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Electrochemical Studies of Sulfur–Nitrogen Compounds. 1. The Trisulfur Trinitride and Tetrasulfur Pentanitride Anions and Further Investigations of Tetrasulfur Tetranitride

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The electrochemical reduction of $S_3N_3^-$, $S_4N_5^-$, and S_4N_4 on mercury or platinum electrodes in acetonitrile containing $M^+ClO_4^-$ ($M = Li, Na, R_4N$, where R = Me, Et, *n*-Bu) has been investigated at various temperatures with use of voltammetric techniques and controlled-potential coulometry. The supporting electrolyte had a marked effect on the reduction of the $S_3N_3^-$ ion, which, in the presence of R_4N^+, accepted two electrons at −2.45 (R = Me) and −2.62 V (R = Et) vs. Ag/0.1 M $AgClO_4$ to give the unstable $S_3N_3^{3-}$ anion. The reduction of $S_4N_5^-$ in the presence of R_4N^+ occurs in two steps, each involving two electrons. The first step produces $S_3N_3^-$, probably via the unstable $S_4N_5^{3-}$ anion, while the second step is the reduction of $S_3N_3^-$. In the presence of R_4N^+ (R = Me, Et) S_4N_4 exhibits three polarographic waves, in addition to a prewave at −0.65 V. The processes involved in these three steps have been identified as (i) $S_4N_4 + e^- \rightarrow S_4N_4^-\cdot$, (ii) $S_4N_4^-\cdot + e^- \rightarrow S_4N_4^{2-}$, and (iii) $S_3N_3^- + 2e^- \rightarrow S_3N_3^{3-}$. The exhaustive electrolysis of S_4N_4 at −2.8 V results in the uptake of eight electrons and the formation of the SN_2^{2-} ion (λ_{max} = 254 nm). The electrochemical oxidation of $S_3N_3^-$ at 0.0 V on a platinum electrode produced S_4N_4 almost quantitatively.

Introduction

Cyclothiazenes and related inorganic heterocycles are π-electron rich.[1] The excess of electrons may be accommodated in π* (or nonbonding) MOs, e.g. $S_3N_3^-$,[2] or by formation of weak cross-ring S–S bonds, e.g. S_4N_4[3] or $S_4N_5^-$.[4] Thus it is not surprising that these ring systems are easily oxidized.[5,6] It is perhaps not so apparent that these π-electron-rich heterocycles and related cage and bicyclic molecules should also be good electron acceptors, as predicted by Fukui et al. for S_4N_4,[7] on account of the relatively low energies of their LUMOs compared to those of the corresponding hydrocarbon systems or cyclophosphazenes.[1]

Although electrochemical techniques are well suited to the elucidation of the redox behavior of π-electron-rich inorganic heterocycles, only a few such studies have been reported and most of these were confined to S_4N_4.[8-13] It has been established that the first reduction step of S_4N_4 (ca. −0.9 V vs. Ag/0.1 M $AgClO_4$ in acetonitrile)[12] involves the uptake of one electron to give the radical anion $S_4N_4^-\cdot$,[8-10] which is unstable above ca. −25 °C with respect to the formation of $S_3N_3^-$. The latter ion is formed almost quantitatively by exhaustive electrolysis of S_4N_4 at ca. −1.2 V.[11,12] One of the present authors also found that $S_4N_4H_4$ is obtained in 80% yield if this electrolytic reduction is carried out in the presence of a large excess of acetic acid.[12] Although additional reduction steps have been observed in polarographic[12,13] and cyclic voltammetric[10] studies of S_4N_4, the processes involved have not been elucidated. Furthermore, there have been no studies of the effect of supporting electrolyte on the electrochemical reduction of S_4N_4.

As part of a study of the redox behavior of π-electron-rich inorganic heterocycles by electrochemical techniques, we have investigated the electrochemical reduction of the $S_3N_3^-$ and $S_4N_5^-$ ions at mercury and platinum electrodes in acetonitrile using a variety of supporting electrolytes, $M^+ClO_4^-$ ($M = Li, Na, R_4N$, where R = Me, Et, *n*-Bu). The results have enabled us to elucidate the main features of the electrochemical reduction of S_4N_4 at potentials <−1.0 V. We have also conducted a brief study of the electrochemical oxidation of $S_3N_3^-$ and $S_4N_5^-$.

