

ELECTROCHEMISTRY IN LIQUID SULFUR DIOXIDE

PART II. OXIDATION OF THIANTHRENE IN THE PRESENCE OF WATER AND ANISOLE

LAWRENCE A. TINKER* and ALLEN J. BARD**

Department of Chemistry, The University of Texas at Austin, Austin, TX 78712 (U.S.A.)

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ABSTRACT

The reaction of electrochemically generated thianthrene radical cation (TH^{•+}) and dication (TH²⁺) with anisole (AnH) and water in liquid sulfur dioxide was investigated by cyclic voltammetry and coulometry. In contrast to behavior in other aprotic solvents, TH^{•+} did not react with either nucleophile on the coulometric time scale (~1 h). However, TH²⁺ reacted rapidly as shown by the formation of a pre-peak on the TH^{•+}/TH²⁺ CV wave. With AnH, this pre-peak was associated with the formation of a (TH-AnH)²⁺ complex in an EC-type reaction ($k \sim 10^8 \text{ M}^{-1} \text{ s}^{-1}$) leading to the final product, (TH-An)^{•+}ClO₄⁻. The reaction of TH²⁺ with water was first order in water and dication ($k_{app} \sim 177 \text{ M}^{-1} \text{ s}^{-1}$) and led to formation of the product thianthrene monoxide. The high stability of TH^{•+} in SO₂ was attributed to the low temperature (-40°C) and high purity of the medium, as well as the strong interaction between SO₂ and the nucleophiles.

INTRODUCTION

A previous study [1] on the oxidation of thianthrene (TH) in liquid sulfur dioxide demonstrated that stable solutions of both the radical cation and dication could be electrogenerated in this solvent. Since the reactions of these species with nucleophiles in such solvents as acetonitrile and dichloromethane have been of considerable interest [2-7], we undertook similar studies in liquid SO₂.

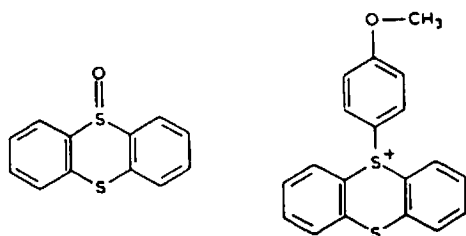
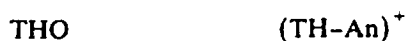
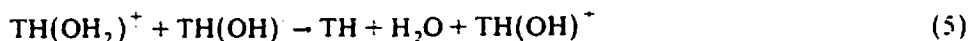
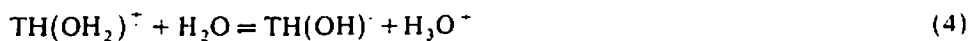
Past work has led to several different reaction mechanisms for these reactions. For example, Shine and Murata [2] proposed that the reaction of thianthrene radical cation (TH^{•+}) with water involved a disproportionation to the reactive dication (TH²⁺) which then reacted, according to eqns. (1) and (2):



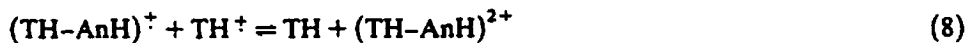
* Present address: Ballard Research, Inc., North Vancouver, B.C., Canada.

** To whom correspondence should be addressed.

Parker and Ebersson [3] later presented evidence indicating that the hydroxylation proceeds via the direct reaction of the radical cation with water and that disproportionation was not a likely pathway. More recently, Evans and Blount [4] reported results which support a general "half-regeneration" mechanism (eqns. 3-6) involving formation of a radical cation-nucleophile adduct with eqn. (5) being the rate-determining step:



In related studies, Silber and Shine [5] reported that the anisylation of $\text{TH}^{\cdot+}$ produced a sulfonium salt, $(\text{TH-An})^+$, in a reaction that was second order in radical cation and inhibited by unoxidized substrate. Although this evidence supported a disproportionation mechanism (eqns. 1 and 2) with anisole (AnH) instead of H_2O as nucleophile, more recent work by Parker and co-workers [6] showed that the disproportionation reaction was probably not an important pathway and a half-regeneration reaction pathway involving adduct formation between $\text{TH}^{\cdot+}$ and AnH was proposed (eqns. 7-9):



More recently Dusserre and Genies [7] investigated the $\text{TH}^{\cdot+}$ -AnH reaction in MeCN and considered five possible reaction mechanisms. They concluded that the half-regeneration mechanism gave a good fit to the experimental data.

