JOURNAL OF APPLIED ELECTROCHEMISTRY **10** (1980) 97–107

# *Anodic oxidation of N-anions. III*. Anodic oxidation of the N-anions of diacylimides: a search for a new electrochemical synthesis of hydrazine*

Z. ALI, R. BAUER, W. SCHÖN, H. WENDT

*Institut für Chemische Technologie der Technischen Hochschule, Darmstadt, West Germany*

Received 8 January 1979

---

The anodic oxidation of N-anions of diacylimides which are acidic enough to be deprotonated by relatively weak bases in protic solvents was investigated with respect to the electrode kinetics and preparative aspects. All imide anions are oxidized in a one-electron step to the respective imide radicals. Of the imides investigated, two were cyclic carboxylic imides (succinimide and phthalimide) three were sulphonyl imides (di-*p*-toluene and di-benzene sulphimide, dimethane sulphimide) and one was a mixed carboxylate–sulphonate imide (saccharate). The imide radicals produced by anodic oxidation of the dicarboxylate imides do not couple to form a hydrazine derivative but induce solvent oxidation by H-abstraction. The disulphonyl imides couple to unstable hydrazine derivatives although H-abstraction occurs to more than 80%. Only the anodic coupling of the N-anion of imido-disulphonic acid to hydrazine tetrasulphonate discovered by Grinstead [3] can be performed with good selectivity and current and mass yields. The optimum conditions for this reaction are determined in order to show that it may serve in the future as one step in a new hydrazine process.

---

## 1. Introduction

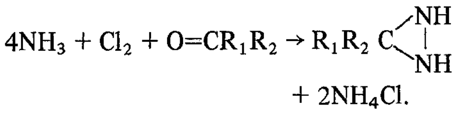
All technical and most of the laboratory-scale processes which are used today for the production and preparation of hydrazine and substituted hydrazines are based on the Raschig process [4]. The Raschig process makes use of the anodic production of chloramine by hypochlorite oxidation of ammonia (or amines)

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O \qquad (1)$$

and the reaction of chloramine and ammonia then forms the desired hydrazine

$$NH_2Cl + NH_3 \rightarrow N_2H_4 + HCl. \qquad (2)$$

One of the more modern versions of hydrazine synthesis, the so-called Bergbau process [3], uses this principle by converting ammonia and chlorine in the presence of an oxy-compound to diaziridines



$$4NH_3 + Cl_2 + O{=}CR_1R_2 \rightarrow R_1R_2C\begin{matrix}\diagup NH\\ |\\ \diagdown NH\end{matrix} + 2NH_4Cl. \qquad (3)$$

Since all such processes are based on the electrochemical production of chlorine, it seems reasonable to question whether a direct anodic conversion of ammonia or appropriate ammonia derivatives to hydrazine can be used instead. Indeed, it was shown recently that the anodic oxidation of amide anions in aprotic solvents yields azo- and hydrazo-compounds [1].

However, performing electrosynthetic reactions in aprotic solvents is not a promising procedure for technical application. Protic solvents are to be preferred. Therefore ammonia (or alkyl and arylamines) should be substituted by appropriate compounds which make the N-protons sufficiently acidic that they can be abstracted by bases of moderate strength in protic solvents like methanol or water. For example in 1957 Grinstead [5] showed that the N-anion of the imido-disulphonic acid (which as an N-acid possesses a p$K_a$ of 8.5) can be coupled anodically in aqueous solutions at Pt, $PbO_2$ or carbon anodes to the hydrazine tetrasulphonate, although with relatively low current yields

$$2(SO_3)_2N^{3-} - 2e \rightarrow [(SO_3)_2N{-}N(SO_3)_2]^{4-}. \qquad (4)$$

---

* For parts I and II see [1] and [2].

0021–891X/80/010097–11$03.10/0

Current yields are: at Pt, 37%; at $PbO_2$, 15%; at C, 4% with a current density of 15 mA $cm^{-2}$.

Bauer and Wendt [2] extended this synthesis to NN′-disubstituted sulphamides and showed that the N-anions of these compounds are oxidized anodically in methanol to form an intramolecular N–N coupling product which decomposes thermally to $SO_2$ and the respective azo-compound.

It is the aim of this paper to investigate more systematically the anodic behaviour of the N-anions of different di-acylimides which are acidic enough to be deprotonated in protic solvents. A more detailed investigation of the Grinstead reaction (Equation 4) was performed in order to find the optimal conditions and it is shown that, indeed, it may serve as the basis for a completely new electrochemical hydrazine process.

## 2. Choice of selected imides

If di-acylimides were to be used as the starting materials for hydrazine production they should satisfy the following demands.

(a) The di-acylimide should be acidic enough to be converted to its N-anion in water or in organic protic solvents such as methanol.

(b) The anodic N–N coupling reaction of the imide anions should be performed with good current and mass yields (more than 50% current and better than 70% mass yield).

(c) The starting imide should be cheap and easily available by a well-established technical synthesis.

(d) It should be possible to convert the anodically produced N–N coupling product to hydrazine by a simple reaction with a high yield.

(e) All auxiliary substances used in the N–N coupling and subsequent hydrazine conversion reaction should lend themselves to recycling, so that in a closed loop only ammonia is introduced and hydrazine and hydrogen is produced electrochemically

$$2NH_3 \xrightarrow{2F} N_2H_4 + H_2 \qquad (5)$$

Thus imides were chosen with $pK_a$ values below 9.9, as shown in Table 1.

