The Calculation of the Primary Radiolysis Yield of Water Vapor Irradiated by 10-keV Electrons

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The yields for the ionization and excitation from each molecular orbital of a water molecule irradiated by 10 keV electrons were calculated using the classical binary-encounter approximation. On further assuming fragmentation processes of the excited or ionized states consistent with the photochemical and mass spectrometrical results in the literature, we obtained, as the radiolysis yields of water vapor: G(electron)=2.96; $G(OH^-)$=0.04; $G(H_3O^+)$=3.00; G(H)=4.83—5.21, including G('hot' H-atoms)$\leq$0.87; $G(H_2)$=0.28—1.15; G(O)=0.83—1.21; G(OH)=6.70—7.08, and $G(-H_2O)=G$(ionized water)$+G$(excited water)=2.91+4.96=7.87.

The ideal study of radiation chemistry consists of (i) the experimental determination of the radiation-chemical products, and (ii) the interpretation of their formation by means of a detailed analysis, specifying the primary products in the physical stage[1] (chiefly molecules in the electronically excited or ionized state) and following their fate in temporal sequence until observable chemical changes appear. Thus, a knowledge of the nature and yields of the primary products is extremely important to radiation chemists.

The primary products are formed as a result of the interaction of molecules with electrons in an energy distribution given by the degradation spectrum.[2,3] Fast electrons in the degradation spectrum interact with molecules in an "optical" collision, for which the cross section is expressed by the Bethe-Born approximation. For slow electrons of the degradation spectrum ($T \lesssim 100$ eV), however, this approximation loses its validity.[4]

We have chosen another possible approach to this problem of the calculation of the primary yields. Our method is a combination of the binary-encounter collision theory and a procedure for calculating the degradation spectrum. We previously applied it to the case of noble gases from He to Xe[5,6] and obtained results in reasonable agreement with the experimental ones.

The present paper is an extension of our work to a molecular system. The G-values of the ionization and excitation from each molecular orbital of the water molecule will be given. Then, we assume the mode with which the primary products decompose to give fragments on the basis of knowledge from photochemistry, mass spectrometry, and photoelectron spectroscopy. The yields of the fragments thus obtained may be compared with those estimated from the experimental work. The agreements are quite satisfactory, as will be shown later.

Method of Calculation

The "binary-encounter" collision theory, first presented by Thomas in 1927[7] and formulated and discussed in detail by Gryzinski,[8,9] Vriens,[10] and Burgess,[11] involves the following approximations:[10]

(i) the incident electron interacts with only one electron in the molecule.

(ii) the interaction between the molecular electrons and nucleus can be disregarded during the collision. In other wors, the collision takes place in a region small compared to the molecular dimensions. Thomas cosidered[7] the case of an electron with a kinetic energy of T moving through a cloud of free target electrons moving in random directions with kinetic energy of E_i. He gave this differential cross section per unit of energy interval for transferring an energy, E, to a target electron:

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

for $T+I_i \geq E$. Here, I_i is the binding energy of the target electron in the i-th molecular orbital (M.O.). The target electron on receiving the energy, E, may jump to a higher M.O. with the excitation energy, E_n, if $E \geq E_n$. Ionization occurs if E is larger than I_i, the kinetic energy of the ejected electron being $E-I_i$. One may also apply the above formula to an excitation induced by the exchange between the incident electron and a molecular electron ($\sigma_{E,exc}$). In this case, E in Eq. I should be replaced by $T+I_i-E$.

The stopping power, the degradation spectrum, and the total number of the primary products were all calculated on the basis of Eq. I. The details of the formulation were the same as those presented previously,[6] except for a slight modification of the stopping power formula (Eq. IV in Ref. 6).

Stopping Power. In the present work we used the stopping power expressed as follows:

$$S(T) = N\sum_i S_i(T)$$

$$S_i(T) = n_i\left\{\int_{E_{si}}^{(T+I_i)/2} E(\sigma_{E,dir}+\sigma_{E,exc})dE + \frac{1}{2}\int_{E_{ti}}^{E_{si}} E\sigma_{E,exc}dE\right\} \qquad (II)$$

for $T \geq I_i$. Here, N is the number of molecules in a unit of volume, $S_i(T)$ is the stopping power due to the n_i-electrons in the i-th M.O., and E_{si} and E_{ti} are the excitation energies of the lowest singlet and triplet levels respectively for the electrons in the i-th M.O. When $T \leq I_i$, the upper limit of the first integral should be replaced by T. When $T < E_{si}$, the first term disappears and the E_{si} in the second integral should be replaced by T.

