

## EFFECTS OF TWO NEW ADDITIVES ON THE INITIAL RATE OF PEROXODISULPHATE ELECTROSYNTHESIS

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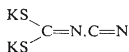
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Two new additives, dipotassium cyanimidodithiocarbonate (DKDK) and 5-thio-2-imido-3,4-disulphazolidine (TIDSAL), were tested for the effect they have on the initial rate of peroxodisulphate ion formation in 5M-H<sub>2</sub>SO<sub>4</sub> solution. The concentrations of the additives ranged from 10<sup>-4</sup> to 10<sup>-2</sup> mol dm<sup>-3</sup>. Both substances were found to increase current yields of peroxodisulphates as well as oxygen overpotential on the platinum anode. The additive concentration at which a maximum increase was achieved was about 1 · 10<sup>-2</sup> mol dm<sup>-3</sup> in both cases. Maximum current yields attained under the applied reaction conditions were, however, somewhat lower than those observed with an optimum addition of SCN<sup>-</sup>.

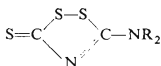
In technical electrosynthesis of concentrated solutions of peroxodisulphuric acid or peroxodisulphates as intermediates of the electrochemical production of hydrogen peroxide or the production of crystalline peroxodisulphates, it is common practice<sup>1-5</sup> to add into anodic compartments small quantities of substances which increase the oxygen overpotential on the platinum anode, thus enabling sufficiently high current yields to be attained. Although a diversity of substances of various compositions<sup>1-10</sup> have been tested and recommended for the given purpose, the additives most widely used in industrial practice are ammonium thiocyanate and alkali metal thiocyanates, sometimes in combination with hydrochloric acid, in concentrations of the order of 10<sup>-2</sup> to 10<sup>-3</sup> mol dm<sup>-3</sup>. Nevertheless, continued research effort is being expended to discover an additive not only of greater effectiveness but, if possible, with a greater long-term stability.

It is a well-known fact<sup>9,10</sup> that the effect of these compounds, which is due to their relatively strong chemisorption onto the surface of oxide-covered platinum anode, is not much persistent and gradually vanishes.

The present communication reports results of investigation of the effects of two new additives, dipotassium cyanimidodithiocarbonate of the structural formula



(further designated as DKDK), and 5-thio-2-imido-3,4-disulphazolidine of the structural formula



(further designated as TIDSAL), where R can be hydrogen or an acyl or an alkyl group, on the initial rate of peroxodisulphate ion formation in a basic 5M-H<sub>2</sub>SO<sub>4</sub> solution under otherwise the same conditions as in our previous work<sup>8</sup>.

## EXPERIMENTAL

*Procedure:* The measurements were carried out in the same all-glass apparatus as used in previous studies on the effect of various factors on the initial rate of anodic formation of peroxodisulphates<sup>8,11</sup>. The working procedure and the way in which the platinum anode was pretreated were also the same. A stock solution of 5M-H<sub>2</sub>SO<sub>4</sub> was made up from concentrated acid of analytical grade and distilled water. In order to maintain the degree of sulphate-to-peroxodisulphate conversion as low as possible ( $\alpha < 0.05$ ), the solution under investigation was periodically replaced by the fresh one without switching off the electric current. The platinum anode was potentiostatically kept at a chosen potential measured with respect to an Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrode in 5M-H<sub>2</sub>SO<sub>4</sub> solution, and the current was read off after its value had become steady. The anode potential was corrected for the IR voltage drop between the platinum anode surface and the tip of the Luggin capillary, determined by the interrupting technique at the end of the measurement at the given potential. The potential values given in this paper are referred to a hydrogen electrode in the same basic solution (R.H.E.). After the measured current had reached a steady value, the current yield of anodic evolution of oxygen accompanying the anodic formation of peroxodisulphate was determined by gas analysis. The current yield of peroxodisulphate was calculated from the relation

$$\chi_{S_2O_8} = 100 - \chi_{O_2} (\%). \quad (1)$$

In view of earlier results<sup>12</sup>, the content of ozone in the evolved oxygen was considered negligible. In some cases, the current yield of peroxodisulphate was determined on the basis of chemical analysis of the anolyte. The results of the two methods lay within the limits of the reproducibility of the measurements ( $\pm 3\%$ ). The current yields of oxygen and peroxodisulphate permitted us to determine the portions of the total anodic current associated with the two main anodic reactions, and on this basis to divide the total anodic polarization curve into the polarization curves for oxygen evolution and peroxodisulphate formation.

Current densities were calculated with respect to the true surface area of the platinum anode, determined by measuring the charging curves in the double-layer region. The roughness factor of the platinum anode treated as described in ref.<sup>11</sup> was found to be  $f_r = 1.5 \pm 0.07$ . All the measurements were carried out at  $25 \pm 0.1^\circ\text{C}$ .

