

Preliminary note

AN IN SITU INFRARED STUDY OF THE OXIDATION OF SULFUR DIOXIDE ON PLATINUM ELECTRODES

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The oxidation of sulfur dioxide on metal electrodes is of interest for its application in a variety of industrial processes, particularly in operations involving degradation of automobile emissions, production of energy, and winning of sulfide ores. The oxidation of sulfur dioxide by electrochemical methods is a complex process in which intermediates and products are formed which strongly adsorb on the electrode surface. A large number of electrochemical investigations have appeared which employ voltammetric techniques to obtain mechanistic information about the process [1–6]. However, the oxidation process at platinum electrodes is a strong function of electrode pretreatment at the more negative potentials; thus, the electrochemical studies are not all in agreement.

Studies using cyclic voltammetry indicate that when SO_2 is introduced into an aqueous acid solution held at potentials about +0.25 V (SCE) (near the open circuit potential), oxidation of SO_2 begins at about +0.5 V (SCE) and is rapidly poisoned by formation of surface oxide species at more positive potentials [3,5,6]. Separate mechanisms have been proposed for the oxidation on clean and oxide covered platinum surfaces at these potentials. When the potential is swept negative following the initial oxidation sweep, an anodic peak appears at about 0.6 V (SCE) [5,6]. At potentials in the hydrogen evolution region, two cathodic waves appear which have been assigned to reduction of SO_2 to form adsorbed sulfur species which alter the electrochemistry of subsequent oxidation cycles. The nature of this surface species and the effect on the oxidation process have been the target of several electrochemical investigations [3,6].

In this analysis, an in situ infrared spectroscopic study of the oxidation of sulfur dioxide on platinum electrodes is undertaken. The focus of this investigation is on

the oxidation processes which occur at potentials in the double layer region and where platinum oxide is formed. Also presented are spectra collected at negative potentials, where the surface activating sulfur species is believed to form.

The experiments were performed in a three electrode cell made from a glass syringe (JAS Instrument Systems) [7]. A CaF_2 infrared transparent window was mounted on the front of the cell and the electrode–window distance was made as small as possible (about $1\ \mu\text{m}$). The working electrode was constructed from a disk of platinum (about 9 mm dia.) which was sealed in glass and polished to a mirror finish with alumina in decreasing particle sizes down to $0.05\ \mu\text{m}$. The electrode was cleaned by continuous cycling between $-0.25\ \text{V}$ and $+1.2\ \text{V}$ (SCE) until sharp hydrogen waves were obtained. Following cycling, the electrode potential was held at $+0.3\ \text{V}$ (SCE) and sulfur dioxide was released into the cell. All reported potentials are with reference to the saturated calomel electrode.

Infrared spectra were obtained using the method of subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) [7]. As the electrode processes are irreversible, a staircase potential step scheme was used to prevent elimination of spectral information by signal averaging [8]. All spectra are computed from the average of 512 interferograms and normalized to a reference spectrum obtained at $+0.3\ \text{V}$. Positive going bands are due to species present at $+0.3\ \text{V}$ and negative going bands arise from species formed at the new potential. Infrared spectra were obtained using an IBM IR/98 Series infrared spectrometer.

Solutions were prepared from analytical grade sulfuric acid (J.T. Baker) and triply distilled water. Sulfur dioxide (99.98% Matheson) was used without further purification. The electrochemistry was controlled using a potentiostat and waveform generator (Hi-Tek Instruments).

The cyclic voltammetry of SO_2 in $1.0\ \text{M}\ \text{H}_2\text{SO}_4$ is shown in Fig. 1. According to the voltammetry, on the first positive sweep from $+0.3\ \text{V}$, SO_2 oxidation begins at about $+0.5\ \text{V}$ and is poisoned at more positive potentials corresponding to the onset of platinum oxide formation. On the negative sweep, an anodic peak is observed which has been assigned to continuing oxidation of SO_2 in the presence of the platinum oxide [6]. At potentials more negative than $+0.3\ \text{V}$ two reduction peaks are observed in the voltammetry. The cathodic waves have been assigned to reduction of SO_2 to form a surface activating sulfur species. On the second sweep, both SO_2 oxidation and platinum oxide formation are diminished, behavior most likely due to an adsorbed species formed at the negative potentials.

The SNIFTIRS spectrum for the oxidation of SO_2 on clean (in the absence of platinum oxide) platinum is shown in Fig. 2. The strong band appearing at $1332\ \text{cm}^{-1}$ and the weaker band at $1151\ \text{cm}^{-1}$ correspond to SO_2 in solution [9]. The band appearing at $1168\ \text{cm}^{-1}$ is formed as a product of SO_2 oxidation at these potentials. The spectral region between 1400 and $2000\ \text{cm}^{-1}$ is shown in Fig. 3. The sharp structure appearing in the figure is due to absorption of atmospheric water vapor. The broad band appearing at about $1650\ \text{cm}^{-1}$ is due to loss of liquid water at the more positive potential. The broad band at $1800\ \text{cm}^{-1}$ arises from a product of the oxidation.

