

Application of ESE spectroscopy to the study of radical reactions in solids

Tsuneki Ichikawa

Faculty of Engineering, Hokkaido University, Sapporo, 060 Japan

Abstract - ESE spectroscopy is shown to be a powerful method for studying radical reactions in solids. Overlapping EPR spectra are possible to be differentiated into each spectral component by utilizing the difference of paramagnetic relaxation rates due to the difference of molecular motion. Informations on the motion of molecules affecting radical reactions are also obtained. The ESE technique is applied to alkyl radicals generated from normal and branched alkanes by γ -irradiation at cryogenic temperature for elucidating the mechanism of selective radical formation by the detachment of C-H hydrogen. It is concluded that the selectivity is strongly dependent on the easiness of C-C-C bending motion assisting the detachment of hydrogen.

INTRODUCTION

Recent progress of ESE spectroscopy makes us possible to use many sophisticated pulse sequences for the detection of paramagnetic species. However the new techniques are not necessarily used widely among chemists except for spectroscopists, probably because the progress is too fast for chemists to recognize the utility of the new techniques. It is therefore worthwhile to demonstrate the usefulness of the ESE spectroscopy to the study of chemistry. The present paper summarizes our recent study on radical reactions in organic solids obtained by the application of the ESE spectroscopy. Although the ESE technique used here is rather classical, the ESE spectroscopy plays a crucial role in the study.

Irradiation of organic solids by ionizing radiations and UV light causes the formation of several types of free radicals which can be stably trapped at cryogenic temperature and detected by EPR. Ambiguity in the identification of radicals in solids by EPR arises from line broadening due to distribution of hyperfine coupling constants (hfcc). The distribution is caused by dynamic and static distortion of radical conformations. If several radical species coexist in a solid sample and their EPR spectra overlap with each other, it is very difficult to differentiate and identify the EPR spectrum of each radical specimen. The computer simulation of the spectrum is not so effective as is expected, since the hfcc of, especially, β protons is very sensitive to the location of the protons with respect to the orbital of a singly-occupied electron and ranges from 0 to 4 mT. Thus, it is not an easy task to study radical reactions in organic solids only by applying conventional CW EPR spectroscopy.

Overlapping EPR spectra can be examined by separating them into each component with an ESE spectroscopy based on the difference in the rate of transverse and longitudinal relaxations. For organic radicals the relaxations are mainly induced by spectral diffusion which in turn is induced by the time fluctuation of hfcc due to thermal motion of radicals. The relaxation rates are therefore sensitive to the

geometrical structure of radicals. The ESE spectroscopy detects the magnetization of unrelaxed on-resonant spins as a function of a waiting time after the excitation. Therefore, if coexisting radicals have different relaxation rates, the overlapping spectra is possible to be differentiated into each component by measuring the intensity of ESE signals while sweeping the external field very slowly. The relaxation rates reflect the motion of radical species in matrices, so that the ESE method is also useful for understanding the relation between molecular motion and radical reaction.

COMPARISON OF CW AND ESE-DETECTED EPR SPECTRA

Fig. 1 shows the sequence of microwave pulses used for the measurement of transverse and longitudinal relaxations. The transverse relaxation is observed by measuring the intensity $E(t_2)$ of two-pulse ESE signals as a function of time interval τ between the first and the second pulses. Since the transverse relaxation takes place between the first pulse and the time of ESE observation, $t_2 = 2\tau$ is the time interval for the transverse relaxation. To observe the longitudinal relaxation, the total magnetization of on-resonant spins under thermal equilibrium is first detected at a fixed τ by the two-pulse method. After time t_0 , long enough for complete relaxation of the spin system, a saturation pulse is applied to saturate the on-resonant spins. The total magnetization is then detected after time t_1 by the two-pulse method. The difference in the ESE intensity with and without the saturation pulse, $E_s(t_1)$, is equal to the amount of longitudinally unrelaxed spins at t_1 after the saturation pulse. The EPR spectra of $E(t_2)$ and $E_s(t_1)$ are obtained by sweeping the external magnetic field very slowly while fixing t_2 and t_1 . The spectra thus obtained will be designated as t_2 and t_1 -dependent EPR spectra.

