MECHANISM OF FORMATION OF PEROXOMONOSULPHURIC ACID DURING ELECTROLYTIC PREPARATION OF PEROXODISULPHATES

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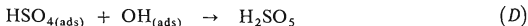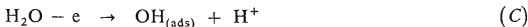*Czechoslovak Academy of Sciences, 160 00 Prague 6*

The content of peroxomonosulphuric acid in the anolyte flowing out from a continual flow-through laboratory electrolyser for the preparation of concentrated ammonium peroxodisulphate solutions was always lower than would correspond to its rate of formation by spontaneous hydrolysis of $S_2O_8^{2-}$ ions in acid medium. Hence, peroxomonosulphuric acid is formed during electrosynthesis of peroxodisulphates only by reactions taking place also in hydrolysis of $S_2O_8^{2-}$ ions. The formation of peroxomonosulphuric acid by direct anodic discharge of HSO_4^- ions is improbable. A modified mechanism of the formation of H_2SO_5 either during hydrolysis or during electrolytic manufacture of peroxodisulphates is proposed.

It is known[1-3] that during electrolytic manufacture of concentrated solutions of peroxodisulphuric acid or its salts, a certain quantity of peroxomonosulphuric acid, H_2SO_5, is formed, and this the more the more acidic is the solution or the longer is the duration of electrolysis (in the case of discontinually operating batch electrolysers). The formation of this acid has been generally attributed to the hydrolytic decomposition of the primarily formed $S_2O_8^{2-}$ ions according to

$$S_2O_8^{2-} + H_2O \rightarrow H_2SO_5 + SO_4^{2-}. \qquad (A)$$
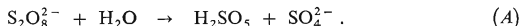
This reaction is catalysed by hydrogen ions[4,5]. Recently Smit and Hoogland[6] assumed that peroxomonosulphuric acid is formed during electrolysis of peroxodisulphates also by direct anodic oxidation of HSO_4^- ions with the participation of an intermediate product of the simultaneous anodic oxygen evolution. Although they did not give a corresponding reaction mechanism, it can be apparently written as follows:

$$HSO_4^- - e \rightarrow HSO_{4(ads)} \qquad (B)$$

$$H_2O - e \rightarrow OH_{(ads)} + H^+ \qquad (C)$$

$$HSO_{4(ads)} + OH_{(ads)} \rightarrow H_2SO_5 \qquad (D)$$

or

$$HSO_{4(ads)} + H_2O - e \rightarrow H_2SO_5 + H^+ . \qquad (E)$$

Based on the known relevant publications[1-5,7-13], it is not possible to compare directly the rates of formation of H_2SO_5 in the electrolysis proper and in the spontaneous hydrolysis, Eq. (A). Namely, the temperature of electrolysis is kept rather low $(10-35°C)$, whereas the rate of hydrolysis of $S_2O_8^{2-}$ ions was studied at temperatures of 50°C and higher (in ref.[11], the temperature is not given) and often at different concentrations. Extrapolation of such kinetic data to lower temperatures and other concentrations is uncertain with respect to, *e.g.*, the catalytic effect of trace metal ions[11-13] whose content was probably different in individual studies.

Our aim was to measure the rates of formation of peroxomonosulphuric acid both during electrolysis of mixed solutions of sulphuric acid and ammonium sulphate and during hydrolysis of $S_2O_8^{2-}$ ions in solutions corresponding to the anolyte flowing out from a continuously operating electrolyser, at initial zero content of H_2SO_5 at the same temperature. The object was to derive a mechanism of formation of this acid during the electrolysis.

EXPERIMENTAL

Apparatus: Concentrated peroxodisulphate solutions were prepared in a laboratory flow-through integral electrolyser of monopolar type with two lateral cathode compartments and one central anode compartment. Its characteristic parameters (current density, current concentration, anode construction, ceramic diaphragms, temperature) were close to those used in large-scale production of H_2O_2 by the Löwenstein's method. The electrolyser had the shape of a prism whose walls and other parts were made of plexi glass. The anode was made of several smooth platinum foils which were 0·05 cm thick, 7 cm long and 0·15 cm wide, and were point-welded to tantalum supports serving as current leads. The cathodes were plates of hard lead, whose dimensions were $10 \times 10 \times 0·2$ cm. The anode and cathode compartments were provided with glass coolers flowed through with water of a constant temperature of 20°C. The anodic current density was kept at 0·416 A/cm² and the cathodic one at 0·045 A/cm² (referred to one side of the cathode facing the anode). The total current load of 9 A corresponded to an anodic current concentration of 27 A/dm³. The stationary temperature of the anolyte was 21·5°C, that of the catholyte 20·5°C.

