The Application of the Spin Trap, Phenyl *t*-Butyl Nitrone, to the Study of the γ-Radiolysis of Cyclohexane

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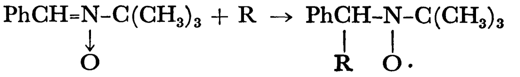
It was shown that cyclohexyl radicals formed by the γ-radiolysis of cyclohexane were trapped by phenyl *t*-butyl nitrone (PBN) to give a nitroxide with a well defined ESR spectrum. We measured the yield of this nitroxide. In order to establish the radical and electron scavenging properties of PBN, we measured the effect of this compound on the yields of hydrogen and nitrogen by adding dinitrogen oxide in cyclohexane together with PBN. The results suggested that PBN is able to scavenge not only free radicals but also electrons. The following relative rates were obtained: $k(e^- + PBN \rightarrow PBN^-)/k(e^- + N_2O \rightarrow N_2O^-) = 0.7$ and $k(H + PBN \rightarrow HPBN)/k(H + C_6H_{12} \rightarrow H_2 + C_6H_{11}) \approx 200$ at room temperature. The *G*-value of the scavengeable hydrogen atoms from cyclohexane was estimated to be 3.4 ± 0.4.

The spin trapping technique has been applied to detect the short-lived free-radicals produced in various chemical reactions.[1] Since Eiben and Fessenden[2] used this technique in the study of the three primary species (e^-_{aq}, H, OH) produced in the radiolysis of water, this technique has been used in radiation chemistry, especially for the radiolysis of aqueous solutions,[3] water,[4] and alcohols.[5,6] So far, there seems to have been only one report about liquid alkanes.[7] Here, we wish to report the results obtained in the γ-radiolysis of cyclohexane using phenyl *t*-butyl nitrone (PBN) as a spin trap.

The radiolysis of cyclohexane has been studied extensively in many laboratories and it is now well known that the main radicals produced in the primary reaction are cyclohexyl radicals and hydrogen atoms. PBN as a spin trap reacts easily with free-radicals to produce relatively stable nitroxide and this nitroxide has a characteristic ESR spectrum.



$$\mathrm{PhCH{=}\underset{\underset{O}{\downarrow}}{N}{-}C(CH_3)_3} + \mathrm{R} \rightarrow \mathrm{Ph\underset{\underset{R}{|}}{CH}{-}\underset{\underset{O\cdot}{|}}{N}{-}C(CH_3)_3} \qquad (1)$$

When we apply this technique to the study of the mechanism of the γ-radiolysis of liquid alkane, it is necessary to check the reactivity of PBN with free-radicals and electrons.

Experimental

PBN was prepared by the method of Emmons.[8] Cyclohexane (pure grade, Tokyo Kasei Kogyo Co.) was purified by being passed through an activated silica gel column.

For the ESR measurement, a constant volume (0.25 ml) of cyclohexane containing a certain concentration of PBN was sealed in a 4 mm i.d. Suprasil quartz tube in a mercury-free vacuum system. These samples were γ-irradiated with ^{60}Co γ-rays at a dose rate of 3.4×10^{17}—5.5×10^{18} eV g^{-1} h^{-1} at room temperature to a total dose 5×10^{15}—5×10^{17} eV g^{-1}. These samples were measured with a JEP-1 X-band ESR spectrometer with a field modulation of 100 kHz. The spin concentration was estimated by comparing integrated area of the spectrum with that of DPPH.

For the product analysis, 1 ml of cyclohexane–PBN solution was γ-irradiated. The yields of hydrogen and nitrogen were measured with a Toepler-McLeod gauge which was attached to a cuprous oxide furnace. The columns used for the gas chromatographic analysis were PEG-600: 2 m long for bicyclohexyl and dimethylsulfolane: 6 m long for cyclohexene.

Results

The γ-radiolysis of 0.1 M PBN solution in cyclohexane at room temperature gave the spectrum shown in Fig. 1. The spin adduct was quite stable at room temperature; no appreciable decay could be observed over one day. The spectrum was a triplet of doublets with $a^N \approx 14.5 \pm 0.2$ G and $a^H{}_\beta \approx 2.2 \pm 0.2$ G, which are characteristic to a cyclohexyl radical spin adduct. However, no hydrogen atom and electron spin adducts were detected.

