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Kinetic Studies of Spin Trapping Reactions.
II. Radiolysis of Cyclohexane

Takahisa Doba, Shoji Noda, and Hiroshi Yoshida*
Faculty of Engineering, Hokkaido University, Kita-ku, Sapporo 060

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In order to extend kinetic utilization of the spin-trapping techniques in radiation chemistry, γ-radiolysis of cyclohexane has been studied at room temperature using pentamethylnitrosobenzene as a spin trap. With increasing radiation dose, the cyclohexyl radical spin adduct has been found by ESR to form and then decay. Consumption of the spin trap has also been monitored by observing the optical absorption. The observed kinetic aspects indicate that the radiation-generated cyclohexyl radicals are completely trapped by $1.3\times10^{-4}-6.6\times10^{-4}$ mol dm^{-3} of the spin trap, and their *G*-value is 3.0. The spin-trapping rate constant has been determined to be 1.6×10^{7} mol^{-1} dm^{3} s^{-1} at 299 K based on the reported rate constant for the reaction between the cyclohexyl radical and tributylstannane. From the optical absorption study, dimeric pentamethylnitrosobenzene has been found to dissociate into the monomer, effective in the spin-trapping, with an equilibrium constant of 8×10^{-4} mol dm^{-3} in cyclohexane at 299 K. The monomer has an absorption coefficient of 48 mol^{-1} dm^{3} cm^{-1} at its absorption peak of 790 nm.

The spin-trapping technique has been developed recently[1,2] and widely used for the identification of free radical intermediates in radiation-chemical,[3–5] photochemical,[6–8] and thermal reactions.[9,10] A recent photochemical study[11] has revealed the problems inherent in this technique: the rate constant of spin-trapping reactions varies widely,[12–17] from 10^3 to 5×10^8 mol^{-1} dm^3 s^{-1}, they generally compete in a complex way with other radical reactions, and spin adduct radicals subsequently react with free radicals to be spin-trapped.[11] Therefore, knowledge of the reactivities of spin traps and spin adduct radicals is needed for the quantitative utilization of the technique.

The radiolysis of cyclohexane is one of the simplest radiation-chemical reaction systems where only atomic hydrogen and cyclohexyl radicals as free radical intermediates are expected. It has been one of the most extensively studied systems.[18–22] This appears as a model reaction system where the validity of the spin-trapping technique can be tested on a quantitative base. Iwahashi *et al.*[23] have applied the technique to this system using *N*-*t*-butyl-α-phenylnitrone (phenyl-*t*-butyl nitrone, PBN) as a spin trap and concluded that "the utilization of the spin trap for the quantitative estimation of products in the radiolysis of hydrocarbons is not a very good technique." In the present study, the spin-trapping technique has been applied to the radiolysis of cyclohexane by using pentamethylnitrosobenzene (PMNB). PMNB reacts with alkyl radicals with a rate constant two orders of magnitude greater than that of PBN so that the kinetic aspects of the spin-trapping are expected to be simpler for PMNB than for PBN.

Experimental

PMNB was synthesized from pentamethylbenzene through $C_6(CH_3)_5Tl(OCOCF_3)_2$,[24,25] and purified by recrystallization from acetone solution. Spectrograde cyclohexane was used without further purification. The monomer-dimer equilibrium and optical absorption of PMNB in cyclohexane solution were studied in the manner as described before.[25] For spin-trapping experiments, solutions of PMNB in cyclohexane were degassed by the freeze-pump-thaw technique at a vacuum of 10^{-5} Torr and sealed in sample cells, which consisted of a quartz ESR tube at one end and quartz optical absorption cell at the other.

Irradiations were conducted with ^{60}Co γ-rays at a dose rate of 2.0—14 krad/min at room temperature, *ca.* 300 K. The concentration of PMNB and that of the spin adduct radicals were simultaneously monitored by a recording spectrophotometer and an X-band ESR spectrometer, respectively.

