MATHEMATICAL SIMULATION OF RADIOLYSIS PROCESS IN WATER UNDER THE INFLUENCE OF LOW-ENERGY ELECTRONS

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ABSTRACT

The physical (10^{-16}-10^{-15} sec.) and physicochemical (10^{-14}-10^{-11} sec.) stage of radiolysis process in liquid water under the influence of low-energy electrons were mathematically simulated using Monte-Carlo and single collision methods. Radiation-chemical yields of the products, formed from their conversions in short-living electron-excited state created by inelastic collision between electrons and water molecules in physical stage of the process, in direct single ionization of different molecular orbitals (H_2O^+...e^- ion pair) and later in physicochemical stage were calculated.

1. INTRODUCTION

Low- (0.05÷10 keV) or high-energy (10÷100 keV) electrons gradually lose their kinetic energy while passing through substance, in elastic and inelastic collision with its molecules (atoms). According to the mechanism of radiation energy loss, decrease of electrone's kinetic energy in inelastic collision is applied on the formation of short-living intermediate particles such as H_2O^+...e^- ion pair created mainly by electron-excited states of different types (it also includes hyperexcitability states) and direct single ionization of several molecular orbitals (MO). As the particles obtained make a strong influence on the processes going in substance (physical, chemical, biological and so on), it gives opportunity to predict cases which are likely to happen in the future, by studuing their roles in different fields of science (plasma physics, astrophysics, modelling of atmospheric phenomena, radiobiology, radiochemistry etc.). Intermediate particles have very short living period (10^{-15}-10^{-13} sec.), therefore their experimental study makes great difficulties. That's why theoretical solution of those particles' formation and application still stays as one of the main problems.

Authors experimentally determined the dependence of effective cross-section (single and double differential values of effective cross-section) in target (liquid water and water vapour) ionization by electron impact (e,2e) on primary energy and their scattering angle [1,2] by EMS (elektron momentum spektroscopy) method. The values of single ionization's effective cross-section, obtained during experiments coincide with the values obtained in the course of theoretical calculations performed by authors from different aspects [3-10] in big energy values, but there is gap in small values. Authors dealt with both experimental and theoretical solution of different electron-excited states in water and water vapour under the influence of electrons [11-16]. Authors [11-16] calculated theoretically radiation-chemical yields of the products formed in physical and physicochemical stage of radiolysis process going in water and water vapour under the influence of electrons having different energy values from several points of view. There is some coincidence between the results obtained from theoretical calculations and experimental results.

In this work radiation-chemical yields of the products generated in physical (10^{-16}-10^{-15} sec.) and physicochemical (10^{-14}-10^{-12} sec.) stage of radyolisis process going in liquid water under the impact of low-energy electrons (T=1, 5, 10 keV) were determined by mathematically simulating both of these phases. More improved form of Mott equation [3] was used for effective cross-section of ionization in inelastic collision, but for effective cross-sections of electron-excited states' different types Kim equation [5, 10] was used. Calculations were made on the base of Mathcad program, using Monte-Carlo and single collision methods.

2. METHODOLOGY

If low-energy electrons collide with water electrons inelastically, the energy balance between them can be expressed in the following simplest way:

$$T = E_s + \Delta E \qquad (1)$$

Here T and E_s are accordingly kinetic energies of electron before and after collision, ΔE-is the energy transferred to water molecule by electron during collision. This energy is applied on different electron and extreme excitation of water molecule

$$e_0 + A \rightarrow A^* \left(A^{**}\right) + e_s \qquad \left(\Delta E = E_{0n}\right) \qquad (2)$$

and direct single ionization of different molecular orbitals (MO).

$$e_0 + A \rightarrow A^+ + e_s + e_e \qquad (\Delta E = W + B_j) \qquad (3)$$

Here e_0, e_s, e_e - are appropriately incident, scattered and ejected electrons, A-molecules of substance, A^+, A^*, A^{**} - are correspondingly ionization, excitation and extreme excitation states. Transmitted energy (ΔE) in these processes equals to excitation energy of molecule (E_{0n}) in (2) case, the sum of kinetic energy of absorbed electron (W) from molecular orbital j and bound energy (B_j) of correspondent orbital in (3) case. Kinetic energies of scattered and ejected electrons may accordingly change from $E_S = 0$ to $E_s^{\max} = T - B_j$ or from $W = 0$ to $W^{\max} = (T - B_j)/2$.

