

Vanadium(V) complexes of sulfonated 1,5,10-tris(2,3-dihydroxybenzoyl)-1,5,10-triazadecane as catalysts for the Stretford process

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Abstract

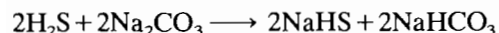
The reaction of the V(V) complex of sulfonated 1,5,10-tris(2,3-dihydroxybenzoyl)-1,5,10-triazadecane (3,4 LICAMS) with H₂S has been studied as a model for the Stretford process. Oxidation of the hydrogen sulfide is found to occur in two steps. The first involves the pH dependent formation of a V(V) LICAMS–H₂S intermediate while the second is a pH independent electron transfer to produce elemental sulfur and V(IV) LICAMS. Rate constants have been measured and the significance of these data to the design of new catalysts is discussed.

Introduction

Increasing environmental concerns have led to the need to remove objectionable impurities such as H₂S from gas streams prior to their sale or use. The Stretford process is a liquid phase gas scrubbing process which absorbs and oxidizes hydrogen sulfide to produce elemental sulfur. It was developed over 25 years ago and is based on complex, liquid phase, oxidation–reduction reactions involving oxygen, hydrogen sulfide ion, vanadium and anthraquinone disulfonic acid [1–5]. The process can treat gases with varying H₂S concentrations in the input stream to produce off-gas with less than 10 ppm H₂S. This flexibility has found important commercial use in treating a variety of different gas streams, including natural gas, Coke oven gas, Claus tail gas, geothermal vent gas and synthetic natural gas [6]. Direct treatment of gas streams eliminates the need for a separate acid gas removal unit. Very low energy requirements, capital costs and operating expenses have lead to its widespread use with ~ 107 plants operating, under construction, or being designed, as of 1988 [7].

As is frequently the case for proprietary industrial procedures, the chemistry involved in the Stretford process is well understood in a general sense but details are sketchy and imprecise. The chemistry is typically summarized according to the following steps.

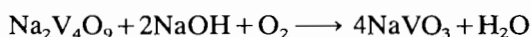
(1) Absorption of H₂S from gas stream



(2) Oxidation of hydrosulfide by vanadate to yield elemental sulfur



(3) Reoxidation of vanadium by molecular oxygen in the presence of anthraquinone disulfonic acid



Despite this seeming simplicity it is clear from a variety of operating problems that the process is far more complex. Previous work on the chemistry of the Stretford process has centered on trying to establish by various means, including ⁵¹V NMR, the exact speciation of the V(V) in ‘Stretford-like’ solution as a function of variables such as pH and concentration [8]. The aqueous chemistry of vanadate is known to be very complex hence this approach has the inherent problem that even if the speciation can be established exactly, the question will remain as to which of the many forms of V(V) known to be present will be the catalytically active one [9, 10]. The key to our efforts at improving the Stretford process lies in sequestering all the V(V) into a single form so that an unambiguous mechanism can be determined. Complexing agents capable of doing this must meet several criteria: (i) very high binding constants for both V(V) and V(IV) so that at an appropriate pH all the vanadium will be complexed, (ii) appropriate thermodynamic redox potential so as to effectively oxidize HS[−] to elemental sulfur and, in turn, be reoxidizable by molecular oxygen, (iii) easy synthetic modifiability to allow for tuning of

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redox potentials by substitution on the ligand moiety. Multidentate phenolates and catecholates fulfill all of these criteria. The chemistry of multidentate phenolate and catecholate ligands with vanadium has been studied previously and has shown that they are excellent ligands for both V(IV) and (V) and generally undergo reversible electrochemistry [11–13]. Hence we have chosen the sulfonated catecholamide ligand 1,5,10-tris(2,3 dihydroxybenzoyl)-1,5,10-triazadecane (3,4 LICAMS) as our initial sequesterent (Fig. 1)*. The results of our studies on the use of the V(V) complex of this ligand as a catalyst for the Stretford Process are reported herein.

Materials and methods

3,4 LICAMS was prepared by a modification of the method of Fish and Tannous [14]. Sulfonation of the ligand was accomplished by a previously reported procedure [15]. Sodium vanadate (Fisher), sodium hydrosulfide hydrate (Aldrich) and KNO_3 (Aldrich) were all used as received.

