Articles

Contribution from the Department of Chemistry,
The University of Calgary, Calgary, Alberta, Canada T2N 1N4

Electrochemical Studies of Sulfur–Nitrogen Compounds. 2. The S_4N^- and S_3N^- Ions, S_7NH, $1,4\text{-}S_6(NH)_2$, $S_4N_4H_4$, and $1,3\text{-}S_4N_2$

T. CHIVERS* and M. HOJO

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The electrochemical reduction of the S_4N^- and S_3N^- ions, S_7NH, $1,4\text{-}S_6(NH)_2$, $S_4N_4H_4$, and $1,3\text{-}S_4N_2$ on mercury and platinum electrodes in acetonitrile containing 0.1 M $M^+ClO_4^-$ ($M^+ = Li^+$, Na^+, or R_4N^+ where R = Me, Et, or *n*-Bu) has been investigated, and the identity of the products was determined by polarography and UV–visible spectroscopy. The reduction of the S_4N^- ion (λ_{max} 580 nm) on a mercury-pool electrode in acetonitrile–0.1 M $Et_4N^+ClO_4^-$ at −1.8 V (vs. Ag/0.1 M $AgClO_4$–MeCN) produced S_3N^- (λ_{max} 465 nm) and consumed more than 1 e/mol. Further reduction of the S_3N^- ion at −2.2 V produced a new binary sulfur–nitrogen anion (λ_{max} 375 nm) tentatively assigned as the S_2N^- ion. A similar sequence of reductions occurred at the platinum electrode. The electrochemical reduction of S_7NH at −1.45 V on a mercury pool resulted in the uptake of 1 e and the formation of S_4N^-, S_3N^-, and HgS, while at a platinum electrode at −1.75 V the products were the 375-nm species and $S_3^{-}\cdot$, in addition to S_4N^- and S_3N^-, and the *n* value was 4. The behavior of $1,4\text{-}S_6(NH)_2$ on electrochemical reduction was similar to that of S_7NH except that no $S_3^{-}\cdot$ was formed and the ratio S_3N^-:S_4N^- was greater for $1,4\text{-}S_6(NH)_2$. The exhaustive electrolysis of $S_4N_4H_4$ at −2.8 V in acetonitrile–0.05 M Me_4NClO_4 gave an *n* value of ca. 8 and produced the SN_2^{2-} ion. The reduction of $1,3\text{-}S_4N_2$ at −1.2 V on a mercury pool produced only $S_3N_3^-$ and HgS and an *n* value of ca. 0.7, while electrolysis at a platinum electrode at −1.4 V gave both S_4N^- and $S_3N_3^-$ and an *n* value slightly greater than unity.

Introduction

In a previous paper in this series, we described the electrochemical reduction of the electron-rich heterocycle $S_3N_3^-$ and the cage species S_4N_4 and $S_4N_5^-$ in acetonitrile.[1] These studies provided direct evidence for the predicted electron-accepting capability of S–N heterocycles arising from the availability of relatively low-energy LUMOs.[2,3] Thus, the polarographic reduction of S_4N_4 proceeds via the radical anion $S_4N_4^{-}\cdot$ to give $S_3N_3^-$, which, in turn, takes up two electrons at −2.45 V (vs. Ag/0.1 M $AgClO_4$–MeCN) and yields the unstable $S_3N_3^{3-}$ ion. Exhaustive electrolysis of S_4N_4 at −2.8 V gives a coulometric *n* value of 8 and produces the SN_2^{2-} ion.[4]

Preliminary results for the voltammetric reduction of the saturated sulfur–nitrogen heterocycle S_7NH and the unsaturated six-membered ring $1,3\text{-}S_4N_2$[5] have been reported recently by Tweh and Turner,[6] but the electrochemical reduction products were not conclusively identified. Reduction of S_7NH in acetonitrile at a platinum electrode was observed to produce a blue species proposed to be S_4N^- and/or $S_3^{-}\cdot$.[7,8] The electrochemical reduction of $1,3\text{-}S_4N_2$ at −20 °C was reported to occur via two successive one-electron steps to give the ions $S_4N_2^-$ and $S_4N_2^{2-}$, which were not characterized. In view of our interest in sulfur–nitrogen anions,[9] we have investigated the electrochemical reduction of S_7NH, $1,4\text{-}S_6(NH)_2$, and $1,3\text{-}S_4N_2$ at mercury and platinum electrodes in acetonitrile using a variety of supporting electrolytes $M^+ClO_4^-$ (M = Li, Na, or R_4N where R = Me, Et, or *n*-Bu). For comparison with the other cyclic sulfur imides we included $S_4N_4H_4$ in this study, and the binary anions S_4N^-[7a] and S_3N^-[10] were investigated in view of their importance in equilibria involving anions derived from the deprotonation of sulfur imides.[9,11] Indeed, the results for these two anions will be presented first since they provide the foundation for understanding the behavior of S_7NH, $1,4\text{-}S_6(NH)_2$, and $1,3\text{-}S_4N_2$ on electrochemical reduction.

Experimental Section

The compounds $PPN^+S_4N^-$ (PPN = Ph_3PNPPh_3),[7a] $PPN^+S_3N^-$,[10] S_7NH,[11,12] $1,4\text{-}S_6(NH)_2$,[11] $S_4N_4H_4$,[13] and $1,3\text{-}S_4N_2$[14] were prepared by the literature methods. The procedures used for the purification and drying of acetonitrile[15] and for the preparation and purification of supporting electrolytes[16] have been described elsewhere.