Experimental Section

Materials. The compounds S_4N_4,[14] $Bu_4N^+S_4N_5$,[15] $PPN^+S_4N_5^-$ (PPN = $(Ph_3P)_2N$),[16] and $Me_4N^+S_3N_3^-$[15] were prepared by literature methods. The $S_3N_3^-$ ion was also prepared by electrochemical reduction of S_4N_4 at −1.2 V on a platinum-gauze electrode in acetonitrile containing $R_4N^+ClO_4^-$ (R = Me, Et, *n*-Bu) as supporting electrolyte.[11,12] 2,1,3-Benzothiadiazole (Eastman) was a commercial sample used as received. The procedures used for the purification and drying of acetonitrile[17] and for the preparation and purification of supporting electrolytes[18] have been described elsewhere.

Apparatus and Procedure. A Princeton Applied Research (PAR) Model 174A polarographic analyzer with a PAR X-Y recorder (Model RE0074) was used for voltammetric measurements with a dropping mercury electrode (dme) or a rotating platinum electrode (rpe), which was a Metrohm Type EA682 operating at 750 rpm. The polarographic cell was an H-type with a fine-porosity sintered-glass frit between the two compartments. The dme had the following open-circuit characteristics: $m = 2.96$ mg s^{-1} and $\tau = 2.72$ s in 0.1 M $Et_4N^+ClO_4^-$–acetonitrile solution at $h = 50$ cm and $T = 23$ °C. In some experiments, a PAR Model 1747 drop timer was used for dc polarography.

Controlled-potential coulometry was performed with a PAR Model 173 potentiostat and Model 179 digital coulometer. The current was monitored by the X-Y recorder with a PAR Model 175 universal programmer. A conventional three-compartment cell was used with either a mercury pool or a platinum gauze as the working electrode. All potentials were measured with reference to a Ag/0.1 M $AgClO_4$–acetonitrile electrode. High-purity nitrogen gas (99.99%)

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Table I. Polarographic Half-Wave Potentials (V) of S_4N_4, $S_3N_3^-$, and $S_4N_5^-$

$[S_4N_4] = 0.20$ mM

supporting electrolyte[a]	prewave $E_{1/2}$[b] (μA)[c]	first wave $E_{1/2}$ (μA)	first wave slope[d]	intermediate wave $E_{1/2}$ (μA)	intermediate wave slope	second wave $E_{1/2}$ (μA)	second wave slope
Li^+	−0.57 (0.2)	−0.90 (1.65)	57.9			−1.06 (5.5)	83.3
Na^+	−0.65 (0.35)	−0.95 (1.2)	58.8			−1.74 (2.4)	120
Me_4N^+[e]	−0.65 (0.2)	−0.94 (1.7)	60.0	−2.02 (0.75)	68.4	−2.44 (3.05)	92.9
Et_4N^+	−0.64 (0.1)	−0.93 (1.8)	58.0	−2.14 (0.6)	84.0	−2.62 (2.6)	120
Bu_4N^+	−0.66 (0.1)	−0.93 (1.85)	62.5	[f]		>−3.0 (−)[g]	

$[S_3N_3^-] = 0.25$ mM

supporting electrolyte[h]	anodic wave $E_{1/2}$ (μA)	cathodic wave $E_{1/2}$ (μA)	cathodic wave slope	supporting electrolyte[h]	anodic wave $E_{1/2}$ (μA)	cathodic wave $E_{1/2}$ (μA)	cathodic wave slope
Li^+	−0.27[i] (1.2)	(−)[j]		Et_4N^+	−0.28 (0.85)	−2.615 (2.7)	85.9
Na^+	−0.28[i] (1.6)	no wave		Bu_4N^+	−0.275 (0.7)	−3.0 (−)[g]	
Me_4N^+[k]	−0.28 (1.0)	−2.455 (3.3)	48.9				

$[Bu_4N^+][S_4N_5^-] = 0.15$ mM

supporting electrolyte	anodic wave $E_{1/2}$ (μA)	first wave $E_{1/2}$ (μA)	first wave slope	second wave $E_{1/2}$ (μA)	second wave slope
Li^+	(−)[l]	−1.65 (4.6)	33.3		
Na^+	(−)[l]	−1.85 (3.4)	41.1		
Me_4N^+[e]	−0.125 (0.5)	−2.06 (2.25)	44.5	−2.45 (2.1)	52.5
Et_4N^+	−0.12 (0.3)	−2.105 (2.25)	52.4	−2.625 (1.75)	88.9
Bu_4N^+	−0.10 (0.25)	−2.12 (1.9)	53	>−3.0 (−)[g]	

[a] Concentration is 0.1 M unless otherwise stated. [b] Vs. Ag/0.1 M $AgClO_4$. [c] Current without correction for changes in drop time. [d] log $[i/(i_d - i)]$ vs. E. [e] 0.05 M. [f] Ill-defined wave at −2.75 V. [g] Small current. [h] 0.09 M except Me_4N^+. [i] Chemically synthesized $Me_4N^+S_3N_3^-$; concentration is 0.3 mM for Li^+ and 0.4 mM for Na^+. [j] Small cathodic waves at −0.67, −1.02, and −1.27 V. [k] 0.045 M in Me_4N^+ and 0.045 M in Bu_4N^+. [l] Not clear.

was saturated with acetonitrile vapor prior to passage into the electrochemical cell. Temperatures below 0 °C were achieved with use of a CCl_4–liquid-nitrogen slush bath.

