Magnetic Field Effect on Photochromism. Recombination of 2,3,4,5-Tetraphenylpyrrolyl Radicals

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Photochromism of the dimer of 2,3,4,5-tetraphenylpyrrolyl radical consists of coloration by photochemical scission and decoloration by thermal recombination of radicals. Application of external magnetic field gave a pronounced retarding effect on the second-order recombination rate constant of escaped radicals.

Photochromic compounds continue to attract a great deal of current attention in view of their high potentiality as optical information storage materials. Among many types of photochromic compounds, the dimer of 2,3,4,5-tetraphenylpyrrolyl radical (TPPR) investigated by Maeda et al.[1] is peculiar in that its coloration/decoloration is the result of photochemical scission into free radicals and their recombination by thermal energy. The coloring reaction can be controlled by irradiation intensity. However, the thermal back reaction is difficult to control. Since recombination of escaped radicals should involve singlet-triplet intersystem crossing (ISC) in the course of reaction, we have a chance to control the ISC process and, in turn, decoloration reaction by application of external magnetic field. Magnetic field effect on chemical reactions has been the target of intensive research.[2,3] However, most of these works are on the short-time behavior before escaped radicals are formed, or on the relative yield of "cage" (geminal)/escaped radical recombination products, to the best of our knowledge. Real-time investigation on the time course of recombination of escaped radicals has been scarcely reported, except for the early trial of Sato et al.[4] on the dimer of 2,4,5-triphenylimidazolyl radical in a polymer medium and recent report of Sakaguchi and Hayashi[5] on short-lived (<4 μs) escaped radicals from 10-methylphenothiazine/tetrafluoro-1,4-dicyanobenzene electron-transfer pair in 2-propanol. In the latter case observed magnetic field effect saturated below ca. 0.1 T (read from figures) and was considered to involve the hyperfine coupling mechanism. In this Letter the magnetic field effect on TPPR in benzene solution is reported. This system is in stark contrast to the Sakaguchi and Hayashi's case: (1) the radical is remarkably long-lived (hundreds of minutes) in a fluid solution, probably due to its steric crowdedness, and (2) magnetic field effect does not saturate up to 0.5 T.

Two dimers among six of TPPR are known to be photochromic.[1] The photo-dimer (PD) was prepared by Kuhn's oxidation procedure[6] of 2,3,4,5-tetraphenyl-1*H*-pyrrole (TPP) which was synthesized after Davidson.[7] Because of the air-sensitive nature of PD, its preparation was carried out under nitrogen atmosphere in the dark. Purity of TPP and PD thus prepared was checked by ^{1}H- and ^{13}C-NMR and FTIR.

UV irradiation of degassed benzene solution of PD (3.75×10^{-4} M) was carried out by an Ushio USH-500 high-pressure mercury lamp. It gave violet colored TPPR with an absorption maximum at 563 nm. The solution in a 1cm × 1cm quartz cell was set in a temperature-controlled water jacket (30±0.2 °C) located between poles of a Tokin SEE-9G electromagnet. Diameter of magnetic poles was 60 mm. Distance between the poles was 48 mm. The electromagnet was cooled by running water. Magnetic field strength was measured by an F.W. Bell model 4048 gauss meter. Residual magnetic field was cancelled by the use of a home-made Helmholtz coil. UV irradiation was made for a total of 180 s, with intermittent (every 15 s) interchange of irradiated surface of the quartz cell and shaking of the solution to attain coloration as homogeneous as possible. Then the time evolution of absorbance at 563 nm was monitored using a tungsten lamp (Noma 10V, 4A) with a cut-off filter (cutting off $\lambda<520$ nm) as a probe light and a monochromator (American ISA)/photomultipher (Hamamatsu 1P28). The intensity of the lamp was monitored simultaneously. Two outputs were fed to a split-chart recorder.

