Redox chemistry of H_2S oxidation by the British Gas Stretford process
Part V: Aspects of the process chemistry

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Stretford processes use air to oxidize H_2S in process and natural gases to elemental sulphur, by absorption in aqueous solution at about pH 9 and reaction of the resulting HS^- ions with dissolved oxygen, in the presence of anthraquinone disulphonates (AQDS) and vanadium (v) species, which act as catalysts. Kinetic measurements of the reactions (AQ27DS + HS^- ions), (V(v) + HS^- ions) and (AQ27DSH$^-$ + O_2), primarily used stopped flow spectrophotometry, as reported here, following papers on the electrochemical behaviour of the individual redox couples in Stretford Processes. The course of reaction (AQ27DS + HS^- ions) was also followed with a gold bead indicator electrode, the potential of which was determined essentially by the AQ27DS/AQ27DSH$^-$ couple as the former species were reduced to the latter. Attempts to use ^{51}V NMR to characterize aqueous vanadium–sulphur complexes were inconclusive. A possible mechanism for Stretford Processes is postulated, involving polysulphide (S_n^{2-}) ions as intermediates, which are oxidized to elemental sulphur by another intermediate, H_2O_2, formed by reaction of AQ27DSH$^-$ ions and dissolved oxygen.

1. Introduction

As described elsewhere [1–3], Stretford Processes oxidize hydrogen sulphide in process gases to elemental sulphur. The H_2S-containing gas is contacted with an alkaline solution containing vanadium (v) salts and anthraquinone disulphonates. H_2S dissolves and deprotonates in the alkaline solution; the resulting HS^- ions react with the two oxidizing agents. The reduced solution is then passed to an oxidation reactor, in which air is passed through the process solution, reoxidizing it and forming elemental sulphur. The sulphur particles' natural hydrophobicity, enhanced by suitable adsorbed surfactants, causes them to concentrate in the froth layer at the liquid surface, from where they are recovered and filtered. The oxidized solution is recycled to the gas absorber where it contacts more hydrogen sulphide.

In the process there are four linked redox couples; S(-II)/S(0) [4, 5], V(v)/V(IV) [6], anthraquinone/ anthraquinol [7] and O_2/H_2O, which were investigated separately using electrochemical techniques. This paper is concerned with the interaction between the individual redox couples, to elucidate some aspects of the mechanisms of the Stretford Process.

Kinetic experiments involved:
(i) stopped flow u.v.–visible spectrophotometry,
(ii) gold indicator electrode potential measurements,
(iii) cyclic voltammetry.

^{51}V NMR spectroscopy and conventional chemical analyses were used to determine reaction products.
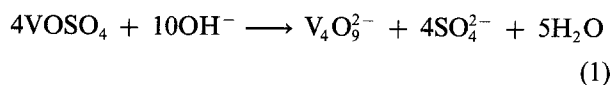
2. Experimental details

pH 9.3 carbonate buffer solutions, containing 59 mol Na_2CO_3 + 0.223 kmol $NaHCO_3$ + 0.10 kmol Na_2SO_4 m^{-3} and pH 9.2 borate buffer solutions, containing 12.5 mol $Na_2B_4O_7 \cdot 10H_2O$ + 0.9 mol NaOH + 0.1 kmol Na_2SO_4 m^{-3}, were prepared from analytical grade materials (BDH, Merck Ltd) in triply distilled water. Sulphide stock solutions containing 0.1 kmol HS^- m^{-3} were prepared by dissolving transparent (i.e., unoxidized) dried crystals of analytical grade sodium sulphide (BDH, Merck Ltd) in the appropriate deoxygenated buffer solution. The molarity of this stock solution was checked by iodate titration [8] and was diluted with the appropriate volume of oxygen-free buffer before use.

Polysulphide solutions were prepared either by dissolving Na_2S_4 in an oxygen-free buffer, or by dissolving elemental sulphur in sodium sulphide solution. Stock solutions were prepared containing 0.1 kmol S m^{-3} and were diluted for use with oxygen-free buffer solution.
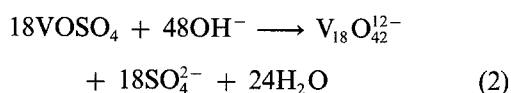
Vanadium (v) solutions, containing 0.1 kmol V(v) m^{-3}, were prepared by dissolving $NaVO_3$ or V_2O_5 (BDH, Merck Ltd) in carbonate buffer or dilute sodium hydroxide solution and diluted with the appropriate buffer solution before use. Vanadium (IV) solutions containing 10 mol vanadium (IV) m^{-3} were prepared by dissolving blue vanadyl sulphate, $VOSO_4 \cdot 6H_2O$ (BDH, Merck Ltd), in oxygen-free carbonate buffer, adding an appropriate volume of 1 kmol NaOH m^{-3} to compensate for the hydroxide

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ion consumption by reactions such as:

$$4VOSO_4 + 10OH^- \longrightarrow V_4O_9^{2-} + 4SO_4^{2-} + 5H_2O \tag{1}$$

and/or

$$18VOSO_4 + 48OH^- \longrightarrow V_{18}O_{42}^{12-}$$
$$+ 18SO_4^{2-} + 24H_2O \tag{2}$$

The resulting solutions were dark brown, but became green and eventually colourless if exposed to air.

Di-sodium 2,7 anthraquinone disulphonate (AQ27DS) (L.B. Holliday Co. Ltd., Huddersfield, UK) was purified as described elsewhere [7], to give a 99.1% pure product.

2.1. Stopped flow apparatus

A Hi-Tech SFA-11 stopped flow attachment was modified for use with oxygen-sensitive solutions by using glass syringes and PTFE-lined stainless steel tubing throughout. The attached quartz cell had four optical faces, giving 2 or 10 mm path lengths. Spectra were recorded after fixed time intervals following the mixing of the reagents using a Hewlett Packard 8451A diode array spectrophotometer, which recorded a 190–820 nm spectrum in 0.1 s. The Hewlett Packard program KINETICM was used to recall spectra from disc, determine absorbance values at particular wavelengths and do kinetic analyses of data.

