

# Mechanism of the Oscillating Chemiluminescence Reaction Using Luminol

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Luminol exhibits repeatedly strong and momentary chemiluminescence in the presence of  $\text{SCN}^-$  and low  $\text{Cu}^{2+}$  concentrations, which is typically ascribed to the formation of  $\text{HO}_2$ . However, the decrease of the oxidation-reduction potential (ORP) and the origin of the strong chemiluminescence is not fully understood. This reaction is considered to involve (i) strong chemiluminescence by the reaction of luminol and  $\cdot\text{OS}(\text{O})\text{CN}$  involved in the feedback loop of  $-\text{OS}(\text{O})\text{CN}$ , (ii) a decrease in the ORP due to a decrease in  $[\cdot\text{OS}(\text{O})\text{CN}]/[-\text{OS}(\text{O})\text{CN}]$ , and (iii) strong chemiluminescence originating from the  $\text{Cu}^+(\text{SCN})_n$  concentration. To verify these hypotheses, three experiments were performed: (i) simultaneous measurement of  $[\text{Cu}^{2+}]$ , the ORP, and the chemiluminescence with variation in the concentration of each solution, (ii) simultaneous measurement of the ORP and absorbance at 450 nm, which is the absorption of  $\text{HO}_2\text{-Cu(I)}$ , and (iii) simulation of the concentration change at the time of the strong chemiluminescence. The strong chemiluminescence is related to the  $\cdot\text{OS}(\text{O})\text{CN}$  concentration in the feedback loop;  $[\text{Cu}^{2+}]$  increased and the ORP decreased during the strong chemiluminescence, and  $[\text{SCN}^-]$  was higher than  $[\text{Cu}^{2+}]$ . Therefore, the increase in  $[\cdot\text{OS}(\text{O})\text{CN}]$  contributed to the ORP decrease, as given by  $E = E_0 + 0.059 \log [\cdot\text{OS}(\text{O})\text{CN}]/[-\text{OS}(\text{O})\text{CN}]$ . The strong and momentary chemiluminescence occurred when the absorbance at 450 nm decreased to a certain level, which suggests that  $\text{HO}_2\text{-Cu(I)}$  decreased and  $\text{Cu}^+(\text{SCN})_n$  increased, and the feedback loop reaction increased rapidly. Simulation confirmed that  $[\cdot\text{OS}(\text{O})\text{CN}]$  increased sharply. This reaction system could thus be applied to the quantitative analysis of low  $\text{Cu}^{2+}$  concentrations simply by measuring the oscillation period.