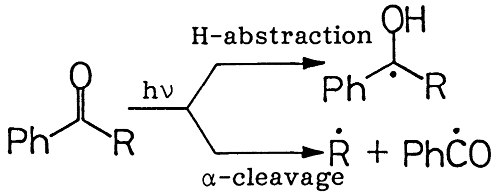
CHEMISTRY LETTERS, pp. 1491-1494, 1990. © 1990 The Chemical Society of Japan

CIDEP Studies on Radicals Produced from Photochemical Reactions of Some Aromatic Carbonyl Compounds

Tadaaki IKOMA, Kimio AKIYAMA, Shozo TERO-KUBOTA, and Yusaku IKEGAMI*
Chemical Research Institute of Non-Aqueous Solutions,
Tohoku University, Katahira 2-1-1, Aobaku, Sendai 980

CIDEP spectra of radicals generated from photoinduced hydrogen abstraction and α-cleavage reactions of several alkyl phenyl ketones were studied. The participation of radical pair mechanism on the spectra was discussed from the magnitude of hyperfine interaction.

It has been well established that chemically induced dynamic electron spin polarization (CIDEP) is induced by two mechanisms, triplet mechanism (TM) and radical pair mechanism (RPM). Transient radicals produced from the excited triplet states often exhibit the CIDEP spectra originated from the both mechanisms. The contribution ratio of these mechanisms is significantly affected by several factors such as the lifetime and spin relaxation rate of the T_1 states, reaction rate for radical production, and radical spin-lattice relaxation time. In the present study, CIDEP spectra from the photolysis of aromatic carbonyl compounds were measured to clarify the main factor of electron polarization in this fundamental reaction. In the photochemistry of alkyl phenyl ketones, there are two competitive reaction pathways, hydrogen abstraction and α-cleavage from the T_1 states, in which the reaction rates and yields depend on the α-substituents.[1-2] Thus, we examined photolytic behaviors of acetophenone (AP), propiophenone (PP), isopropyl phenyl ketone (PPK), and t-butyl phenyl ketone (BPK).



R = CH_3 : AP
C_2H_5 : PP
$CH(CH_3)_2$: PPK
$C(CH_3)_3$: BPK

Commercial carbonyl compounds were purified by distillation under reduced pressure. All sample solutions were prepared at concentration of 0.1 mol dm^{-3} and deoxygenated by bubbling with argon gas before the CIDEP measurements. The solutions were flowed in a quartz tube within the cavity of a Varian E 109E X-band EPR spectrometer. An excimer laser (Lumonics

HE-420, XeCl 308 nm) was used as the light source. Time-resolved EPR (TREPR) system used was described previously.[3)]

Figure 1 shows the observed and simulated CIDEP spectra obtained from the laser excitation of aromatic carbonyl molecules in light paraffin at room temperature. These signals exhibit relatively slow growth time to reach the maximum at 2 μs because of the slow reaction rates and high viscosity. The transient radicals were assigned to the corresponding ketyl and solvent radicals, based on the steady state EPR results reported previously,[4)] except the BPK system. In BPK, α-cleavage reaction efficiently occurred to produce t-butyl radical.[5)] The present CIDEP spectrum was well

