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Abstract

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ON THE DEPENDENCE OF THE YIELD OF MOLECULAR PRODUCTS OF WATER RADIOLYSIS ON THE CONCENTRATION OF RADICAL ACCEPTORS

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As has been found experimentally for many systems, as the concentration of an acceptor of H and OH radicals in an irradiated solution increases, the yield of H_2 and H_2O_2 (the number of molecules formed, referred to 100 eV of energy absorbed by the solution) decreases (^{1}). This effect has been studied most fully in radiolysis under the action of hard γ-rays (Co^{60}). It has been established empirically that the decrease in G_{M}—the yield of molecular products (H_2 and H_2O_2)—occurs linearly as a function of the cube root of the concentration C_A of acceptor A (see Figs. 1 and 2). If G_{M}^0 (the subscript M denotes H_2 or H_2O_2) is the yield extrapolated to zero acceptor concentration, then, as is seen from the figures, the relation holds

$$G_{\mathrm{M}} = G_{\mathrm{M}}^0 - qC_A^{1/3}, \tag{1}$$

where q is a parameter found from experiment for each radical acceptor and molecular product.

1. In theoretical works on the influence of radical acceptors on the yield of H_2 and H_2O_2, no special significance is attached to the form of equation (1), and its agreement with experiment is regarded as accidental (see, for example, (^{2})).

We have attempted to derive relation (1) on the basis of the model of water radiolysis now generally accepted. According to this model, under the action of radiation, active particles—H and OH radicals capable of reacting with dissolved substances and with one another—are formed in separate spherical microregions of the irradiated solution, spurs, arising along the path of the ionizing particle. Recombination of radicals gives H_2 and H_2O_2 molecules. The presence in the solution of an appreciable concentration of acceptor prevents radicals from different spurs from meeting. Therefore it is sufficient to consider the process of radical recombination in an isolated spur.

If the concentration of radicals at point $\mathbf{r}$ at time t is denoted by $C(\mathbf{r}, t)$, their diffusion coefficient by D, and the recombination constant by k, then the equation for $C(\mathbf{r}, t)$ has the following form:

$$\frac{\partial C}{\partial t} = D\Delta C - kC^2 - k_A C_A C, \tag{2}$$

where k_A is the rate constant of the reaction of radicals with their acceptor, and Δ is the Laplace operator.

We represent $C(\mathbf{r}, t)$ in the form

$$C(\mathbf{r}, t) = n(t)w(\mathbf{r}, t), \qquad \int w(\mathbf{r}, t)\, dv = 1 \tag{3}$$

($n(t)$ is the total number of radicals at time t, $w(\mathbf{r}, t)$ is the probabil—

the probability of finding a radical at point $\mathbf{r}$ at time t). Then integration of equation (2) over the entire volume gives

$$\frac{dn}{dt} = -k\frac{n^2}{V} - k_A C_A^0 n \int w \frac{C_A}{C_A^0}\, dv, \tag{4}$$

where C_A^0 is the initial concentration of the acceptor, and

$$V \equiv \frac{1}{\int w^2(\mathbf{r}, t)\, dv} \tag{5}$$

has the dimensions of volume.

The distribution of radicals at the initial instant of time (the moment of spur formation) is usually specified by a Gaussian law. In addition, we shall assume that it remains so throughout the entire time, i.e.

$$w(r, t) = \frac{e^{-r^2/4Dt+a^2}}{\left[\pi(4Dt + a^2)\right]^{3/2}}, \tag{6}$$

where a is the initial width of the distribution.

Analysis $^{(2)}$ shows that expression (6) describes the spatial distribution of radicals over the entire time fairly well. In a rigorous solution of the problem under consideration it is necessary to supplement equation (2) with the equation

$$\frac{\partial C_A}{\partial t} = D_A \Delta C_A - k_A C_A C,$$

Fig. 1. Dependence of $G_{\mathrm{H_2O_2}}$ on the concentration C_A of acceptors of OH radicals (1): a—Br^-; —Cl^-; —NO_2^-; —J^-; —Tl^+

Figure 1: Fig. 1. Dependence of $G_{\mathrm{H_2O_2}}$ on the concentration C_A of acceptors of OH radicals (1): a—Br^-; —Cl^-; —NO_2^-; —J^-; —Tl^+

Figure 2

Figure 2: Figure 2

which takes into account the diffusion of the acceptor particles (D_A is their diffusion coefficient), and to consider them jointly. However, attempts to obtain the "cube-root law" in this way apparently did not give a result $^{(2)}$. Below we shall set forth an approximate method.

