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Secondary Electrons in the Radiolysis of Cyclohexane

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Carbon dioxide and sulfur hexafluoride have been used as electron scavengers in the γ-radiolysis of cyclohexane. The dependence of $G(H_2)$ on the concentrations of additives can be interpreted satisfactorily in terms of diffusion-controlled reactions between electrons and the additives. A simple calculation was made using a function proportional to $r^2\exp(-\alpha r^2)$ for the initial distribution of secondary electrons. The distribution constant α and the value of G(electrons) were adjusted to make the calculated curve of $G(H_2)$ *vs.* scanvenger concentration coincide with the observed one. The average initial separation of the secondary electron from the parent positive ion was found to be about 50 Å, and $G(\text{electrons})=3$.

In recent years, much knowledge of the behavior of electrons formed in the radiolysis of condensed system has been gained using techniques of spectroscopy,[1] ESR[2] and conductivity measurements[3].

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[1] M. R. Ronane, J. P. Guarino and W. H. Hamill, *J. Am. Chem. Soc.,* **84**, 4230 (1962).

[2] D. R. Smith and J. J. Pieroni, *Can. J. Chem.*, **43**, 876 (1965).

[3] A. O. Allen and A. Hummel, *Discussions Faraday Soc.*, **36**, 95 (1963).

In paraffinic hydrocarbons, however, ionic species formed have such short lifetimes that indirect techniques must be employed to study their behavior.

Williams used ND_3 as a positive ion detector in the radiolysis of cyclohexane⁴⁾ and estimated the time interval elapsed for the recombination of electrons with the parent positive ions. The estimated time of 10^{-7}—10^{-9} sec was much larger than that calculated from theory by Samuel and Magee ten years ago.⁵⁾ Freeman calculated with good accuracy G-values of free electrons formed in the radiolysis of water and cyclohexane.⁶⁾ He used numerical tables published by Lea⁷⁾ to estimate the distribution of secondary electrons. His method was also applied successfully to explain Williams' results,⁸⁾ although this was criticized by Williams with regard to the estimation of the collision number.⁹⁾

We have recently investigated the effect of nitrous oxide on the radiolysis of hydrocarbons¹⁰⁾ and concluded that its effect is due to electron scavenging. Carbon dioxide and sulfur hexafluoride are well known to be unreactive to free radicals, while both gases, especially the latter, are known to react with thermalized electrons.¹¹⁾ This paper reports the effects of these gases on the radiolysis of cyclohexane and a theoretical treatment of these systems.

Experimental

Experimental procedure was almost the same as reported in the previous paper¹⁰⁾ except for a few details described below.

Carbon dioxide and sulfur hexafluoride were used as supplied by Takachiho Shoji Co. without further purification.

To analyze ethylene when carbon dioxide was present, the gas volatile at −120°C was admitted to a tube containing ascarlite to absorb the carbon dioxide and the remaining gas was analyzed by gas chromatography.

Solubilities of carbon dioxide and sulfur hexafluoride in cyclohexane have been measured at several temperatures.¹²⁾ The results are listed in Table 1.

TABLE 1. OSTWALD ABSORPTION COEFFICIENTS, α, OF CARBON DIOXIDE AND SULFUR HEXAFLUORIDE IN CYCLOHEXANE

Carbon dioxide			
T°C	10.9	15.5	22.5
α	1.87	1.46	1.16

Sulfur hexafluoride					
T°C	13.0	16.2	20.0	23.0	26.0
α	1.47	1.39	1.39	1.30	1.25

Results

In Fig. 1, G-values of hydrogen, carbon monoxide and ethylene are shown as a function of the concentration of carbon dioxide present in cyclohexane. The decreasing curve of $G(H_2)$ is very similar to that obtained by the addition of nitrous oxide. To compare the effects of carbon dioxide and nitrous oxide, one experiment was done with cyclohexane in the presence of both gases. The result is shown in Table 2.