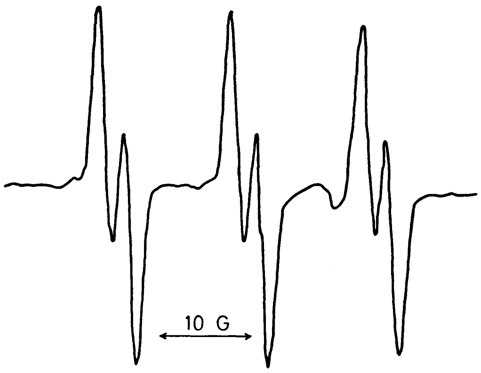


Fig. 1. A typical ESR spectrum of 0.1M PBN solution in cyclohexane after γ-radiolysis at room temperature.

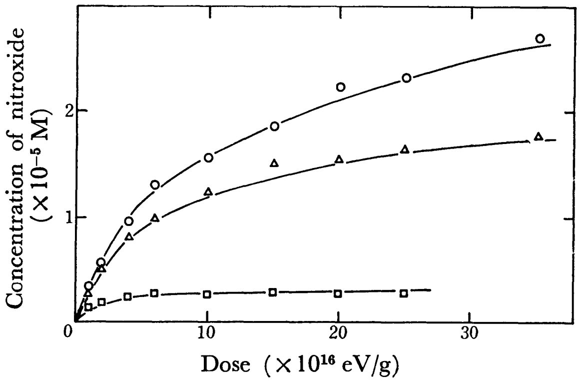


Fig. 2. The yield of nitroxide I as a function of radiation dose. PBN concentration; ○: 0.1 M, △: 0.05 M, □: 0.01 M.

Figure 2 shows the yields of the spin adduct as functions of the irradiation dose for 0.1, 0.05, and 0.01 M PBN solutions in cyclohexane. The yields are not linear with dose. This suggests that secondary reactions which destroy the spin adduct are occurring during the radiolysis. As the dose increases, the increasing rate of the yield decreases and the yield has a tendency to saturate. The saturating values are dependent on the PBN concentration.

Figure 3 shows the relation between the yield of the spin adduct and the dose rate for 0.1 M PBN solution. The yields show little dependence on the dose rate. This suggests that the reaction between two cyclohexyl radicals is not important compared with the reaction of cyclohexyl radicals with PBN to produce spin adducts.

Figure 4 shows the reciprocal of the *G*-value of spin adduct *vs.* the irradiation dose. Extrapolation to zero dose gives the results for the primary *G*-values of 3.1±0.5, 2.9±0.5, and 2.8±0.5 respectively for 0.1, 0.05, and 0.01 M solutions.

In order to study the reaction of PBN in the radiolysis of cyclohexane, we measured the yields of several products from the γ-irradiated solutions. Figure 5 shows the yield of hydrogen. Figures 6 and 7 compare the yields of nitrogen and hydrogen respectively *vs.* the concentration of dinitrogen oxide in cyclohexane without PBN and with 0.1 M PBN. Solid lines are theoret-

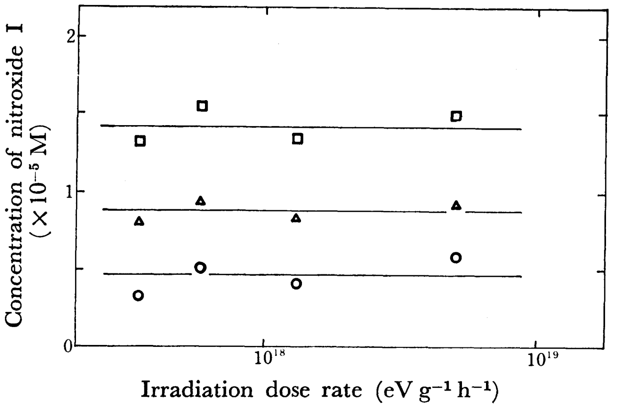


Fig. 3. The yield of nitroxide I as a function of radiation dose rate. Total dose; ○: 3.0×10^{16}, △: 5.0×10^{16}, □: 1.0×10^{17} eV g^{-1} at room temperature.

