A Comparison of the Primary Processes of the Radiolyses Induced by α-, β-, and γ-Rays

Shin SATO, Ken-ichi KOWARI, and Kiyoshi OKAZAKI
Department of Applied Physics, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152
(Received November 22, 1975)

By using the cross sections derived by the binary encounter collision theory and the assumption of a continuous slowing down, the G-values for the ionization and excitation of helium gas irradiated by α-, β-, and γ-rays have been calculated. In the radiolysis by high-energy electrons, the G-values started to decrease at an incident electron energy of about 10^3 eV with a decrease in the energy. Calculation showed that, if the radiation energy is extremely high, the G-values are independent of the kind of radiation. In the radiolysis induced by α-particles, the ratio of the yield resulting from the direct interaction with α-particles to that due to the secondary electrons was calculated as a function of the energy of the incident α-particles. When the energy was 8 MeV, the ratio for ionization was calculated to be 1.31.

There are several naive questions when we consider the primary process of the radiolyses induced by different ionizing radiations.

1) In radiation chemistry, the radiolysis yield obtained by the irradiation of high-energy electrons is believed to be independent of the energy of the incident electrons if they are high in energy. Then, what eV is the threshold value for calling electrons "high-energy electrons"—10^2, 10^3, or 10^4 eV?

2) It is believed that the chemical reaction induced in such materials as organic compounds by the irradiation of γ-rays from ^{60}Co is exactly the same as the reaction induced by the irradiation of high-energy electrons except for the difference in the penetration of the two ionizing radiations. However, the energy of the secondary electrons produced by the γ-irradiation through the Compton effect distributes down to zero eV. Consequently, the yield obtained by the irradiation of monoenergetic electrons of a high energy, say 100 keV, might not agree quantitatively with the yield obtained by γ-irradiation.

3) According to the experimental data,[1] when the energy of incident radiation is extremely high, the ionization yield in a gas does not depend upon the kind of radiation. However, the interaction of high-energy electrons with a material must be different from the interaction of other particles; for example, an incident electron can replace an electron in a material, but other particles cannot. Such an effect might result in a quantitative difference in the radiolysis yield.

4) When the W-value of a certain gas is measured by using α-particles as the radiation source, a question may be raised—what percentage of the ionization is induced by the direct interaction with α-particles, and what percentage by the interaction with the secondary electrons produced?

In this paper, we will attempt to answer these questions by performing numerical calculations on the radiolysis of helium gas. The calculating method is classical and approximate; however, we believe that the result is not far from the truth.

Radiolysis by High-energy Electrons

Throughout this paper, we will use the following equation, derived from the classical binary encounter theory,[2] for the differential cross section of the energy loss:

$$\sigma_{E,\mathrm{dir}} = \frac{\pi e^4}{T+I_i+E_i}\left(\frac{1}{E^2}+\frac{4E_i}{3E^3}\right) \tag{1}$$

for $T \geq I_i+E$. Here, T is the energy of the incident particle; I_i and E_i are, respectively, the binding energy and the average kinetic energy of the target electron, and E is the energy loss of the incident particle. When the incident particle is an electron and when an exchange with the target electron occurs, the differential cross section ($\sigma_{E,\mathrm{exc}}$) is expressed by replacing E in Eq. 1 with $T+I_i-E$.

For the calculation of the yields of ionization and excitation, we use the concept of the degradation spectrum, $y(T)$, and calculate it on the assumption of a continuous slowing down. The details of this procedure have been discussed previously;[3] therefore, we will only briefly outline them here.

According to the assumption of a continuous slowing down, the degradation spectrum of the incident electron, $y_1(T)$, is expressed as a reciprocal of the stopping power of the incident electron in the target gas. While the degradation spectrum of the incident electron is being formed, the secondary electrons are ejected and form their degradation spectrum, $y_2(T)$. The formulation of $y_2(T)$ can easily be carried out by using the differential cross section in Eq. 1. Similarly, the degradation spectrum of the electrons ejected in later steps can be constructed. The total degradation spectrum, $y(T)$, is obviously the sum of these spectra. Once $y(T)$ is obtained, the yield of any process can be calculated by using the total cross section, $Q_s(T)$, for that process:

$$N_s = Nn_i\int_{T_s}^{T_0} y(T)Q_s(T)\mathrm{d}T \tag{2}$$

Here, N_s is the number of species produced in the s process; N is the number of the target atoms in unit volume; n_i is the number of electrons in the i-th shell; T_s is the threshold energy of the incident electron for the s process, and T_0 is the energy of the primary electron. Then, the G-value of the product is calculated by this equation:

$$G_s = 100\, N_s/T_0 \tag{3}$$

Figure 1 shows the G-values thus calculated for the

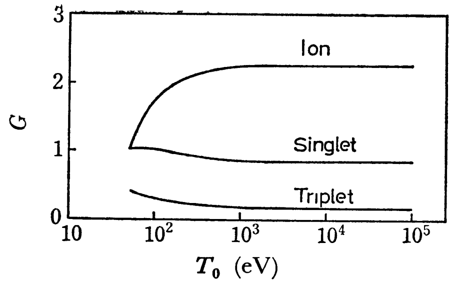

Fig. 1. The G-values for ionization and singlet and triplet excitations as functions of the energy of the primary electron.

Table 1. Constants used for calculation (eV)

Binding energy	$I_i = 24.581$
Singlet excitation energy	$E_s = 21.2$
Triplet excitation energy	$E_t = 19.8$
Average kinetic energy	$E_i = 38.74$

Table 2. Comparison of G-values for ionization and excitations induced by different ionizing radiations

	G_{ion}	G_{singl}	G_{tripl}
High energy electrons ($>10^3$ eV)	2.27	0.86	0.16
γ-Rays from ^{60}Co	2.30	0.86	0.16
α-Particles (8 MeV)	2.24	0.85	0.15

ionization and singlet and triplet excitations in helium gas as functions of the energy of the primary electrons. The constants used for the calculation are summarized in Table 1.[3] Obviously, the G-value of ionization tends to decrease at 10^3 eV with the decrease in the energy of the primary electrons. Above 10^3 eV, the G-values of any process are independent of the energy of the primary electrons. The values are listed in Table 2.

γ-Radiolysis

Energy Distribution of Compton Electrons. When a material consisting of atoms with low atomic numbers is irradiated by γ-rays from ^{60}Co, the primary interaction occurs mainly through the Compton effect. In order to calculate the energy distribution of the Compton electrons, Davison and Evans[4] derived this equation:

$$\frac{d\sigma(T)}{dT} = \frac{\pi r_0^2}{\alpha h\nu}\left[1+\frac{T^2}{(h\nu-T)h\nu}+\left\{1-\frac{T}{\alpha(h\nu-T)}\right\}^2\right] \quad (4)$$

from the famous Klein-Nishina formula.[5] Here, $\sigma(T)$ is the cross section for the formation of Compton electrons with the energy of T, $h\nu$ is the energy of the incident γ-rays, $\alpha=h\nu/mc^2$, and $r_0=e^2/mc^2$. m is the mass of electron, e is the charge, and c is the velocity of light.

Figure 2 shows the calculated energy distribution of the Compton electrons produced by the irradiation of ^{60}Co γ-rays, which consist of two different photons, 1.17 and 1.33 MeV. This figure is the same as that shown in the literature.[6] It is assumed in this calcula-

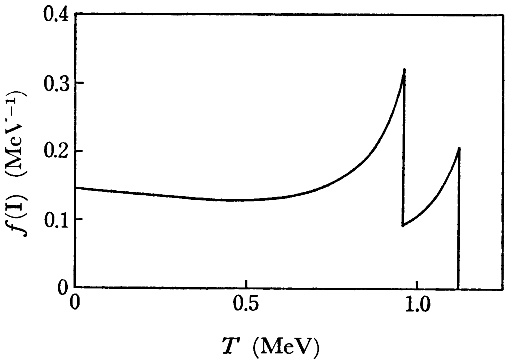

Fig. 2. The energy distribution of Compton electrons produced in helium irradiated by γ-rays from ^{60}Co.

tion that the interaction of γ-rays with the gas occurs only once; *i.e.*, the interaction of the scattered γ-rays is not taken into account. As Fig. 2 shows, because of the momentum conservation, the maximum energy of the Compton electrons is less than the energy of incident radiation.

