2856 © 1980 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 53, 2856—2860 (1980) [Vol. 53, No. 10

The Electrochemical Studies of Tetrasulfur Tetranitride in Acetonitrile

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(Received March 1, 1980)

$S_4(NH)_4$ has been prepared in a good yield (80% or more) by the electrolytic reduction (4-electrons) of S_4N_4 in the presence of a proton donor in acetonitrile. In the proton donor, a fairly high acidity (acetic acid or a stronger acid) and a much higher concentration than would be expected from the stoichiometry was needed. With a low acidity (*e.g.*, phenol) or a low concentration of the proton donor, a side reaction occurred with the formation of H_2S and NH_3. Under these conditions, a blue species was produced in the course of the electrolysis; this species was confirmed to be S_3^-. The re-oxidation of $S_4(NH)_4$, the oxidation of S_4N_4, and the reduction of $S_4(NH)_4$ were also examined in this connection.

The present author and his co-workers have investigated the electrode reaction with disulfur dichloride (S_2Cl_2),[1] which has a bond of sulfur-chlorine, and elemental sulfur (S_8),[2] which has only a bond of sulfur-sulfur. Tetrasulfur tetranitride (S_4N_4) is the best-known nitride of sulfur, and it has formed the starting point of most previous investigations in sulfur-nitrogen chemistry.

The reduction of S_4N_4 with potassium metal in 1,2-dimethoxyethane has been reported by Chapman and Massey[3] to produce a species of color changes attributed to ions of the $S_4N_4^{n-}$ type (n=1—4). Meinzer *et al.*[4] assigned the ESR spectrum produced by the electrochemical reduction of S_4N_4 in acetonitrile to $S_4N_4^{\cdot-}$, which has a structure similar to S_4N_4. It was further demonstrated that this radical anion is only stable at temperatures below *ca.* −25 °C, while above 0 °C rapid decomposition occurs. Prater *et al.*[5] conclusively identified the $S_4N_4^{\cdot-}$ radical and showed that it decayed according to a first-order rate law. However, it was unknown what species was produced by the decomposition of the $S_4N_4^{\cdot-}$ radical. Very recently, Bojes *et al.*[6,7] confirmed the formation of the $S_3N_3^-$ ion as the final product of the electrochemical reduction of S_4N_4 in ethanol at room temperature.

$$S_4N_4 + 4/3e \longrightarrow 4/3\ S_3N_3^-$$

In the present paper, the mechanism of the electrochemical reaction for S_4N_4 and the related compounds in acetonitrile will be reported. The effect of proton donors on the electrode reaction will also be examined in detail.

Experimental

Reagents. S_4N_4 was prepared from S_2Cl_2 and ammonia.[8] IR absorptions (CS_2 solvent) occurred at 940 m and 700 s cm^{-1}. Found: S. 68.83, N, 30.50%. Calcd for S_4N_4: S, 69.59, N, 30.41%. $S_4(NH)_4$ was prepared by the reaction of S_4N_4 with methanolic tin(II) chloride.[9] Its IR spectrum (KBr) was coincident with in the literature.[10] Found: S, 67.88, N, 30.09, H, 2.3% . Calcd for S_4N_4: S, 68.1, N, 29.8, H, 2.1%.

The method of purifying acetonitrile and the method of preparing the Et_4NClO_4 used as a supporting electrolyte has been described elsewhere.[1] The other chemicals were of G. R. grade and were used without further purification.

Apparatus and Procedure. The apparatus and equipment used in the voltammetry, controlled potential coulometry, spectrophotometry, and ESR measurements were the same as those used before.[1,2] IR spectra were measured by a Japan Spectroscopic Co., Ltd., Diffraction Grating Infrared Spectrometer, Model IRA-1. The dropping mercury electrode had the following characteristics: m=0.70 mg/s at 60 cm in the open circuit, τ=4.3 s at −1.1 V *vs.* a Ag/0.1 M** $AgClO_4$–AN electrode in 0.1 M Et_4NClO_4–AN solution. The rotating platinum electrode had a geometric surface area of 0.10 cm^2.

