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Submicrosecond Time-Resolved ESR Study on Photodissociation of 2,2'-Azobis[isobutyronitrile]

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A transient signal of the 2-cyano-2-propyl radical was detected in the laser photolysis of the toluene solution of 2,2'-azobis[isobutyronitrile]. The esr spectrum was of an absorption-emission pattern which is characteristic of CIDEP generated in a geminate radical-pair. A dissociation mechanism was deduced on the basis of experimental results.

A popular initiator, 2,2'-azobis[isobutyronitrile], RN:NR for radical polymerizations and radical reactions has been known to generate a pair of the 2-cyano-2-propyl radicals and a nitrogen molecule by pyrolysis$^{1)}$ or photolysis.$^{2)}$ The esr of 2-cyano-2-propyl radical $(CH_3)_2(CN)C\cdot$, R• has been observed in the steady-state photolysis of the flowing solution of RN:NR.$^{3)}$ In the photogeneration of a short-lived free radical an enhanced esr absorption or emission is frequently observed due to the chemically induced dynamic electron spin polarization (CIDEP).$^{4)}$ The spectral pattern and time profile of esr are very characteristic of the mechanisms for the generation of CIDEP.$^{5)}$ In this letter, time-resolved spectra of CIDEP for the photogenerated R• radical from RN:NR are reported, and the mechanisms of photolysis are discussed on the basis of the analysis of esr spectra.

The toluene solution of 0.24 M(M=mol dm^{-3}) RN:NR was deoxygenized by bubbling of nitrogen (99.99%) and was flowed through a flat quartz cell of internal path length 2.0 mm. The cell was placed in a cylindrical esr cavity of TE_{011} mode with a light-irradiation hole of 7 mm diameter (Tokyo Denki-Seiki Co. Ltd.). The light source was a nitrogen-gas laser of ca. 5 mJ per pulse with a width of ca. 5 ns at a repetition rate of 7.5 Hz (NDC Co. Ltd.). The light extinction coefficient ε of RN:NR in toluene solution was ca. 20 $M^{-1}cm^{-1}$ at the wavelength of 337.1 nm. The esr measurement was made using a home made X-band esr spectrometer equipped with an FET microwave-amplifier of 25 dB gain and a preamplifier of 100 MHz bandwidth (NF Electronic Instruments, BX-31). The overall time resolution was estimated to be ca. 35 ns by separating the dual microwave pulses of various intervals. The further details of esr spectroscopy[6)] and the flow system[7)] were the same as reported before.

The flowing solution showed the esr spectrum of Fig. 1a at the delay time of 200 ns after laser illumination. The low-field side of the spectrum is absorptive and high-field side is emissive. And this A/E pattern was well reproduced by the spectrum simulation (Fig. 1b) assuming RPM by S-T_0 mixing with singlet precursor. In this simulation, the hyperfine coupling constants of 2.1 mT and 0.34 mT were used for six equivalent hydrogen nuclei and a nitrogen nucleus, respectively, in the R• radical.[3)] The linewidth of the esr spectrum was determined to be 0.17 mT by spectrum simulation, and this is larger than the linewidth of ≈ 0.06 mT due to the uncertainty principle in a system with the life time of 10^{-7} s.

In the spin polarized system, however, the apparent linewidth is varying with time and at a later stage of the polarization the line becomes much narrower than that of the early stage.[8)] The central part of the spectrum changed with the delay time as shown in Fig. 2. At 300 ns after laser pulse an A/E pattern became clear. The high-field peak, at 600 ns, showed a complex lineshape, where the center of the peak remained emissive and the robes of the peak turned into absorptive. It became more clear at 700 ns, but whole absorptive at 1.0 μs.