A typical result is shown in Figure 1, in which the reciprocal of absorbance is plotted against time after UV irradiation is

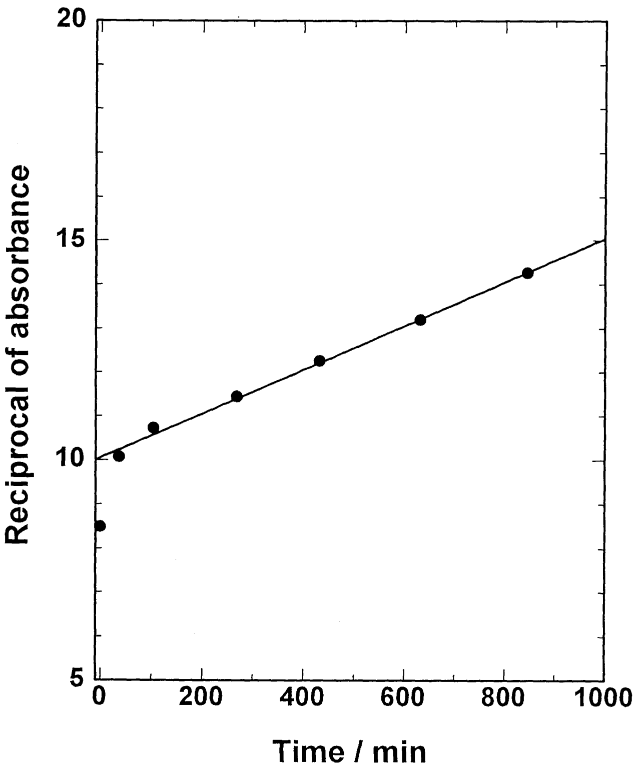

Figure 1. Reciprocal of absorbance vs. time. The slope of straight line gives the relative second-order rate constant (k_2/ε).

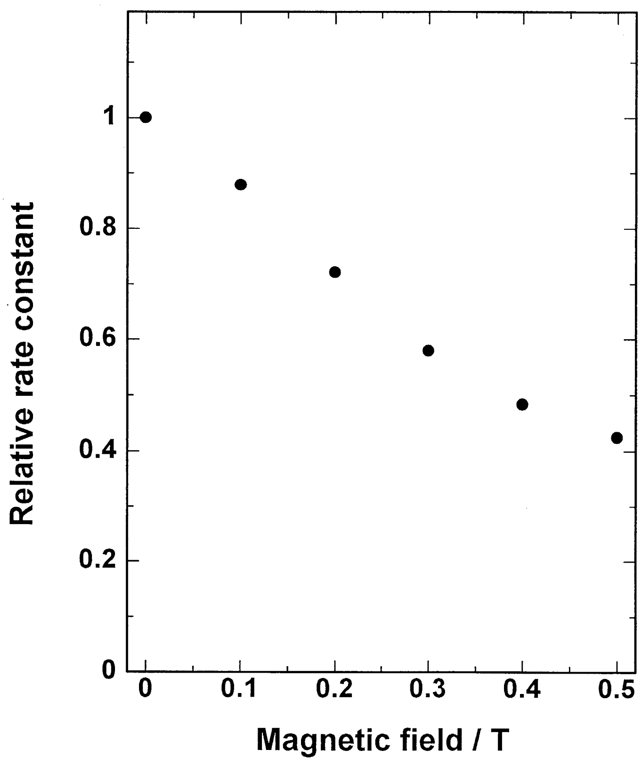

Figure 2. Dependence of relative second-order rate constant (k_2/ε) on applied magnetic field.

ceased. Apparently the decay followed the second-order kinetics, clearly indicating recombination of the random encounter radical pair (RERP) from escaped TPPRs, except for the rapid absorption decay near t=0. The slope of the straight line in the figure gives k_2/ε, where k_2 is the second-order rate constant and ε is the (unknown) extinction coefficient of the radical at 563 nm. Plot of k_2/ε against magnetic field strength is given in Figure 2. The rate constant decreases significantly with magnetic field strength (under the plausible assumption that ε is independent of magnetic field), down to about 40% of the field-free value at 0.5 T.

Although escaped radicals must come across frequently by diffusion, outspread phenyl groups prevent for them to approach close enough to form an RERP in most of the cases. Repeated encounters lead to the formation of an RERP with a very limited probability. Rotational diffusion may play some role in the formation of an RERP. Once an RERP is formed, however, the succeeding process can proceed rather quickly. Singlet: triplet ratio of the RERP is statistically 1:3 on their formation. ISC increases the amount of singlet pair at the expense of the triplet pair. The singlet pair either recombines or again separates into escaped radicals while the triplet pair only separates. External magnetic field impedes ISC and, in turn, recombination of radicals. No staturation of the magnetic field effect is discerned within the used field strength. In view of this finding, the relaxation mechanism[2] provides the most plausible explanation of the observed effect.

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