Spin-trapping Reactions in γ-Irradiated Benzene Solutions. Generation of Authentic Spin-adduct Radicals

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Synopsis. Spin-trapping in γ-irradiated solutions of chlorinated hydrocarbons in benzene by using 2,4,6-tri-*t*-butylnitrosobenzene revealed that transient free radicals are generated almost exclusively by the dissociative electron attachment to the solutes. This provides a simple, useful method for preparing the authentic spin-adducts of hydrocarbon radicals.

The spin-trapping technique has been utilized for the detection of short-lived free radicals involved in chemical reactions. The technique comprises the conversion of the short-lived radicals into the stable nitroxide radicals (spin-adducts) by the reaction with nitroso or nitrone compounds (spin-traps) and the observation of the latter radicals by means of the conventional ESR method. The ESR spectra of authentic spin-adducts are essential for the identification of the spin-trapped short-lived radicals. The authentic spin-adducts have been generated by several methods.[1-4] We wish to report a simple radiation-chemical method which is applicable in spin-trapping studies.

The free radicals were generated by the dissociative electron attachment, $RCl+e^- \rightarrow R\cdot + Cl^-$, to chlorinated hydrocarbons in γ-irradiated benzene solutions. Benzene was chosen as solvent because the radiation-chemical yield of the free radicals from neat benzene (per 100 eV radiation energy absorbed, *G*-value) is as low as 0.4.[5] In contrast, the yield is generally as high as 3 in saturated hydrocarbons, so that the spin-adducts of the solvent radicals sometimes prevent detection of free radicals from solutes in saturated hydrocarbon solvents by the spin-trapping technique.

Experimental

Benzene of spectrograde was used. Reagent grade chlorinated hydrocarbons were used as solutes without further purification. The spin-trap, 2,4,6-tri-*t*-butylnitrosobenzene,[6] was supplied by Dr. Masahiro Tabata, Hokkaido University. The sample solutions were degassed by freeze-pump-thaw cycles, sealed in ESR tubes at 10^{-3} Pa irradiated with ^{60}Co γ-rays, and subjected to measurements with an ESR spectrometer (JEOL, JES-ME-2X). The yield of the spin-adducts was determined by using the DPPH solution in benzene as a standard. All the experimental procedures were carried out at ambient temperture (20±2 °C).

Results and Discussion

The ESR spectrum recorded from benzene containing only the spin-trap is predominantly due to the spin-adduct of phenyl radical[2] (Fig. 1A). The spectral lines indicated by arrows show a minor contribution from unidentified free radicals. The generation of phenyl radical from benzene is necessarily accompanied by the formation of hydrogen atoms. However, they cannot be observed by the spin-trapping technique.

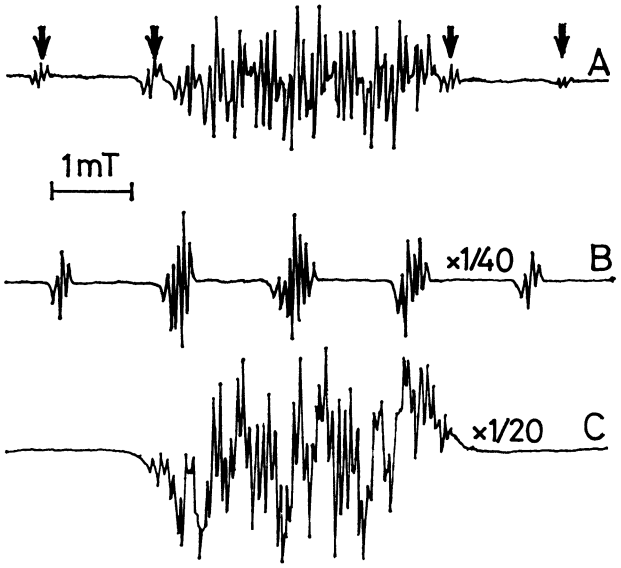

Fig. 1. ESR spectra of spin-adducts generated in benzene containing the 0.01 mol/dm³ spin-trap (A) with no other solute, (B) with benzyl chloride and (C) with *o*-chlorotoluene, γ-irradiated to the dose of 1×10^{19} eV/g.

The concentration of the chlorinated hydrocarbons is 0.2 mol/dm³ for all the samples. Arrows indicate the spectrum due to an unidentified spin-adduct. Relative sensitivity in the ESR measurements is shown in the figure.

Probably they readily react with benzene to form cyclohexadienyl radicals, which are too stable due to the π-conjugation to react with the spin-trap. The *G*-value of the spin-adduct of the phenyl radical is only 0.01 at 0.01 mol/dm³ of the spin-trap.