The concentration of the hydrogen ion in an acetonitrile solution was determined, after a good amount of water had been added to the solution, by titration with Et_4NOH (6.75 mM aqueous solution) using a Horiba glass electrode. Ammonia and hydrogen sulfide were trapped successively in 0.005 M H_2SO_4 and 0.1 M KOH aqueous solutions respectively. The ammonia was analyzed by the Nessler method, while the hydrogen sulfide was detected by the use of sodium nitroprusside and determined by polarography.

Results and Discussion

Reduction of S_4N_4. A polarogram of S_4N_4 in acetonitrile is shown in Fig. 1; it gives main two reduction waves. The half-wave potentials of the two waves were −0.93 and −2.58 V respectively. The limiting currents for both waves were proportional to the concentration in the range from 0.5 to 5×10^{-4} M. In

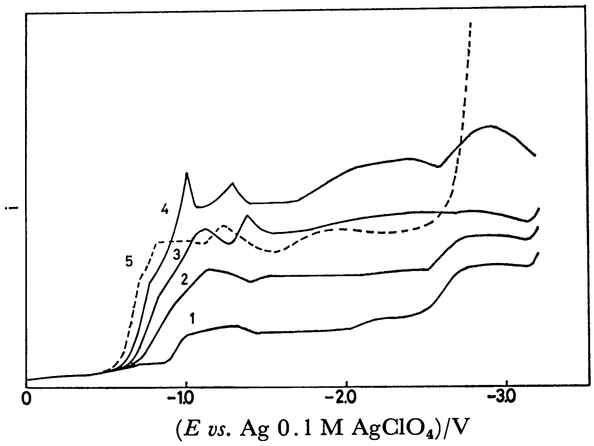

Fig. 1. Polarograms of 0.1 mM S_4N_4 with acetic acid in acetonitrile containing 0.1 M Et_4NClO_4.
(1) 0, (2) 0.2, (3) 0.5, (4) 1.0, (5) 5.0 mM of the acid.

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** Throughout this paper 1 M=1 mol dm^{-3}.

order to determine the number of electrons involved in the reduction, a S_4N_4 solution was electrolyzed at the controlled potential of -1.2 V on a Hg-pool electrode; this gave a *n*-value of 1.3 for the first wave. The electrolyzed solution was pumped into an optical flow-cell, and the absorption spectrum was measured to give a peak at 360 nm. The product can be identified as $S_3N_3^-$ according to the *n*-value and the peak wavelength, with reference to the results in ethanol.[6] The absence of the $S_4N_4^{\cdot -}$ radical in the solution (the initial concn of S_4N_4 was 1—5×10^{-4}) at room temperature was proved by ESR measurements, as predicated by Meinzer *et al.*[4] The further reduction at the second wave caused the solution to turn colorless from yellow, with an *n*-value of 5—6 electrons.

TABLE 1. VOLTAMMETRIC AND COULOMETRIC DATA FOR S_4N_4 AND $S_4(NH)_4$

Electrode	Reduction Hg	Reduction Pt	Oxidation Pt
S_4N_4			
$E_{1/2}$/V	-0.93, -2.58	-0.95, $(-1.48)^{a)}$	$+1.64$
Slope$^{b)}$/mV	57.2, 120	61	170
n-Value$^{c)}$	1.3 (5—6)	1.3	*ca.* 4.0
$S_4(NH)_4$			
$E_{1/2}$/V	$-2.80^{d)}$	—$^{e)}$	$+0.95$, $+1.62$
Slope$^{b)}$/mV	$127^{d)}$		180, 140
n-Value$^{c)}$	(≈6)		4.0

a) A small wave appeared. b) Slope of the $-E$ *vs.* log-$[(i/(i_d-i)]$ plot. c) The number of electrons obtained by coulometry. d) Estimated value attributable to a polarographic maximum. e) With a Pt electrode, the potential can be measured to -2.0 V *vs.* Ag/0.1 M $AgClO_4$–AN at most.

