

RATE OF OZONE FORMATION UNDER THE CONDITIONS OF ELECTROLYTIC PRODUCTION OF PEROXODISULPHATES

J. BALEJ and M. THUMOVÁ

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

Received November 13th, 1973

The rate of formation of ozone on a smooth platinum anode was determined in concentrated solutions of pure sulphuric acid as well as in solutions containing sulphuric acid and ammonium sulphate in various molar ratios, in the range of total current densities $10^{-1} - 10^0$ A/cm² at 15, 20 and 25°C. The dependence of the current yields of ozone, χ , on the total current density, i_{tot} , can be described, for the range of experimental conditions used, by the relation $\log \chi = -2.49(\pm 0.25) + 0.57(\pm 0.05) \log i_{\text{tot}}$, where both the coefficients are, within the limits of experimental errors, independent of the electrolyte composition and of temperature.

It is a well-known fact that in electrolysis of aqueous solutions of oxygen containing acids or their salts as well as in solutions of hydroxides, at higher potentials (over c. 2.2 V (RHE)) ozone is formed on anodes made of platinum group metals besides normal biatomic oxygen. A number of papers¹⁻¹⁴ was devoted to the investigation of the conditions of the formation of ozone, with the result that the highest yields are obtained in rather concentrated solutions of sulphuric or perchloric acids and at the lowest possible temperature. However, it is difficult to compare the results of different authors, because of the differences in their experimental conditions. The results concerning the effect of several factors are sometimes even contradictory. When comparing the respective experimental results it must, however, be borne in mind that processes, taking place on a smooth platinum anode in the region of high anodic potentials, are significantly affected also by the previous history of the electrode, the composition and properties of its surface, the purity of the electrolyte etc. Further, it must be taken into account that the electrode is charged at such high potentials with considerably high currents, causing, especially under insufficient cooling, local overheating of the electrode and of its surroundings which, among other, may be the cause of differing results found by various authors and also of the relatively worse reproducibility of the data.

In view of the fact that no quantitative conclusions can be drawn from the hitherto published data on the rate of ozone formation on a platinum anode under the conditions of electrolytic production of peroxodisulphates, we have undertaken new measurements the results of which are the subject of the present communication.

EXPERIMENTAL

Experimental conditions were chosen so as to imitate as closely as possible the reaction conditions of the electrolytic production of ammonium peroxodisulphate or of peroxodisulphuric acid as

intermediates in the electrochemical preparation of hydrogen peroxide according to Löwenstein's method or according to the Weissenstein procedure¹⁵⁻¹⁷. For this reason the initial solutions used were 12N-H₂SO₄, corresponding roughly to the composition of the electrolyte in the Weissenstein procedure and further the solutions, containing 23.30% H₂SO₄ and 19.64% (NH₄)₂SO₄ (solution A) in which the molar ratio $P_0 = m_{\text{H}_2\text{SO}_4}/m_{(\text{NH}_4)_2\text{SO}_4} = 1.6$ and further 26.90% H₂SO₄ and 16.31% (NH₄)₂SO₄ (solution B) in which $P_0 = 2.25$, corresponding according to previous solubility measurements¹⁸ to the maximum concentration of the initial solutions for the electrochemical production of hydrogen peroxide by Löwenstein's method or by the Schmidt modification, for the temperature of 20°C with the assumed degree of conversion of sulphate to persulphate $\alpha = 0.8$. We also worked with the solution of the composition 22.65% H₂SO₄ and 18.92% (NH₄)₂SO₄ (solution C) corresponding to $P_0 = 1.6$ and to the highest attainable degree of conversion $\alpha = 0.7$ at 15°C.

Measurement of the rate of ozone formation was carried out in an electrolytic vessel similar to that in the previous studies of the formation of different surface oxides on a platinum electrode¹⁹. The measurement was based on the determination of the dependence of the total current on the anodic potential at steady conditions. At the same time, the rate of evolution of gaseous oxygen was measured, in which the content of ozone was determined iodometrically²⁰. The known amount of the anodically evolved gaseous oxygen was thoroughly shaken with buffered solution of potassium iodide and the iodine evolved by the action of ozone was extracted into 2 ml of chloroform. The amount of iodine was then determined with a spectral colorimeter Specol (Zeiss, Jena) by measuring the extinction at 527 μm . Total amounts of both gaseous oxygen and ozone determined as described above, evolved, at known current density i_{tot} , in a known time, served to calculate the partial current densities i_{O_2} and i_{O_3} according to Faraday's laws from the over-all equations



