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Abstract

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A NEW METHOD FOR ESTIMATING RATIOS OF RATE CONSTANTS OF REACTIONS OF RADICALS WITH THEIR ACCEPTORS

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The widely used method for determining the relative rate constants of reactions of H and OH radicals with the aid of two or more competing acceptors presupposes exact knowledge of the mechanism of the chemical transformations occurring in the system, which often include a large number of reactions. Since for almost all systems the mechanism of the processes taking place in them has been insufficiently studied, the relative rate constants of reactions of one and the same pair of acceptors with respect to one and the same radical, as obtained by different authors, often do not agree with one another.

Below we shall set forth a method for determining the ratios of the constants of reactions of radicals with their acceptors that does not require knowledge of all the reactions occurring in the irradiated system. It is based on using the experimental dependence of the yields G_M of molecular products of water radiolysis (H_2 and H_2O_2) on the concentration C_A of acceptors of radicals. In many cases this dependence has the following form:

$$G_M = G_M^0 - qC_A^{1/3}, \tag{1}$$

where q is a parameter depending on the type of acceptor, the type of radiation, and the type of radical and molecular product. As can be seen, the decrease in G_M occurs linearly as a function of the cube root of the concentration of the radical acceptor.

It was shown in ([1]) that such a dependence is obtained when the overwhelming part of the molecular product is formed by recombination of radicals arising in separate microregions, spurs, isolated from one another. In this case, in the approximation of the two-radical model of radiolysis, it can be shown that

$$G_M = G_M^0 - G_M^0 \left(\frac{k_A}{k} \cdot \frac{C_A}{C_0} \right)^{1/3}. \tag{2}$$

Here C_0 is the initial "concentration" of radicals in the spur, k is the rate constant of their recombination, and k_A is the rate constant of the reaction of the radicals with their acceptor.

Equation (2) is identical with the empirical law (1); in this case the coefficient q in (1) acquires a quite definite physical meaning:

$$q \equiv \left(\frac{k_A}{k} \cdot \frac{1}{C_0} \right)^{1/3} \cdot G_M^0. \quad (3)$$

Let q_1 and q_2 be the values of the empirical coefficients in equation (1) for the radical acceptors A_1 and A_2, respectively. Then

$$\frac{k_{A_1}}{k_{A_2}} = \left(\frac{q_1}{q_2} \right)^3. \quad (4)$$

Relation (4) assumes that in the cases being compared the values of k and C_0 are the same. Therefore we are entitled to compare only results obtained under conditions in which these quantities are the same. Consequently, in the cases being compared, the type of radiation, the temperature, and the pH of the solutions must be the same.

As an example for calculating ratios of the constants, a series of acceptors of solvated electrons and H atoms in neutral and acidic solutions was chosen. In the selected systems the irradiation was carried out by γ-

Table 1

Comparison of the ratios of rate constants found by formula (4) and by the method of competing acceptors

Particle	Medium	A_1	A_2	By formula (4): q_1/q_2	By formula (4): k_{A_1}/k_{A_2}	By formula (4): source	By the method of competing acceptors: k_{A_1}/k_{A_2}	By the method of competing acceptors: source
e^-_{aq}	Neutral	NO_3^-	H_2O_2	$\frac{0.40 \pm 0.04}{0.26 \pm 0.07}$	3.6 ± 2	([2–5])	1.0; 1.8	([12]); ([13,14])
e^-_{aq}	Neutral	NO_2^-	H_2O_2	$\frac{0.36 \pm 0.04}{0.26 \pm 0.07}$	2.6 ± 2	([2,3,6])	0.3	([12])

Particle	Medium	A_1	A_2	By formula (4): q_1/q_2	By formula (4): k_{A_1}/k_{A_2}	By formula (4): source	By the method of competing acceptors: k_{A_1}/k_{A_2}	By the method of competing acceptors: source
e_{aq}^-	Neutral	NO_3^-	NO_2^-	$\frac{0.40 \pm 0.04}{0.36 \pm 0.04}$	1.4 ± 0.1	[4–6]	3.3	[12]
e_{aq}^-	Neutral	Cu^{2+}	H_2O_2	$\frac{0.70 \pm 0.03}{0.26 \pm 0.07}$	20 ± 10	[2,3,6]	3 ± 1; 12 ± 4	[15]; [15,16]
H	pH 2	Cu^{2+}	H_2O_2	$\frac{0.23 \pm 0.09}{0.25 \pm 0.07}$	0.8 ± 0.7	[2,3,6]	0.1; 1.45	[17,18]; [13,19]
H	0.4 M HCl	Fe^{3+}	H_2O_2	$\frac{0.61 \pm 0.07}{0.25 \pm 0.07}$	15 ± 5	[7]	5.2	[20–22]
OH	Neutral	Br^-	J^-	$\frac{0.64 \pm 0.11}{0.77 \pm 0.06}$	0.6 ± 0.4	[8,9]	0.2	[23]
OH	0.4 M H_2SO_4	Tl^-	Ce^{3+}	$\frac{0.06 \pm 0.01}{0.30 \pm 0.01}$	44 ± 20	[10,11]	38; 41	[10,24]
OH	0.4 M H_2SO_4	Tl^+	Ce^{3+}	$\frac{1.05 \pm 0.01}{0.23 \pm 0.02}$	98 ± 20	[10]	38; 41	[10,24]

by Co^{60} rays and fast electrons; the hydrogen yield $G^0_{H_2}$ was the same and amounted to 0.45 ± 0.01. The results of the calculations are presented in Table 1.

Similar calculations were also carried out for acceptors of OH radicals, the results of which are likewise presented in Table 1. For comparison, the table gives values of the ratios of constants obtained by the method of competing acceptors.