## 3. Electrode kinetic investigation of the anodic oxidation of different imide anions in THF solutions

It was impossible to record the anodic polarograms for dibenzene and ditoluene sulphimide at Pt-anodes in methanol and water since in these solvents the anodic half-wave potentials of both imides are too anodic to be separated from the electrolyte–solvent oxidation (background) current. Therefore the anodic polarograms of the N-anions of all di-acylimides given in Table 1 (with the exception of imidodisulphonate) were

*Table 1. $pK_a$ values (measured in water) and anodic half-wave potentials measured at C and Pt anodes in THF and methanol solution of some selected diacyl-imides*

| *Imide* | $pK_a$ | *Reference* | $E_{1/2}$ *of imide anions (V versus SCE)* | | |
|---|---|---|---|---|---|
| | | | *in THF* | | *in methanol* |
| | | | *at C anode* | *at Pt anode* | *at C anode* |
| phthalimide | 9.9 | [7, 8] | 0.895 | 0.885 | 1.170 |
| succinimide | 9.35 | [9, 10, 25] | 0.915 | 0.910 | 1.220 |
| conjugate acid of saccharate | 2.41 | [8] | 1.045 | 1.130 | – |
| ditoluene sulphimide | 1.70 | [11] | 1.105 | 1.150 | – |
| dibenzene sulphimide | 1.45 | [11] | 1.120 | 1.160 | – |
| dimethane sulphonimide | 0.90 | this work | – | – | – |
| imido-disulphonate anion* $[HN(SO_3)]^{2-}$ | 8.50 | [12] | – | – | 0.9–1.32* |

* $pK_a$ and $E_{1/2}$ measured in aqueous solution only

measured in THF or THF–methanol solutions in order to obtain comparable half-wave potentials.

Half-wave potentials were measured at platinum anodes as well as at carbon anodes (Sigri P127) in THF and at C-anodes in methanol. At both anode materials irreversible anodic waves were observed in THF $\{dE/d[\log{(i_d - i)/i}] \approx 120\,\mathrm{mV}\}$. The observed half-wave potentials of the imide-anions (with the exception of the imidodisulphonate trisanion and the dimethansulphonimide anion) correlate reasonably with the $pK_a$ value of the diacylimides (as measured in water).

If the aqueous SCE electrode is chosen as the reference electrode the $pK_a$–$E_{1/2}$ correlation at both electrodes can be expressed by the equations: at Pt

$$E_{1/2} = 1.13\,\mathrm{V} - (0.025\,\mathrm{V})\,pK_a \qquad (6a)$$

and at C

$$E_{1/2} = 1.12\,\mathrm{V} - (0.033\,\mathrm{V})\,pK_a. \qquad (6b)$$

The observed small difference in half-wave potential between the two anode materials indicates that adsorption of the imide anions prior to oxidation is only of minor importance for the primary charge transfer.

The correlation of half-wave potentials and $pK_a$ values (the more basic imide anions being somewhat more accessible to oxidation than the less basic ones) can be understood qualitatively since the separation of partial negative charge of the lone electrode pair of the imide anion means a better accessibility of one of the two electrons towards anodic extraction (20–30 mV per $pK_a$ unit). A more quantitative interpretation uses Equation 7 for the half-wave potential of a completely irreversible anodic wave of a charge transfer process with charge transfer coefficient $\alpha$

$$E_{1/2} = E_0 - (RT/\alpha F)\ln{(k_0/k_m)} \qquad (7)$$

where $E_0$ represents the reversible potential of the imide anion/imide radical couple, $\alpha$ is the charge-transfer coefficient and $k_0$ and $k_m$ are the standard charge transfer rate and mass transfer coefficient, respectively. $k_m$ was kept constant in all the experiments ($10^{-2}\,\mathrm{cm\,s^{-1}}$) so that a change in $E_{1/2}$ parallel to a change in the $pK_a$ of the amide may reflect a change in the normal potential as well as a systematic change in the standard charge transfer rate:

$$[dE_{1/2}/d(pK_A)]_{\mathrm{imide}} = dE_0/d(pK_a) - 120\,\mathrm{mV}\,d(\log k_0)/d(pK_a) \qquad (8)$$

The small shift in the half-wave potential with anode material suggests that $k_0$ stays essentially constant for all imide anions and that mainly the weak dependence of $E_0$ with $pK_a$ is measured by the established $E_{1/2}$–$pK_a$ correlation. A correlation factor of approximately 20 mV per $pK_a$ unit is equivalent to only 20/58 = 0.34 for the correlation of the free energy of proton dissociation of the imide in water versus the free energy of anodic oxidation of the imide anion to the imide radical in THF solution. It should be pointed out that this sort of correlation cannot be extended to anions of different structure, e.g. acetylide anions [6] which show remarkably higher half-wave potentials than would be estimated from their $pK_a$ values and the correlations (Equations 6a and b) for the imide anions.

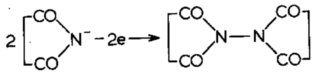
## 4. Preparative anodic oxidation of different imide anions

### 4.1. *Anodic oxidation of the anions of dicarboxylate imides: succinimide and phthalimide*

An anodic oxidation of succinimide and phthalimide anions in aqueous solution turned out to be impossible due to the fast hydrolysis of the imide anions to the anion of amidosuccinic and amidophthalic acid respectively [13]. Anodic oxidations of these anions were therefore performed in THF and in methanol.