Partial current density, corresponding to the anodic formation of peroxodisulphate ion was then calculated using the relation

$$i_{\text{S}_2\text{O}_8^{2-}} = i_{\text{tot}} - i_{\text{O}_2} - i_{\text{O}_3}. \quad (\text{I})$$

In this way it was possible to determine not only the course of the total polarization curve but also the polarization curves of partial anodic reactions. Polarization curves were measured under galvanostatic conditions, *i.e.* the electrolytic vessel was polarized by constant current and after stabilization of the anodic potential its value was read off; the rate of formation of gaseous oxygen was then measured at this current together with the analytical determination of the ozone content. To find the real value of anodic potential, the ohmic drop between the outlet of the Luggin capillary and the anode surface was determined, in most cases using the interruption technique²¹. Since the stabilization of the anodic potential at the chosen current lasted mostly several hours to tens of hours, the content of the simultaneously formed peroxodisulphate ion or of its hydrolytic products increased in the anodic region. In order to prevent their possible effect on the rate of ozone formation, the electrolyte in the anodic region was quickly replaced by a fresh one without interrupting the polarization of the electrode, whereupon the anodic potential, the rate of oxygen evolution as well as the content of ozone were measured.

The electrolytic vessel was supplied by constant current from a stabilized source I SZ 13 (Elektročas), the current was measured with an amperemeter Metra DLI (accuracy class 0.5),

anodic potential against a hydrogen reference electrode immersed into the same initial anolyte was measured using valve voltmeter MV 11 (Clamann & Grahnert, GDR) with precompensation, the accuracy of the measurement being ± 2 mV. Platinum anodes, in the form of wires, (diameter 0.05 cm) were on both ends sealed into the glass to eliminate the edge effect. Their total surface was 0.0785 cm^2 . The relatively small surface area was chosen in order to make, even at current densities of the order of magnitude 10^0 A/cm^2 , the total current and hence also the Joule heat formed in the course of anodic reaction as small as possible. The electrolytic vessel was placed in a thermostat maintained at the desired temperature. within the accuracy of $\pm 0.05^\circ\text{C}$. The anode itself was not cooled so that, especially at the highest current densities, the temperature in the vicinity of anode was by several degrees higher, similarly as it is in production-scale electrolyzers.

Solutions for measurement were prepared from sulphuric acid, reagent grade purity, and from ammonium sulphate, also reagent grade purity, which was additionally purified by recrystallization. The ready solutions were no more purified. The gas burette for measuring the rate of anodic oxygen evolution within the accuracy of $\pm 0.01 \text{ ml}$ was also maintained at the same temperature as the thermostat.

RESULTS AND DISCUSSION

Both the total and partial anodic polarization curves, measured in solutions of the above mentioned composition on a smooth platinum electrode polarized with current densities $10^{-1} - 10^0 \text{ A/cm}^2$ are presented in Figs 1 and 2. Fig. 1 shows the polarization curves in $12\text{N-H}_2\text{SO}_4$ at thermostat temperatures 15, 20 and 25°C and further the polarization curves in the initial solution of electrolytic preparation of ammonium persulphate according to Löwenstein (molar ratio $P_0 = 1.6$) and according to Schmidt ($P_0 = 2.25$) for the assumed degree of conversion of sulphate to per-

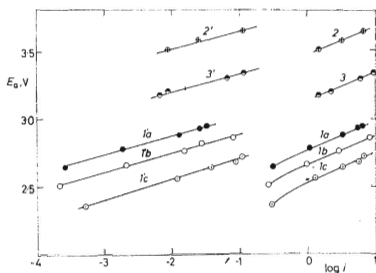


FIG. 1

Course of Total Anodic Polarization Curves (1a-c, 2 and 3) and of Partial Polarization Curves of Ozone Evolution (1'a-c, 2' and 3') on a Smooth Platinum Electrode in Solutions of $12\text{N-H}_2\text{SO}_4$ (1a-c) and in Solutions A (2, 2') and B (3, 3'), at 15°C (1a, 1'a), 20°C (1b, 1'b, 2, 2', 3 and 3') and 25°C (1c, 1'c)

