EFFECT OF CARO'S ACID IN ELECTROLYTIC PREPARATION OF PEROXODISULPHATES

Jan BALEJ

Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 160 00 Prague 6

Received November 10th, 1979

Measurements of the current yield of oxygen and of the anode potential during electrolytic preparation of peroxodisulphates in a continually operating flow-through model electrolyser both in the stationary state and after the beginning of anolyte feeding with an increased content of Caro's acid into the anode space proved that this acid is preferentially oxidised at the anode under evolution of oxygen, whereby the current yield of peroxo compounds is lowered. Owing to this reaction taking place preferentially on the anode, the anode potential is lowered at constant current density, which is denoted as "depolarization effect" of Caro's acid in persulphate electrolysis.

It has been known since long[1,2] that the preparation of peroxodisulphuric acid or its salts by anodic oxidation of concentrated solutions of sulphuric acid or its mixtures with sulphates is negatively influenced by the simultaneously formed peroxomonosulphuric acid (Caro's acid), H_2SO_5. Two reasons for this were considered[1-6]: *a)* The Caro's acid is preferentially oxidized on the anode:

$$H_2SO_5 + H_2O - 2\,e \rightarrow O_2 + H_2SO_4 + 2\,H^+ , \tag{1}$$

causing an adequate decrease of the current yield of peroxo compounds; and *b)* the preferential anodic oxidation (*1*) causes a decrease of the anodic potential (so-called depolarization effect of Caro's acid), whereby the conditions for electrosynthesis of peroxodisulphates become worse.

However, Smit and Hoogland[7] concluded that this opinion about the negative depolarization effect of Caro's acid is not justified since they found during electrolysis with an increased content of this acid even an increase of the anodic potential. According to them, Caro's acid is formed in the electrosynthesis of peroxodisulphates not only by their hydrolysis but also by direct anodic discharge of HSO_4^- ions according to the reaction

$$HSO_{4(ads)} + OH_{(ads)} \rightarrow H_2SO_5 . \tag{2}$$

We proved[8] that this reaction is improbable since the amount of H_2SO_5 in the anolyte of a continually operating flow-through electrolyser is much smaller than would correspond to the spontaneous hydrolysis of $S_2O_8^{2-}$ ions according to the equation:

$$S_2O_8^{2-} + H_2O \rightarrow HSO_5^- + SO_4^{2-} + H^+ \tag{3}$$

outside the electrolyser under the same conditions (temperature and composition).

To elucidate the concept of the "depolarization effect" of Caro's acid in electrosynthesis of peroxodisulphates, we carried out some new measurements which form the subject of the present work.

EXPERIMENTAL

The effect of Caro's acid in electrosynthesis of nearly saturated solutions of $(NH_4)_2S_2O_8$ was measured in a laboratory flow-through electrolyser of a monopolar type used earlier[8]. At first, the course of electrolysis was followed at constant current density $j_a = 0{\cdot}416\ A/cm^2$ on a platinum anode at stationary conditions; temperature of cooling water 20°C, that of anolyte in anodic compartment 21·5°C, temperature of catholyte in cathodic compartment 21·0°C; the rate of flow of electrolyte led in parallel into both cathodic compartments and then, after joining the streams, into the anodic (middle) compartment was in the range 65—69 cm^3/h (owing to fluctuations of the pump power), corresponding to the time of delay of the anolyte in the anodic compartment 4·78—5·08 h. The outflowing anolyte was analysed for the content of peroxo compounds (expressed as $(NH_4)_2S_2O_8$) and for the content of H_2SO_5 besides H_2SO_4 and $(NH_4)_2SO_4$. From this analysis and rate of oxygen evolution on the anode, the current yield of peroxo compounds and oxygen was calculated. For the sake of simplicity, we assumed that the rate of ozone evolution was negligible in accord with earlier measurements[9]. To check the stationary state of the continual electrolysis, we analysed also the catholyte. The anode potential was measured against a Hg/Hg_2SO_4 reference electrode in the same solution as used in electrolysis.

After a sufficiently long time of electrolysis at constant rate of flow, temperature, and current density, we began to collect the catholyte flowing out from both cathodic compartments in a separate vessel and to feed the anodic compartment with a partially hydrolysed anolyte at a rate of flow of 1 230 cm^3/h. This was obtained by hydrolysing at room temperature outside the electrolyser the anolyte collected during the preceding stationary electrolysis. A portion of the $S_2O_8^{2-}$ ions was hydrolysed to the first stage to H_2SO_5 but not to H_2O_2 which could not be found in the hydrolysed anolyte even after three days. The total content of peroxo compounds in the anolyte practically did not change. Except for the changed composition and rate of feeding the solution into the anodic compartment, the conditions of electrolysis did not change. The anode potential and the rate of anodic oxygen evolution were followed systematically during the changed regime of electrolysis. The anolyte was analysed at the end of electrolysis regime.