2.2. Indicator electrode potential measurements

The potential of a gold bead indicator electrode was measured against a saturated calomel reference electrode (SCE) at 600 s intervals during the reaction between anthraquinone 2,7 disulphonate (AQ27DS) and sodium sulphide solution; the SCE potential was assumed to be +0.242 V vs S.H.E. (standard hydrogen electrode). The indicator electrode assembly was connected to the stopped flow apparatus in place of the stop syringe, so that the chamber containing the indicator electrode was flushed with the reaction mixture at the same time as the optical cell was filled, initially with 0.16 mol AQ27DS m^{-3} and 50 mol Na_2S m^{-3} in deoxygenated carbonate buffer.

2.3. Preparation of samples for ^{51}V NMR

Four samples containing:
- (i) 100 mol $NaVO_3$ m^{-3} in carbonate buffer.
- (ii) 10 mol $NaVO_3$ m^{-3} in carbonate buffer.
- (iii) 500 mol $NaVO_3$ + 500 mol Na_2S m^{-3} in carbonate buffer.
- (iv) 5 mol $NaVO_3$ + 500 mol Na_2S m^{-3} in carbonate buffer.

were prepared for ^{51}V NMR on a Bruker 200 NMR spectrometer, using an exciting radiation frequency of 52.6 MHz and liquid $VOCl_3$ as a reference material, against which all chemical shifts are quoted. All the samples were thoroughly deoxygenated before they
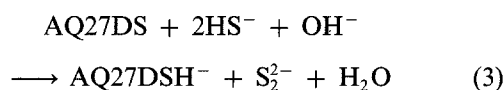
were mixed and were sealed into glass NMR sample tubes under a nitrogen atmosphere. Samples one and two were colourless, sample four became yellow as the reagents were mixed and sample three became dark-brown and a black, hydrophobic solid precipitated from the solution.
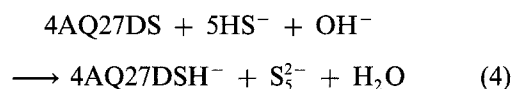
3. Results and discussion

3.1. Stopped flow reaction between AQ27DS and HS⁻ ions

Figure 1 shows the spectra obtained when equal volumes of solutions containing 0.32 mol AQ27DS m^{-3} and 100 mol Na_2S m^{-3} were mixed in the stopped flow apparatus. These were very similar to those obtained during the electrochemical reduction of AQ27DS [7], suggesting that the predominant reduction product (which had an absorbance peak at 410 nm) was the same in both cases and shown elsewhere [7] to be AQ27DSH⁻ ions, which have a pK_a of 10.8 [7]. However, the presence of AQ27DS²⁻ ions was indicated by the minor absorption peak at ≈ 450 nm, at which they absorb strongly [7]; this was confirmed by the absence of a clear isosbestic point at ≈ 360 nm not being maintained during the course of the reaction.

There was no visible formation of elemental sulphur during the reaction; evidently, the difference of about 0.08 V between the reversible potentials of the anthraquinone and sulphur couples, was an insufficient driving force to produce the necessary degree of supersaturation for phase formation, the homogeneous nucleation step being slow. Hence, the HS⁻ ions were probably oxidized to polysulphide ions (S_n^{2-}) by the set of reactions:

$$AQ27DS + 2HS^- + OH^-$$
$$\longrightarrow AQ27DSH^- + S_2^{2-} + H_2O \tag{3}$$

through to

$$4AQ27DS + 5HS^- + OH^-$$
$$\longrightarrow 4AQ27DSH^- + S_5^{2-} + H_2O \tag{4}$$

Polysulphide ions also absorb as shown in Fig. 2, the spectrum of a polysulphide solution prepared by dissolving Na_2S_4 in a carbonate buffer.

However, complete reduction of all the AQ27DS, according to Equation 4, would produce only 0.04 mol S_5^{2-} m^{-3}. Since the molar absorptivity (ε_{max}) at 380 nm was 112.5 m^2 mol^{-1}, the increase in absorbance at this wavelength due to the production of the polysulphide ions would amount to only 0.045 absorbance units, corresponding to less than 10% of the absorbance at 380 nm due to AQ27DSH⁻ ions.

3.2. Reaction rate of AQ27DS and HS⁻ ions

In the presence of an approximately 200 fold excess of HS⁻ ions and for conditions satisfying the Beer–Lambert law, the observed (Fig. 3) logarithmic
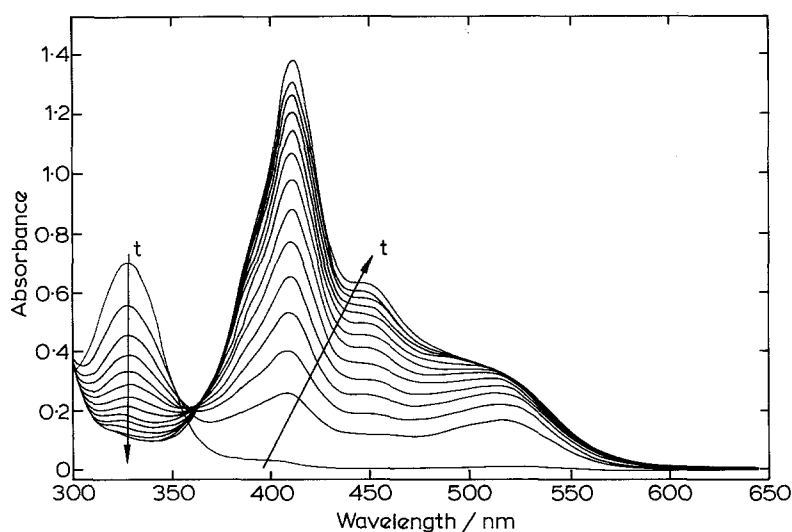
Fig. 1. Spectra taken at 600 s intervals during reaction between AQ27DS and HS^- ions. $[AQ27DS]_0 = 0.16 \, mol \, m^{-3}$, $[HS^-]_0 = 50 \, mol \, m^{-3}$, T 290 K. 10 mm path length.

decrease in AQ27DS concentration (derived from the absorbance at 330 nm) with time, indicated that the reaction was (pseudo) first-order with respect to AQ27DS, following the equation:

$$\ln [AQ27DS]_t = \ln [AQ27DS]_o - kt \qquad (5)$$

where $[AQ27DS]_o$ and $[AQ27DS]_t$ are the initial concentration and that after reaction time t, respectively. Hence, the slope of Fig. 3 gives the first-order rate constant (k), which was found to be $2.5 \times 10^4 \, s^{-1}$ at 290 K.

