Mechanism of Chemiluminescence of 2, 4, 5-Triphenylimidazole

By Taro HAYASHI and Koko MAEDA

(Received October 12, 1962)

Radziszewsky[1] found that lophine exhibits a whitish greenish blue luminescence in an ethanolic solution of potassium hydroxide with molecular oxygen or several oxidizing agents. We have been studying the mechanism of the chemiluminescence of 2, 4, 5-triphenylimidazole (lophine) for several years[2,3], and have found that substitution of its imino-hydrogen[4] prevented luminescence. This fact suggests that the anion produced by the dissociation of the imino-hydrogen is the active agent of chemiluminescence.

The chemiluminescence of lophine with an ethanolic solution of bromine or an aqueous solution of potassium ferricyanide was inhibited by the removal of dissolved oxygen in the solutions and the luminescence was restored immediately upon passing oxygen into the reaction mixture. This indicates that molecular oxygen is necessary for chemiluminescence. When an ethanolic solution of bromine

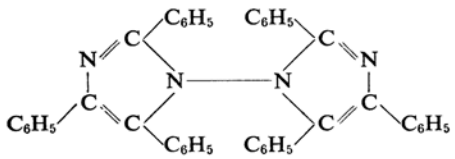
1) B. Radziszewsky (*Ber.*, **10**, 70 (1877)) found that benzoic acid and ammonia were produced with the chemiluminescence of lophine.

2) T. Hayashi and K. Maeda, 1st Joint Meeting of the Societies of Chemistry in Japan, Tokyo, November, 1957; 11th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1958; T. Hayashi, K. Maeda and H. Ojima, Symosium on Mechanism of Organic Reactions, Chem. Soc. Japan, Tokyo, 1959; Shirahama, 1960; Sendai, 1961.

3) The spectrum of luminescence extending over the visible region with a maximum at about 540 mμ will be reported soon.

4) *N*-Methyllophine (m. p. 149~150°C), *N*-ethyllophine (m. p. 125~126°C) and *N*-*n*-butyllophine (m. p. 122~123°C were investigated.

was mixed with a solution of lophine in ethanolic potassium hydroxide, a reddish violet color was produced and soon faded. When an aqueous solution of potassium ferricyanide was mixed with the solution of lophine, a grayish white precipitate was produced[5]. The precipitate was recrystallized from benzene at a temperature below room temperature to give fine pale yellow prisms of $C_{42}H_{30}N_4$, m. p. 199~201°C (decomp.)[5]. Its benzene solution turned reddish violet with ultraviolet irradiation or heating. Electron spin resonance[6], formation of yellow nitroso compound, m. p. 110~113°C (decomp.)[5], molecular weight determination and spectroscopic investigation revealed that the color was due to the free radical 2, 4, 5-triphenylimidazyl $C_{21}H_{15}N_2$ produced by the dissociation of the N–N bond in the dimeric compound $C_{42}H_{30}N_4$[7] (I). The dissociation was increased with ultraviolet radiation or heating.



(I)

These findings suggest that the free radical is the essential intermediate in the process of chemiluminescence. The reddish violet benzene solution showed a luminescence, similar to that of lophine, with the addition of hot ethanolic potassium hydroxide, yielding benzoic acid and ammonia. When the solutions of lophine and potassium ferricyanide or bromine were mixed in the absence of oxygen, no luminescence was observed, although the reddish violet color did appear; and when oxygen was passed into the solution, a luminescence was immediately produced. This fact shows that molecular oxygen is necessary for the luminescence of the free radical. When the solution of the dimeric compound in carbon disulfide was exposed to air in direct sunlight, the reddish violet color, first produced, gradually faded to yellow, giving a yellow solid residue by evaporation of the solvent at room temperature. It melted at about 110~120°C with evolution of gas, presumably oxygen, and it oxidized potassium iodide in acetic acid to iodine. Thus it seems probable that the yellow solid contains the peroxide produced from the free radical and molecular oxygen[8]. The benzene solution of the yellow solid exhibited luminescence, similar to that of lophine, with hot ethanolic potassium hydroxide in the absence of oxygen.

From the facts mentioned above, the probable mechanism of the chemiluminescence of lophine is suggested[9] to be as follows: the anion of lophine formed in ethanolic potassium hydroxide yields the free radical 2, 4, 5-triphenylimidazyl by oxidation, from which the peroxide is produced with molecular oxygen and finally the peroxide emits light to yield benzoic acid and ammonia[10].

Department of Chemistry
Faculty of Science
Ochanomizu University
Bunkyo-ku, Tokyo

5) T. Hayashi and K. Maeda, This Bulletin, 33, 566 (1960). This compound exhibits photochromism in solid and in solutions and also thermochromism in solutions.

6) T. Hayashi, K. Maeda, S. Shida and K. Nakada, *J. Chem. Phys.*, 32, 1568 (1960).

7) The investigation of the constitution by spectroscopy and molecular weight determination will be reported soon.

8) Eosine, exhibited a weak photosensitizing effect on the photo-oxidation and zinc oxide suspended in the solution, also exhibited a weak catalytic action on the photo-oxidation.

9) T. Hayashi, *Chemistry and Industry (Kagaku to Kogyo)*, 14, 225 (1960).

10) The mechanism of the luminescence of the peroxide has not yet been ascertained.