Optical and ESR Studies on Triphenylimidazolyl Radicals Produced by Photolysis and Radiolysis at Low Temperature*[1]

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In a previous paper[1)] we reported that UV-illumination of the photochromic dimer of triphenylimidazolyl (photo-dimer, abbreviated as R_2) in EPA at $-196°C$ induced a coloration which was attributed to the formation of a radical cation of the dimer.[1)] We wish to report here that the coloration should be associated with the formation of triphenylimidazolyl radical R·, as in the case of photolysis of the dimer at room temperature.[2)]

When a colorless solution of photo-dimer in methyltetrahydrofuran (MTHF) in a thin quartz cell was exposed at $-196°C$ to UV-light (λ=240—400 mμ), an absorption with $\lambda_{\max}$ 350, 556 mμ appeared which was almost the same as that of R· in MTHF at room temperature. The ESR spectrum of the solution at $-196°C$ showed a broad doublet which is unambiguously attributable to the fine structure due to the close-lying two radicals. From these observations it is concluded that photo-dimer in MTHF at $-196°C$ dissociates homolytically upon UV-illumination. When the same solution was radiolyzed at $-196°C$ with γ-rays from a ^{60}Co source, an absorption spectrum very similar to that of the photolyzed solution appeared ($\lambda_{\max}$ 347, 552 mμ) indicating the formation of R·. The ESR spectrum of the radiolyzed solution, however, showed no sign of the doublet due to the radical pair but a sharp singlet of $\Delta H_{\mathrm{msl}}=8.1$ gauss. The line width is close to that of the monomeric R· in solutions photolyzed at room temperature. In the radiolysis of the rigid solution, R· is apparently formed not as a geminate radical pair but as a single isolated radical by the reaction $R_2+e^- \rightarrow R\cdot + R^-$. The reaction is consistent with the ESR result as well as several other observations.

When both photolyzed and radiolyzed solutions at $-196°C$ were carefully warmed, a subtle color change was noticed just before the solution thawed. The warmed solution, when quickly dipped again in liquid nitrogen, exhibited another spectrum similar to the original, but with a significant red shift ($\lambda_{\max}$ 354, 566 mμ). In addition to the red shift the absorption bands became narrower and the band structure was more manifested. It is assumed that the newly appearing spectrum is associated with triphenylimidazolyl radical whose phenyl groups are more or less coplanar with the plane of the imidazole ring. The spectrum reported previously as the cation radical of R_2 might have been the spectrum of this conformational isomer of the radical.

We obtained quite analogous results in the studies on tetraphenylpyrryl radical produced by oxidation of tetraphenylpyrrole.

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*[1] Presented at the Symposium on Photochemistry of the Chemical Society of Japan (T. Shida, K. Maeda and T. Hayashi; Oct., 1968, Sendai).

1) T. Hayashi and K. Maeda, This Bulletin, **40**, 2990 (1967).

2) T. Hayashi, K. Maeda and K. Morinaga, *ibid.*, **37**, 1563 (1964).