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Abstract

Full Text

PHYSICAL CHEMISTRY

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REACTION OF THE THERMALIZED ELECTRON IN FROZEN AQUEOUS SOLUTIONS

(Presented by Academician A. N. Frumkin, February 26, 1965)

Studies of the primary products of the radiolysis of various compounds, carried out in recent years, have shown that the thermalized electron plays an important role in radiation-chemical transformations. In liquid polar media—water and alcohols (1)—yields of thermalized electrons that had escaped recombination in spurs and were solvated by the solvent were found, and the rate constants of their reactions with many acceptors were determined. In frozen solutions, both inorganic (2,3) and organic (4,5), ratios were found for the rate constants of reactions of the thermalized electron, formed as a result of the action of ionizing radiation or light, with various substances. In these works the method of stationary concentrations was used to calculate the ratios of the rate constants of the reactions. Apparently, the application of this method for treating kinetic data is fully justified, since the mobility of the thermalized electron is sufficiently high even in solid media, while its stationary concentration is low. Stabilization of the electron, observed in some frozen glassy systems (6–9), may be regarded as its reaction with structural defects, and the stabilized electron in this sense is a reaction product. The main complications in studying kinetics in frozen solutions are the absence of data on the yields of electrons under the action of ionizing radiations and the difficulty of estimating the concentration of some electron acceptors—structural defects, undissociated acid molecules, etc. Therefore, in the published literature for very low temperatures, ratios of the rate constants of reactions of the thermalized electron with acceptors have been determined only for acceptors introduced in a relatively low concentration ($\sim 0.1\,M$), which does not change the composition and yields of the primary products of radiolysis.

In determining the ratios of the rate constants of reactions of the thermalized electron with acceptors present in frozen solutions at high concentration, it is necessary to know the magnitude of the yield of thermalized electrons for each system studied. G_{e^-} can be found from the yield of the transformation product whose appearance is caused by the capture, by one of the components of the system, of all the thermalized electrons.

In the study of the radiolysis of concentrated aqueous solutions of $NaClO_4$, it was shown that in liquid solutions the ion ClO_4^- is destroyed only as a result of the direct action of radiation, the yield of which is 4.0 ions/100 eV absorbed by

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Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

ClO_4^- ions $^{(10)}$. In frozen $NaClO_4$ solutions the yield of reduction of the ClO_4^- ion increases owing to its reaction with the thermalized electron:

$$ClO_4^- + e^- = ClO_4^{2-} \tag{1}$$

with the formation, as was proposed, of the intermediate ion-radical ClO_4^{2-}, which on heating undergoes hydrolysis:

$$2ClO_4^{2-} + H_2O = ClO_4^- + ClO_3^- + 2OH^-. \tag{2}$$

Reaction (1) does not occur in the liquid phase, since its rate constant at 20° is below 10^4 l/mole • sec. Since the yield of direct action, to a first approximation, should not depend on temperature, the yield of thermalized electrons can be calculated from the formula:

$$G_{e^-} = 2\left[G(-ClO_4^-) - G(-ClO_4^-)_{\text{pr}}\right],$$

where $G(-ClO_4^-)$ is the observed yield of perchlorate destruction at −196°, and $G(-ClO_4^-)_{\text{pr}}$ is the yield of destruction by direct action at the given concentration of ClO_4^- ions. The calculated values of G_{e^-} are given below.

Fig. 1. Dependence of $G(\text{H})$ on the acidity of aqueous $NaClO_4$ solutions irradiated at −196°, with total concentration of ClO_4^- ions: 1—2*M*; 2—8*M*; 3—4*M*

Fig. 2. Graphical solution of equation I for: 1—2*M* and 2—8*M* $NaClO_4$ solutions

$NaClO_4$, M	1	2	4	6	8
G_{e^-}, electron/100 eV	0.45	0.97	1.43	1.80	2.10

The influence of the acidity of the medium on the yield of H atoms was studied in $NaClO_4$ solutions irradiated with Co^{60} γ-rays at −196°, containing various amounts of H_3O^+ ions at a constant content of ClO_4^- ions. The yield of H atoms was determined by the EPR method with the aid of an RE-13-01 radiospectrometer. It was found that $G(\text{H})$ depends both on the concentration of H_3O^+ ions and on the concentration of ClO_4^- ions. The observed dependence (see Fig. 1) is explained by competition between reaction (1) and the reaction of the thermalized electron with the hydronium ion:

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Fig. 3 and Fig. 4

Figure 2: Fig. 3 and Fig. 4

$$e^- + H_3O^+ = H + H_2O. \tag{3}$$

Using the steady-state concentration method for competition between ClO_4^- and H_3O^+ ions, we obtain the equation:

$$1 + \frac{k_1[ClO_4^-]}{k_3[H_3O^+]} = \frac{G_{e^-}}{G(H) - G_H}, \tag{I}$$

where k_1 and k_3 are the rate constants of the corresponding reactions, $G(H)$ is the observed yield of H atoms, and G_H is the yield of H atoms in a neutral perchlorate solution, formed by another mechanism (3), which, as

one may assume, does not depend on the acidity of the medium. The concentration of H_3O^+ ions at −196° was taken to be the same as at 20°.