Effects of the addition of solutes to the solution are summarized as follows. No change observed in the spectrum on addition of 0.2 mol/dm³ toluene. The yield of the spin-adduct of phenyl radical increases by four times on addition of 0.2 mol/dm³ chlorobenzene. A spectrum almost exclusively due to the spin-adduct of benzyl radical (Fig. 1B) was observed on addition of 0.2 mol/dm³ benzyl chloride. In contrast, the spin-adduct of a phenyl-type radical (very probably *o*-methylphenyl radical) was observed on addition of *o*-chlorotoluene, but no formation of the benzyl-type radical.

The results indicate that short-lived free radicals are generated by the dissociative attachment of the electrons released by γ-rays to the chlorinated compounds and converted into the stable nitroxide radicals by the spin-trap. An alternative mechanism in which the free radicals are generated by the dissociation of the excited solutes resulting from the energy transfer from the solvent is excluded by the formation of the

phenyl-type radical from *o*-chlorotoluene. The bond energy for the benzyl–hydrogen bond (3.7 eV) is smaller than that for the phenyl–chlorine bond (4.1 eV),[7] so that the benzyl-type radical should be generated from the excited *o*-chlorotoluene.

The total energy for the dissociative electron attachment reaction is given by

$$E = BE(\text{R-Cl}) - EA(\text{Cl}) - E_s(\text{Cl}^-) - E(\text{e}^-), \quad (1)$$

where BE(R–Cl) denotes the C–Cl bond energy, and EA(Cl) the electron affinity of the chlorine atom, 3.6 eV.[7] The solvation energy of the chloride ion, $E_s(\text{Cl}^-)$, can be estimated to be 2.2 eV by the Born formula and from the ionic radius, 1.81 A,[7] and the dielectric constant of benzene, 2.28.[7] The energy of electron in benzene, $E(\text{e}^-)$, is -0.5 eV.[8] Thus eq. 1 is reduced to $E = BE(\text{R-Cl}) - 5.3$ eV. Since the C–Cl bond energy is generally smaller than 5.3 eV, the reaction is exothermic. Thus, the dissociative electron attachment readily occurs to give free radicals from chlorinated hydrocarbon solutes.

Propyl, butyl, α-methylbenzyl, and phenylethyl radicals can actually be generated by the dissociative electron attachment to the corresponding chlorides, and are detected by means of the spin-trapping technique. The hyperfine couplings of spin-adducts thus formed are in good agreement with those reported. The coupling constants for the spin-adduct of benzyl radical, 1.32 mT (two protons), 0.08 mT (two protons), and 1.48 mT (a nitrogen nucleus), differ slightly from the coupling constants observed in toluene solution, 1.362 mT, 0.083 mT, and 1.475 mT.[2] The solvent effect on the coupling constants is appreciable even between benzene and toluene.

Figure 2 shows the relation between radiation dose and the yield of the spin-adduct of butyl radical generated from butyl chloride. No influence of the dose rate indicates that the bimolecular recombination of butyl radicals is practically absent. The gradual decrease in the rate of formation of the spin-adduct with the radiation dose indicates that butyl radicals react competitively with the spin-traps and the spin-adducts. The latter reaction is generally found in spin-trapping studies and is important in the kinetic analysis of the spin-trapping reactions.[3,9]

The yield of the butyl radical spin-adduct is proportional to the concentration of the added butyl chloride: [spin-adduct] $= 1.8 \times 10^{-5}$ [butyl chloride] has been obtained for the spin-trap concentration of 0.01 mol/dm^3, the butyl chloride concentration lower than 0.4 mol/dm^3, and the radiation dose of 1×10^{19} eV g^{-1}.

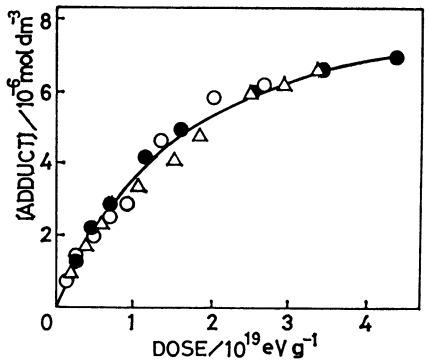

Fig. 2. Effect of dose and dose rate on the yield of the spin-adduct of butyl radical generated in the benzene solution containing the 0.01 mol/dm^3 spin-trap and 0.2 mol/dm^3 butyl chloride.
Key to the dose rate; ○, 3.6×10^{15} eV/g·s; ●, 7.6×10^{15} eV/g·s; △, 15.8×10^{15} eV/g·s.

The linear dependence suggests that the electrons disappear mostly in recombining with cations and only a small fraction of them react with butyl chloride. This is in line with a low G-value of the spin-adduct, 0.04, determined from the initial slope of the curve.

In conclusion, the spin-adducts of various free radicals can be authentically generated by the γ-irradiation of the benzene solutions, when the corresponding chlorinated compounds are available. The advantage of the present method lies in the fact that the ESR spectra of the spin-adducts can be recorded without interference of the spectra due to the by-product spin-adducts.

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