KINETICS OF HYDROLYSIS OF PEROXODISULPHATE IONS IN ACIDIC MEDIUM TO PEROXOMONOSULPHURIC ACID

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The rate of hydrolysis of $S_2O_8^{2-}$ ions in acidic medium to peroxomonosulphuric acid was measured at 20 and 30°C. The composition of the starting solution corresponded to the anolyte flowing out from an electrolyser for production of this acid or its ammonium salt at various degrees of conversion and starting molar ratios of sulphuric acid to ammonium sulphate. The measured data served to calculate the rate constants at both temperatures on the basis of the earlier proposed mechanism of the hydrolysis, and their dependence on the ionic strength was studied.

The anolyte flowing out from a continually operating electrolyser during production of peroxodisulphuric acid or its salts by anodic oxidation of aqueous sulphuric acid or its mixture with sulphates contains a certain quantity of peroxomonosulphuric acid, H_2SO_5. Its formation has been attributed[1-4] mainly to hydrolysis of the primarily anodically formed peroxodisulphate ions

$$S_2O_8^{2-} + H_2O \rightarrow HSO_5^- + SO_4^{2-} + H^+ , \qquad (A)$$

although later authors[5] assumed a direct anodic discharge of SO_4^{2-} or HSO_4^- ions with participation of an intermediate product of the anodic evolution of oxygen, proceeding simultaneously. However, our preceding work[6] showed that peroxomonosulphuric acid is formed under the mentioned conditions mostly by chemical reactions, which take place also during spontaneous hydrolysis of peroxodisulphates in acidic medium outside the electrolyser. Further it was shown[7] that this acid reacts on the platinum anode during electrolytic preparation of peroxodisulphates with the formation of oxygen according to

$$HSO_5^- + H_2O \rightarrow O_2 + HSO_4^- + 2\,H^+ + 2\,e^- . \qquad (B)$$

This reaction is undesirable since it causes a decrease of the content of active oxygen (total content of peroxo compounds) in the outlet solution and a decrease of the anodic potential at a given current density, whereby the electrolysis conditions become less favourable. Therefore, there is a tendency to maintain the content of H_2SO_5 in the anodic compartment of the electrolyser as low as possible.

However, data about the rate of hydrolysis of $S_2O_8^{2-}$ ions to peroxomonosulphuric acid under the conditions of electrolysis, *i.e.*, at 10—35°C, are lacking. Measurements of this rate were done hitherto at temperatures higher or equal to 50°C (refs[8-10]), apparently in connection with the production of hydrogen peroxide[1-4]. Extrapolation of these data to lower temperatures is not possible since the constants of the Arrhenius equations and their eventual dependence on the ionic strength cannot be determined from the published measurements.

The present work deals with the results of measurement of the kinetics of hydrolysis of peroxodisulphate ions to peroxomonosulphuric acid in solutions used in the production of ammonium peroxodisulphate according to Löwenstein (or modified methods) as well as in the electrolytic manufacture of peroxodisulphuric acid[11], and this at 20 and 30°C.

EXPERIMENTAL

The rate of hydrolysis of peroxodisulphates to H_2SO_5 was measured in a thermostated Pyrex glass vessel closed with a Bunsen valve. The solution composition was similar to that used in practice with various molar ratios, P_0, of H_2SO_4 to $(NH_4)_2SO_4$ in the starting solution and with various degrees of conversion, α, of SO_4^{2-} ions to $S_2O_8^{2-}$ (ref.[12]). The solutions were prepared from reagent grade sulphuric acid, doubly recrystallized ammonium sulphate and peroxodisulphate, and distilled water. A solution containing the required quantity of H_2SO_4 and $(NH_4)_2SO_4$ was heated to a temperature by 3—4 K higher than the experimental temperature and then the required quantity of ground $(NH_4)_2S_2O_8$ was added. After its rather rapid dissolution the solution temperature attained the required value, and immediately afterwards a sample for analysis was taken. Further samples were taken at different time intervals. To hinder the hydrolysis, the samples were diluted with distilled water of a known volume about 1 : 30. During the hydrolysis, the solutions were magnetically stirred.

The total concentration of H^+ ions in the samples was determined by titration with 0·1M-NaOH with methyl red as indicator, the content of NH_4^+ ions was determined according to Hanuš[13], and the total content of peroxo compounds (corresponding to the starting content of $S_2O_8^{2-}$ ions) was determined permanganometrically. The content of H_2SO_5 was determined according to Csányi[14]. The difference between the total content of peroxo compounds and H_2SO_5 corresponded to the content of $S_2O_8^{2-}$ ions at the given instant, since no hydrolysis of H_2SO_5 to hydrogen peroxide,

$$HSO_5^- + H_2O \rightarrow HSO_4^- + H_2O_2\,, \qquad (C)$$

was observed at the given reaction conditions.