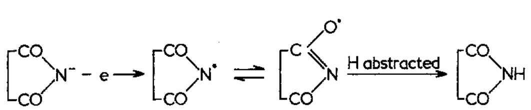
The anodic oxidations were performed in divided cells under potentiostatic conditions at potentials in the lower third of the anodic waves and at potentials in the diffusion-limited region. In all cases the charge consumed exceeded the amount required to oxidize the imide anion present in the electrolyte by more than 10%. Nevertheless in no case was the expected dimeric oxidation product found. The only substances recovered from the electrolyte solutions, except for the imide, were amidophthalic and amidosuccinic acid, products of slow hydrolysis of the imides caused by traces of water in the solvents. When methanol was the solvent, its oxidation product formaldehyde could be detected, i.e. the anodic N-anion oxidation induced nothing other than solvent oxidation.

That the intended N–N coupling of the imides



(9)

fails completely is very likely due to the fact that the produced N(or O)-radicals abstract hydrogen atoms from the solvent rather than dimerize:



(10)

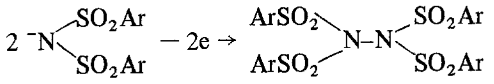
The H-abstraction reaction is then the key reaction for the induced solvent oxidation. Recent investigations showed that imidyl radicals are very effective H-abstractors [14].

### 4.2. *Anodic oxidation of dibenzene and ditoluene sulphimide anions*

The anodic oxidation of the sulphonimide anions was only possible in THF since only in this solvent is the solubility of the Li- and Na-salts of the imides and of the oxidation product high enough to allow for reasonable diffusion-limited current densities ($i_{\text{diff}} \approx 10\,\text{mA cm}^{-2}$ with rotating rod or plate electrodes).

In water and in methanol the anodic wave is so poorly separated from the background current of the solvent–electrolyte system that a controlled anodic reaction cannot be performed.

Since it is well known that the expected reaction products (tetra-arylsulphohydrazides) are very unstable compounds [15–17] which tend to decompose with evolution of nitrogen, the work-up procedure was performed carefully avoiding any heating above 40° C. Nevertheless only an impure mixture, whose main component was the di-aryldisulphone was recovered. It is formed from the N–N coupling product



$$2\ {}^{-}N(SO_2Ar)_2 - 2e \rightarrow (ArSO_2)_2N{-}N(SO_2Ar)_2 \qquad (11a)$$

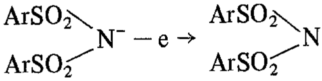
by the reaction

$$(ArSO_2)_4N_2 \rightarrow N_2 + 2\ Ar{-}SO_2{-}SO_2{-}Ar. \qquad (11b)$$

The yield of the anodic coupling (Equation 11a) based on the yield of disulphone, is relatively low. Anodic oxidation of solutions of dibenzene and ditoluene sulphimide alone (only $LiClO_4$ being added as supporting electrolyte), i.e. relying on the supply of imide anions by proton dissociation of the relatively weak N-acid, one obtains no more than 5–6% current yield (90% mass yield) for Reactions 11a and b (concentration of imide, 0.2 M).

Neutralizing half of the imide by addition of 0.1 M benzyl-trimethyl-ammoniumhydroxide and working with the pulsed potentiostatic mode (0–1.35 V versus SCE) increases the yield to approximately 14% (again nearly 90% mass yield).

The observed low current yield and very high mass yield, despite the separation of the *i–E* wave for imide anion oxidation from the background current, is good reason to conclude that the imide radicals (Equation 12a) are not only able to dimerize (with subsequent decomposition) very effectively but that their main reaction is again H-abstraction from the solvent (Equation 11b) regenerating the starting imide.



$$(ArSO_2)_2N^{-} - e \rightarrow (ArSO_2)_2N^{\cdot} \qquad (12a)$$

$$(ArSO_2)_2N^{\cdot} + \text{solvent} \rightarrow (ArSO_2)_2NH + \text{solvent oxidation products} \qquad (12b)$$

Dimethanesulphinimide anions do not oxidize within the available potential range.

### 4.3. *The Grinstead reaction: anodic oxidation of $[N(SO_3)_2]^{3-}$ anions. Systematic investigation of optimal conditions for the anodic coupling of the imido-disulphonate trisanion to the hydrazine–tetrasulphonate tetra-anion*

*4.3.1. Anodic polarography of the imido-disulphonate trisanion in aqueous solutions.* The anodic polarograms of the imido-disulphonate trisanion in aqueous solutions exhibit an irreversible one-electron wave the half-wave potential of which varies with the anode material and the nature of the anion of the supporting electrolyte (Table 2). Hence it is likely that the imido-disulphonate trisanion is oxidized in the adsorbed state: it is, according to Equation 7 the change of standard charge exchange rate for the anodic step $[k_{0(f,b)}]$

