A. K. PIKAEV, P. Ya. GLAZUNOV, Academician Vikt. I. SPITSYN

1963

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

Full Text

A. K. PIKAEV, P. Ya. GLAZUNOV, Academician Vikt. I. SPITSYN

APPROXIMATE VALUES OF THE RATE CONSTANTS OF RADIATION REACTIONS INVOLVING THE HYDRATED ELECTRON

At the present time, questions connected with the participation in radiolytic transformations in aqueous solutions of two forms of reducing radicals formed during the radiolysis of water are being widely discussed in the literature. There is definite evidence that these forms are the hydrated electron e_{aq}^{-} and the hydrogen atom H, the former being converted into the latter as a result of reaction with hydrogen ions. Clearly, investigation of the influence of pH on the yields of radiolytic transformations in aqueous solutions makes it possible in a number of cases to study the reactivity of these intermediate products of radiolysis toward dissolved substances.

Earlier (^{1}), by using two independent methods of kinetic treatment of experimental data obtained in a study of the radiolysis of solutions of ferrous sulfate in 0.4 M H_2SO_4, containing oxygen, under the action of pulsed electron radiation, we estimated the absolute values of the rate constants of the reactions $H + O_2$, $H + OH$, and $Fe^{2+} + OH$. It therefore seemed possible, by studying radiolytic transformations in this system under conditions where reactions involving the hydrated electron proceed, i.e., at sufficiently high pH, to compare the reactivity of e_{aq}^{-} and H.

Fig. 1. Dependence of $G(Fe^{3+})$ on dose rate for a $3 \cdot 10^{-3}$ M Mohr' s salt solution saturated with air:
1—0.4 M H_2SO_4 (^{1});
2—pH 3

Fig. 2. Dependence of $G(Fe^{3+})$ on H_2SO_4 concentration for a $3 \cdot 10^{-3}$ M Mohr' s salt solution saturated with air, at a dose rate of $(1.3—1.5) \cdot 10^{23}$ eV/ml · sec

As the source of ionizing radiation we used a directly accelerated electron tube (^{2}). High dose rates were produced by means of single electron pulses. Their

Fig. 3

Figure 3: Fig. 3

duration was $5 \cdot 10^{-6}$ sec. The electron energy was 1.0 MeV. The methods of generation and measurement of the pulses, as well as the experimental procedure, have been described in our previous communications (^{1,3}). The absolute accuracy of the measurements was ±10%.

The reagents used were of sufficiently high purity. The solutions in all cases were sulfuric-acid solutions and were saturated with air. Trivalent iron was determined spectrophotometrically at a wavelength of 304 mμ.

The molar extinction coefficient of Fe^{3+} in $0.4\,M$ H_2SO_4 at 24°C was taken to be 2170 (^{4}). In the calculations, allowance was made for its dependence on the acidity of the solution (^{5,6}), as well as for its variation with temperature (0.7% per degree). The pH value was measured on an LP-58 potentiometer.

Figure 1 shows the dependence of $G(Fe^{3+})$ for a $3 \cdot 10^{-3}\,M$ solution of Mohr's salt at pH 3 on the dose rate (curve 2). The same figure gives, for comparison, the analogous dependence for $0.4\,M$ H_2SO_4 (curve 1), which we obtained earlier (^{1}). Figure 2 illustrates the dependence of $G(Fe^{3+})$ on pH for a Mohr' s salt solution of the same concentration at a dose rate of $(1.3—1.5) \cdot 10^{23}$ eV/ml · sec. Finally, Fig. 3 gives the dependence of $G(Fe^{3+})$ on the solution concentration at a dose rate of $3 \cdot 10^{22}$ eV/ml · sec and at different pH values*: curve 1—$0.4\,M$ H_2SO_4, curve 2—pH 2, and curve 3—pH 3. As is evident from these figures, $G(Fe^{3+})$ at a constant concentration of Fe^{2+} ions decreases with increasing pH. A similar course of the dependence of $G(Fe^{3+})$ was also observed in (^{8}) for the case of low dose rates.

