Studies on the anodic decomposition products of sulfamate

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The anodic oxidation of sulfamate, products of which are known to significantly affect the quality of nickel deposits in a nickel electroforming bath, has been studied. Sulfamate was oxidized electrochemically at a platinum electrode in aqueous solution of initial pH 12 and 2, and one of the decomposition products produced therefrom, which had not been identified in the literature, was separated by means of paper chromatographic methods and subjected to spectroscopic analysis. The compound is produced at an applied potential more positive than 1.2 and 1.8 V vs Ag/AgCl, saturated KCl electrode in alkaline and acidic media, respectively. The analysis indicates that the compound has spectroscopic and chromatographic characteristics consistent with a new, thus far unknown compound, diimide S-sulfonate, $H_2N=N-S-SO_3$ which may have two different tautomeric structures. An oxidation mechanism for sulfamate consistent with the generation of this product is proposed.

1. Introduction

Anodic decomposition products of sulfamate ions have been known to exert significant effects on the quality of electroformed nickel deposits in nickel electroforming baths. Klingenmaier [1] reported that an oxidation product, which decreased tensile stress and increased the sulfur content of the deposit, was formed during the anodic polarization. Marti [2] noticed a similar phenomenon in a nickel sulfamate bath with passive or insoluble anodes and suspected that it was due to the effect of sulfite, which was produced during the anodic decomposition. Greene [3] detected sulfite and sulfate, and found a u.v. peak at 245 nm. He speculated that this peak was due to azodisulfonate, which decreased the stress and increased the sulfur content. This explanation has been well accepted [4]. However, Kendrick and Watson [5, 6] claimed that the decomposition reaction was different at a passivated nickel anode from that at the platinum electrode. Although the tensile stress of the deposit was decreased in both cases, the sulfur content of the deposit was increased only at the platinum anode.

Zeng, Zhang and Li [7, 8] detected hydrazinedisulfonate and dithionate in the anodic decomposition products using differential pulse polarography and i.r. spectroscopy. They also found there was another stable species absorbing at 245 nm, but this was not azodisulfonate. Therefore, they believed there must be an unknown species responsible for the u.v. peak at 245 nm. The species was found to be produced at both the nickel and platinum anodes. In this work, we have investigated the anodic process of sulfamate at a platinum electrode and report results on the separation and identification of the anodic decomposition product absorbing at 245 nm.

2. Experimental details

A two-compartment electrochemical cell was used to separate anolyte and catholyte. The working electrode was a platinum foil with area of about 75 cm^2 for exhaustive electrolysis experiments or 2.0 cm^2 for cyclic voltammetry (CV) experiments. A platinum wire spiral was used as a counter electrode. The reference electrode was a Ag/AgCl (saturated KCl) electrode. A 1 M sodium sulfamate solution was prepared by dissolving 1 mol of sulfamic acid (Sigma ACS reagent) in water and adding 1 mol of NaOH (Baker Analyzed reagent). The pH of the solution was adjusted using sulfamic acid or NaOH. Previous investigators have shown that anodic decomposition products in sodium sulfamate solutions are basically the same as those in nickel sulfamate solutions [7, 8].

A PAR model 173 potentiostat/galvanostat was used for large scale electrolysis and CV experiments. A Pine model RDE3 bipotentiostat was used as a function generator for the potentiostat. The u.v. spectra were recorded with a Perkin–Elmer Lambda-5 u.v./vis. spectrophotometer. The i.r. spectra were recorded with a Perkin–Elmer 783 infrared spectrometer. Paper chromatography experiments were performed in a developing chamber of size 30 cm × 9.5 cm × 28 cm. Paper 597 from Schleicher & Schuell was used to load and develop samples.

Fast atomic bombardment mass spectra were obtained at the mass spectrometry facility at the Michigan State University.
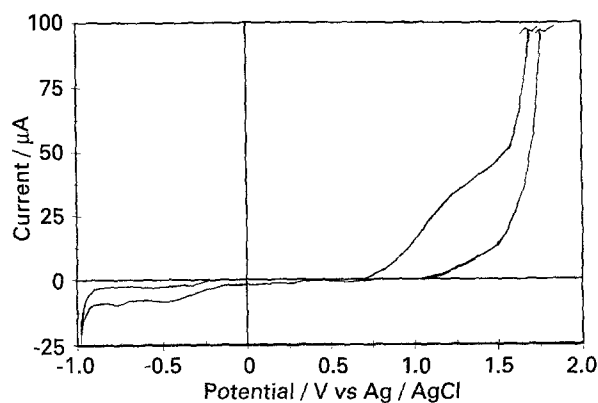
Fig. 1. Cyclic voltammogram of 1 M sodium sulfamate solution at pH 12 recorded at a scan rate of 10 mV s⁻¹.