The results of the voltammetry and coulometry with a platinum electrode were similar to those with mercury electrode for the first wave, as shown in Table 1, except that the absorbance at 360 nm due to $S_3N_3^-$ by the electrolysis on Hg-pool was a little smaller than that on Pt-electrode. This difference may be caused by the interaction between $S_3N_3^-$ and mercury. The molar absorptivity of $S_3N_3^-$ at 360 nm was estimated to be *ca.* 8.2×10^3 in acetonitrile, based on the experiments with Pt-gauze.

By the addition of acetic acid as a proton donor to a S_4N_4 solution, the wave height of the first wave increased and the half-wave potential shifted positively (see Fig. 1). Similar results were also obtained with benzoic acid of a degree of acidity similar to that of acetic acid.

Figure 2 shows the dependence of the wave height of the first wave on the concentration of the proton donor. With the addition of acetic acid or chloroacetic acid, the wave height increased by a factor 5—6, compared to that without a proton donor. The wave height decreased upon the further addition of the acids and then attained a constant value (*ca.* 3.5—4 times). With phenol, which is a much weaker acid, the wave height increased by a factor of 4—5. The effect of water on the polarogram of S_4N_4 was very small. The presence of 5% water in acetonitrile made the first wave height increase by only a foctor of 1.6, while the second wave was not changed.

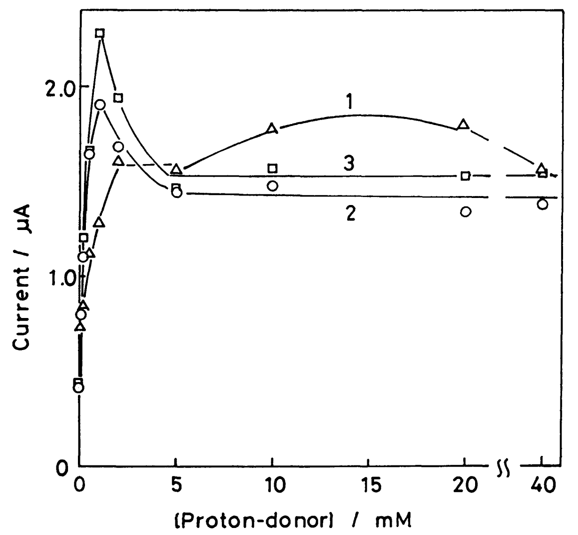


Fig. 2. Effect of proton-donor on the first wave height of S_4N_4. $[S_4N_4]=0.1$ mM, (1) phenol, (2) acetic acid, (3) monochloroacetic acid.

The increase in the wave height in the presence of proton donors suggested an increase in the *n*-value in the electrode precess. Figure 3 shows the *n*-values in the controlled potential coulometry with the Hg-pool electrode in the presence of proton donors. Without a proton donor, the *n*-value is 1.3, as mentioned above. However, the *n*-value increased to 8.2 with the addition of 5 mM of acetic acid to 0.1 mM of S_4N_4, and attained a constant value of 4.0 with 400 times acid, as much, when electrolyzed at -1.2 V. At -1.8 V, the *n*-value exceeded 10 with 2 mM of the acid and then decreased with more acid, but it never reached as law as 4.0.