The graphical solution of equation (I), using as an example two solutions with different concentrations of the ClO_4^- ion, is shown in Fig. 2. As can be seen, the experimental data in these coordinates fit a straight line well. The slope of the straight line in this and subsequent cases was found by the method of least squares. The values

Fig. 3

Fig. 4

Fig. 3. Graphical solution of equation II

Fig. 4. Graphical solution of equation III for systems: 1—5M $HClO_4$; 2—2M $HClO_4 + 6M$ $NaClO_4$

of the ratios k_1/k_3 are given in Table 1. The mean value of k_1/k_3 is 0.42 ± 0.15.

It was shown previously that $G(-ClO_4^-)$ decreases with increasing concentration of H_3O^+ ions in a $NaClO_4$ solution with a total content of the ion

Table 1

Ratios of constants in perchlorate systems at −196°

System	Measured parameter	Variable acceptor	$G_{e^-}^*$	k_1/k_3	k_4/k_3	k_1/k_4
$NaClO_4$+ $HClO_4$, $[ClO_4^-] = 2M$	$G(H)$	H_3O^+	0.97	0.47		
$NaClO_4$+ $HClO_4$, $[ClO_4^-] = 4M$	$G(H)$	H_3O^+	1.45	0.31		
$NaClO_4$+ $HClO_4$, $[ClO_4^-] = 8M$	$G(H)$	H_3O^+	2.10	0.56		
$NaClO_4$+ $HClO_4$, $[ClO_4^-] = 4M$	$G(-ClO_4^-)$	H_3O^+	1.45	0.31		
$1.25M$ $HClO_4$+ 0.01–$0.2M$ H_2O_2	$G(H)$	H_2O_2	0.55	0.32	80	0.004
$2.5M$ $HClO_4$+ 0.01–$0.3M$ H_2O_2	$G(H)$	H_2O_2	1.13	0.31	52	0.006
$5.0M$ $HClO_4$+ 0.02–$0.45M$ H_2O_2	$G(H)$	H_2O_2	1.63	0.20	60	0.003
$2M$ $HClO_4$+ $6M$ $NaClO_4$+ 0.01–$0.15M$ H_2O_2	$G(H)$	H_2O_2	2.10	0.39	44	0.009

* The yields G_{e^-} in acid solutions were taken to be the same as in the corresponding $NaClO_4$ solutions of the same concentration.

ClO_4^- $4M$. In this case there is also competition between reactions (1) and (3). The steady-state concentration method in this case leads to the equation:

$$1 + \frac{k_3[H_3O^+]}{k_1[ClO_4^-]} = \frac{G_{e^-}}{2\left[G(-ClO_4^-) - G(-ClO_4^-)_{\text{pr}}\right]}, \tag{II}$$

where $G(-ClO_4^-)$ is the yield of destruction of the ClO_4^- ion at the given acid concentration. The graphical solution of equation (II) is presented in Fig. 3.

The ratio k_1/k_3 from these data is 0.31 ± 0.05, which, within the experimental error, agrees with k_1/k_3 determined from the dependence of $G(\mathrm{H})$ on the acidity of the medium.

The effect of the concentration of hydrogen peroxide on the yield of H atoms in $HClO_4$ solutions irradiated with γ-rays from Co^{60} at $-196°$ was also studied. It was found that the addition of hydrogen peroxide, which in liquid solutions is a very active electron acceptor (^{1}), lowers $G(\mathrm{H})$, and the decrease in $G(\mathrm{H})$

is the greater, the higher the concentration of H_2O_2 and the lower the acid concentration. The observed effect can be explained by competition among reactions (1), (3), and (4):

$$e^- + H_2O_2 = OH + OH^-. \tag{4}$$

The steady-state concentration method for this case leads to the equation:

$$1 + \frac{k_1[ClO_4^-]}{k_3[H_3O^+]} + \frac{k_4[H_2O_2]}{k_3[H_3O^+]} = \frac{G_{e^-}}{G(H)}. \tag{III}$$

When solved graphically, the equation obtained makes it possible simultaneously to calculate the ratio k_1/k_3 from the intercept cut off by the straight line on the ordinate axis, and the ratio k_4/k_3 from the tangent of the angle of inclination. Figure 4 gives the graphical solution for two systems. The average value of k_1/k_3 from these experiments is 0.31 ± 0.10, which is in good agreement with k_1/k_3 for systems not containing peroxide. The average value of the ratio k_4/k_3 is 62 ± 20. In aqueous solutions at 20°, the ratio $k_4/k_3 \simeq 0.7$ (^{1}), i.e., two orders of magnitude lower than in frozen solutions. These data show that the reactivity of the thermalized electron with respect to the same pair of acceptors can differ substantially.

The values of the ratios of the constants k_1/k_3 and k_4/k_3, within experimental error, coincide for different systems. The coincidence of these ratios shows that in frozen solutions the value of the ratio of the rate constants of the reactions of two acceptors does not depend on the composition of the perchloric or chloric-acid matrix for glassy samples.

Thus, provided that the value of the yield of thermalized electrons that have escaped recombination in the spur is determined, it is possible to calculate, in frozen solutions, the ratios of the rate constants of reactions of the thermalized electron with various acceptors present in the system at any concentration; the resulting values of the ratios of the constants do not depend on the composition of the system.

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