Results and Discussion

Monomer-Dimer Equilibrium of PMNB in Cyclohexane. PMNB dissolved in cyclohexane is in part present in the dimeric form. Monomeric PMNB has a weak optical absorption with a maximum at 790 nm, while dimeric PMNB has a strong absorption band with a maximum at 327 nm. According to the relationship, $c/A=1/2\varepsilon+A/K\varepsilon^2$ where c is the total concentration of PMNB, A is the absorbance at 790 nm, K the equilibrium constant and ε the molar absorption coefficient, K and ε for PMNB are determined to be 8×10^{-4} mol·dm^{-3} and 48 mol^{-1} dm^3 cm^{-1} at 299 K from the observed linear dependence of c/A on A as shown in Fig. 1. Thus, 45 to 80% of PMNB is in the monomeric form and is effective in spin-trapping free radical intermediates, when dissolved in cyclohexane at the total concentration of 10^{-3} to 10^{-4} mol dm^{-3}. This behavior of PMNB is very similar to that reported previously

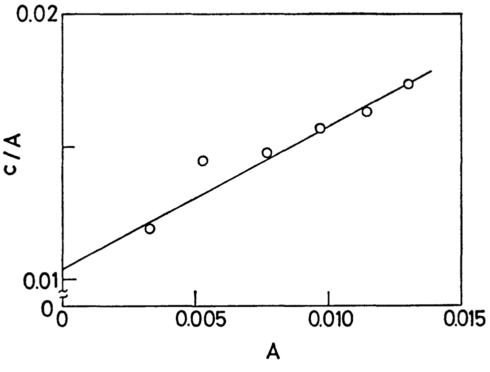

Fig. 1. The relationship between the absorbance, *A*, at 790 nm and the total concentration of PMNB, *c*, in cyclohexane at 299 K.

in benzene solution.[25,26]

Radiation-Chemical Reactions of Cyclohexane Solutions of PMNB. ESR spectra observed from the γ-irradiated solutions show a triple-doublet hyperfine structure, as shown in Fig. 2, with coupling constants of 1.40 and 0.76 mT. These have been attributed to the spin adducts of the cyclohexyl radical. Neither the spin adduct of hydrogen nor that of other free radicals could be observed by ESR. The cyclohexyl radical spin adducts decay after γ-irradiation to *ca.* 70% of the initial amount during the first hour, and then remain almost unchanged. The decay cannot be attributed to either the self-decomposition of the spin adducts or their recombination, but is probably due to reactions with some radiolytic products.

The dependence of the yield of spin adducts on the radiation dose is shown, typically in Fig. 3 for a dose rate of 14 krad/min. The yield increases at first with the initial slope independent of the PMNB concentration in the range of 6.6×10^{-4}—1.3×10^{-4} mol dm^{-3}, reaching a maximum dependent on the PMNB concentration, and then decreases to zero. The *G*-value of the spin adduct formation determined to be 3.0 from the initial slope independent of the PMNB concentration. The decrease of the dose rate to 3.3 krad/min gives no change in the *G*-value. Thus, the cyclohexyl radicals are believed to be effectively spin-trapped by PMNB, and the recombination reactions between themselves is absent at the dose rates examined.

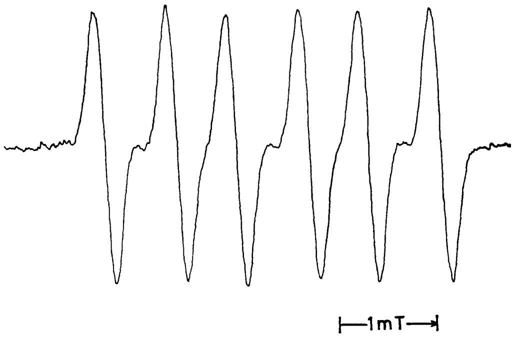

Fig. 2. ESR spectrum of pentamethylphenyl cyclohexyl nitroxide (spin adduct radical) obtained from the γ-radiolysis of cyclohexane in the presence of PMNB at room temperature.

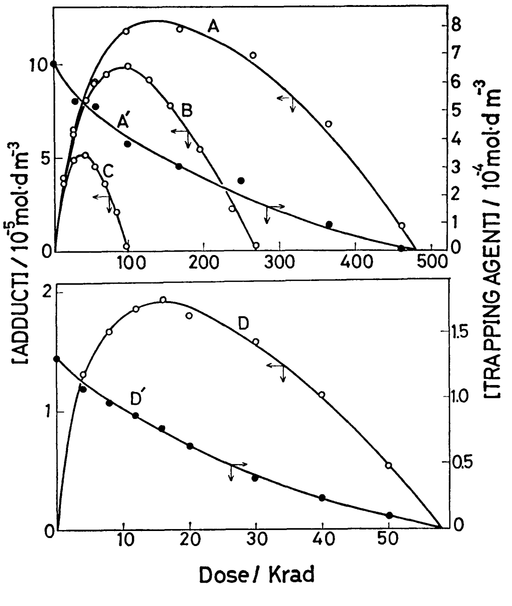

Fig. 3. The dependence of the concentration of the spin adducts (○) and that of the spin trap (●), PMNB, on the radiation dose, at the PMNB concentration (A, A′) 6.6×10^{-4}, (B) 4.4×10^{-4}, (C) 2.2×10^{-4}, and (D, D′) 1.3×10^{-4} mol dm^{-3}.

