BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (7), 1670—1673 (1977)

The Electron Capture by Bromobenzene in the γ-Radiolyses of Cyclohexane and 2,2,4-Trimethylpentane

Hidetoshi KARASAWA, Eung-Ryul KIM, and Shin SATO

Department of Applied Physics, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

(Received November 22, 1976)

The γ-radiolyses of cyclohexane and 2,2,4-trimethylpentane have been reinvestigated. Bromobenzene was used as the electron scavenger. The analysis of the G-values of benzene obtained at high concentrations of bromobenzene showed that the empirical formula proposed by Hummel for the electron scavenging

$$G = G_{\mathrm{fi}} + G_{\mathrm{gi}}\{1-\exp(-\sqrt{\alpha S})\}$$

is better than that proposed by Warman *et al.* The values of $G_{\mathrm{fi}}+G_{\mathrm{gi}}$ thus obtained were 3.7 ± 0.3 for cyclohexane and 3.5 ± 0.2 for 2,2,4-trimethylpentane. The bromobenzene-concentration dependence of the G-values of hydrogen and methane from 2,2,4-trimethylpentane was well explained by the hypothesis that the lifetimes of the 2,2,4-trimethylpentane ion for the decomposition are in the same order as the time needed for the geminate recombination.

Bromobenzene is an efficient electron scavenger in the radiolysis of hydrocarbon. As the product of the electron scavenging reaction, benzene is formed, in amounts which can easily be estimated by gas chromatography.[1] In this paper we wish to report the G-values of benzene, hydrogen, and methane from cyclohexane and 2,2,4-trimethylpentane solutions as functions of the concentration of bromobenzene.

Such studies have been carried out by many radiation chemists in order to clarify the initial process of the radiation chemistry of hydrocarbons. Although many aspects of the initial process have been clarified by this method, one of the most interesting values has not yet been finally assessed—the total G-value of electrons. In the gas phase, the G-value of electrons can easily be measured by the current-saturation-method. However, in the liquid phase, this method cannot easily be applied. Moreover, the definition of the ionization in the liquid phase itself is somewhat obscure; *i.e.*, the ionized state and the highly excited state are not clearly distinguishable in the liquid phase.

When we use the electron-scavenging method, the value we can determine is the G-value of scavengeable electrons, which might not equal the total G-value of the electrons. For example, a certain highly excited state might be quenched by the electron transfer to the scavenger.[2,3] Moreover, when we use the electron-scavenging method, we have to face the problem of extrapolation. If there are two different equations which fit the data at low concentrations of the scavenger, the extrapolation to an infinite concentration would give two different values of the total G-value of the scavengeable electrons. From this point of view, bromobenzene is one of the most useful electron scavengers, because we can make experiments with pure bromobenzene and, therefore, can apply the extrapolation technique from both sides, from lower concentrations and from higher concentrations, when the direct radiolysis of bromobenzene becomes important. In this paper, we wish to show that, in order to obtain a self-consistent value, the empirical formula proposed by Hummel[4] for the electron scavenging is better than that proposed by Warman *et al.*[5]

Experimental

The cyclohexane (Wako Pure Chemical Co. and Tokyo Kagaku Seiki Co.) and 2,2,4-trimethylpentane (Koso Chemical Co. and Tokyo Kagaku Seiki Co.) were used after being passed through 1-m-long silica gel columns. The bromobenzene (Wako Pure Chemical Co.) was purified by fractional distillation before use.

The 2-ml solutions *in vacuo* were irradiated by ^{60}Co γ-rays. The dose rate was 3—9×10^{19} eV/g h, and the total dose ranged from 1 to 15×10^{19} eV.

The products noncondensable at the temperature of liquid nitrogen, hydrogen and methane, were collected in a Toepler-McLeod apparatus and the amount measured by means of a gas buret. The gas was circulated through a cuprous oxide furnace maintained at 260 °C and a liquid nitrogen trap to convert the hydrogen into water. The residual gas, methane, was then collected again, and its amount was measured.

The condensable products were measured gas-chromatographically. The following columns were used: the 4-m tricresyl phosphate column at 60 °C for benzene, the 5-m dimethylsulfolane column at room temperature for cyclohexene, and the 2-m polyethylene glycol column at 80 °C for bicyclohexyl. As the standard compound, toluene or hexane was used.