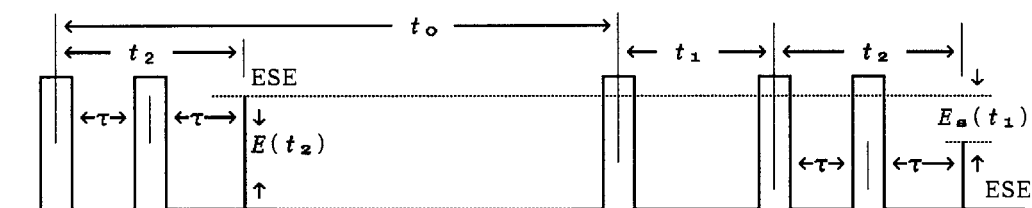


Fig.1. Sequences of microwave pulses used for the measurement of transverse and longitudinal relaxations.

The shape of an ESE-detected EPR spectrum is not necessarily the same as that of the corresponding CW EPR spectrum. An extreme case is the EPR spectrum of 1-hydroxyethyl radical in a γ -irradiated ethanol matrix at 77 K (ref. 1). As is shown in Fig. 2, the CW EPR spectrum of the radical is composed of five lines due to hyperfine interactions with one α proton and three methyl β protons. The hyperfine interaction depends on the location of the β protons with respect to the p orbital of the unpaired electron. However, the observed hyperfine coupling constant is the same for all the β protons because of quick rotation of the methyl group in the time scale of the CW EPR measurement. On the other hand, the ESE-detected EPR spectrum is composed of four lines due to hyperfine interactions with three β protons of the spin state $\pm(1/2, 1/2, 1/2)$ and one α protons of the spin state $\pm 1/2$. The rotation of the methyl group with the nuclear spin state other than $\pm(1/2, 1/2, 1/2)$ causes the fluctuation of the hyperfine interactions. The rotation is not fast enough to average out the fluctuation of the hyperfine interaction but is fast enough to induce complete phase relaxation during time t_2 . The 1-hydroxyethyl radicals with the methyl protons of the spin state other than $\pm(1/2, 1/2, 1/2)$ is therefore not observed by the ESE-detected EPR.

An ESE-detected EPR spectrum occasionally changes with t_1 and/or t_2 . An example is alkyl radicals in n-hexane (Fig. 2). Two types of secondary alkyl radicals are known to be generated and stabilized in γ -irradiated n-alkane crystals at 77 K. They are the penultimate alkyl radical with the unpaired electron on a carbon second to the end of the carbon chain and the internal alkyl radical with the unpaired electron on a carbon farther than the second one. Although the irradiated crystals show the overlapping CW EPR spectra of these radicals, the ESE-detected EPR show the spectrum of only the internal 1-ethylbutyl radical. This difference arises from the fast paramagnetic relaxation of the penultimate radical induced by time fluctuation of the EPR spectrum due to molecular motion, that is, spectral diffusion. The spectral diffusion of the penultimate radical is much faster than the internal one, because the twisting motion of the C-CH-C bond, the source of the fluctuation of the β proton hfcc, is faster for the penultimate radical (ref. 2, 3).

The resolution of the ESE-detected EPR spectrum increases with t_1 , which implies that the longitudinal relaxation is slower for the spins near the peak of the spectrum. The resolution enhancement is well explained by taking the spectral diffusion-induced relaxation into account. When an EPR spectrum is broadened due to spectral diffusion, the relative intensity of the spectrum is inversely proportional to the diffusion rate at the observed spectral position. The longitudinal relaxation due to the spectral diffusion is therefore slower for the spins near the peak of the spectrum.

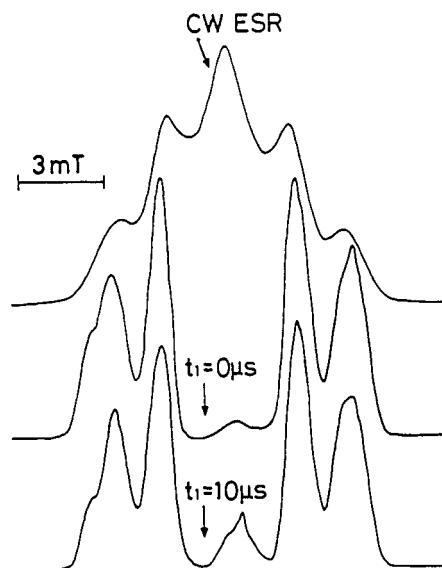


Fig. 2. CW and t_1 -dependent EPR spectra of hydroxyethyl radical at 77 K in γ -irradiated ethanol glass.