As is seen from Table 1, both methods give ratios of constants that agree in order of magnitude. In comparing the results it should be borne in mind that the error in calculating the ratio k_{A_1}/k_{A_2} from equation (4) is determined only by the error in the quantity $\left(\frac{q_1}{q_2}\right)^3$, whereas in calculating the ratio of constants by the method of competing acceptors the magnitude of the error is determined by the impossibility of accurately taking into account all reactions occurring in the system. In addition, the method set forth in the present work makes it possible to determine the ratio of constants directly for any pair of acceptors and, in principle, with the same error. In the method of competing acceptors, however, only some ratios of constants are obtained directly; the remaining ratios of constants have to be recalculated, which can sometimes introduce a considerable additional error.

Table 2

Calculation of ratios of rate constants by formula (4)

Particle	Medium	A$_1$	A$_2$	q_1/q_2	k_{A_1}/k_{A_2}	Source
H	0.4 M H_2SO_4	Ce^{4+}	H_2O_2	$\frac{0.33 \pm 0.02}{0.25 \pm 0.07}$	2.3 ± 2.0	(2,3,25)
H	0.4 M H_2SO_4	Ce^{4+}	H_2O_2	$\frac{0.27 \pm 0.05}{0.25 \pm 0.07}$	1.3 ± 1.0	(2,3,26)
OH	0.4 M H_2SO_4	Br^-	Cl^-	$\frac{1.01 \pm 0.12}{0.54 \pm 0.02}$	7 ± 3	(27,28)
OH	0.4 M H_2SO_4	Br^-	Tl^+	$\frac{1.01 \pm 0.12}{1.06 \pm 0.01}$	0.9 ± 0.3	(10,27)
OH	pH 1	Hydroquinone	Br^-	$\frac{0.92 \pm 0.12}{0.96 \pm 0.12}$	0.9 ± 0.4	(10,29)
e^-_{aq}	Neutral	Acrylamide	Cu^{2+}	$\frac{0.70 \pm 0.03}{0.70 \pm 0.03}$	1.0 ± 0.2	(6,30)
OH	Neutral	NO_2^-	J^-	$\frac{0.61 \pm 0.05}{0.77 \pm 0.06}$	0.5 ± 0.2	(6,9)

Using the data on the influence of acceptors on the values of k_{A_1} and k_{A_2}, we also calculated, by equation (4), the ratios of rate constants of reactions for which data are absent in the literature. The results of these calculations are given in Table 2.

Table 3

Approximate values of absolute rate constants of reactions

Reaction	Medium	K, l/mol · s — present work	K, l/mol · s — literature data	Notes
$e^-_{aq} + Cu^{2+}$	Neutral	—	$3.0 \cdot 10^{10}$ (15)	Direct determination
$e^-_{aq} + H_2O_2$	Neutral	$1.5 \cdot 10^9$	$1.2 \cdot 10^{10}$ (15)	Direct determination
$e^-_{aq} + NO_2^-$	Neutral	$3.9 \cdot 10^9$	—	
$e^-_{aq} + NO_3^-$	Neutral	$5.4 \cdot 10^9$	—	
e^-_{aq}+ acrylamide	Neutral	$3.0 \cdot 10^9$	—	

Reaction	Medium	K, l/mol · s — present work	K, l/mol · s — literature data	Notes
$H + H_2O_2$	0.4 M H_2SO_4	—	$4 \cdot 10^7$ (31, 32)	Calculation at high dose rate
$H + Ce^{4+}$	Same	$7.2 \cdot 10^7$	—	
$H + Cu^{++}$	0.01 M H_2SO_4	$3.2 \cdot 10^7$	—	
$H + Fe^{3+}$	0.4 M HCl	$6 \cdot 10^9$	—	
$OH + Ce^{3+}$	0.4 M H_2SO_4	—	$3.2 \cdot 10^8$ (32)	Calculation at high dose rate
$OH + Br^-$	0.4 M H_2SO_4	$1.6 \cdot 10^{10}$	$7.2 \cdot 10^7$ (33)	Calculation at low dose rate
$OH + Cl^-$	Same	$2.3 \cdot 10^9$	$1.6 \cdot 10^{10}$ (32)	Calculation at high dose rate
$OH + Tl^+$	Same	$1.45 \cdot 10^{10}$	$2.7 \cdot 10^9$ (33)	Calculation at low dose rate
OH+ hydroquinone	0.1 M H_2SO_4	$1.45 \cdot 10^{10}$	—	
$OH + Br^-$	Neutral	$0.65 \cdot 10^{10}$	—	
$OH + J^-$	Neutral	$1.1 \cdot 10^{10}$	$2.5 \cdot 10^9$ (33)	Calculation at low dose rate
$OH + NO_2^-$	Neutral	$5.5 \cdot 10^9$	$1.1 \cdot 10^{10}$ (32)	Calculation at high dose rate

The new ratios between reaction constants obtained above make it possible to give a table of approximate values of the rate constants of the reactions of the solvated electron and of the radicals H and OH with various compounds. Taking as initial values $k_{e^-_{aq}+Cu^{2+}} = 3.0 \cdot 10^{10}$ mol/l · s (15) for a neutral medium and $k_{H+H_2O_2} = 4 \cdot 10^7$ mol/l · s (31) for an acid medium, and $k_{OH+Ce^{3+}} = 3.2 \cdot 10^8$ mol/l · s (32) in neutral and acid media, we obtain the approximate absolute values of the reaction-rate constants listed in Table 3. For comparison, the table includes absolute rate constants determined by other methods.

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