Details of the equipment and procedures used for electrochemical and spectrophotometric measurements have been described previously.[1] All coulometric reductions were repeated, at least in duplicate, until consistent *n* values were obtained. All potentials are quoted with

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(1) Chivers, T.; Hojo, M. *Inorg. Chem.* **1984**, *23*, 1526.

(2) Tanaka, K.; Yamabe, T.; Tachibana, A.; Kato, H.; Fukui, K. *J. Phys. Chem.* **1978**, *82*, 2121.

(3) Chivers, T. *Acc. Chem. Res.* **1984**, *17*, 166.

(4) Herberhold, M.; Ehrenreich, W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 633.

(5) In this context, saturated refers to S–N heterocycles containing three-coordinate nitrogen and unsaturated applies to S–N ring systems in which nitrogen is two-coordinate: Heal, H. G. "The Inorganic Heterocyclic Chemistry of Sulfur, Nitrogen, and Phosphorus"; Academic Press: London, **1980**.

(6) Tweh, J. W.; Turner, A. G. *Inorg. Chim. Acta* **1981**, *47*, 121.

(7) Although both S_4N^- and $S_3^{-}\cdot$ are blue, it should be possible to distinguish these ions by their visible spectra. In acetonitrile the S_4N^- ion shows a smooth visible absorption band at 582 nm,[7a] while the band for $S_3^{-}\cdot$ occurs at 613 nm and exhibits fine structure.[7b] (a) Chivers, T.; Laidlaw, W. G.; Oakley, R. T.; Trsic, M. *J. Am. Chem. Soc.* **1980**, *102*, 5773. (b) Fujinaga, T.; Kuwamoto, T.; Okazaki, S.; Hojo, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2851.

(8) The formation of $S_3^{-}\cdot$ in the presence of S_4N^- can also be detected by Raman spectroscopy: Chivers, T.; Lau, C. *Inorg. Chem.* **1982**, *21*, 453.

(9) Chivers, T.; Oakley, R. T.; *Top. Curr. Chem.* **1982**, *102*, 117.

(10) Bojes, J.; Chivers, T.; Laidlaw, W. G.; Trsic, M. *J. Am. Chem. Soc.* **1982**, *104*, 4837.

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(13) Brauer, G. "Handbook of Preparative Inorganic Chemistry", 2nd ed.; Academic Press: New York, 1963; Vol. 1, p 411.

(14) Chivers, T.; Codding, P. W.; Laidlaw, W. G.; Liblong, S. W.; Oakley, R. T.; Trsic, M. *J. Am. Chem. Soc.* **1983**, *105*, 1186.

(15) Fuminaga, T.; Okazaki, S.; Hojo, M. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *44*, 89.

(16) Fujinaga, T.; Okazaki, S.; Hojo, M. *Bull. Inst. Chem. Res., Kyoto Univ.* **1978**, *56*, 139.

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Table I. Polarographic Data for S_4N^-, S_3N^-, S_7NH, and 1,4-$S_6(NH)_2$

supporting electrolyte[a]	anodic $E_{1/2}$[b] (i[c])	cathodic				
		$E_{1/2}$ (i)	$E_{1/2}$ (i)	slope[d]	$E_{1/2}$ (i)	slope
		$[S_4N^-]$ = 0.40 mM				
Li^+	−0.83 (0.7)		−1.30 (5.9)		−1.89 (2.1)	
Na^+	−0.74 (0.8)		*e*			
Me_4N^+	−0.71 (1.3)		−1.70 (7.7)	*f*	−2.17 (1.3)	58
Et_4N^+	−0.64 (1.7)		−1.575 (3.1)	63	−2.03 (3.5)	144
Bu_4N^+	−0.64 (1.5)		−1.565 (2.3)	58	−2.46 (3.3)[g]	
		$[S_3N^-]$ = 0.28 mM				
Me_4N^+					−1.84 (3.1)[h]	177
Et_4N^+					−2.07 (2.4)	59
Bu_4N^+					−2.09 (1.0)	53
		$[S_7NH]$ = 0.39 mM				
Li^+		−1.32 (10.4)				
Na^+		−1.24 (3.3)	−1.48 (5.0)		−1.64 (5.2)[i]	
Me_4N^+		−1.19 (2.0)	−1.64 (10.1)[j]		−2.23 (2.5)	
Et_4N^+		−1.25 (1.8)	−1.59 (5.7)		−2.09 (1.5)	
Bu_4N^+		−1.32 (1.9)	−1.59 (4.1)		−2.11 (1.4)	
		$[1,4\text{-}S_6(NH)_2]$ = 0.38 mM				
Me_4N^+		−1.32 (2.9)	−1.70 (8.6)[j]		−2.21 (3.8)	
Et_4N^+		−1.32 (2.8)	−1.61 (2.1)		−2.08 (1.8)	
Bu_4N^+		−1.32 (2.3)	−1.54 (1.1)		−2.04 (1.8)	

[a] Concentration is 0.1 M perchlorate except for Me_4N^+ (0.05 M). [b] In V. [c] In μA. [d] E vs. log $[(i_d - i)/i]$, in mV. [e] Three waves were observed at −1.24 V (2.0 μA), −1.47 V (2.3 μA), and −1.62 V (3.8 μA). [f] Not evaluated because of a sharp polarographic maximum. [g] Close to the reduction wave of PPN^+. [h] Additional small wave at −2.20 V (0.9 μA) 53 mV. [i] Sharp maximum. [j] Maximum at intermediate of the wave.