Interest in the electrochemical properties of substances in SO_2 [1,8] and its very different properties compared to MeCN and CH_2Cl_2 suggested that a study of these same reactions in SO_2 would be of interest. We show here that $\text{TH}^{\cdot+}$ does not react on the time-scale ~ 1 h with either H_2O or AnH, but that a rapid reaction of the TH^{2+} with these nucleophiles occurs.

EXPERIMENTAL

The general experimental procedures along with solvent purification and handling techniques, and a detailed description of the electrochemical cell used has been reported previously [1].

Thianthrene (Aldrich Chemical Co., Milwaukee, WI, 97%) was recrystallized from benzene and sublimed prior to use. Anisole (Matheson, Coleman and Bell) was used without further purification. For experiments in which water was used as the nucleophile, distilled water was degassed with nitrogen prior to use. Liquid samples used as nucleophiles (e.g. H₂O, AnH) were introduced to the cell by injection with a microliter syringe through a side port fitted with a rubber septum.

All electrochemical measurements were performed at -40°C with tetra-*n*-butylammonium perchlorate (TBAP) as supporting electrolyte using a P.A.R. Model 173 (Princeton Applied Research, Princeton, NJ) potentiostat employing positive feedback for *iR* compensation, a Model 179 digital coulometer and a Model 175 signal programmer. Voltammograms obtained for scan rates < 500 mV s⁻¹ were recorded on a Model 200 X-Y recorder (Houston Instruments, Austin, Texas). Those at scan rates of 500 mV s⁻¹ and greater were recorded on a Model 564 storage oscilloscope (Tektronix, Inc., Beaverton, OR).

Thianthrene-5-oxide (THO) was prepared by the method of Fries and Voght [9] and recrystallized from methanol. THO formed during bulk electrolysis at +0.8 V of 4.8 mM TH in the presence of excess water was isolated and identified as follows. The solvent was allowed to boil off leaving a mixture of supporting electrolyte, product and starting material. The electrolyte in this experiment, tetramethylammonium tetrafluoroborate (TMABF₄), was removed by dissolving it in warm water and filtering off the residue of organic material. This material was then recrystallized from methanol and thin-layer chromatography was used to separate TH and THO. The TH, recrystallized from benzene, had a mp of 154-155°C (lit. value 156°C). The THO (mp 141-142°C; lit. 143°C) was identified by its ultraviolet spectrum in MeCN ($\lambda_{\max} = 241$; $\epsilon = 1.83 \times 10^4$) as compared to that of authentic THO, and by infrared spectroscopy (S-O band, 1078 cm⁻¹).

RESULTS

Reaction of TH with AnH

Typical voltammograms for the oxidation of TH at a platinum disk electrode (area 0.074 cm²) in the presence of different amounts of AnH are shown in Fig. 1a-e. The voltammogram observed in the absence of any AnH (Fig. 1a) shows only the waves for the reversible generation of TH^{•+} (wave O₁/R₁) and TH²⁺ (wave O₂/R₂). The addition of a small amount of AnH ([AnH]/[TH] = 0.2) did not affect the first charge-transfer reaction (O₁/R₁). However, a pre-peak (O'₂) was produced at the foot of the O₂/R₂ wave, and a new oxidation wave, O₃, was observed at a more positive potential. On the reverse scan, the R₂ wave was still visible and a new