*Table 2. Half-wave potentials of imido-disulphonate trisanion measured in aqueous solutions at different anode materials in the presence of different supporting electrolyte anion* ($k_m$: *0.5 × $10^{-2}$ cm $s^{-1}$*) ($E_{1/2}$ *mV) measured versus SCE*

| *Supporting electrolyte anion* | *Anode material* | | | |
|---|---|---|---|---|
| | *Pt* | *C* | *PbO$_2$* | *Au* |
| $Cl^-$ | 910 | 950 | 900 | – |
| $F^-$ | 1000 | 950 | 1100 | 1320 |
| $SO_4^{2-}$ | 1020 | 980 | 1030 | 940 |
| $NO_3^-$ | 1040 | 950 | 1030 | 950 |
| $ClO_4^-$ | 1100 | 1020 | 1150 | 1250 |

$$[(SO_3)_2N]^{3-} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [(SO_3)_2N]^{2-} + e \qquad (13)$$

which determines the position of the half-wave potential of the irreversible imid-anion oxidation wave [18]. It is remarkable that using different anode materials the half-wave potential is lowest in the presence of chloride anions and highest in presence of perchlorate anions. The effect of perchlorate anions may be due to the electrosorption of these bulky anions and the consequent decrease of the surface concentration of imide anions. The low value of the half-wave potential in the presence of chloride anions, however, is very unlikely to be due to an especially low adsorbability of chloride anions (which are known to be adsorbed strongly at Pt, C and Au anodes at potentials around 800–1000 mV versus SCE) [19, 20]. Instead this effect must be explained by induced or catalytic oxidation of the imide anions by adsorbed Cl' radicals which may be formed by underpotential deposition at the anode especially at platinum and lead dioxide anode. (The potential for anodic $Cl_2$ evolution is approximately 1100 mV). It should be stressed that especially on Pt anodes the anodic N–N coupling is more effective in the presence of $Cl^-$ (see below). The anodic polarographic data are important so far as they show whether there is a well-defined separation for the imide ion oxidation from the solvent–electrolyte system background current at all electrode materials. Indeed this is the case for freshly prepared anodes. At all electrode materials there is at least 100 mV between the foot potential of the imide anion oxidation and the electrolyte–solvent oxidation.

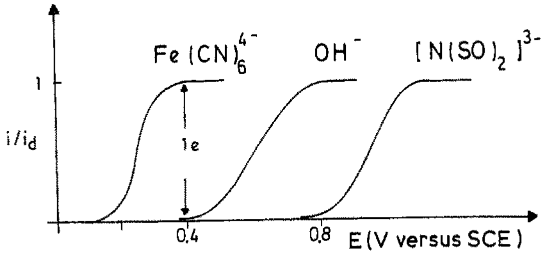


Fig. 1. Schematic representation of anodic polarograms for hexacyanoferrate (reversible), hydroxyl ions and imido-disulphonate anions.

However, on ageing the anodes during prolonged electrolysis, the current–voltage curves of the imido-disulphonate trisanion oxidation becomes more irreversible and consequently with aged electrodes there is the danger of co-oxidation of water, i.e. evolution of $O_2$.

A second question of supreme importance for a practical electrolytic oxidation of the $[N(SO_3)_2]^{3-}$ anions is the oxidation potential of hydroxyl ions, since these anions might be either present in the electrolyte due to over-alkalination in the preparation procedure, or might be generated in the course of the electrolysis at the cathode ($H_2O + e \rightarrow 1/2\, H_2 + OH^-$). Unfortunately at all anode materials used, the anodic half-wave potentials for the hydroxyl ion oxidation lies at least 150 mV more cathodic than for the imido-disulphonate trisanion oxidation (see Fig. 1). Therefore in a practical electrolysis $OH^-$ ions must be either excluded or the $OH^-$ ions must be kept away from the anode in order to obtain attractive current efficiencies. On the other hand an acidification of the electrolyte has to be avoided for chemical reasons. At pH values below 9.5 a relatively fast self-catalysed hydrolysis of imido-disulphonate anions leads to rapid decomposition of the depolarizer and relatively low mass yields for the electrolytic coupling process:

$$[N(SO_3)_2]^{3-} + 2H_2O \xrightarrow{H^+} NH_3 + HSO_4^- + SO_4^{2-}. \qquad (14)$$

*4.3.2. Parametric optimization of the anodic oxidation of imido-disulphonate trisanions in aqueous solution.* The current yield for the anodic coupling reaction (Reaction 11a) depends on the anode material and the nature of the supporting electrolyte. For the conditions: $i = 10\,\mathrm{mA\,cm^{-2}}$, 0.2 M $K_3N(SO_3)_2$ and 0.2 M KF as supporting

*Table 3. Current yields for $[N(SO_3)_2]^{3-}$ oxidation in aqueous solutions without supporting electrolyte: galvanostatic, i = 10 mA cm$^{-2}$, 20° C, pH = 11–11.5, conversion 25–30%, glass-diaphragm divided cell*

| *Electrolyte composition* | *C anode* | *Pt anode* |
|---|---|---|
| A 2 M $Li_3N(SO_3)_2$ | 20–30% | 50–60% |
| B 2 M $Li_3N(SO_3)_2$<br>+ 0.1 $Mg(ClO_4)_2$ | 45–55%<br>47–50%* | 60–65%<br>48–52%* |

* undivided capillary gap cell

electrolyte, with a divided cell, the following order for the electrodes in terms of decreasing current yield (which is shown in brackets) was obtained: Pt (45–50%) > C (25–35%) > $PbO_2$ (16–25%) > Au (0%). Gold anodes are not effective since they become covered completely with gold oxide, identified by its dark brown colour, and then only oxygen is evolved.

Grinstead certainly found similar results although in his paper Pt and $PbO_2$ became transposed due to a misprint. For the conditions: $i = 10\,\mathrm{mA\,cm^{-2}} \approx 10^{-1} i_d$, 0.1 M $K_3N(SO_3)_2$, with Pt anodes and 20° C, the following current yields with differing supporting electrolyte anions were obtained: with $Cl^-$ 45–47%, with $F^-$ 44–45%, with $SO_4$ 30–33% and with $ClO_4^-$ 20–25%. These results clearly demonstrate the advantage of $Cl^-$ and $F^-$ and comparable yields (~ 45%) are obtained. With sulphate and perchlorate the yields decrease remarkably.

