

## KINETICS AND MECHANISM OF REDUCTION OF VANADIUM(V) BY THIOPHENOL IN AQUEOUS PERCHLORIC ACID MEDIUM

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### Abstract

*Kinetics and mechanism of the oxidation of thiophenol by ammonium trioxovanadate (V),  $\text{NH}_4\text{VO}_3$ , was investigated in 40% (V/V) aqueous ethanol and  $0.01 \text{ mol dm}^{-3} \text{ HClO}_4$ . Vanadium(V) was reduced to the corresponding V(IV) whereas thiophenol was oxidized to diphenyldisulphide at  $27^\circ \text{C}$  and  $I = 0.0101 \text{ mol dm}^{-3} (\text{NaClO}_4)$ . Stoichiometric studies indicated that one mole of V(V) was reduced per mole of thiophenol oxidized. The reaction was determined to be first order in [oxidant] and [reductant]. The rate of reaction was positively affected on varying  $[\text{H}^+]$  at  $1 \times 10^{-3} \leq [\text{H}^+] \leq 0.1 \text{ mol dm}^{-3}$ . Plot of acid-dependant rate constants  $k_{\text{H}^+}$  ( $k_2$ ) against the  $[\text{H}^+]^2$  was linear without intercept. The rate of the reaction remained invariant on varying the ionic strength of the medium. Addition of small amounts of anions and cations did not affect the rate of reaction. The reaction has been rationalized on the basis of an inner-sphere reaction pathway.*

**Keywords:** Reduction, Vanadium(V), Thiophenol, Kinetics and Mechanism

### Introduction

Vanadium(V) is reportedly toxic. Administration of ammonium trioxovanadate(V),  $\text{NH}_4\text{VO}_3$ , in rats has been reported to have negative effects on fertility, reproduction and progeny [1]. It crosses the placenta barrier and accumulate in the fetuses especially fetal skeleton causing visceral and skeletal anomalies. At high doses V(V) causes cytotoxicity and reduced growth [2,3]. V(V) has also been employed as a sensor for N-acetyltransferase activity in human hepatocytes [4] and its teratogenic effect on Swiss albino mice documented[5]. Investigation into the mode of V(V) toxicity revealed that the degree of toxicity correlates with the depletion of cellular glutathione and related non-protein thiols[6]. The reports posit that V(V) and thionyl radicals were generated in the reactions. Further investigation based on the reaction of V(V) and glutathione, cysteine,  $\mu$ -acetylcystein and penicilliamine using ESR Spin trapping also revealed the production of V(V) complexes[7]. Intermediate of the form V(V) - thiolate were also isolated.

Interesting results have been obtained for the reactions of V(V) with some thiols under biological conditions [8,9] in which the reduction of V(V) to V(IV) was accompanied by formation of V(V) and V(IV) complexes. Mercaptoethanol as the model reductant, formed V(IV)-sulphur complexes of 2:2 stoichiometry at neutral to alkaline pH, but at lower pH and high solute concentrations, V(V) oxidized the thiol and V(IV)-thiol complex was formed. In another report, it was shown that NADPH conjugates the reduction of V(V) to V(IV) and it was possible to reduce V(IV) to V(III) using cysteine methyl ester [10]. Implication of V-thioester intermediate in the reaction of V(V) with thiols was reinforced by the work of Legrum [11] involving glutathione and cysteine where an intense blue coloured complex that absorbed at 750 nm was formed at  $\text{pH} < 5$ . Recently, the redox kinetics of heteropolyoxo  $[\text{MnV}_{13}\text{O}_{38}]^+$  was reported [12]. In acetate buffer of pH 3.25-4.30, the heteropoly V(V) ion was reduced to the V(IV) ion,  $\text{VO}^{2+}$  and mercaptoethanol oxidized to 2-

hydroxyethylidisedisulphide. The reaction was first order in [thiol] and V(V) and showed a triphasic nature.