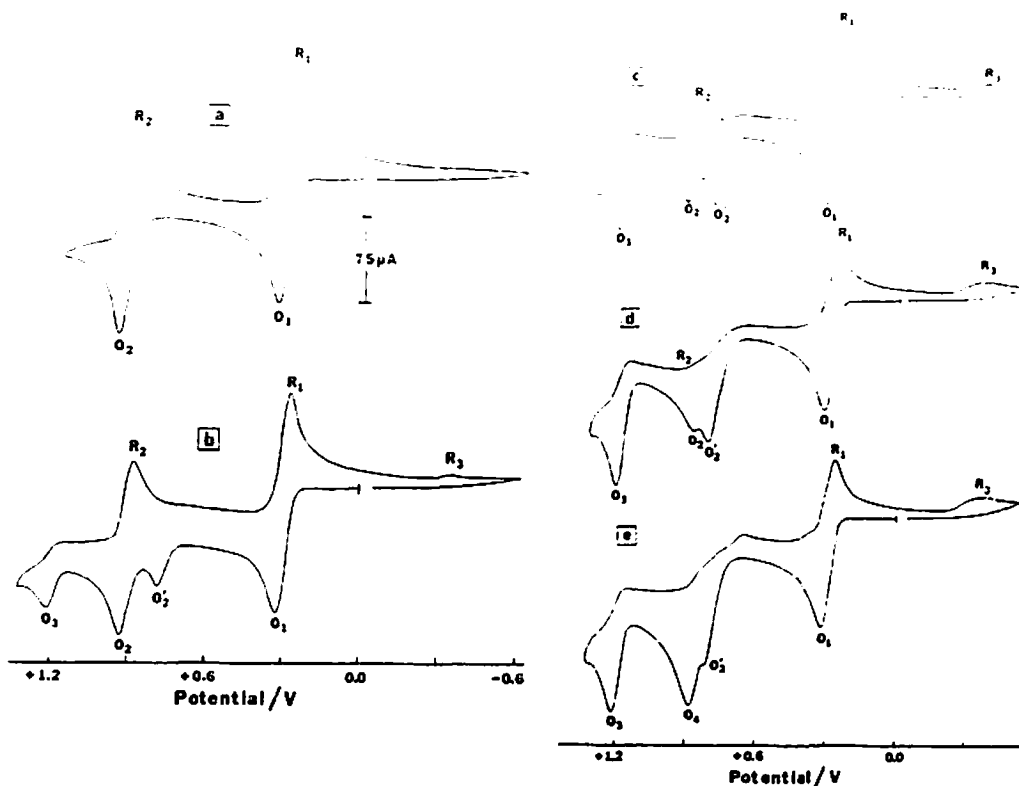


Fig. 1. Cyclic voltammograms of 5 mM TH at Pt electrode in 0.1 M TEAP-liquid SO_2 solution with different AnH concentrations. $[\text{AnH}]/[\text{TH}]$: (a) 0.0; (b) 0.2; (c) 0.4; (d) 0.8; (e) 1.0; $v = 100 \text{ mV s}^{-1}$.

small reduction wave, R_3 , appeared. As more AnH was added (Fig. 1c), the height of the pre-peak, O_2' , increased at the expense of the $\text{TH}^{\dot{+}}$ oxidation wave O_2 . When the potential scan was reversed after O_1 , the R_1/O_1 peak current ratio (i_{pc}/i_{pa}) remained equal to unity, and no change in peak potentials was observed. At an $[\text{An}]/[\text{TH}]$ ratio of 0.8 (Fig. 1d) the O_2/R_2 couple was barely visible. Further addition of AnH ($[\text{AnH}]/[\text{TH}]$ slightly greater than unity) had no effect on the height of the pre-peak. However, a new wave, O_4 , corresponding to the oxidation of excess AnH appeared (Fig. 1e). The characteristics of the O_1/R_1 wave remained unchanged, even in the presence of an excess of AnH.

Controlled potential coulometry (CPC) carried out at +0.50 V with complete oxidation of TH to $\text{TH}^{\dot{+}}$ in the presence of AnH ($[\text{AnH}]/[\text{TH}] \approx 1$) produced a dark purple solution with an n_{app} (number of faradays per mole of TH) of 0.98. The radical cation concentration was monitored by the cyclic voltammetric reduction of $\text{TH}^{\dot{+}}$. The i_{pc} was the same as in the absence of AnH and remained unchanged for time periods of at least 1 h. CPC carried out to reduce completely the $\text{TH}^{\dot{+}}$ solution

gave $n_{app} = 0.97$ and the O_1 wave returned to essentially its original height. Alternatively, coulometric generation of the radical cation followed by addition of an excess of AnH again showed no decrease in the concentration of $TH^{\cdot+}$. Clearly, $TH^{\cdot+}$ is highly stable in the presence of AnH in liquid SO_2 .