However, for a technical electrolysis of imidodisulphonate the use of a supporting electrolyte is an undesired complication. Therefore Table 3 gathers typical current efficiencies obtained by use of 2 M solutions of the tris-lithium salt of the imido-disulphonate trisanion but without any addition of supporting electrolyte. The results at Pt anodes are even better than those obtained under otherwise identical conditions in the presence of $F^-$ and $Cl^-$ anions and on carbon anodes current yields are essentially the same as those obtained in the presence of chloride and fluoride anions.

There are several possible reasons for the low current efficiencies obtained:

(a) The loss in current efficiency is due to hydrolysis of the hydrazine tetrasulphonate and further oxidation of the resulting hydrazine to nitrogen.

(b) Part of the primarily produced N-radicals react with water by hydrogen abstraction and thus induce water oxidation and oxygen evolution.

(c) Due to the relatively high pH value which is necessary to stabilize the imido-disulphonate anion (pH = 11.5) hydroxyl ions are co-oxidized and oxygen is evolved.

By establishing a complete balance of all nitrogen-containing substances involved in the process it can be shown that hydrazine tetrasulphonate hydrolysis and subsequent anodic nitrogen evolution from hydrazine is negligible and possibility (a) need not be considered. A choice between possibilities (b) and (c), which both result in oxygen evolution, can be made by careful buffering of the anolyte solution during the relatively long electrolysis (1–3 h) during which part of the cathodically produced hydroxyl ions may be transferred to the anolyte.

A very effective way to buffer solutions at a pH value of betwen 10 and 11 is to add excess magnesium ion. Then the pH is controlled by the solubility product of $Mg(OH)_2$ at around 10.

Certainly current efficiencies obtained after addition of magnesium perchlorate are higher than the results which are obtained without magnesium ions (Table 3). A similar improvement of the current yield is obtained by using a self-buffering solution of 25% imido-disulphonate di-anion and 75% imido-disulphonate trisanion (total 2 M) but this is at the expense of mass yield since under these conditions (lower pH) a relatively fast hydrolytic decomposition of the imido-disulphonate according to Reaction 14 cannot be avoided.

It is easily shown by cathodic polarographic investigations that the product, hydrazine tetrasulphonate anions, cannot be reduced cathodically even with potentials as negative as – 2 V versus SCE. This allows the use of undivided cells.

*4.3.3. Anodic production of hydrazine tetrasulphonate in undivided cells by continuous electrolysis.* For a technical process which aims at producing hydrazine tetrasulphonate or its alkali salt, it is desirable to use as simple and as cheap an electrolysis cell construction as possible, i.e. it is desirable to use an undivided cell.

The capillary gap cell which was developed by Beck [21] and whose mass transfer properties are quite well understood [22, 23], lends itself for the performance of a continuous oxidation of imidosulphonate trisanions. Furthermore a comparison of current yields obtained in the capillary gap cell under optimal working conditions (see below) shows that graphitic carbon anodes (Diabon P127) give as good results as platinum anodes so that there is no further need to use noble metal anodes (Table 3, B).

The performance of the anodic Reaction 4 in an undivided cell with a cathode at which hydrogen and hydroxyl ions are produced leads to the difficulty of competing anodic oxygen evolution since on continuous electrolysis more and more of the imido-disulphonate is replaced by hydroxyl ions

$$2[N(SO_3)_2]^{3-} + 2H_2O \xrightarrow{2\,F} [N_2(SO_3)_4]^{4-} + 2OH^- + H_2. \qquad (15)$$

Furthermore it is necessary to use as high current densities as possible in order to keep the partial current densities for hydroxyl ion and water oxidation low.

Therefore, in order to minimize current efficiency losses due to hydroxyl ion oxidation it is necessary to start with a high concentration of imido-disulphonate anions and to convert them according to Equation 14 only to a limited extent (e.g. 10–20%). As can be seen from the solubility data of di- and trisalkali salts (Table 4) of the imido-disulphonic acid it is only possible by use of lithium and potassium salts to reach concentrations of more than 1 M $[N(SO_3)_2]^{3-}$ in aqueous solutions at 20° C. So these salts have to be used for a technical electrolysis in order to obtain good current yields.

Secondly it is desirable to use an appropriate buffer system, to keep the $OH^-$ concentration as high as possible in order to avoid excessive loss of imido-disulphonate due to hydrolysis (for which a low working temperature around 25–30° C is additionally important) but as low as possible in order to minimize hydroxyl ion co-oxidation.

An appropriate buffer system is the $Mg^{2+}/Mg(OH)_2$ system. With a capillary gap cell, the technical conditions for obtaining simultaneously the optimal current and mass yields (low degree of hydrolysis) and reaching a conversion of approximately 20%, can only be defined experimentally since the interaction of the different process parameters is too complicated to be handled by a purely physicochemical model. A gap width between anode and cathode of 0.6 mm (which again is an empirical optimum with respect both to overall cell voltage and obtained current yield) was chosen and the dependence of the current yield on current density at different flow rates is shown in Figs. 2a and b. That the observed optimum is mainly dependent on competing mass transport of imido-disulphonate and $OH^-$ anions to the anode is evident by the dependence of the optimum current density on $[N(SO_3)_2]^{2-}$ concentration (Fig. 2b).