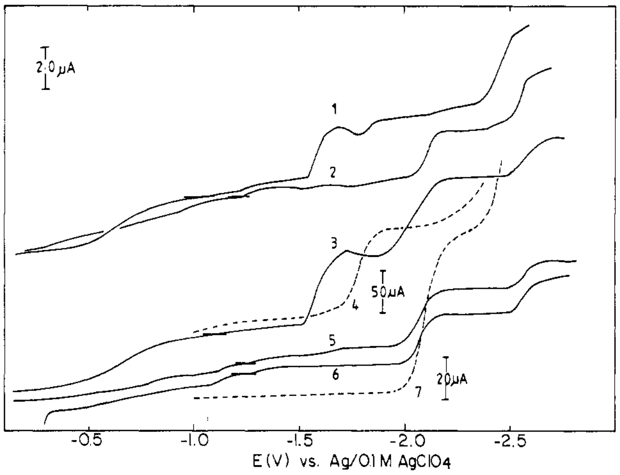


Figure 1. Voltammograms of S_4N^- and S_3N^- in acetonitrile at 23 °C on the DME unless otherwise indicated: (1) 0.40 mM $PPN^+S_4N^-$ (0.1 M Bu_4NClO_4); (2) 1 mM Ph_3P addition to 1; (3) 0.40 mM $PPN^+S_4N^-$ (0.1 M Et_4NClO_4); (4) on RPE for 3; (5) 0.28 mM $PPN^+S_3N^-$ (0.1 M Et_4NClO_4); (6) 1 mM Ph_3P addition to 5; (7) on RPE for 6. Waves after −2.5 V are due to the reduction of the PPN^+ cation.

reference to a Ag/0.1 M $AgClO_4$–MeCN electrode.

Results and Discussion

Electrochemical Reduction of the S_4N^- Anion. Polarographic data for 0.40 mM $PPN^+S_4N^-$ in acetonitrile at 23 °C containing various supporting electrolytes are given in Table I, and voltammograms for $PPN^+S_4N^-$ in the presence of 0.1 M n-Bu_4NClO_4, and 0.1 M Et_4NClO_4 electrodes are shown in Figure 1. In the latter case two cathodic waves were observed at −1.58 and −2.03 V for the dropping-mercury electrode (DME). The $E_{1/2}$ value for the first wave shifted positively when $[S_4N^-] \leq 0.2$ mM. The height of the second wave was slightly greater than that of the first, and the heights of both waves showed a linear relationship with $[S_4N^-]$. The first wave was shown to be diffusion controlled by the linear relationship of i_l with $h^{1/2}$, but the second wave was neither reversible nor diffusion controlled. With 0.1 M n-Bu_4NClO_4 the first wave for $PPN^+S_4N^-$ also occurred at −1.57 V, but the second wave was shifted to more negative potentials, −2.46 V, so that it overlapped the reduction wave for the PPN^+ cation. With 0.05 M Me_4NClO_4, the height of the first wave at −1.70 V was considerably enhanced and it was accompanied by a polarographic maximum. A complicated sequence of polarographic waves, suggesting decomposition, was observed with $LiClO_4$, or $NaClO_4$ as supporting electrolytes.

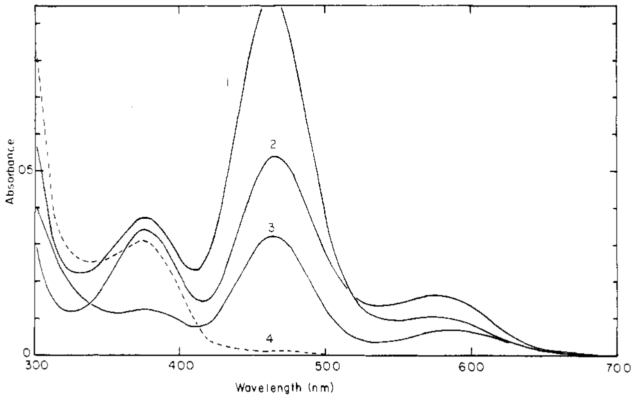
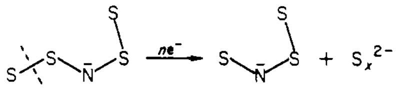


Figure 2. Absorption spectra after electrolysis of S_4N^-, S_7NH, and 1,4-$S_6(NH)_2$ in acetonitrile–0.1 M Et_4NClO_4: (1) [1,4-$S_6(NH)_2$] = 0.13 mM, Pt gauze at −1.8 V, n = 2.9; (2) $[PPN^+S_4N^-]$ = 0.11 mM, Pt gauze at −2.0 V, n = 1.5; (3) $[S_7NH]$ = 0.073 mM, Pt gauze at −1.75 V, n = 4.0; (4) $[PPN^+S_4N^-]$ = 0.14 mM, Hg pool at −2.2 V, n = 3.0.