The dication, TH^{2+} , however, reacted rapidly with AnH as shown by the appearance of the pre-peak, O'_2 . The observation of a pre-peak in voltammetry [10] can be caused by two possible mechanisms. The first involves an initial pre-equilibrium between substrate and nucleophile, forming a product which is easier to oxidize than $TH^{\cdot+}$ itself, e.g. eqns. (7)–(9). However, this mechanism would result in changes in the O_1/R_1 waves because the reaction in eqn. (10) would affect the $TH^{\cdot+}$ concentration (i.e. the reactions at the first wave would be an EC sequence) [11]. Another mechanism which gives the same voltammetric results is an ECC reaction between the dication and nucleophile (eqns. 10–12):



The pre-peak is caused by the rapid removal of TH^{2+} in eqn. (11) which leads to further oxidation of substrate and additional anodic current to maintain the $[TH^{2+}]/[TH^{\cdot+}]$ ratio at the level required by the Nernst equation. This case has been treated for stirred solution voltammetry [12] and cyclic voltammetry [11,13]. When the nucleophile-to-substrate ratio is less than unity, the theoretical current-potential curves for the general E_rC_i reaction scheme with the following chemical reaction very fast, show that the pre-peak current is limited by the diffusion of AnH. As long as the diffusion coefficients of the species involved are approximately equal, the sum of the two peak currents, $i_p(O'_2) + i_p(O_2)$ is practically constant. As the concentration of AnH is increased, the peak height of O'_2 increases until, at an $[AnH]/[TH]$ ratio of about unity, it becomes limited by diffusion of $TH^{\cdot+}$. A plot of the experimental ratio $i_p(O'_2)/i_p(O_2)$ where $i_p(O_2)$ is the peak height of O_2 prior to addition of AnH vs. $[AnH]/[TH]$, shown in Fig. 2, generally follows this behavior. When $[AnH]/[TH] \sim 1.0$ only the oxidation peak O'_2 and peak O_4 were observed. The rate constant k_3 , for the reaction between TH^{2+} and AnH (eqn. 14) was estimated for the case where $[AnH]/[TH] = 2$, assuming, as a first approximation, that the reaction could be considered pseudo-first order in AnH [11,13]. Higher concentration ratios could not be employed because the direct oxidation of AnH in wave O_4 masks the wave of interest, O'_2 . Based on the peak shift of O'_2 from O_2 as a function of scan rate, one can estimate $4 \times 10^6 M^{-1} s^{-1} < k_3 < 10^8 M^{-1} s^{-1}$.

CPC carried out to oxidize completely the mixed solution ($[AnH]/[TH] = 1$) at the potential of the pre-peak wave gave $n_{app} = 2.01$. Voltammetric analysis after coulometry showed one oxidation wave corresponding to O_3 , no other oxidation waves and one reduction wave, R_3 , corresponding to proton reduction (Fig. 3). The

peak height of O_3 was 85% of the original height of O_2 , showing considerable conversion to a stable product. This product has been identified as the sulfonium salt produced from addition of AnH to sulfur with subsequent bond formation and expulsion of a proton from the AnH ring, leaving $(TH-An)^+ ClO_4^-$ [6b].

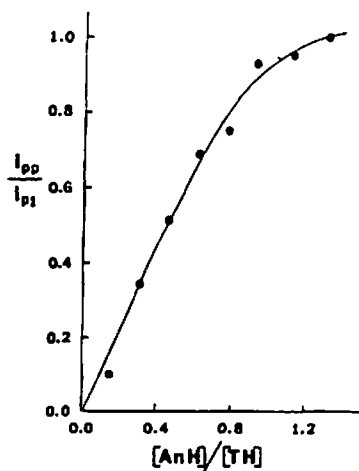


Fig. 2. Ratio of peak current for pre-peak to that for oxidation of TH vs. $[AnH]/[TH]$.