In Fig. 3 the capillary gap cell is illustrated and the optimum conditons are given. In Table 5 current, and mass efficiencies are given for repeated recycling (extended electrolysis time) of $Li_3N(SO_3)$ solutions without and with addition of 0.1 M $Mg(ClO_4)_2$ as buffer. The recycling was continued until an approximate 20% conversion was obtained, since an 0.1 M concentration of $Li_4N_2(SO_3)_4$ is the minimum concentration limit which is necessary to precipitate $Li_4N_2(SO_3)_4$ by cooling the electrolyte down to 0° C.

The integral current yields (40% without and 60% with addition of $MgClO_4$) are encouraging and so are the mass yields which are in the range 65–70% with 30–35% losses due to imido-disulphonate hydrolysis. The differential current yields of as high as 80% show that the hydrogen abstraction reaction, which is predominant in the anodic oxidation of the anions of dicarboxyl imides, is probably of minor or no importance in the oxidation of the imido-disulphonate anion.

The use of an amalgam cathode instead of a hydrogen-evolving steel cathode is even more attractive for the following reasons:

(a) Only trace amounts of hydroxyl ion are evolved at the cathode, so that the optimal pH conditions for the anode reaction can be easily

*Table 4. Solubilities of imido-disulphonate di- and trialkali salts with different alkali cations in aqueous solution at 20° C*

| *Salt* | *Solubility* (mol $l^{-1}$) | *Reference* |
|---|---|---|
| $Li_2HN(SO_3)_2$ | 4.1 | – |
| $Li_3N(SO_3)_2$ | 2.2 | – |
| $Na_2HN(SO_3)_2$ | 3.6 | [24] |
| $Na_3N(SO_3)_2$ | 0.32 | [24] |
| $K_2HN(SO_3)_2$ | 0.09 | [24] |
| $K_3N(SO_3)_2$ | 1.26 | [24] |

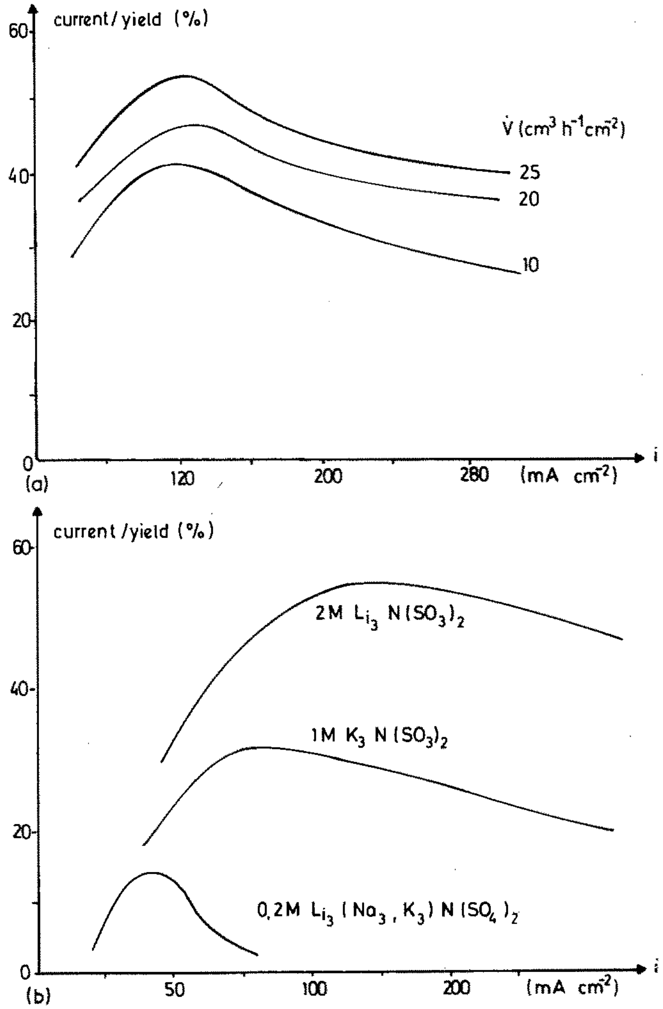
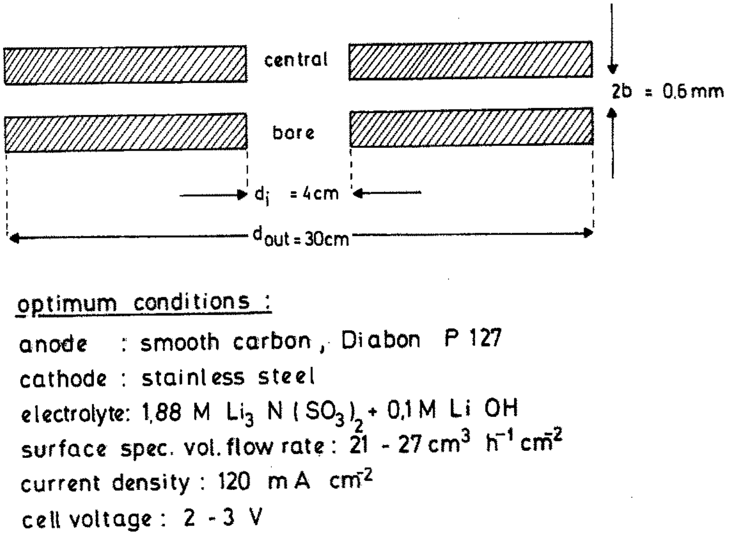


