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Polarized ESR Spectra of the Triplet Enols Generated from *o*-Methylacetophenone and Related Compounds

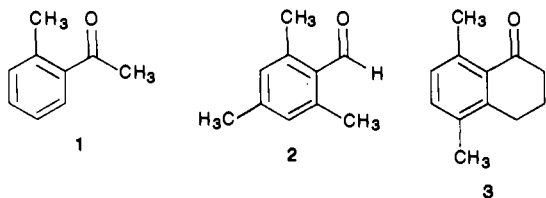
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Reaction sequence of the photoenolization of *o*-methylacetophenone has been proposed on the basis of the nanosecond flash photolysis.¹ Intramolecular hydrogen transfer in the photoexcited $^3n\pi^*$ state of this molecule leads to the formation of a short-lived biradical which decays to produce the unstable enol. Although a 1,4-biradical is a key intermediate in this reaction, no direct observation of the intermediate by ESR technique has been reported, to our best knowledge.

In this communication, we present the results of application of a time-resolved ESR technique to the photochemistry of *o*-methylacetophenone (1) and the related compounds, 2,4,6-trimethylbenzaldehyde (2) and 5,8-dimethyl-1-tetralone (3),² in glassy matrix. Generation of the transient species during the photoenolization and chemical quenching of the biradical in the presence of an electron acceptor in solution have been demonstrated.



All substances were purified by distillation under reduced pressure. Solvent toluene, ethanol, and methylcyclohexane were spectrograde and used without further purification. The sample solution prepared at a concentration of 5×10^{-2} M was degassed by using five freeze-thaw cycles. The method to detect transient ESR signals has been described previously.³ A nitrogen laser (5 mJ/pulse, 10-Hz repetition rate) was used for the light source. A high-pressure Hg lamp (500 W) equipped with a UV-31 glass filter was used for continuous irradiation.

Continuous irradiation of each solution containing 1-3 in the mixed solvent of toluene/ethanol (1:1, v/v) at 77 K showed no ESR signal except a small one due to free radical. On the other hand, the transient species in the photoreaction was detected by applying the time-resolved ESR method. Figure 1a shows the ESR spectrum observed for the solution of 1 at 1 μ s after the light pulse irradiation. The weak emission signal at about 1500 G corresponds to the $|\Delta M_S| = 2$ transition of the triplet molecule. The $|\Delta M_S| = 1$ transitions show the phases of AEA at the low-field half and of EAE at the high-field half (A, absorption; E, emission). The estimated zero-field parameters, $|D|$ and $|E|$, are 0.060 and 0.0025 cm^{-1} , respectively. These values are different from those of the excited triplet states of acetophenone derivatives.^{4,5} Similar

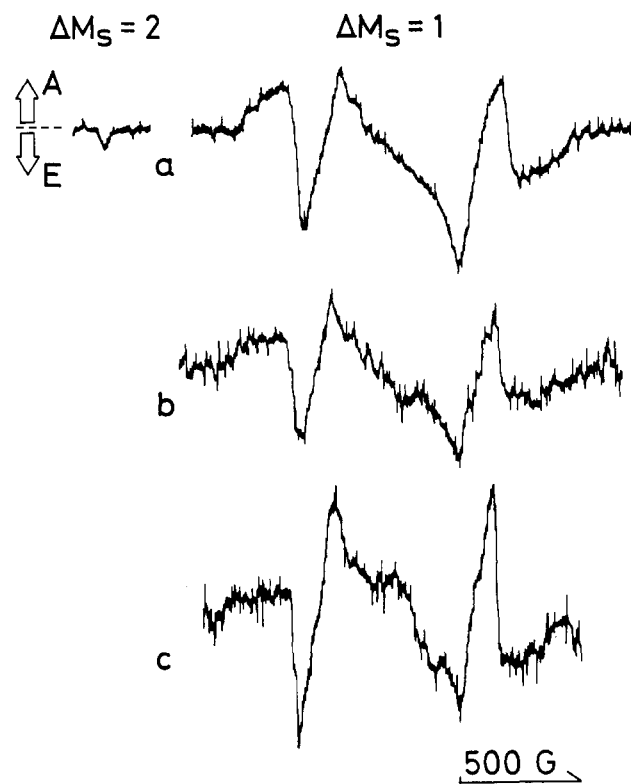


Figure 1. Transient ESR spectra of the intermediate biradicals generated by the laser pulse irradiation of 1 (a), 2 (b), and 3 (c) in toluene/ethanol (1 : 1) at 77 K. The spectra were taken at 1 μ s after the laser pulse.