Reaction of TH with water

Typical cyclic voltammograms observed for the oxidation of TH upon addition of water to the SO_2 solution (Fig. 4) are characterized by the disappearance of R_2

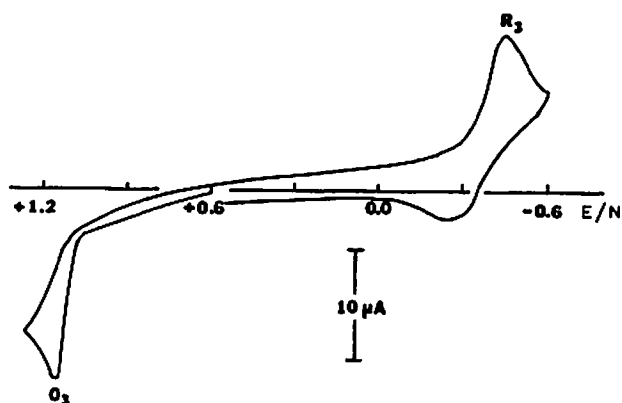


Fig. 3. Cyclic voltammetry of a 3.0 mM TH solution after electrolysis to the dication in the presence of excess AnH; $\nu = 100 \text{ mV s}^{-1}$.

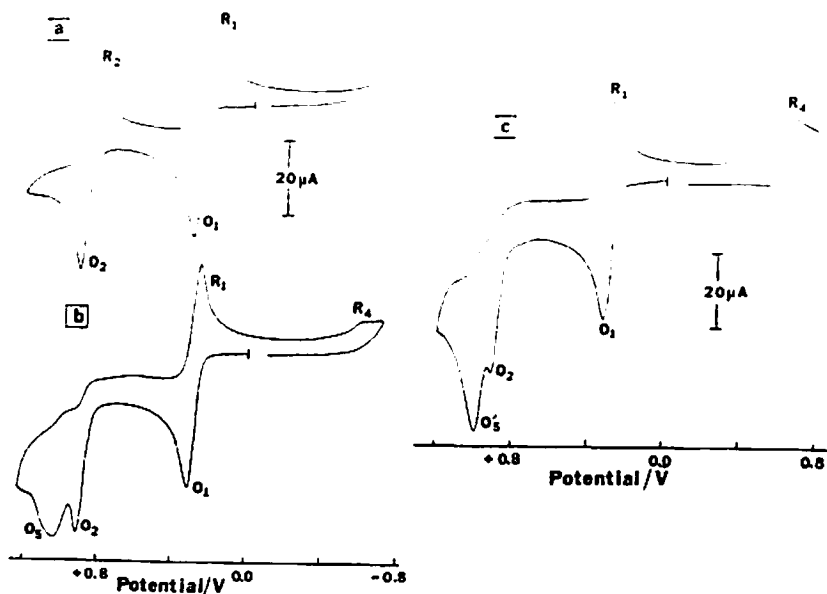


Fig. 4. Cyclic voltammetry of 3.34 mM TH in liquid SO_2 -0.15 M TBAP in the presence of excess water. $[\text{H}_2\text{O}]/[\text{TH}]$: (a) 0.0; (b) 5; (c) 10; $\nu = 100 \text{ mV s}^{-1}$.

(reduction of TH^{2+}) and the appearance of a new oxidation wave, O_3 , and a new reduction wave, R_4 . Wave O_3 at $[\text{H}_2\text{O}]/[\text{TH}] \sim 5$ was broad, somewhat rounded at the peak and appeared to have a shoulder on one side, suggesting that it involved two electrochemical processes that occur at nearly the same potential ($\Delta E_p \sim 100 \text{ mV}$). However, at $[\text{H}_2\text{O}]/[\text{TH}] = 10$ the shape of the new wave resembled that of a single electrochemical process (O_3') with E_{pa} at slightly more negative potentials than that of O_3 . In both cases the R_4 wave was present, and became larger with increasing water concentration. This wave can be attributed to proton reduction, since addition of 70% perchloric acid to SO_2 solutions caused an increase in the height of the R_4 wave proportional to the acid concentration. Note that even in the presence of a large excess of water ($[\text{H}_2\text{O}]/[\text{TH}] = 25$) the O_1/R_1 wave remained unchanged from that of the original, water-free, solution.