Kinetic studies

Rates were estimated from measurement of absorbance changes using a Hi-Tech SFA-12 stopped-flow apparatus attached to an HP 8520 diode array spectrophotometer which was interfaced with a Compaq 386 microcomputer running OLIS supplied software for data collection and analysis. Reactions were monitored at wavelengths as shown in the figures or text. Reactions were carried out under pseudo-first order conditions with the ratio of hydrosulfide to vanadium greater than 10/1. Acidities were regulated by acetate and/or phosphate buffers at a final concentration of 0.08 M. Values of pH for the mixtures were checked experimentally at the conclusion of each reaction. Ionic strength was regulated at 0.5 M by addition of KNO_3 . The desired temperature (± 1 °C) was controlled by a RTF-210 water circulator.

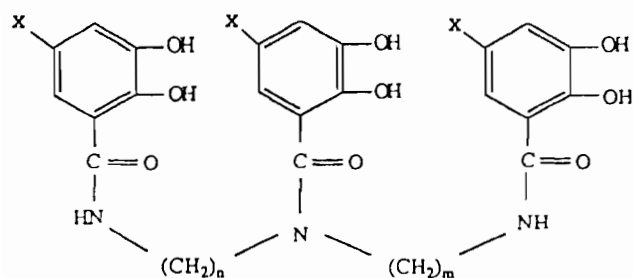


Fig. 1. Structure of 3,4 LICAMS where $n = 3$, $m = 4$ and $x = \text{SO}_3^-$

*Abbreviations 3,4 LICAMS stands for linear-catecholamide-sulfonated. The 3 and 4 refer to the number of carbon atoms in the triamine backbone

Results

Vanadium(V) LICAMS displays a characteristic and intense optical spectrum at neutral to modestly acidic pH. Monitoring the absorbance at a variety of wavelengths shows that the reaction of V(V) LICAMS with hydrosulfide is clearly biphasic. Depending on the pH there is initially a rapid decrease in absorbance in the 480–720 nm region followed by a slower increase. This behavior is consistent with the formation of an intermediate. By choosing the appropriate conditions it proved possible to dissect the kinetics into the two well behaved first order steps. The rapid formation of the intermediate was monitored at 600 nm using stopped flow spectrophotometry. The temperature was lowered to 15 °C in order to achieve decay times within the range of our apparatus. The reaction was carried out under pseudo-first order conditions using a 10-fold excess of hydrosulfide. Rapid scan spectrophotometry shows that the deep green color caused by LMCT transitions of the V(V) catecholate is bleached, yielding a relatively featureless spectrum for the intermediate. Kinetic data reveal that the reaction is first order in both V(V) complex and in hydrosulfide. Plots of k_{obs} versus pH over the range 5.15–6.61 (Fig. 2) gave a straight line indicating a reaction first order in $[\text{H}^+]$ and gave a second order rate constant of $1.08 \times 10^7 \text{ m}^{-2} \text{ s}^{-1}$.

The second, and much slower reaction, was studied at room temperature and was monitored at 670 nm. Rapid scan spectrophotometry clearly shows formation of the features characteristic of the optical spectrum of V(IV) catechols [11, 16]. The spectrum of the final deep blue product is identical to that of an authentic sample of equimolar V(IV) LICAMS indicating complete one-electron reduction V(V). This is confirmed by the presence of the characteristic EPR spectrum of

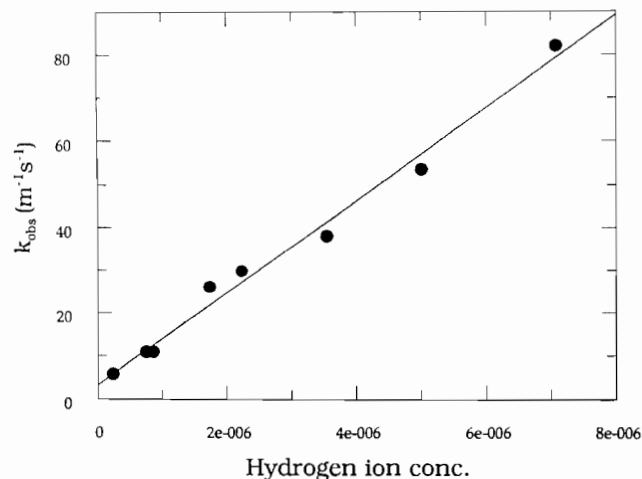


Fig 2 Plot of k_{obs} vs $[\text{H}^+]$ at 15 °C for the initial rapid phase of the reaction of V(V) LICAMS with H_2S

