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EVIDENCE OF THE SINGLET RADICAL PAIR PRECURSOR IN THE PHOTOLYTIC GENERATION OF 1,4-DIMETHYLPYRIDINYL RADICAL FROM ITS DIMER.

A CIDEP STUDY

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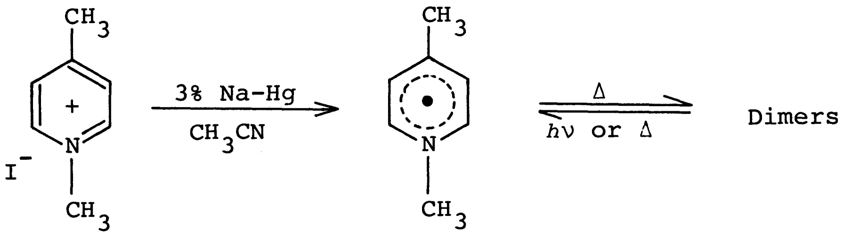
Time-resolved ESR spectra of the 1,4-dimethylpyridinyl radical were observed after the photolysis of its dimer with a N_2 laser. Since the transient ESR spectra exhibited the A/E polarization, singlet radical pair is proposed as the precursor of the present radical on the basis of simple sign rule.

A time-resolved ESR technique is useful to elucidate the photochemical process from the observation of CIDEP (chemically induced dynamic electron spin polarization) phenomena,[1)] and the theoretical and experimental studies revealed that the electron spin polarization is caused by two major mechanisms, namely, radical pair mechanism (RPM)[2)] and triplet mechanism (TM).[3)] There are three types of radical pair (RP): triplet pair, singlet pair, and free pair with the uncorrelated spins. All of the CIDEP spectra reported are referred to TM or triplet geminate and free pairs in RPM, except a few cases.[4)] This paper presents that the singlet RP is the precursor for the generation of 1,4-dimethylpyridinyl radical from its dimer by photolysis, since the time-resolved ESR spectra exhibit an enhanced absorption and emission (A/E) pattern.

The 1,4-dimethylpyridinyl radical was prepared and purified by a similar procedure to the preparation of 1-methyl-4-phenylpyridinyl.[5)] Reduction of the corresponding pyridinium iodide with 3% sodium amalgam in degassed acetonitrile, followed by distillation under vacuum, afforded the radical, but the radical solution dissolved in acetonitrile or 2-methyltetrahydrofuran (MTHF) showed no ESR signal at room temperature because of the dimerization. ESR signal due to the radical appeared during a continuous irradiation of the dimer with the light of near UV region or by thermal cleavage of it at temperatures above +60 °C. Figure 1 shows the ESR spectrum obtained during continuous irradiation of the



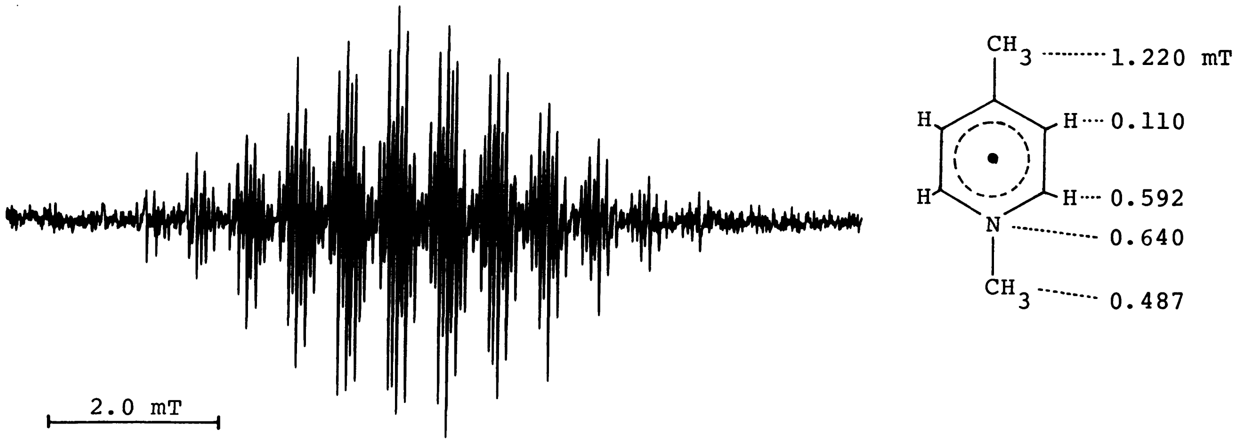


Fig. 1. ESR spectrum and hyperfine splitting constants of 1,4-dimethylpyridinyl radical in 2-propanol at -40 °C.