UV–visible spectra were recorded with a Cary 219 spectrophotometer using a sample of electrolyzed solution that was transferred, by suction under a nitrogen atmosphere, into a 1-cm quartz optical flow cell.

Results and Discussion

Effect of Supporting Electrolyte on the Electrochemical Reduction of S_4N_4. Polarograms of S_4N_4 in acetonitrile containing various supporting electrolytes at 23 °C are shown in Figure 1. With 0.05 M Me_4NClO_4 or 0.1 M Et_4NClO_4 as supporting electrolyte four waves were observed: the first polarographic wave at ca. −0.9 V, accompanied by a prewave at ca. −0.65 V, an intermediate wave at ca. −2.1 V, and the second polarographic wave. The additional prewave at ca. −0.4 V, reported by Tweh and Turner,[13] was not observed for the concentrations of S_4N_4, <0.5 mM, used in this study. The half-wave potentials are listed in Table I The $E_{1/2}$ value for the first polarographic wave, which involved the formation of $S_4N_4^-\cdot$,[8-10] is almost unaffected by a change in supporting electrolyte. In contrast, the nature of the cation has a marked effect on the $E_{1/2}$ and i_l values for the second polarographic wave. Thus the intermediate and second waves were not well-defined at 23 °C in the presence of Bu_4NClO_4, while with $LiClO_4$ the second wave appeared just after the first wave and the wave height was ca. 3 times the height of the first wave. A third wave was observed at ca. −1.8 V when $[Li^+] \geqslant 0.1$ M. With $NaClO_4$ (0.1 M) as supporting electrolyte, the second wave appeared at −1.74 V.

The height of the prewave showed a nonlinear relationship with concentration of S_4N_4 and increased relative to the height of the first polarographic wave at low temperatures. On this basis it was concluded that the prewave is due to adsorption. The highest current value for the prewave was found for $NaClO_4$.

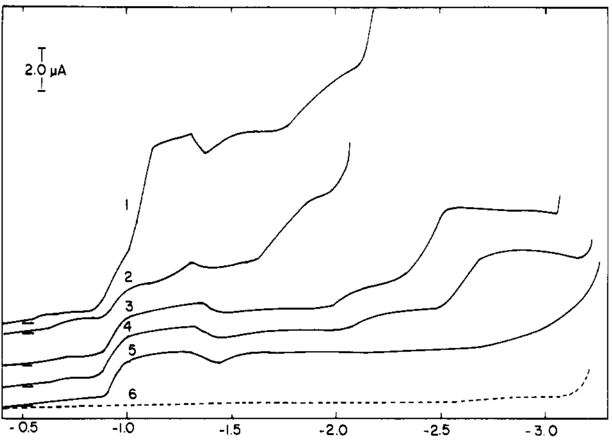


Figure 1. Polarograms of 0.20 mM S_4N_4 in MeCN containing $MClO_4$ at 23 °C: (1) M = Li; (2) M = Na; (3) M = Me_4N; (4) M = Et_4N; (5) M = n-Bu_4N; (6) base current for 0.1 M n-Bu_4NClO_4.

The prewave was not observed for the reduction of S_4N_4 on the rpe, and the first wave occurred in the range −0.93 to −0.97 V for all supporting electrolytes. The second wave was difficult to discern, even for Me_4NClO_4 or Et_4NClO_4, due to its proximity to the negative-potential limit for the rpe. With $LiClO_4$ or $NaClO_4$, the current of the first wave decreased gradually with increasing negative potentials and the second wave was not observed.

