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# The Voltammetric Reduction of Tetrasulfur Tetranitride in Non-Aqueous Solvent Systems*

J. W. TWEH and A. G. TURNER**

*Department of Chemistry and Chemical Engineering, University of Detroit, Detroit, Mich. 48221, U.S.A.*

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*The reduction of tetrasulfur tetranitride at the dropping mercury and platinum electrodes in the solvents acetonitrile, dimethylsulfoxide and pyridine has been studied at different temperatures. In acetonitrile three polarographic waves are observed, one of which corresponds to the formation of the tetrasulfur tetranitride anion. A single wave was observed in dimethylsulfoxide corresponding to $S_4N_4^-$, enthalpy of activation 23.8 kcal/mol. Two waves were observed in pyridine corresponding to the formation of $S_4N_4^-$ and possibly the denegative anion, $S_4N_4^{2-}$.*

## Introduction

Tetrasulfur tetranitride has been observed to undergo a series of color transformations when treated with potassium metal in dimethoxyethane at room temperature [1]. The changes have been ascribed to the formation of negative ions in the sequence:

$$S_4N_4 \xrightarrow{e^-} S_4N_4^- \xrightarrow{e^-} S_4N_4^{2-} \xrightarrow{e^-}$$

$$S_4N_4^{3-} \xrightarrow{e^-} S_4N_4^{4-}$$

This is consistent with molecular orbital calculations which show that there are two low-lying vacant molecular orbitals of E symmetry which are antibonding with respect to the two sulfur atoms [2]. *In situ* ESR experiments gave successive spectra consisting of nine, five, and three lines indicating that some of the reduction products are radical anions. The nine, five, and three-line spectra result respectively from electron interaction with four equivalent, two equivalent, and one equivalent nitrogen atoms [3]. Furthermore, it has been concluded that below 0 °C, the nine-line spectrum is attributable to $S_4N_4^-$ while the presence of the nine-line spectrum above 0 °C is due to further reduction products of $S_4N_4^-$ in which all four nitrogen atoms are equivalent [4]. Above 0 °C and without further reduction, the $S_4N_4^-$ ion decomposes into fragments which give rise to five and three-line spectra [4]. In more recent electrochemical studies of $S_4N_4$ at −25 °C, the initial reduction step has been shown to be a one-electron process by cyclic voltammetry [5] and by coulometry [6].

There does not seem to be any convincing evidence for the direct addition of more than one electron to $S_4N_4$ [7]. The following reaction has been carried out and the sodium salt is thought to contain the $S_4N_4^{4-}$ anion [8]:

$$6(C_6H_5)_3CNa + 2S_4N_4H_4 \rightarrow$$

$$Na_2H_2S_4N_4 + Na_4S_4N_4 + 6(C_6H_5)_3CH$$

The validity of the above reaction concerning the formation of $H_2S_4N_4^{2-}$ and $S_4N_4^{4-}$ has been questioned by other workers [4, 9].

The electrochemical techniques of polarography and voltammetry at the stationary and rotating disk electrodes can provide direct evidence for the stepwise formation of $S_4N_4^-$, $S_4N_4^{2-}$, $S_4N_4^{3-}$, and $S_4N_4^{4-}$ from the number of reduction waves and the number of electrons transferred. The investigation of the reduction process as a function of temperature can yield values of enthalpy of activation the magnitude of which may serve to determine whether the electron transfer involves bond rupture.

With this expectation, we have undertaken to investigate the electrochemical reduction of $S_4N_4$ at the dropping mercury electrode (dme) and the platinum electrode in the solvents acetonitrile, dimethylsulfoxide (DMSO), and pyridine at different temperatures.

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**Author to whom correspondence should be addressed.

## Experimental

### *Chemicals*

Tetrasulfur tetranitride was prepared according to standard methods [10]. The crude product was purified by recrystallization from benzene melting point, 180 °C. Reagent grade acetonitrile was purified by the procedure of Coetzee *et al.* [11]. The solvent purity was monitored by NMR, UV cutoff, and conductance measurements. Products showing a single NMR peak, and a conductance less than $10^{-7}$ $\text{ohm}^{-1}$ $\text{cm}^{-1}$ was considered to be pure. Dimethylsulfoxide was purified based on recommended methods in the literature [12]. The reagent DMSO was shaken with type 4A molecular sieves for two days then decanted into a flask containing calcium hydride. It was then warmed under dry nitrogen and reduced pressure while in contact with the base to decompose any dimethylsulfide present [13]. The solvent was distilled slowly under nitrogen and reduced pressure. The purity of the solvent was monitored by observing a single peak of the DMSO methyl protons which appeared at about 7.5 ppm [14]. Pyridine was purified according to the following procedure [15, 16]: the analytical reagent grade pyridine was shaken with activated Linde molecular sieves type 4A and was left standing for one day. The solvent was decanted into a flask containing solid potassium hydroxide and was left standing for one hour and then distilled into a flask containing barium oxide. Subsequently, the distillate was refluxed over the barium oxide for one hour and then slowly distilled. This treatment produced colorless solvent which showed negligible infrared absorption peaks for water at 3450 $\text{cm}^{-1}$ [16].