The content of NH_4^+ ions in the hydrolysed samples could not be determined by the method after Hanuš, since the added formaldehyde was oxidized with H_2SO_5 to formic acid and the consumption of the titrating agent, a solution of NaOH, was higher. Since the content of NH_4^+ ions did not change during hydrolysis, Eq. (*A*), it was sufficient to determine them only at the beginning of hydrolysis. The duration of the measurement did not exceed 24 h.

RESULTS AND DISCUSSION

The composition of the solutions used in the measurements and the experimental data are summarized in Table I. For a given molar ratio P_0, temperature of the solution 20 to 30°C and the highest attainable degree of conversion of SO_4^{2-} ions to $S_2O_8^{2-}$, $\alpha_{max} = 0{\cdot}8$ with solutions of the highest permissible concentration[12], we chose three actual degrees of conversion $\alpha = 0{\cdot}4, 0{\cdot}55$ and $0{\cdot}7$, which determined the initial composition of the solution for the measurement. Since the decomposition of peroxo compounds to gaseous oxygen was negligible during the hydrolysis (in the

TABLE I

Initial Composition of Solutions Used for Measurement of Rate of Hydrolysis of $S_2O_8^{2-}$ to HSO_5^- and Mean Values of Obtained Rate Constants k

P_0	α	P_a	$c_{0S_2O_8^{2-}}$ mol/dm^3	$c_{0(NH_4)_2SO_4}$ mol/dm^3	c_{0H^+} mol/dm^3	I mol/dm^3	β	$k \cdot 10^2$ h^{-1} mol^{-1} . dm^3
				Temperature 20°C				
1·0	0·4	1·0	0·9494	1·5031	2·9776	11·857	0·090	0·144
	0·55	1·0	1·2973	1·1476	2·2055	10·687	0·082	0·134
	0·7	1·0	1·6310	0·6457	1·468	9·054	0·042	0·123
1·5	0·4	1·83	0·790	1·187	4·326	12·491	0·235	0·243
	0·55	2·11	1·0195	0·8919	3·671	11·272	0·054	0·236
	0·7	2·67	1·3060	0·6617	3·1453	10·716	0·169	0·210
2·0	0·4	2·67	0·6340	1·0152	5·198	12·823	0·336	0·352
	0·55	3·22	0·8806	0·7621	4·6945	12·068	0·307	0·347
	0·7	4·33	1·2284	0·8484	4·8895	13·676	0·514	0·334
2·5	0·4	3·50	0·5520	0·9194	5·9502	13·441	0·492	0·529
	0·55	4·33	0·7754	0·6923	5·5303	12·834	0·462	0·479
	0·7	6·00	0·9956	0·5059	5·4798	12·804	0·161	0·621
∞	—	∞	0·1778	0·000	11·549	17·725	—	2·023
				Temperature 30°C				
1·0	0·4	1·0	1·0291	1·6826	3·4208	13·418	0·413	1·024
	0·55	1·0	1·1524	1·000	1·9677	9·472	0·173	0·570
	0·7	1·0	1·6972	0·8305	1·5903	10·020	0·051	0·521
1·5	0·4	1·83	0·8480	1·3221	4·6184	13·672	0·645	1·021
	0·55	2·11	1·1764	0·8207	4·0377	12·448	0·650	0·977
	0·7	2·67	1·4743	0·6836	3·3138	11·807	0·616	1·008
2·0	0·4	2·67	0·7320	1·1418	5·5803	14·129	0·388	1·469
	0·55	3·22	0·9760	0·8722	5·2500	13·810	0·855	1·500
	0·7	4·33	1·2307	0·5948	4·7050	12·969	0·732	1·459
2·5	0·4	3·50	0·6302	0·9570	6·3382	14·554	0·866	1·941
	0·55	4·33	0·8365	0·7380	6·0140	14·086	0·807	1·745
	0·7	6·00	1·1059	0·5553	5·6872	14·000	0·800	1·719
∞	—	∞	0·650	0·000	11·53	17·400	—	7·17

most unfavourable case, $P_0 = \infty$, at 30°C the loss of peroxo compounds was less than 3% after 24 h), we assumed that the rate of consumption of $S_2O_8^{2-}$ ions was equal to the rate of production of SO_5^{2-} ions, *i.e.*

$$-\mathrm{d}c_{S_2O_8^{2-}}/\mathrm{d}t = \mathrm{d}c_{HSO_5^-}/\mathrm{d}t\,. \qquad (1)$$

