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Concerning the Cube-root Dependence of the
Molecular Yield on Scavenger Concentration in
the Radiolysis of Water

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Abstract

It has been shown rigorously that, within the diffusion model, the reduction of the molecular yield by competitive scavenger reaction always follows a Square-root law in the limit of small scavenger concentration, and not a cube-root law. The error of earlier demonstration of the cube-root dependence using diffusion kinetics by Byakov has been traced to several reasons. The most important reason is the neglect of competition between scavenging and recombination reaction within the characteristic time t_1 which, in the limit of small concentration of the scavenger, proceeds to infinity.

In the radiolysis of water and dilute aqueous solutions the observable molecular products, H_2 and H_2O_2 , are formed by the recombination of reactive primary radicals, including the hydrated electron. When radical scavengers are present there is a competition between recombination and scavenging reactions, the extent of the competition being determined by the concentration of the scavenger and the rate constant of the scavenging reaction.

During the early stage of the development of the radiolysis of aqueous solutions it was empirically established by experiments that the reduction in the molecular yield follows an approximate cube-root relation with the concentration of the scavenger as follows.¹

$$G(R_2) = G^0(R_2) - \alpha C_s^{1/3} \quad (1)$$

In equation (1) R_2 stands for a molecular product, H_2 or H_2O_2 , C_s is the scavenger concentration and α is a constant specific to the scavenger and the molecular product concerned. For quite some time this cube-root relationship was considered fortuitous and it was not possible to derive it from a sound theoretical point of view.^{2,3} In the meantime a great deal of refined theoretical⁴ and experimental⁵ work has been performed on electron scavenging in the γ -radiolysis of liquid hydrocarbons. In these systems the electron-electron reaction does

not occur; however, it has been shown rather rigorously that one theoretically expects an enhancement of the scavenging reaction proportional to the square-root of the scavenger concentration as long as the latter is small.⁴ This theoretical demonstration is very general, depending only on two factors. The first is a Laplace-transformation relationship between the yield of the scavenging reaction (or, in the aqueous case, a reduction in the molecular yield) and the probability, as a function of time, of survival against recombination in the absence of scavengers. The second factor relates to free diffusion in the infinite-time limit which, by the Laplace transformation, is related to the behavior of scavenger reaction at small concentrations.

Recently it has been brought to this writer's attention⁶ that Byakov⁷ had already attempted to derive equation (1) for the radiolysis of aqueous solutions utilizing diffusion kinetics. Besides the usual assumptions inherent in the diffusion model, Byakov introduces further approximations^{7,8} and the results are carried through to a recent publication.⁹ The purpose of the present article is to show that even in the radiolysis of aqueous solutions one rigorously expects a square-root dependence given by

$$G(R_2) = G^0(R_2) - \beta C_s^{1/2}, \quad (2)$$

where β is a suitable constant. We shall first derive equation (2) utilizing diffusion kinetics. This will be followed by an attempt

to analyse the subtle error which led Byakov to the derivation of equation (1).

We consider a one-radical (R) model spur within which the competition between recombination and scavenging reactions may be described as follows.

Following Ganguly and Magee¹⁰ the number of radicals in the spur at time t , $n(t)$, may be given by

$$n(t) = \exp(-\lambda t) [n_0^{-1} + k \int_0^t V(t')^{-1} \exp(-\lambda t') dt']^{-1}. \quad (3)$$

In equation (3) n_0 is the initial number of radicals in the spur, k is the rate constant of reaction (a), $\lambda = k_s c_s$ with k_s as the rate constant of the scavenging reaction (b) and $V(t)$ stands for the effective volume of the spur at time t . Exactly speaking $V(t)$ is given by^{7,10}

$$V(t)^{-1} = \int c^2 dv / n^2(t), \quad (4a)$$

where c is the concentration of radicals and the integration is to be carried over the entire volume. In the Gaussian prescribed diffusion approximation applied to a spherical spur $V(t)$ may be expressed as follows^{7,10}