The *G*-value of the cyclohexyl radical spin adducts has been reported to be 3 for the γ-radiolysis of cyclohexane containing PBN as a spin trap.[23] In that case, the *G*-value is slightly dependent on the PBN concentration in the range 0.1—0.01 mol dm^{-3} due to the low reactivity of PBN towards alkyl radicals.[11] It is worth noting that the *G*-values determined by the spin-trapping techniques are generally smaller than the *G*-value of 4.0 determined by using iodine as a radical scavenger.[19]

The change of the PMNB concentration with increasing radiation dose is shown in Fig. 3, representatively for the highest and the lowest initial concentrations of PMNB. The spin traps are completely consumed at the time when the spin adduct concentration reaches zero. Such an exact coincidence indicates that the same entities are responsible for both the formation and the decay of the spin adducts. Therefore, the spin adducts and the spin traps compete with each other in reacting with cyclohexyl radicals. Such a situation is very much like that previously reported for 2-methyl-2-nitrosopropane and *t*-butyl radical in a photochemical reaction system.[11]

Rate Constants and Reaction Kinetics. The change in the spin adduct concentration can essentially be expressed by the following two processes,

$$\mathrm{R}\cdot + \mathrm{T} \xrightarrow{k_1} \mathrm{A}, \tag{1}$$

$$\mathrm{R}\cdot + \mathrm{A} \xrightarrow{k_2} \text{diamagnetic product(s)}, \tag{2}$$

where R·, T, and A represent the cyclohexyl radical, the spin trap (PMNB), and the spin adduct, respectively. Assuming that PMNB is entirely monomeric, the rate equation

$$\frac{d[\mathrm{A}]}{d[\mathrm{T}]} = \frac{k_2}{k_1}\cdot\frac{[\mathrm{A}]}{[\mathrm{T}]} - 1 \tag{3}$$

is readily derived and integrated as

$$\frac{[\mathrm{A}]}{[\mathrm{T}]_0} = \frac{1}{\alpha-1}\cdot\frac{[\mathrm{T}]}{[\mathrm{T}]_0}\left\{1-\left(\frac{[\mathrm{T}]}{[\mathrm{T}]_0}\right)^{\alpha-1}\right\} \tag{4}$$

with the initial condition that $[\mathrm{A}]=0$ for $[\mathrm{T}]=[\mathrm{T}]_0$. α is the ratio of the rate constants, k_2/k_1. According to the above equation, the dependence of [A] on [T] is shown by the plots in Fig. 4 for several values of the variable parameter α. Figure 4 shows some of the aspects of general importance in the spin-trapping technique. As the spin-trapping reaction proceeds (the $[\mathrm{T}]/[\mathrm{T}]_0$ value decreases from unity to zero), the adduct radical concentration reaches a maximum value which is proportional to the initial spin trap concentration. If α is too large, the adduct radical concentration cannot be enough for the ESR detection of the adduct radical.

The dependence of [A] on [T] has been experimen-

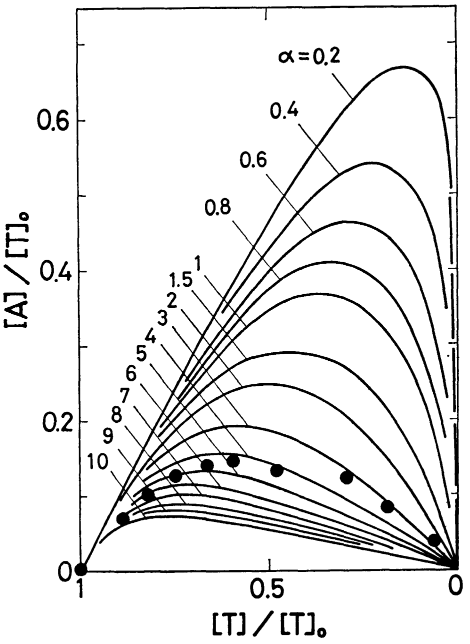

Fig. 4. The relationship between the concentration of the spin adduct and that of the spin trap, PMNB, normarlized by the initial concentration of PMNB. Theoretical curves are derived for several α values based on the Eq. 4, and experimental results (●) are obtained for the initial concentration of PMNB of 1.3×10^{-4} mol dm^{-3} at room temperature.