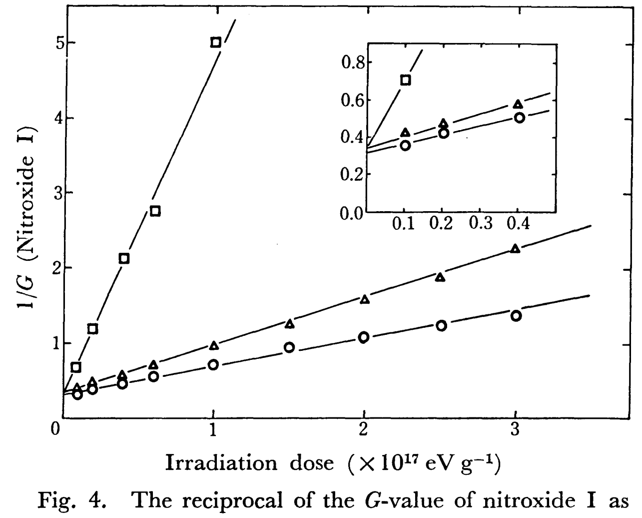


Fig. 4. The reciprocal of the *G*-value of nitroxide I as a function of radiation dose. PBN concentration; ○: 0.1 M, △: 0.05 M, □: 0.01 M.

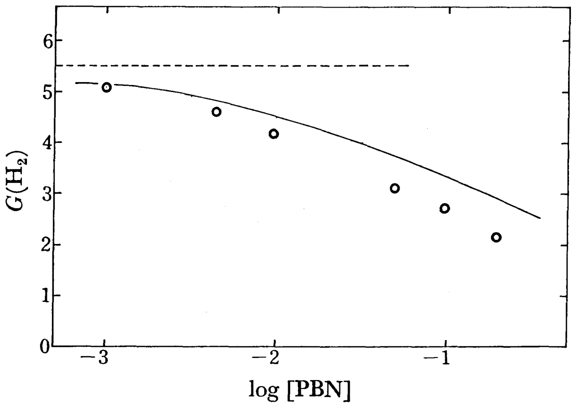


Fig. 5. The *G*-value of hydrogen molecule as a function of PBN concentration. The solid line is the theoretical fit (see in the text).

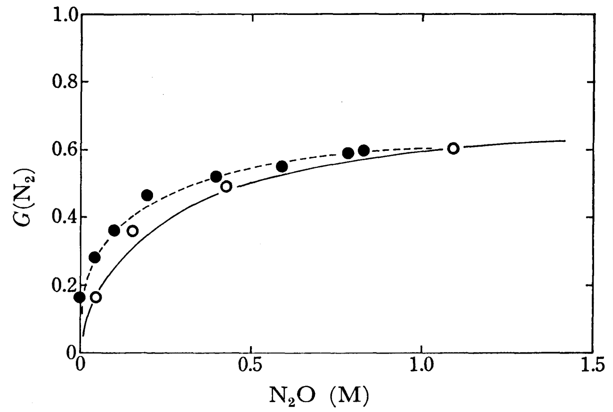


Fig. 6. The *G*-value of nitrogen as a function of the concentration of dinitrogen oxide. The total dose is 5.2×10^{19} eV g^{-1} at room temperature (○). The plots of cyclohexane without PBN refers to the paper of Takeuchi *et al.* (●).[13] The solid line is obtained from the relation proposed by Schuler *et al.*[11,12]

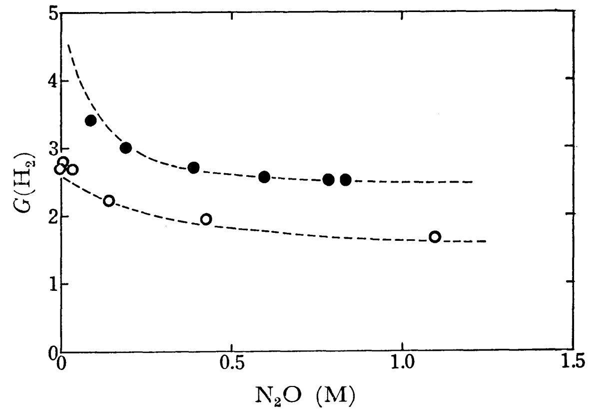


Fig. 7. The *G*-value of hydrogen molecule as a function of the concentration of dinitrogen oxide. The total dose is 5.2×10^{19} eV g^{-1} at room temperature (○). The plots of cyclohexane without PBN refers to the paper of Takeuchi *et al.* (●).[13]

TABLE 1. THE EFFECTS OF THE RADICAL SCAVENGERS ON THE G-VALUES OF PRODUCTS IN THE γ-RADIOLYSIS OF CYCLOHEXANE

Radical scavenger	Total dose (eV g^{-1})	Products	
		(c-C_6H_{11})$_2$	c-C_6H_{10}
$C_3H_7SSC_3H_7$[17]	1.0×10^{19}	0.15	1.10
C_3H_7SH[18]	1.5×10^{19}	0.26	1.57
O_2[15]	$\geq2.5\times10^{19}$	0.29	1.49
p-Benzoquinone[15]	12.8×10^{19}	0.29	1.54
PBN (This work)	5.4×10^{19}	0.34	1.52

ical fits (see Discussion). Table 1 summarizes the yields of bicyclohexyl and cyclohexene in a γ-irradiated cyclohexane containing 0.1 M PBN together with the yields obtained by using different radical scavengers.