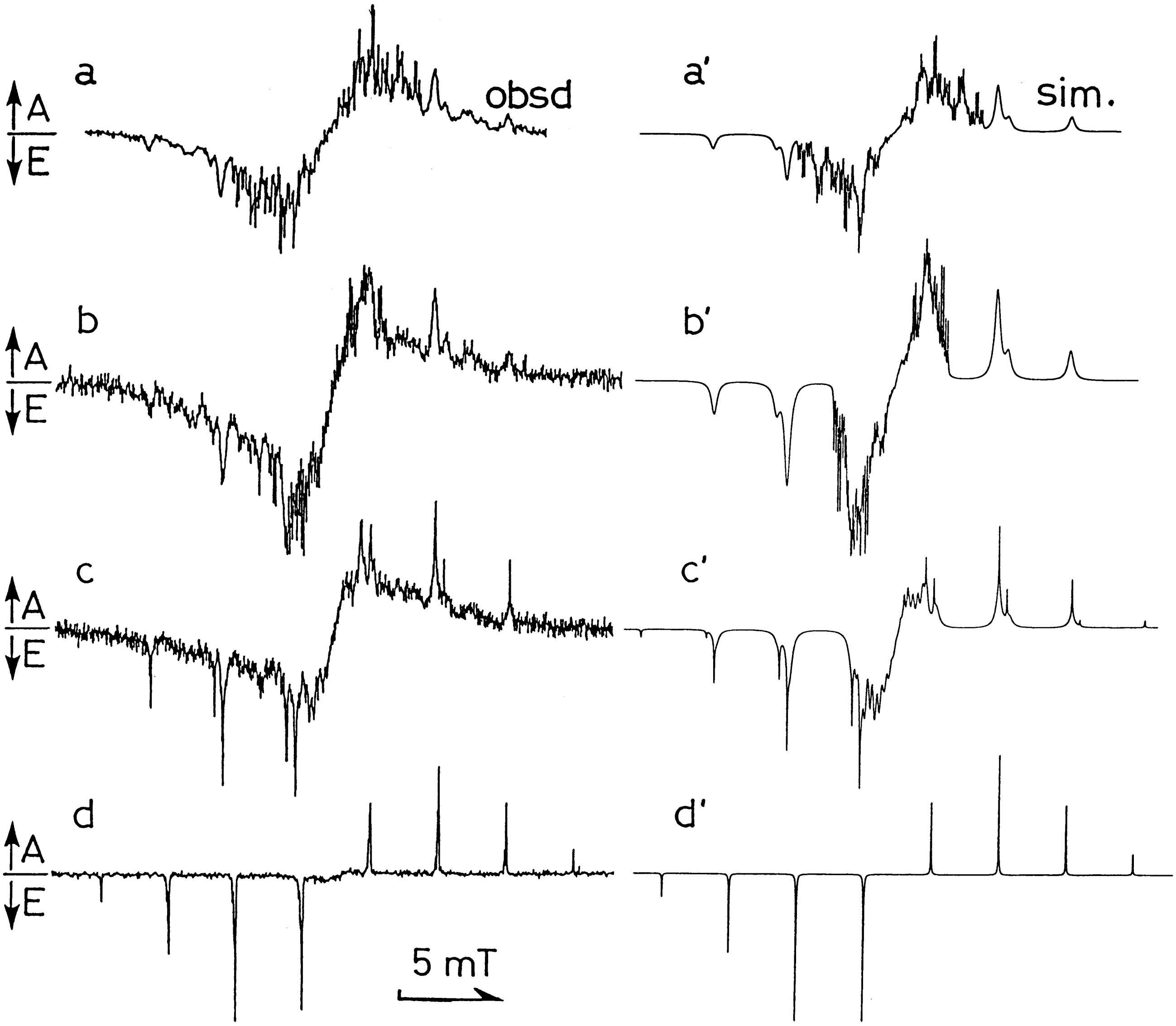
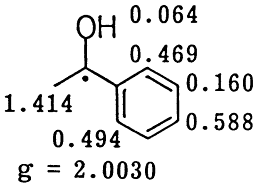


Fig. 1. Observed (a-d) and simulated (a'-d') CIDEP spectra obtained from the photolyses of acetophenone (a), propiophenone (b), isopropyl phenyl ketone (c), and t-butyl phenyl ketone (d) in light paraffin. The spectra were observed at 1.7 μs after laser irradiation at room temperature.

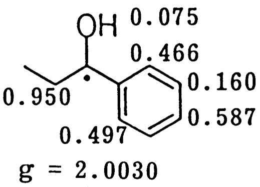
reproduced by pure RPM, in which benzoyl and t-butyl radicals were taken into account as the geminate pair (Fig. 1d'). Apparent excess E polarization arose from the difference of their g-factors. On the other hand, the PPK system showed the free radicals generated from both reactions of hydrogen abstraction and α-cleavage suggesting comparable reaction rates of these pathways. Very slow rate of the α-cleavage ($7.4\text{x}10^3$ s^{-1}) has been obtained for PPK from the quenching experiment.6) The isopropyl radical exhibited narrower line width and shorter lifetime than those of solvent radical. In Table 1 is shown the hyperfine coupling (hfc) constants of the observed radicals determined by computer simulation. Unknown broad E/A signals were observed in the present systems.