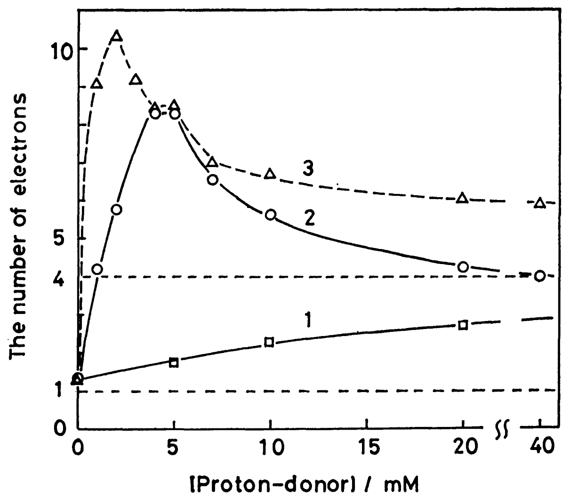


Fig. 3. The number of electrons in controlled potential coulometry. $[S_4N_4]=0.1$ mM, on Hg-pool electrode, (1) with phenol, potential at -1.2 V, (2) acetic acid, at -1.2 V, (3) acetic acid, at -1.8 V.

With phenol at −1.2 V, although the *n*-value increased from 1.3 toward a large value, a black solid was formed over the mercury electrode surface. The same black solid was also observed in the case of the presence of less than 2 mM of acetic acid.

The formation of $S_4(NH)_4$ was suggested by the *n*-value of 4 in the presence of acetic acid. The absorption spectrum of the solution electrolyzed at −1.2 V with 40 mM of acetic acid to 0.1 mM of S_4N_4 is shown in Fig. 4. $S_4(NH)_4$ gave a shoulder near 235 nm with a molar absorptivity of *ca.* 1.9×10^3 in acetonitrile, and the electrolyzed S_4N_4 solution showed the same spectrum as $S_4(NH)_4$. The yield was directly estimated to be about 90%, but the intensity of the shoulder was so small that an error may have occurred. Accordingly, the tetraimide produced was re-oxidized back to S_4N_4 at +1.2 V on the Pt electrode, and the absorbance at 250 nm was compared with that of the initial S_4N_4. The molar absorptivity of S_4N_4 at 250 nm was *ca.* 1.6×10^4. The yield in an experiment was 81%. As will be described in detail in the following section, the re-oxidation, that is, the oxidation of $S_4(NH)_4$ to S_4N_4 was established to proceed almost quantitatively. The formation of $S_4(NH)_4$ was confirmed also by voltammetry with a platinum electrode.

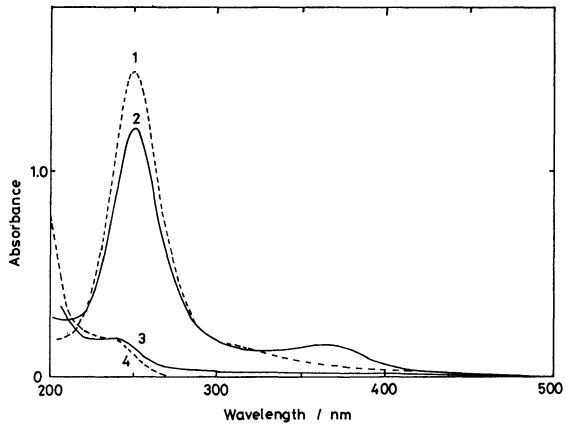


Fig. 4. Absorption spectra of the product from S_4N_4. (1) original 0.1 mM S_4N_4 solution. (2) oxidation (+1.2 V) product from (3), (3) reduction (−1.2 V) product from S_4N_4 with 40 mM acetic acid, (4) 0.1 mM $S_4(NH)_4$ solution. The absorption of the acid is corrected for (2) and (3).

For a higher concentration of S_4N_4 (*e.g.*, 0.2 or 0.5 mM), the tetraimide was obtained with about 400 times as much acid as S_4N_4. The product was isolated by being evaporated to dryness at room temperature; it was then washed with distilled water to remove the supporting electrolyte and the residues of the solvent and the acid. The IR spectrum of the product coincided with that of $S_4(NH)_4$ prepared chemically.