On the rotating platinum electrode (RPE), $PPN^+S_4N^-$ gave a single wave at ca. −1.8 V with Et_4NClO_4 or n-Bu_4NClO_4 and at −1.74 V with Me_4NClO_4. In the latter case the wave height decreased at more negative potentials. Smaller waves were observed for $LiClO_4$ and $NaClO_4$, possibly due to deposition of decomposition products on the electrode surface.

Controlled-potential coulometry of 0.11 mM $PPN^+S_4N^-$ in acetonitrile–0.1 M Et_4NClO_4 was performed on a platinum-gauze electrode at −2.0 V. After the uptake of 1 e, the blue solution had become green. At n = 1.5, the UV–visible spectrum of the yellow electrolyzed solution (see Figure 2) showed a strong absorption band at 465 nm (Cf. lit.[10] λ_{max} 465 nm for S_3N^-) together with a medium intensity band at 375 nm and a weak band at 580 nm (S_4N^-).[7a] When the electrolysis of S_4N^- was carried out at −2.3 V (the potential at which S_3N^- is reduced on a Pt electrode; vide infra), the only absorption band in the UV–visible spectrum of the electrolyzed solution was at 375 nm and the coulometric *n* value was 3.

The electrolysis of 0.08 mM $PPN^+S_4N^-$ on a mercury pool at −1.8 V gave *n* values of 1.3–1.5, and the UV–visible spectrum showed bands at 465 (S_3N^-) and 375 nm. If the electrolysis was stopped after the uptake of 0.6 e, the absorption spectrum of the blue-black solution exhibited bands at 580 (absorbance 0.16, S_4N^-) and 465 nm (absorbance 0.48). However, this solution became yellow on standing for 30 min, and the 580-nm band in the visible spectrum was replaced by a band at 375 nm. This observation suggested that either mercury or (poly)sulfide anions, S_x^{2-}, formed by the electrochemical reduction of S_4N^- can react with S_4N^- (or S_3N^-) to produce the 375-nm species. Thus the electrochemical reduction of S_4N^- involves the scission of an S–S bond to give S_3N^- (eq 1).



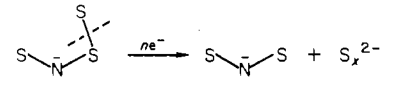
(1)

The true *n* value for this process is difficult to obtain due to the slow reaction of the other reduction product, S_x^{2-}, with S_4N^-.

When the electrolysis of $PPN^+S_4N^-$ was carried out at −2.2 V on a mercury pool, the coulometric *n* value was 3. During the course of the electrolysis the color of the solution changed from blue (*n* = 0) through pale green (*n* = 1) and yellow (*n* = 1.5) to colorless (*n* = 3), and the UV–visible spectrum of the final solution exhibited a single peak at 375 nm.

Electrochemical Reduction of the S_3N^- Anion. A solution of $PPN^+S_3N^-$ (0.28 mM) in acetonitrile–0.1 M Et_4NClO_4 exhibited a greenish yellow color and gave two cathodic waves prior to the reduction of the PPN^+ cation on the DME (see Figure 1). The smaller first wave ($E_{1/2}$ = −1.63 V, 0.3 μA) was due to the presence of a small amount of the S_4N^- ion, which is formed spontaneously from S_3N^- in solution.[10] The second wave ($E_{1/2}$ = −2.065 V, 2.55 μA, slope 65 mV) is due to the reduction of the S_3N^- ion. The addition of Ph_3P (1 mM in acetonitrile) to the solution converted all the S_4N^- to S_3N^- as determined by the polarogram and the visible spectrum of the resulting yellow solution. The remaining polarographic wave ($E_{1/2}$ = −2.07 V, 2.4 μA, slope 58 mV) was found to be diffusion controlled by the linear relationship of i_l with $h^{1/2}$.[17] Controlled-potential electrolysis of $PPN^+S_3N^-$ (prepared from S_4N^- and Ph_3P) on a mercury-pool electrode at −2.2 V gave *n* values of 1.4–1.8, and the UV–visible spectrum of the electrolyzed solution showed a single band at 375 nm.

By analogy with S_4N^- (vide supra) we propose that the electrochemical reduction of S_3N^- also results in the scission of an S–S bond to give the 375-nm species (eq 2), which is



(2)

tentatively attributed to the S_2N^- ion.[18,19]

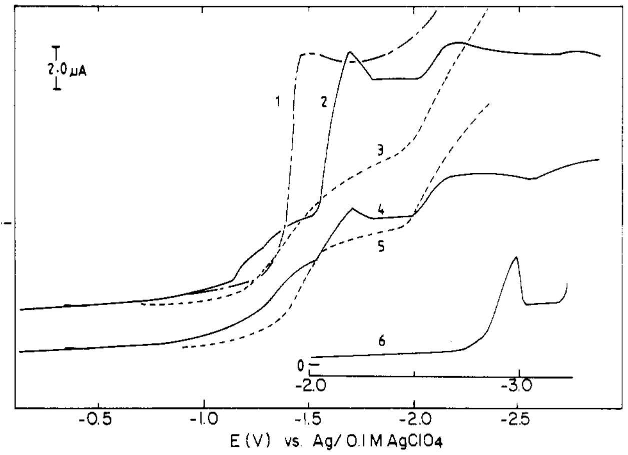


Figure 3. Voltammograms of S_7NH, 1,4-$S_6(NH)_2$, and $S_4(NH)_4$ in acetonitrile at 23 °C on the DME and with 0.1 M Et_4NClO_4 unless otherwise indicated: (1) 0.40 mM S_7NH (0.1 M $LiClO_4$); (2) 0.40 mM S_7NH; (3) on RPE for 2; (4) 0.35 mM 1,4-$S_6(NH)_2$; (5) on RPE for 4; (6) 0.37 mM $S_4(NH)_4$.

