Chemiluminescence of 2, 3, 4, 5-Tetraphenylpyrrole

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We have been studying[1] the mechanism of the chemiluminescence of 2, 4, 5-triphenylimidazole (lophine) and have already proposed a mechanism involving free radical and peroxide[2]. Recently an investigation of the electron spin resonance of the free radical 2, 3, 4, 5-tetraphenylpyrryl, a solution of which was prepared by oxidation of tetraphenylpyrrole, was reported[3].

Lophine and tetraphenylpyrrole resemble each other in several aspects. They are both nitrogen-containing, unsaturated, five-membered heterocyclic compounds in which each of the carbon atoms of the ring combines with a phenyl group; and they both produce a free

1) T. Hayashi and K. Maeda, This Bulletin, **33**, 566 (1960): T. Hayashi, K. Maeda, S. Shida and K. Nakada, *J. Chem. Phys*, **32**, 1568 (1960).

2) T. Hayashi, *Chemistry and Industry* (*Kagaku to Kogyo*), **14**, 225 (1960); T. Hayashi and K. Maeda, This Bulletin, **35**, 2057 (1962).

3) S. M. Blinder, M. L. Peller, N. W. Lord, L. L. Aamodt and N. S. Ivanchukov, *J. Chem. Phys.*, **36**, 540 (1962).

radical by oxidation, which reacts with molecular oxygen to produce a peroxide. Tetraphenylpyrrole was therefore expected to exhibit chemiluminescence on oxidation as lophine does. As expected, a solution of tetraphenylpyrrole (0.1 g.) in 20 cc. of 2 N ethanolic solution of potassium hydroxide produced a weak greenish blue luminescence[4] at about 60°C upon addition of 3% aqueous hydrogen peroxide solution followed by 2% aqueous potassium ferricyanide solution, or 2% aqueous potassium ferricyanide solution only, or 2% ethanolic solution of bromine. When dissolved oxygen in the solutions in the latter two cases was removed by a stream of nitrogen, no luminescence was shown, and when oxygen was passed into the reaction mixture, a luminescence appeared immediately. Therefore it seems probable that molecular oxygen is necessary for the luminescence of tetraphenylpyrrole.

By oxidation of the benzene solution of tetraphenylpyrrole containing 2 N ethanolic potassium hydroxide with 2% aqueous solution of potassium ferricyanide in nitrogen, a pink benzene solution was obtained containing the free radical 2, 3, 4, 5-tetraphenylpyrryl, with optical absorption maxima at 524 mμ and 563 mμ[3]. The benzene solution containing the free radical produced a weak greenish blue luminescence when 2 N ethanolic potassium hydroxide was added with a stream of oxygen at about 60°C. Thus it appears probable that the free radical tetraphenylpyrryl is the intermediate stage of the chemiluminescence process of tetraphenylpyrrole.

The pink solution of the free radical tetraphenylpyrryl in benzene reacted with molecular oxygen to turn yellow. The reaction was promoted markedly by irradiation with ultraviolet light. The yellow solution was evaporated under reduced pressure to leave a yellow solid residue which melted at about 70~80°C with evolution of gas, presumably oxygen, and proved positive in the starch test for iodine when treated with potassium iodide. Hence the yellow residue seemed sure to contain the peroxide. When 2 N ethanolic potassium hydroxide was added to the benzene solution of this yellow residue at about 60°C in the absence of oxygen, a weak greenish blue luminescence was produced. This fact shows that the peroxide of tetraphenylpyrryl produces a luminescence in ethanolic potassium hydroxide in the absence of oxygen.

Accordingly, the mechanism of the chemiluminescence of tetraphenylpyrrole appears probable that tetraphenylpyrrole in the first step produces the free radical tetraphenylpyrryl with oxidizing agent, and then the free radical produces the peroxide with molecular oxygen and the peroxide exhibits a luminescence without molecular oxygen. This free radical-peroxide mechanism is analogous to that of lophine[2,5]. It is considered that this mechanism would be general for luminescence, at least for that of nitrogen-containing unsaturated heterocyclic compounds requiring molecular oxygen, and would be involved in the mechanism of bioluminescence.

When the solution of the peroxide in ethanolic potassium hydroxide was heated at about 60°C in nitrogen atmosphere for several hours, ammonia, benzoic acid and 2, 3, 4, 4-tetraphenyl-5-oxo-2-pyrroline were detected. The mechanism of the luminescence of the peroxide has not yet been determined.

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4) The luminescence was far weaker than that of lophine. No luminescence of tetraphenylpyrrole was observed with molecular oxygen.

5) For the chemiluminescence of 3-amino-phthalhydrazide (luminol) and 10, 10'-dimethyl-9, 9'-biacridium dinitrate (lucigenin), speculative mechanisms involving free radical and peroxide have been proposed. (T. Bremer, *Bull. soc. chim. Belg.*, 62, 569 (1953); H. Eyring et al., "The Luminescence of Biological Systems", A. A. A. S. (1955), p. 75); B. Tamamushi and H. Akiyama, *Trans. Faraday Soc.*, 35, 491 (1939).