A New Phenomenon of Storage Light Energy by Solution of Photochromatic 1,1'-Bi(2,4,5-triphenylimidazyl) at Low Temperatures

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(Received May 30, 1963)

In a study of the mechanism of the chemiluminescence of 2,4,5-triphenylimidazole (lophine), 1,1'-bi(2,4,5-triphenylimidazyl) (I) (m. p. 199∼201°C), was obtained as fine, pale yellow prisms. It exhibits both photochromism and thermochromism in a solution and in a solid state[1]. These phenomena were due to the reversible formation of a reddish purple free radical, 2,4,5-triphenylimidazyl-(II), by the dissociation of an N-N bond of compound I with irradiation or heating[2]. This communication deals with a new phenomenon which was found in solutions of this compound and its photochromatic substituted derivatives at low temperatures.

A pale yellow 10^{-3} M benzene solution of 1,1'-bi(2,4,5-triphenylimidazyl) (I) which had been prepared in the dark and sealed in a glass tube after removal of oxygen, was frozen at about −20°C in the dark to a nearly white solid, which soon became a pale yellow solution when kept at room temperature in the dark. The frozen solution did not acquire a reddish-purple color on being irradiated for several minutes with sunlight at −20°C. When this irradiated white solid was, immediately after irradiation, immersed in water at about 15°C in the dark, a reddish-purple color appeared as soon as the solid began to liquefy. In about 15 min. the irradiated frozen solid liquefied to be a deep reddish-purple solution, the color of which was nearly as deep as that acquired by an original pale yellow solution with irradiation at room temperature; it then gradually faded to the original pale yellow when kept in the dark at room temperature. A similar phenomenon was observed when the frozen solution was irradiated at −70°C. The reddish-purple color was attributed to the free radicals (II) produced by the splitting of the N-N bond of compound I, because the solution gave a strong electron spin resonance signal (g=2.003) and the free radical which gave the ESR signal was identified as 2,4,5-triphenylimidazyl (II) by a study of the absorption spectrum. It has, therefore, been concluded that light energy is stored in the frozen solution, to be used later for the splitting of the N-N bond. This phenomenon is a new effect of storage light energy by a frozen solution of the photochromatic compound. It was observed irrespective of the concentration of the solution and of the kind of solvent; it was found, for example, in a 10^{-2} or 10^{-4} M solution in benzene, cyclohexane or carbon tetrachloride.

A pale yellow 10^{-3} M toluene solution of compound I, which, unlike a benzene solution, did not freeze at −20°C, immediately acquired

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 and K. Maeda, This Bulletin, 35, 2057 (1962).

a deep reddish-purple color when irradiated at about -20°C. From this fact the phenomenon of the storage of light energy seems to be characteristic of a frozen solution. However, the toluene solution did not acquire a reddish-purple color with irradiation at about -70°C. But it did begin to acquire a faint reddish-purple color when kept in a dark room at a temperature near -30°C, the color becoming deeper with a further rise in the temperature. Therefore, the storage of light energy can occur in both a frozen solution and a fluid solution. This phenomenon is primarily to be attributed to the photochromatic molecule in a solution cooled at a low temperature. A similar phenomenon was observed in a solution in *n*-heptane. The freezing of the solution seems to facilitate the storage at a higher temperature to some extent, because a frozen solution in benzene or cyclohexane did not acquire a reddish-purple color upon irradiation at about -20°C but stored light energy to split the N–N bond when the frozen solution liquefied in the dark.

A frozen toluene solution of compound I, which had been cooled at -195°C with liquid nitrogen in the dark, immediately acquired a faint reddish-purple color upon being irradiated at about -195°C. When the temperature rose to about -70°C in the dark or under irradiation, this solid lost its color and became a nearly colorless solution which began to acquire a reddish-purple color near about -30°C in the dark. A similar phenomenon was also observed near -195°C in a frozen solution in benzene, *n*-heptane, cyclohexane or EPA which trapped free radicals formed upon irradiation.

The duration of the storage of light energy by a frozen solution of compound I in benzene, irradiated at -20°C, was measured at -70°C and 0°C. It was found that light energy absorbed could be stored for 100 hr. or more at -70°C, whereas it was completely dissipated in about 6 hr. at 0°C. A fluid toluene solution was also found to be able to store light energy at -70°C for more than 100 hr.

A phenomenon of the storage of light energy, similar to that mentioned above, was also observed in solutions of substituted derivatives of compound I, such as 2-*p*-methylphenyl, 2-*p*-methoxylphenyl, 2-*p*-chlorophenyl, 2, 4, 5-tri-*p*-methylphenyl and 2, 4, 5-tri-*p*-chlorophenyl derivatives which were prepared by the method similar to that of compound I.

From the foregoing facts, the following is considered to be the mechanism of the storage of light energy at a low temperature. On irradiation in solution at a low temperature, 1,1′-bi(2, 4, 5-triphenylimidazyl) must be excited to an unusual metastable state, which is favorably affected by a low, ambient temperature or, especially, by the freezing of the solution. This state may be related to some peculiar state of the N–N bond or to a particular spatial disposition of the two imidazole rings which is related to the temperature. The light energy thus stored in the excited molecule, however, is a little insufficient for the splitting of the N–N bond; therefore, for the effective splitting of the bond, some thermal energy may have to be provided by an elevation of the temperature. The mechanism of the phenomenon observed at -195°C, which, considering from the preliminary investigation of the absorption spectrum, seems to be related to the spatial disposition of the imidazole rings and to that of the phenyl nuclei in the frozen solution, is unknown to us at the present time.

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