Reagent grade anhydrous sodium perchlorate, lithium perchlorate, and silver perchlorate were obtained from G. Frederick Smith Chemical Company, Columbus, Ohio. These chemicals were used without further treatment except for drying in the oven. They were always stored over Drierite in a desiccator. Mercury was purified according to standard methods [17].

### *Instruments*

The voltammetric data were recorded with the Princeton Applied Research Corporation Model 364 Polarographic Analyzer in conjunction with a three-electrode cell and Hewlett-Packard X–Y Recorder Model 7035 B. The reference electrode was a silver wire sealed into a male ground glass joint. The glass capillaries for the dme were obtained from Sargent-Welch Equipment Co., Chicago, Illinois. A constant temperature bath was used at 25 °C. The –20 °C temperature was obtained with a $CCl_4$– dry ice slush bath. The –38 °C temperature was obtained with a dimethyl formamide–dry ice slush bath. A Leeds and Northrup Student Potentiometer was used in all potentiometric measurements.

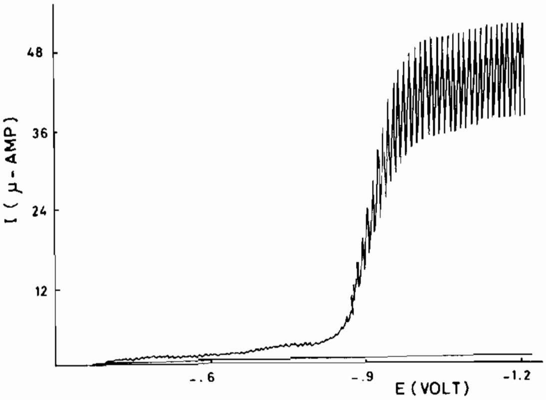

Fig. 1. Polarographic wave for tetrasulfur tetranitride (2.5 m*M*) in acetonitrile and at 25 °C. $E_{1/2}$ = –0.890 V (after correction for IR drop).

The polarographic results were obtained at mercury column heights of 138 cm, 78 cm, and 43 cm. The drop life at each column height was essentially constant within the potential range from 0.00 V to –1.00 V. Therefore, average values of the dropping mercury electrode characteristics were used in all calculations where they were required.

The diffusion coefficients of tetrasulfur tetranitride were calculated using the Stokes–Einstein relation. In these calculations, 1.78 Å was used as the radius of $S_4N_4$ and the viscosity of the pure solvent was used. The values obtained for acetonitrile are: –20 °C, 1.86 × $10^{-5}$ $\text{cm}^2$/sec; 0 °C, 2.54 × $10^{-5}$ $\text{cm}^2$/sec; 25 °C, 3.60 × $10^{-5}$ $\text{cm}^2$/sec.

The Ag/0.01 *M* $AgClO_4$ was used as the reference electrode throughout this investigation. The formal potential of this couple in each solvent was estimated using its measured values [15, 18, 19] and the Debye-Huckel calculations for strong electrolytes. The values at 25 °C and 0.1 *M* supporting electrolyte are: Acetonitrile: 0.508 V; DMSO: 0.405 V; Pyridine: 0.502 V. These values were also employed at temperatures other than 25 °C.

## Results and Discussion

### *The $S_4N_4$–Acetonitrile System*

Within the potential range 0.00 V to –1.50 V and over the concentration range 0.5 m*M* to 4.9 m*M*, the reduction of $S_4N_4$ solutions yielded three waves at –20 °C, 0 °C and 25 °C (Figs. 1 and 2). Tenth molar sodium perchlorate was used as supporting electrolyte. The polarographic half-wave potentials ($E_{1/2}$) are –0.380 V, –0.670 V, and –0.890 V respectively. The polarographic diffusion currents for

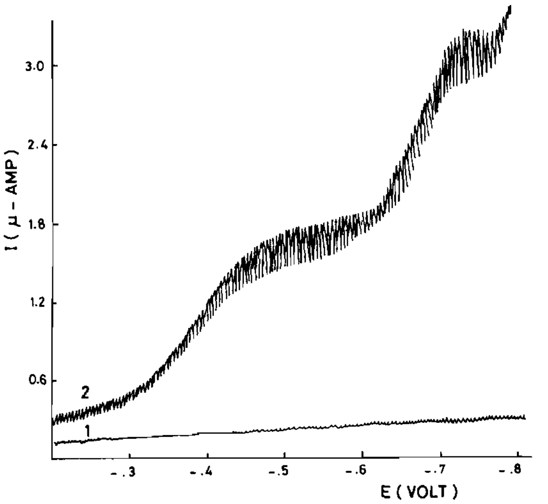

Fig. 2. Polarographic waves for tetrasulfur tetranitride (2.5 m$M$) at 25 °C. $E_{1/2}$ = –0.380 V and $E_{1/2}$ = –0.670 V.

