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Energy Transfer in γ-Irradiated Cyclohexane-Benzene Mixture Studied by Spin Trapping-ESR Technique

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Synopsis. Cyclohexyl and phenyl radicals were detected in γ-irradiated cyclohexane–benzene mixtures by a spin trapping-ESR technique. The dependence of the radical yields upon mixture composition showed that energy transfer occurs efficiently from cyclohexane to benzene with the transfer efficiency of *ca.* 0.5 dm^3 mol^{-1}.

The rate of energy transfer in cyclohexane solutions is equal to or larger than that expected for a diffusion process,1,2) so that the energy transfer will play an important role in the radiation chemistry of the cyclohexane–benzene mixture. The cyclohexane–benzene mixture is one of the typical systems in which the role of the energy transfer in radiation-chemical reactions has been the most extensively studied.3) However, there still remains an ambiguity about the efficiency of the energy transfer from an excited cyclohexane to benzene.2–4)

In this study, the spin trapping technique was utilized to detect cyclohexyl and phenyl radicals produced from cyclohexane and benzene, respectively, and to elucidate further the energy transfer in γ-irradiated cyclohexane-benzene mixture. The spin trapping has been demonstrated to be a pertinent technique to study free radicals in γ-irradiated systems not only qualitatively but also quantitatively.5,6) The present spin trapping study will supplement the conventional product analysis methods,3) and the fluorescence spectroscopic method7) which have been used in the previous studies on the energy transfer. Pentamethylnitrosobenzene (PMNB) is an efficient spin-trap for carbon-centered radicals8) and is used in this study.

Experimental

Cyclohexane and benzene of spectrograde were used as received. PMNB was synthesized and purified as described previously.8) Each solution was degassed by the freeze-pump-thaw technique at a vacuum of 10^{-3} Pa and sealed in a quartz ESR tube. The sample was γ-irradiated and the ESR spectrum was recorded by a conventional x-band ESR spectrometer, both at ambient temperature.

Results and Discussion

The spin adduct of cyclohexyl radical was detected from the γ-irradiated cyclohexane solution containing PMNB; its *G*-value (yield for 100 eV energy absorbed) was 2.9, as reported previously.5) The spin adduct of phenyl radical was detected from the γ-irradiated benzene solution containing PMNB; its *G*-value was found to be 0.06. The spin adducts of both the radicals were observed from cyclohexane–benzene mixtures. A typical ESR signal is shown in Fig. 1; the signal is the superposition of a broad six-line spectrum due to the cyclohexyl radical-spin adduct and a sharp multiplet one due to the phenyl radical-spin adduct.8,9)

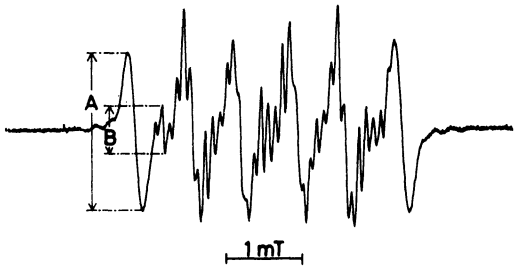


Fig. 1. ESR spectrum recorded from γ-irradiated cyclohexane–benzene mixture (benzene mole fraction, $f_{\mathrm{B}}=0.55$) containing 10^{-2} mol dm^{-3} PMNB at room temperature. *G*-values of cyclohexyl and phenyl radicals were calculated from the line intensities, A and B, in referring to the spectra due to the spin adducts of these radicals recorded from cyclohexane or benzene solution.

Although the yield of the spin adducts depended on the PMNB concentration, 10^{-2} mol dm^{-3} of PMNB was found to be sufficient to trap all the scavengeable radicals in the γ-irradiated cyclohexane–benzene mixtures. The yields of spin adducts increased linearly with dose up to ≈200 Gy. Therefore, the *G*-values were determined by irradiating 10^{-2} mol dm^{-3} PMNB solutions to a dose of 100 Gy. The decay of the spin adducts was so slow that it need not to be taken into account for the present determination of the yields of the free radicals by the spin trapping technique.

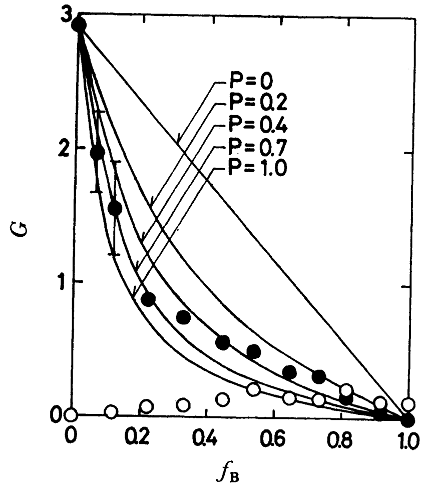
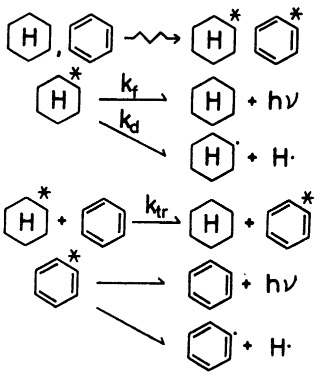