Method: The electrolyte of a given composition was fed at a chosen rate to both cathode compartments in parallel, where hydrogen evolution took place as the main reaction. The diffusion resistance of the diaphragms used was so high that no $S_2O_8^{2-}$ ions were transferred from the anode into the cathode space. This was evidenced by gasometrically found 100% current yields of hydrogen at arbitrarily high concentrations of $S_2O_8^{2-}$ ions in the anode compartment. After passing through the cathode compartments, both catholytes flowing out were joined and led to the central anode compartment where $S_2O_8^{2-}$ ions and partly ozonized oxygen[14] were formed on the anode. From there the anolyte flowed out as the final product, which was then chemically analysed to determine the total content of peroxo compounds and individual components. The current yields of peroxo compounds (calculated as $(NH_4)_2S_2O_8$) in total and of their components were calculated from the known charge passed and the quantity of electro-

lyte flowed through. The results of analyses after attainment of the stationary state in the flow-through electrolyser were used to evaluate the dependences under study. The electrolysis was carried out without any addition of NH_4CNS or other compounds used in industrial cells to increase the current yield of peroxodisulphate, in order to avoid their influence on the content of peroxomonosulphuric acid with which they react mostly rapidly.

The rate of hydrolysis of the $(NH_4)_2S_2O_8$–H_2SO_4–$(NH_4)_2SO_4$–H_2O system was measured *a)* in the anolyte flowing out from the anode compartment immediately after finishing the electrolysis which had proceeded for many hours at stationary conditions, and *b)* in solutions prepared from recrystallized reagent grade $(NH_4)_2S_2O_8$, $(NH_4)_2SO_4$ and H_2SO_4, and distilled water. The latter measurements were carried out in thermostated Pyrex glass vessel during stirring; samples were taken off at different time intervals and analysed. The temperature of measurement was $20 \pm 0.05°C$.

Solutions: To follow the rate of formation of H_2SO_5 during the electrolytic process, we used as a starting solution 22·6% H_2SO_4 and 20·3% $(NH_4)_2SO_4$. This corresponds to the maximum allowable concentration in order to obtain a nearly saturated $(NH_4)_2S_2O_8$ besides the remaining acid and ammonium sulphate[15,16] assuming that the molar ratio P_0 between the two is 1·5 in the starting solution, the maximum conversion of the sulphate to peroxodisulphate $\alpha_{max} = 0.8$, and the temperature of the cooling water 20°C. To measure the hydrolysis rate in the synthesized solution, the chosen starting concentrations were 14·24% H_2SO_4 + 9·31% $(NH_4)_2SO_4$ + + 18·60% $(NH_4)_2S_2O_8$. This was nearly in accord with the outflowing anolyte in the case where the starting solution had been electrolysed to form ammonium peroxodisulphate with a real degree of conversion $\alpha = 0.55$.

Analytical: The total acidity of electrolyte samples was determined by titration with 0·1M-NaOH with methylred as indicator, the total content of peroxo compounds by adding an excess of Fe^{2+} ions and titrating manganometrically according to LeBlanc and Eckardt[17], H_2SO_5 was determined iodometrically according to Palme[4], and NH_4^+ ions by the method of Hanuš[18].

RESULTS

The composition of the anolyte flowing out from the described electrolyser at stationary conditions for various rates of flow is given in Table I. Certain fluctuations of the composition are apparently due to inconstancy of the rate of flow, which influenced the degree of conversion as well as the current yield. Variations of the total content of peroxo compounds (denoted as $(NH_4)_2S_2O_{8,tot}$) and other components with the rate of flow of electrolyte corresponded to the mass balance of the electrolysis and were directly proportional to the conversion degree[16], whereas the content of H_2SO_5 varied only slightly in the range $0.09-0.13m$ H_2SO_5 (about $1-2\%$ of the total content of peroxosulphates). No hydrogen peroxide was found in the outflowing anolyte.