The assignment of the 375-nm species as a new binary sulfur–nitrogen anion, probably S_2N^-, is supported by the observation that addition of a solution of *c*-S_8 in acetonitrile to a solution of the 375-nm species generates S_4N^- (λ_{max} 580 nm) immediately. Only a very small amount of S_3N^- (λ_{max} 465 nm) is formed, but the S_3N^- ion also reacts rapidly with *c*-S_8 to produce S_4N^-.

We have previously proposed the S_2N^- ion as an intermediate in the formation of S_4N^- by thermolysis of a solution of the $S_3N_3^-$ ion in acetonitrile at reflux (eq 3).[7a]

$$S_3N_3^- \rightarrow S_2N^- + \text{“NSN”} \quad (3)$$

The sulfur produced by the disproportionation of NSN would be in a much more reactive state than *c*-S_8 and might be expected to react instantaneously with the S_2N^- ion in boiling acetonitrile (eq 4). This accounts for the lack of

$$S_2N^- + 2S^0 \rightarrow S_4N^- \quad (4)$$

evidence for an intermediate species in the UV–visible spectrum of solutions of $S_3N_3^-$ during thermolysis. A well-defined isosbestic point is observed for the absorption bands at 365 ($S_3N_3^-$) and 582 nm (S_4N^-). We have been unable to prepare S_2N^- by the reaction of S_3N^- with triphenylphosphine.[10] However, the electrochemical results suggest that it should be possible to prepare S_2N^- by treatment of S_3N^- (or S_4N^-) with a suitable reducing agent. Such experiments are in progress.

On the RPE, S_3N^- gave a single cathodic wave at −2.10 V (slope 79 mV) with 0.1 M Et_4NClO_4 as supporting electrolyte. Irreversible and poorly behaved waves were observed at −2.04 and −2.4 V for Me_4NClO_4 and *n*-Bu_4NClO_4, respectively.

Electrochemical Reduction of S_7NH and 1,4-$S_6(NH)_2$. Polarographic data for S_7NH and 1,4-$S_6(NH)_2$ in acetonitrile containing various supporting electrolytes are given in Table I, and some typical voltammograms are illustrated in Figure 3. Heptasulfur imide, S_7NH, gave three cathodic waves on the DME in the presence of 0.1 M Et_4NClO_4. The $E_{1/2}$ values of the second and third waves are very close to those observed for S_4N^-, suggesting that this ion is produced at the first

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[17] The compounds Ph_3P and Ph_3PS did not interfere with the observation of the polarographic waves of $PPN^+S_3N^-$ since these compounds are reduced at more negative potentials than the PPN^+ cation: Dessy, R. E.; Chivers, T.; Kitching, W. *J. Am. Chem. Soc.* **1966**, *88*, 467.

[18] The cleavage of a S–S bond in the electrochemical reduction of S_3N^- and S_4N^- can be understood from a consideration of the LUMOs for these anions. In both cases, the LUMOs are strongly antibonding with respect to S–S linkages.[7a,10]

[19] Ab initio MO calculations, using the Hartree–Fock–Slater SCF procedure, for various geometries of the S_2N^- ion show the bent symmetrical form of SNS^- (C_{2v}) to be more stable than an unsymmetrical arrangement SSN^- (C_s) by ca. 50 kcal mol⁻¹. The calculated values for the lowest energy transitions of SNS^- (C_{2v}) are 410 and 393 nm for SNS = 110 and 120°, respectively: Laidlaw, W. G.; Trsic, M., personal communication.

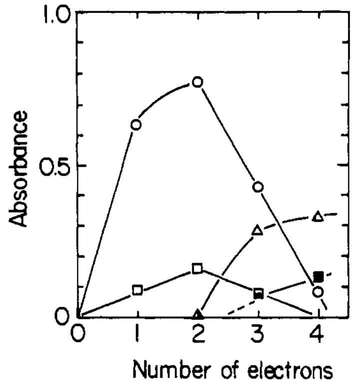
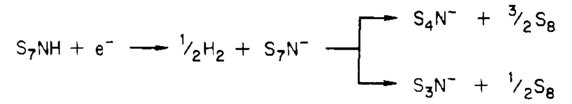


Figure 4. Variation of visible absorption bands as a function of electron uptake in the electrolysis of S_7NH (7.1×10^{-5}M) with 0.1 M Et_4NClO_4 (Pt gauze at −1.75 V): (○) 580–590 nm ($S_4N^- + S_3^{-}\cdot$); (△) 465 nm (S_3N^-); (□) 370 nm (S_4N^-); (■) 375 nm.

polarographic wave. Controlled-potential electrolysis of a solution of S_7NH on a mercury-pool electrode at −1.45 V gave an *n* value of 1.0 and produced S_4N^- (λ_{max} 580 nm), S_3N^- (λ_{max} 465 nm), and a precipitate of HgS. The pH of the electrolyzed solution, after addition of distilled water, was not significantly different from that of water itself.