polarized spectra were also obtained in nonpolar solvents such as methylcyclohexane and toluene/ethanol (10:1, v/v), though the additional E-polarized lines due to the transient free radicals appeared at the $g = 2$ region.

In order to certify the above transient species, measurements were performed for 2 and 3, both having a similar structural situation between the carbonyl and methyl groups to that of 1. The compound 3 has a fixed structure, while 1 and 2 form syn and anti conformations. Light pulse irradiation to the solutions of 2 and 3 afforded the spin-polarized spectra shown in Figure 1b and 1c, respectively. The polarization patterns and zero-field parameters of these spectra agreed well with those of Figure 1a. Thus, the results clearly indicate the generation of triplet biradical species in these photochemical reactions. A similar examination carried out for 2-methylbenzophenone (4) gave only a spectrum similar to those of the excited triplet states of benzophenone derivatives.⁶ The short reported lifetime of the biradical generated from the syn form of 4⁷ would make the detection by our time-resolved ESR system difficult, while the excited triplet state has a relatively long lifetime.

Spin polarization of excited triplet states usually arises from the anisotropic intersystem crossing (ISC) to the triplet sublevels.⁸ According to the qualitative consideration to the phase of CIDEP at the $|\Delta M_S| = 1$ region, two physically realizable situations are necessary to interpret the AEA/EAE pattern with the signs of *D* and *E* regarding the manner of ISC. We assume simply the same signs of *D* and *E*. Then the zero-field energies W_x , W_y , and W_z are in the order $W_y > W_x > W_z$ for $D > 0$ and $W_z > W_x > W_y$ for $D < 0$. When the highly populated state in the sublevels is T_z and T_y for $D > 0$ or T_x for $D < 0$, the phase pattern of the

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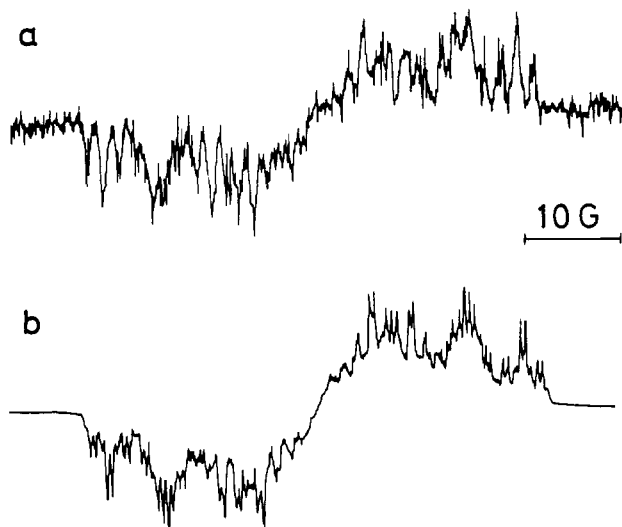


Figure 2. (a) Transient ESR spectrum observed at 1 μ s after the laser pulse irradiation of the wet methanol solution containing **1** and methylviologen dichloride at -70 $^{\circ}$ C. (b) The simulated spectrum with E/A polarization. Hyperfine splitting constants for the 2-acetylbenzyl radical: 15.5 (2 H), 5.25 (1 H), 6.25 (1 H), 1.75 (2 H), and 0.50 G (3 H).

observed CIDEP can be reproduced. Since the phase of the $[\Delta M_S] = 2$ line is emissive, the most populated sublevel would be the upper one. In the present case, the E value is small, so the latter case can be neglected because of a small difference between W_x and W_y . Consequently, it may be suggested that the anisotropic ISC occurred so as to make a spin distribution $P_y > P_z \gg P_x$, where P_i is the population of a triplet sublevel.