TABLE I

Values of the Constants of Kinetic Equation (5) for the Dependence of Current Yields of Ozone on Total Current Density in Various Solutions and at Various Temperatures

Solution	$t, ^\circ\text{C}$	b'	b''	E'	E''	A	B
12N-H ₂ SO ₄	15	0.212	0.135	2.772	3.142	-2.740	0.570
	20	0.215	0.136	2.662	3.012	-2.573	0.580
	25	0.224	0.143	2.527	2.842	-2.202	0.568
A	20	0.210	0.133	3.478	3.786	-2.317	0.579
B	20	0.210	0.134	3.139	3.468	-2.455	0.568
C	15	0.220	0.152	3.080	3.455	-2.468	0.474
	20	0.226	0.154	2.946	3.334	-2.520	0.468
	25	0.276	0.160	2.760	3.182	-2.455	0.568
				<i>Average</i>		-2.49 ¹	0.57
						± 0.25	± 0.05

sulphate $\alpha = 0.8$ at 20°C . This figure shows, in addition to the total polarization curves, further only the partial polarization curves of ozone evolution which are most important in our present studies. Fig. 2, illustrating analogous results for initial solutions of the electrolytic preparation of peroxodisulphate according to Löwenstein with the assumed degree of conversion $\alpha = 0.7$ or 0.8 , shows in addition to the total polarization curve also the polarization curves of all anodic processes, *i.e.* of the formation of normal oxygen, of ozone and peroxodisulphate.

These results in which each point represents an average of at least five measurements show that the course of both the total polarization curve and the partial polarization

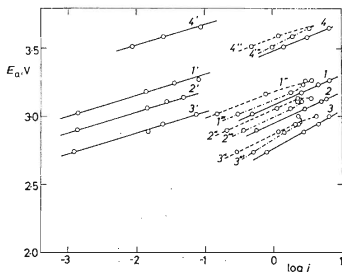


FIG. 2

Course of Total Anodic Polarization Curves (1-4) and of Partial Polarization Curves of Ozone Evolution (1'-4'), Oxygen Evolution (1'' to 4'') and Peroxodisulphate Formation (1''' to 4''') in Solutions A at 20°C (4) and C at 15°C (1), 20°C (2) and 25°C (3)

curve of ozone evolution is in all cases approximately linear (in the usual semi-logarithmic plot). The non-linearity of the polarization curves of the formation of peroxodisulphates as well as of the evolution of normal oxygen at high current densities is evidently caused by local over-heating of the anode surface and by the acceleration of chemical decomposition of the formed peroxodisulphate. The slope of the over-all polarization curve amounts the values between 0.21–0.27 V/log unit of the current density, whereas for the polarization curve of ozone evolution this quantity lies between 0.13–0.16 V. This range of values of the slope b , which is relatively narrow with respect to the reproducibility of the data, indicates that the rate limiting process of anodic ozone evolution is a one-electron reaction with the charge transfer coefficient $\alpha = 0.37–0.45$. In spite of this, the true kinetic parameters of this reaction cannot so far be determined from the course of these partial polarization curves of ozone evolution decisively enough, since it has not been as yet unambiguously proved in which over-all electrode reaction this product is formed and, consequently, what is the value of its equilibrium potential. The value of the standard equilibrium potential for the hitherto often proposed reaction



is $E^\circ = 2.076$ V, whereas for reaction (B) the resulting value is $E^\circ = 1.510$ V (see²²).

For our purposes, however, the most important task was to determine the dependence of the current yield of ozone formation on the total current density under various conditions existing in the electrolytic production of peroxodisulphates. To derive the respective quantitative relations the fact can be taken into account that both the total polarization curve and the curve of anodic ozone evolution can be expressed by the equations (analogous to Tafel's equations)

$$E = E' + b' \log i_{\text{tot}}, \quad \text{or} \quad E = E'' + b'' \log i_{\text{O}_3}, \quad (2), (3)$$

in which E' and E'' denote potentials at which the total current density, i_{tot} , and the partial current density, i_{O_3} , respectively, attain the value $1\text{A}/\text{cm}^2$. The value of the partial current density of ozone evolution at i_{tot} and the corresponding anodic potential E is then given by the expression

$$E' + b' \log i_{\text{tot}} = E'' + b'' \log i_{\text{O}_3}, \quad (4)$$

which upon transformation can yield the desired expression for the dependence of the current yield of ozone $\chi_{\text{O}_3} = i_{\text{O}_3}/i_{\text{tot}}$

$$\log \chi_{\text{O}_3} = A + B \log i_{\text{tot}}, \quad (5)$$

where

$$A = (E' - E'')/b'' \quad (6)$$

and

$$B = (b' - b'')/b'' \quad (7)$$

The values of coefficients A and B can in general be a function of the variable reaction conditions, particularly of the composition of the electrolyte and of temperature.