The rate of hydrolysis of $S_2O_8^{2-}$ ions to HSO_5^- in acidic medium is catalysed with hydrogen ions[8-10]. According to Palme[8], the dependence of the rate constant calculated for Eq. (*A*) from the first-order kinetics,

$$\ln\left[c_{0S_2O_8^{2-}}/c_{S_2O_8^{2-}}\right] = kt\,, \qquad (2)$$

is not a linear, but an exponential function of the concentration of hydrogen ions with an exponent larger than one; its value was not indicated. Neither the overall equation (*A*), used in the discussion, nor the mechanism of formation of peroxomonosulphuric acid according to Kolthoff and Miller[10] involving the formation of sulphur tetraoxide as an intermediate elucidates the catalytic effect of hydrogen ions. This mechanism was opposed by Soviet authors on the basis of isotopic measurements[15,16], but their interpretation based on the overall reaction (*A*) also brings no elucidation of the catalytic effect of hydrogen ions; and they did not measure the rate of hydrolysis.

We proposed[6] a modified mechanism of formation of H_2SO_5 during electrolytic manufacture of peroxodisulphates as well as during their spontaneous hydrolysis outside the electrolyser, which enables to elucidate the catalytic influence of hydrogen ions. Accordingly, the kinetics of hydrolysis obeys the equation

$$\mathrm{d}c_{HSO_5^-}/\mathrm{d}t = kc_{H^+}\,.\,c_{S_2O_8^{2-}}\,, \qquad (3)$$

whence the effect of hydrogen ions is obvious.

The same final form of kinetic equation (*3*) as derived for the proposed mechanism[6] may also be obtained by assuming other reaction schemes:

$$S_2O_8^{2-} + H^+ \xrightarrow{k_D} HS_2O_8^- \quad \text{(slow)} \qquad (D)$$

$$HS_2O_8^- + H_2O \xrightarrow{k_E} HSO_5^- + HSO_4^- + H^+ \quad \text{(fast)} \qquad (E)$$

$$r = k_D\,.\,c_{H^+}\,.\,c_{S_2O_8^{2-}} \qquad (3a)$$

or:

$$S_2O_8^{2-} + H^+ \overset{K_F}{\rightleftarrows} HS_2O_8^- \quad \text{(fast)} \qquad (F)$$

$$HS_2O_8^- + H_2O \xrightarrow{k_G} HSO_5^- + HSO_4^- + H^+ \quad \text{(slow)} \tag{G}$$

$$r = k'_G \,.\, c_+ \,.\, c_{S_2O_8^{2-}} \,, \tag{3b}$$

where

$$k'_G = k_G \,.\, a_{H_2O} \,.\, K_F \tag{3c}$$

K_F being the equilibrium constant of reaction (*F*). The mechanism involving steps (*D*) and (*E*) has also been considered by House[17]. From the experimental results, however, it cannot be decided which of the proposed mechanisms is the most probable one.

The dependence of the composition of the studied samples on the time was obtained by integrating Eq. (*3*) with respect to (*1*). After substituting the boundary condition and new symbols,

$$c_{S_2O_8^{2-}} = x \,, \quad c_{H^+} + c_{S_2O_8^{2-}} = a = \text{const.} \,,$$

$$t = 0 \,, \quad x = x_0 \,,$$

we obtain

$$dx/dt = k(x^2 - ax) \tag{4}$$

and on integrating from $t = 0$ to t

$$\ln\left[x_0(a - x)/x(a - x_0)\right] = a \,.\, k \,.\, t \;. \tag{5}$$

This equation served to calculate the rate constant k from the experiments for a given solution. The concentration of hydrogen ions was set approximately equal to that determined by titration, since the true value was not known. The ionic strength of the solutions was calculated analogously. The mean values of k determined in this way are given in Table I. It is seen that the values of k at different instants of hydrolysis are fairly constant.

The final degree of hydrolysis, β, at the end of the measurement (Table I) varied in rather wide limits from 0·042 to 0·866 depending at a given temperature mainly on the molar ratio Pa.