The rate of the spontaneous hydrolysis of the anolyte after finishing the electrolysis, its initial composition being identical with the final composition given in Table I after 101 h of electrolysis, is illustrated by the data in Table II and Fig. 1. In this table is shown also the course of hydrolysis of the synthesized anolyte (*cf.* Experimental).

Since no H_2O_2 was ever found in the analysed solutions, we can assume that the hydrolysis of $S_2O_8^{2-}$ ions proceeds under the given conditions only to the first stage

with the formation of H_2SO_5 according to the overall equation (A). Thus, its rate of formation can be calculated as

$$d[H_2SO_5]/d\tau = -d[S_2O_8^{2-}]/d\tau = k'[S_2O_8^{2-}] \tag{1}$$

and after integration

$$\ln\left([S_2O_8^{2-}]_0/[S_2O_8^{2-}]\right) = k'\tau . \tag{2}$$

The calculated values of k' for both solutions under study are given in Table II.

DISCUSSION

Is is seen from Tables I and II and Fig. 1 that the rate of formation of peroxomonosulphuric acid by spontaneous hydrolysis of the anolyte after finishing the electrolysis is much higher than would correspond to the content of this acid in the anodic compartment of the electrolyser at the corresponding time of delay. The hydrolytic rate constant of the synthesized anolyte is under the same conditions somewhat smaller than in the case of the anolyte flowed out from the electrolyser owing apparently to a catalytic effect of traces of anodically dissolved platinum (which was not present in the synthesized anolyte). Nevertheless, even the hydrolysis of the synthesized anolyte leads to a several times higher content of H_2SO_5 than found in the anolyte flowed out during electrolysis at the corresponding temperature and rate of flow. (In reality, the anolyte temperature in the anodic compartment was even by 1·5°C higher than during hydrolysis of the synthesized anolyte.)

Our finding that the rate of spontaneous hydrolysis of $S_2O_8^{2-}$ ions is several times higher than would correspond to the final content of H_2SO_5 in the outflowing anolyte

Fig. 1

Dependence of Total Content of Peroxosulphates (as $(NH_4)_2S_2O_{8,tot}$) (1) and of Peroxomonosulphuric Acid (2) on Time of Delay of Anolyte in the Anode Compartment of a Flow-Through Electrolyser, and Dependence of the Increment of the Content of this Acid in Flowed-out Electrolyte on Time of Subsequent Spontaneous Hydrolysis (3)
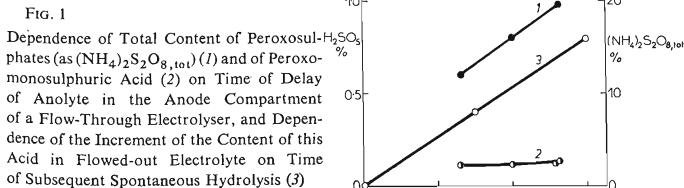
TABLE I

Composition of Anolyte Flowing out from a Laboratory Flow-through Electrolyser at Stationary Conditions at Different Flow Rates ($P_0 = 1.5$, $\alpha_{max} = 0.8$, $t = 20°C$, $i_a = 0.416$ A/cm², $I = 9$ A, Pt anode)

Electrol. time, h	Voltage E, V	Flow rate cm³/h	Anolyte composition, %				α	P_a	Current yield, %	Time of delay in an. com. h
			H_2SO_4	$(NH_4)_2SO_4$	$(NH_4)_2S_2O_{8,tot}$	H_2SO_5				
26	4.22	122.0	17.71	13.52	12.25	0.11	0.344	1.76	49.54	2.62
32	4.22	122.5	17.53	13.49	12.08	0.12	0.341	1.75	49.08	2.61
54	4.28	79.0	16.04	10.93	16.23	0.12	0.462	1.98	45.28	4.05
71	4.29	81.0	16.11	11.25	16.14	0.11	0.454	1.93	42.23	3.95
96	4.33	61.0	14.77	9.07	19.98	0.12	0.561	2.19	44.02	5.25
101	4.33	62.0	14.84	9.12	19.89	0.135	0.558	2.19	41.06	5.16

at corresponding conditions is at variance with the conclusion of Smit and Hoogland[6] according to which this acid is formed during electrosynthesis of peroxodisulphates also by anodic oxidation of HSO_4^- ions. If this conclusion was true, then the quantity of H_2SO_5 in the outflowing anolyte of a flow-through electrolyser would have to be larger than that formed at the corresponding conditions by sole hydrolysis of $S_2O_8^{2-}$ ions.