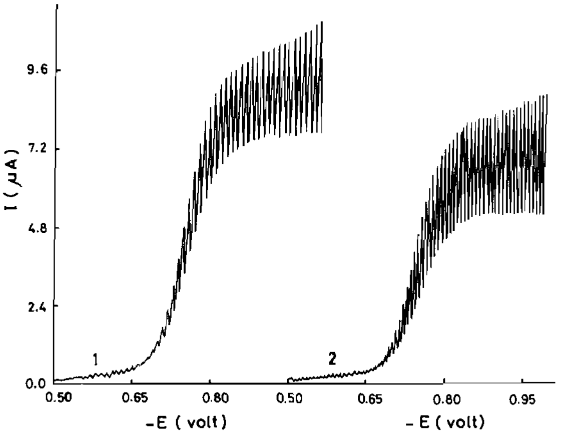

Fig. 3. Polarographic waves for tetrasulfur tetranitride (2.0 m$M$) in dimethylsulfoxide at 25 °C. $E_{1/2}$ = –0.731 V (after correction for IR drop). 1. Height of mercury column = 138 cm. 2. Height of mercury column = 78 cm.

the wave occurring at $E_{1/2}$ = –0.890 V were consistently larger then those of the other two waves by a factor of ten; whereas the diffusion currents of the waves at $E_{1/2}$ = –0.380 V and $E_{1/2}$ = –0.670 V were approximately the same. The diffusion currents of the waves at $E_{1/2}$ = –0.380 V and $E_{1/2}$ = –0.670 V did not show direct proportionality with the concentration of $S_4N_4$ in all solutions investigated and the waves themselves could be obtained only at high currents sensitivity. Equally important, the observed diffusion currents for the wave at $E_{1/2}$ = –0.890 V and diffusion currents calculated from a form of the Ilkovic equation were approximately the same. The calculated values were slightly larger than the observed values. This agreement is considered as evidence that the wave occurring at $E_{1/2}$ = 0.890 V involves the transfer of one electron. On the other hand, one must invoke the involvement of at least ten electrons if similar agreement between the observed and calculated diffusion currents is to be achieved for the waves at $E_{1/2}$ = –0.380 V and $E_{1/2}$ = –.0.670 V.

The current-potential data were analyzed by plotting E *vs.* $\log(I/I_d - I)$). The half-wave potentials were determined from the linear plots as the value of E at which $\log (I/(I_d - I)) = 0$. If the wave which occurs at $E_{1/2}$ = –0.890 V involves the addition of one electron to $S_4N_4$, then the transfer coefficient can be evaluated from the slope of the linear plots. This calculation yielded 0.87 ± 0.0 as the average transfer coefficient for all temperatures investigated. With the average value of the transfer coefficient, the values of the forward heterogeneous rate constants were calculated relative to the formal potential of Ag/0.01 *M* $AgClO_4$ reference electrode in acetonitrile. The enthalpy of activation was calculated from the slope of a plot of $-\log k_{f,h}$ *vs.* 1/T. A value of 5.35 kcal/mole was obtained.

The investigations of Williford *et al.* [5] and Brown [6] have shown that the first wave ($E_{1/2}$ = –0.380 V) involved the transfer of one electron. If this finding applies in this case for the wave which occurs at $E_{1/2}$ = –0.380 V, then the estimated transfer coefficient is 0.67 ± 0.03 as determined from the slopes of the linear plots for all temperatures.

Since the diffusion currents are approximately the same for the waves which occur at $E_{1/2}$ = –0.380 V and $E_{1/2}$ = –0.670 V, then one electron must be involved in the rate determining step for the electrode process which yielded the second wave. Consequently, the average transfer coefficient is 1.19 ± 0.22 for all temperatures investigated. This rather high value of the transfer coefficient is probably due to the effects of adsorption exhibited by the wave. The enthalpy of activation could not be calculated for the wave because the estimated rate constants were essentially temperature independent.