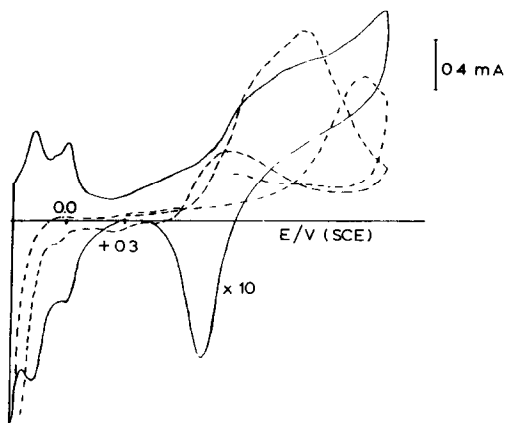


Fig. 1. Cyclic voltammetry of 1.0 M H_2SO_4 (—) and SO_2 in 1.0 M H_2SO_4 (---) at a platinum electrode. (-·-·-) Second voltammetric sweep in the solution containing SO_2 . The current scale for the solution containing H_2SO_4 only is expanded by a factor of 10. All potentials are with reference to SCE.

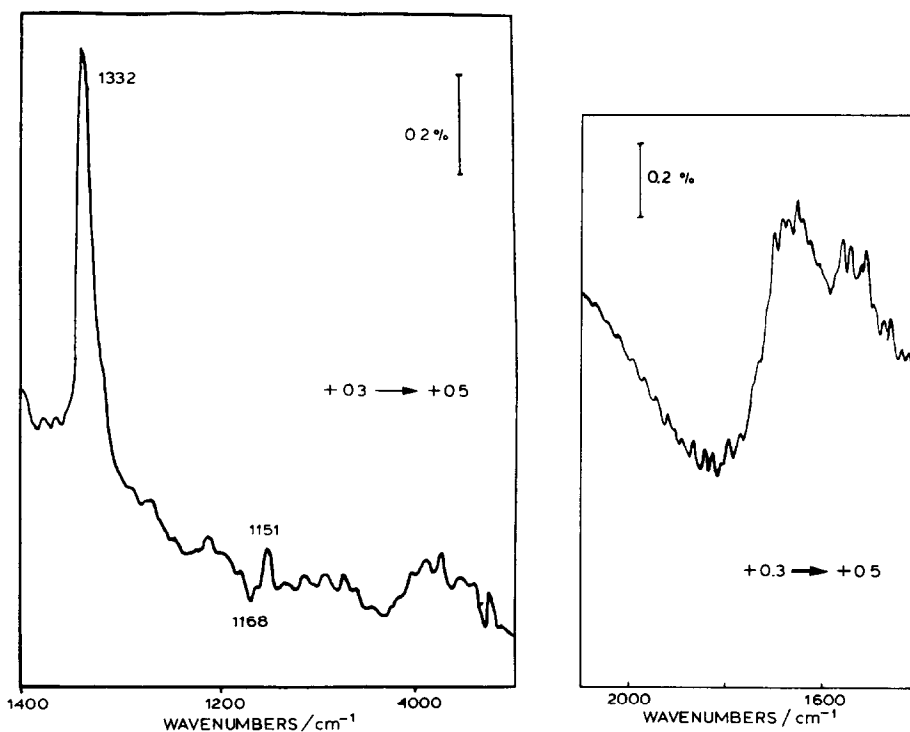


Fig. 2. SNIFTIRS spectra of the oxidation of SO_2 at a platinum electrode at +0.5 V and normalized to a base potential of +0.3 V (SCE). Bands pointing upward correspond to species present at the base potential.

Fig. 3. Same as Fig. 2 showing a higher energy spectral region.

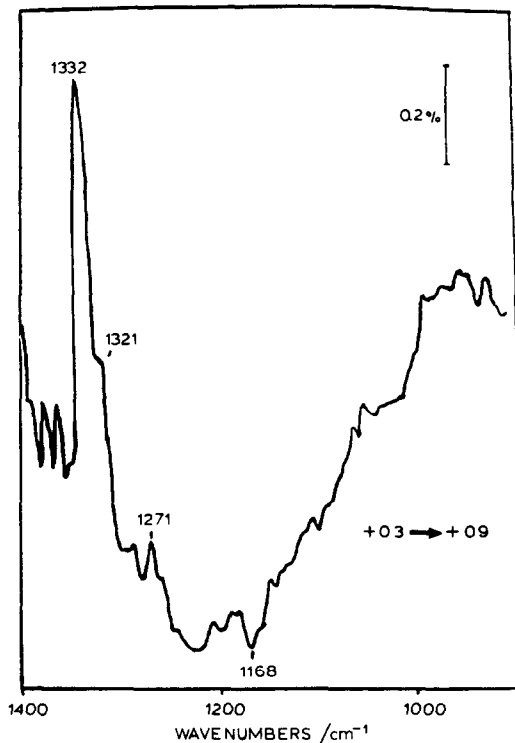


Fig. 4. SNIFTIRS spectra of the oxidation of SO_2 at a platinum electrode at +0.9 V and normalized to a base potential of +0.3 V (SCE). Bands pointing upward correspond to species present at the base potential.