3. Results and discussion

3.1. Oxidation and reduction potential of unknown species

A cyclic voltammogram (CV) of a 1 M sodium sulfamate solution at an initial pH 12 is shown in Fig. 1. There is a shoulder in the anodic range; then current increases rapidly due to oxygen evolution. On the cathodic side, hydrogen evolution occurs at about −1.0 V vs Ag/AgCl electrode. There are two other small shoulders, one of which at about −0.75 V is most likely due to the reduction of the platinum oxide. These seem to be irrelevant to the unknown species under investigation in this study. No further investigation was performed on them.

To find at which potential the unknown species with an absorption peak at 245 nm is anodically produced, the solution was electrolysed at several electrode potentials, 0.8, 1.2 and 1.6 V. The anolyte was regularly sampled for u.v. spectral measurements. Figures 2 and 3 show the u.v. spectra. In these spectra, a sodium sulfamate solution without electrolysis was used as a blank solution. When the electrolysis was conducted at 0.80 V, no trace of the absorption peak at 245 nm was detected from the solution. There is a peak appearing at about 217 nm, which undergoes a shift to a slightly longer wavelength with its intensity increased (not shown). It appears that this is due to some solvent effects, because we observe a peak by

Fig. 3. Difference u.v. spectra of sulfamate solution after the electrolysis at 1.2 V vs Ag/AgCl. Other conditions are the same as those in Fig. 2.

slightly changing the pH of the solution. A shoulder absorption band develops at 245 nm when the potential is held at 1.2 V, as shown in Fig. 2. Difference spectra were obtained by normalizing absorbances of spectra to that of the peak at 226 nm and subtracting them from those of lower electrolysis times. The results are shown in Fig. 3. This reveals that the unknown species with an u.v. peak at 245 nm is produced at 1.2 V. Further increase in the electrode potential results in an apparent increase of the peak at 245 nm; see Fig. 4. Therefore, in a solution with initial pH of 12, the unknown species begins to be produced at 1.2 V, but it is produced in a significant amount only at more positive potentials where oxygen is produced.

Similar experiments were conducted in an acidic solution. The CV for a solution with an initial pH of 2 is shown in Fig. 5. The current increases rapidly when the potential increases and the anodic decomposition current peaks as shown in Fig. 1 are covered by the oxygen evolution current. In this solution, the spectral peak at 245 nm is detected when it is electrolyzed at above 1.6 V. However, a sizable amount of the unknown species is produced at 1.8 V in the solution of initial pH 2.

To see whether this species is reduced at the cathode, the working electrode was held at a few different negative potentials. No change was detected for the band at 245 nm, when the preelectrolysed solution containing the unknown species was reduced at
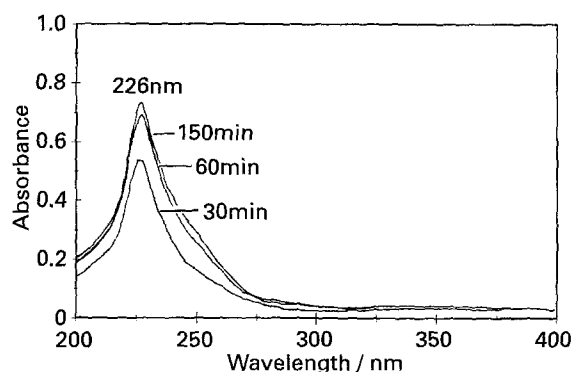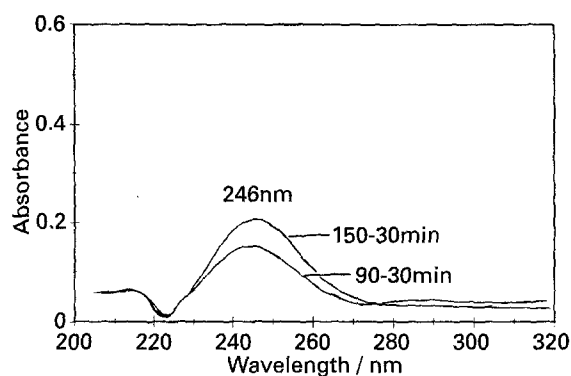