Discussion

The transient radicals produced in the radiolysis of cyclohexane are cyclohexane ion, electron, hydrogen atom, and cyclohexyl radical.[9] In the present experiment, the cyclohexyl radicals were identified as the nitroxide I:

$$C_6H_{11} + PBN \rightarrow (PBN)\text{-}C_6H_{11}\,. \qquad \text{I} \quad (2)$$

However, no other nitroxides could be observed, even though they were thought to be formed by the trapping of $C_6H_{12}^+$, e^-, and H by PBN. This does not necessarily mean that PBN does not react with them. In the study of the radiolysis of water in the presence of PBN, Sargent and Gardy suggested the existence of $(PBN)^-$.[4] On the other hand, the formation of (PBN)-H has been actually observed by ESR in the γ-radiolysis of methanol at low temperature[6] and during the radiolysis of water.[4] In the γ-radiolysis of hydrocarbon at room temperature, however, the formation of (PBN)-H has not been reported, except for the paper by Mao and Kevan.[7] Consequently, we think that nitroxides II and III are unstable and decay before the ESR measurement at room temperature:

$$e^- + PBN \rightarrow (PBN)^- \qquad \text{II} \quad (3)$$

$$H + PBN \rightarrow (PBN)\text{-}H\,. \qquad \text{III} \quad (4)$$

The curves shown in Fig. 2 have the same tendency as that obtained by Mao and Kevan in the γ-irradiated methanol containing PBN.[6] The nitroxide I may be attacked by cyclohexyl radicals or hydrogen atoms during the γ-irradiation:

$$(PBN)\text{-}C_6H_{11} + C_6H_{11} \rightarrow X\,, \qquad (5)$$

$$(PBN)\text{-}C_6H_{11} + H \rightarrow Y\,. \qquad (6)$$

As the concentration of PBN can be thought to change little during the γ-irradiation, the rate of formation of nitroxide I may be constant (Reaction 2). If this nitroxide I is consumed by the secondary reactions 5 and 6, we can derive the following relation for the steady-state treatment:

$$[(PBN)\text{-}C_6H_{11}] = A[PBN](1-\exp(-Bt))\,. \qquad (I)$$

Here, A stands for $k_2[C_6H_{11}]/(k_5[C_6H_{11}]+k_6[H])$ and B for $k_5[C_6H_{11}]+k_6[H]$. This relation can explain qualitatively the experimental result that saturating values are proportional to the concentration of PBN.

The hydrogen producing process in the γ-radiolysis of cyclohexane may be described as follows:

$$C_6H_{12} \rightsquigarrow C_6H_{12}^+ + e^- \rightarrow C_6H_{11} + H\,, \qquad (7)$$

$$\rightarrow C_6H_{10} + H_2\,, \qquad (8)$$

$$\rightarrow (C_6H_{11})_2 + H_2\,, \qquad (9)$$

$$\rightsquigarrow C_6H_{12}^* \rightarrow C_6H_{11} + H\,, \qquad (10)$$

$$\rightarrow C_6H_{10} + H_2\,, \qquad (11)$$

$$\rightarrow (C_6H_{11})_2 + H_2\,, \qquad (12)$$

$$H + C_6H_{12} \rightarrow H_2 + C_6H_{11}\,. \qquad (13)$$

Reactions 9 and 12 explain the formation of bicyclohexyl which is not suppressed by the presence of radical scavenger (Table 1). There are two processes in which PBN disturbs the formation of hydrogen: one is the capture of electrons produced in Reaction 7 and the other is the capture of hydrogen atoms produced in Reactions 7 and 10.