The values of k (Table I) at a given temperature are somewhat variable owing not to experimental errors but also apparently to variable ionic strength of the solutions. According to the mechanism proposed earlier[6], the rate-controlling reaction involves both ions and uncharged molecules, hence the dependence of the rate constant on the ionic strength at a given temperature can be expected to be given as

$$\log k = \log k_0 + BI \,. \tag{6}$$

This equation holds for the corresponding reaction types[16]. The ionic strength of the studied solutions increased somewhat during the hydrolysis, Eq. (*A*), and was calculated as

$$I = 3\left[c_{0\mathrm{H_2SO_4}} + c_{0\mathrm{(NH_4)_2SO_4}} + c_{0\mathrm{(NH_4)_2S_2O_8}}\right] + c_{\mathrm{H_2SO_5}} = I_0 + c_{\mathrm{H_2SO_5}}\,, \qquad (7)$$

where c_0 and I_0 denote initial concentration and ionic strength for $c_{0\mathrm{H_2SO_5}} = 0$. We assume throughout that H_2SO_5 dissociates only to the first degree.

The correlation of the calculated values of k with Eq. (*6*) is shown in Fig. 1 for all measured solutions at 20 and 30°C. It is seen that the regression lines fit well the experimental points; they can be expressed as (for k in $\mathrm{h^{-1}\,mol^{-1}\,dm^3}$)

$$\log k = -4{\cdot}3209 + 0{\cdot}1470\, I \quad (20°\mathrm{C})\,, \qquad (8)$$

$$\log k = -3{\cdot}7791 + 0{\cdot}1421\, I \quad (30°\mathrm{C})\,. \qquad (9)$$

It is seen that the slopes of these linear dependences are similar; and with respect to a certain scatter of the experimental rate constants we can assume that the slope is the same for both temperatures. Hence, the activation energy of the studied reaction is in this temperature interval constant and independent of the ionic strength. If we use the mean value of the slope, $B = 0{\cdot}1445$, then Eqs (*8*) and (*9*) are replaced

$$\log k = -4{\cdot}2896 + 0{\cdot}1445\, I \quad (20°\mathrm{C})\,, \qquad (10)$$

$$\log k = -3{\cdot}7952 + 0{\cdot}1445\, I \quad (30°\mathrm{C})\,. \qquad (11)$$

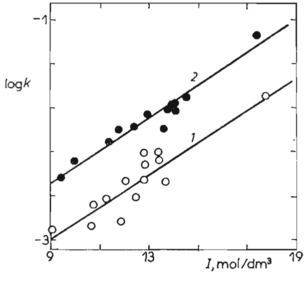

FIG. 1

Dependence of log *k* on Mean Ionic Strength for Hydrolysis of $S_2O_8^{2-}$ Ions to H_2SO_5 at 20°C *1* and 30°C *2*

Then we obtain the values of the activation energy and frequency factor: $\Delta H^{\ddagger} = 84{\cdot}11$ kJ/mol, $A = 4{\cdot}99 \,.\, 10^{10}$ $(I = 0)$. Hence, the dependence of the rate constant for hydrolysis of $S_2O_8^{2-}$ ions to H_2SO_5 in acidic medium on the temperature and ionic strength can be at our conditions expressed as

$$\log k = 10{\cdot}6978 - 4\,394/T + 0{\cdot}1445\, I\,. \qquad (12)$$

It is difficult to compare our results with those of other authors since the conditions of measurement were different. According to Kolthoff and Miller[10], the rate constant is equal to $1{\cdot}5\ \text{min}^{-1}$ in 5M-$HClO_4$ at 50°C, as determined from the initial slope of the dependence of $\log c_{S_2O_8^{2-}}$ on t; this dependence was not linear during further course of the hydrolytic reaction in contrast to our data. If we calculate their rate constant, k', from Eq. (*12*), we obtain $k' = 6 \,.\, 10^{-4}\ \text{min}^{-1}$ at the given conditions[10]; the relation between k' and k used in the present paper is $k' = kc_{H^+}$. The agreement is hence satisfactory in spite of the different reaction conditions. Besides it is not clear whether the nonlinear dependence of $\log c_{S_2O_8^{2-}}$ on t in ref.[10] led to an increase or decrease of the value of k' obtained from the initial value of the slope.

The discrepancy between Eq. (*12*) and the data of Palme[8] is larger and the same applies for the comparison of his data with those of Kolthoff and Miller[10] so far as possible. Another work[9], dealing with hydrolysis of peroxodisulphates at 80 to 100°C, does not bring any possibility to evaluate the rate constant.

It can be concluded that our results enable to determine the rate of formation of peroxomonosulphuric acid by hydrolysis of $S_2O_8^{2-}$ ions in acidic medium under various conditions of manufacture of peroxodisulphuric acid or its salts by electrolysis of sulphuric acid solutions or its mixtures with sulphates. The presence of H_2SO_5 in the anolyte of industrial electrolysers is undesirable; the mentioned results enable to find technically and economically suitable measures for suppressing its concentration (*e.g.*, low temperature of electrolysis, addition of compounds reacting with H_2SO_5 but not with $H_2S_2O_8$).

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