Since S_4N^- is not reduced at −1.45 V, the S_3N^- ion probably results either from direct reaction of S_4N^- with mercury or from decomposition of the initially formed S_7N^- ion (eq 5 and 6).[20]



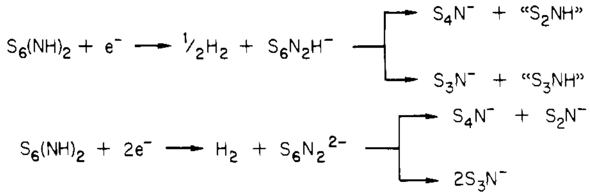
$$S_7NH + e^- \longrightarrow \tfrac{1}{2}H_2 + S_7N^- \longrightarrow \begin{cases} S_4N^- + \tfrac{3}{2}S_8 & (5) \\ S_3N^- + \tfrac{1}{2}S_8 & (6) \end{cases}$$

The sulfur so formed will react with mercury to form HgS or, on a platinum electrode, will be reduced to polysulfide ions (vide infra).

At the RPE, 0.4 mM S_7NH in acetonitrile–0.1 M Et_4NClO_4 showed two irreversible cathodic waves at −1.39 (62.5 μA, 163 mV) and −2.12 V (42.5 μA, 100 mV). Coulometric reduction of S_7NH (0.07 mM) at −1.75 V on a platinum gauze electrode gave an *n* value of 4. During the electrolysis, the initially colorless solution first became blue, then green, and finally yellow at $n = 4$. The absorption spectra of the electrolyzed solution, measured as a function of electron uptake, are displayed in Figure 4. The product at $n = 4$ was mainly S_3N^- (λ_{max} 465 nm) accompanied by a small amount of the 375-nm species, which does not appear in the UV–visible spectrum until after the uptake of 2 e. The band at 370 nm, observed prior to the $n = 2$ stage, is associated with S_4N^-. At $n > 2$, the major S_4N^- band at 580 nm was shifted to a longer wavelength due to the formation of $S_3^{-}\cdot$ (613 nm). Elemental sulfur formed by the electrolysis of S_7NH at a platinum electrode will be reduced to polysulfide ions, and hence $S_3^{-}\cdot$, at this potential.[7b] In this connection it should be mentioned that two maxima, at $n = 0.7$ and $n = 2$, were observed in the current–time curve during the controlled potential electrolysis of S_7NH at −1.75 V on a platinum electrode. In the electrochemical reduction of *c*-S_8, a similar maximum was observed at an *n* value of ca. 2.5.[7b]

The hexasulfur dimide, 1,4-$S_6(NH)_2$, gave three polarographic waves in the presence of R_4N^+ cations (see Table I). The $E_{1/2}$ values of the second and third waves were very similar to those of S_7NH. Coulometric reduction on a mercury pool at −1.5 V (the first wave) gave an *n* value of 1.3, and a precipitate of HgS was formed. The UV–visible spectrum of the electrolyzed solution showed that the major product was S_3N^- (λ_{max} 465 nm), accompanied by smaller amounts of S_4N^- (λ_{max} 580 nm). On the RPE, 1,4-$S_6(NH)_2$ showed two irreversible cathodic waves at −1.57 and −2.18 V. Controlled-potential electrolysis of 0.13 mM 1,4-$S_6(NH)_2$ at −1.8 V on a platinum-gauze electrode gave an *n* value of 3. The UV–visible spectrum of the electrolyzed solution showed bands at 465 (S_3N^-, absorbance 0.97), 580 (S_4N^-, absorbance 0.11), and 375 nm (absorbance 0.38). The changes in the absorption spectrum as a function of *n* during the electrolysis were qualitatively similar to those observed for S_7NH (see Figure 4) with the exception that no $S_3^{-}\cdot$ was formed from 1,4-$S_6(NH)_2$. Consistent with this observation, no maximum due to the formation of *c*-S_8 was observed in the current–time curve, which did not exhibit a smooth logarithmic decay. Finally, the amount of S_3N^- formed from 1,4-$S_6(NH)_2$ was ca. 1.7 times larger than that formed from S_7NH.

These results can be explained by a combination of the reduction processes shown in eq 7–10, the relative importance of which is unknown.



$$S_6(NH)_2 + e^- \longrightarrow \tfrac{1}{2}H_2 + S_6N_2H^- \longrightarrow \begin{cases} S_4N^- + \text{“}S_2NH\text{”} & (7) \\ S_3N^- + \text{“}S_3NH\text{”} & (8) \end{cases}$$

$$S_6(NH)_2 + 2e^- \longrightarrow H_2 + S_6N_2{}^{2-} \longrightarrow \begin{cases} S_4N^- + S_2N^- & (9) \\ 2S_3N^- & (10) \end{cases}$$

In order to generate the $S_6N_2H^-$ and $S_6N_2{}^{2-}$ ions, a 10^{-4} M solution of 1,4-$S_6(NH)_2$ in acetonitrile was treated with *n*-Bu_4NOH in methanol and the UV–visible spectra of the resulting solutions were measured after the addition of 1, 2, 3, 4, and 5 molar equiv of base. The changes in the absorption spectrum as a function of added base were very similar to the changes observed for electrolyzed solutions of 1,4-$S_6(NH)_2$ as a function of electron uptake (vide supra). The 585-nm band (S_4N^-) rapidly reached a maximum at $[OH^-]$:[1,4-$S_6(NH)_2$] = 2, while the 465-nm band (S_3N^-) grew steadily and reached a plateau when this ratio was ca. 3; at this point the 375-nm band first appeared. The intensity of the latter band increased steadily (and the 585-nm band decreased) as more base was added. The absorption spectra of the final solution revealed that S_3N^- (465 nm) is converted to the 375-nm species on standing in the presence of OH^-.