Fig. 2. (a) Dependence of current yield for $[N_2(SO_3)_4]^{4-}$ synthesis on current density for three different surface-specific volumetric flow rates [Electrolyte: 2 M $Li_3N(SO_3)_2$]. (b) Determination of optimum current density for $[N_2(SO_3)_4]^{4-}$ synthesis in a capillary gap cell with optimal specific flow rate [$(\dot{V}_{opt})_{spec}$ = 21–27 cm$^3$ cm$^{-2}$ h$^{-1}$].



optimum conditions :

anode : smooth carbon, Diabon P 127
cathode : stainless steel
electrolyte: 1,88 M $Li_3N(SO_3)_2$ + 0,1 M LiOH
surface spec. vol. flow rate : 21 - 27 cm$^3$ h$^{-1}$ cm$^{-2}$
current density : 120 mA cm$^{-2}$
cell voltage : 2 - 3 V

Fig. 3. Schematic diagram and actual dimensions of capillary gap cell with optimal working conditions for anodic $[N_2(SO_3)_4]^{4-}$ synthesis.

*Table 5. Results of the continuous anodic oxidation of* $[N(SO_3)_2]^{3-}$ *at C anodes (Diabon P127) in capillary gap cell. [Electrolyte: 1.8 M* $K_3N(SO_3)_2$*, run B (5 and 6) with addition of 0.24 M* $Mg(ClO)_2$*; cathode: stainless steel (V2A), gap width, 0.6 mm,* $\dot{V} = 21\text{–}27\ cm^3\,cm^{-2}\,h^{-1}$*,* $i = 0.123\ A\,cm^{-2}$*]*

| *Analysis number* | *Time* (h) | *Current yield (%)* | *Mass yield (%)* | *Hydrazine concentration* (M) |
|---|---|---|---|---|
| *Run A: 1.88 M* $K_3N(SO_3)_2$*, 0.1 M KOH* | | | | |
| 1 | 0.5 | 68.4 | – | 0.09 |
| 2 | 1.0 | 49.0 | – | 0.12 |
| 3 | 1.5 | 43.6 | – | 0.22 |
| 4 | 2.0 | 43.3 | 69 | 0.20 |
| *Run B: 1.83 M* $K_3N(SO_3)_2$*, 0.1 M KOH, 0.24 M* $Mg(ClO_4)_2$ | | | | |
| 5 | 0.5 | 79.0 | – | 0.10 |
| 6 | 1.0 | 63.0 | 64.5 | 0.20 |

controlled by adding only small amounts of dipotassium or dilithium salts of imido-sulphonate (or LiOH). The addition of $Mg^{2+}$ ions which introduces the complication of $Mg(OH)_2$ precipitation can then be avoided.

(b) According to the overall reaction

$$2Me_3N(SO_3)_2 \rightarrow Me_4N_2(SO_3)_4 + 2(Me)_{amalg.}$$

one third of the initially used alkali metal is recovered as the amalgam and can be recycled directly by reaction with the di-alkali salt to the tri-alkali salt of imido-disulphonic acid:

$$Me_2HN(SO_3)_2 + (Me)_{amalg} \rightarrow Me_3N(SO_3)_2 + 2H_2.$$

(c) Since no appreciable amount of $H_2$ is evolved at the cathode no additional gas–liquid phase separation is necessary and explosion hazards associated with $H_2$-evolution in the electrolyser (traces of $O_2$ being always evolved at the anode) can be avoided.

(d) The well-established amalgam electrolysis techniques of the chloralkali electrolysis can be used.

Indeed by carefully controlling the electrolyte pH an overall current efficiency of better than 80% can be obtained with a 30–35% conversion of aqueous 1.8 M $Li_3N(SO_3)_2$ solutions using the mercury cathode.

## 5. Recovery of hydrazine, recycling of sulphate and flow sheet of an hydrazine process based on the anodic dimerization of imido-disulphonate anions

The anodic coupling of imido-disulphonate trisanions which can be performed under appropriate pH control with high current and mass yield can be used to produce hydrazine provided it is possible

(a) to separate the lithium or potassium salt of hydrazine tetrasulphonate from the electrolyte;

(b) to convert hydrazine tetrasulphonate by a simple procedure into hydrazine;

(c) to recycle the sulphate–sulphur in order to avoid production of useless alkali sulphate.

It may be noted, however, that:

(a) The separation of $Li(K)_4N_2(SO_3)_4$ is possible simply by cooling 0.3–0.4 M solutions of this salt down to about 0° C. With the same procedure it is possible to separate out alkali sulphates and sulphamates which are generated by slow hydrolysis of imido-disulphonate anions whereas the ammonia produced by hydrolysis may be partly remove by air stripping and partly by co-precipitation of $(NH_4)_2SO_4$ which as an admixture to the hydrazine tetrasulphonate alkali salt is harmless in the further processing.