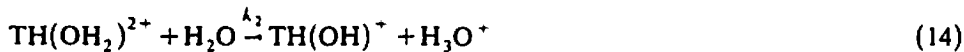
CPC experiments were undertaken to see if reaction of TH^+ with water did occur at longer times. A solution of TH in the presence of excess water ($[\text{H}_2\text{O}]/[\text{TH}] \sim 10$) was electrolyzed at +0.50 V so as to oxidize completely the TH to TH^+ . The n_{app} -value was 0.98 and the radical cation was stable, as shown by CV scans taken with time after coulometry. Reduction back to the parent species gave $n_{app} = 0.97$ and the original voltammogram was regenerated. In another experiment a solution of TH^+ in SO_2 was generated by electrolysis and excess water ($[\text{H}_2\text{O}]/[\text{TH}^+] = 20$) was injected. The concentration of TH^+ , monitored by cyclic voltammetry for a

period of 15 min. showed no changes in wave height or potential. Reversal coulometry showed complete regeneration of the TH solution. Results from these experiments confirm that no reaction of the radical cation with water, at least for times ~ 1 h, occurs.

If coulometry was carried out at -0.850 V where the parent species is oxidized to TH^{2+} , the deep violet color of TH^{2+} , which was visible at the beginning of the electrolysis, disappeared. Voltammetric analysis after electrolysis showed one oxidation wave and one reduction wave corresponding to O'_2 and R_2 respectively (Fig. 5). The height of the O'_2 wave was about 85% of the original TH wave, O_1 , and the n_{app} -value is slightly larger than that expected for a $2e$ reaction. This can probably be attributed to the closeness of the two oxidation waves, O_2 and O'_2 , so that some product oxidation at O'_2 occurred.

The new wave, O'_2 , was ascribed to the oxidation of thianthrene monoxide (THO) formed via the reaction of TH^{2+} and H_2O . This was confirmed by the addition of authentic THO to the solution (Fig. 6) where the only change found in the observed voltammogram was an increase in the height of the O'_2 wave after addition. THO was also identified by bulk electrolysis at the half-peak potential of wave O_2 (chosen to minimize oxidation of the product formed at potentials corresponding to wave O_2). Details are given in the Experimental section.

A mechanism which accounts for the observed results is one in which the dication, TH^{2+} , reacts with water to form a water-dication complex that subsequently loses two protons to form the product (eqns. 13–15):



The O'_2 wave is then caused by the oxidation of THO. The two electrochemical processes which occur at intermediate $[\text{H}_2\text{O}]/[\text{TH}]$ ratios might be the oxidation of THO along with a protonated form of THO, e.g. $\text{TH}(\text{OH})^+$. The change from wave O'_2 to O_2 with addition of water depends upon H_2O being a better base than SO_2 and producing an increase in the rate of the deprotonation steps.

The negative shift in peak potential with increasing water concentration and with changes in scan rate can be used to estimate the observed rate constant for the following chemical reaction [11,13]. The k_{obs} obtained from this calculation is a function of the water concentration, as shown in Fig. 7. The plot of $\log k_{\text{obs}}$ vs. $\log \text{H}_2\text{O}$ is a straight line with a slope of 1.02 (correlation coefficient = 0.98), indicating a first-order dependence on water concentration. This leads to the experimental rate law:

$$-d[\text{TH}]^{2+}/dt = k_{\text{app}}[\text{TH}^{2+}][\text{H}_2\text{O}] \quad (16)$$

