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Preliminary Results for the Voltammetric Reduction of 1,3-Tetrasulfur Dinitride (S_4N_2) and Heptasulfur Imide (S_7NH) in Acetonitrile

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Heptasulfur imide, S_7NH, was reduced in acetonitrile to form the monoanion, S_7NH^{1-}, which then disproportionated to form other products. The reduction occurred at an $E_{1/2}$ potential of about −1.4 volts relative to the Ag/0.01 M *$AgClO_4$ electrode. 1,3-Tetrasulfur diimide was found to undergo reduction to form both the monoanion, $S_4N_2^{1-}$, and the dianion, $S_4N_2^{2-}$. These reductions occurred at −1.43 and −2.03 volts, respectively.*

Introduction

We have investigated the reduction of the titled compounds by controlled potential voltammetry at the dropping mercury electrode, the stationary platinum electrode, and the rotating platinum electrode in the solvent, acetonitrile.

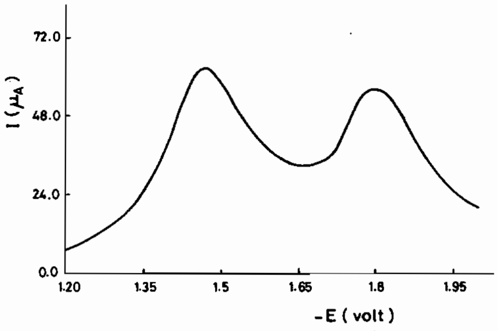

Fig. 1. Differential pulse voltammetric waves for 0.25 m*M* heptasulfur imide (S_7NH) at the stationary platinum wire electrode in acetonitrile and at 25 °C.

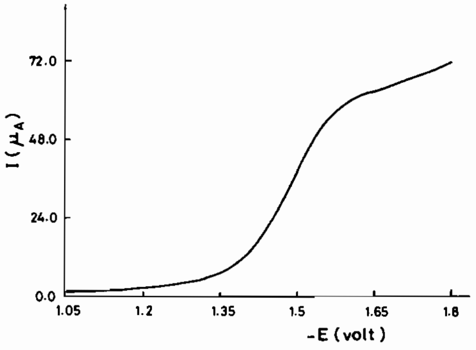

Fig. 2. D. C. voltammetric wave for 0.25 m*M* heptasulfur imide (S_7NH) at the rotating platinum wire electrode in acetonitrile and at 25 °C.

At 25 °C and within the concentration range of 0.25 m*M* to 0.60 m*M*, the reduction of S_7NH at the stationary platinum disk electrode and the rotating platinum disk electrode yielded two waves by differential pulse voltammetry (Fig. 1) and one wave at the rotating platinum wire electrode by dc voltammetry (Fig. 2). The current-potential data which result from the reduction at the rotating electrodes were analyzed by plotting E *vs* log $(I/I_L - I))$, where I and I_L are respectively the current and the limiting current in microamp, and E is voltage relative to Ag/0.01 *M* $AgClO_4$ electrode in acetonitrile. $E_{1/2}$ was then determined from the plots as the value of E at which $\log (I/(I_L - I)) = 0$. This procedure yielded – 1.460 V as the half-wave potential and – 0.074 V as the slope of the linear plot for the dc voltammetric wave. The values of $E_{1/2}$ estimated from the differential pulse data were −1.227 V and −1.495 V respectively, and the values of the corresponding slopes of the linear plots were −0.067 V and −0.058 V. In addition, the peak potentials for the reduction at the stationary electrode by differential pulse voltammetry occurred at −1.455 V and −1.785 V respectively. All potentials are relative to the Ag/0.01 *M* $AgClO_4$ reference electrode. One tenth molar tetra-n-butyl ammonium perchlorate was used as the supporting electrolyte.

The slopes of the log plots are close to the theoretical value of 2.303 RT/F (=0.0592 V) so that the waves may be considered to each correspond to the transfer of one electron. Furthermore, during the electrolysis in the potential region of the second

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wave, a blue solution was observed to form at the surface of the stationary disk electrode. This observation suggests that the reduction of S_7NH at the platinum electrode results in the formation of a blue colored species possibly S_4N^- which is formed when a solution of S_7NH is prepared in basic solvents such as dimethylformamide (1). Another possibility is the formation of S_3^- which is obtained when untreated hexamethylphosphotriamide (HMPTA) is used as solvent (1).

