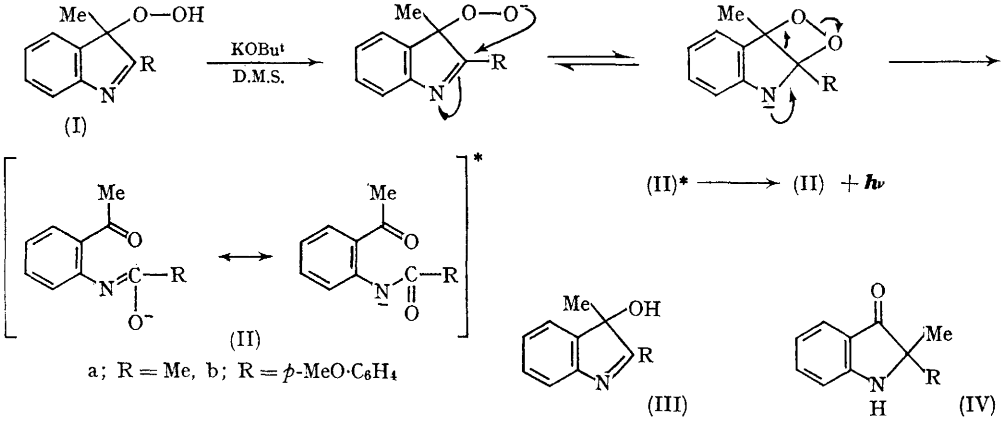
Chemiluminescence of Indolyl Peroxides

By FRANK MCCAPRA and Y. C. CHANG
(*University of British Columbia, Vancouver, Canada*)

INTEREST in the chemiluminescence of simple indoles[1,2] has recently been increased by reports[3,4] of the occurrence of the indole moiety in the luciferin of bioluminescent marine organisms. The mechanism of the chemiluminescence has remained obscure, although our earlier work[1] suggested the intermediacy of a 3-indolyl hydroperoxide. We now report evidence which establishes the salient features of the light-producing reaction involving these peroxides.

Using standard methods,[5] eleven variously substituted 3-indolyl hydroperoxides have been prepared, but a discussion of the influence of substitution is deferred to the full paper. Detailed investigation of two of the brightest peroxides (Ia; R = Me) and (Ib; R = p-MeO·C_6H_4·) gives the following results.



a; R = Me, b; R = p-MeO·C_6H_4

A beautiful green light is observed on treatment of a solution of either (Ia) or (Ib) (usually 10^{-4}M) in dimethyl sulphoxide (D.M.S.) with potassium t-butoxide also in D.M.S. (10^{-3}M). Stronger solutions (10^{-1}M) were easily visible in daylight. The only products (t.l.c.) isolated were shown to be (II), (III), and (IV). The last compound is slowly formed from (III) under the influence of base and is probably not a product of the light reaction.

The major product of the reaction is (II) (60—70% yield) and its fluorescence spectrum has a maximum at 518 mμ, superimposable upon the chemiluminescence spectrum of (Ia). Similarly, the chemiluminescence of (Ib) is identical to the fluorescence of (IIb), the maximum of both occurring at 495 mμ in this case. The ratio of the chemiluminescence intensities of (Ia): (Ib) is equal to the ratio of fluorescence intensities of the corresponding excited products (IIa) : (IIb) (about 10 : 1 in each case). The reaction is perfectly of first order with respect to peroxide (using an excess of base) over at least 80% of the reaction time and the total light intensity varies linearly with peroxide concentration, eliminating a mechanism involving the collision of two peroxide-derived molecules in the production of light. Thus a recent general proposal[6] does not apply in this case. It is interesting that the neutral amide formed by protonation of (II) is not visibly fluorescent, and both chemiluminescence and fluorescence are destroyed by small amounts of protic solvents. All other products of the reaction either do not fluoresce or else have maxima very different from that of the chemiluminescence.

Synthesis of the peroxide (Ib) using $^{18}O_2$ (16% enrichment) and treatment with base gave the amide related to (IIb), with total retention of ^{18}O in the amide carbonyl. We therefore feel that the mechanism shown (or a simple variant) reasonably explains the chemiluminescence of these peroxides, and by extension, the chemiluminescence of the parent indoles under the same conditions. It is related to a mechanism suggested for the chemiluminescence of imidazolyl peroxides,[7,8] and is compatible with our general theory[9] previously suggested for this type of chemiluminescent peroxide reaction.

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