Double Collision. A molecule undergoing interac-

tion with an impacting electron may result in a simultaneous excitation and/or ionization of two electrons. Gryzinski formulated two such processes:[9] one in which two electrons in the molecule are excited and/or ionized by two successive collisions of the incident electron, and another in which the incident electron ejects the first electron, which in turn excites or ionizes the second electron in the same molecule. According to the treatment of Gryzinski,[9] and using Eq. I as the cross sections for transferring energy on collision, we derived the cross-section formulas[12] for double ionization (designated as $\sigma(H_2O^{++})$), double excitation $\sigma(H_2O^{ee})$, and simultaneous excitation and ionization $\sigma(H_2O^{e+})$ in order to estimate their yields with the help of the degradation spectrum obtained on the basis of single collisions alone.

Constants Used for Calculation

The ground-state electronic configuration of the H_2O molecule is:

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2, \quad {}^1A_1$$

For the present calculation, we must know the binding energies, I_i, of the electrons in each M.O., their average kinetic energies, E_i, and their lowest singlet and triplet excitation energies, E_{si} and E_{ti}. Table 1 summarizes the values used. The lowest excited states:

$$\cdots (1b_2)^2(3a_1)^2(1b_1)(4a_1), \quad {}^3B_1\,(5\text{ eV}), \quad {}^1B_1(7.5\text{ eV})$$

$$\cdots (1b_2)^2(3a_1)(1b_1)^2(4a_1), \quad {}^1A_1\,(9.6\text{ eV})$$

heve been identified by UV-absorption or electron-impact experiments.[14-16] The E_{si} values of the other M.O.'s given in Table 1 were estimated from the differences in the I_i-values. Selection rules for transitions were taken into account. All the E_{ti}-values, except for the lowest, were set equal to the respective E_{si} values; they are only provisional.

TABLE 1. THE BINDING ENERGY (I_i), THE KINETIC ENERGY (E_i), AND THE LOWEST SINGLET (E_{si}) AND TRIPLET (E_{ti}) LEVELS OF ELECTRONS IN THE WATER MOLECULE (IN eV)

M.O.	I_i	E_i	E_{si}	E_{ti}
$1b_1$	12.6	70.4	7.5	5.0
$3a_1$	14.7	42.0	9.6	9.6
$1b_2$	18.4	42.0	13.3	13.3
$2a_1$	32.2	70.4	27.1	27.1
$1a_1$	540	806	535	535

More difficult to ascertain are the average kinetic energies, E_i. Since the M.O. $1a_1$, $2a_1$, and $1b_1$ are composed mainly of the atomic orbitals of oxygen (1s, 2s+2pz, and 2px respectively), the E_i values of these M.O.'s may be calculated using Slater's rule.[17] The E_i values for $1b_2$ and $3a_1$ were set equal to the mean of the kinetic energies calculated for the corresponding atomic orbitals of oxygen and hydrogen.[18]

For the calculation of the double-collision cross-sections, we assumed, to simplify the computation, that double collisions occur only among the 6-electrons in the $1b_1$, $3a_1$, and $1b_2$ orbitals. The 6-electrons are situated uniformly on the surface of the sphere with a radius of 0.5 Å, so that the mean distance between two of these electrons is 0.8 Å. The first ionization energy, $\bar{I}(\mathrm{I})$, the first excitation energy, $\bar{E}_s(\mathrm{I})$, and the kinetic energy, $\bar{E}_i$, are taken to be the averages of the respective values of the $1b_1$, $3a_1$, and $1b_2$ electrons. The second ionization energy, $\bar{I}(\mathrm{II})$, and the second excitation energy, $\bar{E}_s(\mathrm{II})$, are tentatively taken to be $2\times\bar{I}(\mathrm{I})$ and $2\times\bar{E}_s(\mathrm{I})$ respectively.

Results

Figure 1 shows the $y(T)$ for a 10 keV electron in H_2O (1 atm, 0 °C). Once $y(T)$ is obtained, the calculation of the yields of the ionization and excitation is straightforward if we use the total cross-section, $Q_s(T)$, for each process.[6] Figures 2 and 3 show the $T\cdot y(T)\cdot Q_s(T)$ *vs.* $\ln T$ plots; according to Platzman[2] the area under the curve is proportional to the yield of the s process (Fig. 2 refers to ionizations, while Fig. 3 refers to excitations).

Tables 2—4 summarize the *G*-values of all the primary products obtained in the present calculation. All the integrations were carried out by means of a computer, HITAC 8700, with a mesh of $(0.5)^{1/40}$ for the energy.