V(IV) catechol [17]. This slow reaction is first order in both SH^- and V(V) (Table 1) but is independent of pH with a second order rate constant of $5.58 \times 10^{-1} \text{ m}^{-1} \text{ s}^{-1}$. Concomitant with the appearance of V(IV) LICAMS is the formation of a white precipitate of colloidal sulfur.

The data as outlined above are consistent with two consecutive first order reactions where the initial reaction is identified with the relatively rapid and pH dependent formation of a V(V) LICAMS hydrosulfide intermediate. The lack of either the optical or ESR spectrum characteristic of V(IV) suggests that electron transfer has *not* taken place in the intermediate. An alternative scheme where the intermediate represents a V(III) complex produced by the two-electron reduction of V(V) seems unlikely given the extreme air sensitivity of V(III) catecholates and not seen with the intermediate. The model is also supported by examination of the rapid scan optical spectra as a function of pH. At low pH (4.40) and at 25 °C the reaction forming the intermediate is very fast leading to there being essentially only two species present in solution at any time; the intermediate and the final product. This suggests an isobestic point ought to be maintained. Figure 3 clearly shows that one is indeed present after the first 10–20 s of the reaction. As the pH is raised, the reaction forming the intermediate is slowed so that at pH 5.90 starting material, intermediate and final product are all present. Figure 4 shows that both the formation of the intermediate (decrease in absorbance at 600 nm) and its subsequent conversion to product (increase in absorbance at 600 nm) are observable.

The overall process can be made cyclic by bubbling air through the solution containing the reduced vanadium. Approximately 80–90% reoxidation of V(IV) to V(V) occurred at pH 6.00 after 30 min. Reoxidation in this manner regenerates the initial V(V) LICAMS spectrum.

TABLE 1 Kinetic data for the 'slow' reaction

V(V) complex $\times 10^4$	$[\text{HS}^-]$ $\times 10^3$	$[\text{H}^+]$ $\times 10^6$	k_{obs} ($\text{m}^{-1} \text{ s}^{-1}$)
1.0	2.0	5.01	0.69
1.0	4.0	5.01	0.52
1.0	6.0	5.01	0.36
0.5	4.0	5.01	0.39
1.0	4.0	2.23	0.58
1.0	4.0	0.89	0.62
1.0	4.0	0.67	0.62
1.0	4.0	0.36	0.69

Kinetic runs were carried out at 25 ± 1 °C; $\mu = 0.5$ (KNO_3). Experiments were monitored at 670 nm using stopped flow

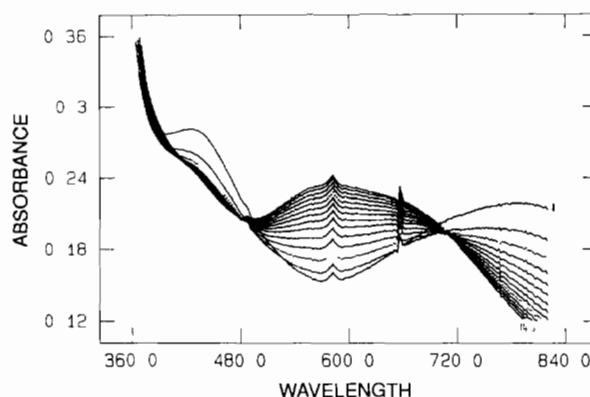


Fig. 3. A series of rapid scan visible spectra for the reaction between H_2S and V(V) 3,4 LICAMS at pH 4.4. Spectra are at 8.5 s intervals