DKDK was prepared in the following way: to a stirred solution containing 84 g (1.0 mol) of 50% aqueous cyanamide, 200 ml of ethanol, and 84 g (1.1 mol) of carbon disulphide, 126 g (2.0 mol) of 90% potassium hydroxide in 500 ml of ethanol was added slowly at 0–15°C over a 15 min period. After stirring at 25–30°C for 1 h, the precipitate was collected by filtration,

washed with 500 ml of pure ethanol and dried at 45–50°C. TIDSAL was prepared according to the procedure described in ref.<sup>13</sup>.

Since DKDK decomposes to some extent in aqueous solution (see below), only fresh solutions, prepared immediately before each run, were used in the measurements.

TIDSAL is soluble practically only in concentrated sulphuric acid. The desired concentrations of TIDSAL in the 5M-H<sub>2</sub>SO<sub>4</sub> solution were therefore obtained by adding appropriate amounts of a concentrated stock solution of TIDSAL in sulphuric acid.

## RESULTS AND DISCUSSION

DKDK was found to decompose slowly in aqueous solution, as evidenced by a variation in the current yield of peroxodisulphate, under otherwise the same conditions, with the "age" of DKDK basic solution before its addition into the measured 5M-H<sub>2</sub>SO<sub>4</sub> solution. This observation is documented in Fig. 1 showing a plot of the current yield of peroxodisulphate at a DKDK concentration of  $5 \cdot 10^{-3} \text{ mol dm}^{-3}$ , achieved at a total anodic current density  $j_a = 0.5 \text{ A cm}^{-2}$ , against the age of DKDK solution. As can be seen from the figure, the decrease in the current yield is greatest during the first day, becoming less marked afterwards. The broken line represents the current yield obtained under the same conditions for the basic 5M-H<sub>2</sub>SO<sub>4</sub> solution without any additive. Because of the ageing effect, fresh solutions, made up by dissolving solid DKDK in the solution studied, were always used in examining the effect of this additive. The measurement on each solution lasted a maximum of 2 h, the solution being subsequently changed for the fresh one without interrupting the anode polarization.

Figs 2 and 3 show the total anodic polarization curves and the polarization curves due to oxygen evolution and peroxodisulphate formation in the basic 5M-H<sub>2</sub>SO<sub>4</sub> solution containing  $1 \cdot 10^{-2} \text{ mol dm}^{-3}$  DKDK and TIDSAL, respectively. Also included in both figures is the total polarization curve for the basic solution without

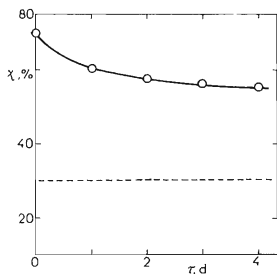


FIG. 1

Dependence of the current yield of peroxodisulphate on the age of DKDK solution.  $c_{\text{DKDK}} = 5 \cdot 10^{-3} \text{ mol dm}^{-3}$ ;  $j_a = 0.5 \text{ A cm}^{-2}$ ; dashed line: steady-state current yield in 5M-H<sub>2</sub>SO<sub>4</sub> solution without additive

any additive. It is seen that additions of both substances produce shifts of the total polarization curve towards higher anodic potentials. Its overall character is, however, unaltered and similar to that observed with previously investigated additives<sup>8,11</sup>.

The polarization curves for concentrations of the additives within the range  $5 \cdot 10^{-4}$  to  $5 \cdot 10^{-2}$  mol dm<sup>-3</sup> have analogous shapes. The determination of these curves was based on the dependences of the current yield of peroxodisulphate on the total anodic current density determined at given concentrations of DKDK and TIDSAL (see Figs 4 and 5, respectively). In each case the current yield passed through a maximum whose position for each additive concentration lay within the current density range from 0.5 to 0.65 A cm<sup>-2</sup>.

As the additive concentration is increased, there is a rise in the maximum current yield of peroxodisulphate until a certain most effective additive concentration is reached, followed by a gradual decrease. This is illustrated in Fig. 6 which includes, for comparison, also an analogous plot for ammonium thiocyanate based on results of an earlier work<sup>8</sup>. Obviously, both DKDK and TIDSAL are very effective polarizers, as the current yields of peroxodisulphate attained in their presence are very close to those resulting from the use of ammonium thiocyanate, particularly at concentrations close to  $1 \cdot 10^{-2}$  mol dm<sup>-3</sup>. At very low degrees of sulphate-to-peroxodisulphate conversion, maximum current yields are attained at a DKDK or TIDSAL concentration of about  $1 \cdot 10^{-2}$  mol dm<sup>-3</sup>. A further increase in the concentration

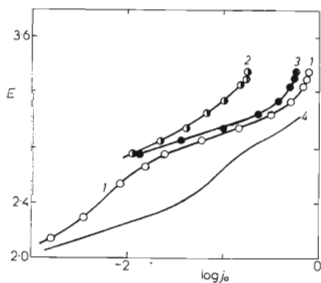


Fig. 2

Effect of DKDK addition ( $0.01$  mol dm<sup>-3</sup>) on the total polarization curve 1 and partial polarization curves for oxygen evolution 2 and peroxodisulphate formation 3; 4 total polarization curve for  $5M-H_2SO_4$  solution