Fig. 1. Dependence of $G_{\mathrm{H_2O_2}}$ on the concentration C_A of acceptors of OH radicals (1): a—Br^-; —Cl^-; —NO_2^-; —J^-; —Tl^+

Let us note that, for times sufficiently close to the moment of spur formation, the second term on the right-hand side of equation (4) is much smaller than the first, since under the experimental conditions the concentration of radicals greatly exceeds the concentration of the acceptor, and $k_A \ll k$. Therefore, during some interval of time $0 \le t < t_1$, while

$$k\frac{n^2}{V} \gg k_A C_A^0 n \int w \frac{C_A}{C_A^0}\, dv, \tag{7}$$

the loss of radicals in the spur will occur mainly only as a result of their recombination. The number of radicals in the spur at any instant of time from this interval will be determined with good accuracy from the solution of equation (4), if the second term on the right-hand side is set equal to zero. Starting from definition (5) and assumption (6), we find that the characteristic volume of the spur is

$$V = \left[8\pi D t + 2\pi a^2\right]^{3/2}. \tag{8}$$

Substituting (8) into (4) and integrating for the number of radicals at the time $0 \le t < t_1$, we obtain, for $c_A = 0$:

$$\frac{n(t)}{n_0} = \frac{1}{1 + L\left(1 - 1/\sqrt{1 + 4Dt/a^2}\right)}. \tag{9}$$

Here $L = (2/\pi)^{1/2} k n_0 / 8\pi D a$, and n_0 is the initial number of radicals in the spur.

Fig. 2. Dependence of G_{H2} on the concentration C_A of acceptors of H atoms (1):
a—$\mathrm{NO_2^-}$; b—$\mathrm{H_2O_2}$; v—$\mathrm{NO_3^-}$;
g—$\mathrm{FeCl_3}$; d—$\mathrm{Cu^{2+}}$; e—$\mathrm{CH_2{=}CH{-}CONH_2}$.

For times when inequality (7) has the opposite sign, recombination of radicals no longer plays a role, and they disappear only through interaction with acceptor particles. Thus, approximately, it may be assumed that recombination of radicals occurs only during the time interval $0 \le t < t_1$, where t_1, in order of magnitude, is found from the condition

$$k\frac{n^2(t_1)}{V(t_1)} = k_A n(t_1)\overline{C}_A(t_1), \tag{10}$$

where $\overline{C}_A(t_1)$ is the acceptor concentration averaged over the spur volume at time t_1.

From expression (9), which in the absence of an acceptor is valid throughout the whole process $0 \le t < \infty$, it is seen that as $t \to \infty$ the number of radicals $n(t)$ that have avoided recombination tends to a definite limiting value $n_\infty = n_0/(1+L)$. Obviously, $n_\infty \le n(t_1) \le n_0$. According to the estimate made in (3), $L \ll 1$, i.e., the quantities n_∞ and n_0 are close. Taking $\overline{C}_A(t_1) \simeq C_A^0$ and using expression (8) for $V(t_1)$, from (10) we obtain

$$t_1 = \frac{a^2}{4D}\left(\frac{k}{k_A}\frac{n_0}{C_A^0 V_0}\right)^{2/3}, \tag{11}$$

where, in accordance with (8), $V_0 = (2\pi a^2)^{3/2}$.

The fraction of radicals that recombined during the time $0 \le t < t_1$, according to (9), is equal to

$$\frac{n_0 - n(t_1)}{n_0} = L\left(1 - \frac{1}{\sqrt{1 + 4Dt_1/a^2}}\right). \tag{12}$$

From (12) it follows that

$$\frac{G_M}{G_M^0} = 1 - \sqrt{\frac{a^2}{4Dt_1}}\,\frac{1}{\sqrt{1 + a^2/4Dt_1}}.$$

Substituting here for t_1 its expression from (10), we finally find:

$$\frac{G_M}{G_M^0} = 1 - \left(\frac{k_A}{k}\frac{V_0 C_A^0}{n_0}\right)^{1/3} \frac{1}{\sqrt{1 + \left(\frac{k_A}{k}\frac{V_0 C_A^0}{n_0}\right)^{-1/3}}}. \tag{13}$$

The justification for the approximate calculation presented is the fulfillment of the following conditions: 1) the number of radicals captured by the acceptor during the time $0 \leq t < t_1$ is small in comparison with the number of recombi-

recombined during the same time; 2) the number of radicals that have recombined during the time $t_1 < t < \infty$ is small compared with the number captured by the acceptor during the same time.

Simple estimates show that these conditions are satisfied if the inequality

$$\left(\frac{k_A}{k}\frac{C_A^0 V_0}{n_0}\right)^{1/3} \ll 1. \tag{14}$$

holds. Assuming, in accordance with generally accepted estimates ⁽²⁾, $k_A \lesssim k$ and $n_0/V_0 \simeq 1$ mole/l, we find that (14) will be satisfied for $C_A^0 \ll 1$ mole/l. In this case equation (13) can be rewritten in the form

$$G_M = G_M^0 = 1 - \left(\frac{k_A}{k}\frac{C_A^0 V_0}{n_0}\right)^{1/3}. \tag{15}$$

Equation (15) is identical with the empirical law (1); in this case the coefficient q in (1) acquires a clear physical meaning:

$$q = \left(\frac{k_A}{k}\frac{V_0}{n_0}\right)^{1/3} G_M^0.$$

For $k_A \simeq k$ and $n_0/V_0 \simeq 1$ mole/l, we obtain $q = 1$ (mole/l)$^{-1/3}$ and $G_M/G_M^0 \simeq 1 - [C_A^0 \text{ mole/l}]^{1/3}$. Hence, for example, at $C_A^{1/3} = 0.3$ (mole/l)$^{1/3}$, the yield decreases by 30% ($G_M/G_M^0 = 0.7$), which is in good agreement with the data of Figs. 1 and 2.

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

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