Electrochemical Reduction of $S_4N_4H_4$. A preliminary investigation of the electrochemical reduction of $S_4N_4H_4$ revealed a polarographic maximum at $E_{1/2} \sim -2.8$ V.[21] In this study, the supporting electrolyte was shown to have a significant effect on the polarographic reduction potential for $S_4N_4H_4$. $E_{1/2}$ values of −2.6, −2.8, and −3.2 V were found for Me_4NClO_4, Et_4NClO_4, and *n*-Bu_4NClO_4, respectively. These values are approximate because of polarographic maxima (Me_4N^+ and Et_4N^+) and closeness to the limit of the polarographic window (*n*-Bu_4N^+). Controlled-potential electrolysis at −2.8 or −3.0 V in the presence of 0.05 M Me_4NClO_4 and 0.1 M Et_4NClO_4, respectively, gave an *n* value of ca. 8, and the UV–visible spectrum of the electrolyzed solution showed an absorption maximum at 254 nm (cf. S_4N_4).[4,22] These results suggest the overall reduction process eq 11 (cf. S_4N_4).[1] When the electrolysis was stopped at the $n = 1$ stage, the pale purple solution exhibited a strong visible absorption band at 390 nm and a weaker band at 510 nm. The identity of the species responsible for these bands is unknown,[23] but

$$S_4N_4H_4 + 8e^- \rightarrow 2SN_2{}^{2-} + 2S^{2-} + 2H_2 \qquad (11)$$

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[20] We have previously established the formation of S_4N^- via the unstable S_7N^- ion in solutions of S_7NH in basic solvents, e.g. DMF or HMPA: Chivers, T.; Drummond, I. *Inorg. Chem.* **1974**, *13*, 1222.

[21] Hojo, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2856.

[22] In acetonitrile, K_2SN_2 exhibits a smooth absorption band at 253 nm: Herberhold, M., personal communication.

Table II. Polarographic Data for $1,3\text{-}S_4N_2$ ($[1,3\text{-}S_4N_2] = 0.27$ mM)

supporting electrolyte[a]	$E_{1/2}$[b] (i[c])	$E_{1/2}$ (i)	$E_{1/2}$ (i)	$E_{1/2}$ (i)
Li^+	*d*			
Na^+	*e*			
Me_4N^+	−0.90 (2.1)	−1.60 (1.9)[f]	−2.20 (1.0)	−2.425 (1.1)
Et_4N^+	−0.90 (2.1)	−1.60 (1.7)	−2.20 (1.7)	−2.61 (0.9)
Bu_4N^+	−0.89 (1.8)	−1.56 (1.0)	−2.11 (0.8)	no wave

[a] Concentration is 0.1 M perchlorate except for Me_4N^+ (0.05 M). [b] In V. [c] In μA. [d] Ill-defined waves at −0.97 V (4.3 μA), −1.33 V (4.5 μA), and −1.95 V (1.6 μA). [e] Four waves at −0.98 V (1.9 μA), −1.28 V (1.7 μA), −1.46 V (1.6 μA), and −1.61 V (2.0 μA). [f] Accompanied by a polarographic maximum.

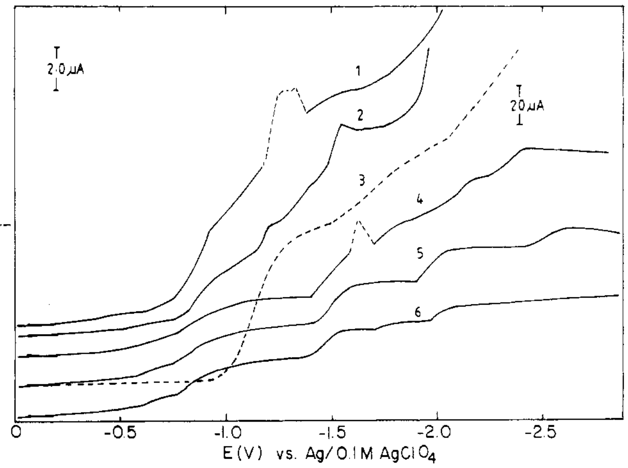

Figure 5. Voltammograms of $1,3\text{-}S_4N_2$ in acetonitrile with various supporting electrolytes (0.1 M) at 23 °C: (1) Li^+; (2) Na^+; (3) Et_4N^+ on RPE; (4) 0.05 M Me_4N^+; (5) Et_4N^+; (6) Bu_4N^+. $[1,3\text{-}S_4N_2] =$ 0.31 mM for waves 1–3 and 0.27 mM for waves 4–6 (all except wave 3 on the DME).

it is pertinent to note that the UV–visible spectrum exhibited a band at 580 nm (S_4N^-) after 30 min at 23 °C in the presence of air. Broad maxima were observed in the current–time curves from the coulometric experiments.

