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Abstract

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A METHOD FOR THE APPROXIMATE ESTIMATION OF THE ABSOLUTE VALUES OF RATE CONSTANTS OF RADIATION REACTIONS IN AQUEOUS SOLUTIONS

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Earlier, in work (^{1}), carried out with the participation of the author of the present article, the absolute values of the rate constants of the reactions $H+OH$, $H+O_2$, and $Fe^{2+}+OH$ were approximately estimated. The method for calculating them consisted in using two independent methods of kinetic treatment of experimental data obtained in the study of the pulse radiolysis of aqueous ferrosulfate solutions containing oxygen. The first method is based on the application of the method of stationary concentrations, and the second on the assumption that reactions in the bulk of the solution do not occur during the action of the electron pulse (duration $5 \cdot 10^{-6}$ sec).

In the present work this method is used to calculate the rate constants of a number of other reactions. For this purpose, experimental data obtained in the study of the pulse radiolysis of the following aqueous systems were treated: Ce^{4+}—Ce^{3+} (^{2,3}), Br^-—O_2^*, NO_3^-—NO_2 (^{4}), and H_2O_2 (^{5}). It was found that in all cases the method under consideration gives realistic values of the constants.

As is known ($^{1-13}$), the yields of radiolytic transformations at sufficiently high absorbed-dose rates produced by pulsed electron radiation, owing to competition in the bulk of the solution between radical-radical and radical-dissolved-substance reactions, change substantially in comparison with low absorbed-dose rates. In the simplest case this change in yields is due to competition between the reactions:

$$R + R \rightarrow R_2, \tag{1}$$

$$R + S \rightarrow \text{product}, \tag{2}$$

where R is a radical, R_2 is a molecular product, and S is the dissolved substance. Then the following equations can be obtained (^{5,7,11}):

$$[\mathrm{R}] = \frac{K_2[\mathrm{S}][\mathrm{R}]_0}{(K_2[\mathrm{S}] + 2K_1[\mathrm{R}]_0)e^{K_2[\mathrm{S}]t} - 2K_1[\mathrm{R}]_0}, \tag{3}$$

$$f = \frac{K_2[\mathrm{S}]}{2K_1[\mathrm{R}]_0} \ln\left(1 + \frac{2K_1[\mathrm{R}]_0}{K_2[\mathrm{S}]}\right), \tag{4}$$

where [R] is the concentration of R at any time t after the pulse; [S] is the concentration of S; $[\mathrm{R}]_0$ is the concentration of R immediately after the pulse (it is assumed that during the action of the pulse no reactions occur in the bulk of the solution), K_1 and K_2 are the rate constants of reactions (1) and (2); f is the fraction of radicals R reacting with S. Obviously,

$$[\mathrm{R}]_0 = G_R \frac{D}{100N}, \tag{5}$$

where G_R is the yield of R, D is the dose per pulse (in eV/l), and N is Avogadro's number. Thus, with the aid of equation (4), it is possible, on the basis of experimental data, to calculate K_1/K_2.

On the other hand, the method of stationary concentrations as applied to reactions (1) and (2) gives, in the general form, the following equation:

$$\frac{I\sqrt{2G}}{(G_R - G)^{1/2}} = \frac{K_2}{K_1^{1/2}}[\mathrm{S}]\left(\frac{100N}{I}\right)^{1/2}, \tag{6}$$

* Experimental data on the radiolysis of this system, obtained with the participation of the author of the present article, will be set forth in detail in a subsequent publication.

where G is the yield of the product of reaction (2), and I is the absorbed dose rate (in eV/l · sec). Thus, knowing G at various I or $[S]$, one can find $K_2/K_1^{1/2}$ from equation (6). By comparing K_2/K_1 with $K_2/K_1^{1/2}$, it is evidently possible to determine K_2 and K_1.

For the systems indicated above, the yields in the absence of dissolved substances capable of interacting with radicals R (reaction (2)) are higher under pulse irradiation conditions than at low dose rates. In the presence of sufficient amounts of such a substance, the yields decrease.