This value means that, in the presence of 50 mol $HS^- \, m^{-3}$, half the anthraquinone would be reduced after 45 min (i.e. $t_{1/2} = 45 \, min$), implying a requirement for long residence times, although these would decrease with increasing temperature, depending on the reaction activation energy. Early Stretford plants used only anthraquinone disulphonates as catalysts, resulting in long residence time requirements (in the absorber and reactor vessels) and low H_2S through-puts.

3.3. Reaction of AQ27DS and HS⁻ ions: Electrode potential measurements

A gold indicator electrode was used to measure the

mixed potential of the reacting solution containing the AQ27DS oxidizing agent and HS^- reducing agent. Previously, oxidation of HS^- ions at a gold electrode was shown to be highly irreversible [5], whereas reduction of AQ27DS was reversible [7]. Therefore, under the non-equilibrium conditions in the reacting system, the observed mixed potential of the gold bead electrode in a reacting mixture of AQ27DS and HS^- ions will lie close to the equilibrium potential of the $AQ27DS/AQ27DSH^-$ couple, due to its fast kinetics; the (time-dependent) relative concentrations of the anthraquinone and anthraquinol determine the value of the mixed potential.

Assuming that only the AQ27DS and $AQ27DSH^-$ concentrations/activities determine the potential of the gold indicator electrode, that this potential is attained rapidly (i.e., the couple has a high exchange current density on gold) compared to the rate of change of concentrations and that the reduction is a first order process in a perfectly mixed system, then the indicator electrode potential will be given by the Nernst equation [7]:

$$E_h/V = E^0 + \frac{RT}{zF} \ln \left\{ \frac{[AQ27DS][H^+]}{[AQ27DSH^-]} \right\} \qquad (6)$$

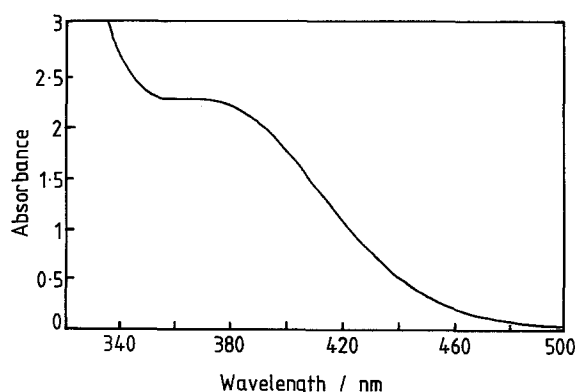Fig. 2. U.v.–visible spectrum of $10 \, mol \, m^{-3}$ sodium polysulphide (NaS_4) in pH 9.3 sodium carbonate buffer solution. 2 mm path length.
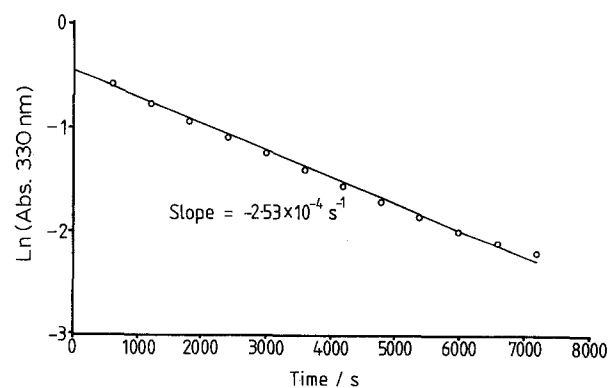

Fig. 3. Plot of ln (Absorbance at 330 nm) against time during reduction of AQ27DS with HS^- ions. $[AQ27DS]_0 = 0.16$, $[HS^-]_0 = 50 \, mol \, m^{-3}$, 290 K. 10 mm path length.
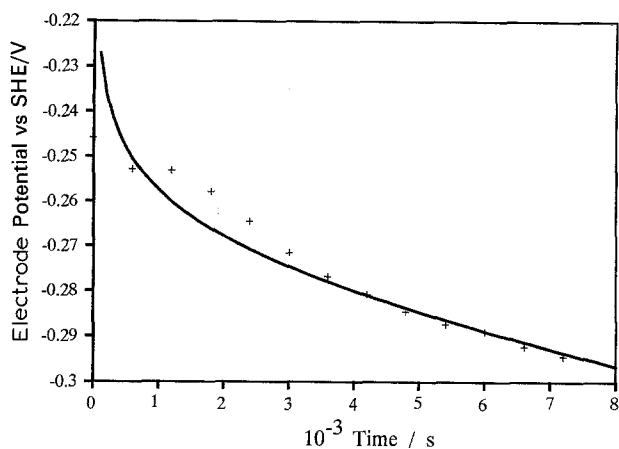
Fig. 4. Measured (+) and theoretical (——) gold indicator electrode potentials against time during reaction of AQ27DS with HS⁻ ions. Solution conditions as in Fig. 1.

From Equation 5

$$[AQ27DS]_t = [AQ27DS]_o \exp(-kt) \quad (7)$$

and so

$$[AQ27DSH^-]_t = [AQ27DS]_o\{1 - \exp(-kt)\} \quad (8)$$

Hence

$$E_{-0.0296\,pH}/V = E^0_{-0.0296\,pH}$$

$$+ \frac{RT}{zF} \ln \left\{ \frac{\exp(-kt)}{1 - \exp(-kt)} \right\} \quad (9)$$