Fig. 2. U.v. spectra of the sulfamate solution recorded after electrolysis at 1.2 V vs Ag/AgCl. Initial solution: pH 12. Reference solution is sulfamate solution without electrolysis.
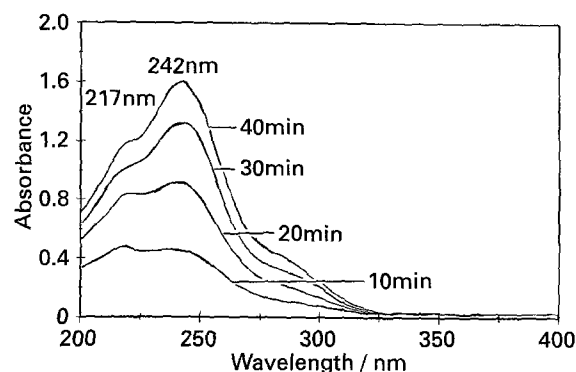

Fig. 4. U.v. spectra of the sulfamate solution after the electrolysis at 1.6 V vs Ag/AgCl. Other conditions are the same as those in Fig. 2.
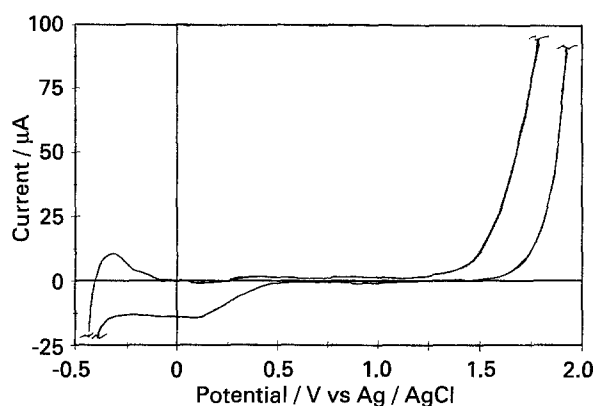
Fig. 5. Cyclic voltammogram of a 1 M sodium sulfamate solution at pH 2 recorded at a scan rate of $10\,\mathrm{mV\,s^{-1}}$.

$-1.20\,\mathrm{V}$ for 60 min. When the potential was reduced at $-1.6\,\mathrm{V}$, it was reduced and the 245 nm band showed a decrease. For an electrolyzed solution of initial pH 2, the unknown species was shown to decrease at $-0.80\,\mathrm{V}$. These spectra are shown in Fig. 6.

These phenomena suggest that the rate-determining step for the anodic production of this compound should include a proton for each electron transfer. For a reaction involving an oxidant (Ox) and reductant (Red), as in

$$Ox + nH^+ + ne^- = Red \qquad (1)$$
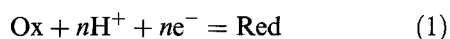
where n is a coefficient for the proton and electron, the following relationship exists:

$$E = E^\circ + \frac{RT}{nF}\ln\frac{[Ox]}{[Red]} - \frac{RT}{F}\mathrm{pH} \qquad (2)$$

For solutions with different pHs, with the same ratio of [Ox] to [Red], there is a potential difference of

$$\Delta E = -0.059\,\Delta\mathrm{pH} \qquad (3)$$

at 25° C. In the present cases, ΔpH is $12 - 2 = 10$; so ΔE should be $-0.59\,\mathrm{V}$. The potential for the anodic production of this species is about $1.2\,\mathrm{V}$ in the solution with an initial pH of 12 and about $1.8\,\mathrm{V}$ at pH 2. The results agree well with expected values from the above calculations.

