

Mechanism of the Oscillating Chemiluminescence Reaction Using Luminol

Toki, Erika

Nakamura, Misato

Osaki, Shiori

Luminol exhibits repeatedly strong and momentary chemiluminescence in the presence of SCN^- and low Cu^{2+} concentrations, which is typically ascribed to the formation of 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 Cu^{2+} concentrations simply by measuring the oscillation period.