Using $k = 2.53 \times 10^{-4}\,s^{-1}$ derived from Fig. 3 and values of $E^0 = -0.273\,V$ vs S.H.E. and $z = 2$ [7], the variation of the potential with time can be predicted from Equation 9, shown in Fig. 4 to give reasonable agreement with experimentally observed potentials. As the reduction of the AQ27DS proceeded, these potentials decreased by an amount congruent with that expected if $z = 2$ in Equation 9, corresponding to the reaction:

$$AQ27DS + H^+ + 2e^- \longrightarrow AQ27DSH^- \quad (10)$$
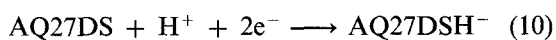
If the radical anion had been produced:

$$AQ27DS + e^- \longrightarrow AQ27DS^{\cdot-} \quad (11)$$
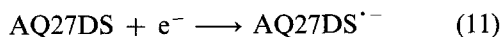
$z = 1$, so then a decrease in potential twice that observed would be predicted. Hence, these measurements provide further evidence that AQ27DS is reduced in a two electron process [7].
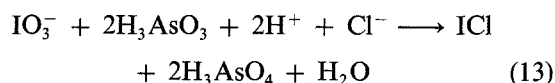
However, the agreement between theory and experiment was not sufficiently close to allow the potential measurements to be used to predict the concentrations of the reduced and oxidized forms, nor to determine the first-order rate constant with adequate precision. The discrepancies (Fig. 4) were largest at the start of the reaction, when AQ27DS⁻ species were predicted [7] to predominate over AQ27DSH⁻ ions.

3.4. Oxidation of AQ27DSH⁻ ions with oxygen

Hydrogen peroxide is a metastable intermediate in the electrochemical reduction of oxygen [9] and can also be produced when reduced anthraquinones react with

oxygen in aqueous solution [10]. Hence, its possible role in the Stretford Process was investigated by analysing for H_2O_2 during the oxidation of solutions of AQ27DSH⁻ ions with oxygen.

H_2O_2 is known to oxidize As(III) to As(v); unreacted As(III) can then be back-titrated in acid solution with iodate [8] and hence the concentration of H_2O_2 can be determined:

$$AsO_2^- + H_2O_2 \longrightarrow HAsO_4^{2-} + H^+ \quad (12)$$

$$IO_3^- + 2H_3AsO_3 + 2H^+ + Cl^- \longrightarrow ICl$$

$$+ 2H_3AsO_4 + H_2O \quad (13)$$

Preliminary checks were made to ensure that As(III) could not be oxidized at a significant rate either through prolonged aeration or by direct reaction with anthraquinone 2,7 disulphonate (AQ27DS).

A solution of AQ27DS was reduced electrochemically at constant potential [3, 7] and then re-oxidized externally by mixing the solution with pure oxygen in a gas syringe and recording the volume of gas absorbed. The re-oxidized solution was then titrated with As(III) to detect the presence of hydrogen peroxide.

It was found that the reduced solution absorbed oxygen in a 1 (O_2):2 (AQ27DSH⁻) molar ratio; no hydrogen peroxide was detected in the re-oxidized solution, suggesting that oxygen was reduced to form hydroxide ions in a four electron process:

$$2AQDSH^- + O_2 \longrightarrow 2AQ27DS + 2OH^- \quad (14)$$

However, if AQDSH⁻ ions were injected into an aerated solution of As(III), under conditions of excess oxygen, then hydrogen peroxide was detected quantitatively as an oxygen reduction intermediate, according to the reaction:

$$AQ27DSH^- + O_2 + H_2O \longrightarrow AQ27DS$$

$$+ H_2O_2 + OH^- \quad (15)$$
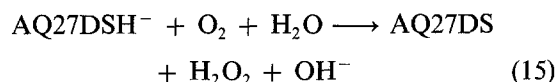
In a solution containing As(III), any hydrogen peroxide produced would react immediately according to Reaction 12. In the presence of As(III) and AQ27DSH⁻ ions, H_2O_2 oxidized them to AQ27DS and As(v), respectively. Hence, in the Stretford Process, the reaction between AQ27DSH⁻ ions and oxygen is likely to produce hydrogen peroxide, which is capable of producing elemental sulphur from polysulphide solutions and oxidizing V(IV) to V(v).

3.5. Stopped flow reaction between V(v) and HS⁻ ions

The application of u.v.-visible spectrophotometry to the study of the reactions of vanadium (v) was limited by the high optical absorption of V(v) (and V(IV)) solutions in the u.v. region; a 10 mm cuvette containing a solution of 10 mol $NaVO_3$ m⁻³ showed complete light absorbance below 370 nm (dilution showed that $\lambda_{max} = 270\,nm$, $\varepsilon = 320\,m^2\,mol^{-1}$). Hence, it was not possible to study the reactions of vanadium (v) solutions at concentrations such as those used in the Stretford Process ([V(v)] typically $= 32\,mol\,m^{-3}$), using
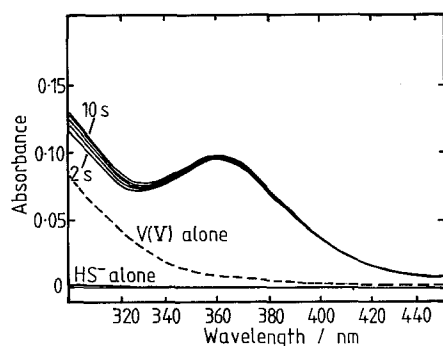
Fig. 5. Spectra taken at 2 s intervals during reaction between V(v) and HS⁻ ions. $[V(v)]_0 = 0.5\,mol\,m^{-3}$, $[HS^-]_0 = 44\,mol\,m^{-3}$; T 290 K; 2 mm path length.

the stopped flow apparatus. However, the 2 mm optical path length was short enough to allow a study of the reaction between a solution containing 0.5 mol V(v) m^{-3} and excess HS⁻ ions (44 mol m^{-3}).

Figure 5 shows the spectra taken at two second intervals during this reaction, which was extremely rapid, an absorbance peak at 360 nm appearing within 2 s. Attempting to decrease the rate of reaction by decreasing the HS⁻ concentration by a factor of ten succeeded only in decreasing the magnitude of the absorbance maximum. This behaviour suggested that an equilibrium was established rapidly between the $HV_2O_7^{3-}$ and HS⁻ ions:
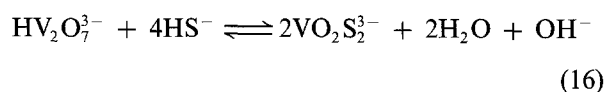
$$HV_2O_7^{3-} + 4HS^- \rightleftharpoons 2VO_2S_2^{3-} + 2H_2O + OH^- \tag{16}$$

Table 1, summarizing some of the spectroscopic properties of known thiovanadate complexes [11], shows that $VO_2S_2^{3-}$ ions exhibit an absorbance maximum at 360 nm.

