

FERRICINIUM ION AS THE OXIDIZING REAGENT IN THE CHEMILUMINESCENCE
REACTION OF LUMINOL IN ORGANIC SOLVENT-WATER MIXTURES

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In the presence of ferricinium ion, the chemiluminescence of luminol is observed in alkaline acetonitrile-water and methanol-water mixtures. The emission intensity is as strong as that observed in the presence of ferricyanide ion. The luminescence decays exponentially within a second.

The role of oxidizing reagents in the chemiluminescence reaction of luminol has been the subject of numerous investigations¹⁾ since its discovery. Among the oxidizing reagents, hemin, ferricyanide ion and numerous complex ions were used frequently in many works. However, the use of these reagents is limited to aqueous solutions because of their low solubilities in other solvents.

Recently, in the course of the studies of ferrocene-ferricinium couple in non-aqueous solvents, we tested the use of ferricinium ion for the chemical oxidation of luminol. The importance of the ferrocene-ferricinium couple is well recognized in homogeneous electron transfer reactions²⁾ as well as in oxidation-reduction titrations in non-aqueous solvents³⁾.

In this paper, we deal with the appearance of the luminescence of luminol in the presence of ferricinium ion in alkaline acetonitrile-water and methanol-water mixtures. In both solvents, the water content was 50 volume %. Ferricinium ion was prepared by the oxidation of the ferrocene solution with solid lead peroxide. For the observation of luminescence, the alkaline luminol solutions of various concentration (0.02 to 0.5 mM/l) were added to the ferricinium-ion solution (0.81 mM/l) by the sudden replacement of the injection syringe. The emission was measured by using a photomultiplier (HAMAMATSU R-136) and an oscilloscope (MATSUSHITA VP-541A). The decay curves of the total emission are illustrated in Fig.1.

The luminescence appeared sharply within ten or more msec after mixing, and decayed rapidly. The initial part of the curve obeys the exponential-type decay, and the decay mode is almost the same for both solvents. However, the decay time constant in acetonitrile-water solvent is much greater than that in methanol-water solvent. For comparison, the luminescence due to the oxidation by ferricyanide ion is also shown in the same figure. It is worth noting that the rise time is greater than that for the oxidation by ferricinium ion. From the results shown in Fig.1 it is clear that ferricinium ion is more effective than the ferricyanide ion as an oxidizing reagent for the chemiluminescence reaction of luminol.

In Fig.2 the concentration dependency of luminol on the maximum emission intensity is shown. In the concentration range of luminol, the logarithm of luminol concentration shows a linear relationship with the maximum emission intensity.

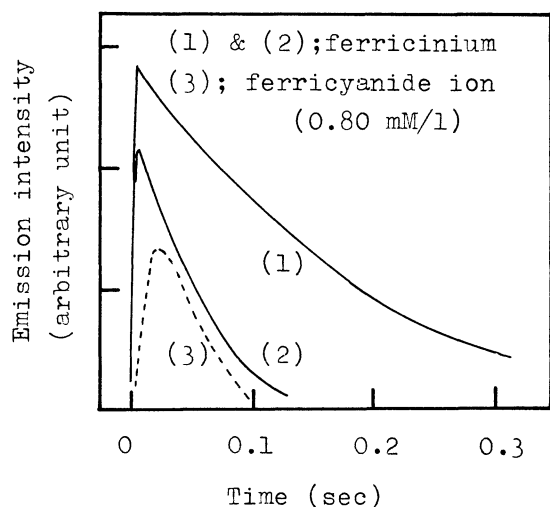


Fig.1 Decay of emission intensity.

$$[\text{luminol}] = 0.5 \text{ mM/l}$$

Solvent: (1) acetonitrile-water

(2) methanol-water

(3) methanol-water

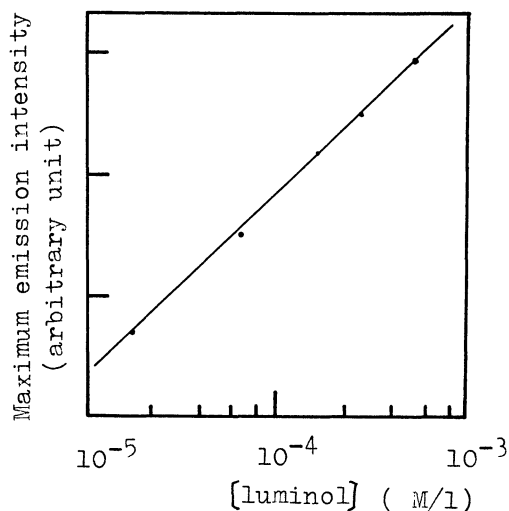


Fig.2 Relationship between maximum emission intensity and $\log[\text{luminol}]$.

$$[\text{ferricinium}] = 0.81 \text{ mM/l}$$

Solvent: acetonitrile-water

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