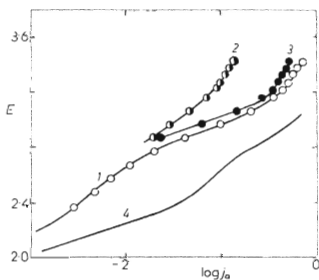


FIG. 3

Effect of TIDSAL addition ( $0.01$  mol dm<sup>-3</sup>) on the total polarization curve 1 and partial polarization curves for oxygen evolution 2 and peroxodisulphate formation 3; 4 total polarisation curve for  $5M-H_2SO_4$  solution

of each additive results in a rather marked decrease in the current yield, as opposed to the case of  $\text{NH}_4\text{SCN}$  where the decrease in the current yield, once the optimum additive concentration has been exceeded, is much slower. Besides, the optimum concentration of DKDK and TIDSAL,  $c_{\text{max}} = 1 \cdot 10^{-2} \text{ mol dm}^{-3}$ , is lower than that established under the same reaction conditions for  $\text{NH}_4\text{SCN}$  ( $c_{\text{max}} \cong 6 \cdot 10^{-2} \text{ mol dm}^{-3}$ ).

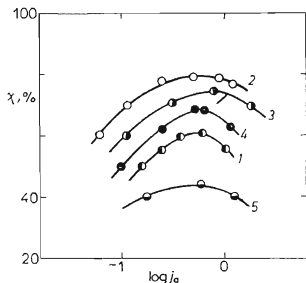


FIG. 4

Current yield of peroxodisulphates as a function of total current density  $j_a$  ( $\text{A cm}^{-2}$ ) at various concentrations of DKDK ( $\text{mol} \cdot \text{dm}^{-3}$ ): Curve 1 0.05; 2 0.01; 3 0.005; 4 0.002; 5 0.0005

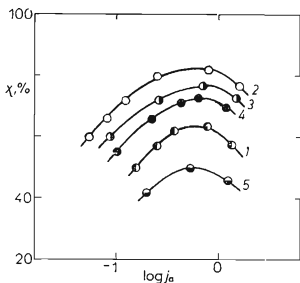


FIG. 5

Current yield of peroxodisulphate as a function of total current density  $j_a$  ( $\text{A cm}^{-2}$ ) at various concentrations of TIDSAL ( $\text{mol} \cdot \text{dm}^{-3}$ ): Curve 1 0.05; 2 0.01; 3 0.005; 4 0.002; 5 0.0005

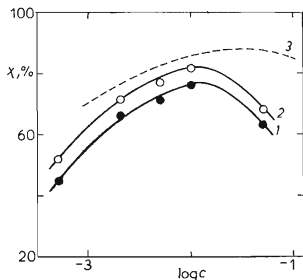


FIG. 6

Current yield of peroxodisulphate as a function of additive concentration at optimum current densities. Curve 1 DKDK; 2 TIDSAL; 3  $\text{NH}_4\text{SCN}$  (ref.<sup>8</sup>)

It is seen from Fig. 6 that TIDSAL is slightly more effective than DKDK. This is probably due to instability of DKDK solutions resulting in a distinct reduction of their effectiveness after as little as a few hours. The cause of this behaviour remains in need of further investigation. Considering the results obtained and the effects of previously studied additives<sup>8-11,14,15</sup>, we may only infer that the positive effects of DKDK and TIDSAL are due to their strong chemisorption onto the surface of the oxide-covered platinum anode, primarily on the active centres for anodic oxygen evolution whose overpotential is largely increased on addition of both compounds (see Figs 2 and 3). The optimum concentration of DKDK and TIDSAL,  $c_{\max} = 1 \cdot 10^{-2} \text{ mol dm}^{-3}$ , identical with that found for a number of previously tested organic additives<sup>8</sup>, presumably corresponds to a limiting coverage of the platinum surface in the region of high anodic potentials.

The high effectiveness of DKDK and TIDSAL, comparable in the concentration range from  $5 \cdot 10^{-4}$  to  $1 \cdot 10^{-2} \text{ mol dm}^{-3}$  with that of  $\text{SCN}^-$ ,  $\text{CN}^-$ ,  $\text{CO}(\text{NH}_2)_2$ ,  $\text{CS}(\text{NH}_2)_2$  and  $\text{CH}_3\text{CN}$  (see ref.<sup>8</sup>), essentially confirms the current views that substances containing groups such as  $\text{—C=N}$  and  $\text{S=C}$  are very effective in promoting the electrosynthesis of peroxodisulphates<sup>1</sup>. However, the present observations indicate that a more complicated configuration of bonding between S, C and N, such as occurs in TIDSAL, does not lead to any further increase in oxygen overpotential as compared with the simpler groups  $\text{CN}^-$  and  $\text{SCN}^-$ .

The study of the effects of DKDK and TIDSAL on the initial rate of anodic formation of peroxodisulphates has confirmed our previous findings<sup>8</sup> that the net effect of an additive on the process studied varies with reaction conditions, depending primarily on the total current density and on the additive whose optimum concentration depends on its nature.

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