3.2. Separation of unknown species from sulfamate

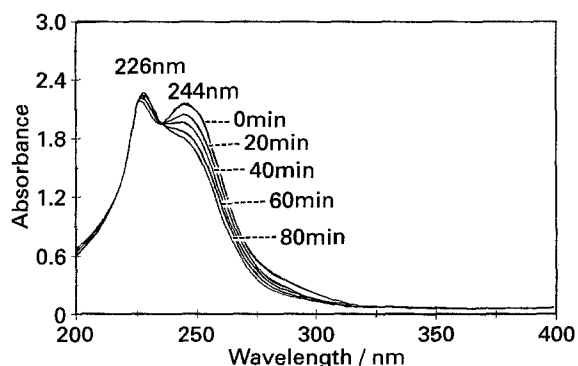The decomposition products, such as sulfite, azodisul-

Fig. 6. U.v. spectra of the electrolysis product solution reduced at $-1.6\,\mathrm{V}$ vs Ag/AgCl for different times. Other conditions are the same as those in Fig. 2.
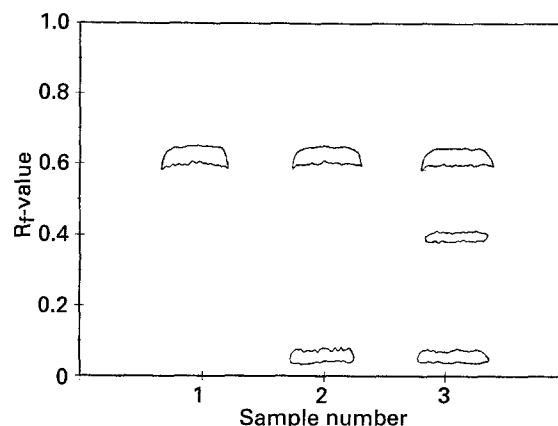

Fig. 7. Paper chromatogram. (1) Sodium sulfamate solution without electrolysis; (2) same solution as in 1 with sulfate added; (3) same solution as in 1 but after electrolysis. The developing solution is dioxane-water-ammonia (68.5:31.4:1). The spray reagent is bromophenol blue. The developed paper was visualized both by the spray reagent and an u.v. lamp.

fonate (ADS), and hydrazinedisulfonate (HDS) can be removed from the electrolyzed solution by chemical methods [7, 8]. However, the separation of the unknown species from sulfamate has not been reported. It is not precipitated by inorganic ions such as barium ions; the extraction methods by organic reagents are not known. Because its concentration is low, the separation by removing sulfamate is also difficult. Lehmann and Kempe [9] demonstrated that imides and amides of sulfur can be separated by paper chromatography. Later, Ito [10] improved the separation method. We separated the unknown species from the electrolysed sodium sulfamate solution by this method. After the sodium sulfamate solution was electrolysed and the u.v. peak at 245 nm was confirmed, sulfite, ADS and HDS were removed by methods mentioned in [7] and [8]. The solution sample was then loaded on a filter paper and developed in a solvent mixture of dioxane–water–ammonia (68.5:31.4:1). Figure 7 shows the results. The sulfamate is shown to have a large R_f value on the paper. The sulfate appears to interact strongly with the stationary phase. The unknown species appears at about the middle of the paper. The last part of the paper was cut off and extracted with water. The liquid collected in a beaker was then dried in an oven at a temperature below 80° C. Control experiments have shown that the unknown species does not undergo chemical change at 80° C. After the solvent (water) was evaporated, a pale yellow solid was recovered. The u.v. spectrum (not shown) agreed with that of the unknown species. A barium salt test shows that it does not contain sulfate. Its i.r. spectrum is different from those of sulfamate and dithionate, which indicates that both sulfamate and dithionate have been removed (see Fig. 8).