We obtained TM/RPM ratio7) by computer simulation to discuss about the electron spin polarization mechanism. Although TM was inactive for AP, some contribution was observed for PP (TM/RPM = 1/9) and for PPK (2/8). It can be considered that the hydrogen abstraction rates (k_H) decrease in the order of AP > PP > PPK in the light paraffin, since the k_Hs with 2-PrOH have been reported as $6.8\text{x}10^6$, $4.4\text{x}10^6$, and $0.9\text{x}10^6$ mol^{-1} dm^3 s^{-1} for AP, PP, and PPK in benzene, respectively.1) Present results indicate that the TM contribution in ketyl radicals increases with decreasing of the k_H values. Therefore, electron spin relaxation rates of the T_1 states and/or ketyl radicals are principal factors in determining the present CIDEP pattern. The electron spin relaxation time of the T_1 state in a fluid solution depends on the zero field splitting (zfs) parameters and the rotational correlation time. The present carbonyl molecules (AP, PP, and PPK) have large zfs values in organic solvents. Any TREPR spectra due to the T_1 states were not observed in alcoholic matrices, though they were obtained in matrices containing water. The phosphorescence spectra show clear carbonyl progression and relatively short lifetimes (3.5, 4.3, and 3.4 ms for AP, PP, and PPK, respectively, in an ethanol glassy matrix at 77 K). Then, we conclude that the T_1 states of PP and PPK, as well as AP, have a mixed character between $n\pi^*$ and $\pi\pi^*$ states in alcoholic solvents resulting in large D values.8) Rotational correlation time tends to increase in the order of AP < PP < PPK. As depicted in Table 1, hfc constants of α-protons in **2** and **3** are smaller than that of methyl proton of **1** suggesting hindered rotation of the ethyl and isopropyl groups. When radicals have larger hfc constants, RPM works more effectively as deduced from the CIDEP theory9) leading to a decrease of the TM/RPM ratio. Furthermore, the small modulation of the hfc by the intramolecular rotation induces only a little effect on the electron spin relaxation process. While initial polarization by TM decays with the spin relaxation rate of the radical, CIDEP by RPM is generated during the bimolecular interaction.

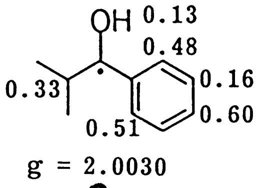
Table 1. Proton hyperfine coupling constants (a^H/mT) and g-factors of radicals determined by simulation.



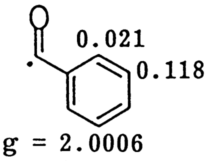
1



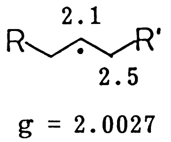
2



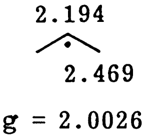
3



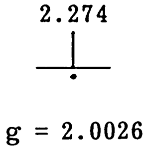
4



5



6



7

Since the polarization rises very slowly in the present system, electron spin relaxation rate of the ketyl radicals would be principal factor in determining the CIDEP pattern, though the effect of T_1 state relaxation rate may not be neglected.

Pure RPM was observed in the CIDEP spectrum of t-butyl radical regardless of the fast photolytic reaction (rate constant $k_\alpha = 10^7$ s^{-1}).1) In the early stage of the signal growing (within 1 μs), no contribution of TM was detected. In the PPK system, **4** and **6** also showed similar results in spite of the participation of TM in ketyl **3**. As noted above, RPM can effectively induce the polarization in these radicals because of the large hfc constants. Detailed study on the time profile of **7** is in progress.

References

1) F. D. Lewis and J. G. Magyar, J. Org. Chem., **37**, 2102 (1972).

2) E. A. Lissi and M. V. Encinas, "Handbook of Organic Photochemistry II," ed by J. C. Scaiano, CRC Press, Boca Raton, Florida (1989), p. 137.

3) T. Ikoma, K. Akiyama, S. Tero-Kubota, and Y. Ikegami, J. Phys. Chem., **93**, 7087 (1989).

4) H. Paul and Fischer, Helv. Chim. Acta, **56**, 1575 (1973).

5) P. W. Atkins, A. J. Dobbs, and K. A. McLauchlan, J. Chem. Soc., Faraday Trans. 2, **71**, 1269 (1975); I. Carmichael and H. Paul, Chem. Phys. Lett., **67**, 519 (1979); L. T. Muus, Chem. Phys. Lett., **160**, 17 (1989); F. Jent and H. Paul, Chem. Phys. Lett., **160**, 632 (1989).

6) M. V. Encina, E. A. Lissi, E. Lemp, A. Zanocco, and J. C. Scaiano, J. Am. Chem. Soc., **105**, 1856 (1983).

7) Ratio of contributions from both TM and RPM to the intensity of observed CIDEP spectrum.

8) T. Ikoma, K. Akiyama, S. Tero-Kubota, and Y. Ikegami, Symp. Molecular Structure (Japan) 1988.

9) F. J. Adrian, J. Chem. Phys., **54**, 3918 (1971).

(Received April 18, 1990)