$$T_{max} = \frac{2\alpha}{1+2\alpha}h\nu \quad (5)$$

Comparison with the Radiolysis Induced by High-energy Electrons. Since the energy distribution of the primary electrons produced by the Compton effect has been obtained, the degradation spectrum of electrons in helium irradiated by γ-rays can be calculated in a manner similar to that shown in the previous section. The degradation spectrum of the primary electrons, $y_1(T)$,[7] and the total energy, T_0, absorbed by helium in the present case are expressed as follows:

$$y_1(T) = \int_T^{T_{max}} f(T)dT/S(T) \quad (6)$$

and

$$T_0 = \int_0^{T_{max}} Tf(T)dT \quad (7)$$

Here, $f(T)$ is the fraction of the primary electrons with the energy of T, and $S(T)$ is the stopping power of helium gas for the electrons with the energy of T. $S(T)$ is formulated as follows:[8]

$$S(T) = \sum_i n_i\left\{\int_{E_{si}}^{(T+I_i)/2} E(\sigma_{E,dir}+\sigma_{E,exc})dE + \frac{1}{2}\int_{E_{ti}}^{E_{si}} E\sigma_{E,exc}dE\right. \quad (8)$$

E_{si} and E_{ti} are the energies of the singlet and triplet excitations for the electron in the i-th shell.

Figure 3 shows the total degradation spectrum, $y(T)$, thus calculated. The calculated G-values for ionization and excitations are summarized in Table 2. Practically no difference can be seen in the G-values calculated for the γ-radiolysis and for the radiolysis by high-energy electrons. The difference of 1% in the G-value of ionization is within the limits of error of the calculation technique.

Radiolysis by α-Particles

According to the binary encounter theory, the differential cross-section for the energy loss of the incident-

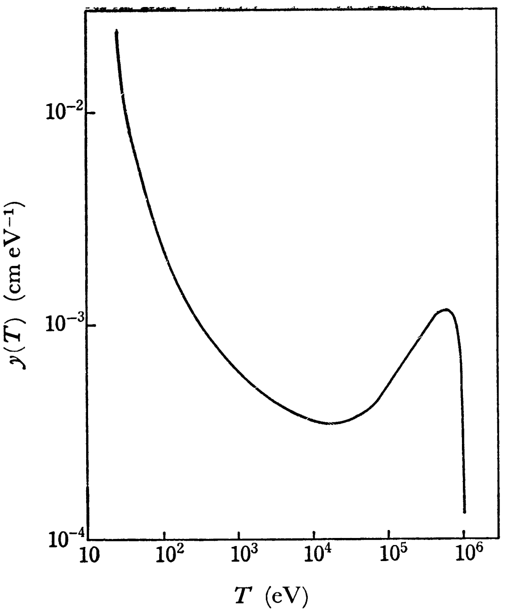

Fig. 3. The degradation spectrum of electrons in helium irradiated by γ-rays from ^{60}Co.

heavy-charged particles can be formulated in a manner similar to that used for electrons. Using the notations of Vriens,[9] the differential cross-sections are expressed as follows:

$$\sigma_1(E) = \frac{\pi Z^2 e^4}{3V_1^2 V_2 E^3}\left\{4V_1^3 - \frac{1}{2}(V_2' - V_2)^3\right\} \tag{9}$$

for $2\,mV_1(V_1 - V_2) \leq E \leq 2\,mV_1(V_1 + V_2)$. Here, $\sigma_1(E)$ is the differential cross section for the energy loss, E; Ze is the charge of the incident particle; V_1 is the incident velocity; V_2 is the velocity of the target electron, and V_2' is that after the collision with the heavy-charged particle. When $E \leq 2\,mV_1(V_1 - V_2)$, the differential cross section has to be modified to this form:

$$\sigma_2(E) = \frac{2\pi Z^2 e^4}{mV_1^2}\left(\frac{1}{E^2} + \frac{2mV_2^2}{E^3}\right) \tag{10}$$

The formulation for these cross-sections has already been reported in detail.[10]