dimer solution with a high-pressure 500 W Hg-lamp, to which a UV-31 glass filter was equipped. Hyperfine structure of the spectrum was analyzed with five splitting constants, as confirmed by computer simulation, and the assignments were made tentatively according to the type of splitting and by comparing them with the calculated spin densities by the McLachlan procedure. Temperature dependence of the splitting constants was scarcely observed, while other pyridinyl radicals with polarizable substituent showed significant dependence.6)

Structure of the dimer was determined by the analysis of the ^{1}H- and ^{13}C-NMR measurements. Isomeric 2,2-, 2,4-, and 4,4-dimers were recognized in solution and the major component was 4,4-dimer (80% at 25 °C).

Time-resolved ESR spectra were observed with a direct detection (no field modulation) method using a Varian E-109E EPR spectrometer. ESR signal from the preamplifier was amplified to +40 dB by a hand-made wide-band amplifier (10 kHz —20 MHz). The signal was taken into a two-channel boxcar integrator (NF BX-531) at arbitrary times after the laser pulse. Nitrogen laser (5 mJ per pulse, 10 Hz repetition rate) was used as a source of the light pulse.

Figure 2 shows the time-resolved ESR spectra of the present radical in 2-propanol taken at the indicated times after the light pulse. These transient spectra exhibit the enhanced absorption at low-field half and the emission at the high-field half (A/E polarization). Since these hyperfine structures completely coincide with that of the steady-state ESR spectrum (Fig. 1), the observed CIDEP spectra are obviously due to 1,4-dimethylpyridinyl. Half-life of the polarization was about 1 μs in 2-propanol at -40 °C under the microwave power of 0.5 mW, and no signal due to any other species appeared. Significant line broadening observed in the growth of CIDEP has been discussed with the derivation from the modified Bloch equation.7) The effect of overlapping of the hyperfine lines may also cause the broadening.8) Since the observed CIDEP spectra showed an A/E pattern, the electron polarization is caused by RPM. The spectra are completely antisymmetric regarding the spectral center, because