Figure 4 shows the SNIFTIRS spectrum of SO_2 oxidation at potentials where platinum oxide formation occurs. The 1332 cm^{-1} band is still apparent and formation of the 1168 cm^{-1} species still occurs. However, a shoulder at 1321 cm^{-1} now appears in the spectrum and a new band is present at 1271 cm^{-1} . The shoulder corresponds to surface SO_2 that is bonded to the platinum surface through one oxygen atom, and the 1271 cm^{-1} band occurs at energies appropriate for S-bonded SO_2 [9]. Also apparent in the spectrum is a broad shift in baseline at about 1200 cm^{-1} . The position and shape of the band is characteristic of surface bound sulfate [10]. Inspection of the higher energy region of the spectrum (not shown) reveals loss of water and the broad band at 1800 cm^{-1} is apparent. A visible white film forms on the electrode surface when the electrode is held at this potential for long (> 10 min) periods of time.

Following collection of spectra at the more positive potentials, the electrode potential was returned to +0.3 V and a new set of reference spectra was collected. The potential was then stepped, according to the staircase method, to more negative potentials. The spectra collected at -0.1 V and -0.15 V are shown in Fig. 5. The

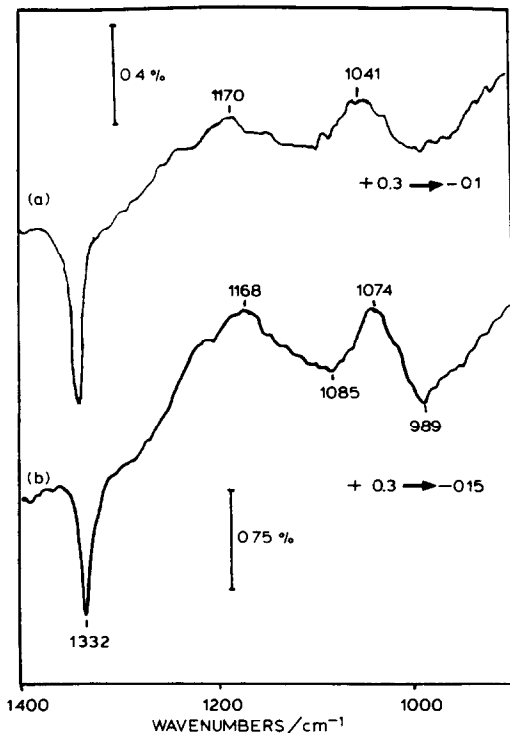


Fig. 5. SNIFTIRS spectra at (a) -1.0 V and (b) -1.5 V (SCE) following a potential step to more positive potentials ($+0.9$ V). The base potential is $+0.3$ V. The solution contains SO_2 in 1.0 M H_2SO_4 .

striking feature is loss of the 1168 cm^{-1} species to regenerate solution SO_2 as evidenced by formation of the 1332 cm^{-1} band. Also, broad bands at 1085 cm^{-1} and 989 cm^{-1} appear which correspond to formation of solution sulfate [9]. Figure 6 shows a higher energy region of the spectrum. Broad bands appear at 2127 cm^{-1} , 1650 cm^{-1} , and 1800 cm^{-1} . The 1650 cm^{-1} band is due to formation of liquid water and the 1800 cm^{-1} band indicates loss of the oxidation product at these negative potentials. The 2127 cm^{-1} band is probably attributable to formation of a reduced sulfur species, possibly the species responsible for surface activation at negative potentials [3,6].

By analysis of the infrared spectra it appears that SO_2 is the electroactive species when the oxidation is carried out in aqueous solution. Further, it is apparent that two separate mechanisms operate for oxidation at potentials in the double layer region and at more positive potentials where platinum oxide formation occurs. The bands pointing upward at 1332 cm^{-1} and 1151 cm^{-1} in Figs. 2 and 4 arise from oxidation of solution SO_2 at $+0.5$ V and $+0.9$ V. In the absence of platinum oxide, it appears that solution SO_2 is oxidized to form a species characterized by absorp-