The mentioned difference between the content of H_2SO_5 in solution during spontaneous hydrolysis of $S_2O_8^{2-}$ ions and its content in the anolyte during electrolysis can be attributed only to the following anodic reaction[1-3]:

$$H_2SO_5 + H_2O - 2e \rightarrow O_2 + H_2SO_4 + 2H^+ . \qquad (F)$$
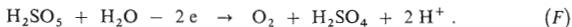
Its rate is under the common conditions of technical electrosynthesis of $S_2O_8^{2-}$ ions obviously higher than the rate of the eventual formation of H_2SO_5 by anodic discharge of HSO_4^- ions according to Smit and Hoogland[6]. According to these authors, their theory is supported by the results of another study[19], which, however, refers to alkaline and not acidic medium used by Smit and Hoogland[6], hence their reasoning is not correct.

With respect to the present and earlier results[1-3], we propose a modified mechanism of formation of peroxomonosulphuric acid both during electrosynthesis of peroxo-

TABLE II

Course of Hydrolysis of Anolyte Flowed out from the Electrolyser after 101 h Electrolysis, and of Synthesized Anolyte with Almost Identical Initial Composition (see Experimental) at 20°C
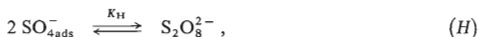
h	H_2SO_4 %	$(NH_4)_2SO_4$ %	$(NH_4)_2S_2O_{8,tot}$ %	H_2SO_5 %	ΔH_2SO_5 %	$k' . 10^2$ s^{-1}
			Anolyte flowed out from the electrolyser			
0	14·84	9·12	19·80	0·135	0·0	—
3	14·86	—	19·76	0·535	0·40	1·38
4	14·88	—	19·75	0·928	0·793	1·39
					mean value	*1·39*
			Synthesized anolyte			
0	14·24	9·31	18·60	0·00		—
4	14·52	—	18·56	0·335		0·920
6	14·59	—	18·49	0·496		0·916
					mean value	*0·92*

disulphates and during their hydrolysis in acidic medium. We do not consider sulphur tetraoxide, SO_4, proposed by Kolthoff and Miller[5] in the hydrolysis mechanism, as a possible intermediate particle under the conditions of electrosynthesis of $S_2O_8^{2-}$ ions; its existence was not proved by the later work[20,21], and only recently, it was synthesized[22] by electrolysis of $7.5M-H_2SO_4 + 1M-HClO_4$ on a platinum anode at high anodic potentials $(4-6\text{ V})$ and at low temperature $(-30°C)$, i.e. at quite different experimental conditions.
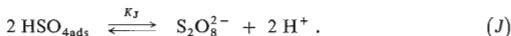
We assume that the rate-controlling reaction in the formation of H_2SO_5 may be the disproportionation of particles:

$$SO_4^- + HSO_4 + H_2O \xrightarrow{k_G} H_2SO_5 + HSO_4^- \qquad (G)$$

which are formed during electrosynthesis of $S_2O_8^{2-}$ ions mainly by anodic discharge of SO_4^{2-} and HSO_4^- ions and undergo rapid dimerization[23]:

$$2\ SO_{4\,ads}^- \overset{K_H}{\rightleftharpoons} S_2O_8^{2-}, \qquad (H)$$

or

$$2\ HSO_{4\,ads} \overset{K_J}{\rightleftharpoons} S_2O_8^{2-} + 2\ H^+ . \qquad (J)$$

The HSO_4 or SO_4^- particles may be formed partly also in the bulk of the electrolyte by hydrolysis of $S_2O_8^{2-}$ ions whose first step is reaction (H) and (J) proceeding backwards. These are also the only reaction path possible outside the electrolyser to form these particles.

Accordingly, the rate of reaction (G) determining the rate of formation of peroxomonosulphuric acid can be expressed as

$$dc_{H_2SO_5}/d\tau = k_G \cdot c_{SO_4^-} \cdot c_{HSO_4} \cdot a_{H_2O} = k_G' \cdot c_{SO_4^-} \cdot c_{HSO_4} . \qquad (3)$$

(We set activities approximately equal to concentrations.) If we replace the concentrations in the rate-controlling step by equilibrium concentrations for reactions (H) and (J), we obtain

$$r = k_G'' \cdot c_{H^+} \cdot c_{S_2O_8^{2-}} \qquad (4)$$

which, for $c_{H^+} = const$, is identical with the experimentally proved Eq. (1), and in which

$$k_G'' = k_G'/(K_H K_J)^{0.5} . \qquad (5)$$

Eq. (4) elucidates theoretically the known catalytic effect of H^+ ions on the rate of formation of H_2SO_5 by hydrolysis of $S_2O_8^{2-}$ ions[4,5,9-13].

