

ANODIC OXIDATION OF SULPHITES

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The anodic behaviour of sulphites has been studied by a number of authors¹⁻²¹ mostly on smooth platinum electrodes^{1-16,19,20}. Some authors used also electrodes covered with platinum black^{5,8,19,20}, or electrodes made of nickel⁸, gold^{8,17,19}, silver¹¹, and graphite^{8,11,21}. They found among the anodic oxidation products sulphate or dithionate besides oxygen according to the composition of starting solutions, pH, conditions of electrolysis and state of the electrode surface.

Rozental and Veselovskij¹³ proposed to utilize analytically the linear dependence of the anodic limiting current on sulphur dioxide concentration in the range $10^{-4} - 10^{-2}$ mol/l. The method was elaborated later by other authors^{14,15,18} who all stated that the results thus obtained are largely dependent on the pretreatment of the platinum electrode used, mainly on its anodic-cathodic prepolarization. The mechanism of the anodic process at the platinum electrode is disputable, the yield of the anodic oxidation varies and is always below 100%.

We therefore studied the mentioned problem anew aiming to define conditions for a current efficiency of hundred percent. The principal condition for electrolysis due to a single electrode reaction is the occurrence of a corresponding separated wave on the polarographic curve. Therefore we measured polarization curves under various conditions.

EXPERIMENTAL

Chemicals and Solutions

Standard aqueous solutions of sulphite were prepared from reagent grade Na_2SO_3 (Lachema, Brno) with the addition of 5% ethyl alcohol (aldehyde-free). The content of Na_2SO_3 was determined iodometrically, the iodine solution was standardized by thiosulphate and this in turn by potassium bromate. All chemicals were of highest purity and the concentrations of solutions were, when necessary, determined by standard methods of volumetric analysis.

Apparatus and Equipment

Polarization curves were recorded manually with the use of a potentiometer and a type DL 02 microamperemeter (Metra, Blansko).

To measure the yield of the electrode reaction, an electromechanical potentiostat was used whose basic circuit is shown in Fig. 1. The potential difference between the working E_1 and reference E_2 electrodes was fed to the input of an electronic millivoltmeter 1 of the type Multiscop V (Laboratorní přístroje, Prague) with a high input impedance. Its output signal was fed to the coil of a sensitive depéz relay 2 of the type RD 10, 20 μA (Metra, Blansko), which controlled a transistor relay 3 of the type R 583 (Závody průmyslové automatizace, Prague) serving as a switch for servomotor 5 of the type K 7 A 1 (MEZ, Náchod). The transistor relay was adapted so as to enable reversion of the servomotor. The latter was fed from rectifier 4 and drove a 13 Ω potentiometric drum 6 with twenty windings. The revolution rate was controlled by a 70 Ω

rheostat 8. The potentiometer was connected to a 12 V storage battery 7. The current flowing through the working electrode was measured with a type DL 02 milliamperemeter 9 (Metra, Blansko). The maximum error in potential control was ± 5 mV at 1.4 revolutions of the servomotor per second and at an applied voltage of 5.3 V.

The electrolytic vessel (Fig. 2) made of "Sial" glass consisted of two compartments, 1 and 2, joined with a ground-glass joint. The lower part 1 was provided with an outlet capillary stopcock 3 and joints for reference electrode 4 and counter-electrode 5. The upper part 2 was provided by inlet 7 for addition of reagents, closed by a soft rubber stopper 8. Working electrode 9 was fixed by silicon rubber in tube 6. Reservoir 15 with a base electrolyte was closed by stopcock 10. Solutions were agitated by magnetic stirrer 11. The vessel had a volume of 33.2 ml and could be filled without any residual gas bubble to eliminate errors due to escapement of sulphur dioxide from the solution.

The vessel was filled with a base electrolyte deoxygenated by purified nitrogen. After gas bubbles had been removed, a freshly analyzed sulphite solution was added by means of a calibrated microsyringe (0–0.476 ml) whose hollow steel needle was inserted through stopper 8 close to the

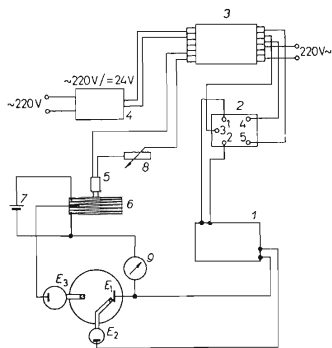


FIG. 1

Basic Circuit of Electromechanical Potentiostat

E_1 Working electrode, E_2 reference electrode, E_3 counter-electrode, 1 electronic millivoltmeter, 2 deprez relay, 3 transistor relay, 4 rectifier, 5 servomotor, 6 potentiometric drum, 7 accumulator, 8 rheostat, 9 milliamperemeter.

