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Ionic Species in the Radiolysis of Cyclohexane

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A diffusion model proposed in the previous paper (*Bull. Chem. Soc. Japan,* **40**, 1818 (1967)) has been applied to explain the ionic reactions occurring in the γ-radiolysis of cyclohexane. The effects of an electron scavenger (N_2O) and a positive ion detector (CH_3OD) were consistently interpreted. The ratio of the diffusion coefficient of electrons to that of parent positive ions has been estimated from the calculation to be in the range of 4 to 5. The calculating method has been compared with that recently published by Freeman (*J. Chem. Phys.,* **46**, 2822 (1967)).

γ-Radiolysis of liquid occurs through two processes; one, ionic, the other, non-ionic. The ratio probably depends upon the molecular structure of the liquid. In cyclohexane, roughly 1 to 1 has been estimated for the ratio of the two processes which contribute to the formation of hydrogen.[1]

Ionic species produced in cyclohexane by γ-ray irradiation are electrons and the parent positive ions. Their excess energies are dissipated in a short time, probably of the order of 10^{-13} sec, through many collisions with solvent molecules. Thus thermalized electrons and the parent positive ions are distributed in the solvent, but not homogeneously; each pair being attracted by the Coulombic interaction which depends on the dielectric property of the solvent. In the previous paper,[2] the function proportional to $r^2 \exp(-\alpha r^2)$ was proposed for the initial distribution of the pair and 50 Å was estimated for the average separation in cyclohexane. Thus ion pairs drift towards each other and neutralize. The heat of neutralization leads to the decomposition of a cyclohexane molecule, as follows.

$$c\text{-}C_6H_{12}^+ + e \rightarrow H \text{ or } H_2 + \text{residue} \tag{1}$$

$$H + c\text{-}C_6H_{12} \rightarrow H_2 + c\text{-}C_6H_{11} \tag{2}$$

One neutralization reaction corresponds to the formation of a hydrogen molecule.[1]

Since the average time interval for the neutralization is estimated to be 10^{-9} sec,[2] electrons can react with electron scavengers in the solution, if present. When nitrous oxide is used as the scavenger, the following reactions seem to occur.[1]

$$e + N_2O \rightarrow N_2 + O^- \tag{3}$$

$$O^- + N_2O \rightarrow N_2 + O_2^- \tag{4}$$

Neutralization reaction between O^- or O_2^- and $c\text{-}C_6H_{12}^+$ does not lead to the formation of hydrogen. The reactions may be as follows, but have not been studied thoroughly.

$$c\text{-}C_6H_{12}^+ + O^- \text{ or } O_2^- \rightarrow c\text{-}C_6H_{11} + OH \text{ or } HO_2 \tag{5}$$

Anyway, the yield of nitrogen can be used as an indicator for the reaction of electrons ejected from cyclohexane molecules.

If a positive ion detector such as CH_3OD is present in the system,[*1] the following reaction occurs and produces a constant fraction of deuterated hydrogen.

$$c\text{-}C_6H_{12}^+ + CH_3OD \rightarrow c\text{-}C_6H_{11} + CH_3ODH^+ \tag{6}$$

The yield of deuterated hydrogen can be used as an indicator for the reaction of parent positive ions.[3]

Data is now available for the reactions described above. This paper reports that the diffusion model proposed in the previous paper can explain these data consistently.

Calculation

In the previous paper,[2] only electrons were treated as a diffusing species. Obviously, parent positive ions can also diffuse in the system. Therefore, a modification is needed in the formulation. When electrons and the parent positive ions diffuse in the system, the number of jumps which both entities make in the diffusion before the neutralization may be approximated as follows,[2]

$$n_{\pm} = \gamma_{\pm}(2r^3/\sigma^2 r_c)$$

Here, the subscripts + and − correspond to positive

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[1] S. Sato, R. Yugeta, K. Shinsaka and T. Terao, This Bulletin, **39**, 156 (1966).

[2] S. Sato, T. Terao, M. Kono and S. Shida, *ibid.*, **40**, 1818 (1967).

[*1] Deuterated ammonia, ND_3, was also used by Williams.[4] This compound is about 3 times less efficient as a scavenger than CH_3OD. The reaction, therefore, may not be diffusion controlled.

[3] J. W. Buchanan and F. Williams, *J. Chem. Phys.*, **44**, 4377 (1966).

[4] F. Williams, *J. Am. Chem. Soc.*, **86**, 3954 (1964).

