Mechanism of the Oscillating Chemiluminescence Reaction Using Luminol

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Luminol exhibits repeatedly strong and momentary chemiluminescence in the presence of SCN- and low Cu2+ concentrations, which is typically ascribed to the formation of HO2. 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 ·OS(O)CN involved in the feedback loop of -OS(O)CN, (ii) a decrease in the ORP due to a decrease in [·OS(O)CN]/[-OS(O)CN], and (iii) strong chemiluminescence originating from the Cu+(SCN-)n concentration. To verify these hypotheses, three experiments were performed: (i) simultaneous measurement of [Cu2+], 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 HO2-Cu(I), and (iii) simulation of the concentration change at the time of the strong chemiluminescence. The strong chemiluminescence is related to the ·OS(O)CN concentration in the feedback loop; [Cu2+] increased and the ORP decreased during the strong chemiluminescence, and [SCN-] was higher than [Cu2+]. Therefore, the increase in [-OS(O)CN] contributed to the ORP decrease, as given by E=E0+0.059log[·OS(O)CN]/[-OS(O)CN]. The strong and momentary chemiluminescence occurred when the absorbance at 450 nm decreased to a certain level, which suggests that HO2-Cu(I) decreased and Cu+(SCN-)n increased, and the feedback loop reaction increased rapidly. Simulation confirmed that [·OS(O)CN] increased sharply. This reaction system could thus be applied to the quantitative analysis of low Cu2+ concentrations simply by measuring the oscillation period.