Fig. 3. Dependence of $G(Fe^{3+})$ on the concentration of Fe^{2+} ions in air-saturated solutions (dose rate $3 \cdot 10^{22}$ eV/ml · sec): 1—$0.4\,M$ H_2SO_4; 2—pH 2; 3 —pH 3

Earlier (^{1}) we showed that the decrease in $G(Fe^{3+})$ in $0.4\,M$ sulfuric-acid solutions containing oxygen, in the case of high absorbed-dose rates, is satisfactorily explained by competition among reactions 3, 4, and 5:

$$H_2O \rightsquigarrow H,\ OH,\ e^-_{aq};\ H_2,\ H_2O_2, \tag{1}$$

$$e^-_{aq} + H_3O^+ \rightarrow H + H_2O, \tag{2}$$

$$H + O_2 \rightarrow HO_2, \tag{3}$$

$$\mathrm{H} + \mathrm{OH} \rightarrow \mathrm{H_2O}, \tag{4}$$

$$\mathrm{Fe^{2+}} + \mathrm{OH} \rightarrow \mathrm{Fe^{3+}} + \mathrm{OH^-}, \tag{5}$$

$$\mathrm{H^+} + \mathrm{Fe^{2+}} + \mathrm{HO_2} \rightarrow \mathrm{Fe^{3+}} + \mathrm{H_2O_2}, \tag{6}$$

$$\mathrm{Fe^{2+}} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe^{3+}} + \mathrm{OH} + \mathrm{OH^-}. \tag{7}$$

Obviously, in $0.4\,M$ H_2SO_4 the hydrated electrons are completely converted into H atoms. At $\mathrm{pH} \geq 2$, reactions (8) and (9) may apparently compete with reaction (2):

$$e^-_{\mathrm{aq}} + \mathrm{O_2} \rightarrow \mathrm{O_2}^-, \tag{8}$$

$$e^-_{\mathrm{aq}} + \mathrm{OH} \rightarrow \mathrm{OH^-}, \tag{9}$$

$$\mathrm{O_2}^- + \mathrm{H^+} \rightleftarrows \mathrm{HO_2}. \tag{10}$$

If it is assumed that the mechanism of oxidation of Fe^{2+} ions in the presence of oxygen at $\mathrm{pH} \geq 2$ is expressed by reactions (1–9), and if it is further assumed that $K_3 = K_8$ and $K_4 = K_9$, then, using the steady-state method, the following equation can be obtained:

$$\frac{\left[{}^1/_2\, G(\mathrm{Fe^{3+}}) + G_{\mathrm{H_2}} - G_{\mathrm{H_2O_2}}\right]\left[G(\mathrm{Fe^{3+}}) - 2G_{\mathrm{H_2}}\right]}{3G_{\mathrm{red}} + G_{\mathrm{OH}} + 2G_{\mathrm{H_2O_2}} - G(\mathrm{Fe^{3+}})} = \frac{K'K_5}{K''}\,(\mathrm{Fe^{2+}})(\mathrm{O_2})\left(\frac{100N}{I}\right), \tag{11}$$

where $K' = K_3 = K_8$, $K'' = K_4 = K_9$, and K_5 are the rate constants of the corresponding reactions; G_{red}, G_{OH}, $G_{\mathrm{H_2}}$, and $G_{\mathrm{H_2O_2}}$ are the initial yields, respectively, of reducing radicals, OH, H_2, and H_2O_2; $(\mathrm{Fe^{2+}})$ and $(\mathrm{O_2})$ are the molar concentrations of Fe^{2+} and O_2; I is the dose rate (in $\mathrm{eV/l \cdot sec}$) and N is Avogadro' s number. We obtained the same equation for $0.4\,M$ H_2SO_4 (^{1}), except that in it, instead of the constants K' and K'', the constants K_3 and K_4 appeared. Obviously, our assumption that the constants are equal will be correct only if the relative constant $K'K_5/K''$ proves equal to the ratio K_3K_5/K_4.

---

* In all cases, the ferrous sulfate solutions used did not contain NaCl. In the presence of chloride ions, $G(\mathrm{Fe}^{3+})$ decreases (7,1).

The value of the constant $K'K_5/K''$, calculated from equation (11) using the experimental data shown in Figs. 1-3, proved to be equal to $(3.8 \pm 1.5) \cdot 10^7$ liters/mole • sec* . In the case of $0.4\,M$ H_2SO_4, $K_3K_5/K_4 = (3.2 \pm 1.2) \cdot 10^7$ liters/mole • sec (1). Thus, it may be assumed that $K_3 \approx K_8$ and $K_4 \approx K_9$.

In our preceding communication (1) it was shown that $K_3 = 5.3 \times 10^9$ liters/mole • sec and $K_4 = 4.5 \cdot 10^{10}$ liters/mole • sec. Then, evidently, $K_8 \approx 5 \times 10^9$ liters/mole • sec** and $K_9 \approx 4 \cdot 10^{10}$ liters/mole • sec. There are many data in the literature on the relative rate constants of reactions involving the hydrated electron. Therefore it is possible, starting from $K_8 = 5 \cdot 10^9$ liters/mole • sec, to estimate approximately the absolute values of the rate constants of some of these reactions. Table 1 gives the values of the constants obtained in this way.