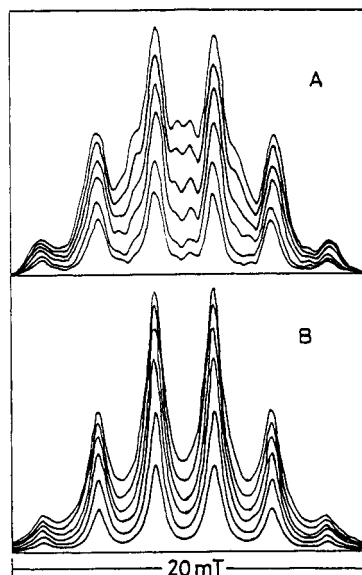
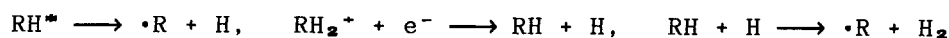


Fig. 3. Comparison of (A) observed and (B) simulated t_1 -dependent EPR spectra of 1-ethylbutyl radical in n-hexane single crystal at 77 K.

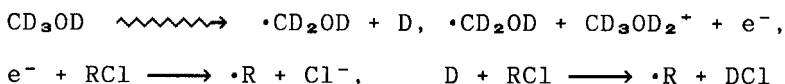
SELECTIVE FORMATION OF ALKYL RADICALS FROM SOLID ALKANES

Irradiation of alkanes by ionizing radiations causes the formation of alkyl radicals. Since the energy of radiations is much higher than bond dissociation energies, several types of radicals are expected to be formed by random scission of chemical bonds. However this is not usually the case. Although a C-C bond is weaker than a C-H bond, due to the cage effect, major radicals formed in condensed media are those generated by the scission of a C-H bond by reactions,



Although a tertiary C-H bond is the weakest, major radicals generated in the glassy solids of branched alkanes are not tertiary alkyl radicals but secondary penultimate radicals. However, no reason has been given for the preferential formation of the radicals. Moreover it is still not certain whether the penultimate radicals are exclusively formed or not, since the CW EPR spectroscopy used is not powerful for differentiating overlapping spectra.

Several types of alkyl radicals are expected to be formed and stabilized in γ -irradiated solid alkanes. For example, five types of alkyl radicals are expected to be formed from 2-methylpentane by the scission of a C-H bond. These are expressed as Me(2)R(1), Me(2)R(2), Me(2)R(3), Me(4)R(2) and Me(4)R(1), where the values of m and n in Me(m)R(n) denote the location of the main chain carbons possessing the methyl group and the unpaired electron, respectively. Since the proton hfcc of these radicals are similar, it is not easy to identify the radicals from the CW EPR spectra of irradiated 2-methylpentane. The identification of the radicals can be achieved more clearly by utilizing the difference of the paramagnetic relaxation rates. Fig. 4 shows the longitudinal relaxation of these radicals at 77 K in perdeuterated methanol generated from chlorinated 2-methylpentanes by reactions,



The relaxation rate decreases with increasing intramolecular distance between the radical carbon and the terminal one. The main process of the longitudinal relaxation is therefore spectral diffusion due to molecular motion of β protons with respect to the p orbital of the unpaired electron. A longer carbon chain is more difficult to move than the shorter one, so that the rate of spectral diffusion decreases with increasing length of chains attaching to the radical carbon.

Since the relaxation rates are not the same for these radicals, by measuring t_1 -dependent EPR spectra, it is possible to judge whether a sample contains several types of radicals or not. Figure 5 shows the t_1 -dependent EPR spectrum for neat 2-methylpentane at 1 week after γ -irradiation. The relative shape of the spectrum does not depend on t_1 , which implies that only one type of the radical remains in the sample. The remaining radical is obviously Me(4)R(2) with 8 EPR lines.

