

A New Series of Chemiluminescent Reactions

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DURING the course of a study of overcrowded aromatic systems, we have found that the addition of base to solutions of the bisquaternary salts of the 1,1'-bisoquinolines (I)—(IV) in hydroxylic solvents produces a blue chemiluminescence (Figure). The quantum efficiency of the chemiluminescence of (I) (0.15%) is of the same order as that of lucigenin¹ (0.30%), but the efficiency falls successively through nine orders of magnitude in the series (I) > (II) > (III) > (IV). The efficiencies were measured relative to that of lucigenin¹ from the integrated band areas of the recordings of chemiluminescence intensity against time given by standard solutions of (I)—(IV) on treatment with base in a cell adjacent to a IP 28 photomultiplier linked to an electronic recorder. The recordings show that the decay of the chemiluminescence is first order, with a half-life of ~ 1 –100 sec., depending upon the solvent and the bisquaternary salt studied.

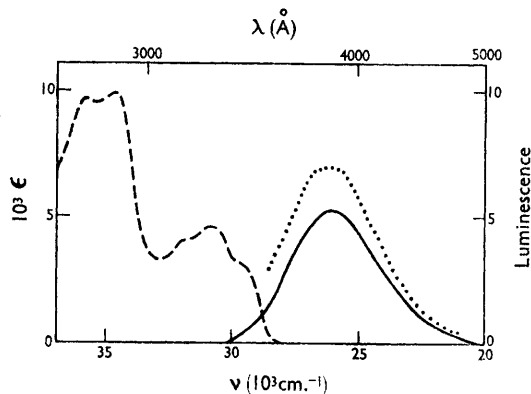
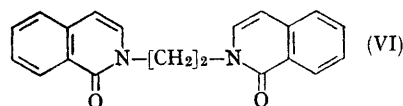
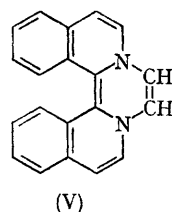
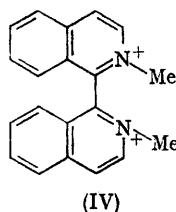
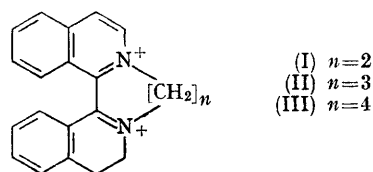


FIGURE. The spectral distribution of the chemiluminescence from the reaction of (I) with alkaline peroxide (—), and the absorption (---) and the fluorescence spectrum (.....) of (VI) and of the product of the chemiluminescent reaction from (I).

The intensity of the chemiluminescence is greater, and its lifetime is longer, in alcohols than in aqueous solution, following the order, methanol > ethanol > propan-2-ol > *t*-butyl alcohol \sim water, but the most intense emission is produced by the addition of alkaline peroxide to aqueous solutions of the salts (I)—(IV) to give a final pH greater

than 11. Nonhydroxylic solvents, such as acetonitrile or dimethyl sulphoxide, give a chemiluminescence intensity similar to that observed in peroxide-free aqueous solution. These solvent effects are similar to those observed in the chemiluminescent reactions of lucigenin and related acridinium derivatives.²



When a degassed solution of (I) in methanol or acetonitrile and aqueous sodium hydroxide are mixed *in vacuo* no chemiluminescence is observed, and a red intermediate is formed which is stable in the absence of oxygen. On the admission of air to the system, strong chemiluminescence appears at the surface and subsequently in the body of the solution, and simultaneously the red colour disappears progressively downwards from the surface of the solution. On treating an aqueous solution of the 2,2'-bipyridyl analogue³ of (I) with base an air-stable red substance is produced with absorption maxima at 20,800 and 28,600 cm^{-1} , but no chemiluminescence is observed. The probable structure of the red intermediate derived from (I) is the bisanhydro-base (V) or the corresponding

monoprotonated conjugate acid. The salts (II)—(IV) are sterically more hindered and are conformationally more labile than (I) and the conjugation between the isoquinoline residues in (V) is greater than that in the analogous intermediates derived from (II)—(IV). Fluorescence efficiency is low in conformationally labile systems, and in nonconjugated dimers, and it is probable that chemiluminescence efficiency is governed, in the series considered, by similar factors.

The major product of the chemiluminescent

reaction of (I) is the 1-isoquinolone dimer (VI), as the product and a synthetic specimen of (VI) have the same absorption and emission spectra (Figure) and the same R_F -value (0.9) in a thin-layer chromatogram on silica gel developed with ethanol. The chemiluminescent spectrum of (I) has the same spectroscopic characteristics, ν_{\max} , 26,100 cm^{-1} and band half-width 4200 cm^{-1} as the fluorescence spectrum of (VI) (Figure).

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² F. McCapra, *Quart. Rev.*, 1966, 20, 485.

³ R. F. Homer and T. E. Tomlinson, *J. Chem. Soc.*, 1960, 2498.