$$V(t) = [2\pi(a^2 + 4Dt)]^{3/2}, \quad (4b)$$

where D is the diffusion coefficient of the radicals and a is the "width" of their initial Gaussian distribution. The number of radicals undergoing scavenging reaction per unit volume per unit time at t equals $k_s c_s c = \lambda c$. Therefore the total amount of scavenging reactions is given by

$$N(\lambda) = \iint \lambda c dv dt = \lambda \int_0^\infty n(t) dt, \quad (5)$$

since $n(t) = \int c(r, t) dv$. Substituting equation (3) into equation (5) we then obtain

$$N(\lambda) = \lambda \int_0^\infty \exp(-\lambda t) [n_0^{-1} + k \int_0^t v(t')^{-1} \exp(-\lambda t') dt']^{-1} dt. \quad (6)$$

If we want to assess the correct law of the reduction of molecular yield at small scavenger concentration we must take the limit of equation (6) as $\lambda \rightarrow 0$. In this limit the inner exponential in equation (6) can be put equal to unity because even a linear expansion will contribute a term of higher order to $N(\lambda)$. Thus

$$\lim_{\lambda \rightarrow 0} N(\lambda) = \lambda \int_0^\infty \exp(-\lambda t) [n_0^{-1} + k \int_0^t \frac{dt'}{v(t')}]^{-1} dt. \quad (7)$$

The integral in equation (7) has the standard form of a Laplacian transformation. Further, using the theorem that if

$\lim_{t \rightarrow \infty} F(t) = g(t)$ then $\lim_{\lambda \rightarrow 0} (\text{LT of } F) = \text{LT of } g$, we get

$$\lim_{\lambda \rightarrow 0} N(\lambda) = \lambda \cdot \text{LT of } \lim_{t \rightarrow \infty} \{ [n_0^{-1} + k \int_0^t \frac{dt'}{v(t')}]^{-1} \}. \quad (8)$$

Using equation (4b) and taking the necessary limit of equation (8) we recover the square-root law as follows.

$$\lim_{\lambda \rightarrow 0} N(\lambda) = \frac{n_0}{(1 + \gamma n_0)} \left[1 + \lambda^{1/2} \frac{a \gamma n_0}{(1 + \gamma n_0)} \left(\frac{\pi}{4D} \right)^{1/2} \right], \quad (9)$$

where $\gamma = k / [(2\pi)^{3/2} (2aD)] = L/n_0$ (in Byakov's notation). The yield of the molecular product, $G(\lambda)$, in the presence of a scavenger is proportional to $n_0 - N(\lambda)$. Thus

$$\lim_{\lambda \rightarrow 0} G(\lambda) \propto \frac{\gamma n_0^2}{(1 + \gamma n_0)} - \left(\frac{\pi \lambda}{4D} \right)^{1/2} a \frac{\gamma n_0^2}{(1 + \gamma n_0)^2}. \quad (10)$$

From equation (10) we obtain

$$\lim_{\lambda \rightarrow 0} G(\lambda) = G(0) \left[1 - a(\pi \lambda / 4D)^{1/2} / (1 + \gamma n_0) \right]. \quad (11)$$

Equation (11) has the same form as eq. (2) with $\beta = aG_0(\pi k_s / 4D)^{1/2} / (1 + \gamma n_0)$.

In Byakov's treatment⁷ of the cube-root dependence (cf. eq. 1) there are several approximations in addition to the prescribed diffusion approximation. They may be divided into two groups; the first group contains incidental features whereas the approximations in the second group have serious consequences. We will first briefly describe the first group approximations and later consider the second group more fully.

The inequality (7) of I apparently depends on time only and signifies that at earlier times recombination predominates over scavenging. Although this may be true its basis is not

necessarily correctly derived; for referring to eq. (2) of (I) the relative importance of various terms on the right hand side depends both on r and t . What it means is that although the radical concentration may "greatly exceed" scavenger concentration in a defined small volume the same may not be true everywhere. The concentration in a Gaussian distribution falls very rapidly whereas the scavenger concentration is independent of r . Therefore at any finite scavenger concentration one can always find a large volume within which the specified inequality will not hold.