Electrolytic Reduction of S_4N_4 at the First Wave. The coulometric reduction of S_4N_4 at −1.2 V on a platinum-gauze electrode in the presence of R_4NClO_4 (R = Me, Et, n-Bu) produced $S_3N_3^-$ ($\lambda_{max} = 360$ nm, $\epsilon = 8.2 \times 10^3$ M^{-1} cm^{-1})[2a,12] quantitatively (n value 1.3). At a mercury working electrode a small amount of the $S_3N_3^-$ formed was consumed by reaction with mercury. With $NaClO_4$ as supporting electrolyte the n values were 1.4 on both the mercury-pool and the platinum-gauze electrodes. The visible spectrum of the purple electrolyzed solution (Pt gauze) indicated the presence of small amounts of other products ($\lambda_{max} = 580$ nm, S_4N^-,[16] and λ_{max}

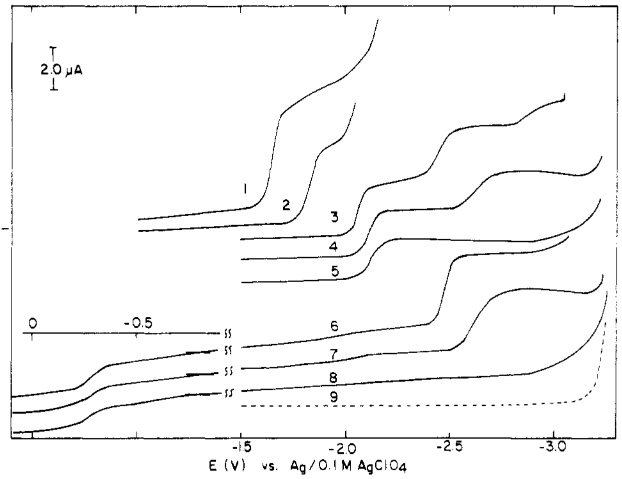


Figure 2. Polarograms of 0.15 mM $S_4N_5^-$ (1–5) and 0.25 mM $S_3N_3^-$ (6–8) in MeCN containing $MClO_4$ at 23 °C: (1) M = Li; (2) M = Na; (3) M = Me_4N; (4) M = Et_4N; (5) M = Bu_4N; (6) M = 0.05 M Me_4N^+ + 0.05 M Bu_4N^+; (7) M = Et_4N; (8) M = Bu_4N; (9) base current of 0.1 M Bu_4NClO_4.

= 510 nm, $S_3N_3O^-$ [19]) in addition to $S_3N_3^-$. In the case of $LiClO_4$ the n value was 1.7–1.8 on the platinum-gauze electrode and the blue solution showed a visible absorption band at 580 nm (S_4N^-)[16] in addition to 360 nm ($S_3N_3^-$). Values of n of ca. 3–4 electrons were found for the coulometric reduction of S_4N_4 at −1.2 V on a mercury-pool electrode in acetonitrile containing 0.1 M $LiClO_4$. The electrolyzed solution had an absorption band at 358 nm with a much lower extinction coefficient than the 360-nm band of $S_3N_3^-$. This 358-nm species was also formed in the electrochemical reduction of $S_4N_5^-$ (vide infra).

Electrochemical Reduction of $S_3N_3^-$. A polarographic wave for the reduction of $S_3N_3^-$ was observed at −2.45 and −2.61 V for Me_4ClO_4 and Et_4NClO_4, respectively (see Table I and Figure 2). This wave was shown to be diffusion controlled by the linear relationship of i_l with $h^{1/2}$. With n-Bu_4NClO_4 this wave occurred at −3.06 V, close to the negative-potential limit of the system, and no corresponding wave was observed in the case of $LiClO_4$ or $NaClO_4$. However, the addition of a small amount of Et_4NClO_4 (0.05 mM) or Me_4NClO_4 to an acetonitrile solution of $S_3N_3^-$ (0.25 mM) containing n-Bu_4NClO_4 (0.1 M) caused the wave to shift to a less negative potential. Increasing the concentration of Et_4N^+ led to a more pronounced change in potential while the current reached a constant value. This behavior suggests an interaction between Et_4N^+ (or Me_4N^+) and the product of the reduction of $S_3N_3^-$ (ion-pair formation).[20]

For such complex formation the equation

$$(E_{1/2})_c = (E_{1/2})_s + (0.059/n)\log K_p + (0.059/n)p\log[\mathrm{Me_4N^+}]$$

relates the shift in $E_{1/2}$ values to the concentration of the complexing agent (Me_4N^+ or Et_4N^+ in this case), where p = the number of cations involved in complex formation, K_p = the stability constant of the complex, $(E_{1/2})_s$ = $E_{1/2}$ of $S_3N_3^-$ with 0.1 M Bu_4NClO_4, and $(E_{1/2})_c$ = $E_{1/2}$ of $S_3N_3^-$ in the presence of added Me_4N^+ ions. It is assumed that the species involved in complex formation have equal diffusion coefficients and activity coefficients of unity.