3.3. Mass spectroscopic analysis

Fast atomic bombardment mass spectroscopy (FAB–MS) experiments were conducted on the separated product. Figure 9 shows the positively charged
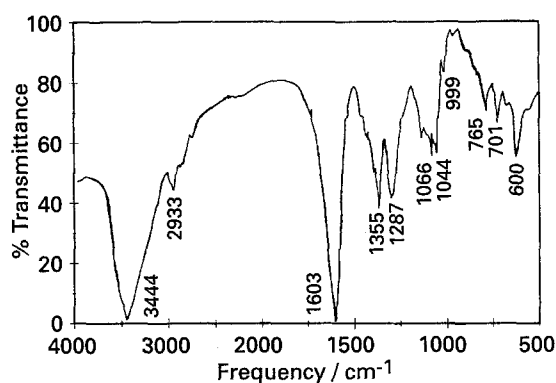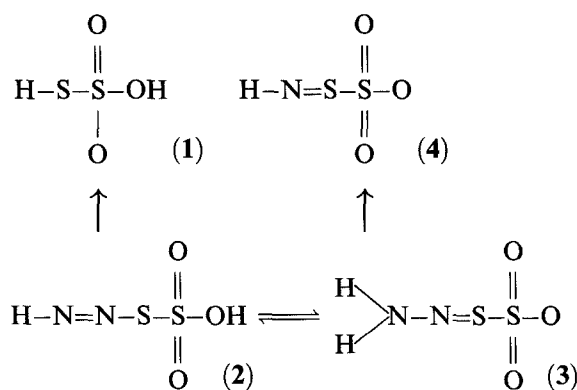
Fig. 8. I.r. spectrum of the separated product.

tionships given in Scheme 1.

Scheme 1

FAB–MS spectrum. The spectrum is fairly complicated, but mass/charge (M/Z) lines can be divided into three groups: the first group contains spectral lines with M/Z values of 115, 137, and 159; the second one with 127 and 149; and the third one with 143, 165, and 187. Within each group, the differences in M/Z-values between two nearby lines are 22, which indicate that the fragment with the larger M/Z value has one more sodium ion and one less proton. Usually the first one in each group is considered a molecular ion or $M + 1$ ion. Therefore, the separated product appears to contain three species that have molecular weights of 114 or 115, 126 or 127, and 142 or 143. In negatively charged FAB–MS spectrum, protons can be taken away from molecules to form negative ions. Although it is difficult to explain every line in a spectrum of an inorganic salt, it should offer information on M or $M - 1$ ion. Figure 10 shows that there are spectral lines at 113, 127 and 141. When this result is compared with those from positive charged FAB–MS, it can be concluded that the separated product should contain three species with molecular weights of 114, 127, and 142, respectively.

The species was allocated a formula of $Na_aH_bO_cS_dN_e$, where Na, H, O, S and N represent sodium, hydrogen, oxygen, sulfur and nitrogen with a, b, c, d and e being their respective atomic ratios. A computer calculation was performed to find all the possible combinations. The only reasonable compounds obtained from the calculation are $S_2O_3H_2$ (114), S_2O_3NH (127), and $S_2O_3N_2H_2$ (142). We speculate that these species have the structures and rela-

In other words, $S_2O_3N_2H_2$ may exist in tautomeric forms (2) and (3). Such a compound with these resonance structures explains many observations. It allows interpretation of most spectral lines of the FAB–MS spectra. In addition to the lines mentioned above, $M/Z = 63$ may be due to a fragment $(H_2NNS)H^+$. In the i.r. spectrum (Fig. 8), absorption peaks around 999, 1044, 1064, 1126, and 1287 cm^{-1} are noted. These bands may correspond to a $-SO_3-$ or $-S-SO_3-$ group [11]. However, no line is shown around M/Z 81 in FAB–MS, which would appear if the fragment $(SO_3)H^+$ existed. Therefore, the molecule with an $-S-SO_3-$ group is more reasonable for these spectral features. In the electrolysed solution, no similar chemical behaviour to that of thiosulfate could be detected. It is therefore likely, that (2) has a tautomeric form (3), and (3) may play an important role in determining the final state of the molecule. The lack of an absorption band in the 1500 cm^{-1} region also suggests that the N–N bond has a considerable single bond character. This argument is similar to that for explaining the structure of the dinitrosulfite ion [12]. The fact that structure (3) has a double bond between N and S, as well as between S and O, explains the tautomeric structures shown by (2) and (3), and thus, the compound should be stable. Molecules with the structure of (2), (3), and (4) have not been reported. However, thiohydroxylamine S-sulfonate with a structure as H_2NSSO_3 has been investigated [11]. Amido- and imido-sulfonates are divided into several classes [9]. There are a series of
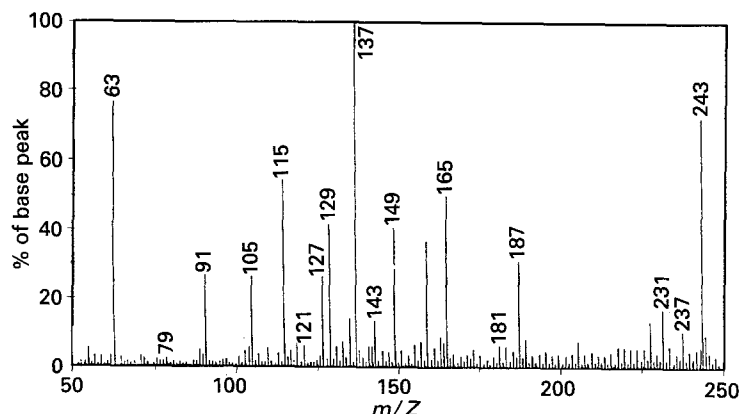