Among the reported reactions of thiols with V(V), the redox kinetics of thiophenol with V(V) ion has not been investigated. This is probably due to its objectionable odor and low solubility in water. In our earlier reports we investigated the redox kinetics of Ce(IV) with thiophenol. The reaction which followed the inner-sphere path and was first order in both oxidant and reductant[13]. Ce(IV) was reduced to Ce(III) and thiophenol oxidized to diphenyl disulphide.

Insight into the interaction of V(V) with important biomolecules especially thiols is very crucial for a better understanding of the cytotoxicity of V(V). RSH/RSSR redox couple acts as a buffer in regulating biological sites[14]. The variable nature of the redox potentials which in most cases are pH dependent leads to changes in protein reactivity, structure orientations, enzymatic activity and transport activity in cells[15]. In this article we report an investigation of the dynamics of the oxidation of a hitherto relatively uninvestigated thiol (thiophenol), by V(V). We hope the results obtained in this study will lead to better insight into the behaviour of V(V) at cellular sites.

### Materials and Methods

All reagents were of analytical grade and were used as supplied without further purification unless otherwise stated. Thiophenol (99.5%  $\text{C}_6\text{H}_5\text{SH}$ , Fluka) herein after referred to as PhSH was used as the reductant. Its solutions were prepared in degassed 1:1 ethanol/water mixture. Ammonium trioxovanadate(V) (ammonium metavanadate  $\geq 99.0\% \text{ w/w}$ ,  $\text{NH}_4\text{VO}_3$ , Fluka) was used as the oxidant. Its solutions were prepared fresh for each kinetic run using doubly distilled deionized water. Analar grade  $\text{NaClO}_4$  was used in maintaining constant ionic strength.

The stoichiometry of the reaction of thiophenol with ammonium trioxovanadate(V) was determined by spectrophotometric titration based on the mole ratio method [16]. The concentration of PhS was kept constant at  $1 \times 10^{-4} \text{ mol dm}^{-3}$  and the concentration of

$\text{NH}_4\text{VO}_3$  varied between  $1 \times 10^{-5}$  to  $1 \times 10^{-3}$  mol  $\text{dm}^{-3}$  at  $[\text{H}^+] = 0.01$  mol  $\text{dm}^{-3}$  ( $\text{HClO}_4$ ),  $I = 0.02$  mol  $\text{dm}^{-3}$  ( $\text{NaClO}_4$ ) and  $T = 27^\circ\text{C}$ . At the completion of the reaction, the absorbances of reaction solutions were obtained at 305 nm. The  $\lambda_{\text{max}}$  of 305 nm was determined on running UV spectrum (Figure 1) of 0.001 mol  $\text{dm}^{-3}$   $\text{NH}_4\text{VO}_3$  in  $\text{HClO}_4$ . All kinetic runs were based on this  $\lambda_{\text{max}}$ . A point of inflexion on the curve obtained on plot of absorbances against mole ratio  $\text{NH}_4\text{VO}_3$ :PhSH gave the stoichiometry of the reaction.

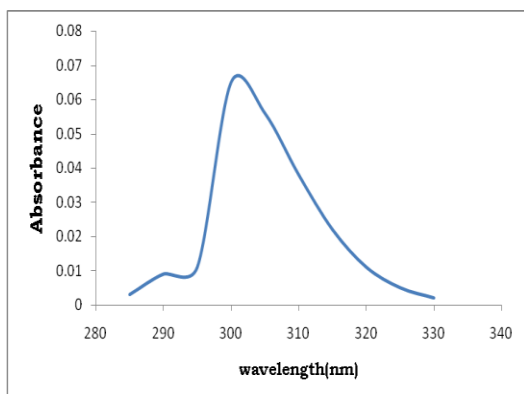


Figure 1. UV spectrum of V(V) in dilute acid medium

Kinetic runs were done under pseudo-first order conditions of [PhSH] being in at least 20-fold excess of the  $[\text{NH}_4\text{VO}_3]$ . The decrease in absorbance of  $\text{NH}_4\text{VO}_3$  at 305 nm were read from a Jenway 6405 UV/Visible Spectrophotometer. Pseudo-first order rate constants,  $k_{\text{obs}}$  were obtained from the gradients of the plot of  $\log(\text{At}-\text{A}\infty)$  against time based on the equation  $A = A_0 + a(1 - e^{-kt})$  [8].  $A_t$  = absorbance at time,  $t$  and  $A\infty$  = absorbance at the completion of the reaction. Plot of kinetic decays were linear for at least 85% extent of the reaction. Second order rate constants,  $k_2$ , were determined as the ratio of  $k_{\text{obs}}/[\text{PhSH}]$ .

