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Abstract

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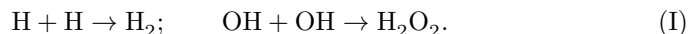
PHYSICAL CHEMISTRY

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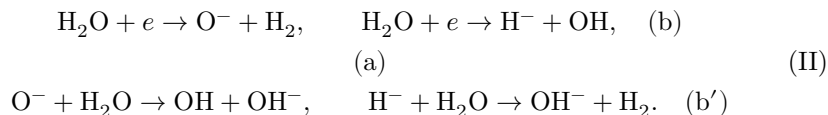
ON THE MECHANISM OF FORMATION OF MOLECULAR PRODUCTS IN THE RADIOLYSIS OF WATER

(Presented by Academician A. I. Alikhanov, July 4, 1963)

At present, various opinions are expressed in the literature concerning the mechanism of formation of the primary molecular products of water radiolysis— H_2 and H_2O_2 . It is often assumed that they are formed by recombination of two active particles ⁽¹⁾, for example:



Along with this, the possibilities of formation of molecular products with direct participation of water molecules in the reaction are also discussed. Thus, according to Hayhinsky and Maga ⁽²⁾, the formation of hydrogen molecules occurs according to one of the following schemes:



Scheme (b) has recently been examined in detail by Platzman ⁽³⁾. He considers that electrons with energy < 6.8 eV (the lower excitation level of water molecules) are captured by water molecules according to reaction (IIb), and then, by reaction (IIb'), H_2 molecules are formed. From his calculation it follows that, in the radiolysis of water under the action of γ -rays and fast electrons, the yield of molecular hydrogen by reactions (IIb') should be 0.2 ± 0.1 molecules per 100 eV, which is of the same order as the experimental value, equal to 0.4 molecules per 100 eV.

In other works ⁽⁴⁾, formation of H_2 and H_2O_2 molecules is considered possible in the interaction of an excited and an ordinary H_2O molecule:

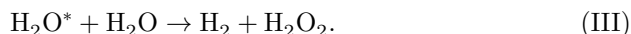
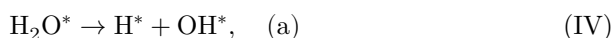


Figure 1

Figure 1: Figure 1

A similar conception of the origin of molecular products was developed also by V. V. Voevodskii ⁽⁵⁾, who assumed that the energy transferred to a water molecule by an ionizing particle then migrates through the solution to some disturbance in the structure of water. The excited molecule H_2O^* that has arisen near such a disturbance decomposes into two excited radicals:



and the latter rapidly enter into reactions:



A common feature of mechanisms (II), (III), and (IV), distinguishing them from mechanism (I), is the idea that H_2 and H_2O_2 molecules can arise as a result of interaction with a water molecule of some one active particle (H^- , H_2O^* , H^* , OH^*).

To identify the mechanism of formation of molecular products that actually takes place, let us consider the dependence of the yield G_M of H_2 and H_2O_2 molecules (the index M denotes H_2 and H_2O_2) on the concentration of acceptors of active particles.

For all systems studied so far in solution irradiated with γ -rays or fast electrons, the values of G_M decrease linearly as a function of the cube root of the acceptor concentration ⁽¹⁾

$$G_M = G_M^0 - qC_A^{1/3}, \quad (1)$$

where G_M^0 is the yield of the molecular product extrapolated to zero acceptor concentration, and q is a constant found experimentally.

Fig. 1. Dependence of $G_{\text{H}_2\text{O}_2}$ on the concentration C_A of acceptors of OH radicals ⁽¹⁾:

a — Br^- ; b — Cl^- ; v — NO_2^- ; g — J^- ; d — Tl^+

The fulfillment of relation (1) is illustrated in Figs. 1 and 2, taken from ⁽¹⁾.

Let us consider what types of dependence $G_M(C_A)$ are produced by the mechanisms of formation of H_2 and H_2O_2 listed above. We first dwell on schemes (II) and (III). According to the accepted model of radiolysis ⁽²⁻⁴⁾, the active particles (H^- , H_2O^*) are formed in separate microregions, spurs. To determine the concentration C of such particles in a spur, one may write the equation

Figure 2

Figure 2: Figure 2

$$\frac{\partial C}{\partial t} = D\Delta C - k[\text{H}_2\text{O}]C - k_A C_A C - \lambda C. \quad (2)$$

