone, whereas Cr(III) and Co(II) showed a shorter delay time than did Cu(II) alone. On the other hand, all of the metal ions remarkably reduced the CL intensity when compared with that by Cu(II) alone. These results suggest that the metal ions give rise to significant effects on the oxidation rate of cysteamine as well as the decomposition rate of $H_2O_2$.

We then determined the amounts of $H_2O_2$ formed and consumed during the delayed CL reaction. The time courses for $H_2O_2$ formation and decomposition are shown in Fig. 2. The time at the beginning of $H_2O_2$ decomposition was in accordance with the delay time observed in the delayed-luminol CL in the presence of the respective metal ions. Nickel(II) did not affect the oxidation rate when compared with that by Cu(II) alone. However, a remarkable decrease of the oxidation rate was observed in the presence of Mn(II). On the other hand, the presence of Co(II) and Cr(III) enhanced the oxidation rate. No catalytic oxidation of cysteamine by these metal ions proceeded under the same conditions. Therefore, the delay time is probably influenced by the difference of the effect of the metal ion on the catalytic activity of Cu(II) for the oxidation of cysteamine.

In Fig. 2, the amounts of $H_2O_2$ formed during cysteamine oxidation were about the same as in Cu(II) alone, regardless of the metal ion added, except for the mixture of Mn(II). However, the decomposition rate of $H_2O_2$ decreased markedly in the presence of metal ions. No catalytic decomposition of $H_2O_2$ by Cr(III), Co(II), and Ni(II) proceeds under the same conditions. On the other hand, Mn(II) catalyzed the decomposition of $H_2O_2$. Consequently, the remarkable decrease in the amounts of $H_2O_2$ formed in the presence of Mn(II) is probably due to the progress of the $H_2O_2$ decomposition by Mn(II) during cysteamine oxidation.

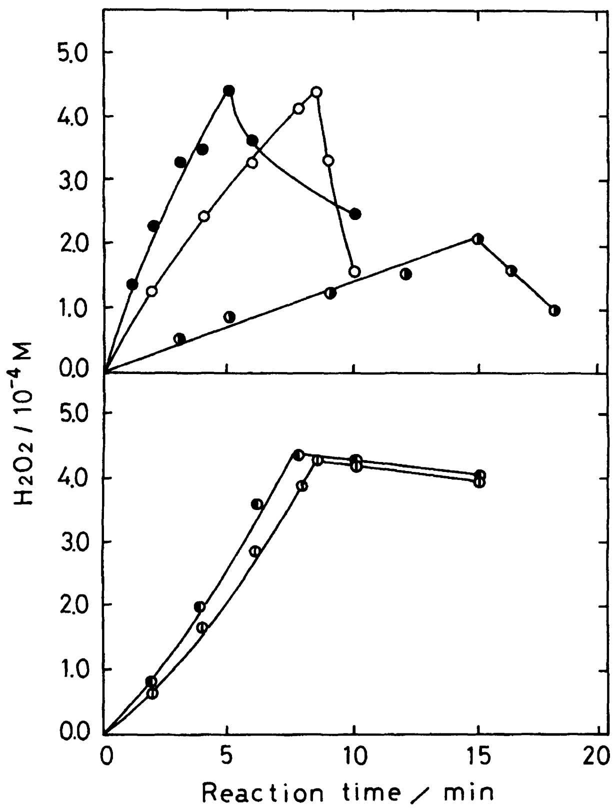

Fig. 2. Time course of hydrogen peroxide formation and decomposition. ○: Cu(II) only, ●: Cu(II)+Co(II), ◑: Cu(II)+Mn(II), ◐: Cu(II)+Cr(III), ⦶: Cu(II)+Ni(II). Conditions: $1.0\times10^{-5}$ M Cu(II), $1.0\times10^{-4}$ M foreign metal ion, $1.0\times10^{-3}$ M cysteamine.

In order to confirm their effect on the deactivation of Cu(II) for the decomposition of $H_2O_2$, we then examined the decomposition of $H_2O_2$ by Cu(II) alone or by the combined use of Cu(II) with the metal ions according to the analytical procedure for $H_2O_2$, except that a $1.0\times10^{-3}$ M $H_2O_2$ solution was employed in place of a cysteamine solution. The concentration of the metal ion added was 10-times greater than that of Cu(II). The decomposition yield of $H_2O_2$ by Cu(II) alone was 61% after 30 s from the start of the reaction. Under the same conditions, those by the combined use of Cu(II) with Co(II), Mn(II), Ni(II), and Cr(III) were 25, 25, 18, and 12%, respectively. These results support the idea that metal ions lower the catalytic activity of Cu(II) for the decomposition of $H_2O_2$.

The CL intensity generally increases with increasing $H_2O_2$ concentration and the decomposition rate of $H_2O_2$. Therefore, the decrease in the CL intensity in the presence of metal ions could be explained in terms of their effect on the deactivation of Cu(II) for the decomposition of $H_2O_2$. Meanwhile, the decrease in the CL intensity in the presence of Mn(II) may be interpreted by taking into account the catalytic decomposition of $H_2O_2$ by Mn(II), in addition to the effect mentioned above.

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