CHEMILUMINESCENCE OF A BY-PRODUCT IN THE FIREFLY CHEMILUMINESCENCE

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The structure of 2-(6'-hydroxy-2'-benzoazolyl)-4-isopropylidene-4-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 (τ₁/₂ ~ 1100 sec) than the luciferin ester (τ₁/₂ ~ 9 sec), permitting its accumulation in the reaction mixture. The only fluorescent compound formed in the chemiluminescence of 4 is oxyluciferin 2. A reaction 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 ~ 2.5 x 10⁻² and for B=OH, QY ~ 1.2 x 10⁻⁴. The lower value for B=OH presumably is a result of ionization of the carboxyl group.

In dilute solutions (1.2 x 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 x 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.