Since the cross-sections for the dissociative-electron capture of the H_2O molecule have been previously reported,[19] we can estimate the order of magnitude of the yield of this process using the $y(T)$-curve obtained

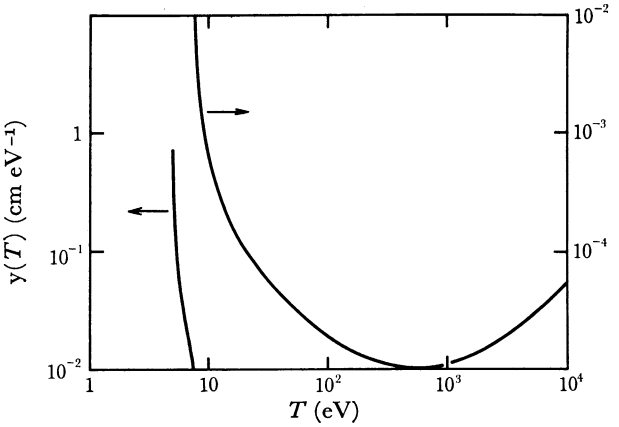

Fig. 1. The degradation spectrum for a 10 keV electron in water vapor (0 °C, 1 atm).

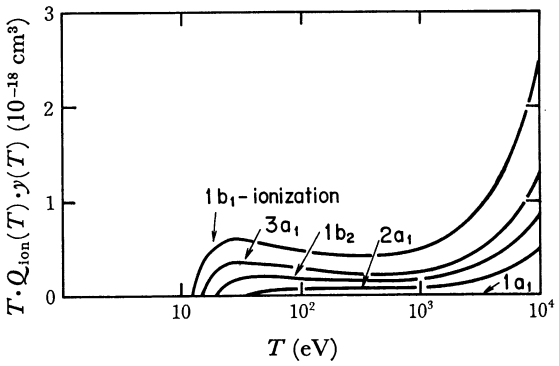

Fig. 2. Contribution of different portions of the electron degradation spectrum to ionizations from each M.O. in H_2O.

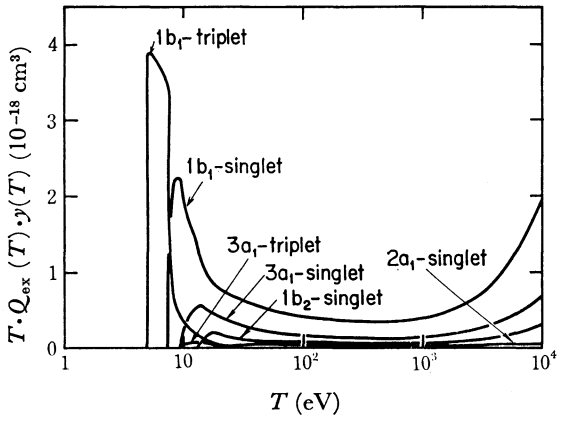

Fig. 3. Contribution of different portions of the electron degradation spectrum to excitations from each M.O. in H_2O.

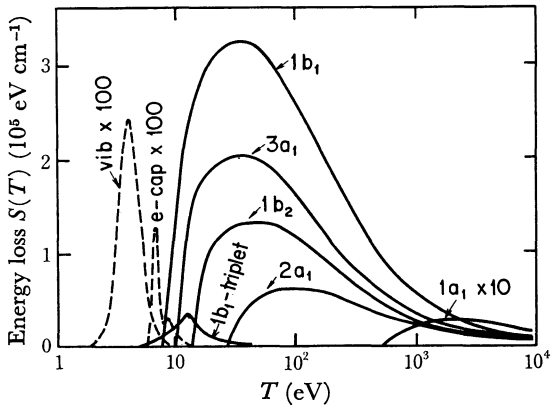

Fig. 4. The stopping power for electrons in water vapor. The contribution from electronic excitation and ionization of each M.O., dissociative electron capture (e-cap) and vibrational excitation (vib) of the H_2O molecule.

Table 2. The G-values of excitations in the H_2O molecule

M.O.	Singlet	Triplet	Mode of decomposition
$1b_1$	2.80	1.00	H+OH
$3a_1$	0.96	0.029	H+OH* (75%), H_2+O (25%)
$1b_2$	0.39	0.011	"hot H"+OH, or H_2+O*
$2a_1$	0.076	0.0016	Ion. frag.[a]
$1a_1$	0.000079	1.5×10^{-6}	Ion. frag.

a) Ionizing fragmentation.