In order to determine the ability of PBN to capture electrons, we measured the yield of nitrogen from the 0.1 M PBN solution in the presence of dinitrogen oxide, which is a well known electron scavenger:[10]

$$e^- + N_2O \rightarrow N_2O^- \rightarrow \delta N_2\,. \qquad (14)$$

$$(1\leq\delta\leq2)$$

Figure 6 shows the results. Obviously, the yield of nitrogen was decreased by the presence of PBN. Schuler *et al.*[11,12] proposed an analytical treatment for the radiolysis system in which two electron scavengers are present. Using their technique, we estimated that $k_3=1.7\times10^{12}\ M^{-1}\ s^{-1}$. Here, we assumed $k_{14}=2.4\times10^{12}\ M^{-1}\ s^{-1}$.[13]

With k_3 estimated, we can calculate the G-value of hydrogen in the presence of PBN, if PBN does not scavenge hydrogen atoms. The calculated result is shown in Fig. 5 as the solid line. The difference between the solid line and the experimental plots must be due to the hydrogen-atom-scavenging by PBN.

The decrease in the G-value of hydrogen, $\Delta G(H_2)$, can easily be derived from the steady-state treatment of Reactions 4 and 7—13:

$$\Delta G(H_2) = \Delta G(H_2)_r + \Delta G(H_2)_i\,,$$

$$= G_0(H) - \frac{k_{13}[C_6H_{12}]}{k_4[PBN]}\Delta G(H_2)_r. \qquad (II)$$

Here, $G_0(H)$ stands for the G-value of hydrogen atoms in the γ-radiolysis of pure cyclohexane, $\Delta G(H_2)_i$ for the decrease of hydrogen due to the electron scavenging by PBN, and $\Delta G(H_2)_r$ for the decrease due to the hydrogen-atom-scavenging by PBN. $\Delta G(H_2)_i$ can be calculated with the value of k_3, while $\Delta G(H_2)_r$ can be estimated from the experimental data. Figure 8 shows the plots between $\Delta G(H_2)$ and $\Delta G(H_2)_r/[PBN]$. From this linear relationship, we can estimate the following values: $G_0(H)=3.4\pm0.4$ and $k_{13}/k_4=(6.0\pm0.6)\times10^{-3}$.

The decrease in the G-value of hydrogen in the presence of dinitrogen oxide together with PBN is shown in Fig. 7. The difference between the G-value with PBN and without PBN must be due to the hydrogen-atom-scavenging by PBN.

The effect of PBN on the yields of bicyclohexyl and cyclohexene is shown in Table 1, together with some

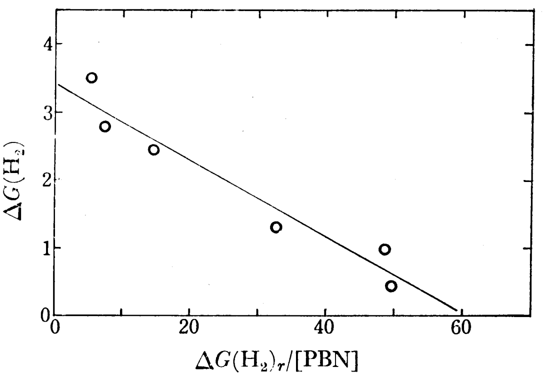


Fig. 8. The decrease in the G-value of hydrogen molecule as a function of $\Delta G(H_2)_r/[PBN]$. (Relation (II))

past data of radical scavengers. There is little difference between them, except in the case of di-*n*-propyl disulfide. It can thus be understood that PBN is one of the good radical scavengers.

Cyclohexane is probably the most popular hydrocarbon for the study of radiolysis. In spite of a large number of investigations, however, the quantitative assessment of the yields of the products from the radiolysis of cyclohexane such as the G-values of electrons, hydrogen atoms, and cyclohexyl radicals have not been settled yet. Only the G-value of hydrogen molecules seems to have reached a final assessment: $G(H_2)=5.7\pm0.2$.[14,15] For the G-value of electrons two values are proposed: One is about 4.0,[11] the other is around 5.2.[16] Both values were estimated by extrapolation to the infinite concentration of radical scavenger on the assumption of a certain reaction mechanism. The discrepancy between the two values is obviously beyond the experimental error. This difference is strongly connected to the fundamental interpretation of the radiolysis of hydrocarbons.

In the present study, we have estimated the G-value of hydrogen atoms. So far, this value has been estimated from the effect of the radical scavenger on the G-value of the hydrogen molecules produced; however, as is well known, the reaction of each radical scavenger is not clear cut. As has been stated above, the reaction of the spin trap, PBN, is also not clear cut; moreover, the spin adducts produced are not stable for reactive species. This fact complicates the analysis. Consequently, we regretfully have to say that the utilization of the spin trap for the quantitative estimation of the products in the radiolysis of hydrocarbons is not a very good technique.

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