The results of the determined values of A and B under various reaction conditions are summarized in Table I. The measured values obviously do not differ too much from each other and for one measured solution and for a given range of experimental conditions no effect of the electrolyte composition or temperature could be proved. Therefore the mean values of coefficients A and B were calculated from the measured values A and B , $A = -2.49 \pm 0.25$ and $B = 0.57 \pm 0.05$. With respect to the reproducibility of the experimental results themselves the conclusion can be drawn that the current yield of ozone evolution under the conditions of the technical electrolytic production of peroxodisulphuric acid or ammonium peroxodisulphate as intermediates in the electrochemical production of hydrogen peroxide is, in the studied range of current densities, electrolyte composition and temperature, practically only a function of the total current density according to equation (5). In this relation coefficients A and B are practically independent of the reaction conditions. The verification of this conclusion by comparison with experimental results is illustrated in Fig. 3, in which full line denotes the dependence according to Eq. (5) with the mean values A and B , and the different points correspond to the actual experimental mean values in the described electrolyzer, where the content of peroxodisulphate was negligible. Fig. 3 also shows the result of measurement on a laboratory-scale flow model of electrolyzer for the preparation of concentrated solutions of

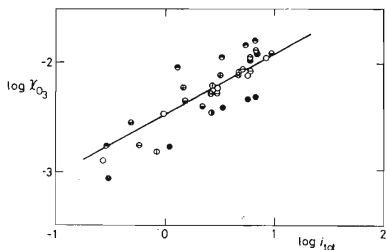


FIG. 3

Dependence of the Ozone Current Yields on Total Current Density in Solutions of 12N- H_2SO_4 at 15°C (●), 20°C (○) and 25°C (◐), in Solution A (⊙) and B (⊖) at 20°C, in Solution C at 15°C (⊗), 20°C (⊕) and 25°C (⊘) and in Solution D (⊙) at 10°C

ammonium peroxodisulphate^{2,3}. In this experiment the initial solution for electrolysis had the molar ratio $P_0 = 2.0$ for the presumed over-all degree of conversion $\alpha = 0.8$ (solution D); the electrolysis was carried out with current density 2.7 A/cm^2 at 10°C , and the real degree of conversion at the chosen flow of electrolyte was $\alpha = 0.76$. As can be seen, even this result (point **o**) in which the leaving anolyte contained 18.05% H_2SO_4 , 3.57% $(\text{NH}_4)_2\text{SO}_4$ and 19.05% $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and the current yield of peroxodisulphates amounted 49.5%, lies within the range of experimental values, obtained in the described non-flow small electrolyzer. This finding also supports the earlier result that the presence of peroxodisulphates has practically no effect on the rate of anodic ozone evolution^{1,11,12}. The fact that the current yields of ozone evolution are, in the range of chosen experimental conditions practically a function of the initial current density only, although the individual polarization curves show distinctly the dependence on both composition of the electrolyte and on temperature, can be explained by the assumption that both these factors affect the course of the total polarization curve and of the partial anodic process of ozone formation relatively in the same extent. Since the current yield of ozone represents the ratio of both the mentioned current densities under the given reaction conditions, their effect cannot appear in the final dependence, at least not in the rather narrow studied range of experimental conditions.