More improved form of Mott equation was used to calculate effective cross-section of MO j single ionization during inelastic collision [3]:

$$\frac{d\sigma_j(W,T)}{dW} = \frac{S}{B_j(t+u+1)}\left\{\frac{1}{(w+1)^2} + \frac{1}{(t-w)^2} - \frac{1}{(w+1)(t+w)} + \frac{4u}{3}\left[\frac{1}{(w+1)^3} + \frac{1}{(t-w)^3}\right]\right\} \qquad (4)$$

here, $t = \frac{T}{B_j}$, $w = \frac{W}{B_j}$, $u = \frac{U_j}{B_j}$, $S = 4\pi a_0^2 N_j \left(\frac{R}{B_J}\right)^2$, U_j and N_j are kinetic energy and number of electron correspondent to MO j, a_0-Bohr radius, R=13.61 eV is Rydberg energy. Numbers of B_j, N_j and U_j according to different MO are given in Table 2.

If we integrate the expression (4) according to all possible values of absorbed electrons' energies, it means from W=0 to W^{max}, we can get the expression describing the dependence of electron primary energy of ionization effective cross-section in inelastic collisison conformable to MO j:

$$\sigma_j(T) = \int_0^{W^{\max}} \frac{d\sigma_j(W,T)}{dW} dW \qquad (5)$$

In order to get complete effective cross-section of ionization we should to sum the expression (5) according to the number of MO [17]:

$$\sigma = \sum_{j=1}^{N_{MO}} \sigma_j(T) \qquad (6)$$

Here N_{MO}=5 is the number of MOs ($1a_1$, $2a_1$, $1b_2$, $3a_1$, $1b_1$) of water molecules.

During inelastic collision between low-energy primary electrons and water molecules the effective cross-section of transformation from ground state (0) of electron to (n) excited state was calculated basing on the following expression [6, 7, 9, 13]:

$$\sigma_{0n} = \frac{4\pi a_0^2 R}{T + B + E_{0n}}\left[a \ln\left(\frac{T}{R}\right) + b + c\frac{R}{T}\right] \qquad (7)$$

Here a, b and c, are constants corresponding to $0 \rightarrow n$ passage. Values of each passage have been chosen according to the values of radiation-chemical yield obtained from experiments and E_{0n} [10,13] is excitation energy conformable to this passage. The values of constants and E_{0n} which have been used in calculations are given in Table 1.

Incident electrons or first generation δ-electrons formed by them lose some part of their energy in each inelastic collision and this process continues till the next inelastic collision that electron energy may cause. Electron the temperature of which equals to T in inelastic collididng with water molecules, the value of moderate energy lost in each event $\Delta E(T)$, has been taken equivalent to the following expression [18, 19]:

$$\Delta E(T) = \sum_n P_{0n}(T) E_n + \sum_j P_j(T) \varepsilon_j(T) \qquad (4)$$

here $P_{0n}(T) = \frac{\sigma_{0n}(T)}{\sigma_{tot}(T)}$ is probability of occurrence of transformation into n excited state, $P_j(T) = \frac{\sigma_j(T)}{\sigma_{tot}(T)}$ is probability of occurence of events corresponding to ionization of j MO, $\sigma_{tot}(T) = \sum_n \sigma_{0n}(T) + \sum_j \sigma_j(T)$ -total effective cross-section, $\varepsilon_j(T) = \int_{B_j}^{T} \varepsilon \frac{d\sigma_j(T)}{d\varepsilon} d\varepsilon$ -moderate energy calculated for forming one electron-positive ion pair in j MO by the electron the temperature of which is equal to T.

The active intermediate particles formed in in elastic collision between low-energy electrons and real molecules in physical phase of radiation-chemical process can be illustrated schematically in the following way [18, 19]:

$$A + e_0^- \rightarrow \left(nA^+, mA^*, lA^{**}\right) + (n+1)e^- \quad (5)$$

Here n, m, l- are correspondingly numbers of ionization, excitation and extreme excitation states caused by every primary electron in substance in physical phase of radiation-chemical process.

3. RESULTS AND DISCUSSION

On the base of our model calculations were made for six electron-excited states of water molecule in liquid phase and its five MOs. The radiation-chemical yields of six A^1B_1, B^1A_1, Rydberg states (Ry), diffuse bands (db), dissosiative excitations (ds) and collective excitation (plasmon) states (es) of water molecule were given in Table 1.

Table 1. The radiation-chemical yields of electron-excited states formed in water (A_1B_1, B_1A_1, Rydberg states (Ry), diffuse bands (db), dissosiative excitations (ds) and collective excitation (ce) states) under the influence of low-energy electrons.

