# *A Kinetic Study of the Photochromism of 2,2′,4,4′,5,5′-Hexaphenyl-1,1′-biimidazolyl with Electron Spin Resonance*

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The mechanism the of photochromism[1] of 2, 2′, 4, 4′, 5, 5′- hexaphenyl - 1, 1′ - biimidazolyl, m. p. 199∼201°C, in a solution has been studied with electron spin resonance. In a benzene solution ($C=1.48\times10^{-4}$ mol./l.) which turned from pale yellow to reddish purple when irradiated with a mercury vapor lamp for 3 min., the ESR was measured.[2] The line width (peak to peak) of the ESR signal (*w* in Fig. 1) was 9.1 gauss, and its *g* value was measured as 2.003. The intensity of the ESR signal, *h* in Fig. 1, gradually decreased with time in the dark, while its line width scarcely changed in 20 min. When the recording of the first signal had been almost finished, the sweep direction of the magnetic field was reversed and an ESR signal was immediately recorded. When this was followed by a similar procedure, the chart shown in Fig. 1 was obtained. The signal intensity, *h*, and the time, *t*, at which a signal curve intersected the base line was measured for every ESR signal on the chart. A graph of the reciprocal of *h* versus the time, *t*, gave a straight line, as is shown in Fig. 2.

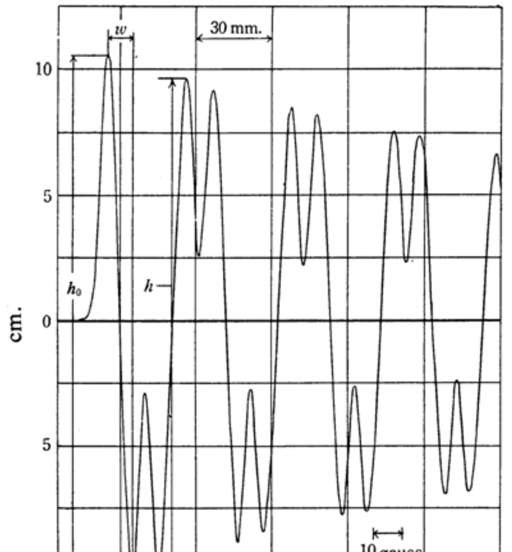

Fig. 1. Intensity change of an ESR signal of a benzene solution of hexaphenyl-biimidazolyl ($C=1.48\times10^{-4}$ mol./l.) with time in the dark at 23°C.
Gain, −34 db; modulation width, 3 gauss

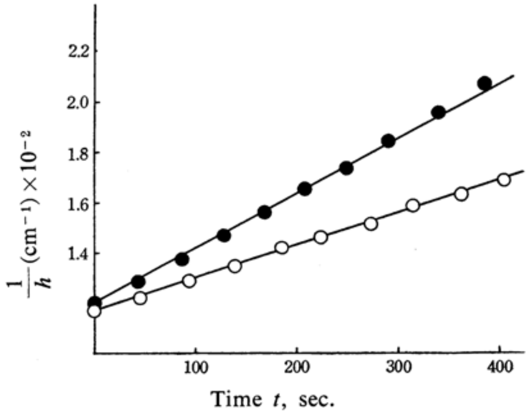

Fig. 2. A graph of $1/h$ vs. time *t*.
*h*: the intensity (cm.) of an ESR signal in Fig. 1.

-●- hexaphenyl-biimidazolyl
-○- hexa-*p*-tolyl-biimidazolyl

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[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); T. Hayashi and K. Maeda, This Bulletin, 35, 2057 (1962); T. Hayashi, K. Maeda and K. Morinaga, ibid., in press.

[2] An electron spin resonance instrument of the Japan Electron Optics Laboratory Co., type JES-3BX (standard frequency 9400 Mc; modulation frequency 100 kc).

The linearity shows that the reaction which diminishes an ESR signal is a second-order radical reaction, since the signal intensity, $h$, is assumed to be approximately proportional to the concentration of free radicals, provided that the line width does not change, as in the present case. The radical reaction is considered to be a recombination of triphenylimidazolyl radicals. This conclusion agrees with the mechanism of photochromism, which has been confirmed1) to be the homolytic dissociation of an N–N bond of hexaphenyl-biimidazolyl to triphenyl-imidazolyl.

A similar kinetic study of the photochromism of 2, 2′, 4, 4′, 5, 5′-hexa-*p*-tolyl-1, 1′-biimidazolyl, m. p. 194∼195°C, with an ESR signal gave a similar conclusion, showing that the substitution of methyl groups diminished the rate of the recombination of free radicals.

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