The above result can be summarized as follows: in the presence of a proper proton donor, S_4N_4 is reduced, and then the proton addition occurs, forming tetrasulfur tetraimide:

$$S_4N_4 + 4HA + 4e \longrightarrow S_4(NH)_4 + 4A^- \qquad (1)$$

Acetic acid is such a weak acid in acetonitrile ($pK_d=22.3$ by Kolthoff and Chantooni[11]) that it does not dissociate by itself to proton and acetate ions. The polarograms of the electrolyzed solution which formed $S_4(NH)_4$ showed a complicated anodic wave of mercury dissolution. This wave is thought to be caused by the acetate ion (A^-) or HA_2^-. The acetate ion is very active in an aprotic solvent. Kolthoff and Chantooni[11] have represented the constant of $K_{homo}=4.7\times10^3$ for the following homoconjugation reaction for acetic acid in acetonitrile: $A^- + HA \rightleftarrows AHA^-$

The fact that the yield of the tetraimide formation decreases, and the *n*-value far exceeds 4, with low concentrations of acetic acid suggests that the decomposition of S_4N_4 occurs as one of the side reactions. In the presence of about 40 times as much acetic acid as S_4N_4, the following reaction was confirmed to occur about 30% from the analysis of H_2S and NH_3:

$$S_4N_4 + 20HA + 20e \longrightarrow 4H_2S + 4NH_3 + 20A^- \qquad (2)$$

The anodic wave in the polarogram of the solution after the electrolysis which formed H_2S and NH_3 was much higher than that in the case of Eq. 1. The acetate ion thus produced was determined by means of amperometric titration with 0.1 M $HClO_4$–AN solution. Under the conditions in which the reaction of Eq. 1 proceeds fully, the electrolyzed solution consumed 4 equivalents of the perchloric acid. On the other hand, with 40 times as much acetic acid as S_4N_4, the electrolyzed solution consumed 8 equivalents, which corresponds to the *n*-value in coulometry.

Another evidence of the decomposition reaction is the fact that the solution turned blue in the course of the electrolysis when 2—5 mM of acetic acid or 5—20 mM of phenol was added to 0.1 mM of S_4N_4. The absorption spectra gave a peak at 613 nm, as is shown in Fig. 5, with acetic acid. (The spectra with 2 mM

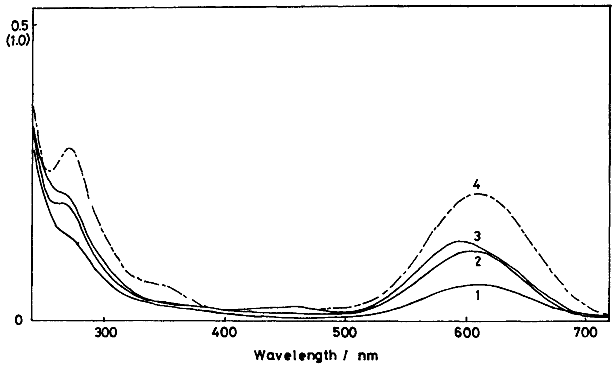
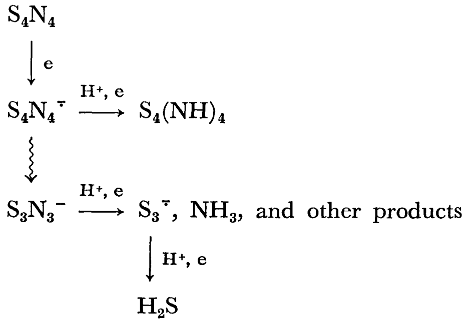


Fig. 5. Absorption spectra of S_4N_4 and S_8 solution in the course of electrolysis at −1.8 V[†]. (1) $[S_4N_4]=0.1$ mM, with acetic acid 5 mM, $Z=$*ca.* 6.9, (2) with acetic acid 3 mM, $Z=$*ca.* 7.7 (3) with acetic acid 2 mM, $Z=$*ca.* 7.8, (4) $[S_8]=0.05$ mM, $Z=2.66$.[††] The enlarged scale of absorbance should be used only for (4).