The starting solution which was fed during normal electrolysis into both cathodic compartments and then into the anodic one was 22·69wt% H_2SO_4 + 20·34wt% $(NH_4)_2SO_4$. This was the highest possible concentration[10] for a temperature of 20°C, molar ratio of the acid to the sulphate $P_0 = 1{\cdot}5$, and assumed maximum degree of conversion to ammonium peroxodisulphate $\alpha_{max} = 0{\cdot}8$. We did not use any additions to increase the current yield of peroxodisulphates since we wanted to prevent any possible side reactions of Caro's acid which would distort the results.

The anode potential, measured as given above, was not corrected for the IR drop between the tip of the Luggin capillary and the anode surface; it was recalculated against hydrogen electrode in the same solution and is given here on this scale. The current yield of oxygen was calculated in all cases on the assumption of a four-electron anodic reaction, although only two electrons are involved in reaction (*1*) leading to gaseous oxygen.

RESULTS AND DISCUSSION

The results of measurements shown in Fig. 1 give the course of the current yield of oxygen evolution (curve *1*) and of the anodic potential (curve 2) in different stages of electrolysis. The first stage, lasting for 100 h, corresponds to the normal course of electrolysis under the given conditions. It is apparent from Fig. 1 that both mentioned quantities attained their stationary values already after some 20 h of electrolysis which did not change during another 80 h. The current yield of peroxodisulphate determined by chemical analysis was on the average 50·0 ± 0·5% in good agreement with the values found gasometrically for anodic evolution of oxygen. The total content of peroxo compounds expressed as $(NH_4)_2S_2O_8$ was on the average 22·8wt% (*i.e.*, 1·27 mol/dm^3) corresponding to the mean degree of conversion of sulphate to peroxodisulphate $\alpha = 0{\cdot}65$. The content of Caro's acid was on the average 0·20 ± 0·01wt% (0·022 mol/dm^3) corresponding to only 1·75% of the total content of peroxo compounds in the outflowing anolyte.

The values of the anodic potential shown in Fig. 1 are the average values from two measured points differing by not more than 10 mV. It is seen that the noncorrected anode potential was during stationary electrolysis equal to 3·09 ± 0·005 V.

When the partially hydrolysed anolyte began to flow into the anodic compartments both measured quantities indicated a change in the course of electrolysis. The inlet composition corresponded to 22·5wt% $(NH_4)_2S_2O_8$ (1·25M-$(NH_4)_2S_2O_8$), the content of Caro's acid attaining 5·84wt% H_2SO_5 or 0·65 mol/l. This corresponded to 51% hydrolysis of $S_2O_8^{2-}$ ions originally present to HSO_5^-. It is seen from the diagram that the increased concentration of Caro's acid in the anode compartment leads to accelerated evolution of oxygen by the preferred reaction (*1*) and to a gradual lowering of the anodic potential. During this stage, lasting for 75 min, both quantities approached slowly their stationary values corresponding to the changed electrolysis conditions. Thus, the current yield of oxygen (assuming four electron oxidation of water) attained 120%, while the anode potential dropped finally by 65 mV.

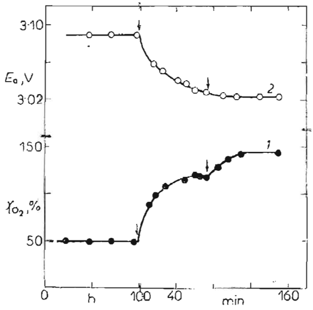

FIG. 1

Time Dependence of Current Yield of Oxygen *1* and Anode Potential *2* in Different Stages of Persulphate Electrolysis

The concentration of Caro's acid in the anode space of the flow-through electrolyser was changed in the instants denoted by arrows.

That the current yield of oxygen exceeded 100% during this stage suggests that its essential part was due to anodic oxidation of Caro's acid, the rate of reaction (*1*) being higher than the rate of formation of peroxo compounds by anodic oxidation of SO_4^{2-} to $S_2O_8^{2-}$ ions. As a result, the total content of peroxo compounds in the flowing anolyte grew smaller, namely finally to 22·05wt% or 1·226M-$(NH_4)_2S_2O_8$, the difference being 0·024 mol/l. At the same time, the concentration of Caro's acid dropped to 5·15wt% or 0·572 mol/l, *i.e.*, by 0·078 mol/l. Hence it is obvious that the concentration of $S_2O_8^{2-}$ ions increased during flow through the anode space by 0·054 mol/l and the total decrease of peroxo compounds was caused only by the loss of Caro's acid through reaction (*1*).