Results

Figures 1 and 2 show the G-values of benzene, hydrogen, and methane from the bromobenzene solutions in cyclohexane and 2,2,4-trimethylpentane as functions of the concentration of bromobenzene, where the concentration of bromobenzene is lower than 1 mol l^{-1}.

In order to subtract the contribution of the direct

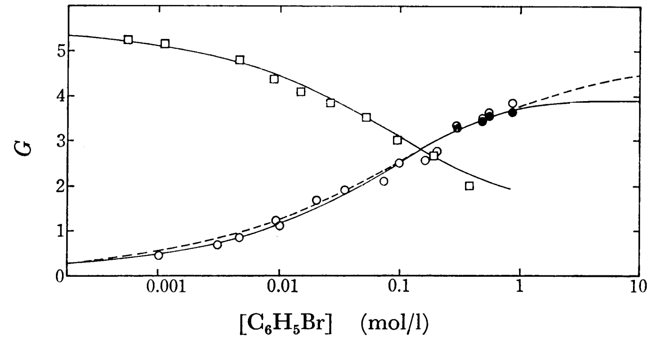

Fig. 1. The G-values of benzene (○) and hydrogen (□) from the bromobenzene solution in cyclohexane. For the filled circles and the curves, see the text.

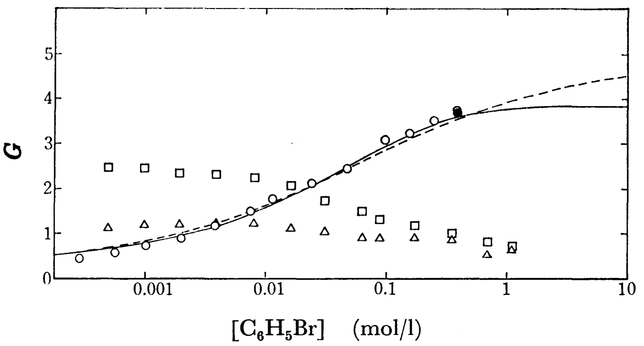

Fig. 2. The G-values of benzene (○), hydrogen (□), and methane (△) from the bromobenzene solution in 2,2,4-trimethylpentane. For the filled circle and the curves, see the text.

radiolysis of bromobenzene, we assumed that the G-value of benzene from pure bromobenzene is 1.2 (see below) and that the energy absorption occurs proportionally to the electron fraction. The filled signs in Figs. 1 and 2 represent the corrected values.

The two kinds of curves for the G-values of benzene, solid and dashed, shown in Figs. 1 and 2, were drawn by using the following two empirical equations; for the solid curves,

$$G(C_6H_6) = G_{fi} + G_{gi}\{1-\exp(-\sqrt{\alpha S})\} \tag{1}$$

and for the dashed curves,

$$G(C_6H_6) = G_{fi} + G_{gi}\frac{\sqrt{\alpha S}}{1+\sqrt{\alpha S}}. \tag{2}$$

Here, S is the concentration of bromobenzene. G_{fi}, G_{gi}, and α are empirical constants, whose values are summarized in Table 1. Since the two equations coincide with each other at the low-concentration limit, the G_{fi}'s in both equations should be the same.

Figures 3 and 4 show the G-values of benzene observed at the concentrations higher than 1 mol l^{-1}. The abscissa is the electron fraction of bromobenzene. Obviously, the G-value of benzene has its maximum value at about 1 mol l^{-1} of bromobenzene. The solid lines correspond to the equation

$$G(C_6H_6) = g_B(C_6H_6)\varepsilon_B + g_H(C_6H_6)\varepsilon_H, \tag{3}$$

where ε_B and ε_H are the electron fractions of bromobenzene and the hydrocarbon used. The g_B and g_H values thus obtained may be summarized as follows; $g_B=1.2\pm0.3$, $g_H=3.7\pm0.3$ for cyclohexane and $g_B=1.0\pm0.2$, $g_H=3.5\pm0.2$ for 2,2,4-trimethylpentane. Since g_H corresponds to the total G-value of benzene when ideal electron scavenging occurs in a pure hydrocarbon, the g_H should be equal to the sum of G_{fi} and G_{gi}.

TABLE 1. EMPIRICAL CONSTANTS OBTAINED BY FITTING THE DATA TO Eq. 1 AND TO Eq. 2.