$E_{1/2}$ values for the reduction of $S_3N_3^-$ were measured for concentrations of Me_4N^+ and Et_4N^+ ranging from 0.05 to 5 mM. From the slope of the plot of $(E_{1/2})_c$ vs. log [Me_4N^+] (see Figure 3) a value of 1.58 was obtained for p/n. The n value for the reduction of $S_3N_3^-$ was determined to be 2 by comparison of the wave height with that of the standard compound, 2,1,3-benzothiadiazole,[21] or the first wave of S_4N_4 with corrections being made for the drop time. Thus $p = 3$ and $n = 2$ suggest the formation of the complex $(Me_4N^+)_3(S_3N_3^{3-})$:

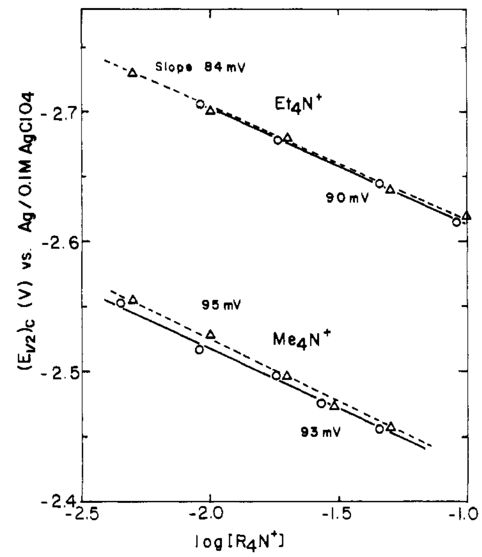
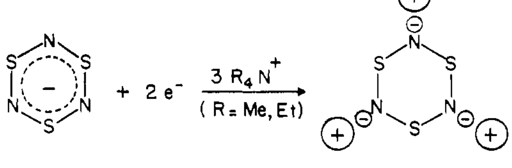


Figure 3. Effect of [Me_4N^+] and [Et_4N^+] on the half-wave potentials of $S_3N_3^-$ and $S_4N_5^-$: (△) 0.27 mM $Bu_4N^+S_4N_5^-$; (○) 0.25 mM $S_3N_3^-$. Total ionic strength was maintained at 0.09 M for $S_3N_3^-$ and 0.1 M for $S_4N_5^-$ by addition of Bu_4NClO_4.

$$S_3N_3^{3-} + 3Me_4N^+ \overset{K_p}{\rightleftarrows} (Me_4N^+)_3(S_3N_3^{3-})$$

Assuming no interaction between Bu_4N^+ and $S_3N_3^{3-}$ and neglecting changes in the reversibility of the wave (the slope of log $i/(i_d - i)$ vs. E changes from 49 to 58 mV as the concentration of Me_4N^+ changes from 0.05 M to 5 mM, and all the waves were diffusion controlled in this concentration range), log K_p for ion-pair formation is ca. 25, indicating a very strong ion association. Similar experiments were carried out with Et_4NClO_4 as supporting electrolyte (see Figure 3), and the values of p and log K_p were found to be 3.05 and 19, respectively.

Addition of two electrons to the LUMO $(2a_2'')^2$ of the 10-π-electron system of $S_3N_3^-$ to give $S_3N_3^{3-}$ will lead to a "valence-saturated" electronic structure, since all π and π^* levels will be fully occupied.[22] Thus one might envisage that the charges in $S_3N_3^{3-}$ are located primarily on nitrogen and the species is stabilized by ion-pair formation in contrast to $S_3N_3^-$, which is a fully delocalized system. In this connection it should be noted that the $E_{1/2}$ values for the oxidation of $S_3N_3^-$ (Table I) are independent of supporting electrolyte, suggesting there is no interaction between $S_3N_3^-$ and the cation.[23]



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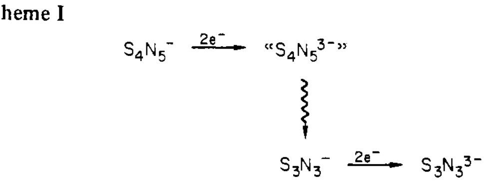
Scheme I



Electrochemical Reduction of $S_4N_5^-$. The effect of supporting electrolyte on the polarographic half-wave potentials of the $S_4N_5^-$ ion is summarized in Table I and Figure 2. With use of 0.1 M Et_4NClO_4 two cathodic waves at ca. −2.1 and −2.6 V were observed for $Bu_4N^+S_4N_5^-$ at 23 °C. Both waves were diffusion controlled, and the wave heights varied linearly with concentration for $[S_4N_5^-]$ = 0.1–0.7 mM. The number of electrons involved in each of these reductions was estimated to be 2 by comparison of the wave heights with that of the standard 2,1,3-benzothiadiazole.