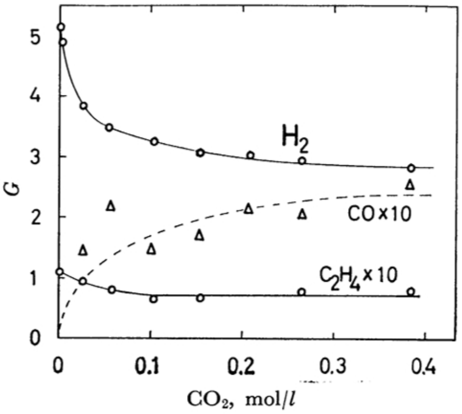

Fig. 1. G-Values of H_2, CO and C_2H_4 as a function of the concentration of CO_2.

TABLE 2. THE EFFECT OF CARBON DIOXIDE ON THE RADIOLYSIS OF A CYCLOHEXANE SOLUTION OF NITROUS OXIDE

Nitrous oxide mol/l	Carbon dioxide mol/l	$G(N_2)$	$G(H_2)$
0.19	0.0	5.39	2.87
0.19	0.20	3.58	2.49

With sulfur hexafluoride, only its effect on the G-value of hydrogen from cyclohexane has been measured. The results are listed in Table 3.

Figure 2 shows the G-values of hydrogen and nitrogen from a solution of 0.09 mol/l nitrous oxide in cyclohexane as a function of the concentration of sulfur hexafluoride. This curve will be discussed later.

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

5) A. H. Samuel and J. L. Magee, *J. Chem. Phys.*, **21**, 1080 (1953).

6) G. R. Freeman and J. M. Fayadh, *ibid.*, **43**, 86 (1965).

7) D. E. Lea, "Actions of Radiations on Living Cells," Cambridge Univ. Press, Cambridge (1955).

8) G. R. Freeman, *J. Chem. Phys.*, **43**, 93 (1965).

9) J. W. Buchanan and F. Williams, *ibid.*, **44**, 4377 (1966).

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

11) D. C. Frost and C. A. McDowell, *J. Chem. Phys.*, **29**, 964 (1958).

12) K. Kikuchi, S. Sato, S. Shida, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **84**, 561 (1963).

TABLE 3. G-VALUES OF HYDROGEN FROM CYCLOHEXANE SOLUTIONS OF SULFUR HEXAFLUORIDE

$\text{mol}/l\times10^{-2}$	$G(H_2)$	$\text{mol}/l\times10^{-2}$	$G(H_2)$
0.0	5.2	5.8	3.6
1.0	5.0	7.8	3.5
3.1	4.1	17.1	3.0
3.8	3.8	24.8	2.8
4.7	3.8	28.4	2.8
5.0	3.9	40.5	2.4

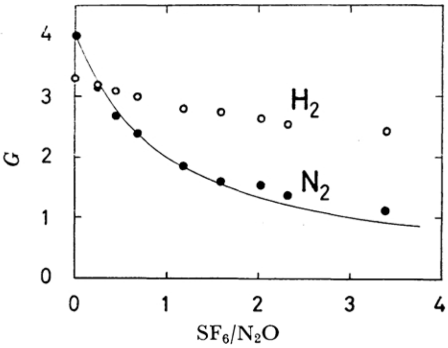

Fig. 2. G-Values of N_2 and H_2 from a cyclohexane solution of 0.09 mol/l nitrous oxide as a function of the concentration of sulfur hexafluoride (see the text for the curve).

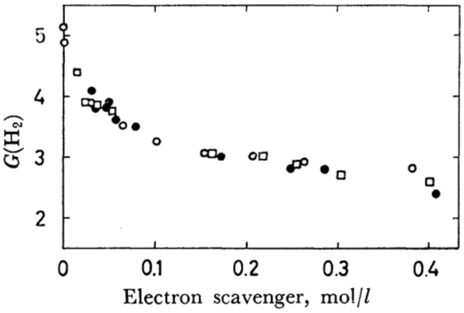

Fig. 3. G-Values of hydrogen as a function of the concentrations of electron scavengers.
○ CO_2 ● SF_6 □ N_2O

Discussion of the Experimental Results

In the radiolysis of cyclohexane, two processes have been postulated to lead to the formation of hydrogen10); one is the ionic process (1), the other is the excitation process (2).