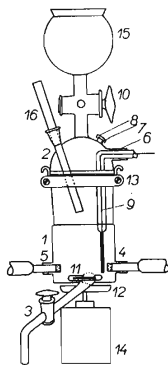


FIG. 2

Electrolytic Vessel

1 Lower compartment, 2 upper compartment, 3 outlet stopcock, 4 joint for reference electrode, 5 joint for auxiliary cathode, 6 joint for working electrode, 7 inlet for injecting reagents, 8 rubber stopper, 9 working electrode, 10 reservoir stopcock, 11 stirrer, 12 permanent magnet, 13 metal fitting, 14 electric motor, 15 electrolyte reservoir, 16 polarographic capillary.

bottom of the vessel, stopcock 10 being opened. The latter was closed after injecting the chosen amount and the stirrer was switched on.

A mercurous sulphate electrode with 1M-H₂SO₄ of a pencil type served as reference. It was provided with a salt bridge whose end, closed by sintered glass, was placed in close proximity of the working electrode. Another mercurous sulphate electrode with 1M-H₂SO₄ and with a mercury pool of 33 cm² surface area, covered with a thick layer of mercurous sulphate²², served as cathode. It was separated from the electrolytic compartment by a sintered glass disc.

Smooth platinum covered with platinum black, smooth gold, and platinum wire with a deposit of lead dioxide were used as working electrodes. They were neither mechanically nor chemically treated before use. Various methods of pretreatment recommended by certain authors^{13,18} cause the electrode to have desirable properties only temporarily and therefore were not used in view of possible applications of our results in continual analysis.

Platinum and gold electrodes were made from pure metal wires, 0.4 mm in diameter and 20 mm in length, by sealing into glass. Platinum black was deposited electrolytically with an addition of lead acetate. Lead dioxide was deposited electrolytically onto a platinum wire 0.5 or 1 mm in diameter and 20 mm in length. Before the deposition of lead dioxide the platinum wire was polished by emery paper (Schröder 6/0 and 6/0 F), treated for 15 min by chromosulphuric acid,

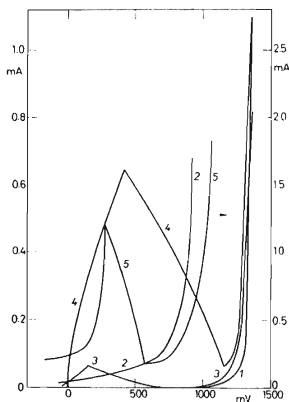


FIG. 3

Polarization Curves

0.5M-H₂SO₄ + 2 · 10⁻³M-Na₂SO₃; 1 and 2 without sulphite. 1 Smooth platinum or gold electrode; 2 platinized platinum electrode; 3 smooth platinum electrode; 4 smooth gold electrode; 5 platinized platinum (see current scale on right-hand side).

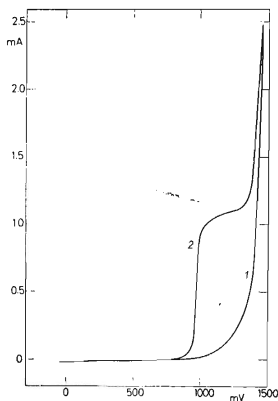


FIG. 4

Polarization Curve on PbO₂ Anode

1 0.5M-H₂SO₄; 2 0.5M-H₂SO₄ + 1.81 × 10⁻³M-Na₂SO₃.

rinsed with distilled water, polarized anodically for 10 min in 50% H_2SO_4 by a current of 2 A, rinsed with distilled water and finally plated with lead dioxide. This pretreatment of the platinum wire resulted in an equal and well-adhering deposit. Lead dioxide was deposited at 1 mA/cm^2 for 100 hours from a solution of $0.5\text{M-Pb}(\text{NO}_3)_2 + 0.5\text{M-HNO}_3$ after Sugino²³. The layer thus obtained was about 0.4 mm in thickness and consisted after Sugino²³ of $\beta\text{-PbO}_2$ which is more stable in acid medium than the α modification²⁴. After finishing the electrodeposition, the electrode was stored for 12 hours in distilled water before use. In the meantime between successive measurements it was also stored in distilled water.

Some electrodes thus prepared gave rise to bubbles of oxygen on the place of contact between lead dioxide and glass during anodic polarization. This phenomenon was attributed to creeping of electrolyte along the glass surface to the platinum enabling evolution of oxygen at a lower overpotential than on the lead dioxide. Good functioning of the electrode was thus hindered. Therefore, the neck of the dry electrode was sealed by a polyester resin under vacuum to ensure filling of pores with the resin which solidified after about two hours.

During recording the polarization curves, the polarizing voltage was changed in 100 mV steps and the stationary current values were recorded. The solutions were stirred at a constant rate. One series of measurements was always performed with solutions of sodium sulphite in 0.5M-NaOH, the other in 0.5M- H_2SO_4 .