Controlled-potential coulometry of n-$Bu_4N^+S_4N_5^-$ at −2.2 V in the presence of 0.1 M Et_4NClO_4 gave an n value of 2.5 and produced $S_3N_3^-$ (λ_{max} = 360 nm) and SN_2^{2-} (λ_{max} = 254 nm).[24] The polarogram of the reduced solution showed a wave at −2.6 V for the reduction of $S_3N_3^-$. Electrolysis of $PPN^+S_4N_5^-$ under similar conditions yielded n = 2.6. On the basis of the known extinction coefficient of $S_3N_3^-$[2a,12] and that estimated for SN_2^{2-} (vide infra), the yield of $S_3N_3^-$ is essentially quantitative and that of SN_2^{2-} is <50% of the amount expected on the basis of the reduction process

$$S_4N_5^- \xrightarrow{2e^-} \text{“}S_4N_5^{3-}\text{”} \rightarrow S_3N_3^- + SN_2^{2-}$$

In contrast to the behavior of $S_3N_3^-$, the different R_4N^+ cations (R = Me, Et, n-Bu) had little effect on the first polarographic reduction of $S_4N_5^-$ (Table I). Consequently it was not possible to obtain definite evidence for the formation of $S_4N_5^{3-}$, e.g. by ion-pair formation. Alkali-metal ions, however, had a dramatic effect on the first wave. Thus the $E_{1/2}$ was shifted to −1.65 and −1.85 V for Li^+ and Na^+, respectively, and the wave heights were ca. 2 and 1.5 times larger than those found for R_4N^+ cations. Coulometric reduction of $S_4N_5^-$ at 1.8 V on a mercury pool in the presence of 0.1 M $LiClO_4$ gave an n value of ca. 5. The electrolyzed solution showed an absorption maximum at 358 nm (cf. the electrolytic reduction of S_4N_4 in the presence of $LiClO_4$, which gave n values of 3–4). The identity of this species is unknown.

As indicated in Table I, the second polarographic wave of $S_4N_5^-$ shows characteristics ($E_{1/2}$ and wave height) very similar to those of the cathodic wave of $S_3N_3^-$. Furthermore, the second wave of $S_4N_5^-$ shows a similar dependence on $[R_4N^+]$ (R = Me, Et; Figure 3), from which p values of 3.22 (Me_4N^+) and 2.85 (Et_4N^+) were obtained. Thus the polarographic reduction of $S_4N_5^-$ can be described as shown in Scheme I. However, the nonintegral n values and the low yields of SN_2^{2-} suggested that the process involved in the large-scale electrolysis of $S_4N_5^-$ is more complex than indicated above.[25]

Electrolytic Reduction of Tetrasulfur Tetranitride at the Intermediate and Second Waves. As indicated in Table I and Figure 1, a small intermediate wave was observed between the first and second polarographic waves of S_4N_4 at 23 °C when Me_4NClO_4 or Et_4NClO_4 were the supporting electrolytes. The wave height showed a linear relation with $[S_4N_4]$, suggesting a Faradaic process rather than adsorption.

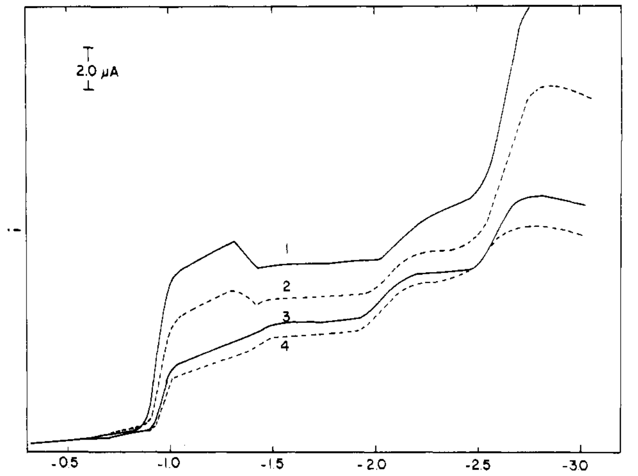


Figure 4. Effect of temperature on the polarogram of 0.80 mM S_4N_4 in MeCN containing 0.1 M Et_4NClO_4: (1) +20 °C; (2) −6 °C; (3) −23 °C; (4) −30 °C.