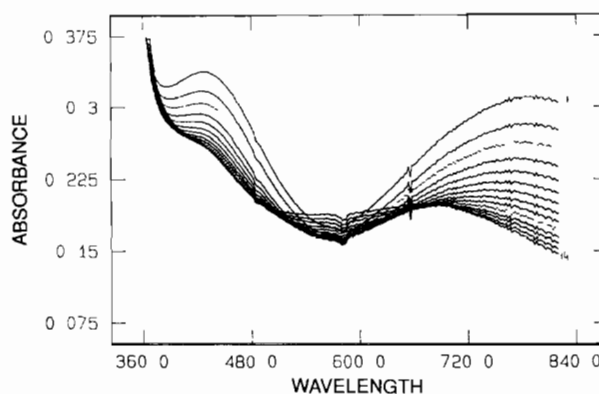
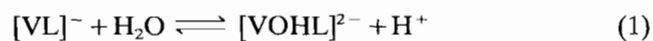


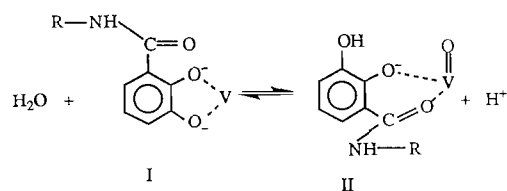
Fig. 4. A series of rapid scan visible spectra for the reaction between H_2S and V(V) 3,4 LICAMS at pH 5.9. Other conditions as in Fig 3. The absorbance at 600 nm initially decreases then increases

Discussion

The presence of an intermediate in the reaction between V(V) LICAMS and H_2S strongly suggests that the redox reaction is an inner sphere process. The initial reaction is most probably formation of a V(V)–SH complex which then undergoes internal electron transfer. At first glance this is somewhat surprising since the V(V) LICAMS was expected to have a coordinatively saturated 'triscatecholato' structure and to undergo a simple outer sphere electron transfer [11, 16, 18]. However in a previous study of the chemistry of V(V) LICAMS we have found that the triscatecholato is stable only at low pH [19]. As the pH is raised it undergoes hydrolysis according to eqn. (1):



It is this species that represents > 90% of the vanadium over the pH range 4.40–6.60 where this study was conducted. The exact nature of the hydrolyzed species is speculative since no X-ray data is available, but it



Scheme 1.

is likely a vanadium oxo complex with a protonated catechol arm similar to the 'salicylate' mode of bonding proposed for protonated Fe^{3+} -LICAMS (Scheme 1) [20, 21]. It is easy to envision attack by the H_2S on the carbonyl site leading to formation of a sulfide complex with displacement of a ligand arm.

In a detailed study of a related chelated iron-based liquid redox process for removal of hydrogen sulfide, DeBerry has investigated the kinetics of the iron EDTA- H_2S system [22]. The process is complex but appears to go through a sulfur bridged dinuclear species prior to electron transfer. Oxidation of sulfide occurs much more slowly. One of the major pathways for sulfur formation involves formation of polysulfide-bridged $\text{Fe}(\text{III})$ chelate dimers. Oxidative ring formation is the final slow step. Polysulfide intermediates comprise another pathway for sulfur formation. Either route circumvents the energetically unfavorable one-electron formation of bisulfide radical. Although the lack of a useful spectral signature for the intermediate, in the case reported here, precludes a direct assessment of its stoichiometry, it seems likely that it represents a sulfide/polysulfide bridged dimer of $\text{V}(\text{V})$ LICAMS.

Conclusions

$\text{V}(\text{V})$ complexes of 3,4 LICAMS proved to be effective redox catalysts for the oxidative removal of H_2S , producing elemental sulfur efficiently even at low pH. $\text{V}(\text{IV})$ LICAMS produced in the redox reaction can be oxidized readily by molecular oxygen to regenerate the $\text{V}(\text{V})$ complex thereby producing a viable catalytic cycle. Standard Stretford chemistry typically functions at pH 8–10 which leads to problems with further

oxidation of the sulfur to soluble sulfate and thiosulfate which eventually have to be removed from the process stream. Operating improvements can therefore be had by lowering the process pH if efficiency can be kept up by new catalysts such as $\text{V}(\text{V})$ 3,4 LICAMS.

Acknowledgements

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