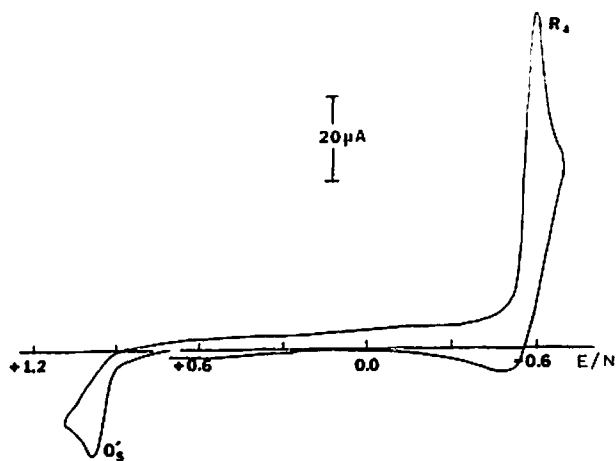


Fig. 5. Cyclic voltammetry of 3.2 *mM* TH in liquid SO_2 -0.15 *M* TBAP after electrolysis to the dication in the presence of excess water $[\text{H}_2\text{O}]/[\text{TH}] = 10$; $\nu = 100 \text{ mV s}^{-1}$.

The apparent rate constant calculated from the observed rate constant is $k_{\text{app}} = 1.77 (\pm 0.35) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$.

As an additional test of the reaction mechanism, theoretical cyclic voltammograms for TH oxidation in the presence of various concentrations of water at different scan rates were obtained by digital simulation techniques [14,15]. The proposed mechanism in eqns. (13)-(15) was assumed, with $k_1 = k_{\text{app}}$ and k_2 and k_3 taken as equal and adjusted for the best fit. Only TH, TH^+ , TH^{2+} and THO were assumed electroactive and, as a first approximation, various possible coproportiona-

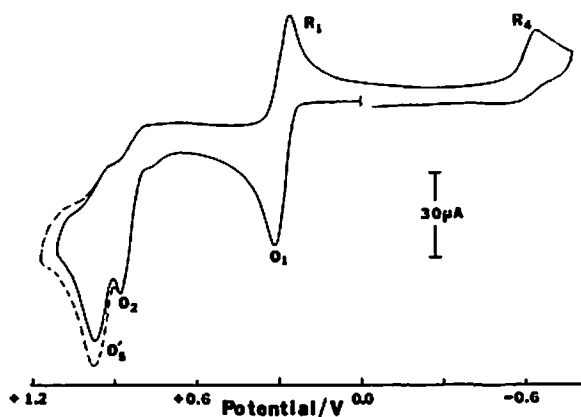


Fig. 6. Cyclic voltammetry of 3.2 *mM* TH in liquid SO_2 -0.15 *M* TBAP in the presence of excess water ($[\text{H}_2\text{O}]/[\text{TH}] \sim 10$) before and after addition of authentic THO; $\nu = 100 \text{ mV s}^{-1}$.

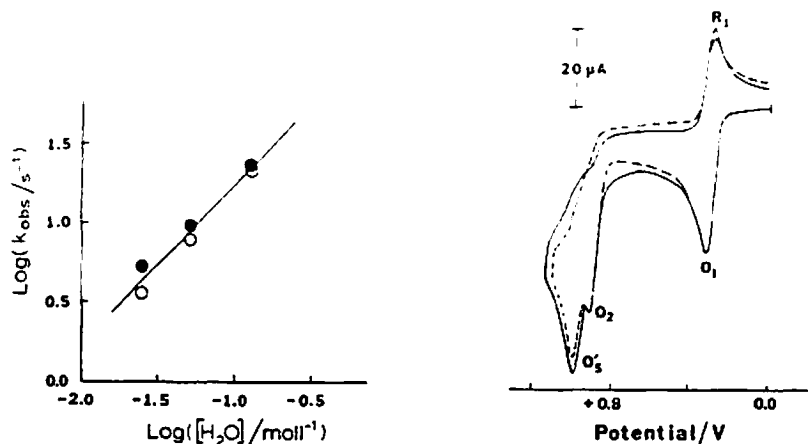


Fig. 7. Dependence of the pseudo-first-order rate constant, k_{obs} , on water concentration for the reaction of TH^{2+} with water in SO_2 ; k_{obs} calculated from the O_5^{\dagger} peak potential shift. (O) $v = 0.1 \text{ V s}^{-1}$; (●) $v = 0.2 \text{ V s}^{-1}$. $[\text{TH}] = 4.9 \text{ mM}$; $T = -40^\circ\text{C}$.