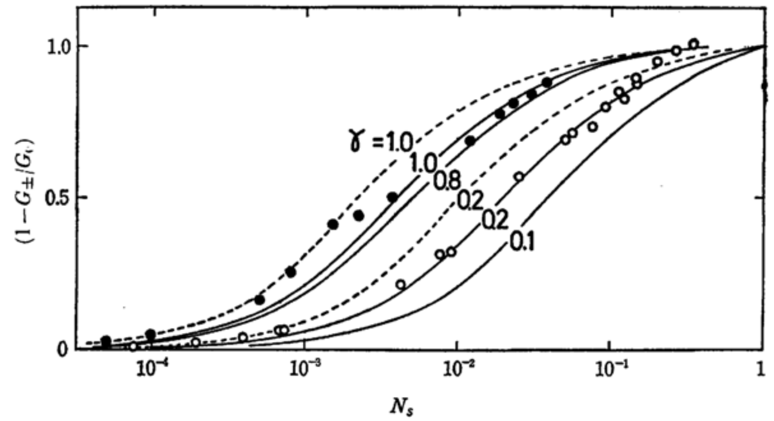

Fig. 1. Comparison of the calculated curves with the experimental data. ○: the fraction of positive ions scavenged by CH_3OD. ●: the fraction of electrons scavenged by N_2O. Full lines for $r_{av}=50$Å. Dashed lines for $r_{av}=60$Å.

ion and electron. r is an initial distance between the two entities. σ is the diameter of the solvent molecule. r_c is defined by the relation, $r_c=e^2/\varepsilon kT$. $\gamma_{\pm}$ is the fraction of the sum of two diffusion coefficients, D_+ and D_-.

Other formulations are the same as those in the previous paper,2) except that the fraction $(1-N_s)^{zn_{\pm}}$ is used in place of $(1-zN_s)^{n_{\pm}}$, since, as Freeman stated,5) the former expression is more exact than the latter. Thus, the G-values of positive ions (G_+) and electrons (G_-) which escape from scavenging are expressed by the relation,

$$G_{\pm} = G_0\frac{1}{N}\int_0^{\infty}\phi(r)(1-N_s)^{zn_{\pm}}\mathrm{d}r$$

G_0 is the G-value of the initial ion pairs. z is the coordination number. N_s is the mole fraction of the scavenger. N is the normalization factor. $\phi(r)$ is the distribution function, for which we proposed the function, $r^2\exp(-\alpha r^2)$, in the previous paper.2) As stated in the previous paper, G-value of electrons which escape geminate recombination in a non-polar solvent such as cyclohexane, is negligibly small compared with the total G-value of ejected electrons. In the case of a polar solvent, however, G-value of such electrons may be much larger. The function $\phi(r)$ should be modified as follows,

$$\phi(r) = r^2\exp(-\alpha r^2)(1-\exp(-r_c/r))$$

where, the fraction $\exp(-r_c/r)$ shows the probability of electrons which escape from the field of the parent positive ion.6)

Figure 1 shows a typical result of the calculation, where $\gamma_{\pm}$ is used as a parameter. A pair of curves obtained for $\gamma_+ + \gamma_- = 1$ should be compared with the experimental data. Filled circles in Fig. 1 show the ratios, $G(N_2)/G_0(N_2)$. Here, $G_0(N_2)=6$ is assumed because the G-value of electrons has been estimated to be 3.2) The data shown at the concentrations lower than 10^{-2} mol/l of nitrous oxide is newly obtained for this paper. Open circles are quoted from the data reported by Buchanan and Williams.3),*2 Obviously, a pair of curves for $\gamma_+=0.8$ and $\gamma_-=0.2$ coincides best with the experimental results.

In Fig. 1, 50 and 60 Å are used as the average initial distances between a positive ion and the electron. Different distances can also be used for the calculation but the coincidence with the experimental results is never obtained unless r_{av} is in the range of 50 to 60 Å and the ratio of γ_-/γ_+ in the range of 4 to 5.

Discussion

The basic idea of the calculation presented here is the same as that proposed by Freeman.5) The difference is in the assumption of the initial distribution of ion pairs produced in the system. Figure 2 compares the two distributions. Although the distribution used in the present calculation appears to be more plausible than that of Freeman, further examinations are needed to determine which is a better approximation.

Recently, Mozumder and Magee showed that,7),8) in addition to isolated spurs, more densely charged spurs, namely, short tracks and blobs play important roles even in the γ-radiolysis of liquids. If this is taken into account in the calculation, the present formulation has to be modified, because, in this formulation, each ion pair is assumed to be independent from other pairs The modification

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5) G. R. Freeman, *J. Chem. Phys.*, **46**, 2822 (1967).
6) L. Onsager, *Phys. Rev.*, **54**, 554 (1938).

*2 Plotted values are the ratios of corrected G-values for deuterated hydrogen to the maximum value, 1.55.
7) A. Mozumder and J. L. Magee, *Radiation Res.*, **28**, 203 (1966).
8) A. Mozumder and J. L. Magee, *J. Chem. Phys.*, **45**, 3332 (1966).