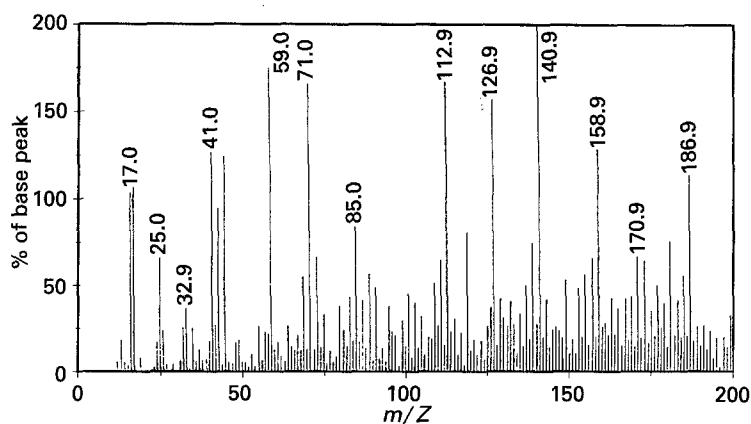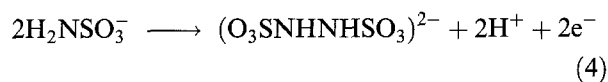Fig. 9. Positively charged fast atomic bombardment mass spectra of the separated product.

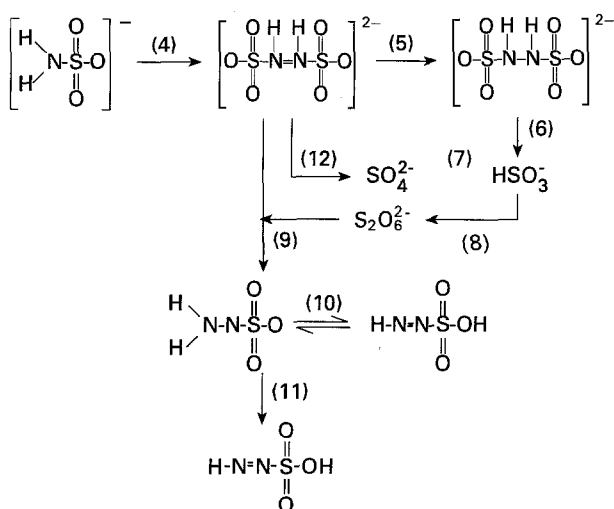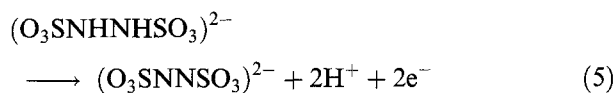Fig. 10. Negatively charged fast atomic bombardment mass spectra of the separated product.
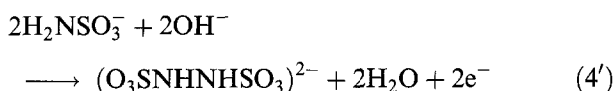
compounds in each class, but only one compound has been reported in the class of thiohydroxylamine S-sulfonate. The present compound may be an additional member of the class. We have examined many known sulfur–nitrogen compounds, such as imidodisulfonate, sulfamide, and hydroxylamine sulfonate. None of them shows the characteristics of the unknown species.

Because thiosulfate has not been detected in the electrolysed solution, $H_2S_2O_3$ (1) detected in FAB–MS should have been produced after the separation in the mass spectrometer chamber.

