

## Luminol Amidine

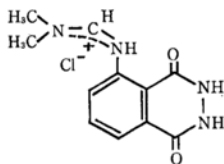
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Luminol, one of the most popular chemiluminescent compounds, has been used as an indicator in titration analysis.<sup>1)</sup> Recently luminol was shown to be a mixture and not a pure compound, as had usually been believed.<sup>2)</sup> It is very difficult to purify commercial luminol by recrystallization because it is sparingly soluble in most solvents.

During the course of synthetic studies of luminol derivatives we found that luminol reacts with the Vilsmeier reagent from dimethylformamide (DMF) and thionyl chloride to afford luminol amidine (I), which is moderately soluble in water and which is easily purified by recrystallization from water.



The luminol amidine (*N,N*-dimethyl-*N'*-diketophthalazine-5-yl-formamidine) was prepared as follows: 1.77 g of luminol was dissolved in 20 ml of DMF, into which the Vilsmeier reagent from 2.19 g of DMF and 3.57 g of thionyl chloride was stirred. The precipitates which appeared were recrystallized from water to give colorless needles, mp 271–272°C (dec).

Found: C, 49.15; H, 4.94; N, 20.93%. Calcd for  $C_{11}H_{13}O_2N_4Cl$ : C, 49.16; H, 4.87; N, 20.85%. UV:  $\lambda_{\text{max}}^{H_2O}$  nm (log  $\epsilon$ ), 228 (4.53), 283 (4.17) and

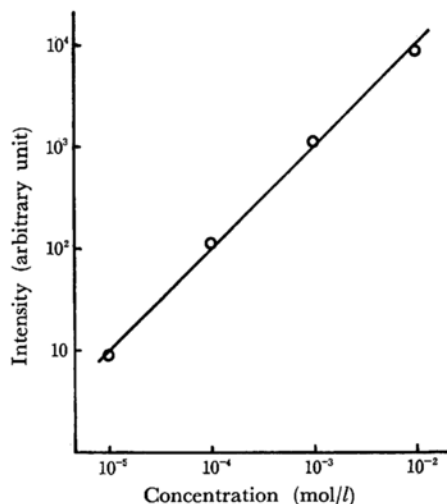


Fig. 1. The chemiluminescence intensity of luminol amidine (I) against molar concentration when the mixture of 0.3% aqueous hydrogen peroxide (0.5 ml) and 0.3% potassium ferricyanide aqueous solution (0.5 ml) was added to the solution of I in 0.1 N sodium hydroxide aqueous solution.

318 (4.17). IR:  $\nu_{\text{max}}^{KBr}$   $\text{cm}^{-1}$  1705, 1645. NMR  $\delta^{D_{2O}}$  3.35 (3H, s), 3.55 (3H, s), 7.7–7.9 (3H, m) and 8.87 (1H, s).

The chemiluminescence of luminol amidine was measured by Hitachi Photomultiplier. The relative intensity of light emission of luminol amidine is about one twenty-fifth that of luminol itself, the maximum of the chemiluminescence spectrum is 452 nm. The plot of the chemiluminescence intensity with the variation in concentration between  $10^{-2}$  and  $10^{-5}$  mol/l shows a straight line (Fig. 1). This suggests that luminol amidine will be useful as a standard compound for the chemiluminescence measurement.

1) F. Kenny and R. B. Kurtz, *Anal. Chem.*, **24**, 1218 (1952); L. Erdey and I. Buzas, *Anal. Chim. Acta*, **22**, 524 (1960).

2) D. S. Bersis and J. Nikokavouras, *Nature*, **217**, 451 (1968).