Chemiluminescence of Indole Derivatives. II. On the Mechanism of the Chemiluminescence of 2, 3-Dimethylindole in the DMSO-KOH System*

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We studied1) the relative light intensities (RLI) of 42 indole derivatives in the following two systems:

(A) Sample-EtOH-KOH-H_2O_2-$K_3Fe(CN)_6$
(B) Sample-DMSO-KOH-Air

From our study, it was found that 2, 3-dimethyl-3-hydroperoxyindolenine (II),2) which was easily produced by the reaction of 2, 3-dimethylindole (I) with air in petroleum ether, emitted a strong light. Therefore, we used I and II for the study of the chemiluminescent reaction mechanism of indoles in the (B) system.

In order to get an accurate emission spectrum it is necessary to make the emission period as long and the light intensity as strong as possible. From our experiments it was found that the best way to do this is to add a solution of I or II in DMSO to the granular KOH.

It was found that I and II (both 10^{-1} mol/*l*) emit light in an oxygen stream, that in a hydrogen stream II emits light while I does not, and that I and II emit nearly the same total amount of light. Further, it was observed that the emission period of I is longer, while the maximum intensity is weaker, than the values of II. Therefore, it may be suggested that the oxidation of I to II by oxygen is the rate-controlling step in the chemiluminescent reaction of I.

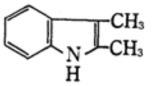
The maxima of the emission spectra of I and II (10^{-2} and 10^{-3} mol/*l*, respectively) were both 520 mμ. This coincidence suggests that the same emitting species are concerned in the chemiluminescent reaction of I and II. This was further supported by the following experiments.

By the addition of the DMSO solution of I or II to KOH, the UV absorption maxima of I (284 and 292 mμ) or that of II (260 mμ) shifted to 259, 267 and 325 mμ, values which were the same as those of *o*-acetamidoacetophenone (IV). Furthermore, the fluorescence spectra of I and II varied similarly with the time and both showed a maximum at 520 mμ, a value which completely coincided with that of IV.

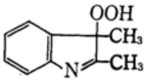
Therefore, it may be concluded that:

1) II is the intermediate of the chemiluminescent reaction of I. 2) The product of this chemiluminescent reaction is IV. 3) The emitting species of the chemiluminescent reactions of I and II are the same. The species may be the excited state of IV because the maximum of the Fl spectra of IV completely coincides with that of the emission spectra of I and II.

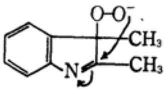
We propose the following mechanism for the chemiluminescent reaction of 2, 3-dimethylindole in the DMSO-KOH-O_2 system; Compound I is autoxidized to II, an intermediate of this reaction, this is followed by the decomposition with KOH, as is shown in III, to an excited state of IV, which then falls to the ground state with the emission of light.



I



II



III

The details will be published elsewhere.

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