Electrochemical Reduction of $1,3\text{-}S_4N_2$. The $1,3\text{-}S_4N_2$ molecule has recently been shown to consist of a six-membered ring in a half-chair conformation.[24] In acetonitrile–0.1 M Et_4NClO_4, four cathodic waves were observed on the DME (see Table II and Figure 5). The height of the first wave varied linearly with concentration for $[S_4N_2] = 0.15$–0.6 mM. The second wave was accompanied by a polarographic maximum. The $E_{1/2}$ values for the second and third waves are close to the values observed for S_4N^- (see Table I), and the $E_{1/2}$ values for the fourth wave correspond with those reported for the $S_3N_3^-$ ion.[1]

Controlled-potential coulometry of 0.11 mM S_4N_2 in acetonitrile-0.1 M Et_4NClO_4 at −1.2 V (the first wave) on a mercury-pool electrode gave an *n* value of ca. 0.7. The UV–visible spectrum of the electrolyzed solution showed a band at 360 nm and a cathodic wave at −2.61 V in polarography due to $S_3N_3^-$. No S_4N^- was detected, and the yield of $S_3N_3^-$ was estimated to be ca. 70% on the basis of the known extinction coefficient[21,25] and polarographic current.[1] Some precipitation of HgS was observed during the electrolysis. The overall reaction shown in eq 12 for the coulometric reduction of S_4N_2 on a mercury electrode is indicated by these results.

$$S_4N_2 + {}^2/_3e^- + 2Hg \rightarrow {}^2/_3S_3N_3^- + 2HgS \qquad (12)$$

On the RPE, in the presence of 0.1 M Et_4NClO_4, S_4N_2 gave two cathodic waves at −1.14 and −1.59 V (see Figure 5). The slope of the first wave was 121 mV and the second wave was ill-defined. Coulometry on a platinum-gauze electrode at −1.4 V gave an *n* value of 1.1–1.2. The polarogram of the solution after electrolysis showed reduction waves at −1.64 and −2.04 V (S_4N^-) and at −2.62 V ($S_3N_3^-$). The presence of these two ions was confirmed by the observation of UV–visible absorption bands at 580 (S_4N^-) and 360 nm ($S_3N_3^-$). The overall scheme shown in eq 13 is suggested to account for the electrochemical reduction of S_4N_2 on a platinum electrode.

$$9S_4N_2 + 10e^- \rightarrow 6S_4N^- + 4S_3N_3^- \qquad (13)$$

In fact, the amounts of S_4N^- and $S_3N_3^-$ formed (calculated from their known extinction coefficients)[20,21,25] corresponded to stoichiometric coefficients of 5 for both ions in eq 13. The additional $S_3N_3^-$ may be formed by the electrochemical reduction of S_4N_4[1] present as a minor impurity in the sample of $1,3\text{-}S_4N_2$ used for electrolysis.

It is clear from these results that the initial reduction product of $1,3\text{-}S_4N_2$, presumably the radical anion $1,3\text{-}S_4N_2^-\cdot$, is unstable with respect to disproportionation to other binary sulfur–nitrogen anions. It is not known whether this decomposition involves an intramolecular bond rupture, as was found for $S_4N_4^-\cdot \rightarrow S_3N_3^-$,[1,26] or a bimolecular reaction. However, the prospects for preparing a stable salt of the dianion $1,3\text{-}S_4N_2^{2-}$, which has been the subject of recent CNDO/2 MO calculations,[27] are not encouraging.

Conclusion

The major product of the electrochemical reduction of S_7NH at mercury or platinum electrodes is the S_4N^- ion. Smaller amounts of the S_3N^- ion are also formed, and the latter is the predominant product from the reduction of $1,4\text{-}S_6(NH)_2$. The S_4N^- ion can be reduced electrochemically to the S_3N^- ion, a process that involves the cleavage of a S–S bond. By analogy, the electrochemical reduction product (λ_{max} 375 nm) of the S_3N^- ion is tentatively assigned as the S_2N^- ion. The electrochemical results suggest that it should be possible to prepare the 375-nm species by treatment of S_4N^- or S_3N^- with a suitable reducing agent.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support, Kochi University for granting a leave of absence to M.H., and Professor R. T. Oakley and Hans Koenig for generous gifts of S_4N_2 and $PPN^+S_4N^-$.

Registry No. S_4N^-, 74273-17-9; $PPN^+S_4N^-$, 74273-18-0; S_3N^-, 76468-83-2; $PPN^+S_3N^-$, 76468-84-3; S_7NH, 293-42-5; $1,4\text{-}S_6(NH)_2$, 1003-76-5; $S_4N_4H_4$, 293-40-3; $1,3\text{-}S_4N_2$, 79796-31-9; S_2N^-, 91054-03-4; HgS, 1344-48-5; $S_3^-\cdot$, 12597-04-5; SN_2^{2-}, 79796-15-9; $S_3N_3^-$, 65107-36-0; $LiClO_4$, 7791-03-9; $NaClO_4$, 7601-89-0; Me_4NClO_4, 2537-36-2; Et_4NClO_4, 2567-83-1; Bu_4NClO_4, 1923-70-2; S, 7704-34-9; Hg, 7439-97-6; Pt, 7440-06-4.

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[23] By analogy with the electrochemical reduction of S_7NH and $1,4\text{-}S_6(NH)_2$ it is, of course, conceivable that these bands are due to the $S_4N_4H_3^-$ ion and/or its decomposition product(s). $S_4N_4H_4 + e^- \rightarrow S_4N_4H_3^- + {}^1/_2H_2$.

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