After the rapid formation of the absorbance maximum at 360 nm, there was a small increase in the optical absorbance in the spectral region 300–380 nm with time. Polysulphide species, which absorb in this spectral range, are likely to have been responsible, as separate experiments had shown that such an increase was observed when HS⁻ ions reacted with dissolved oxygen in an aerated buffer solution.

At pH 9.2, $V_{18}O_{42}^{12-}$ polyanions [13] form in vanadium (IV) solutions in the absence of sulphide, giving rise to an intense absorption throughout the whole

u.v.–visible spectral range corresponding to a brown colouration, rather than the observed absorbance maximum at 360 nm. Hence, $V_{18}O_{42}^{12-}$ ions were not formed in the reaction between V(v) and excess HS⁻ ions under the conditions reported above.

The ^{51}V NMR spectra of 10 mol V(v) m^{-3} showed peaks at -547, -562 and -573 p.p.m. against $VOCl_3$; these were attributed to $H_2V_2O_7^{2-}$, $HV_2O_7^{3-}$ and $V_3O_9^{3-}$ ions, respectively. On reaction with sulphide solutions, all these peaks disappeared, which is consistent with the formation of thio complexes. However, no peak at 184 p.p.m. (attributed [11] to $VO_2S_2^{3-}$ ions) could be detected, although it was not clear whether the detection limits of the spectrometer would be exceeded at this relatively low concentration (5 mol V m^{-3}). The spectrum was not scanned above 300 p.p.m., so it is not possible to preclude the presence of other thio complexes (see Table 1).

3.6. Vanadium (V) reduction

At higher vanadium (v) concentrations it was not possible to follow the reaction between V(v) species and HS⁻ ions using u.v.–visible stopped flow spectrophotometry, because of the strong absorbances of the V(v) and V(IV). However, the following observations could be made.

(i) When a solution containing 10–100 ml V(v) m^{-3} was reacted with an equal volume of equimolar Na_2S, the mixture instantly turned a green–brown colour. If a large excess of sulphide was added, after several minutes a brown–black solid began to precipitate from the solution.

(ii) If this brown–black solid was separated and dissolved in hydrochloric acid, it dissolved to form a blue solution.

(iii) When hydrogen peroxide was added to the green–brown solutions, the solution instantly turned turbid, and a yellow solid (which was identified as sulphur) could be separated from a clear solution.

These observations imply that when more concentrated solutions of vanadium (v) were used, reduction of the vanadium (v) to vanadium (IV) was achieved. Vanadium (IV) solutions (prepared from $VOSO_4$) appeared brown, but when they were exposed

Table 1. Summary of spectroscopic behaviour of thiovanadates [11, 12].

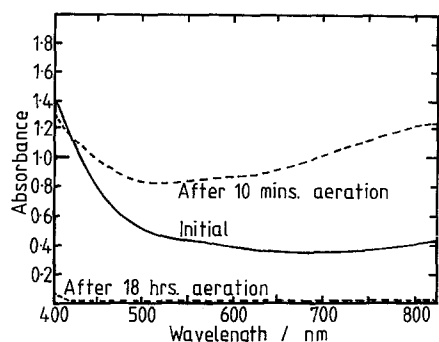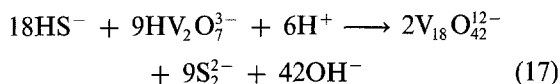| Species	Colour	U.v.–visible absorbances λ_{max}/nm ($\varepsilon/m^2\,mol^{-1}$)	^{51}V NMR chemical shift /p.p.m. (VOCl₃)
VO_4^{3-}	Colourless		-541
$VO_3(OH)^{2-}$	Colourless		-539
VO_3S^{3-}	(Orange)	305, 442 (in methanol)	-250
HVO_3S^{2-}			-121
$VO_2S_2^{3-}$	Yellow/red	305, 360 ($\varepsilon \sim 400$), 460 (weak)	184
$HVO_2S_2^{2-}$			<230
VOS_3^{3-}	Red	295, 325, 459 ($\varepsilon \sim 600$), 521	740
$HVOS_3^{2-}$			748
VS_4^{3-}	Violet	267, 351, 394, 538	1395
HVS_4^{2-}			1392

Fig. 6. Spectra of 10 mol V(IV) m^{-3} before and after aeration. pH 9.3; T = 290 K; 10 mm path length.
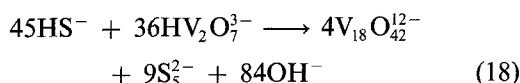
to air they became a blue–green colour. After prolonged exposure to the atmosphere they turned colourless. The u.v.–visible spectra of vanadium (IV) solutions before and after exposure to the atmosphere are shown in Fig. 6.

This behaviour suggests that vanadium (IV) solutions, which probably contain $V_{18}O_{42}^{12-}$ anions, can be oxidized initially to form mixed valence V(V)/V(IV) ions in solution. Mixed valence anions that are blue and green are known, though still poorly characterized [14]. Prolonged aeration formed the V(V) ions, $HV_2O_7^{3-}$.

It is likely that the brown-coloured solutions that resulted when V(V) (at > 10 mol m^{-3}) and HS$^-$ ions are mixed, contain $V_{18}O_{42}^{12-}$ ions [13] formed by the set of reactions:

$$18HS^- + 9HV_2O_7^{3-} + 6H^+ \longrightarrow 2V_{18}O_{42}^{12-}$$
$$+ 9S_2^{2-} + 42OH^- \qquad (17)$$

through to

$$45HS^- + 36HV_2O_7^{3-} \longrightarrow 4V_{18}O_{42}^{12-}$$
$$+ 9S_5^{2-} + 84OH^- \qquad (18)$$

These reactions appear to produce predominantly polysulphides, rather than elemental sulphur, since the precipitation of sulphur was not observed, unless a large excess of vanadium (V) was used.