By using Eqs. 9 and 10, we can derive the total cross-sections for ionization and excitation (Q_{ion} and Q_{exc}):

$$Q_{ion} = \int_{2mV_1(V_1-V_2)}^{2mV_1(V_1+V_2)} \sigma_1(E)\mathrm{d}E + \int_{I_i}^{2mV_1(V_1-V_2)} \sigma_2(E)\mathrm{d}E \tag{11}$$

for $I_i \leq 2\,mV_1(V_1 - V_2)$. Here, I_i is the binding energy of the target electron. When the binding energy is higher than $2\,mV_1(V_1 - V_2)$, the term for σ_2 in Eq. 11 dissappears and Q_{ion} is expressed as follows:

$$Q_{ion} = \int_{I_i}^{2mV_1(V_1+V_2)} \sigma_1(E)\mathrm{d}E$$

for $2\,mV_1(V_1 + V_2) \geq I_i \geq 2\,mV_1(V_1 - V_2)$. In a similar manner, the total cross-sections for excitations can be formulated:

$$Q_{exc} = \int_{E_s}^{I_i} \sigma_2(E)\mathrm{d}E$$

for $2\,mV_1(V_1 - V_2) \geq I_i$, and

$$Q_{exc} = \int_{2mV_1(V_1-V_2)}^{I_i} \sigma_1(E)\mathrm{d}E + \int_{E_s}^{2mV_1(V_1-V_2)} \sigma_2(E)\mathrm{d}E$$

for $2\,mV_1(V_1 + V_2) \geq I_i \geq 2\,mV_1(V_1 - V_2) \geq E_s$, where E_s is the threshold energy for the excitation.

$$Q_{exc} = \int_{E_s}^{I_i} \sigma_1(E)\mathrm{d}E$$

for $2\,mV_1(V_1 + V_2) \geq I_i \geq E_s \geq 2\,mV_1(V_1 - V_2)$, and

$$Q_{exc} = \int_{E_s}^{2mV_1(V_1+V_2)} \sigma_1(E)\mathrm{d}E$$

for $I_i \geq 2\,mV_1(V_1 + V_2) \geq E_s \geq 2\,mV_1(V_1 - V_2)$. In the treatment of the binary encounter theory, the excitation into the triplet state results from the exchange between the incident electron and the target electron. Therefore, in the present case, the formation of the triplet state cannot be taken into account.

In a manner similar to that used for electrons, the stopping power for heavy-charged particles is expressed in this form:

$$S(T) = N\sum_i n_i \left\{\int_{2mV_1(V_1-V_{2i})}^{2mV_1(V_1+V_{2i})} E\sigma_1 \mathrm{d}E + \int_{E_{si}}^{2mV_1(V_1-V_{2i})} E\sigma_2 \mathrm{d}E\right\} \tag{12}$$

Then, the degradation spectrum of the incident-heavy-charged particle may be expressed as follows:

$$y_0(T) = 1/S(T)$$

and the yield of the product formed through the s process in the collision of heavy-charged particles can be calculated by using Eq. 2.

In the radiolysis induced by the irradiation of heavy-charged particles, the secondary electrons ejected play an important role. The treatment on these electrons is similar to that for the Compton electrons produced by the γ-irradiation.

Figure 4 shows the $Ty(T)Q_s(T)$ values as a function of ln T. The incident radiation is 8 MeV α-particles. The solid lines correspond to the direct interaction of α-particles, and the dashed lines, to that of the secondary electrons. The ratio of the G-value for ionization due to the interaction with α-particles to that due to the secondary electrons is 1.31. Similar calculations can also be made for the excitation. The results are summarized in Table 3. Obviously the fraction due to the direct interaction increases with the decrease in the incident energy.

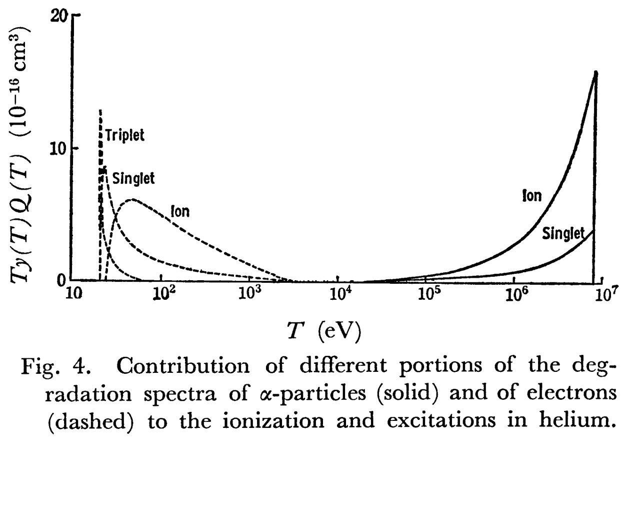

Fig. 4. Contribution of different portions of the degradation spectra of α-particles (solid) and of electrons (dashed) to the ionization and excitations in helium.

