SHORT COMMUNICATION

*The Mechanism of the Photochromism and Thermochromism of 2, 2', 4, 4', 5, 5'-Hexaphenyl-1, 1'-biimidazolyl**

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We previously found[1,2] that 2, 2', 4, 4', 5, 5'-hexaphenyl-1, 1'-biimidazolyl (I) ($C_{42}H_{30}N_4$, fine pale yellow prisms, m. p. 199~201°C (decomp.)) and its various substitution compounds exhibited photochromism and thermochromism in both a solution and a solid state. A pale yellow benzene solution of I showed an absorption maximum at 280 mμ (ε=28500) at 15°C, while the solution which turned reddish purple upon irradiation with sunlight at 15°C or upon heating on a water bath in the dark showed new absorption maxima at 347 mμ (ε=1100), 520 mμ (shoulder) and 554 mμ (ε=190) with a decrease in the absorbance of 280 mμ and was found to exhibit an electron spin resonance (g value: 2.003). When the solution irradiated was immediately placed in a dark room, the absorbance of 347 mμ and 554 mμ gradually decreased with the recovery of the absorbance of 280 mμ, an isosbestic point being shown at 309 mμ, and a decrease in the electron spin resonance was also found.

In a benzene solution of I (C=1.49×10^{-5} mol./l.) the absorbance of 347 mμ was measured in the dark at 19.0, 36.1, 45.5 and 50.5°C in order to measure the absorbance due only to thermochromism, A_1. In the same solution when irradiated for 3 min. with a mercury vapor lamp at the temperatures mentioned above, a decrease in the absorbance of 347 mμ, A_2, due both to photochromism and thermochromism with time, was measured beginning immediately after irradiation at the temperatures mentioned above. When the difference between A_2 and A_1 of the same temperature, which was the decrease in the absorbance due

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1) T. Hayashi and K. Maeda, This Bulletin, 33, 566 (1960).

2) T. Hayashi, K. Maeda, S. Shida and K. Nakada, *J. Chem. Phys.*, 32, 1568 (1960); T. Hayashi and K. Maeda, This Bulletin, 35, 2057 (1962).

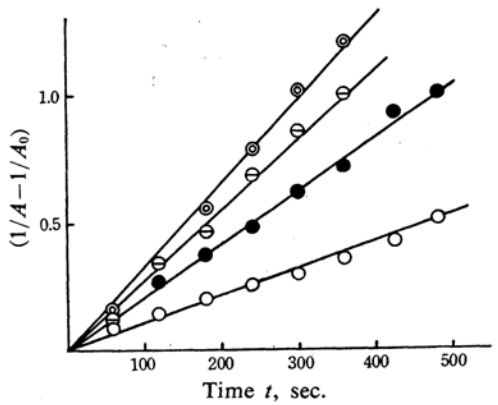
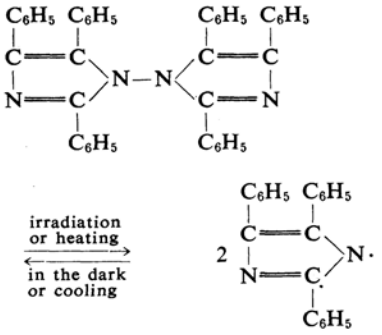


Fig. 1. The rate of the decrease of the absorbance A of 347 mμ in a solution ($C=1.49\times10^{-5}$ mol./l.) of hexaphenylbiimidazolyl.
A_0 : A at $t=0$
—◎— 50.5°C —⊖— 45.5°C
—●— 36.1°C —○— 19.0°C

only to photochromism, A, was calculated, the reciprocal of A was found to decrease linearly with time, as is shown in Fig. 1. The linearity shows that the reaction which causes absorbance A to decrease obeys the rate law for a second-order reaction, since the absorbance of 347 mμ was confirmed to obey Beer's law in a benzene solution of a concentration lower than about 10^{-5} mol./l. at 15°C. This finding suggests that this reaction is a recombination of 2, 4, 5-triphenylimidazolyl radicals formed by the homolytic dissociation of I and that the mechanisms of the photochromism and thermochromism of hexaphenyl-biimidazolyl (I) may be represented by the following equation:



This mechanism was supported by the determination of the molecular weight in a benzene solution ($C=0.0124$ mol./l.) with a macro-cryoscopic method carried out in a dark room, which showed a decrease in molecular weight from 600 to 440 with irradiation. From the rate constants which were obtained from the measurements shown in Fig. 1, the activation energy for the recombination of 2, 4, 5-triphenylimidazolyl radicals was determined to be 7.3 kcal./mol. The equilibrium constants for the thermal homolytic dissociation of I were estimated to be approximately 3.1×10^{-4} (49.0°C), 4.7×10^{-4} (53.8°C) and 1.1×10^{-3} (60.4°C) from the absorbance of 554 mμ due to thermochromism by the mass action law and Beer's law and from the equilibrium constants, ΔH for this reaction was estimated to be about 23 kcal./mol.

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