tally examined for the initial PMNB concentration, $[T]_0$, of 1.3×10^{-4} mol dm^{-3} and the plot is shown in Fig. 4. At this $[T]_0$ value, more than 75% of PMNB is monomeric. The plots fall in the range of $\alpha=3$ to 5. The determined value of α includes errors due to the assumptions of totally monomeric PMNB, and the disregard of the instability of the spin adduct, but it indicates undoubtedly that $k_2 > k_1$. The assumed negligibility of the bimolecular recombination of the cyclohexyl radicals (important when the PMNB concentration becomes very low) and the possible effects of hydrogen atoms may also be explain the experimental plot's derivation from the single curve expected from Eq. 4.

The spin-trapping rate constant, k_1, can generally be determined by competition experiments with reactions having known rate constant, *e.g.* the reaction of the cyclohexyl radical with tributylstannane,

$$\dot{C}_6H_{11} + (C_4H_9)_3SnH \xrightarrow{k_5} C_6H_{12} + (C_4H_9)_3Sn\cdot, \qquad (5)$$

was chosen as a reference reaction, for which the rate constant has been reported to be 1.2×10^6 mol^{-1} dm^3 s^{-1} at 298 K in cyclohexane.[27] The ratio of the initial slope of spin adduct concentration *vs.* radiation dose curve in the absence and presence of tributylstannane was found to agree with the expected linear relationship,

$$\frac{d[A]}{d[A]'} = 1 + \frac{k_5[S]}{k_1[T]}, \qquad (6)$$

as shown in Fig. 5, where $[A]'$ represents the concentrations of the spin adducts generated in the presence of tributylstannane, S. The rate constant, k_1, obtained from the slope of the straight line was found to be 1.6×10^7 mol^{-1} dm^3 s^{-1}. This value is smaller than that for the spin-trapping of *t*-butyl radicals by PMNB in benzene solution determined by using the same reference reaction, 9×10^7 mol^{-1} dm^3 s^{-1}.[11,25]

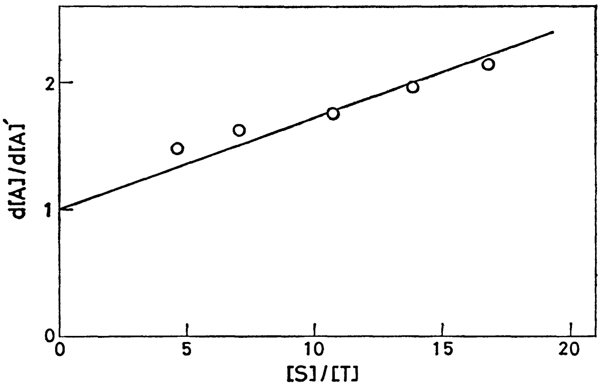

Fig. 5. The dependence of the rate of the spin adduct formation on the concentration of radical scavenger, tributylstannane, in cyclohexane at 299 K.

Conclusion

Simultaneous monitoring of both the spin traps and the spin adducts revealed radiation-chemical processes in the γ-radiolysis of cyclohexane solutions of PMNB. The most significant results are: (1) PMNB is an efficient spin trap such that the cyclohexyl radicals generated with *G*-value of 3.0 are thoroughly spin-trapped, (2) the cyclohexyl radical spin adducts readily disappear in the subsequent reaction with the cyclohexyl radicals. The explanation for the *G*-value of the cyclohexyl radical determined by the spin-trapping technique being smaller than the generally accepted value of ≈ 4 remains unknown.[28] The former results implies however that the spin-trapping technique has a future in the kinetic studies of radiation chemistry with the proper choice of the spin trap based on the rate data of the spin-trapping reactions to be accumulated further. The latter further complicates the kinetic aspects of the spin-trapping. Generally, the data on PMNB, such as the absorptivity, the monomer–dimer equilibrium, and the spin-trapping rate constant, serve as a basis to extend the spin-trapping technique to study the kinetics of free radical intermediates.

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