The increase in $G(\mathrm{Ce}^{3+})$ for a Ce^{4+} solution, $G(\mathrm{H_2O_2})$ for an $\mathrm{O_2}$ solution, and $G(\mathrm{NO_2^-})$ for a $\mathrm{NO_3^-}$ solution is mainly explained by the increased role of recombination of OH radicals ($^{2-4}$):

$$\mathrm{OH} + \mathrm{OH} \rightarrow \mathrm{H_2O_2}. \tag{7}$$

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

Fig. 1. Dependence of $G(\mathrm{Ce}^{3+})$ on the concentration of Ce^{3+} in a 0.4 M sulfuric acid solution of Ce^{4+} ($[\mathrm{Ce}^{4+}] = 2 \cdot 10^{-4}$ M, dose rate $1.5 \cdot 10^{23}$ eV/ml • sec). Points—experimental data (3); curve calculated at $K_9/K_7 = 3 \cdot 10^{-2}$.

Fig. 2. Dependence of $G(\mathrm{H_2O_2})$ on the concentration of KBr in a 0.4 M $\mathrm{H_2SO_4}$ solution saturated with air (dose rate $2.9 \cdot 10^{23}$ eV/ml • sec). Points—experimental data; curve calculated at $K_{10}/K_7 = 2.5$.

The increase in $G(\mathrm{H_2})$ for deaerated acidic water is due chiefly to recombination of H atoms (5,11):*

$$\mathrm{H} + \mathrm{H} \leftarrow \mathrm{H_2}. \tag{8}$$

Addition to the indicated solutions of Ce^{3+}, Br^-, $\mathrm{NO_2^-}$, and $\mathrm{H_2O_2}$, as a result of the occurrence of the reactions:

$$\mathrm{Ce}^{3+} + \mathrm{OH} \rightarrow \mathrm{Ce}^{4+} + \mathrm{OH}^-, \tag{9}$$

$$\mathrm{Br}^- + \mathrm{OH} \rightarrow \mathrm{Br} + \mathrm{OH}^-, \tag{10}$$

$$\mathrm{NO_2^-} + \mathrm{OH} \rightarrow \mathrm{NO_2} + \mathrm{OH}^-, \tag{11}$$

$$\mathrm{H} + \mathrm{H_2O_2} \rightarrow \mathrm{OH} + \mathrm{H_2O} \tag{12}$$

leads, respectively, to a decrease in $G(\mathrm{Ce}^{3+})$, $G(\mathrm{H_2O_2})$, $G(\mathrm{NO_2^-})$, and $G(\mathrm{H_2})$.

In these cases the yields G of the products at a given concentration S and dose rate are related to the quantity f by the following relation:

$$G = (1 - f)(G_0 - G_0') + G_0', \tag{13}$$

where G_0 is the product yield at the given high dose rate in the absence of S, and G_0' is the yield of the same product at a low dose rate, likewise in the absence of S. In Figs. 1-3 the experimental values and the values calculated from equations (4) and (13) of $G(\mathrm{Ce}^{3+})$, $G(\mathrm{H_2O_2})$, and $G(\mathrm{NO_2^-})$ are compared at $K_9/K_7 = 3 \cdot 10^{-2}$, $K_{10}/K_7 = 2.5$, and $K_{11}/K_7 = 1.5$, respectively. As can be seen, the agreement is satisfactory. In the Ce^{4+}—Ce^{3+} system, as was shown

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* In sufficiently acidic solutions, hydrated electrons are converted into H atoms:

$$e^-_{\mathrm{aq}} + \mathrm{H}^+ \rightarrow \mathrm{H}.$$

in work (3), the products of the interaction of OH radicals with sulfuric acid play an important role. Therefore, a more accurate value of K_9/K_7 can be obtained at sufficiently high concentrations of Ce^{3+}, when the reaction of OH with HSO_4^- is suppressed. For this concentration range of Ce^{3+} ($[\mathrm{Ce}^{3+}] \geqslant 5 \cdot 10^{-3}\ M$), $K_9/K_7 = 4 \cdot 10^{-2}$. The value of the constant K_{12}/K_8 was calculated in a similar way by J. Thomas and E. Hart (5). It is equal to $8 \cdot 10^{-3}$.