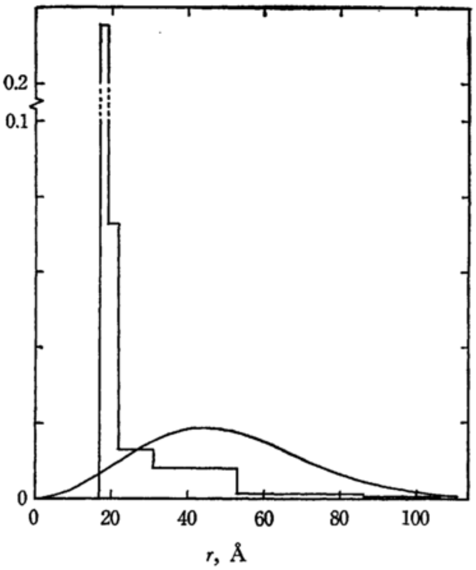

Fig. 2. Comparison of the initial distribution of ion pairs assumed in the present calculation (r_{av}=50Å) with that estimated by Freeman.

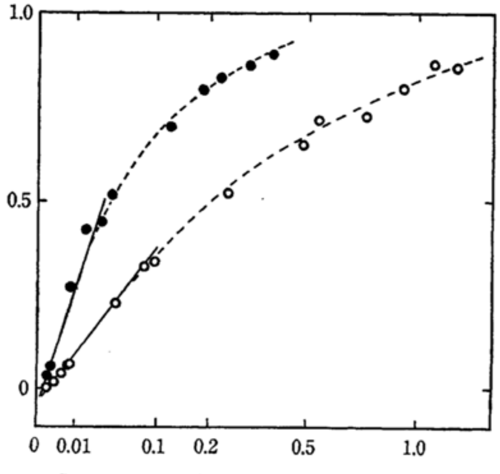

Fig. 3. Concentration-dependence of the effect of scavengers.
○: for CH_3OD. ●: for N_2O.

may be very much intricate.

In the present calculation, adjustable parameters are the distribution constant, α (or r_{av}) and the fraction, $\gamma_{\pm}$ from which the diffusion coefficient of electrons can be estimated if the diffusion coefficient for positive ions is known. This value is not known but may be equal to that of cyclohexane molecule itself, which is reported to be 1.38×10^{-5} cm^2 sec^{-1} at 25°C. According to the result calculated in the previous section, the diffusion coefficient of electrons in cyclohexane should be 4 or 5 times larger than that of the positive ions. This is very much smaller than that expected if the electron is not solvated and diffuses freely in the solution. Freeman assumed that $D_-/D_+\approx 5$ in his calculation.[5]

Using a photoelectronic technique to produce electrons in n-hexane, LeBlanc has measured the mobility of electrons at room temperature.[9] The value obtained was 1.4×10^{-3} cm^{2}V^{-1}sec^{-1}, which corresponds to a diffusion coefficient of 3.5×10^{-5} cm^2 sec^{-1}. Such a small value has led LeBlanc to conclude that electrons in n-hexane must be partially solvated by the solvent molecules. This is consistent with our present findings. Quantitatively, however, the ratio of $D_-/D_+=2.5$ ($=3.5\times 10^{-5}/1.38\times 10^{-5}$) calculated from LeBlanc's results, assuming that the diffusion coefficient for electrons in cyclohexane is equal to that in n-hexane, is about one half of that estimated in the present calculation. The discrepancy might arise from the speculations involved in the present treatment, but it is also possible that it may arise from the experimental error on D_-, although the recent measurement of conductivity of n-hexane irradiated by X-rays gave the value[10] consistent with that of LeBlanc.

In homogeneous systems, the rate of a reaction is proportional to the product of reactant concentrations, but this does not always hold in heterogeneous systems. Noyes has shown that the effect of a scavenger on a geminate recombination reaction is almost proportional to the square root of the scavenger concentration.[11] In the reaction of ND_3 with cyclohexane positive ion, Williams showed that this was the case.[4] However, when CH_3OD is used as a scavenger, Noyes' prediction does not fit well, probably because the range of the CH_3OD concentration is too wide to apply his approximation. This is shown in Fig. 3 along with the similar test for electron scavenging by nitrous oxide. Obviously, the proportionality to the square root of concentration holds only in a narrow range (from 0.002 to 0.02 mol/l for electrons and from 0.01 to 0.1 mol/l for positive ions) and a small negative intercept exists.

Even in a heterogeneous reaction, we are apt to assume that the rate of reaction with a scavenger is proportional to the concentration if it is very low. This was found to be correct even in the present case, but the maximum concentration used was quite low $\sim 10^{-3}$ mol/l. Therefore, we must be careful when we apply homogeneous kinetics to the radiolysis of a solution such as a liquid scintillator, where ionic species play an important role.[12]

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[9] O. H. LeBlanc, *ibid.*, **30**, 1443 (1959).

[10] A. Hummel and A. O. Allen, *ibid.*, **44**, 3421 (1966).

[11] R. M. Noyes, "Progress in Reaction Kinetics," Vol. 1, G. Porter Ed., Pergamon Press, Oxford (1961), p. 129.

[12] T. Yoshida and S. Sato, This Bulletin, **40**, 2216 (1967).