Equation	Cyclohexane			2,2,4-Trimethylpentane		
	G_{fi} a)	G_{gi}	α b)	G_{fi} a)	G_{gi}	α b)
(1)	0.15	3.8	10	0.33	3.5	18
(2)	0.15	4.8	10	0.33	4.5	16

a) Determined by the conductivity method.10)
b) 1 mol^{-1}.

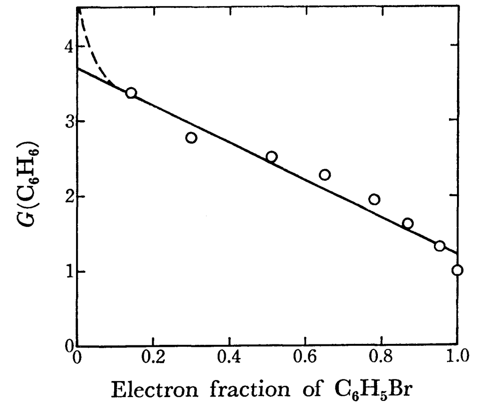

Fig. 3. The G-values of benzene from the bromobenzene solution in cyclohexane at the high concentrations of bromobenzene. For the solid and dashed lines, see the text.

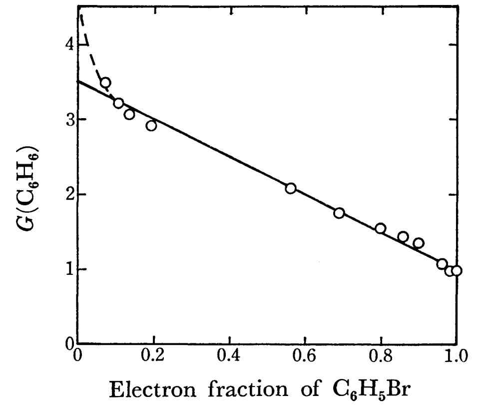

Fig. 4. The G-values of benzene from the bromobenzene solution in 2,2,4-trimethylpentane at the high concentrations of bromobenzene. For the solid and dashed lines, see the text.

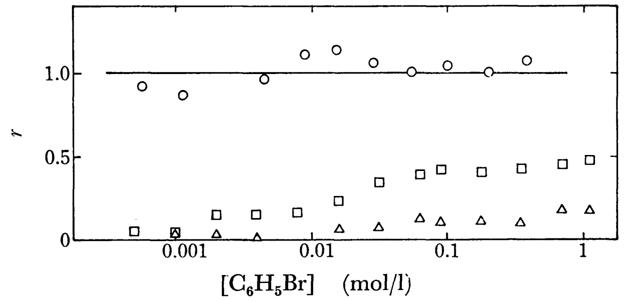

Fig. 5. Compensation between the G-value of benzene and the G-value of noncondensable products. ○: r_{H_2} from cyclohexane solution, □: r_{H_2} from 2,2,4-trimethylpentane solution, and △: r_{CH_4} from 2,2,4-trimethylpentane solution.

Comparing the g_H's shown above with the values in Table 1, we can conclude that Eq. 1 gives more self-consistent values than does Eq. 2.

Figure 5 shows the following ratios;

$$r_{H_2} = \{G_0(H_2) - G(H_2)\}/G(C_6H_6), \tag{4}$$

and

$$r_{CH_4} = \{G_0(CH_4) - G(CH_4)\}/G(C_6H_6). \tag{5}$$

TABLE 2. G-VALUES OF CYCLOHEXENE, BICYCLOHEXYL, AND CYCLOHEXYL BROMIDE FROM THE BROMOBENZENE SOLUTION IN CYCLOHEXANE

Bromobenzene (mol l^{-1})	$G(C_6H_{10})$	$G(C_{12}H_{22})$	$G(C_6H_{11}Br)$
0	3.01	1.95	
0.00045	0	0.49	
0.42	0	0.31	0.75
1.06	0	0.23	0.72

Here, G_0 stands for the G-value from a pure hydrocarbon. Obviously, in the case of cyclohexane, the $G(H_2)$ are compensated by the $G(C_6H_6)$. The G-values of hydrogen and methane from 2,2,4-trimethylpentane solution will be discussed later.

A few experiments were made in the measurement of the G-values of cyclohexene, bicyclohexyl, and cyclohexyl bromide in the presence of bromobenzene. The results obtained are summarized in Table 2.