Fig. 8. Comparison of experimental with simulated cyclic voltammogram for oxidation of TH in the presence of water; $k_1 = 200 \text{ M}^{-1} \text{ s}^{-1}$, $k_2 = k_3 = 1.6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$; $[\text{H}_2\text{O}]/[\text{TH}] = 10.0$; $v = 0.1 \text{ V s}^{-1}$.

tion reactions (e.g. between TH^{2+} and TH) were neglected. Details of the method and results are available [16]. A typical simulated voltammogram, compared to an experimental one, for $k_1 = 200 \text{ M}^{-1} \text{ s}^{-1}$, $k_2 = k_3 = 1.6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, $v = 0.1 \text{ V s}^{-1}$ at $[\text{H}_2\text{O}]/[\text{TH}] = 10$, is shown in Fig. 8. Differences between the simulated and experimental curves can be ascribed to differences in the residual current caused by the addition of water to SO_2 and perhaps to neglect of the effect of side reactions. While a more complete study would clearly be required to obtain a detailed reaction mechanism, the results here appear to confirm the general aspects of the electrochemical oxidation of TH in SO_2 in the presence of water.

DISCUSSION

Although the results obtained for the $\text{TH}^{2+} - \text{AnH}$ and $\text{TH}^{2+} - \text{H}_2\text{O}$ reactions in SO_2 are in many ways comparable to those previously found in other aprotic solvents, an important difference is the lack of reactivity of TH^{\dagger} in SO_2 . For example, the cyclic voltammetric results found by Parker et al [6b] for TH-AnH in MeCN-trifluoroacetic acid (TFA) anhydride and CH_2Cl_2 -TFA-TFA anhydride were similar to those in SO_2 , but reaction of TH^{\dagger} with AnH was found on a coulometric time scale (e.g. in MeCN-TFA anhydride, 99:1, at 0.44 mM TH an observed rate constant of $165 \text{ M}^{-1} \text{ s}^{-1}$ was reported). The proposed mechanism was the half-regeneration mechanism (eqns. 7-9), which leads to the same species, TH-AnH^{2+} , proposed for the $\text{TH}^{2+} - \text{AnH}$ reaction (eqns. 14 and 15). The rate

constant for the reaction of $\text{TH}^{\cdot+}$ and AnH in these solvents, $10^7 \text{ M}^{-1} \text{ s}^{-1}$ [6b] is of the order of that found in SO_2 . Similarly, Evans and Blount [4] showed that $\text{TH}^{\cdot+}$ reacted with water in MeCN with a half-life of the order of minutes ($[\text{TH}^{\cdot+}] = 0.6 \text{ mM}$, $[\text{H}_2\text{O}] = 50 \text{ mM}$), with formation of THO. The reaction of $\text{TH}^{\cdot+}$ with trace water (1-3 mM) in MeCN was so rapid that no reversal wave for $\text{TH}^{\cdot+}$ was observed in the cyclic voltammogram (150 mV s^{-1}).

The lower reactivity of $\text{TH}^{\cdot+}$ with nucleophiles in SO_2 compared to MeCN and CH_2Cl_2 can partially be ascribed to the lower temperature of the SO_2 medium and probably to the greater ease of removal of trace water and impurities from it. Another factor, however, is the solvent interaction with the species. Previous work on liquid SO_2 [17] has shown that there is little or no interaction of SO_2 with cations, so that strong stabilization by solvent interaction with $\text{TH}^{\cdot+}$ is unlikely. However, there are strong interactions between SO_2 and donor molecules such as water and aromatics. Wickert [18] reported the formation of the compound $\text{SO}_2 \cdot \text{H}_2\text{O}$ which remained as a stable residue after evaporation of the solvent at 0°C . Thus, a major factor in the remarkable stability of radical cations and dications in liquid SO_2 is the high degree of solvation of nucleophiles. These factors, coupled with the resistance of the solvent to oxidation and the wide window towards positive potentials make SO_2 a very useful solvent for electrochemical studies of highly oxidized substances.

ACKNOWLEDGEMENT

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