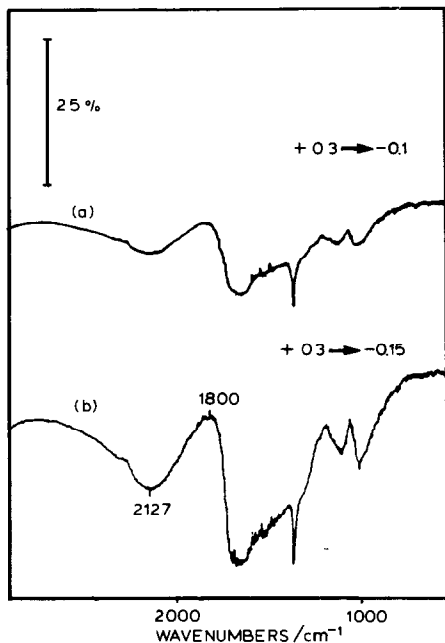


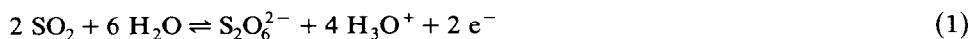
Fig. 6. Same as Fig. 5 showing a higher energy spectral region.

tion bands at 1168 cm^{-1} and 1800 cm^{-1} . When the oxidation is carried out at potentials where oxide is present on the platinum surface ($+0.9\text{ V}$), the spectra indicate displacement of adsorbed SO_2 , possibly by reaction with platinum oxide. A likely product of the reaction is adsorbed sulfate, as evidenced by the broad shift in base line at about 1200 cm^{-1} . A band of this type is characteristic of sulfate adsorbed on a platinum electrode [10]. It is unlikely that the increase in surface sulfate concentration is due to migration of sulfate from solution, as the sulfate concentration is low in solutions of sulfuric acid. The reaction of solution SO_2 also occurs at these potentials, as the 1168 cm^{-1} and 1800 cm^{-1} bands have grown, and oxidation of solution SO_2 is evident.

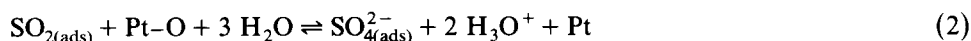
The oxidation of SO_2 in aqueous acid solutions gives rise to a product characterized by absorption bands at 1168 cm^{-1} and 1800 cm^{-1} . Further, reduction of this species forms solution SO_2 and water. The exact nature of this species is in question; however, electrochemical studies have suggested dithionate as a possible oxidation product [4,5]. Infrared spectra obtained from Nujol mulls of sodium dithionate show absorption bands between 2300 cm^{-1} and 2000 cm^{-1} , and another strong absorption at about 1240 cm^{-1} [11]. Adsorption of the dithionate species on the platinum surface could account for the strong red shifting of the infrared bands. Reduction of the species to form SO_2 and water lends further support that an adsorbed dithionate species may be involved (see eqn. 3 below); however, the exact

assignment of these bands is inconclusive at the present time and further studies are under way. Reactions of adsorbed SO_2 and oxygen at platinum surfaces have been studied under vacuum conditions [12,13]. The authors report formation of a sulfur-oxygen containing compound which decomposes to SO_2 and oxygen when heated; however, no identification of the product was proposed.

Assuming that adsorbed dithionate is indeed a product of SO_2 oxidation, the following mechanism is proposed from the infrared spectra:



when the reaction occurs on clean platinum at potentials in the double layer region and



when the reaction occurs in the presence of platinum oxide. Studies suggest that SO_2 oxidation occurs through an SO_3^{2-} intermediate [6]. However, this species was not observed in the infrared spectra, as evidenced by the absence of bands at 1010 cm^{-1} and 961 cm^{-1} in Figs. 2 and 4 [9]; nevertheless, this intermediate may be too short lived to detect under these conditions.

The spectra obtained when the electrode is held at more negative potentials indicate that reaction of the 1168 cm^{-1} species occurs to form solution sulfate as indicated by broad bands at 1085 cm^{-1} and 989 cm^{-1} [9], and regenerate solution SO_2 and water. A possible mechanism for the decomposition of dithionate is given by



which would explain the increased concentration of solution SO_2 and appearance of solution sulfate.

In the lower potential limit a new species is formed which absorbs at 2127 cm^{-1} and is likely due to formation of an adsorbed sulfur species. Reduction of SO_2 may compete with the dithionate reaction at these potentials. This may explain the appearance of the 2127 cm^{-1} band; however, a positive assignment of this band cannot be made with these limited spectral data.

In conclusion, a SNIFTIRS study of the oxidation of SO_2 on platinum electrodes confirms electrochemical studies which suggest that separate mechanisms operate when oxidation occurs on clean and oxide covered platinum surfaces. Infrared spectra of a major product of the oxidation are presented and the assignment of these bands to adsorbed dithionate is proposed. Further, the reduction of this product forms solution SO_2 and water, a process not previously observed using electrochemical methods.

ACKNOWLEDGEMENTS

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