In conclusion, the polarographic reduction of $S_4N_4$ in acetonitrile yielded three waves. The values of diffusion currents do not indicate that the three waves result from the successive reduction of the same electroactive species, as $S_4N_4$. The positions of the first two waves are in agreement with those previously observed by other investigators. The third wave which appears at $E_{1/2}$ = –0.890 V has not been reported before and we believe that this wave results from the addition of one electron to $S_4N_4$, whereas the first two waves result from the successive reduction of a species that is derived from the reaction of $S_4N_4$ with another chemical species in the system, *i.e.* acetonitrile, *etc.* This species may contain the $S_4N_4$ nucleus and is very stable. The magnitudes of the enthalpy of activation suggest that the electron transfer to $S_4N_4$ to $S_4N_4^-$ does not involve a bond rupture. We did not observe any change

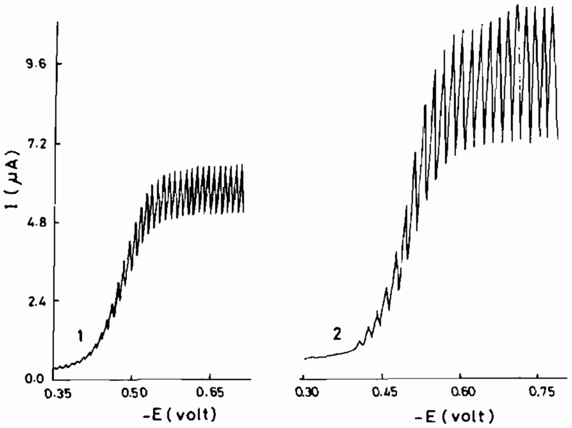

Fig. 4. Polarographic waves for tetrasulfur tetranitride (2.3 m*M*) in pyridine. $E_{1/2}$ = −0.491 V. 1. T = −38 °C; 2. T = 0 °C.

in coloration of the already yellow $S_4N_4$ solutions.

### *The $S_4N_4$–DMSO System*

The polarographic reduction of $S_4N_4$ over the concentration range 1.9 m*M* to 4.1 m*M* and from 20 °C to 55 °C yielded one well-defined wave at each of the temperatures investigated (Fig. 3). Tenth molar sodium perchlorate was used as supporting electrolyte. The slopes of the E *vs.* $\log(I/(I_d - I))$ plots were sufficiently close to the theoretical values at the various temperatures that the reduction of $S_4N_4$ which yielded the wave may be considered to involve the transfer of one electron in the rate determining step. Further evidence for the one electron involvement is indicated by the excellent agreement obtained between the observed and calculated diffusion currents using a form of the Ilkovic equation. Over the temperature range of 20 °C to 55 °C and relative to the reference potential of 0.405 V, the forward heterogeneous rate constant varied from $1.12 \times 10^{-9}$ cm/sec to $7.58 \times 10^{-8}$ cm/sec from which the enthalpy of activation was calculated to be 23.8 kcal/mole.

In summary, the polarographic reduction of $S_4N_4$ in DMSO yielded one wave which occurred at $E_{1/2}$ = −0.731 V with transfer coefficient of 1.04 ± 0.03 and involved the addition of one electron to $S_4N_4$ to form perhaps $S_4N_4^-$.

### *The $S_4N_4$–Pyridine System*

The electrochemical reduction of $S_4N_4$ was investigated in pyridine solutions ranging from 1.2 m*M* to 4.4 m*M* at −38 °C, −20 °C, 0 °C, 25 °C, and 47 °C using 0.1 *M* $LiClO_4$ 0.1 *M* $NaClO_4$ as supporting electrolyte. Within the potential range of 0.00 V to −1.50 V, the reduction at the dme yielded most often one well-defined wave which exhibited extensive broadening at more negative potential beyond the diffusion plateau (Fig. 4). A second ill defined wave appeared between −1.05 V to −1.50 V with an $E_{1/2}$ = −1.310 V. The application of the Ilkovic equation indicates that the waves involved the transfer of one electron. The position of the first wave occurs at $E_{1/2}$ = −0.491 V with an estimated transfer coefficient of 0.84 ± 0.06. The heterogeneous rate constants for the first wave ranged from $0.60 \times 10^{-3}$ cm/sec at −38 °C to $1.93 \times 10^{-3}$ cm/sec at 47 °C from which the enthalpy of activation was calculated to be 4.82 kcal/mole. A similar analysis cannot be carried out for the second wave because it was only observed at 25 °C and did not appear at the other temperature.

In summary, the polarographic reduction of $S_4N_4$ results in two waves at 25 °C indicating the formation of the monoanion and possibly the dianion. The formation of the dianion probably involves an irreversible electrode process.

In conclusion, tetrasulfur tetranitride can be reduced at the dme electrode to the monoanion in acetonitrile, DMSO, and pyridine solutions. The values of the enthalpy of activation suggest that the addition of one electron does not involve bond rupture. No direct evidence for further reduction of the tetrasulfur tetranitride anion to a more negatively charged species (*e.g.* $S_4N_4^{2-}$, $S_4N_4^{2-}$, etc.) can be found in the solvents investigated.

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