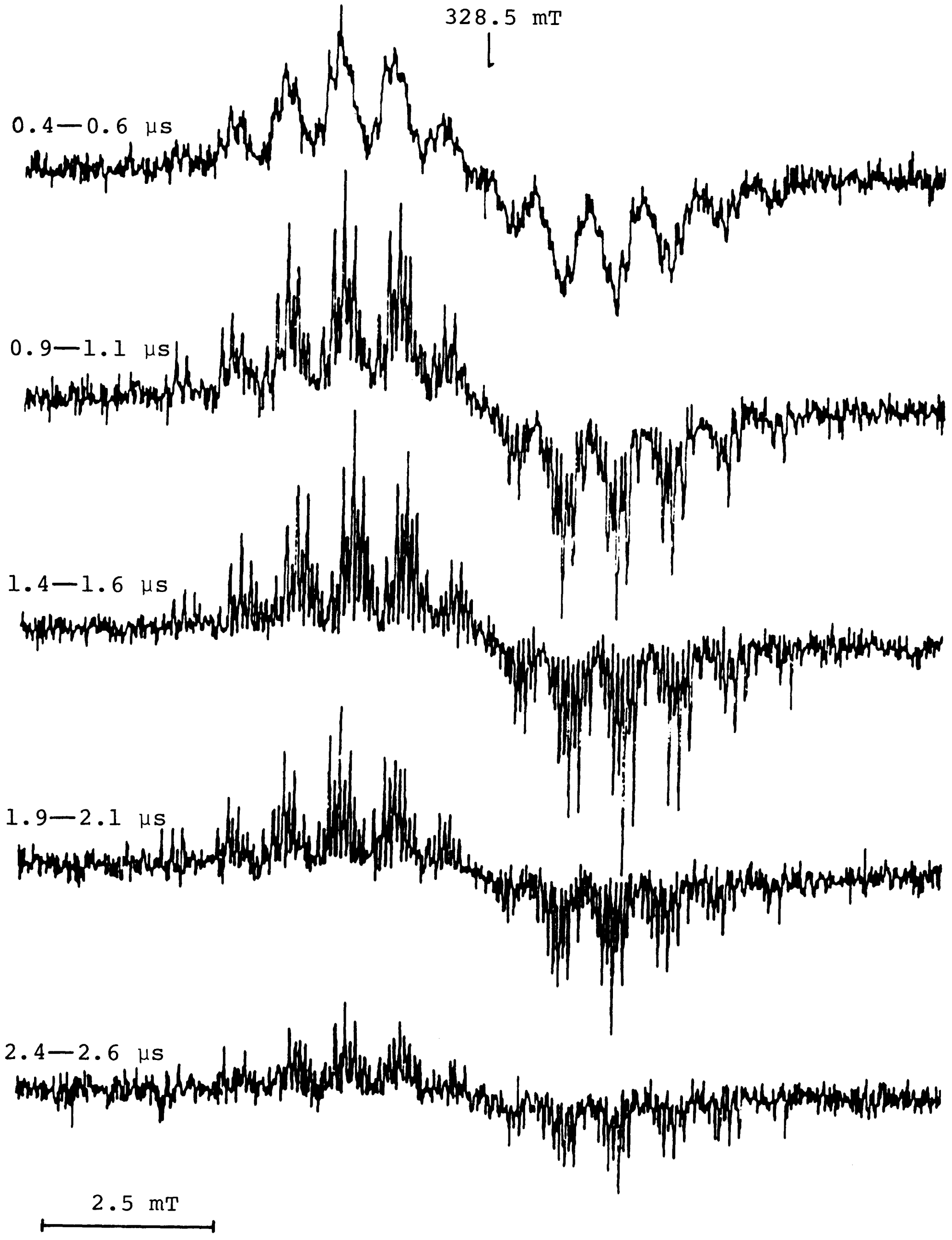


Fig. 2. Time-resolved ESR spectra of 1,4-dimethylpyridinyl radical generated on irradiation of the dimer in 2-propanol at -40 °C. The spectra were taken at the indicated times after laser pulse.

the photolysis of the dimer generates a pair of the radicals, in which the difference of g-values of both radicals is zero.

The spin state of RP precursor can be obtained from the simple sign rule, $\Gamma_{me} = \mu J$, where Γ_{me} is positive for A/E polarization and negative for E/A one.8) Positive value of μ means triplet or free pair, while the negative one is due to singlet RP. If the exchange integral, J, is negative value, which is reasonable to the usual cases where the bonding state of RP is singlet, μ becomes negative because of the positive Γ_{me} (A/E polarization). Therefore, we can propose the singlet RP as the precursor for the present radical.

Only a few observations of A/E polarization have been reported.4) It is interesting that the precursor of the present radical is a singlet RP and the pair has relatively long lifetime enough to cause ST_0 mixing in solvent cage. The dienes of two dihydropyridine rings of the dimer would be involved in the photochemical cleavage from the singlet excited state, as seen in the photo-sigmatropic rearrangement of some dienes systems.10) The long lifetime of the singlet RP may be ascribed to the low frequency factor of the recombination regardless of its small activation energy.11)

Intensity of the polarization depends on the power of incident microwave and also on temperature. Torrey nutation was observed at high microwave power. The details of the behavior will be reported elsewhere.

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11) The dimerization rate of 1-methyl-4-t-butylpyridinyl radical has been determined by our kinetic ESR study: $\log (k/M^{-1}s^{-1}) = 8.55 - 2020/2.303\,RT$. Similar parameters were observed for the dimerization of 1,4-dimethylpyridinyl radical, but the refinement of the values is under way.

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