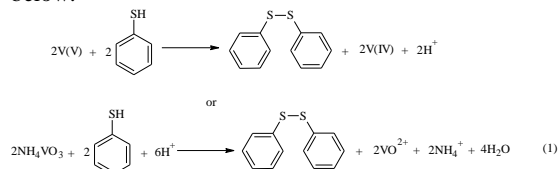
The effect of  $[\text{H}^+]$  on the rate of reaction was investigated using  $\text{HClO}_4$ . The concentration of the acid was varied between  $0.001 \leq [\text{H}^+] \leq 0.10$  mol  $\text{dm}^{-3}$ , while the concentration of oxidant, reductant and ionic strength was kept constant at  $T = 27^\circ\text{C}$  and  $\lambda_{\text{max}} = 305$  nm. The results indicated increase in rate of reaction with  $[\text{H}^+]$ .

The effect of ionic strength on the rate of reaction was determined using  $\text{NaClO}_4$ . The ionic strength was varied within 0.011 to 0.05 mol  $\text{dm}^{-3}$  ( $\text{NaClO}_4$ ) and concentrations of oxidant, reductant,  $\text{H}^+$  were kept constant at  $T = 27^\circ\text{C}$  and  $\lambda_{\text{max}} = 305$  nm. The rate of reaction remained invariant on varying the ionic strength of the reaction media.

Effect of presence of added ions on the rate of reaction was investigated using  $\text{Cl}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$ . The concentrations of the ions were varied between 0.005 to 0.05 mol  $\text{dm}^{-3}$  and other parameters kept. The results indicate that these were unable to catalyse the reaction. Varying the dielectric constant of the medium from 68.22 to 74.16, using propan-2-one, and other parameters kept constant, the rate of reaction increased with increase in dielectric constant.

## Results and Discussion

Plot of absorbance versus mole ratio following spectrophotometric titration gave a point of inflexion at approximately 1.0 indicating a 1:1 reductant:oxidant mole ratio. The results are consistent with equation (1) below.



The stoichiometry of 1:1 is in accord with one-electron transfer and has been reported for other reactions of thiols with V(V) [4,8,9,17,10-12]. Production of the V(IV) ion,  $\text{VO}^{2+}$  as the inorganic product is consistent with earlier reports [11,12]. On mixing a large excess of  $\text{NH}_4\text{VO}_3$  with PhSH at 0.01 mol  $\text{dm}^{-3}$   $\text{HClO}_4$  and ensuring that all PhSH was consumed after 4 h, and extracting with diethyl ether several times, two layers were obtained. The UV- spectrum of the aqueous phase (Figure 1) gave a prominent peak at 305 nm indicating presence of excess V(V) but no peak of V(III) around 403 nm and above. V(V) is  $d^0$  and shows no d-d transition but charge transfer band from 266 – 305 nm [18,19]. This is in conformity with earlier reports that reduction of V(V) with thiols yields V(IV) [9,11,17,12,18,19]. Evaporation of ether from the organic extract yielded an off white crystalline solid. Infrared spectrum of this organic product showed no peak between 2000 – 2700  $\text{cm}^{-1}$  indicating absence of  $\nu(\text{S-H})$  of thiols but the presence of a weak band centered around 722  $\text{cm}^{-1}$  is confirmatory of  $\nu(\text{C-S})$  of disulphides. This same observation was reported for the reaction of Ce(IV) with PhSH [13].