The brown solid that precipitates when vanadium (V) is in prolonged contact with sulphide solutions must contain vanadium in the (IV) oxidation state or lower; the blue solutions that were produced when the solid was dissolved in acid are characteristic of blue vanadyl (VO^{2+}) ions. The possibility that the solid was a vanadium sulphide is remote, since the potential–pH diagram for the vanadium–sulphur–water system [6] shows no area of thermodynamic stability for a sulphide phase at pH 9.3. That diagram predicts V_3O_5 to be the first solid phase to be encountered as the solution redox potential is decreased at pH 9.3; this would be expected to dissolve in acid to form blue VO^{2+} and green V^{3+} ions, which would be oxidized on exposure to the atmosphere forming more vanadyl ions:
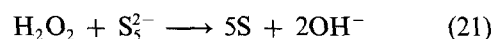
$$V_3O_5 + 8H^+ \longrightarrow VO^{2+} + 2V^{3+} + 4H_2O \quad (19)$$
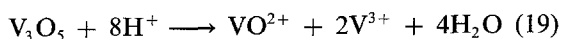
It is also possible that the solid may have been a mixed-valence salt.

3.7. Oxidations involving H_2O_2

Hydrogen peroxide reacted rapidly with polysulphide solutions, producing elemental sulphur by the set of reactions:

$$H_2O_2 + S_2^{2-} \longrightarrow 2S + 2OH^- \qquad (20)$$

through to

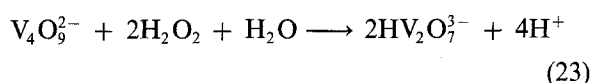$$H_2O_2 + S_5^{2-} \longrightarrow 5S + 2OH^- \qquad (21)$$
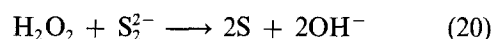
The much greater driving force available compared with that with AQ27DS enables elemental sulphur phase formation to occur.
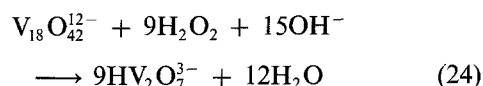
By contrast, when hydrogen peroxide was added to solutions containing HS$^-$ ions at pH 9.3, sulphoxy compounds such as thiosulphate ions rather than sulphur were produced:

$$4H_2O_2 + 2HS^- \longrightarrow S_2O_3^{2-} + 5H_2O \quad (22)$$

However, when H_2O_2 was added to the green–brown solution, produced by mixing equal volumes of 10 mol m^{-3} V(V) and HS$^-$, elemental sulphur was again produced. This suggested that polysulphides were produced during the reaction between V(V) and HS$^-$ ions and that these were oxidized to sulphur by H_2O_2. Hydrogen peroxide was also a sufficiently strong oxidant to convert vanadium (IV) to vanadium (V), forming a colourless solution:
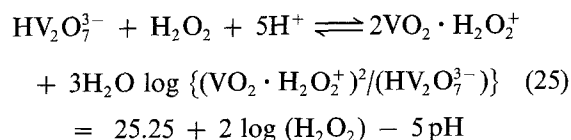
$$V_4O_9^{2-} + 2H_2O_2 + H_2O \longrightarrow 2HV_2O_7^{3-} + 4H^+$$
$$(23)$$

and/or

$$V_{18}O_{42}^{12-} + 9H_2O_2 + 15OH^-$$
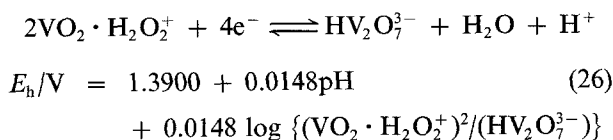$$\longrightarrow 9HV_2O_7^{3-} + 12H_2O \qquad (24)$$

Therefore, the addition of hydrogen peroxide to a reduced solution, containing vanadium (IV) and polysulphide ions, can produce elemental sulphur and vanadium (V) ions.

However, $HV_2O_7^{3-}$ ions may be further oxidized by H_2O_2 [6]:

$$HV_2O_7^{3-} + H_2O_2 + 5H^+ \rightleftharpoons 2VO_2 \cdot H_2O_2^+$$
$$+ 3H_2O \log \{(VO_2 \cdot H_2O_2^+)^2/(HV_2O_7^{3-})\} \quad (25)$$
$$= 25.25 + 2 \log (H_2O_2) - 5pH$$

to produce a peroxy complex which, as a strong oxidant, will also re-oxidize the various reduced species:

$$2VO_2 \cdot H_2O_2^+ + 4e^- \rightleftharpoons HV_2O_7^{3-} + H_2O + H^+$$

$$E_h/V = 1.3900 + 0.0148pH \qquad (26)$$
$$+ 0.0148 \log \{(VO_2 \cdot H_2O_2^+)^2/(HV_2O_7^{3-})\}$$

3.8. Stretford solution chemistry: Electrochemical results

When a Stretford Process solution containing 33 mol V(V) m^{-3} and 8 mol AQ27DS m^{-3} in a carbonate buffer was reacted with 10 mol HS$^-$ m^{-3}, the solution
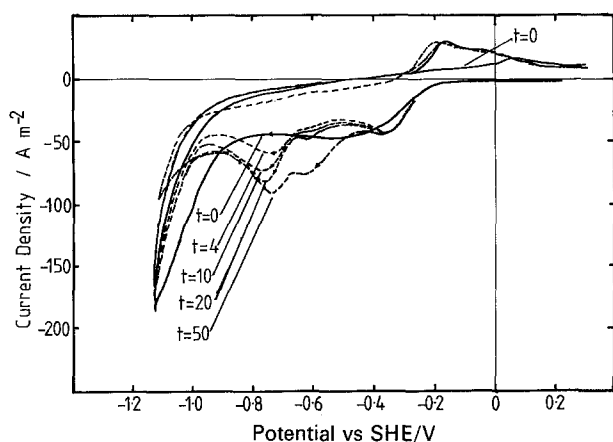
Fig. 7. Voltammetry of gold electrode as a function of time (minutes) in a Stretford solution during reduction of 8 mol AQ27DS m^{-3} and 33 mol V(v) m^{-3} by 10 mol HS⁻ m^{-3}. pH 9.3; potential sweep rate $= 0.2 \, V \, s^{-1}$.

instantly turned a turbid dark brown colour. Over the succeeding 20 min this turbidity disappeared, leaving a dark-brown coloured solution. Both vanadium (IV) and AQ27DSH⁻ ions absorb strongly in the visible region, and together would produce such a brown colouration. The turbidity may have been due to reduced vanadium oxide such as V_3O_5 [6], in the form of a colloidal dispersion.