We propose that the single wave observed at the rotating disk electrode by dc voltammetry results from the following reduction process at the electrode:

$$S_7NH\ \text{(solvated)} + e^- \longrightarrow S_7NH^-\ \text{(solvated)}$$

The S_7NH^- may disproportionate in any number of ways as follows:

$$\begin{aligned} S_7NH^- &\longrightarrow 3/8S_8^- + S_4N^- + H^+ \\ &\longrightarrow 3/8S_8 + S_4N^{2-} + H^+ \\ &\longrightarrow S_3^- + S_4N^- + H^+ \end{aligned}$$

The two successive reduction waves may involve the following processes:

$$\begin{aligned} &S_7NH\ \text{(solvated)} + e^- \longrightarrow S_7NH^-\ \text{(solvated)} && \text{1st wave} \\ &S_7NH^-\ \text{(solvated)} \longrightarrow 3/8S_8^- + S_4N^- + H^+ && \\ &S_4N^- + e^- \longrightarrow S_4N^{2-} && \\ &\qquad \text{or} && \text{2nd wave} \\ &S_8^- + e^- \longrightarrow S_8^{2-} && \end{aligned}$$

An alternative is the following sequence of reactions:

$$\begin{aligned} &S_7NH\ \text{(solvated)} \longrightarrow S_7NH^-\ \text{(solvated)} && \text{1st wave} \\ &S_7NH^-\ \text{(solvated)} \longrightarrow S_3^- + S_4N^- + H^+ && \\ &S_3^- + e^- \longrightarrow S_3^{2-} && \\ &\qquad \text{or} && \text{2nd wave} \\ &S_4N^- + e^- \longrightarrow S_4N^{2-} && \end{aligned}$$

Further experiments are necessary to distinguish between these possibilities.

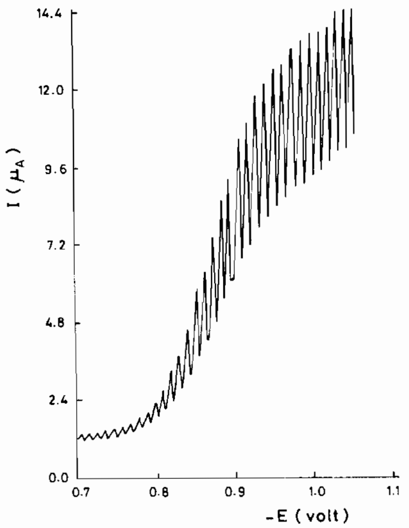

Fig. 3. Polarographic wave for 1.54 m*M* 1,3-tetrasulfur dinitride (S_4N_2) in acetonitrile at 25 °C. $E_{1/2} = -0.866$ V.

The reduction of 1,3-tetrasulfur dinitride was studied by polarography and by voltammetry at the rotating and the stationary platinum electrodes. The polarographic reduction of S_4N_2 was investigated at −20 °C and 25 °C using 0.1 *M* $NaClO_4$ as the supporting electrolyte. Within the potential range 0.0 V to −1.20 V the polarographic reduction of S_4N_2 yielded one wave (Fig. 3) at each temperature. The current-potential data obtained at each temperature were analyzed by plotting E *vs* log $(I/(I_d - I))$. The E *vs* log $(I/I_d - I))$ plots were linear. The $E_{1/2}$ value estimated from the data at 20 °C is −0.880 V and the corresponding value at 25 °C is −0.866 V. The slopes of the linear plots were −0.064 V and −0.068 V at the respective temperatures −20 °C and 25 °C.

Ilkovic equation calculations (2) of the diffusion currents gave the same values as the observed diffusion currents at both temperatures. This agreement between the calculated and the observed diffusion currents indicates that the electron transfer process at both temperatures involved the addition of one electron to S_4N_2 to form $S_4N_2^-$.

In 0.1 *M* tetra-n butyl ammonium perchlorate as the supporting electrolyte, the reduction of S_4N_2 at the rotating platinum wire electrode by dc voltammetry yielded one wave (Fig. 4) at 20 °C and 25 °C. The current-potential data were analyzed in the same manner as before. The values of $E_{1/2}$ at − 20 °C and 25 °C are respectively −1.485 V and −1.265 V and

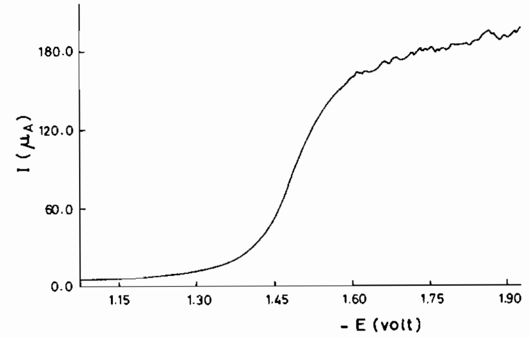

Fig. 4. D. C. voltammetric wave for 1.54 m*M* 1,3-tetrasulfur dinitride (S_4N_2) at the rotating platinum wire electrode in acetonitrile at 20 °C.

value of the corresponding slopes of the linear plots are –0.094 V and –0.183 V respectively. The high values of the respective slopes suggest that the reduction of S_4N_2 at the rotating platinum electrode at both temperatures proceeds irreversibly.