## Kinetics and Reaction Order

Under pseudo-first order conditions of  $[\text{PhSH}] \gg [\text{V(V)}]$ , plots of  $\log(\text{At}-\text{A}\infty)$  versus time was linear to about 85% extent of reaction, indicating first order dependence of rate on  $[\text{V(V)}]$ . It also suggest no inhibition of the reaction by the products for this extent of reaction. Pseudo-first order and second order rate constants are shown in Table 1. Pseudo-first order rate constants,  $k_{\text{obs}}$ , increased with increase in  $[\text{PhSH}]$  at  $2.0 \times 10^{-3} \leq [\text{PhSH}] \leq 3.0 \times 10^{-3}$  mol  $\text{dm}^{-3}$  with  $[\text{V(V)}] = 1 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ,  $[\text{H}^+] = 0.01$  mol  $\text{dm}^{-3}$ ,  $I = 0.0101$  mol  $\text{dm}^{-3}$  ( $\text{NaClO}_4$ ) and  $T = 27^\circ\text{C}$ . Second order rate constants,  $k_2$ , were obtained as ratio of  $k_{\text{obs}}/[\text{PhSH}]$ . Reported  $k_2$  values are the result of replicate runs and were fairly constant at  $2.61 \pm 0.03$   $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ .

Table 1 Pseudo-First order and Second order rate constants for the reduction of V(V) by thiophenol at  $[\text{V(V)}] = 1 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ,  $[\text{H}^+]$ , 0.0 mol  $\text{dm}^{-3}$ ,  $I = 0.0101$  mol  $\text{dm}^{-3}$  ( $\text{NaClO}_4$ ),  $\lambda_{\text{max}} = 433$  nm and  $T = 27 \pm 1^\circ\text{C}$

| $10^4$ [PhSH]/mol $\text{dm}^{-3}$ | $10^3$ $k_{\text{obs}}/\text{s}^{-1}$ | $k_2/(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$ |
|------------------------------------|---------------------------------------|---|
| 20.0                               | 5.30                                  | 2.65  |
| 22.0                               | 5.64                                  | 2.56  |
| 24.0                               | 6.24                                  | 2.60  |
| 26.0                               | 6.81                                  | 2.62  |
| 30.0                               | 7.92                                  | 2.64  |

The invariant nature of  $k_2$  values also infers that the rate of reaction is first order dependent on [PhSH]. Least square fits ( $r = 0.989$ ) of the plot of  $\log k_{\text{obs}}$  versus  $\log$  [PhSH] gave a straight line (Figure 2) with a slope of approximately 1.0, in accord with first order dependence on [PhSH]. Hence the rate of reaction at constant pH can be described by Equation (2).

$$\frac{-d[V(V)]}{dt} = k_2[V(V)] [PhSH]$$

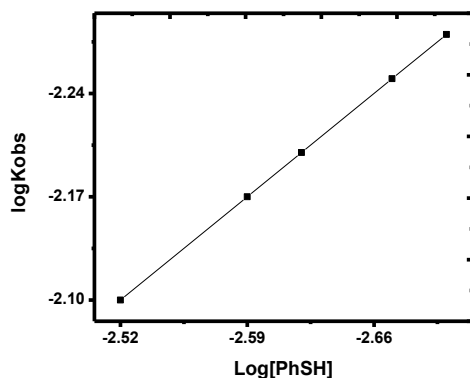


Figure 2 Plot of  $\log K_{\text{obs}}$  versus  $\log$  [PhSH]

First order dependence of [thiols] in most of their redox reactions had been reported [8, 11, 12] and the results here tend to align with earlier reports. This suggests PhSH to be a one- electron reductant.