The A/E pattern of Fig. 1a for the R• radical leads to a conclusion that the precursor of the spin polarized radical is a geminate pair of the singlet state[9)] and the contribution of the triplet mechanism (TM) which causes either of whole emissive or absorptive pattern is discarded. The change in the spectra of Fig. 2 with time demonstrates the rapid decay of the A/E spectrum (from b to d of Fig. 2) leaving the absorption spectrum of the R• radical in the thermally equilibrated spin state (e and f of Fig. 2). The complex lineshape of the peak in the high-field side (c and d of Fig. 2), could be explained as the result of superposing a relatively sharp emissive line of the decaying A/E spectrum on the center of a growing absorptive line of the spectrum for the R• radical in the thermally equilibrated spin state.[8)]

As an additional discussion on the radical pair of the singlet state, the spin multiplicity of a photolytically excited state which leads to the radical pair is estimated to be singlet according to the Wigner spin conservation rule.[10)] The experimental result for the R• radical and the discussions given above could give a reaction scheme as follow:

$$\mathrm{RN{:}NR} \xrightarrow{h\nu} {}^{1}(\mathrm{RN{:}NR}) \longrightarrow {}^{1}[\mathrm{R}\cdot\cdot\mathrm{R}] + \mathrm{N}_2, \quad \{{}^{1}[\mathrm{R}\cdot\cdot\mathrm{R}] \longleftrightarrow {}^{3}[\mathrm{R}\cdot\cdot\mathrm{R}]\} \longrightarrow 2\cdot\mathrm{R},$$

where ^{1}(RN:NR) represents the singlet excited state. ^{1}[R••R] and ^{3}[R••R]

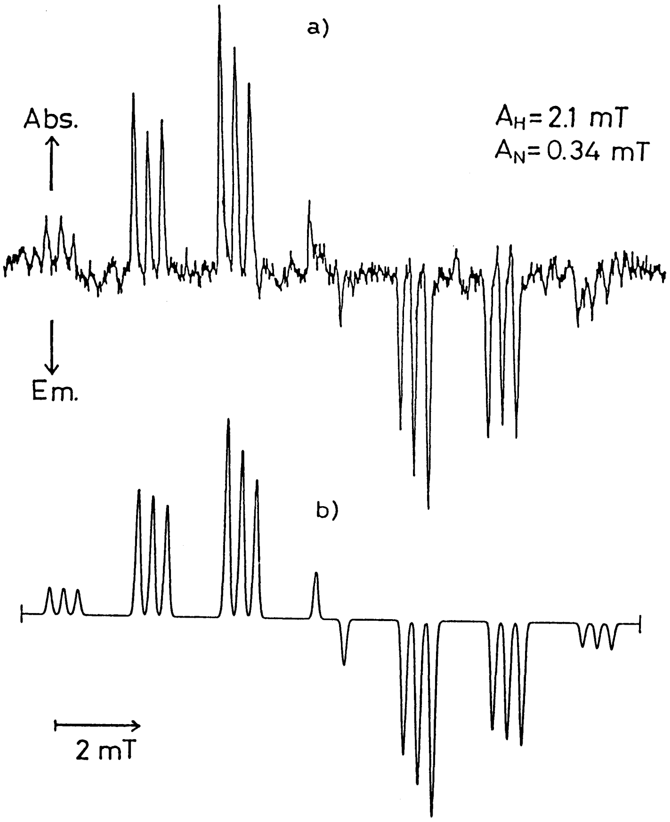

Fig. 1. Esr spectra of the R• radical in toluene at room temperature. a) Observed spectrum with the gate width of 200 ns. b) Simulated spectrum (see text).