Discussion

When Warman *et al.* proposed Eq. 2 for expressing the G-values of the methyl radicals formed by the electron scavenging of methyl bromide in cyclohexane, they compared Eq. 2 with Eq. 1,[6] which had been proposed by Hummel. Since their data beautifully fit Eq. 2, they abandoned Eq. 1. However, the highest concentration they used was 0.5 mol l^{-1}, and the G-value obtained at this concentration was 2.8, which corresponds to 72% of the value of G_{gi} they estimated by applying Eq. 2 to their data. In other words, the G_{gi} value they determined is based on a long extrapolation. Consequently, it is doubtful that the sum of G_{fi} and G_{gi} thus obtained is the true total G-value of scavengeable electrons.

As is shown in Figs. 1 and 2, the present data obtained at lower concentrations of bromobenzene are not reproducible enough to discriminate Eq. 1 from Eq. 2. However, as has been shown above, the extrapolation from the high-scavenger-concentration side seems to be more consistent with Eq. 1 than with Eq. 2.

Theoretically we cannot discuss the merits of the two empirical equations. All we can say at present is that the sum of G_{fi} and G_{gi} obtained by the use of Eq. 1 is closer to the total G-value of scavengeable electrons estimated by the extrapolation from the high-concentration side than that estimated by the use of Eq. 2. Of course, Eq. 3 is also an empirical equation. Therefore, $G(C_6H_6)$ might deviate from Eq. 3 at the low-electron fraction of bromobenzene, as is shown by dashed lines in Figs. 3 and 4. However, we do not think this is plausible.

As Fig. 5 shows, the $G(H_2)$ from the cyclohexane solution are compensated by $G(C_6H_6)$. This seems to substantiate the idea that one neutralization reaction between the cyclohexane ion and electron leads to the formation of one hydrogen molecule. The curve for $G(H_2)$ in Fig. 3 was drawn by the use of the equation

$$G(H_2) = 5.6 - [G_{fi} + G_{gi}\{1 - \exp(-\sqrt{\alpha S})\}]. \tag{6}$$

Here, the value of 5.6 is the G-value of hydrogen from pure cyclohexane.

On the other hand, in the case of 2,2,4-trimethylpentane, the situation is much more complex. The ratios, r, for hydrogen and methane depend on the concentration of bromobenzene. In order to explain this dependence, we propose the following reaction mechanism.

According to the mass-spectrometric analysis, the parent ion of 2,2,4-trimethylpentane is not stable, but easily decomposes into a butyl ion and a butyl radical. If this type of decomposition competes with the geminate recombination between the parent ion and an electron, and if the neutralization reaction between a butyl ion and an electron does not lead to the formation of hydrogen or methane, then we can derive the concentration-dependences of $G(H_2)$ and $G(CH_4)$.

The probability of the electron scavenging by bromobenzene by the time t may be expressed as follows:

$$\int_0^t kS e^{-kSt'} dt' = 1 - e^{-kSt}. \tag{7}$$

Here, k is the rate constant of the electron scavenging by bromobenzene. Then, the fraction of electrons which react with the electron scavenger should be expressed by the equation

$$F(\phi) = \int_0^\infty f(t)(1 - e^{-kSt}) dt = 1 - \int_0^\infty f(t) e^{-kSt} dt. \tag{8}$$

Here, $f(t)$ is the time distribution function of the geminate electrons. If Hummel's empirical equation can be used for expressing the electron scavenging in the present system, the $f(t)$ function should satisfy the following equation:

$$\int_0^\infty f(t) e^{-kSt} dt = \exp(-\sqrt{\alpha S}). \tag{9}$$

The $F(\phi)$ fraction corresponds to the yield of benzene produced by the reaction between bromobenzene and geminate electrons.

When the electron scavenger is absent, the formation of hydrogen depends on the decomposition lifetime of the parent ion ($\tau = 1/k_0$) and on the efficiency of the hydrogen formation from the neutralization reaction (γ):

$$F(H_2) = \gamma \int_0^\infty e^{-k_0 t} f(t) dt. \tag{10}$$

In the presence of bromobenzene, this fraction should be modified as follows:

$$F(H_2)_S = \gamma \int_0^\infty e^{-k_0 t} f(t) e^{-kSt} dt. \tag{11}$$

Therefore, we can easily derive the following equations:

$$r'_{H_2} = \frac{G(H_2)_0 - G(H_2)}{G(\phi) - G_{fi}} = \gamma \frac{\int_0^\infty f(t)\{e^{-k_0 t} - e^{-(k_0 + kS)t}\} dt}{1 - \int_0^\infty f(t) e^{-kSt} dt} = \gamma \frac{\exp(-\sqrt{\beta}) - \exp(-\sqrt{\beta + \alpha S})}{1 - \exp(-\sqrt{\alpha S})}. \tag{12}$$