Table 3. The G-values of ionizations in the H_2O molecule

M.O.	G	Mode of decomposition
$1b_1$	1.26	H_2O^++e
$3a_1$	0.68	H_2O^++e
$1b_2$	0.44	Ion. frag.
$2a_1$	0.21	Ion. frag.
$1a_1$	0.005	H^++OH^++2e *via* HO^{2+}

Table 4. The G-values for double collisions in the H_2O molecule

Primary product	Excitation energy (eV)	G	Mode of fragmentation
H_2O^{++}	45.6	0.09	H^++OH^++2e
H_2O^{ee}	30.6	0.12	H_2O^++e
H_2O^{+e}	35.6	0.31	Ion. frag.

in the present work. This gives $G\approx0.04$ for this reaction:

$$H_2O + e \longrightarrow H^- + OH \quad (1)$$

An alternative mode of dissociation:

$$H_2O + e \longrightarrow H_2 + O^- \quad (2)$$

has a much lower probability.[19]

Figure 4 shows the contribution from the electrons in each M.O. of the H_2O molecule to the stopping power for electrons in water vapor. Here are also shown, for convenience of comparison, the stopping power due to the dissociative-electron capture (Reaction 1) and the stopping power due to the vibrational excitations of water previously estimated by Mozumder.[20]

Yields of the Radiolytic Fragments

In order to obtain the radiolysis yields so as to compare them with the experimental results, we must know the fate or fragmentation process of the primary products listed in Tables 2 to 4.

The Ionized States. As to the ionized states, useful information is available from experimental photoelectron spectroscopy.[21] When an electron is removed from the $1b_1$ orbital, non-bonding in nature, the resulting ion is left practically unexcited. The loss of an electron from $3a_1$ will cause a bending vibration. If an electron is lost from a bonding $2a_1$ or $1b_2$ orbital, the O–H bond strength is weakened and its length is increased. In fact, the peaks of the band corresponding to the ionization from $1b_2$ in the P.E.S. spectrum are diffuse, suggesting a short lifetime prior to dissociation.[21]

The ejection of a $1a_1$-electron produces a doubly-charged ion by a well-known Auger process; the ion will then decompose.[22]

The Excited States. The UV absorption experiments threw light on the neutral excited states listed in Table 3. The continuous band ranging from 7 to 9 eV is due to the $\cdots\cdots(1b_1)^2$, $^1A_1\rightarrow\cdots\cdots(1b_1)(4a_1)$, $^1B_1$ transition, where the higher state is repulsive because of the anti-bonding nature of the $4a_1$ orbital.[23] The photochemical experiments have enabled us to conclude that the fragments are OH and H.[24] The excitation of an electron from $3a_1$, responsible for the bent shape of the molecule, to an anti-bonding $4a_1$ orbital will strain it towards its linear form and at the same time dissociate it. The photochemical experiments show that O, $OH(^2\Sigma^+)$, and $OH(^2\Pi)$ are formed simultaneously, their abundances being 25, 5, and 70% respectively.[24,25]

Nothing is known at present about the fate of the excited water molecules formed by promoting an electron from $1b_2$, $2a_1$, or $1a_1$ to $4a_1$ or a higher orbital. Since the excitation energy in these cases exceeds the lowest ionization energy of H_2O, both ionization and dissocia-

tion are possible. Therefore, we tentatively assume that the excitation of a $1b_2$-electron leads to dissociation to "hot H"+OH or H_2+O, while the excitation of a $2a_1$- or $1a_1$-electron leads to dissociative ionization. In the former case, the "hot H"-atoms might further react with water:

$$\text{"hot H"} + H_2O \longrightarrow H_2 + OH \quad (3)$$

as has been evidenced in the photochemical experiments.[24]

Double Collision. The doubly charged water and the excited water ion, designated as H_2O^{++} and H_2O^{+e} respectively in Table 4, would dissociate because of their large excitation energy. The doubly excited state, H_2O^{ee}, would lead to preionization.

The Ionizing Fragmentation. The yield of the primary products which will produce ionizing fragmentation amounts to $G\approx1$. Mass spectrometry provides information on the fragments. The mass spectrum of water obtained with an extremely high ion-extraction efficiency[26] shows that both H^+ and OH^+ are very abundant ions, about 25—30% of the parent ion, H_2O^+. The intensities of the other ions, O^+ and H_2^+, are low enough to be excluded from the present consideration. Thus, we may assume that the processes designated as Ion. frag. in Tables 2—4 are represented by:

$$H_2O \longrightarrow \begin{cases} H + OH^+ + e\ (50\%) & (4) \\ H^+ + OH + e\ (50\%) & (5) \end{cases}$$

It is possible that these fragments have a kinetic energy or an electronic excitation energy. Thus, the H-atoms formed in Reaction 4 can possibly react further according to Reaction 3.