In the absence of oxygen, no precipitation of elemental sulphur was observed, even after standing for 12 h, although the solution contained a stoichiometric excess of oxidising agents. However, when air or oxygen was bubbled through the solution, sulphur was formed immediately and the red-brown colouration was discharged simultaneously.

Voltammetry of 33 mol V(v) + 8 mol AQ27DS m^{-3} in a carbonate buffer solution using a gold flag electrode, with the potential limits set at $+0.3$ V and -1.2 V vs S.H.E., initially showed a reduction wave at about -0.285 V on the negative-going potential scan; this was attributed to the reduction of AQ27DS. The re-oxidation peak was partially suppressed and occurred at 0.05 V vs S.H.E. Similar patterns were seen during the voltammetry of vanadium (v) solutions at gold electrodes [2, 6] and were attributed to the re-oxidation of vanadium oxide films. This suggested that the formation of such films deactivated the gold electrode towards the re-oxidation of AQDSH⁻ ions.

When 10 mol HS⁻ m^{-3} solution was added, the series of voltammograms shown in Fig. 7 were obtained. Two new reduction peaks at -0.65 and -0.8 V vs S.H.E. appeared and increased in intensity during the 50 min following the addition. When the solution was oxygenated, these same peaks disappeared in about 20 min. The species responsible for the reduction peaks were probably polysulphide ions; cyclic voltammetry of polysulphide solutions at a gold electrode revealed two reduction peaks [5]. The peak potentials in Fig. 7 differ from those observed in polysulphide solutions alone (-0.5 and -0.95 V vs S.H.E.), but this probably reflected the compositional differences and the state of the gold electrode surface,

which is likely to have been covered by films of elemental sulphur, then vanadium oxide(s) as the negative-going potential sweep proceeded.
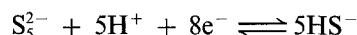
4. A possible mechanism for Stretford Processes

In the absorption reactor

HS⁻ ions are formed by aqueous absorption of H₂S ($pK_a = 7$) at about pH 9:

$$H_2S + OH^- \longrightarrow HS^- + H_2O \qquad (27)$$

Their oxidation is known to occur via polysulphide intermediates [5] and can be written as occurring via S_5^{2-} ions, though a range of polysulphide ions (S_n^{2-}, $2 \leqslant n \leqslant 5$) [4] will be produced in practice:

$$S_5^{2-} + 5H^+ + 8e^- \rightleftharpoons 5HS^-$$

$$E_h/V = 0.0071 - 0.0370 \, pH \qquad (28)$$
$$+ 0.0074 \log (S_5^{2-}) - 0.0370 \log (HS^-)$$

The HS⁻ ions react with anthraquinone disulphonates to form polysulphide ions by reactions such as:

$$4AQDS + 5HS^- + OH^-$$
$$\longrightarrow 4AQDSH^- + S_5^{2-} + H_2O \qquad (4)$$
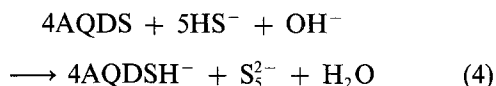
The thermodynamic driving force is greater for the V(v)/HS⁻ reactions:

$$5HS^- + 4HV_2O_7^{3-} + 11H^+ \longrightarrow 2V_4O_9^{2-}$$
$$+ S_5^{2-} + 10H_2O \qquad (29)$$

and/or

$$45HS^- + 36HV_2O_7^{3-} + 3H^+ \longrightarrow 4V_{18}O_{42}^{12-}$$
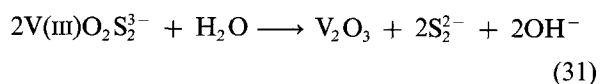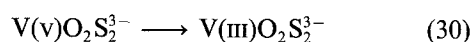$$+ 9S_5^{2-} + 84OH^- \qquad (18)$$
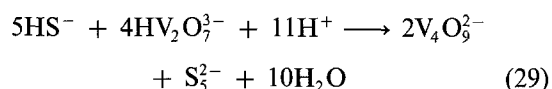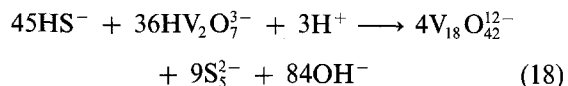
since the standard reversible potential values at pH 9.3 and 289 K are -0.335, -0.333, -0.25 and -0.09 V vs S.H.E. for the HS⁻/S, HS⁻/S_5^{2-}, AQ27DS/ AQ27DSH⁻ and V(v)/V(IV) couples, respectively; (hence, $HV_2O_7^{3-}$ ions could reoxidize AQ27DSH⁻ ions). However, it is likely that the oxidation of hydrosulphide solutions with vanadium (v) proceeds via the formation of a thiovanadate complex; it has been shown that dilute vanadium solutions (<1 mol V(v)m^{-3}) may form $VO_2S_2^{2-}$ ions when contacted with excess HS⁻ ions:

$$HV_2O_7^{3-} + 4HS^- \longrightarrow 2VO_2S_2^{3-} + 2H_2O + OH^-$$
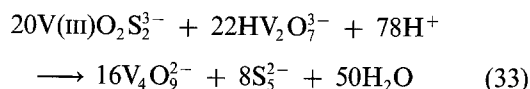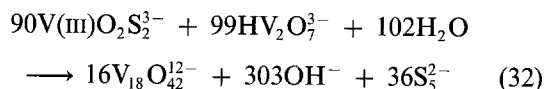$$\qquad (16)$$
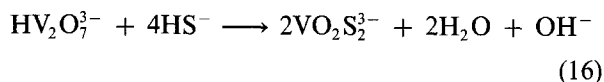
Transition metal thiovanadates are known to undergo intramolecular redox reactions which can give rise to polysulphides and reduced vanadium phases [15]. For example,

