CHEMILUMINESCENCE OF A BY-PRODUCT IN THE FIREFLY CHEMILUMINESCENCE

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The structure of 2-(6'-hydroxy-2'-benzothiazolyl)-4-isopropylidene-Δ^2-thiazolin-5-one (4) is assigned to a by-product formed in the chemiluminescence of esters of the dimethyl derivative of firefly luciferin (3). Compound 4 also proved to be chemiluminescent on reaction with potassium phenoxide and oxygen. The conditions are the same as those used in the chemiluminescence of the luciferin ester 1 that produces 4, but the isopropylidene compound reacts more slowly ($\tau_{1/2} \sim 1100$ sec) than the luciferin ester ($\tau_{1/2} \sim 9$ sec), permitting its accumulation in the reaction mixture. The only fluorescent compound formed in the chemiluminescence of 4 is oxyluciferin 2. A reactiom mechanism for this conversion based on an analogous proposal for the CL of firefly luciferin was proposed.

The quantum yield for the CL of 4 is dependent on the nature of the base B. For $B=PhO^-$, QY $\sim 2.5 \times 10^{-2}$ and for $B=^-OH$, QY $\sim 1.2 \times 10^{-4}$. The lower value for $B=^-OH$ presumably is a result of ionization of the carboxyl group.

In dilute solutions (1.2×10^{-6}M), the CL λ_{max} of 4 is 626 nm, a value close to that of the fluorescence of 2 (631 nm) and the CL emission of the phenyl and AMP esters of 3. The CL of ester 1 occurs at 630 nm. In more concd. solutions (>2×10^{-5}M) the wavelength of CL of 4 shifts to 584 nm. An exiplex emission from 2 + 4 may be involved since the addition of 4 (10^{-4}M) to a fluorescing solution of 2 (10^{-5}M) shifts the emission from 630 to 585 nm. Also, the addition of 4 to a chemiluminescing solution of ester 1 leads to a shift of the emission wavelength from 630 to 584 nm.

The conversion of compound 4 to 13 is in effect the reverse of the conversion of 1 to 4, implying that the thiazoline carboxylic acid ring system of 1 and 13 and the thiazolinone ring system of 4 can be brought into equilibrium with base.