RESULTS AND DISCUSSION

The curves obtained with all electrodes in alkaline solutions were the same in the absence as in the presence of sulphite. The polarization curves obtained in acidic solutions with the platinum, gold and platinized platinum electrodes are shown in Fig. 3. All three curves exhibit practically already at their beginning an increase of current followed by an abrupt decrease. Kljanina and Šlygin²⁰, who observed this effect with a platinized platinum electrode, attributed the current increase to oxidation of sulphur dioxide to sulphuric acid, and the drop of current to adsorption of oxygen on the electrode to such an extent that it hinders the anodic oxidation of sulphur dioxide. At any rate, it is obvious from Fig. 3 that the mentioned electrodes cannot be used for quantitative oxidation of sulphur dioxide.

TABLE I

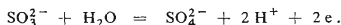
Current Efficiency of Electrooxidation of Na_2SO_3 on Lead Dioxide Electrode

Initial amount of Na_2SO_3 mg	Unconverted Na_2SO_3 mg	Charge passed coulomb	Conversion %	Current efficiency %
18.537	2.80	24.0221	84.88	100.29
24.618	0.90	36.687	96.34	98.97
30.503	1.00	44.896	96.72	100.84
6.845	2.95	6.028	56.90	98.91
6.872	1.65	7.910	75.98	101.06
48.375	5.65	65.412	88.32	99.99
171.257	14.70	235.893	91.41	101.60

In Fig. 4 are shown the polarization curves obtained with the lead dioxide electrode. Curve 1 corresponds to 0.5M-H₂SO₄; curve 2, obtained after addition of sulphite, exhibits a well-defined wave with half-wave potential of 0.965 V (1.64 V against N.H.E.). Its limiting current extends over about 0.3 V. At 1.3 V (against Hg/Hg₂SO₄) the current increases steeply and at 1.39 V oxygen evolution was observed. The half-wave potential is reproducible to ± 15 mV with the same electrode or to ± 25 mV with different electrodes of the same type.

The current efficiency of the electrode reaction was measured at the potential of 1.05 V corresponding to the middle of the horizontal portion of the wave (maintained constant by the potentiostat). The electric charge consumed was measured by an iodine coulometer. Into the electrolytic vessel (Fig. 2) was inserted a dropping mercury electrode which together with the counter-electrode could be connected by means of a switch with a type LP 60 polarograph (Laboratorní přístroje, Prague). The dropping electrode served as cathode to determine the remaining amount of sulphite in the electrolytic vessel after the electrolysis was interrupted. Use was made of the linear dependence of the height of the reduction wave of sulphur dioxide on concentration in acidic medium²⁵⁻²⁷.

The current efficiency values determined from the consumption of sulphite during electrolysis and from the amount of charge are summarized in Table I. We assumed that the anodic reaction proceeded according to the equation^{11,13}



The current efficiency was $100 \pm 1.6\%$ in the range of sulphite concentrations $1.53 \cdot 10^{-3}$ to $3.85 \cdot 10^{-2}$ mol/l. This result is an evidence that the final oxidation product at the lead dioxide electrode is sulphuric acid. If it were dithionate, the current efficiency determined as above would be about 200%, and if it were persulphate the current efficiency would be about 66%.

The mechanism of the electrode reaction, whose study was beyond the scope of the present work, involves obviously a chemical reaction of sulphurous acid with lead dioxide, so that the latter plays a role of a catalyst electrode. Namely at higher sulphite concentrations the originally black lead dioxide turns brown; simultaneously the current decreases and the dependence of current on the concentration of sulphite is no more linear. The electrodes thus passivated can be regenerated by anodic polarization in sulphuric acid solution to restore their original properties.

The described anodic oxidation can be probably utilized in analytical determination of sulphites. A technical application seems possible in production of sulphuric acid from sulphur dioxide²⁸.

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CHEMISTRY OF BORANES. XXII.*

THE ACIDITY OF BORANES

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The acidity of boranes was already observed more than ten years ago¹ but all relative data are rather scant and often mutually contradictory²⁻⁹. The dependence of their acidity on the type of solvent is an interesting feature. While in aqueous ethanol decaborane is a strong monoacid^{1,11}, in ether it is ten times less acid than phenol^{8,9}. It is not known certainly under which conditions it can function as a diacid⁹ and it is not clear which of the possible tautomeric anions $B_{10}H_{13}^-$ and under which conditions they apply¹¹. In addition to the monoanion structure Lipscomb also proposed the structure of the unknown dianion $B_{10}H_{12}^{2-}$ (ref.¹¹) which was recently identified¹².

Still less clear is the situation in the case of borane $n-B_{18}H_{22}^{13}$. The structure of its monoanion $B_{18}H_{21}^-$ was also proposed by Lipscomb¹¹. Later on the existence of dianion $B_{18}H_{20}^{2-}$ (ref.¹³) was also proved.

In order to classify the controversies around higher boranes and the functionality of their anions we investigated the behaviour of decaborane and octadecaborane in some solvents miscible with water potentiometrically.

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