#### Acid Dependence

Within the hydrogen ion concentration range of  $1 \times 10^{-3} \leq [H^+] \leq 1 \times 10^{-1} \text{ mol dm}^{-3}$ , the effect of  $[H^+]$  on the reaction kinetics was investigated with the concentration of oxidant, reductant and ionic strength kept constant. Under these conditions, the rate of reaction increased with  $[H^+]$  as shown in Table 2. A plot of  $k_2$  versus  $[H^+]^2$  was linear with insignificant intercept, conforming to equation (3);

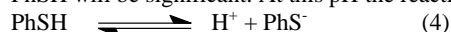
$$K_{H^+} = m [H^+]^2 \quad (3)$$

Table 2 Acid-dependent rate constant from the reduction of V(V) by thiophenol at  $[V(V)] = 1 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[PhSH] = 2.2 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.15 \text{ mol dm}^{-3} (\text{NaClO}_4)$ ,  $\lambda_{\text{max}} = 433 \text{ nm}$  and  $T = 27 \pm 1^\circ \text{C}$

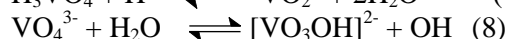
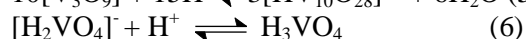
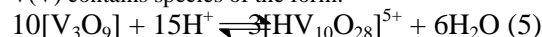
| $[HClO_4]/\text{mol dm}^{-3}$ | $10^3 k_{\text{obs}}/\text{s}^{-1}$ | $k_2/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ |
|-------------------------------|-------------------------------------|---|
| 0.001                         | 5.02                                | 2.28  |
| 0.005                         | 5.25                                | 2.37  |
| 0.010                         | 5.65                                | 2.9   |
| 0.06                          | 9.68                                | 4.40  |
| 0.07                          | 11.04                               | 5.02  |
| 0.08                          | 13.44                               | 6.11  |
| 0.10                          | 15.47                               | 7.03  |
|                               | 20.67                               | 9.42  |

Enhancement of rate of reaction with increase in  $[H^+]$  is not popular with oxidation of thiols by metal ions. Infact most of the reported reactions were inverse acid-dependent[13,15,12,20]. Only very few were acid dependent but at high  $[H^+]$ [21]. The Pka for the

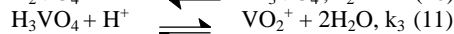
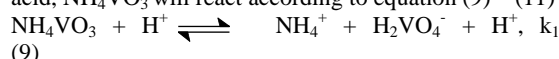
dissociation of PhSH is given to be about 9.93[21]. It is doubtful whether at the prevailing conditions of this reaction (pH between 3.0 and 1.0) the dissociation of PhSH will be significant. At this pH the reaction;



will be subdued leading prefer to the reductant reacting in a non-deprotonated form. It is most likely that the positive acid dependence of the reaction emanates from the various equilibria assumed by V(V) in aqueous solutions of pH 2-5[22,23]. Through pH, cryoscopy, ion-exchange, UV/Visible spectral, IR/ Raman and NMR studies, it has been shown that aqueous acid solution of V(V) contains species of the form:



These reactions are very essential in analyzing the nature of acid-dependence of V(V) reaction in acid solutions. It is the protonation of these species that significantly directs the course of V(V)-PhSH reaction. In aqueous acid,  $NH_4VO_3$  will react according to equation (9) – (11)



The vanadyl cation,  $VO_2^+$  is a major reductant in this reaction. Its reaction with PhSH will lead to formation of a precursor complex of the form  $[PhS-VO_2]$ . In the some reactions this precursor complex manifested as a deep blue complex formed before the electron transfer reaction[11]. In the V(V)-PhSH reaction, a brilliant blue colour appeared on mixing the oxidant and reductant indicating formation of a precursor complex. This complex was short-lived and its subsequent decay led to the redox process.

#### Effects of ionic strength, dielectric constant and added ions

The ionic strength of the reaction was varied from 0.011 to  $0.05 \text{ mol dm}^{-3}$  using  $\text{NaClO}_4$  at  $[V(V)] = 1 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[PhSH] = 2.2 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[H^+] = 0.01 \text{ mol dm}^{-3}$ ,  $\lambda_{\text{max}} = 305 \text{ nm}$  and  $T = 27^\circ \text{C}$ . The results shown in Table 3 indicate that within this prevailing ionic strength, the rate of reaction was not altered. Lack of primary salt effect for reaction of ions in aqueous solution supports a rate determining step where one of the redox partners is a neutral molecule[24] thereby making the product of charges zero. Since the vanadyl ion is a cation, it is most likely the rate determining step will involve  $VO_2^+$  and PhSH or a precursor complex that decompose in the redox in the step.