According to our theory, the mechanism of formation of H_2SO_5 is the same in the anodic compartment of the electrolyser, where $S_2O_8^{2-}$ ions are formed, as outside the electrolyser, where hydrolysis proceeds in concentrated acidic solution. We cannot state definitely the relative participation of the anodic discharge of SO_4^{2-} and HSO_4^- ions and or reactions (H) and (J) proceeding backwards in the formation of the SO_4^- and HSO_4 particles in the anodic compartment.

The fact that the concentration of H_2SO_5 in the anolyte during electrolysis is smaller than during hydrolysis of $S_2O_8^{2-}$ ions at the same temperature and concentrations is an evidence that this acid is irreversibly decomposed on the anode by reaction (F) with the formation of gaseous oxygen, as deduced already from earlier experiments with discontinuous electrolyses[1,10] or from recent experiments with a flow-through electrolyser[24]. Therefore, we cannot imagine that the same compound would be formed simultaneously at the anode by the opposite reaction sequence $(B)-(E)$ as assumed by Smit and Hoogland[6].

REFERENCES

1. Machu W.: *Das Wasserstoffperoxyd und die Perverbindungen*, p. 127. Springer, Wien 1951.
2. Schumb W. C., Satterfield C. N., Wentworth R. L.: *Hydrogen Peroxide*, p. 121. Reinhold, New York 1955.
3. *Gmelin's Handbuch der Anorganischen Chemie*, Syst. Nr. 9, Bd. B, Lf. 2, p. 798 and 810. Verlag Chemie, Weinheim 1960.
4. Palme H.: Z. Anorg. Allg. Chem. *112*, 97 (1920).
5. Kolthoff I. M., Miller I. K.: J. Amer. Chem. Soc. *73*, 3055 (1951).
6. Smit W., Hoogland J. G.: Electrochim. Acta *16*, 1 (1971).
7. Efimov E. A., Izgaryshev N. A.: Dokl. Akad. Nauk SSSR *106*, 1039 (1956); Zh. Fiz. Khim. *31*, 1141 (1957).
8. Elbs O., Schönherr K.: Z. Elektrochem. *1*, 417 (1894—5).
9. Thiele W.: *Thesis*. M. Luther Universität, Halle 1978.
10. Müller E., Schellhaas H.: Z. Elektrochem. *13*, 257 (1907).
11. Rius A., Zuluetta C.: Ann. Real. Soc. Esp. Fís. Quím. *46B*, 79 (1950).
12. Galiba H., Csányi L. J., Szabó Z. G.: Z. Anorg. Allg. Chem. *287*, 152 (1956).
13. House D. A.: Chem. Rev. *62*, 185 (1962).
14. Balej J., Thumová M.: This Journal *39*, 3409 (1974).
15. Pungor E., Schulek E., Trompler J.: Acta Chim. (Budapest) *4*, 411, 417, and 423 (1954).
16. Balej J.: This Journal *30*, 2663 (1965).
17. LeBlanc M., Eckardt M.: Z. Elektrochem. *5*, 355 (1898).
18. Čůta F.: *Analytická chemie odměrná*, p. 295. Published by Nakladatelství ČSAV, Prague 1956.
19. Potemskaya A. P., Lunenok-Burmakina V. A.: Ukr. Khim. Zh. *35*, 339 (1969).
20. Wannagat U., Schwarz R.: Z. Anorg. Allg. Chem. *286*, 81 (1956).
21. Wannagat U., Horn E. M., Valk G., Höfler J.: Z. Anorg. Allg. Chem. *340*, 181 (1965).
22. Potapova G. F., Rakov A. A., Veselovskii V. I.: Elektrokhimiya *9*, 1410 (1973).
23. Balej J., Kadeřávek M.: This Journal *44*, 1510 (1979).
24. Balej J.: This Journal, in press.

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