$$C_6H_{12}\begin{cases}\rightsquigarrow C_6H_{12}^{+} + e \rightarrow \text{H or } H_2 + \text{residue} & (1)\\ \rightsquigarrow C_6H_{12}^{*} \rightarrow \text{H or } H_2 + \text{residue} & (2)\end{cases}$$

Hydrogen atoms produced in either process abstract hydrogen from cyclohexane to form a hydrogen molecule. If solute molecules which are reactive to electrons but not to hydrogen atoms present in this system, the ionic process (1) will be interfered with. In the previous paper, nitrous oxide was used as such a solute and the results were well explained in terms of electron scavenging by nitrous oxide. Carbon dioxide similarly can scavenge electrons, but is much more stable towards decomposition following electron attachment. This is consistent with the very small G-value observed for carbon monoxide, shown in Fig. 1. Sulfur hexafluoride molecules are also well known to be reactive towards thermalized electrons,11) while not reacting with free radicals. Johnson and Warman used sulfur hexafluoride as an electron scavenger in the radiolysis of propane in the gas phase,13) and compared its ability as an electron scavenger with that of other molecules such as nitrous oxide. They found sulfur hexafluoride to be 10^4 times more effective than nitrous oxide. In the liquid phase, however, sulfur hexafluoride does not appear to be a better scavenger than nitrous oxide and carbon dioxide. This is shown in Fig. 3, where G-values of hydrogen are plotted as a function of the concentrations of three additives. All the data lie on a single curve within experimental error. A more direct comparison is made in Fig. 2. If sulfur hexafluoride and nitrous oxide compete for electrons, the following relation holds for the yield of nitrogen from a cyclohexane solution with a constant concentration of nitrous oxide.

$$G(N_2) = G_0(N_2)/(1 + k[SF_6]/k'[N_2O])$$

where k/k' is the ratio of the specific reaction rates of sulfur hexafluoride and nitrous oxide with electrons, and $G_0(N_2)$ is the G-value of nitrogen in the absence of sulfur hexafluoride. The curve shown in Fig. 2 is drawn for $k/k'=1$. These results strongly suggest that electrons produced in cyclohexane drift slowly to their parent ions and that reactions with electron scavengers are diffusion controlled. This conclusion has already been reached by Williams4) and Freeman6) in their studies of different cyclohexane systems.

Calculations based on a Diffusion Model

A simple calculation has been made, based on the following assumptions:

1) Ejected secondary electrons have such large energies that Coulombic forces from the parent ions can be neglected until the electrons become thermalized. If so, the probability of finding an electron ejected with a certain energy, at a distance R from the parent ion, is proportional to $r^2\exp\cdot(-\alpha r^2)=\phi(r)$,14) where α is a distribution constant and is connected with the average separation

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13) G. R. A. Johnson and J. M. Warman, *Nature*, **203**, 73 (1964).

14) W. Feller, "An Introduction to Probability Theory and Its Applications," John Wiley & Sons, New York (1965).

r_{av} in the relation of $r_{av}^2 = 4/(\pi\alpha)$. In the present system, ejected electrons have various energies. Therefore, the proposed function is only a first approximation.*[1]

2) The ejected electrons are assumed not to react with electron scavengers before thermalization.

3) After thermalization, electrons drift slowly to their parent positive ions. On the way, a fraction of them will be captured by the scavengers, the reaction of which will be diffusion controlled.

4) The distance which an electron travels in a single jump in the diffusion is assumed to be the diameter of cyclohexane, 5.4 Å.

These assumptions are almost same as those Freeman[8)] and Williams[9)] used in their calculations. In the present calculation, however, the initial distribution of secondary electrons estimated by Freeman is not used.