Table 1.

Approximate values of the rate constants of reactions of e^-_{aq} with certain dissolved substances

Dissolved substance	K, liters/mole • sec	Source
O_2	$5 \cdot 10^9$	Present work
OH	$4 \cdot 10^{10}$	Present work
H^+	$5 \cdot 10^9$	(11)
H_2O_2	$2.7 \cdot 10^9$	(11)
H_2O_2	$2.3 \cdot 10^9$	(12)
$ClCH_2COOH$	$1.5 \cdot 10^9$	(13)
Acetone	$2.2 \cdot 10^9$	(14)
NO_3^-	$4.9 \cdot 10^9$	(14)
$[Fe(CN)_6]^{3-}$	$4 \cdot 10^9$	(14)
NH_4^+	$2.2 \cdot 10^5$	(14)
$H_2PO_4^-$	$3.8 \cdot 10^6$	(14)
$HF(HF_2^-)$	$6.3 \cdot 10^7$	(14)
N_2O	$6.3 \cdot 10^9$	(15)
CO_2	$1.5 \cdot 10^{10}$	(16)

It should be noted that the mechanism of radiolytic oxidation of Fe^{2+}, expressed by reactions (1-9), is apparently valid only at sufficiently high concentrations of Fe^{2+} ions. For example, for $0.4\,M$ H_2SO_4 the constant K_3K_5/K_4 increases to $6 \cdot 10^7$ liters/mole • sec already in the case of a $10^{-3}\,M$ solution of Fe^{2+} ions. However, as the acidity is lowered, the value of this constant is independent of (Fe^{2+}) over a wider range of Fe^{2+} concentrations. Thus, at pH 3, even for a 10^{-4} solution of ferrous sulfate, $K'K_5/K''$ practically does not differ from the values in the case of higher concentrations ($4.9 \cdot 10^7$ liters/mole • sec). It is still difficult to give any definite explanation of this phenomenon. Perhaps it is associated with the fact that at low Fe^{2+} concentrations the OH radicals interact mainly with sulfuric acid. Clearly, further investigations are necessary for the final resolution of this question.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
14 V 1963

REFERENCES

1. A. K. Pikaev, P. Ya. Glazunov, V. I. Spitsyn, DAN, **150**, 1077 (1963).
2. P. Ya. Glazunov, G. B. Radzievskii, in the collection *The Action of Ionizing Radiations on Inorganic Systems*, Publishing House of the Academy of Sciences of the USSR, 1958, p. 395.
3. P. Ya. Glazunov, A. K. Pikaev, DAN, **130**, 1051 (1960).
4. R. H. Schuler, A. O. Allen, J. Chem. Phys., **24**, 56 (1956).
5. J. Haybittle, R. Saunders, A. Swallow, J. Chem. Phys., **25**, 1213 (1956).
6. C. M. Henderson, N. Miller, Radiation Res., **13**, 641 (1960).
7. J. K. Thomas, E. J. Hart, Radiation Res., **17**, 408 (1962).
8. A. O. Allen, V. D. Hogan, W. G. Rothschild, Radiation Res., **7**, 603 (1957).
9. A. O. Allen, *The Radiation Chemistry of Water and Aqueous Solutions*, N. Y., 1961.
10. J. P. Keene, Nature, **197**, 47 (1963).
11. C. J. Hochanadel, Radiation Res., **17**, 286 (1962).
12. G. Czapski, A. O. Allen, J. Phys. Chem., **66**, 262 (1962).
13. E. Hayon, A. O. Allen, J. Phys. Chem., **65**, 2181 (1961).
14. J. Jortner, M. Ottolenghi et al., J. Chem. Phys., **37**, 2488 (1962).
15. F. S. Dainton, D. B. Peterson, Proc. Roy. Soc., **A267**, 443 (1962).
16. J. T. Allan, N. Getoff et al., J. Inorg. and Nucl. Chem., **19**, 204 (1961).

* In the calculations, the dependence of G_{rest}, G_{OH}, and $G_{H_2O_2}$ on pH (⁹) was taken into account, and the mean values of $G(Fe^{3+})$ in each series of experiments were used.

** An estimate of this constant was also made in work (¹⁰). According to the data of that work, it is equal to $1.5 \cdot 10^{10}$ liters/mole • sec.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.