The Mechanism of the Photochromism and Thermochromism of 2, 2′, 4, 4′, 5, 5′-Hexaphenyl-1, 1′-biimidazolyl in a Solid State

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Photochromism and thermochromism are exhibited by 2, 2′, 4, 4′, 5, 5′-hexaphenyl-1, 1′-biimidazolyl in the solid state as well as in the solution. The pale yellow substance becomes reddish purple upon irradiation or when heated in a solid state[1], although the color is paler than that in the solution. The mechanism of these phenomena in the solution was previously reported[2] to be the reversible dissociation to the free radical, 2, 4, 5-triphenylimidazolyl.

An electron-spin resonance of hexaphenylbiimidazolyl which became pale reddish purple upon irradiation in a solid state with sunlight at 15°C for 10 min. was observed in a solid state at 15.0°C, the first derivative of a single absorption line where the g value is 2.002 and the line width (from peak to peak) is about 7.8 gauss being measured.[3] Since hexaphenylbiimidazolyl which had been kept in the dark after recrystallization exhibited no ESR signal, this ESR measurement shows that the mechanism of the photochromism of hexaphenylbiimidazolyl in a solid state involves a free radical, probably 2, 4, 5-triphenyl-imidazolyl, as in a solution.

The absorption spectrum of hexaphenylbiimidazolyl in a solid state was measured in the visible region immediately after irradiation with a mercury vapor lamp at 15°C for 10 min. with a Hitachi recording spectrophotometer, the absorption maximum (554 mμ) obtained by the reflection spectroscopic method[4] and the absorption maximum (562 mμ) obtained by the opal glass transmission method[5] and the potassium bromide disk method[6] being shown respectively. The absorption maximum (554 mμ) coincides with the one shown by 2, 4, 5-triphenylimidazolyl in an irradiated benzene solution, whereas the absorption maximum measured with the transmission method, the shift may be attributed to a weak absorption, extending from the ultraviolet region to 620 mμ, by hexaphenyl-biimidazolyl, which exists (562 mμ) shows a red shift of 8 mμ. The species exhibiting the photochromic color in a solid state is most probably 2, 4, 5-triphenylimidazolyl, which shows an absorption maximum of 554 mμ in benzene. The mechanism of the photochromism of hexaphenyl-biimidazolyl in a solid state can, therefore, be concluded to be the radical dissociation of its N-N bond to triphenylimidazolyl radicals, similar to the mechanism in a solution.

Considering the thermochromic color in a solid state to be similar to the photochromic color, the exhibition of an ESR signal in the thermochromism in a solid state and the mechanism of the thermochromism in a solution,[2] the same mechanism can be applied to the thermochromism in a solid state.

The photochromic color in a solid state hardly faded in the dark at room temperature, whereas it gradually reverted to its original pale yellow color at about 40°C at which temperature the thermochromism is not observed. The decay rate of the intensity of the first derivative ESR spectrum, which is the rate of the recombination of the free radical, 2, 4, 5-triphenylimidazolyl, was measured in the dark at 46.0 and 62.5°C. Unlike the rate in a benzene solution,[2] the rate in a solid state did not obey the rate expression of the second-order reaction.

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1) The photochromic color appears upon irradiation with sunlight or with a mercury lamp at room temperature, whereas the thermochromic color begins to appear at about 180°C, and the sample becomes intensely reddish purple when fused at 198—200°C. The rate of the disappearance of the color is very slow at room temperature.

2) T. Hayashi, K. Maeda and M. Morinaga, This Bulletin, 37, 1563 (1964); T. Hayashi, K. Maeda and M. Takeuchi, ibid., 37, 1717 (1964).

3) Its spin concentration was about 8×10^{17} spin/g.

4) The mixture of hexaphenyl-biimidazolyl, (0.0149 g.) and magnesium oxide (1 g.) was used.

5) Hexaphenyl-biimidazolyl (1.5 mg.) was used.

6) A mixture of the sample (1.3 mg.) and potassium bromide (200 mg.) was used.