Electron-excited state	Excitation energy, eV	Constants			T, keV		
		a	b	c	1	5	10
A^1B_1	8.4	0.7532	0.4751	-0.0675	0.807	0.802	0.801
B^1A_1	10.1	0.3900	0.1500	0.0015	0.387	0.388	0.388
Ry	12.26	0.0465	0.0282	-0.010	0.049	0.050	0.050
db	11.93	0.2380	0.0010	0.0265	0.209	0.211	0.212
ds	14.1	0.2473	-0.010	0.0150	0.212	0.208	0.214
ce	21.4	1.2951	0.0120	-0.7532	1.076	1.077	1.077

The values of radiation-chemical yields of ionization according to five MOs ($1a_1$, $2a_1$, $1b_2$, $3a_1$, $1b_1$) of water molecule obtained from our calculations were given in Table 2.

Table 2. The radiation-chemical yield of direct ionization according to MO of water molecule under the influence of electrons having different energies.

Molecular orbitals	N	B_j, eV	U_j, eV	T, keV		
				1	5	10
$1a_1$	2	539.7	793.4	1.645	1.649	1.650
$2a_1$	2	36.88	70.71	0.950	0.957	0.961
$1b_2$	2	19.83	48.36	0.704	0.709	0.710
$3a_1$	2	15.57	59.52	0.287	0.288	0.288
$1b_1$	2	12.61	61.91	0.0017	0.0021	0.0025

Short-living active intermediate particles (excitation and extreme excitation states) generated in physical state of radiolysis process convert into products of new type in physicochemical state (10^{-14} san.) as a result of dissociation and autoionization. Singlet excitation states A^1B_1 and B^1A_1 of water molecule create the following products dissociating correspondingly

$$H_2O^*(A^1B_1) \rightarrow H + OH \quad (6)$$
$$H_2O^*(B^1A_1) \rightarrow H_2 + O$$

and ~25% of (6) reaction recombinates and converts into water molecule. Extreme excitation states (Ry, db, ds and ~0,922 part of collective excitation states) are observed by formation of $H_2O^+...e^-$ ion pair as a result of autoionization

$$H_2O^{**} \rightarrow H_2O^+ + e^-$$

The other ~0,072 part of collective excitation state creates highly excited hydrogen atom H^* and OH radical by dissociating.

$$H_2O^{**} \rightarrow H^* + OH$$

H_2O^+ ion creates H_3O^+ ion with high reactionary character as a result of ion-molecular reaction in the period of 10^{-14} sec.

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$$

The electrons the energies of which are not sufficient for inelastic collision lose their energies as a result of dipole relaxation, transform into thermal electrons and solvates in liquid phase 10^{-12} sec. Considering the above-mentioned conditions, the radiation-chemical yields of intermediate products created in radiolysis process during ~10^{-11} sec. can be illustrated in the following form:

$$G(H_3O^+) = g_{H_2O^+} + g_{Rid} + g_{ab} + 0{,}922g_{pl}$$

$$G(OH) = G(H_3O^+) + 0{,}75g_{H_2O^*(A_1B_1)} + 0{,}078g_{pl}$$

$$G(H) = 0{,}75g_{H_2O^*(A_1B_1)}, \quad G(H_2) = G(O) = g_{H_2O^*(B_1A_1)}$$

$$G(H^*) = 0{,}078g_{pl}, \quad G(e_{aq}) = G(H_3O^+)$$

The results of calculations were given in Table 3. in comparison with the results obtained by different authors and in diffrent experiments.

Table 3. The radiation-chemical yields of the products created in physicochemical phase of radiolysis process in water under the influence of low-energy electrons:

Results	Products						
	$G(H_3O^+)$	G(OH)	G(H)	$G(H_2)$	G(O)	$G(H^*)$	$G(e_{aq})$
J.Q.Turner [20]	6.3	8.4	2.1	0.3	0.3	-	6.3
I.Q.Kaplan [11]	5.16	5.85	0.61	0.39	0.39	0.086	5.16
Experiments [20,21]	4.8	5.9	0.7	0.45	-	-	4.7
Our results	5.05	5.74	0.61	0.39	0.39	0.086	5.05

There's coincidence between the radiation-chemical yields of intermediate products calculated on the base of our model for active intermediate products in physical and physicochemical phases of radiolysis process in water and the results of the theoretical calculations and experiments [6,7,11] conducted by [6,7,11] authors from different aspects.

4. REFERENCES

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