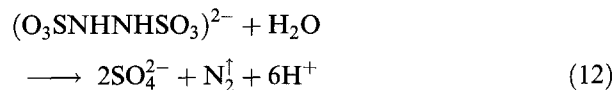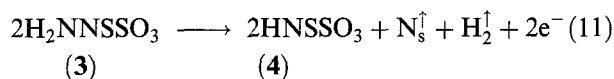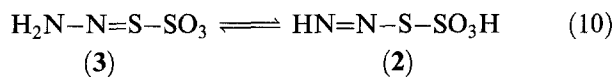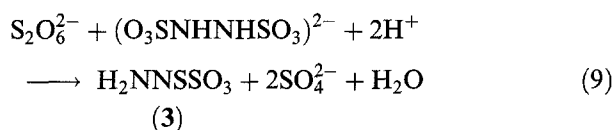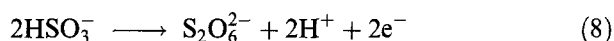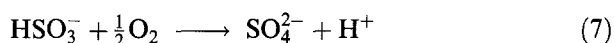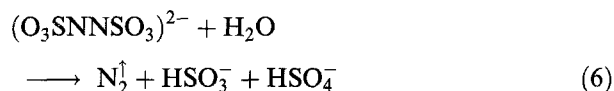A mechanism for the anodic decomposition has been suggested in [7] and [8]. From the present observations the mechanism shown in Scheme 2 is proposed. The numbers shown in Scheme 2 represent the following reactions:

$$2H_2NSO_3^- \longrightarrow (O_3SNHNHSO_3)^{2-} + 2H^+ + 2e^- \tag{4}$$

or, in alkaline solution:

$$2H_2NSO_3^- + 2OH^-$$

$$\longrightarrow (O_3SNHNHSO_3)^{2-} + 2H_2O + 2e^- \tag{4'}$$

$$(O_3SNHNHSO_3)^{2-}$$

$$\longrightarrow (O_3SNNSO_3)^{2-} + 2H^+ + 2e^- \tag{5}$$

Scheme 2.

$$(O_3SNNSO_3)^{2-} + H_2O$$

$$\longrightarrow N_2^\uparrow + HSO_3^- + HSO_4^- \tag{6}$$

$$HSO_3^- + \tfrac{1}{2}O_2 \longrightarrow SO_4^{2-} + H^+ \tag{7}$$

$$2HSO_3^- \longrightarrow S_2O_6^{2-} + 2H^+ + 2e^- \tag{8}$$

$$S_2O_6^{2-} + (O_3SNHNHSO_3)^{2-} + 2H^+$$

$$\longrightarrow H_2NNSSO_3 + 2SO_4^{2-} + H_2O \tag{9}$$
$$\qquad\quad (3)$$

$$H_2N-N{=}S{-}SO_3 \rightleftharpoons HN{=}N{-}S{-}SO_3H \tag{10}$$
$$\quad\;(3) \qquad\qquad\qquad\quad (2)$$

$$2H_2NNSSO_3 \longrightarrow 2HNSSO_3 + N_s^\uparrow + H_2^\uparrow + 2e^- \tag{11}$$
$$\quad\;(3) \qquad\qquad\qquad (4)$$

$$(O_3SNHNHSO_3)^{2-} + H_2O$$

$$\longrightarrow 2SO_4^{2-} + N_2^\uparrow + 6H^+ \tag{12}$$

Most of the intermediates involved, such as HSO_3^- [2–5,7,8], $(O_3SNHNHSO_3)^{2-}$[3,7,8], HSO_4^-[2,3,7,8], $S_2O_6^{2-}$[8], (2), (3), and (4), in this mechanism have been detected. It has been reported [8] that the amount of hydrazinedisulfonate is very small in alkaline solution because of chemical and electrochemical reactions during electrolysis. Therefore, the rate-determining step for producing H_2NNSSO_3 or $HNSSO_3$ should be reaction [4]. The reaction has the same coefficients for the H^+ and electron, which is consistent with the results of the pH effect on oxidation and reduction potentials of the unknown species (see Equations 2 and 3).

Because the mechanism involves compounds that had not previously been reported, more work needs to be done to further confirm the mechanism. It would be desirable to synthesize the compounds to confirm the present findings. The effects of the proposed anodic products on the stress and the sulfur content of the deposit also require investigation once the compound is prepared.

Acknowledgements

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