Ion-molecule Reactions. The ionic fragments produced by the decomposition of the primary products of the water radiolysis may react with a water molecule to yield another ion. The following reactions are well known:[27]

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH \quad (6)$$

$$OH^+ + H_2O \longrightarrow H_3O^+ + O \quad (7)$$

$$H^- + H_2O \longrightarrow H_2 + OH^- \quad (8)$$

The proton may react with several water molecules succesively to form a clustered state. We will represent this state as merely H_3O^+ for the sake of simplicity.

Final Results. We can now use the results shown in Tables 2 to 4 to estimate the G-values of the radiolytic fragments of water vapor in accordance with the above assumptions. The results are summarized in Table 5.

TABLE 5. THE G-VALUES OF THE FRAGMENTS IN THE RADIOLYSIS OF WATER VAPOR

Fragment	G
electron	2.96
OH^-	0.04
H_3O^+	3.00
H	4.83—5.21[a]
H_2[b]	0.28—1.15
O	0.83—1.21
OH	6.70—7.08

$G(-H_2O)=G$(ionized water)$+G$(excited water) $=2.91+4.96=7.87$

a) G("hot H")$\leq$0.87 is included. b) "molecular" H_2.

Discussion

The experimental W values which have been reported for water vapor lie around 30 eV.[27] Thus, G(ionization) $=3.3$. The values of G(electron) can be obtained experimentally from the difference in the radiolytic yields of water vapor with and without added electron scavengers; the values of 3.0 ± 0.4[28] and 2.7 ± 0.6[29] have been reported. The value for $G(-H_2O)$ was estimated by means of the total hydrogen yields from water vapor containing various organic additives. There is a reasonable agreement on $G(-H_2O)=8\pm1$.[27] Molecular hydrogen is also formed,[28,30] with a yield ($G\approx0.6$), not influenced by additives. More recently Boyd *et al.*[31] reported that the yields of hydrogen from the Febetron radiolysis of water vapor with HCl are $G(H_2)=7.9\pm0.2$ and $G(H_2)=4.6\pm0.2$ with 1 mol% SF_6. They combined their results, taking G("molecular" H_2)$=0.45$, with the relative primary ion yields of the radiolysis of water vapor as: $G(e)=3.3$, $G(H)=4.15$, $G(OH)=6.25$, and $G(O)=1.05$. It is of interest to compare all these results with the values compiled in Table 5. The agreement is satisfactory.

The important role of kinetically hot or electronically excited H-atoms has often been noticed.[32,33] According to the scheme discussed above, they are possibly formed either by the decomposition of the excited water molecule (itself formed by the promotion of a $1b_2$-electron) or by way of Reaction 4. Thus, the present results predict 0.9 as the maximum G-value of "hot" or excited H-atoms.

The yield of the doubly charged water, H_2O^{++}, amounting to $G=0.1$ should be noted in view of the radiolysis of frozen aqueous solutions. Molecular decomposition by Coulomb repulsion would bring about the atomic displacement in the solid phase,[34] the result of which may be the formation of trapped species.

The O-atoms, to which little attention has been paid, may be produced with a high yield ($G\approx1$) and may play an important role in the radiation chemistry of water.[35]

It is of some interest to know the mean energy, $\tilde{I}_1$, imparted to the molecule undergoing ionization. In an ionizing collision, the impacting electron loses the energy, E, which is the sum of the energy imparted to the molecule and the kinetic energy of the ejected electron. Using the results in Tables 2 to 4, one obtains:

$$\tilde{I}_i = \frac{\sum(I_i \times G_i)}{\sum G_i} = 19\,\text{eV}$$

which largely exceeds the lowest ionization energy, 12.6 eV. This is due to the electronic excitation of the ions formed or to excitation to repulsive ionic states, leading to the formation of fragments with a high kinetic energy.

We must further note that Santar and Bednar[4] calculated the yields of the excitation and ionization of valence electrons in the water molecule. They

treated separately the contributions to the yield from "fast" and "slow" electrons of the degradation spectrum. They used the available optical data for H_2O to calculate the yields due to "fast" electrons. They also utilized the optical data to ascertain the number and initial kinetic energy of the "slow" electrons, which are produced predominantly by "fast" collisions. They further used the experimental W value for water, considered the energy balance, and finally obtained results which are close to those found experimentally.

The present method is obviously more straightforward and simpler than that employed by Santer and Bednar. It requires neither the optical data nor the W value. Instead, it requires data on the binding energy, the excitation energy, and the kinetic energy of each electron in the molecule. In conclusion, we should mention that the "binary-encounter" approximation may be very useful, not only for getting a general idea about the primary process of radiolysis, but also for estimating non-empirically the radiation-chemical yields.

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