Although a considerable amount of the primary alkyl radicals are observed immediately after the irradiation, they gradually convert to

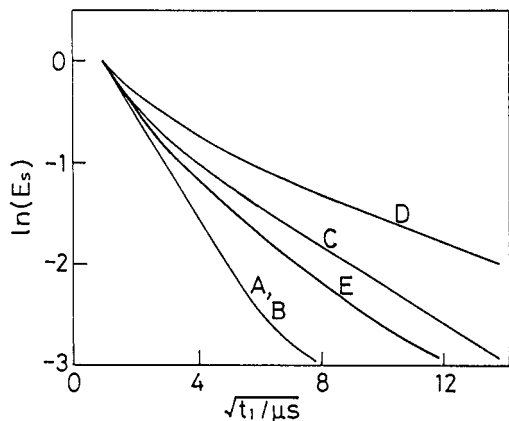


Fig. 4. Longitudinal relaxation of (A) Me(2)R(1), (B) Me(4)R(1), (C) Me(4)R(2), (D) Me(2)R(3), and (E) Me(2)R(2) radicals in perdeuterated methanol at 77K.

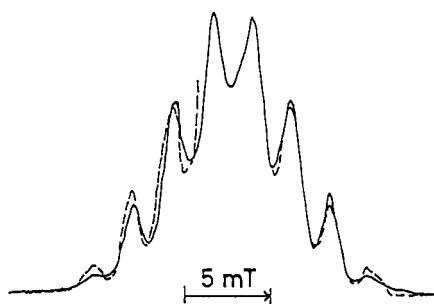


Fig. 5. t_1 -dependent EPR spectra at 77 K for (—) γ -irradiated neat 2-methylpentane and of (---) Me(4)R(2) radical in perdeuterated methanol at $t_1=0$ and 50 μs .

the Me(4)R(2) radical by the abstraction of penultimate secondary C-H hydrogen. The spectrum of alkyl radicals generated from 2-methylpentane in perdeuterated methanol due to abstraction of C-H hydrogen by deuterium atoms agrees with that of the Me(4)R(2) radical. These results indicate the selective abstraction of hydrogen from penultimate carbon by hydrogen atoms and primary alkyl radicals. The tertiary radical and the internal secondary radical generated from chlorinated 2-methylpentanes in 2-methylpentane are stable at 77 K, certifying no formation of these radicals in neat 2-methylpentane glass either from the cation radical or from the excited state of 2-methylpentane. The hydrogen abstraction proceeds via quantum-mechanical hydrogen tunneling process, since only 2 % of 2-methylpentane in perdeuterated methanol gives 20 % of the total radicals. The selective formation of secondary penultimate radicals is also observed for another branched alkanes.

In contrast to the selectivity in solids, the selectivity of alkyl radical formation in alkane liquids simply depends on the strength of the C-H bonds. Spin trapping experiment of γ -irradiated branched alkanes shows that the yield of the spin adduct of tertiary alkyl radicals is comparable with that of secondary alkyl radicals, though the number of tertiary C-H bonds is much smaller.

It is concluded from the above results that the selectivity of radical formation strongly depends on the easiness of molecular motion assisting the scission of a C-H bond. In glassy solids, the conformation change of an excited or ionized molecule from an original state to dissociative states is prevented by surrounding matrix molecules. Since the methyl group located at the end of a molecular chain is the easiest to be deformed, a considerable amount of the primary radical is generated from excited or ionized alkanes though the C-H bond is the strongest. The difficulty of the deformation increases with the length of alkyl chains attached to a carbon atom for C-H bond scission, so that the scission of an internal secondary C-H bond does not take place. Dissociation of a C-H bond on a tertiary carbon atom needs synchronous deformation of the bonds from sp^3 to $sp^2 + p$. The tertiary alkyl radical is therefore not generated though the paramagnetic relaxation is faster than the secondary radical. Asynchronous deformation is enough for the paramagnetic relaxation of the tertiary radical. The situation is the same for the abstraction of hydrogen by hydrogen atoms or the primary radicals. A hydrogen atom on a penultimate carbon is selectively abstracted since the penultimate carbon has moderate flexibility and C-H bond dissociation energy.

Fig. 6 compares the CW and the t_1 -dependent EPR spectra (first derivative) of alkyl radicals generated from 2 % of n-hexane in γ -irradiated perdeuterated n-hexane crystal at 77 K. Difference between the CW and t_1 -dependent EPR spectra arises from the selective detection of the internal radical by the t_1 -dependent EPR, since the relaxation of the internal radical is much slower in the crystal.