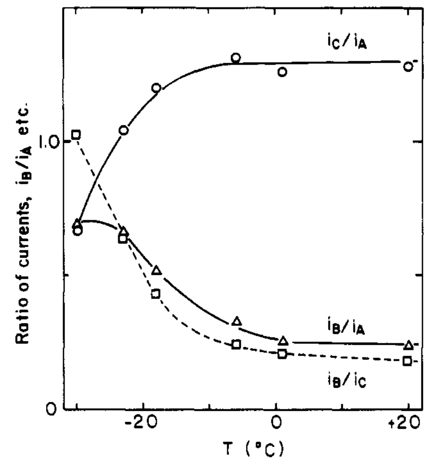
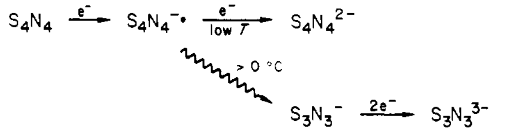


Figure 5. Variation of currents for the three polarographic waves of 0.8 mM S_4N_4 with temperature: (A) first wave; (B) intermediate wave; (C) second wave. No correction was made for changes in drop time with potential.

Scheme II



In their cyclic voltammetric study of S_4N_4 at a platinum electrode in acetonitrile–Et_4NClO_4 at −25 °C Williford et al. reported the observation of an ill-defined and totally irreversible wave at (an unspecified) potential more negative than the $S_4N_4 + e^- \rightarrow S_4N_4^{-}\cdot$ reduction.[10] It was suggested that this process may be production of $S_4N_4^{2-}$. The reduction $S_4N_4^{-}\cdot + e^- \rightarrow S_4N_4^{2-}$ was, therefore, a candidate for the intermediate polarographic wave. In view of the thermal instability of $S_4N_4^{-}\cdot$ above ca. −25 °C,[8,10] we have examined the effect of temperature on the polarographic reduction of S_4N_4. As indicated in Figures 4 and 5, the height of the intermediate wave increased relative to the heights of the first and second waves as the temperature was decreased. These data support the hypothesis that the intermediate wave is due to the reduction of $S_4N_4^{-}\cdot$. Furthermore, an analysis of the shifts in $E_{1/2}$ values of the intermediate wave caused by changing $[R_4N^+]$ (R = Me, Et; Figure 6) gave p = 2.08 (Me_4N^+) or 2.17 (Et_4N^+), suggesting the formation $(R_4N^+)_2(S_4N_4^{2-})$.[26]

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(24) Herberhold, M.; Ehrenreich, W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 633. The SN_2^{2-} ion has recently been isolated as a potassium salt and characterized by its infrared spectrum. In acetonitrile solution, the UV spectrum of K_2SN_2 exhibits a smooth absorption band at 253 nm (Herberhold, M., personal communication).

(25) The LUMO ($7b_1$) of $S_4N_5^-$ is a σ^* orbital, antibonding with respect to the cross-ring S–S bond *and* the S–N framework: Laidlaw, W. G., personal communication.

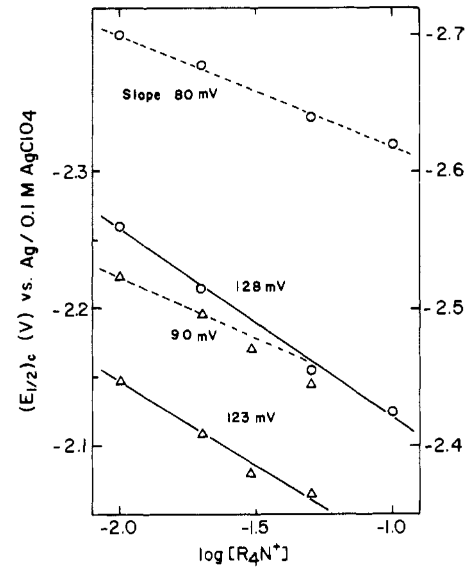

Figure 6. Effect of $[Me_4N^+]$ and $[Et_4N^+]$ on the half-wave potentials of the intermediate (—) and second (---) polarographic waves of 0.20 mM S_4N_4: (△) Me_4N^+; (○) Et_4N^+. Total ionic strength was maintained at 0.1 M by addition of Bu_4NClO_4. The right-hand scale refers to $(E_{1/2})_c$ for the second wave.

As indicated in Table I, the second polarographic wave for S_4N_4 has $E_{1/2}$ values very similar to those observed for $S_3N_3^-$ in the presence of $R_4N^+ClO_4^-$ (R = Me, Et, *n*-Bu), although there are differences in the slopes of these waves. It, therefore, seems reasonable to conclude that the second wave for S_4N_4 is due to the reduction of $S_3N_3^-$, and the effect of changing $[R_4N^+]$ (R = Me, Et) on the $E_{1/2}$ values for the second wave (Figure 6) provides additional support for this contention. The data give *p* values of 3.05 (Me_4N^+) and 2.71 (Et_4N^+) for the second wave of S_4N_4. Thus the overall electrochemical reduction of S_4N_4 can be described by Scheme II.