[†] As the decomposition reaction seemed to proceed more greatly at −1.8 V than −1.2 V according to Fig. 3, the results for −1.8 V are shown here. At −1.2 V, of course, the S_4N_4 solution gives same blue Species as −1.8 V.

[††] S_8 is reduced to $S_3^{\cdot-}$ at $Z=2.66$, see Ref. 2) in detail.

of the acid gave a peak at 590 nm at $Z^{***}=7.8$, but the peak shifted to 613 nm at $Z=8.2$). Here, the blue species was confirmed to be $S_3^{\cdot -}$, for the author and co-workers have previously established[2] that the blue species is $S_3^{\cdot -}$, which gives a peak at 613 nm in the electrolytic reduction of elemental sulfur in acetonitrile. The sulfur produced by the decomposition of S_4N_4 passes through the stable species, $S_3^{\cdot -}$, before being utterly reduced to H_2S.


Proposed reduction mechanism

Scheme 1.

All the experiments suggest the reduction mechanism shown in Scheme 1. $S_4(NH)_4$ would be formed through the $S_4N_4^{\cdot -}$ radical if the radical is surrounded by a large amount of proton donors, so the protonation to $S_4N_4^{\cdot -}$ occurs easily. The protonated species may be reduced further at the same potential, and the protonation and the reduction will continue until $S_4(NH)_4$ is formed. Without a proton donor, $S_4N_4^{\cdot -}$ decomposes to $S_3N_3^-$ very rapidly at room temperature. When the $S_4N_4^{\cdot -}$ is not protonated enough with a small amount of the proton donor, almost all the radicals may decompose to $S_3N_3^-$. The formation of NH_3 or H_2S may occur through the species of $S_3N_3^-$. It seems reasonable to regard the species of $S_3N_3^-$ as the intermediate of the decomposition reaction, because the electrolysis of $S_3N_3^-$ in the presence of a sufficient amount of the acid did not produce the tetraimide any more, but NH_3, H_2S, and others.

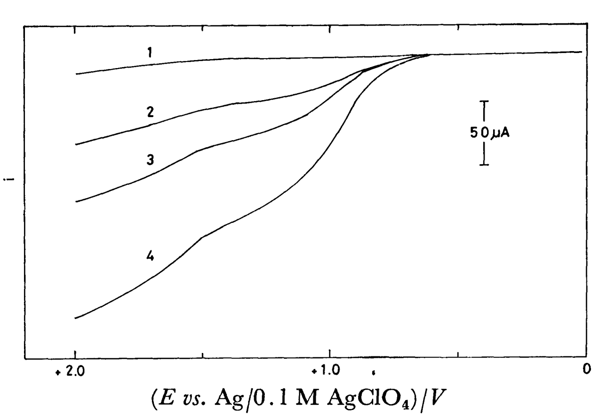


Fig. 6. Anodic waves of $S_4(NH)_4$ in acetonitile containing 0.1 M Et_4NClO_4 on the rotating platinum electrode. (1) 0, (2) 0.1, (3) 0.2, (4) 0.4 mM of $S_4(NH)_4$.

The Oxidation of $S_4(NH)_4$ and S_4N_4, and the Reduction of $S_4(NH)_4$. $S_4(NH)_4$ was oxidized in two steps on the rotating platinum electrode, as is shown in Fig. 6 (see also Table 1). The limiting current of the first wave was proportional to the concentration of the depolarizer in the range of 0.1—0.7 mM. The second wave was much smaller than the first wave. The controlled potential coulometry at +1.2 V on the Pt-gauze electrode gave the *n*-value of 4.0 ± 0.15 for the first wave. The absorption spectrum of the solution just after the electrolysis had a peak at 250 nm, which showed the formation of S_4N_4 in a 96% yield. About 4 equivalents of the hydrogen ion were detected in the solution by acid-base titration. Therefore, the following electrode reaction is proved to occur almost quantitatively at +1.2 V:

$$S_4(NH)_4 \longrightarrow S_4N_4 + 4H^+ + 4e \qquad (3)$$

The yield for this electrode reaction was largely dependent on the potential at which the tetraimide was oxidized. For example, the yield of S_4N_4 fell to 68% at +1.3 V, and S_4N_4 was little detected by means of the UV spectrum at +1.4 V. The absorbance at 250 nm decreased with the passage of time because the proton produced behaved as a strong acid in acetonitrile and reacted with S_4N_4 to decompose. The reaction of the proton may also be related to the fact that the analyzed concentration of the proton was smaller than the calculated value by a factor of more than 10% several hours after the experiment of the electrolysis. When perchloric acid of 5 mM was present in the S_4N_4–AN solution of 0.1 mM, the absorbance at 250 nm decreased by factors of 2.7 and 4.1% after 15 min and 1 h respectively. On the other hand, hydrochloric acid of 1 mM caused the absorbance of S_4N_4 to decrease to half after 5 h. Nair and Murthy[12] reported that, when the sulfur nitride allowed to react with anhydrous hydrogen iodide in nonaqueous solvent like carbon tetrachloride, all the sulfur was reduced to hydrogen sulfide and that all the nitrogen was converted into ammonia as per the equation:

$$S_4N_4 + 20HI \longrightarrow 4H_2S + 4NH_3 + 10I_2$$

As the half-wave potential of the second wave of the imide is close to that of the anodic wave of S_4N_4, as is shown in Table 1, the S_4N_4 derived from $S_4(NH)_4$ may be thought to be further oxidized at the second wave. However, the second wave height of $S_4(NH)_4$ is much smaller than the wave height of S_4N_4, which is probably due to the proton produced at once according to Eq. 3. S_4N_4 was, furthermore, oxidized with a *n*-value of *ca.* 4.0 by controlled-potential coulometry at +2.0 V on the Pt-gauze electrode. The absorption spectrum of the product gave a peak at 280 nm, which might be due to the SN^+ ion, judging from the *n*-value of 4. The species of SN^+ has already been isolated in the $SN^+\cdot AsF_6^-$ form.[13] S_4N_4 may be oxidized as follows:

$$S_4N_4 \longrightarrow 4SN^+(?) + 4e \qquad (4)$$

$S_4(NH)_4$ gave a reduction wave accompanied by a polarographic maximum on a dropping mercury electrode before the cation of the supporting electrolyte (Et_4N^+) was reduced. The wave height was proportional

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*** Z indicates the number of electrons added for S_4N_4.

to the concentration of the depolarizer of 0.1—0.5 mM, and the number of electrons involved in the reduction step was estimated to be unity from the wave height. However, the current showed unusual behavior in coulometry at −3.0 V with a Hg-pool electrode: The current initially decreased in the usual manner, the solution turning pale red-purple. Then the current increased again with the color disappearance just after the 1-electron was consumed, and subsequently went through a maximum. Finally, an *n*-value of near 6 was obtained. This result might suggest that $S_4(NH)_4^{\cdot-}$ is produced by the one-electron reduction of $S_4(NH)_4$ and decomposed by the further addition of electrons. A similar current maximum in coulometry has previously reported for elemental sulfur in acetonitrile.[2]

Conclusion

In a chemical preparation of the tetraimide, water or alcohol gives hydrogen to S_4N_4 to produce $S_4(NH)_4$. However, not even phenol can contribute to the formation of $S_4(NH)_4$; only acetic acid or a stronger acid can do so in an electrochemical reduction.

The author is indebted to Professor Taitiro Fujinaga for his invaluable advice and encouragement. Thanks are also due to Dr. Satoshi Okazaki for some valuable suggestions. The elemental analyses were made in the Laboratory for Organic Elemental Microanalysis Faculty of Pharmaceutical Science, Kyoto University. The author wishes to express his thanks to the Laboratory.

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