Although a considerable amount of internal radicals are generated from protiated solute n-alkanes in γ -irradiated n-alkane crystals, only penultimate secondary radicals, are generated from the solutes in the glassy matrices of deuterated alcohols. Fig. 7 shows the t_1 -dependent EPR spectrum at 77 K of γ -irradiated perdeuterated methanol containing 2 % of n-hexane. The spectral shape does not depend on t_1 (and t_2) which indicates that only one type of radical is generated in the sample. The CW EPR spectrum agree with that of 1-methylpentyl radical generated from 2-chlorohexane. The formation of the solute radicals in crystalline and glassy solids proceeds through tunneling C-H hydrogen abstraction by deuterium atoms, since only 2 % of the protiated solute gives more than 20 % of the total radicals.

The difference of the selectivity between crystalline and glassy solids arises from the effect of solid phase on the bending motion of a C-C-C bond assisting hydrogen tunneling from the central carbon atom. Steric

hindrance to the bending motion increases in glassy solid with increasing length of alkyl chains attached to the a carbon atom to be hydrogen-abstracted, because the alkyl chains stuck into the glass matrix acts to prevent the distortion of the C-C-C bond. However the alkyl chains in n-alkane crystals do not necessary prevent the distortion of the C-C-C bond. In crystalline n-alkanes all the carbon atoms in a molecule are in one molecular plane. The in-plane accordion motion of a flat carbon skeleton is easy to take place, because the accordion motion does not exert much strain to the surrounding. Since the accordion motion causes the simultaneous bending of all the C-C-C bonds in a molecule, the tunneling C-H hydrogen abstraction is possible to take place on penultimate and internal secondary carbon atoms.

Paramagnetic relaxation rate of penultimate alkyl radicals in n-alkane crystals is much faster than that of internal radicals. At a first glance, this contradicts the present conclusion that the rate of C-C-C bending motion for internal carbon is comparable to that for penultimate one. However the molecular motion causing paramagnetic relaxation is the out-of-plane twisting motion of the C-C-C bond. The in-plane bending motion of the C-C-C bond does not cause the relaxation, because the isotropic hfcc of β protons are not modulated by the bending motion. Since an n-alkane molecule is sandwiched by two n-alkane molecules, the rate of twisting motion is very slow for the internal radicals.

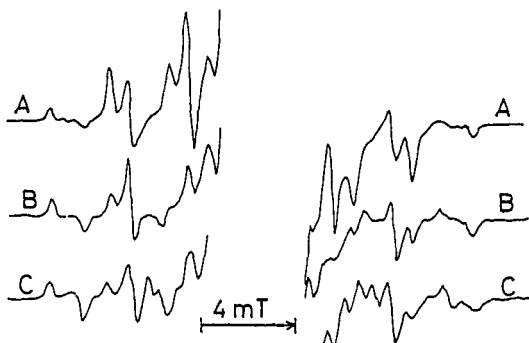


Fig. 6. Comparison of (A) CW and t_1 -pendent first-derivative EPR spectra at (B) $t_1=1\mu s$ and (C) $t_1=100\mu s$ for γ -irradiated perdeuterated n-hexane containing 2% of protiated n-hexane

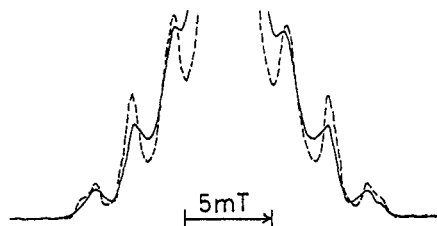


Fig. 7. Comparison of the t_1 -dependent EPR spectra of alkyl radicals generated from (—) n-hexane and (---) 2-chlorohexane in perdeuterated methanol glass at $t_1=1\mu s$. The relative shapes of the spectra do not depend on t_1 .

CONCLUDING REMARKS

It has been exemplified in the present paper that the ESE spectroscopy is quite useful for elucidating the mechanism of radical reactions in solid because of its ability of discriminating overlapping EPR spectrum and determining the rate of molecular motion. This is also useful for investigating radical reactions in polymers. The mechanism of radiation-induced lithogram of poly(methyl methacrylate) was first established by using this technique (ref. 4). I hope many chemists to notice the usefulness of the ESE technique and apply it to their research field, which in turn encourages EPR specialists to find a new pulse technique.

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