According to a conception that the biradicals formed as a result of intramolecular hydrogen abstraction in the triplet excited state of *o*-alkyl-substituted aromatic carbonyl compounds are describable as the triplets of the corresponding photoenols,⁹ the transient species would be assigned to the excited triplet molecule of the enol (i.e., 1,4-biradical).¹⁰ The presence of oxygen in solution significantly reduced the intensity of the polarization, showing a quenching of the transient species by oxygen.

The biradical is quenched by an appropriate electron acceptor to produce the monoradical as follows. Under a steady-state irradiation to the wet methanol (1 : 10, v/v) solution containing **1** (50 mM) and methylviologen (MV^{2+} , 50 mM) at -70 $^{\circ}$ C, the observed ESR spectrum was only due to the cation radical MV^{+} . Time-resolved ESR measurement of the same solution however exhibited the spectrum of another radical species, which showed the E/A pattern of polarization and the g value slightly different from that of MV^{+} (Figure 2a). Since the photolysis of the unsubstituted acetophenone in the presence of MV^{2+} did not exhibit any polarized ESR signal in the same experimental conditions, possibility of the direct electron transfer from the ketone triplet state to the acceptor can be ignored, regardless of an appearance of the ESR signal under a steady-state irradiation. A transient ESR spectrum similar to that of Figure 2a was also obtained for the solution containing **1** and 1-benzyl-4-*tert*-butylpyridinium chloride at room temperature. From the computer simulation (Figure 2b), the generated radical was identified as 2-acetylbenzyl radical, which has been expected as one of the intermediates in the electron-transfer reaction of type II biradicals.⁹ We thus concluded that the observed CIDEP spectrum originated from chemical quenching of the intermediate of photoenolization of **1** by MV^{2+} in solution. Since the polarization depends on the hyperfine splittings, the E/A polarization arises from the ST_0 mixing of the radical pair.

These results support that the observed spectra of Figure 1 are due to the intermediates in the photoenolization of *o*-methyl-

substituted aromatic carbonyl compounds.

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RNA Fragment r(CGm⁵CGCG) That Exhibits Two Conformations in Slow Exchange on the NMR Time Scale in Low Salt Solution

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Examination of the three-dimensional structure of a transfer RNA (tRNA) molecule—by far the best known among nucleic acids—shows that the polynucleotide chain undergoes many changes in direction which are associated with local conformational changes.¹ Several studies suggest that the presence of numerous atypical bases found in tRNAs—such as 5-methylcytosine (m^5C) or pseudouracil (Ψ)—play a specific role in the spatial organization of these molecules. For example, we showed that the substitution of uracil by pseudouracil induces a notable conformational change in an isolated ribonucleotide by favoring the syn orientation of the base;² moreover several works demonstrated that m^5C , which is also found in DNAs, favors the transition from the *B* to the *Z* form.³⁻⁷ Recently it has been shown that the tetramer r(CGCG) is able to adopt a *Z* conformation in high salt solution conditions.⁸

In order to investigate the role of m^5C in tRNA molecules, we have examined the conformation of the self-complementary RNA fragment r(CGm⁵CGCG) in aqueous solution by ¹H and ³¹P NMR at 500 and 202 MHz, respectively.

The hexamer r(CGm⁵CGCG) was synthesized in solution by the phosphotriester method. The purity of the hexamer was checked on a Nucleosil C18 analytical column (99.8%) and by polyacrylamide gel electrophoresis under denaturing conditions. Enzymatic digestion by snake venom phosphodiesterase indicated that r(CGm⁵CGCG) had the expected 3'-5' phosphodiester linkage. ¹H and ³¹P NMR spectra were obtained on a Bruker WM-500 spectrometer.

Figure 1 shows the aromatic portion of the ¹H NMR spectra of r(CGm⁵CGCG) in aqueous solution (0.1 M NaCl) recorded at different temperatures. The high-temperature spectrum exhibits the usual signals of the three guanosine H8 protons and of the three cytosine H6 protons. If the temperature is lowered, several base protons (Figure 1) as well as H1' sugar proton signals (not

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