(b) Acidic hydrolysis of the alkali salt of hydrazine tetrasulphonate anions is a fast reaction which produces aqueous solutions of hydrazine (up to 20%) with almost no loss in hydrazine [5]. But a better procedure would be the ammonium ion catalyzed ammonolysis in a medium temperature (100–130° C) medium pressure process (30–50 bars) which produces a mixture of ammonia and hydrazine which is much easier to separate and concentrate than aqueous hydrazine solutions;

$$Li(K)_4N_2(SO_3)_4 + 4NH_3 \xrightarrow{NH_4^+} N_2H_4 + 4Li(K)SO_3NH_2 \qquad (16)$$

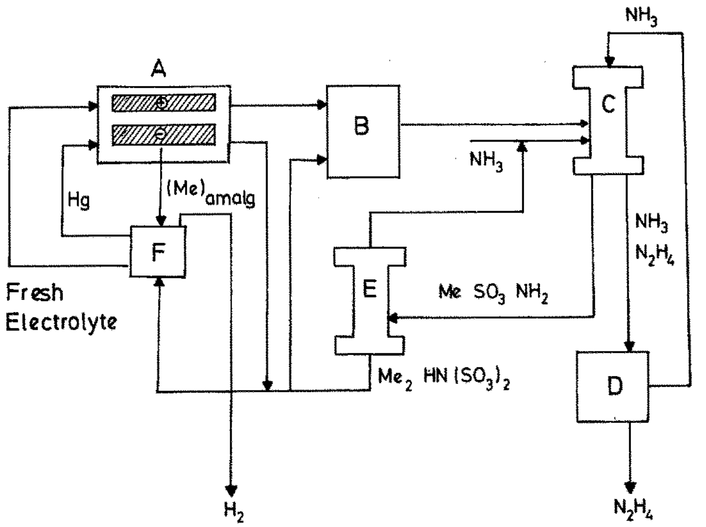


Fig. 4. Proposed flow sheet for hydrazine process: A electrolytic amalgam cell; B crystalliser; C pressure reactor I for ammonolysis of alkali salt of hydrazine tetrasulphonic acid; D distillation column for $NH_3/N_2H_4$ separation; E pressure reactor II for conversion of sulphonate to imido-sulphonate; F pile for amalgam conversion.

(c) The alkali sulphonate which is obtained by ammonolysis of hydrazine tetrasulphonate alkali salts can be recycled by reconversion in a medium temperature, medium pressure process to the imido-disulphonate

$$4Li(K)SO_3NH_2 \rightarrow 2Li(K)_2(SO_3)_2NH + 2NH_3. \qquad (17)$$

Reaction 17 is a well-established reaction for the converison of ammonium amido-sulphonates to di-ammonium imido-disulphonate [25]. Fig. 5 presents the schematic flow sheet of the new hydrazine process which is based on the electo-chemical Grinstead reaction (Equation 4).

## 6. Experimental

Electrode kinetic measurements were performed at rotating rod electodes machined from different anode materials. The aqueous saturated calomel electrode was used as the reference electrode. All organic substances, solvents, and supporting electrolytes were thoroughly purified by recrystallization, distillation and drying. Identification and quantitative determination of organic substances and products was achieved by C, H and S analysis using i.r. and n.m.r. spectroscopy and chromatography, respectively. Hydrazine determination was performed by iodometry [26].

## Acknowledgement

The authors are indebted to the Deutsche Forschungsgemeinschaft for financial support (We 90/9).

## References

[1] R. Bauer and H. Wendt *Angew. Chem. Internat. Edn.* 17 (1978) 202.

[2] *Idem, ibid* 17 (1978) 370.

[3] R. Ohme and A. Zubeck, *Zeitschrift f. Chemie* 8 (1968) 41.

[4] K. Othmer, 'Encyclopedia of Chemical Technology' 2nd edn (edited by E. A. Parolla) Interscience, New York (1966) Vol. II, p. 164.

[5] R. R. Grinstead, *J. Inorg. Nucl. Chem.* 4 (1957) 287.

[6] R. Bauer and H. Wendt, *J. Electroanalyt. Chem.* 80 (1977) 395.

[7] A. R. Butler, *J. Chem. Soc. Perkin Trans.* 2 (1974) 1239.

[8] C. R. Guerillot, *Compt. rend.* **240** (1955) 1107.

[9] J. T. Edward and K. A. Terry, *J. Chem. Soc.* (1957) 3527.

[10] H. F. Walton and A. E. Martell, *J. Amer. Chem. Soc.* 74 (1952) 5745.

[11] G. Dauphin and A. Kergonard, *Bull. Soc. Chim.* 3 (1961) 486.

[12] G. J. Doyh and N. Davidson, *J. Amer. Chem. Soc.* 71 (1949) 3491.

[13] B. Zerne and M. L. Bender *ibid* 83 (1961) 2267.

[14] P. S. Skell, J. C. Day and J. P. Slanga, *Angew. Chem.* 90 (1978) 546.

[15] T. Curtins and F. Lorenzen, *J. prakt. Chem.* 58 (1898) 160.

[16] A. A. Witte, *Rec. trav. chim.* **51** (1931) 299.
[17] F. Lober, *Angew. Chem.* **64** (1952) 65.
[18] M. Katz, P. Reimenschneider and H. Wendt, *Electrochim. Acta* **17** (1972) 1595.
[19] E. Schmidt and S. Stucki, *Ber. Bunsenges. Phys. Chem.* 77 (1973) 913.
[20] S. Gilman, *J. Phys. Chem.* **43** (1969) 425.
[21] F. Beck and H. Guthke, *Chem. Ing. Techn.* **41** (1969) 943.
[22] R. Dworak and H. Wendt, *Ber. Bunsenges. Phys. Chem.* **80** (1976) 77.
[23] *Idem, Chem. Ing. Techn.* **49** (1977) 349.
[24] Y. Ito and Y. Yoshino, *Nippon Kagaku Kaishi* (1975) 1160.
[25] 'Inorganic Synthesis' (edited by W. C. Fernelins) Vol. 2 McGraw Hill, New York (1946) p. 180.
[26] J. M. Kolthoff, *J. Amer. Chem. Soc.* **46** (1924) 2009.