The assumed time-scale of validity of eq. (9) of I is for $t \leq t_1$ where t_1 is given by eq. (11) of I. If k_A (k_S in our notation) is $\sim k$ then t_1 would be approximately independent of the rate constant of scavenging. This cannot be absolutely true since the natural time scale of scavenging is $\tau_S \sim (k_S c_S)^{-1}$. The smaller of t_1 and τ_S is the appropriate time scale. For example if we take $k_A \sim k \sim 10^{10}$ litre/(mole.s), $a \sim 20 \text{ \AA}$, $D \sim 4 \times 10^{-5} \text{ cm}^2/\text{s}$, $n_0 \sim 6$ we estimate $t_1 \sim 10^{-8} \text{ s}$ whereas $\tau_S \sim 10^{-9} \text{ s}$.

The derivation of eq. (11) of I requires that $L \ll 1$. If that is not true one would obtain

$$t_1 = \frac{a^2}{(4D)} \left[\left(\frac{k}{k_A} \cdot \frac{n_0}{C_{AVO}} \right)^{2/3} - 1 \right] (1 + L)^{-2/3}. \quad (12)$$

In another word Byakov's approximation would be consistent if $t_1 \gg a^2/(4D)$, the diffusion time-scale. If the scavenger concentration is very small ($\approx 1 \text{ mM}$) then the approximation will be

justified. With the previously used values for the parameters this approximation starts to be invalid at ~ 40 mM concentration of the scavenger.

The assumptions that $n_{\infty} \leq n(t) \leq n_0$ and that $n_{\infty} = n_0/(1 + L)$ with $L \ll 1$ are not mutually consistent with reduction of molecular yield at a small scavenger concentration. For if these are true and then the molecular yields are very small to start with and any reduction in them is a second-order effect which is not within the purview of the theory. In water radiolysis the total molecular yield (H_2 and $H_2 O_2$) in the absence of scavengers is about 1.2. Taking the initial radical yield as 10, $G_0 = 10$ and $G_0 - G_{\infty} = 2 \times 1.2 = 2.4$ which gives $L = (G_0 - G_{\infty})/G_{\infty} = 0.316$. Ershler and Bykaov⁸ compute L in two typical cases as 0.25 and 0.50. None of these values are actually $\ll 1$.

The most important objection to Byakov's treatment is that equation (12) of I is not correct even when $C_A \rightarrow 0$ ($t_1 \rightarrow \infty$). There is always competitive scavenger reaction between 0 and t_1 . As $C_A \rightarrow 0$, $t_1 \rightarrow \infty$. This means that the reaction velocity with the scavenger is infinitely slow; but since the reaction proceeds over infinitely long time it does not imply that the total scavenger reaction probability is negligible. In fact in the limit $C_A \rightarrow 0$, the reaction probability with the scavenger is just the probability of escape, $(1 + L)^{-1}$ in Byakov's notation. In other words there is a singularity in scavenger reaction at $C_A = 0$. If the scavenger concentration is exactly zero then of course the scavenger reaction probability is zero. But if $C_A \rightarrow 0$ that

reaction probability is the escape probability which in the present case is rather large. It is now evident that there is no clearly defined time-scale t_1 such that all or most recombination reaction occurs between 0 and t_1 and all or most scavenging reactions occurs between t_1 and ∞ . That concept is not correct. The competition between recombination and scavenging occurs over the entire time-scale. If this competition is taken into account in Byakov's procedure exactly the same expressions will be obtained for $n(t)$, $N(\lambda)$ and $G(\lambda)$ as in equations (3), (9) and (11) respectively, valid in their stated limits and approximations.

In conclusion it may be inferred that the square-root law of scavenging is the only correct one within the diffusion model. It however, does not deny the experimental validity of the cube-root law (eq. 1), for which the exact explanation is lacking. In actual practice the radiolysis of water is a very complicated situation involving reactions between various kinds of radicals, ions and scavengers. Conclusions derived from a one-radical, one-solute model may not apply. On the other hand there is some evidence that at least during the early stages of radiolysis of water diffusion kinetics may not play an important role.¹¹ All of these may have an important bearing on scavenging reactions.

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