Here $[\text{H}_2\text{O}]$ is the concentration of water molecules, k and k_A are the corresponding reaction-rate constants, and D is the diffusion coefficient. The last term λC takes into account the possible loss of activity of the particle without formation of molecular products. Recombination of active particles according to the schemes under consideration plays no role. Integrating (2) over the whole volume under the assumption $C_A = \text{const}$, for the total number n of particles in a spur we obtain the equation

$$-\frac{dn}{dt} = n [k[\text{H}_2\text{O}] + k_A C_A + \lambda],$$

whence

$$\frac{n(t)}{n_0} = \exp\left(-\frac{t}{\tau}\right),$$

$$\tau_A = \frac{1}{k[\text{H}_2\text{O}] + k_A C_A + \lambda}. \quad (3)$$

In the absence of acceptor ($C_A = 0$)

$$\frac{n(t)}{n_0} = \exp\left(-\frac{t}{\tau_A}\right),$$

$$\tau = \frac{1}{k[\text{H}_2\text{O}] + \lambda}. \quad (4)$$

Fig. 2. Dependence of G_{H_2} on the concentration C_A of acceptors of H atoms⁽¹⁾:
a— NO_2^- ; *b*— H_2O_2 ; *v*— NO_3^- ; *g*— FeCl_3 ; *v* in 0.4 M HCl; *d*— Cu^{2+} ; *e*— $\text{CH}_2=\text{CH}-\text{CONH}_2$

The yield G_M of molecular products in this model is proportional to the quantity

$$k[\text{H}_2\text{O}] \int_0^\infty n(t) dt.$$

Fig. 3

Figure 3: Fig. 3

Therefore, using (3) and (4), we have:

$$\frac{G_M^0}{G_M} = \frac{\tau}{\tau_A} = 1 + \frac{k_A C_A}{k[\text{H}_2\text{O}] + \lambda}. \quad (5)$$

In V. V. Voevodskii's model (IV) of the radiolysis of water (⁵), the radicals H and OH are formed near disturbances in the homogeneity of the structure of water, i.e., uniformly throughout the volume of the irradiated solution. The concentration of radicals in this case is determined from the equation

$$gI = (k[\text{H}_2\text{O}] + k_A C_A + \lambda) C \equiv \frac{C}{\tau_A}, \quad (6)$$

where I is the dose rate ($\text{eV}/\text{cm}^3 \cdot \text{sec}$), and g is a numerical coefficient. The yield of molecular products, i.e., their number formed during the time t_0 of absorption by the solution of energy $E_0 = 100 \text{ eV}/\text{cm}^3$, is found from the equality

Fig. 3. Dependence of G_M^0/G_M on the concentration C_A of acceptors of the radicals H and OH. The solid curves refer to H_2O_2 , the dashed curves to H_2 . The symbols are the same as in Figs. 1 and 2.

$$G_M = k[\text{H}_2\text{O}]Ct_0, \quad (7)$$

in which t_0 is determined from the condition

$$It_0 = E_0. \quad (8)$$

Substituting into (7), instead of C and t_0 , their expressions from (6) and (8), we obtain

$$G_M = gk[\text{H}_2\text{O}]\tau_A.$$

Hence

$$\frac{G_M^0}{G_M} = \frac{\tau}{\tau_A} = 1 + \frac{k_A C_A}{k[\text{H}_2\text{O}] + \lambda}, \quad (9)$$

a result identical to (5).

It follows from (5) and (9) that, according to mechanisms (II), (III), and (IV), the ratio G_M^0/G_M should increase linearly with increasing acceptor concentration. Such a result cannot be reconciled with experiment (see Fig. 3). On the other hand, the theoretical analysis of model (I) for the formation of H_2 and H_2O_2 by recombination of two active particles, carried out in (6), shows that the dependence of G_M on C_A has the form:

$$\frac{G_M}{G_M^0} = 1 - \left(\frac{k_A V_0 C_A}{k_p n_0} \right)^{1/3} \quad (10)$$

(V_0 is the initial volume of the spur, k_p is the radical recombination constant, n_0 is their number at the moment of formation of the spur), identical with the empirical law (I).

The sharp discrepancy between the results of the analysis of mechanisms (II), (III), and (IV) and the highly reliable experimental data, together with the agreement of the consequences of mechanism (I) with this experiment, is convincing evidence in favor of the latter. Dependence (I), apparently, cannot be explained on the basis of mechanisms (II), (III), and (IV).

Let us note that the above consideration does not exclude the possibility that some fraction of the molecular products of radiolysis is formed as a result of the interaction of some active particle with water, provided that the corresponding reaction-rate constant k greatly exceeds the constant k_A for the rate of interaction of this active particle with dissolved substances. The influence of the latter on the magnitude of the component of the total yield of molecular products formed in this way would then be weak, and the total yield of molecular products at low concentrations of radical acceptors would still depend as the cube root of the acceptor concentration.

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Note: Figure translations are in progress. See original paper for figures.

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