The relative constants $K_9/K_7^{1/2}$ and $K_{10}/K_7^{1/2}$, as it turned out, are equal to $3.6 \cdot 10^3$ $(\mathrm{l/mol \cdot sec})^{1/2}$ and $2 \cdot 10^5$ $(\mathrm{l/mol \cdot sec})^{1/2}$, respectively. The constant $K_{11}/K_7^{1/2}$ can be calculated from the experimental data obtained

[Figure 3 and Figure 4 graphs shown on the page.]

Fig. 3. Dependence of $G(\mathrm{NO}_2^-)$ on the concentration of NO_2^- in $5 \cdot 10^{-3}$ M NaNO_3 solution saturated with air (dose rate $1.5 \cdot 10^{23}$ eV/ml · sec). Points—experimental data (4); curve calculated for $K_{11}/K_7 = 1.5$

Fig. 4. Graphical solution of equation (20) using the data of work (5)

in work (4). If it is assumed that the mechanism of radiolysis of NO_3^- solutions at high absorbed-dose rates includes reactions (7) and (11), as well as the reactions:

$$\mathrm{NO}_3^- + \mathrm{H} \rightarrow \mathrm{NO}_2 + \mathrm{OH}^-, \tag{14}$$

$$\mathrm{NO}_3^- + \mathrm{e}^-_{\mathrm{aq}} \rightarrow \mathrm{NO}_3^{2-}, \tag{15}$$

$$2\mathrm{NO}_2 + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{NO}_2^- + \mathrm{NO}_3^- + 2\mathrm{H}^+, \tag{16}$$

$$2\mathrm{NO}_3^{2-} + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{NO}_2^- + \mathrm{NO}_3^- + 2\mathrm{OH}^-, \tag{17}$$

then, using the steady-state concentration method, one can derive the equation*:

$$\frac{G_{\mathrm{red}} - G(\mathrm{NO}_2^-)}{\left[G(\mathrm{NO}_2^-) + G_{\mathrm{H}_2} - G_{\mathrm{H}_2\mathrm{O}_2}\right]^{1/2}} = \frac{G_{\mathrm{OH}} + 2G_{\mathrm{H}_2\mathrm{O}_2} - 2G(\mathrm{H}_2\mathrm{O}_2)}{\left[G(\mathrm{H}_2\mathrm{O}_2) - G_{\mathrm{H}_2\mathrm{O}_2}\right]^{1/2}} = \frac{K_{11}}{K_7^{1/2}}[\mathrm{NO}_2^-]\left(\frac{100N}{I}\right)^{1/2}. \tag{18}$$

From the data presented in work (4), it follows that

$$K_{11}/K_7^{1/2} = (1.3 \pm 0.7) \cdot 10^5\ (\mathrm{l/mol \cdot sec})^{1/2} **.$$

For calculating the relative constant $K_{12}/K_8^{1/2}$, the results obtained by J. Thomas and E. Hart (^{5}) were used. It was assumed that the value $G(\mathrm{H_2})$ is determined chiefly by reactions (8) and (12), and also by the reaction:

$$\mathrm{H} + \mathrm{OH} \rightarrow \mathrm{H_2O}. \qquad (19)$$

* Here and below the symbol G_{red} denotes the total yield of $\mathrm{e}^-_{\mathrm{aq}}$ and H.

** The calculation of $K_{11}/K_7^{1/2}$ was carried out on the basis of the values $G(\mathrm{NO_2^-})$ and $G(\mathrm{H_2O_2})$ for a $5 \cdot 10^{-3}$ M $\mathrm{NaNO_3}$ solution at dose rates up to 10^{22} eV/ml · sec. In the calculations, dose-rate values averaged over the irradiated volume and arithmetic mean values of the concentrations of the $\mathrm{NO_2^-}$ and $\mathrm{H_2O_2}$ formed were used.