Fig. 2. Dependence of *G*-values of (●) cyclohexyl radical and (○) phenyl radical in γ-irradiated cyclohexane–benzene mixture on the mole fraction of benzene, f_{B}, at room temperature. The dependence was calculated from Eq. 2 for cyclohexyl radical, and shown by curves for the energy transfer efficiency, *P*, of 0, 0.2, 0.4, 0.7, and 1.0.

Figure 2 shows the *G*-values of cyclohexyl and phenyl radicals as a function of the mole fraction of benzene, f_B, in cyclohexane–benzene mixtures. The experimental points without error bars in Fig. 2 have an uncertainty of 20%, which comes from the rapid decay of the spin adducts due to a very minute amount of impurities. The larger error in the low benzene fraction region comes from the steep variation of a yield curve in this region. The addition of a small amount of benzene remarkably reduced the cyclohexyl radical yield, and the further addition of benzene reduced it only slowly. A similar dependence of f_B has been reported for the yields of products³⁾ and of the emission from excited cyclohexane.⁷⁾ The yield of phenyl radical increased with the increasing of f_B, passed a maximum at f_B of about 0.7, and decreased to the value in the pure benzene. These results indicate that the excitation energy transfer occurs efficiently from cyclohexane to benzene.

The relevant reaction scheme will be as follows:



The cyclohexyl and phenyl radicals were spin-trapped and detected. H atoms will form simultaneously and react either with PMNB or with benzene to result in the formation of spin adducts of H or cyclohexadienyl radicals. However, they could not be detected, because the former are unstable(10) and the latter are not reactive with PMNB.(11)

Based on the reaction scheme, the yield of cyclohexyl radical, $G(C_6H_{11}\cdot)$, is given by the following relationship:

$$G(C_6H_{11}\cdot) = G_0(C_6H_{12}^*)\frac{k_d(1-f_B)}{k_f+k_d+k_{tr}[C_6H_6]}, \qquad (1)$$

where $G_0(C_6H_{12}^*)$ represents the yield of singlet-excited cyclohexane in pure cyclohexane. Equation 1 leads to:

$$G(C_6H_{11}\cdot)/G_0(C_6H_{11}\cdot) = (1-f_B)/(1+P[C_6H_6]), \qquad (2)$$

were $G_0(C_6H_{11}\cdot)$ is the yield of cyclohexyl radical in pure cyclohexane ($f_B=0$) and *P* is the energy transfer efficiency, $k_{tr}/(k_f+k_d)$. The curves expected from Eq. 2 are also shown in Fig. 2 for selected values of *P*. Although experimental points do not fall on a single curve, they show that $P=0.5\pm0.3$ mol^{-1} dm^3. The apparent deviation from the additive law (from the straight line for $P=0$) shows that some energy transfer occurs from cyclohexane to benzene.

The energy transfer efficiency has been determined to be 4(2) and 0.65—0.84 mol^{-1} dm^3 (3) by means of the conventional product analysis and 2.8 mol^{-1} dm^3 by using a radical scavenger such as DPPH and the fluorescence spectroscopic method.(7) The *P* values obtained in the present and previous steady-state studies are in satisfactory agreement. In contrast, a *P* value of as large as 60 mol^{-1} dm^3 has been reported based on the pulse radiolysis-transient optical emission study.(4) The reason for such a big difference between steady-state and transient methods is not known at the moment.

The yield of the phenyl radical, $G(C_6H_5\cdot)$, shows a peak at about 0.7 of f_B. The peak should appear if $G_0(C_6H_{12}^*)$ is larger than the yield of the singlet excited benzene in pure benzene ($f_B=1$), $G_1(C_6H_6^*)$, and *P* is larger than $G_1(C_6H_6^*)/\{G_0(C_6H_{12}^*)-G_1(C_6H_6^*)\}$-$[C_6H_6]_1$ ($[C_6H_6]_1$ is the benzene concentration at $f_B=1$). $G_1(C_6H_6^*)$ has been reported to be 1.6.(12) On the other hand, the value of $G_0(C_6H_{12}^*)$ has not been unequivocally determined; it has been reported to be 1.4—1.7(13) and 0.3.(14) The latter value seems to be far too small to fulfill the condition for the $G(C_6H_5\cdot)$ peak to appear.

In conclusion, the spin trapping technique has provided a new approach to the energy transfer in the γ-irradiated cyclohexane–benzene mixture based on the *G*-values of free radicals involved. This study will show the validity of the quantitative, kinetic utilization of the spin trapping technique.

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