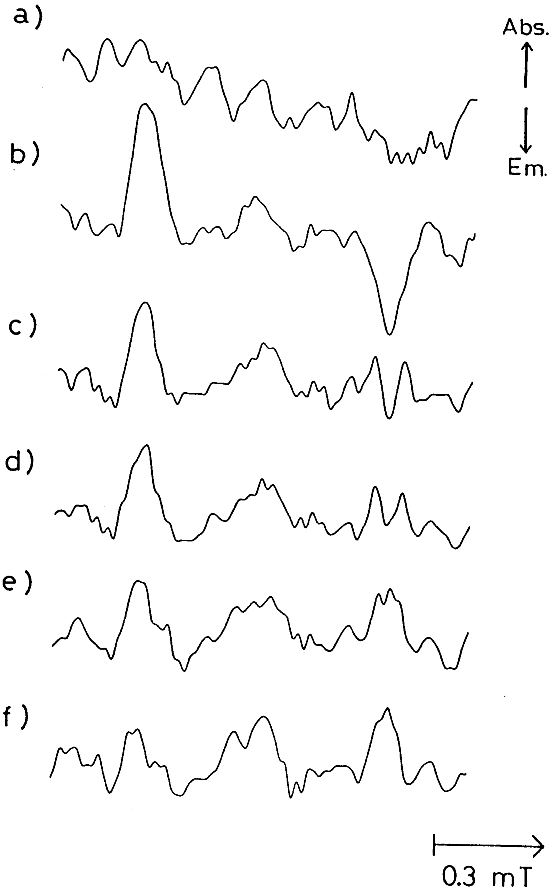

Fig. 2. Esr spectra taken at various delay times. a) 100 ns, b) 300 ns, c) 600 ns, d) 700 ns, e) 1.0 μs, f) 1.4 μs.

represent a radical pair in the singlet state and that in the triplet state, respectively, and $\{^1[R\cdot\cdot R] \longleftrightarrow {}^3[R\cdot\cdot R]\}$ represents the state of S-T_0 mixing which leads to the spin polarized radical.

In the photosensitized dissociation of RN:NR with xanthone which is excited to the triplet state by laser light, an esr spectrum of total emission pattern for the R• radical was observed as shown in Fig. 3. The spectrum is mainly of total emissive pattern which is characteristic of CIDEP by TM, and partly an E/A pattern by RPM with the triplet precursor superimposed on it. The conservation of spin polarization in the triplet-triplet energy transfer has been shown recently,$^{11)}$ then the polarization in the triplet state of xanthone may be transfered to that of RN:NR in the present system. This experimental finding revealed that RN:NR also easily dissociates into two R• radicals from its excited triplet state as follows:

$$X_n \xrightarrow{h\nu} {}^1(X_n) \longrightarrow {}^3(X_n),\ {}^3(X_n) + RN{:}NR \longrightarrow X_n + {}^3(RN{:}NR),\ {}^3(RN{:}NR) \longrightarrow 2R\cdot + N_2,$$

where X_n denotes xanthone.

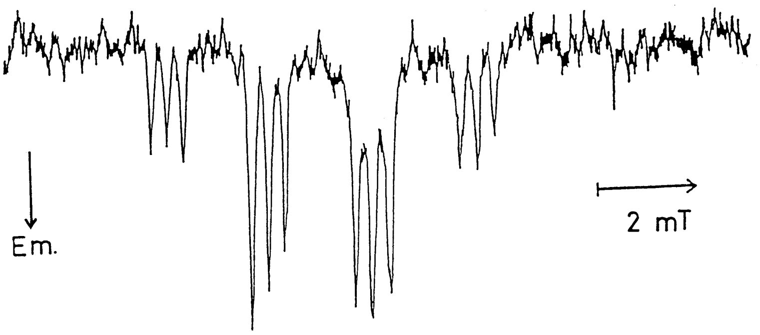

Fig. 3. Esr spectrum of the R• radical in toluene at room temperature in the presence of 0.01 M xanthone, which was taken at the delay time of 200 ns with the gate width of 200 ns.

In conclusion, the CIDEP signal of absorption-emission pattern for the R• radical was observed, and this signal decayed out within several hundreds nanosecond leaving the whole absorptive spectrum for the radical in the thermally equilibrated spin state. By the direct photolysis, the dissociation of RN:NR into two R• radicals takes place from the excited singlet state and the reaction is much faster than the intersystem crossing to the excited triplet state, while in the triplet sensitization the molecule in the excited triplet state easily dissociates into two R• radicals.

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