Applying the method of stationary concentrations, we find:

$$\frac{G_{\mathrm{red}} - G_{\mathrm{OH}} - G(\mathrm{H_2}) + G_{\mathrm{H2}}}{\sqrt{2}\,[G(\mathrm{H_2}) - G_{\mathrm{H2}}]^{1/2}} = \frac{K_{12}}{K_8'^{\,1/2}}[\mathrm{H_2O_2}]\left(\frac{100N}{I}\right)^{1/2}. \qquad (20)$$

Solving equation (20) for $K_{12}/K_8'^{\,1/2}$ using all the data obtained in work (5) is not possible. In that work the values of $G(\mathrm{H_2})$ are given as a function of $[\mathrm{H_2O_2}]$ at various doses per pulse, the dose being expressed as the number of micromoles of $\mathrm{Fe^{3+}}$. It is impossible to calculate the dose rate (in eV/ml • sec) from these data, since in each separate case the pulse duration is not indicated. However, it follows from work (5) that the mechanism including the competition of reactions (8) and (12) operates at dose rates up to 10^{23} eV/ml • sec. Therefore it may be assumed that one of the curves given in Fig. 2 of the cited work, namely the curve plotted at the maximum dose rate at which this mechanism still operates, was obtained at a dose rate of 10^{23} eV/ml • sec. Figure 4 shows the graphical solution of equation (20) using the data corresponding to this curve. In this figure

$$\varphi(G) = \frac{G_{\mathrm{red}} - G_{\mathrm{OH}} - G(\mathrm{H_2}) + G_{\mathrm{H2}}}{\sqrt{2}\,[G(\mathrm{H_2}) - G_{\mathrm{H2}}]^{1/2}}.$$

The tangent of the angle of inclination of the straight line in Fig. 4 is equal to

$$\frac{K_{12}}{K_8'^{\,1/2}}\left(\frac{100N}{I}\right)^{1/2}.$$

Then $K_{12}/K_8'^{\,1/2} = 9.8 \cdot 10^2$ $(\mathrm{l/mol \cdot sec})^{1/2}$.

Table 1

Rate constants of radiation reactions in aqueous solutions

Reactions	K, l/mol • sec
$H + OH$	$4.5 \cdot 10^{10}$ *
$H + O_2$	$5.3 \cdot 10^{9}$ *
$Fe^{2+} + OH$	$2.7 \cdot 10^{8}$ *
$H + H$	$1.4 \cdot 10^{10}$
$OH + OH$	$8.1 \cdot 10^{9}$; $6.4 \cdot 10^{9}$; $7.6 \cdot 10^{9}$***
$H + H_2O_2$	$1.1 \cdot 10^{8}$
$Ce^{3+} + OH$	$3.2 \cdot 10^{8}$
$NO_2^- + OH$	$1.1 \cdot 10^{10}$
$Br^- + OH$	$1.6 \cdot 10^{10}$

* Calculated in work (1).
** From data on the radiolysis of the $Ce^{4+} - Ce^{3+}$ system (at $K_9/K_7 = 4 \cdot 10^{-2}$).
*** From data on the radiolysis of the $Br^- - O_2$ system.
**** From data on the radiolysis of the $NO_3^- - NO_2^-$ system.

Table 1 gives the values of the constants found by comparing the obtained values of the ratios K_2/K_1 and $K_2/K_1'^{1/2}$. It is of interest to compare the constants calculated in the present work with those known in the literature. According to (14), $K_7 = 4 \cdot 10^9$ l/mol • sec, $K_9 = 7.2 \cdot 10^7$ l/mol • sec and $K_{11} = 2.5 \cdot 10^9$ l/mol • sec. As follows from work (5), $K_8 = 5 \cdot 10^9$ l/mol • sec. According to data (15), $K_{Br^- + OH}/K_{H2+OH} = 830$. Since $K_{H2+OH} = 4.5 \cdot 10^7$ l/mol • sec (14), then $K_{10} = 3.7 \cdot 10^{10}$ l/mol • sec. As can be seen, the agreement is satisfactory.

It should be noted that the proposed method for estimating the absolute values of rate constants of radiation reactions is approximate. Obviously, it is most applicable in those cases where the reactions partly proceed during the action of the pulse and end comparatively quickly after its introduction into the irradiated system.

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

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