From an analysis of the polarographic wave heights, it is likely that the decomposition of $S_4N_4^{2-}$ also produces $S_3N_3^-$ and thus contributes to the second wave of S_4N_4, at least in the presence of Me_4N^+. Thus, with 0.05 M Me_4N^+, the height of the second wave was much higher than the value calculated with use of the heights of the first and intermediate waves for regulated drop times and *n* values of 1 and 2 for the first and second waves, respectively.

The $S_3N_3^{3-}$ ion is unstable even in the presence of Me_4N^+ or Et_4N^+ as indicated by the following experiments. Controlled-potential coulometry of a 0.4 mM solution of S_4N_4 in acetonitrile–0.1 M Et_4NClO_4 at −2.8 V on a mercury-pool electrode gave an *n* value of ca. 8, and the electrolyzed solution exhibited a very strong absorption at 254 nm.[24] A similar experiment using 0.02 M Me_4NClO_4 and 0.08 M Bu_4NClO_4 as supporting electrolyte gave an *n* value of ca. 7 and a similar absorption spectrum. These results are consistent with the reduction process

$$S_4N_4 \xrightarrow{8e^-} 2SN_2^{2-} + 2S^{2-}$$

The extinction coefficient of the SN_2^{2-} ion was estimated to be 4×10^4 L mol^{-1} cm^{-1}.

Electrolytic Oxidation of $S_3N_3^-$ and $S_4N_5^-$. A 0.25 mM solution of $[Et_4N^+][S_3N_3^-]$ in acetonitrile containing 0.1 M Et_4NClO_4 showed three successive anodic waves on the rpe at −0.25 V (62.5 μA; the slope of log $i/(i_d - i)$ vs. E is 58 mV), +0.81 V (50 μA; slope 58 mV) accompanied by a maximum, and ca. +1.4 V (75 μA; slope 150 mV). Coulometric oxidation of a 0.25 mM solution of $S_3N_3^-$ at 0.0 V on a platinum-gauze electrode gave an *n* value of 1.1 and produced S_4N_4 in ca. 90% yield, based on the absorbance at 250 nm ($\epsilon = 1.6 \times 10^4$).[12] When the oxidation was carried out at the second wave (+1.0 V), the *n* value increaed to ca. 2.5 and the yield of S_4N_4 decreased to ca. 50%.

A 0.2 mM solution of $PPN^+S_4N_5^-$ in acetonitrile containing 0.1 M Et_4NClO_4 gave an irreversible oxidation wave at +0.032 V (47 μA, slope 115 mV) and a much smaller wave at +0.95 V (8 μA) on the rpe. Under similar conditions, the first wave for a 0.3 mM solution of *n*-$Bu_4N^+S_4N_5^-$ occurred at +0.24 V (77 μA, slope 105 mV) and the second wave at +0.92 V (12 μA). Coulometric oxidation of a 0.23 mM solution of $PPN^+S_4N_5^-$ at +0.75 V (0.1 M Et_4NClO_4–acetonitrile) gave an *n* value of ca. 1.3 and produced an intense yellow solution, λ_{max} = 370nm (cf. S_5N_6 (in CH_2Cl_2), λ_{max} = 375 and 250 nm).[5] The absorption at 250 nm was obscured by bands due to the PPN^+ cation.

Thus it appears that the electrochemical oxidation of the $S_3N_3^-$ and $S_4N_5^-$ anions parallels the oxidation of these anions by mild oxidizing agents in giving S_4N_4[6] and S_5N_6,[5] respectively, as the major oxidation products.

Conclusion

The supporting electrolyte (ion-pair formation) has a decisive influence on the electrochemical reduction of $S_3N_3^-$. In the presence of R_4N^+ (R = Et, Me) a two-electron reduction occurs, providing direct evidence for the *electron-accepting* ability of this electron-rich inorganic heterocycle. The cages S_4N_4 and $S_4N_5^-$ are also good electron acceptors due to the availability of relatively low-energy LUMOs, but the anionic reduction products are unstable with respect to the formation of $S_3N_3^-$. Further electrochemical studies of related heterocycles should provide useful information regarding the redox behavior of electron-rich systems.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support and Kochi University for granting a leave of absence to M.H. We are most grateful to Professor M. Herberhold (Universität Bayreuth) for providing details of the UV spectrum of the SN_2^{2-} ion prior to publication.

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(26) Gleiter, R. *J. Chem. Soc. A* **1970**, 3174. A planar (D_{4h}) $S_4N_4^{2-}$ anion would be a 14-π-electron system with three of the four π^* orbitals occupied. Consequently, $S_4N_4^{2-}$ is expected to prefer a structure with one cross-ring S–S bond and six staggered lone pairs of electrons.