After finishing the second stage of electrolysis lasting for 75 min (Fig. 1), the anodic compartment of the electrolyser was fed at the same rate (1230 cm^3/h) with an anolyte solution with a nearly equal total content of peroxo compounds (22·25wt% or 1·237M-$(NH_4)_2S_2O_8$), whose degree of hydrolysis to Caro's acid was 73·5%, hence it contained 8·17wt% or 0·908M-H_2SO_5. During this third stage, lasting also for 75 min, the current yield of oxygen attained about 140%, while the anode potential dropped initially by 4 mV and did not change any further.

The outflowing anolyte at the end of this third period contained peroxo compounds corresponding to 21·37wt% or 1·20M-$(NH_4)_2S_2O_8$, the concentration of Caro's acid being 6·936wt% or 0·778 mol/l. The total drop of the concentration of peroxo compounds during flow through the anode space was hence 0·037 mol/l while the loss of Caro's acid was 0·130 mol/l. Accordingly, the concentration of $S_2O_8^{2-}$ ions must have increased during the third period by 0·093 mol/l. Also in this case the rate of anodic oxidation of Caro's acid (Eq. (*1*)) was higher than the rate of formation of peroxodisulphates by anodic oxidation of sulphate ions[8].

It follows from our results that Caro's acid formed by hydrolysis of $S_2O_8^{2-}$ ions or by disproportionation of primarily discharged anion radicals according to the proposed mechanism[8] reacts preferentially on the anode with the formation of gaseous oxygen according to reaction (*1*). This process requires less energy than oxidation of SO_4^{2-} ions to $S_2O_8^{2-}$ and brings about a decrease of the anode potential at constant current density, denoted as "depolarization effect of Caro's acid". The fact that the most pronounced decrease of the anode potential was observed immediately after the supply of electrolyte with increased content of Caro's acid had commenced is conceivable since the relative increase of its concentration was highest at that moment: the concentration of Caro's acid in the anolyte in the first stage of electrolysis (0·022 mol/l) was about thirty-times lower than that in the partially hydrolysed inlet electrolyte in the second stage (0·65 mol/l). In comparison, the ratio between the concentration of Caro's acid in the second stage and that in the third (0·908 mol/l) was equal to 0·716. Accordingly, the anode potential drop in the first case was 65 mV and in the second 4 mV. The change of the electrode potential is namely a logarithmic function of the concentration of electroactive particles. The electrode reaction of Caro's acid is, however, not the only reaction determining the anode potential in our case, hence no quantitative correlation can be expected. The ratio between the anode potential drops observed is equal to 16, whereas the logarithm of the concentration ratio of the mentioned acid is equal to 10·1. From the point of view of our results, which are consistent with the findings about the behaviour of Caro's acid in industrial electrolyses, the increase of anode potential by 0·1 V caused by increase of the concentration of Caro's acid from 0·02 to 0·07 mol/dm^3, as reported by Smit and Hoogland[7], is difficult to comprehend.

It can be concluded that the results of our measurements substantiate the earlier concepts about the behaviour of Caro's acid in electrolytic manufacture of peroxodisulphates[1-6]; the newer concept of Smit and Hoogland[7], according to which the formation of this acid under these conditions is attributed also to the anodic discharge of HSO_4^- ions and its "depolarization effect" is considered nonexistent, appears improbable.

REFERENCES

1. Konsortium für Elektrochem. Industrie: DRP 13 987 (1905).
2. Müller E., Schellhaas H.: Z. Elektrochem. *13*, 257 (1907).
3. Foerster F.: *Elektrochemie Wäßeriger Lösungen*, 4. Aufl., p. 842. J. A. Barth, Leipzig 1923.
4. Machu W.: *Das Wasserstoffperoxid und die Perverbindungen*, 2. Aufl., p. 127. Springer, Wien 1951.
5. *Gmelin's Handbuch der Anorganischen Chemie*, Syst. Nr. 9, Teil B, Lief. 2, p. 812. Verlag Chemie, Weinheim 1960.
6. Regner A.: *Technická elektrochemie* I. *Elektrochemie anorganických látek*, p. 569. Academia, Prague 1967.
7. Smit W., Hoogland J. G.: Electrochim. Acta *16*, 1 (1971).
8. Balej J., Thumová M., Kadeřávek M.: This Journal *45*, 3254 (1980).
9. Balej J., Thumová M.: This Journal *39*, 3409 (1974).
10. Balej J.: This Journal *30*, 2663 (1965).

Translated by K. Micka.