TABLE 3. IONIZATION AND EXCITATIONS OF HELIUM BY DIFFERENT ENERGY α-PARTICLES

T_0 (MeV)	G_{ion}	f_d (%)	f_s (%)	G_{singl}	f_d (%)	f_s (%)	G_{tripl}
0.02	1.30	100	0	1.83	100	0	0.0004
0.04	1.78	99.7	0.3	1.50	98.9	1.1	0.015
0.1	2.05	97.1	2.9	1.19	93.2	6.8	0.050
0.3	2.17	91.8	8.2	1.02	83.4	16.6	0.082
0.5	2.20	88.9	11.1	0.96	78.2	21.8	0.094
0.7	2.21	85.4	14.6	0.93	72.5	27.5	0.11
1.0	2.22	80.7	19.3	0.90	66.1	33.9	0.12
1.5	2.22	75.3	24.7	0.88	59.5	40.5	0.13
2.0	2.23	71.5	28.5	0.87	55.1	44.9	0.14
3.0	2.24	66.6	33.4	0.86	49.8	50.2	0.14
5.0	2.24	61.0	39.0	0.85	44.4	55.6	0.15
8.0	2.24	56.6	43.4	0.85	40.4	59.6	0.15

f_d: the fraction due to the direct interaction of α-particles. f_s: the fraction due to secondary electrons.

Conclusion

Let us summarize the answers to four questions proposed in the Introduction. To the first question, the answer is that, from the point of view of the radiation chemist, the lower threshold value for high-energy electrons is about 10^3 eV. The answer to the second question is that the primary process of the γ-radiolysis is certainly the same as that of the radiolysis induced by high-energy electrons. This conclusion has been widely accepted. The present calculation is another support for it. The answer to the third question, regarding the radiation-chemical difference between heavy-charged particles and electrons, is also simple; *i.e.*, if the radiation energies are extremely high, the yield of the primary process is independent of the kind of radiation which induces the reactions. If present, the difference is within a few percent. The answer to the fourth question is shown by the numbers in Table 3. These numbers may be used when discussing the effect of δ-rays on the radiolysis induced by α-particles. Similar calculations can easily be carried out for the radiolysis induced by other heavy-charged particles, such as protons and argon ions. Recently Ohno has made a few such calculations.[11]

The calculating method we have used above is based on two important assumptions, one regarding the cross section for the energy loss, and the other, the assumption of the continuous slowing down. These assumptions probably introduce serious deviations in the numbers. However, the conclusions summarized above may hold nevertheless.

References

1) D. W. Huyton and T. W. Woodward, *Radiat. Res. Rev.*, **2**, 205 (1970).
2) L. H. Thomas, *Proc. Camb. Phil. Soc.*, **23**, 829 (1927).
3) S. Sato, K. Okazaki, and S. Ohno, *Bull. Chem. Soc. Jpn.*, **47**, 2174 (1974).
4) C. M. Davison and R. D. Evans, *Rev. Mod. Phys.*, **24**, 79 (1952).
5) O. Klein and Y. Nishina, *Z. Phys.*, **52**, 853 (1929).
6) H. E. Johns, D. V. Cormack, S. A. Denesuk, and G. F. Whitmore, *Can. J. Phys.*, **30**, 556 (1952).
7) D. V. Cormack, R. W. Hummel, H. E. Johns, and T. W. Spinks, *J. Chem. Phys.*, **22**, 1 (1954).
8) S. Ohno, H. Nagayama, K. Okazaki, and S. Sato, *Bull. Chem. Soc. Jpn.*, **48**, 2153 (1975).
9) L. Vriens, "Case Studies in Atomic Collision Physics I," ed. by E. W. McDaniel *et al.*, North-Holland, Amsterdam (1969), p. 335.
10) L. Vriens, *Proc. Phys. Soc.*, **90**, 935 (1967).
11) S. Ohno, *Bull. Chem. Soc. Jpn.*, **48**, 2229 (1975).