If it is assumed that the reductions at the rotating platinum wire electrode involves the addition of one electron to S_4N_2 as was determined for the dropping mercury electrode case, then the transfer coefficients are 0.53 at 20 °C, and 0.32 at 25 °C.

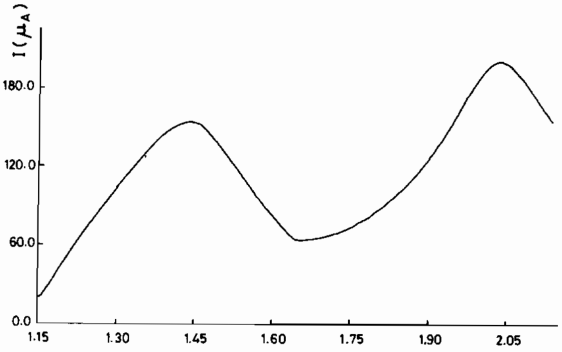

Fig. 5. Differential pulse voltammetric waves for 1.54 m*M* 1,3-tetrasulfur dinitride (S_4N_2) at the stationary platinum wire electrode in acetonitrile and at –20 °C.

Electrochemical reduction of S_4N_2 at –20 °C using the stationary platinum wire electrode yielded two reduction waves (Fig. 5). The peak potentials occurred at –1.428 V and –2.031 V respectively. The rate constants corresponding to the waves were, for the first wave 2.24×10^{-8} cm/sec and for the second wave 3.72×10^{-14} cm/sec. The rate constants were calculated relative to 0.511 V as the standard potential of Ag/0.01 *M* $AgClO_4$ in acetonitrile at 25 °C. Since the wave heights were approximately the same, and if the first wave ($E_{1/2} = -1.428$ V) is identified with the wave observed at rotating platinum electrode, then the reduction of S_4N_2 at the stationary electrode may be considered to occur in two steps to form the monoanion and the dianion:

$$S_4N_2\text{ (solvated)} + e^- \longrightarrow S_4N_2^-\text{ (solvated)}$$

$$S_4N_2^-\text{ (solvated)} + e^- \longrightarrow S_4N_2^{2-}\text{ (solvated)}$$

Experimental

Acetonitrile (Mallinckrodt ACS reagent grade) was purified based on recommended methods in the literature [3, 4]. The solvent purity was monitored by NMR, UV cutoff, and conductance measurements. Product showing a single NMR peak, and a conductance less than 10^{-7} ohm^{-1} cm^{-1} was considered to be pure.

Heptasulfur imide (S_7NH) was prepared by standard methods [5]. Tetrasulfur dinitride (S_4N_2) was prepared and stored according to procedure developed by Adkins [6]. Reagent grade anhydrous sodium perchlorate and silver perchlorate (G. F. Smith Chemical Co., Columbus, Ohio) were used without further purification except for drying for two hours at 110 °C.

A model 364 Polarograph (Princeton Applied Research Corporation, Princeton, N.J.) was used in combination with a Hewlett Packard X-Y Recorder, Model 7035 B. A three-electrode cell was employed. The electrochemical cell was made from 100 ml three-neck flask to which a fourth neck was attached. Provision was made for the cell solution to be out of contact with the atmosphere during transfer from the dry box. Oxygen free nitrogen was used to purge the solution. The polarographic results reported here were obtained using a column height of 140 cm (average drop time of 2 seconds). The capillary used was obtained from Sargent-Welch Equipment Co., Chicago, Illinois. The working platinum disk electrode was made by sealing a thin platinum foil into a glass tubing to give an exposed disk surface area of 0.127 cm^2. The electrode was rotated at a constant speed of 600 rpm with the aid of the Sargent-Welch constant speed synchronous rotator. The 25 °C temperature was maintained with an oil bath. The –20 °C temperature was obtained with CCl_4 – dry ice slush bath.

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