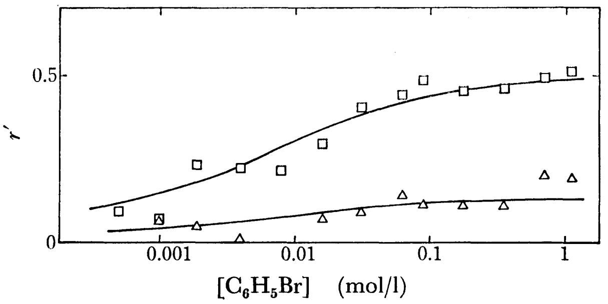

Fig. 6. The interpretation of the formation of hydrogen and methane from 2,2,4-trimethylpentane solution. □: r'_{H_2} and △: r'_{CH_4}.

Here, $\beta = k_0\alpha/k$. The curve for r'_{H_2} in Fig. 6 was drawn by using the following values; $\alpha = 18$ l mol^{-1}, $\beta = 0.052$, and $\gamma = 0.61$. A similar treatment can be applied to r'_{CH_4} ratio. The value of γ used for drawing the curve for methane was 0.16.

In order to estimate the decomposition lifetime of the 2,2,4-trimethylpentane ion, let us assume that $k = 10^{13}$ l mol^{-1} s^{-1}.[7] Then, the lifetime can be estimated to be 2×10^{-11} s.

Freeman and Sambrook commented that, when one uses a bromide compound as an electron scavenger, one has to pay attention to the effect of the product, especially hydrogen bromide, on the electron scavenging process.[8] According to the radiolysis study of pure bromobenzene, the G-value of hydrogen bromide is not small, but ranges from 1.0 to 2.0.[9]

When we measured the G-value of benzene from the bromobenzene solution in cyclohexane, we observed the formation of cyclohexyl bromide as is shown in Table 2. Upon the addition of bromobenzene, the formation of cyclohexene was completely suppressed. This is probably due to the reaction of cyclohexene with the hydrogen bromide eventually produced.

Although we could not clarify the fate of all of the bromine atoms, the final form of bromine atoms may be alkyl bromide. If such products as alkyl bromide should seriously affect the electron scavenging process of bromobenzene, some changes would be needed in the present treatment, especially for the absolute value of G_{gi}. However, since the absolute amount of any product is much smaller than that of bromobenzene added to the solution, we do not think that the effect of a product such as alkyl bromide on the electron-scavenging process of bromobenzene is serious.

References

1) T. Kimura, K. Fueki, and Z. Kuri, *Bull. Chem. Soc. Jpn.*, **43**, 3090 (1970); M. Baba and K. Fueki, *ibid.*, **48**, 3039 (1975).

2) S. Sato and T. Oka, *Bull. Chem. Soc. Jpn.*, **44**, 856 (1971).

3) T. Wada and Y. Hatano, *J. Phys. Chem.*, **79**, 2210 (1975).

4) A. Hummel *J. Chem. Phys.*, **49**, 4840 (1968).

5) J. M. Warman, K. D. Asmus, and R. H. Schuler, *J. Phys. Chem.*, **73**, 931 (1969).

6) S. J. Rzad, P. P. Infelta, J. M. Warman, and R. H. Schuler, *J. Chem. Phys.*, **52**, 3971 (1970).

7) A. O. Allen, T. E. Gangwer, and R. A. Holroyd, *J. Phys. Chem.*, **79**, 25 (1975).

8) G. R. Freeman and T. E. M. Sambrook, *J. Phys. Chem.*, **78**, 102 (1974).

9) S. S. Kumar and J. F. Merklin, *J. Chem. Soc., Faraday Trans. 1*, **69**, 577 (1973); A. F. Everard, J. D. Parrack, G. A. Swan, and P. S. Timmons, *J. Chem. Soc.*, **169**, 905 (1962); R. E. Buhler and J. M. Bossy, *Int. J. Radiat. Phys. Chem.*, **6**, 95 (1974).

10) W. F. Schmidt and A. O. Allen, *J. Chem. Phys.*, **52**, 2345 (1970).