Thus, as derived by Williams,[9)] the G-value of electrons which recombine with the parent ions in the presence of a small amount of electron scavenger, the mol% of which is N_s, may be expressed as follows.

$$G = G_e \frac{1}{N} \int_0^\infty \phi(r)(1 - zN_s)^n \, \mathrm{d}r$$

$$N = \int_0^\infty \phi(r) \, \mathrm{d}r$$

Here, G_e is the G-value of electrons ejected from cyclohexane. z is the coordination number, for which we take 6. n is the collision number, which can be estimated by the following relation.

$$n = 2r^3/(\sigma^2 r_c)$$

where, σ is the diameter of cyclohexane molecule and r_c is the critical distance defined by the relation, $e^2/(\varepsilon r_c) = \boldsymbol{k}T$. Here, e is the charge of an electron and ε is the dielectric constant of the system.

If the electrons captured by the scavengers do not contribute to the formation of hydrogen, then the decrease of $G(H_2)$ in the presence of scavengers is equal to the difference between G_e and G. An example of the calculation is shown in Fig. 4. The curve A shows the initial distribution of electrons, where the average separation is 50 Å. The curve B is the distribution of electrons which recombine with the parent ions. The curve C will be discussed later. In these calculations, adjustable parameters are G_e and α (or r_{av}). In Fig. 5 are shown a few calculated curves for the decrease of $G(H_2)$ as a function of the concentration of the scavenger. These curves should be compared with the plots shown in Fig. 3. The most suitable curve is that obtained with $G_e=3$ and $r_{av}=50$ Å.

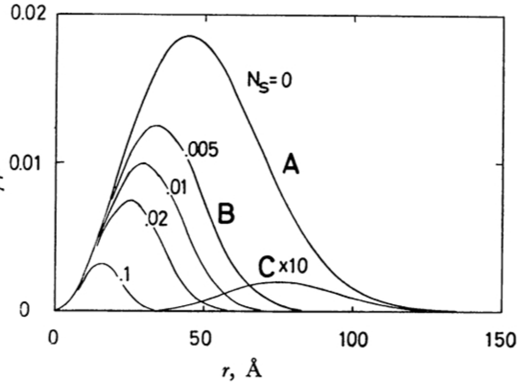

Fig. 4. The distributions of electrons.

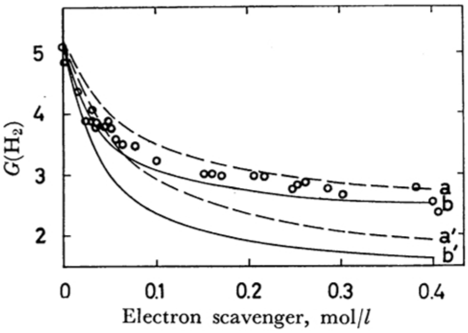

Fig. 5. Calculated G-values of hydrogen as a function of the concentrations of electron scavenger.

a $G_e=3$ $r_{av}=40$ Å	b $G_e=3$ $r_{av}=50$ Å
a' $G_e=4$ $r_{av}=40$ Å	b' $G_e=4$ $r_{av}=50$ Å

Open circles show the experimental results, which are same as shown in Fig. 3.

Discussion of the Calculations

In the present calculation, the motion of the thermalized electron has been treated as that of a negative cyclohexane ion. This reasoning is difficult to establish with our present knowledge, although simple explanations have been reported.[6),9)] We think that thermalized electrons are partially solvated in cyclohexane. Moreover, in the present model, only electrons can diffuse in the system. If positive parent ions also are treated as a diffusing species, the calculation becomes a little more complex. This treatment will be discussed separately.

Since the distribution function has been obtained, the G-value of free electrons in this system can be calculated using the function of $\exp(-r_c/r)$, which was obtained by Onsager[15)] and used by Freeman[8)] to estimate the G-value of free electrons, as follows:

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*[1] The function $\phi(r)$ used in the present calculation is that used by Samuel and Magee for the distribution of radicals in their diffusion theory.[5)]

15) L. Onsager, *Phys. Rev.*, **54**, 554 (1938).

$$G(\text{free electrons}) = G_e \frac{1}{N}\int_0^\infty \phi(r)\exp(-r_c/r)\,\mathrm{d}r$$

The G-value obtained for free electrons is 0.03. The distribution of these electrons is shown in Fig. 4 as the curve C. This value is about one third of that observed by conductivity measurements.3) We don't believe that this disagreement reflects an essential defect in the present calculation.

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