The dependence of the current yields of ozone formation on the total current density, found in paper⁴ had a linear course of the form $\chi_{\text{O}_3} = k \cdot i_{\text{tot}}$, where constant k is indirectly proportional to temperature (in the original paper this constant was not numerically evaluated). This result, slightly different from our data, can be explained so that the range of measured current densities in paper⁴ was narrow, lying between $0.3 - 0.5 \text{ A/cm}^2$. On the other hand in paper³ the current yields of ozone in the range of total current densities $0.05 - 0.3 \text{ A/cm}^2$ in 30% HClO_4 at -45°C were independent of i_{tot} , which is in contradiction both with the results of the cited authors⁴ and with our own results. The relation (5) derived in the present paper, which was also verified experimentally (Fig. 3), is moreover in accordance with further data on the general course of the partial polarization curve of ozone evolution as well as of the total polarization curve in the region of higher anodic potentials²⁴ (over c. 2.5 V). The derived general relation (5) for the dependence of current densities of the partial electrode reaction on the total current density contains only differences of kinetic constants of the assumed partial and total polarization curves and thus it is practically independent of the accuracy of reading off the real electrode potentials, especially at higher current densities, since a possible inaccuracy in determining the ohmic part, IR , of the total measured electrode potential, corresponding to the voltage drop between the electrode surface and the orifice of the Luggin capillary, manifests itself in the same way in both polarization curves and is finally compensated. This also makes possible to explain the practical independence of the final constants A and B on the reaction conditions, even though the

polarization curves proper show such kind of dependence. It is especially valid for the results described in Fig. 2 where not too great differences in the composition of the solutions resulted in a considerable shift of the polarization curves which can most probably be explained by an error in the *IR* term determination.

REFERENCES

1. Briner E., Haefeli R., Paillard H.: *Helv. Chim. Acta* 20, 1510 (1937).
2. Briner E., Yalda A.: *Helv. Chim. Acta* 24, 1328 (1941); 25, 98, 1178 (1942); 26, 1162, 1829 (1943).
3. Putnam G. L., Moulton R. W., Fillmore W. W., Clark L. H.: *Trans. Electrochem. Soc.* 93, 211 (1948).
4. Lash E. I., Hornbeck R. D., Putnam G. L., Boelter E. D.: *J. Electrochem. Soc.* 98, 134 (1951).
5. Beck T. R., Moulton R. W.: *Ind. Eng. Chem.* 43, 1123 (1951).
6. Beck T. R., Moulton R. W.: *J. Electrochem. Soc.* 103, 247 (1956).
7. Saeder J. D., Tobias C. W.: *Ind. Eng. Chem.* 44, 2207 (1952).
8. Rakov A. A., Veselovskij V. I., Nosova K. I.: *Ž. Fiz. Chim.* 32, 2702 (1958).
9. Veselovskij V. I.: *Trudy IV. Soveščanija po Elektrochimii*, p. 247. Mir, Moscow 1959.
10. Rakov A. A., Nosova K. I., Kasatkin E. V.: See 8, p. 834.
11. Lunenok-Burmakina V. A., Potemskaja A. F., Brodskij A. E.: *Dokl. Akad. Nauk SSSR* 137, 1402 (1961).
12. Brodskij A. E., Lunenok-Burmakina V. A.: *Kernenergie* 5, 371 (1962).
13. Gerovič M. A., Kaganovič R. I., Mazitov J. A., Gorochov L. N.: *Dokl. Akad. Nauk SSSR* 137, 634 (1961).
14. Flisskij M. M., Surova L. M.: *Elektrochimija* 1, 1005 (1965).
15. Machu W.: *Das Wasserstoffperoxid und die Perverbindungen*, 2nd Ed., p. 190. Springer, Wien 1951.
16. Schumb W. C., Satterfield C. N., Wentworth R. L.: *Hydrogen Peroxide*, p. 130. Reinhold, New York 1955.
17. Regner A.: *Technická elektrochemie. I. Elektrochemie anorganických látek*, p. 560. Academia, Prague 1967.
18. Balej J.: *This Journal* 30, 2663 (1965).
19. Balej J., Špalek O.: *This Journal* 37, 499 (1972).
20. Zehender F., Stumm W.: *Mitt. Lebensunters. Hyg.* 44, 206 (1953).
21. Vondrák J., Špalek O.: *Chem. listy* 64, 609 (1970).
22. Pourbaix M.: *Atlas d'Equilibres Electrochimiques à 25°C*, p. 99. Gauthier-Villars, Paris 1963.
23. Balej J.: Unpublished results.
24. Veselovskij V. I., Rakov A. A., Kasatkin E. V., Jakovleva A. A. in the book: *Adsorbicija i Dvojnoj Električeskij Sloj v Elektrochimii*, p. 132 (A. N. Frumkin, B. B. Damaskin, Eds). Nauka, Moscow 1972.

Translated by V. Čermáková.