$$V(v)O_2S_2^{3-} \longrightarrow V(III)O_2S_2^{3-} \qquad (30)$$

$$2V(III)O_2S_2^{3-} + H_2O \longrightarrow V_2O_3 + 2S_2^{2-} + 2OH^- \qquad (31)$$

though in the presence of V(v) species and other oxidants, higher polysulphides and V(IV) species ($V_{18}O_{42}^{12-}$

or $V_4O_9^{2-}$ ions) could be produced:

$$90V(III)O_2S_2^{3-} + 99HV_2O_7^{3-} + 102H_2O$$

$$\longrightarrow 16V_{18}O_{42}^{12-} + 303OH^- + 36S_5^{2-} \quad (32)$$

$$20V(III)O_2S_2^{3-} + 22HV_2O_7^{3-} + 78H^+$$

$$\longrightarrow 16V_4O_9^{2-} + 8S_5^{2-} + 50H_2O \quad (33)$$

To minimize blockage of the absorber, its redox conditions should be controlled so that HS^- oxidation is restricted to producing polysulphides, delaying their further oxidation to elemental sulphur until reaching the oxidizer.

In the oxidizer reactor

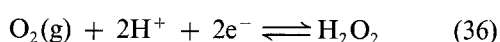Sulphur production by oxidation reactions such as:

$$5S + 2e^- \rightleftharpoons S_5^{2-} \quad (34)$$
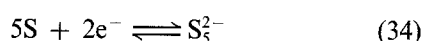
$$E_h/V = -0.3405 - 0.0295 \log (S_5^{2-})$$

are driven ultimately by oxygen reduction:

$$O_2(g) \rightleftharpoons O_2(aq) \quad (35)$$

$$\log (O_2(aq)) = -2.85 + \log p_{O_2}$$

$$O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O_2 \quad (36)$$
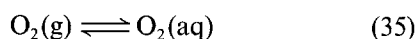
$$E_h/V = 0.695 - 0.00591\,pH - 0.0296 \log (H_2O_2)$$
$$+ 0.0296 \log p_{O_2}$$

$$O_2(aq) + 2H^+ + 2e^- \rightleftharpoons H_2O_2 \quad (37)$$
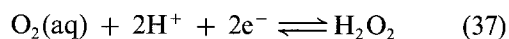
$$E_h/V = 0.7794 - 0.0591\,pH - 0.0296 \log (H_2O_2)$$
$$+ 0.0296 \log (O_2(aq))$$

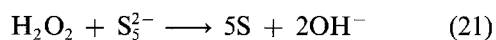$$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O \quad (38)$$
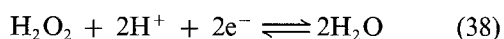
$$E_h/V = 1.763 - 0.0591\,pH + 0.0296 \log (H_2O_2)$$

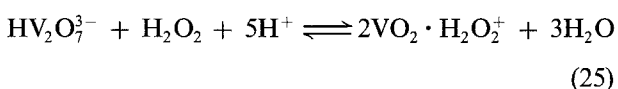Oxygen reduction by $AQDSH^-$ ions (which may be a range of isomers) produces hydrogen peroxide:

$$AQDSH^- + O_2 + H_2O \longrightarrow 2AQDS$$
$$+ H_2O_2 + OH^- \quad (15)$$
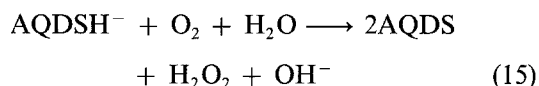
which can oxidize polysulphide ions to elemental sulphur:

$$H_2O_2 + S_5^{2-} \longrightarrow 5S + 2OH^- \quad (21)$$

and assist in the oxidation of the vanadium (IV) species by:

$$V_{18}O_{42}^{12-} + 9H_2O_2 + 15OH^- \longrightarrow 9HV_2O_7^{3-} + 12H_2O$$
$$(24)$$

$HV_2O_7^{3-}$ ions may be further oxidized by H_2O_2:

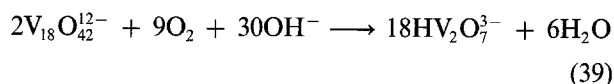$$HV_2O_7^{3-} + H_2O_2 + 5H^+ \rightleftharpoons 2VO_2 \cdot H_2O_2^+ + 3H_2O$$
$$(25)$$
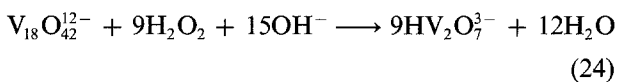
$$\log \{(VO_2 \cdot H_2O_2^+)^2/(HV_2O_7^{3-})\}$$
$$= 25.25 + 2 \log (H_2O_2) - 5\,pH$$

to produce a peroxy complex which, as a strong oxidant, will re-oxidize the various reduced species:

$$2VO_2 \cdot H_2O_2^+ + 4e^- \rightleftharpoons HV_2O_7^{3-} + H_2O + H^+$$
$$(26)$$
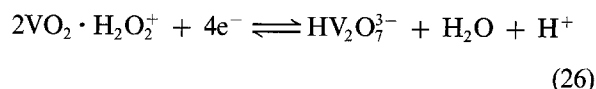
The brown vanadium (IV) species ($V_{18}O_{42}^{12-}$ ions) will also react slowly with dissolved oxygen, eventually to form vanadium (V) ions:

$$2V_{18}O_{42}^{12-} + 9O_2 + 30OH^- \longrightarrow 18HV_2O_7^{3-} + 6H_2O$$
$$(39)$$

The rising air bubbles in the oxidizer also serve to recover the sulphur produced in Reaction 21 by froth flotation, because of the hydrophobic nature of elemental sulphur. The re-oxidized solution is then re-cycled to the absorption reactor to undergo another redox cycle.

5. Conclusions

The formation of polysulphide (S_n^{2-}) ions by the partial oxidation of HS^- ions, inter alia, reduced the anthraquinone to the anthraquinol form, which reacts with oxygen to form H_2O_2. Elemental sulphur is then formed by the reaction of S_n^{2-} ions and H_2O_2. The detail of the mediation of vanadium species is less well defined since V(v) may be reduced and/or complexed by HS^- ions or complexed by H_2O_2.

Acknowledgements

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