Table 3 Effect of ionic strength on V(V)-PhSH at  $[V(V)] = 1 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[PhSH] = 2.2 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[H^+] = 0.01 \text{ mol dm}^{-3}$ ,  $\lambda_{\text{max}} = 433 \text{ nm}$  and  $T = 27 \pm 1^\circ \text{C}$

| $I/\text{mol dm}^{-3}$ | $10^3 k_{\text{obs}}/\text{s}^{-1}$ | $k_2/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ |
|------------------------|-------------------------------------|---|
| 0.011                  | 5.63                                | 2.56  |
| 0.02                   | 5.62                                | 2.55  |
| 0.03                   | 5.65                                | 2.57  |
| 0.04                   | 5.64                                | 2.56  |
| 0.05                   | 5.67                                | 2.58  |

**Table 4** Effect of dielectric constant on V(V)-PhSH at [PhSH] = 2.2 x 10<sup>-3</sup> mol dm<sup>-3</sup>, [V(V)] = 1 x 10<sup>-4</sup> mol dm<sup>-3</sup>, [H<sup>+</sup>] = 0.01 mol dm<sup>-3</sup>, λ<sub>max</sub> = 433 nm and T = 27 ± 1 °C

| Dielectric Constant (D) | 10 <sup>3</sup> k <sub>obs</sub> /s <sup>-1</sup> | k <sub>2</sub> /(dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> ) |
|-------------------------|---|--|
| 68.22                   | 2.87  | 1.30   |
| 70.51                   | 3.85  | 1.75   |
| 71.78                   | 4.53  | 2.06   |
| 72.97                   | 5.06  | 2.30   |
| 74.16                   | 5.26  | 2.39   |

Dielectric constant (D) was varied from 78.16 to 68.22 by adding some portions of Propan-2-one to make up the reaction mixture. Under this condition other parameters were kept constant and the rate of reaction monitored at 27 °C. Results shown in Table 4 are indicative that rate of reaction increase with D. This observation does not support the result obtained on varying ionic strength as it indicates the interaction of anions and cations at the rate determining step. The dependence of rate on D is likely a medium effect arising from the various equilibrium established by V(V) in aqueous acid [18].

The catalytic effect of added ions was investigated by adding various amounts of K<sup>+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup> and CH<sub>3</sub>COO<sup>-</sup> in the range 5.0 x 10<sup>-3</sup> to 5 x 10<sup>-2</sup> mol dm<sup>-3</sup> and concentrations of oxidant, reductant and acid kept constant. The result in Table 5 indicate that the rate of reaction was unaffected by the presence of these ions at the concentration range of investigation. This observation shows lack of catalysis and points to likely formation of a precursor complex with inner-sphere character rather than an outer-sphere path[8,12,25,26]. At the rate determining, the precursor complex, [VO<sub>2</sub>-SPh] undergoes intramolecular electron transfer and subsequent decomposition thereby ruling out any catalysis.

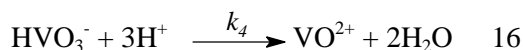
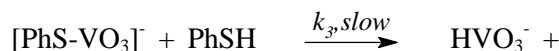
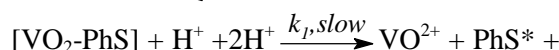
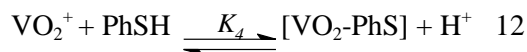
**Table 5** effect of added ions on V(V)-PhSH reaction at [V(V)] = 1x 10<sup>-4</sup> mol dm<sup>-3</sup>, [PhSH] = 2.2 x 10<sup>-3</sup> mol dm<sup>-3</sup>, [H<sup>+</sup>] = 0.01 mol dm<sup>-3</sup>, λ<sub>max</sub> = 433 nm and T = 27 ± 1 °C

| 10 <sup>3</sup> [Cl <sup>-</sup> ]                  | 10 <sup>3</sup> k <sub>obs</sub> /s <sup>-1</sup> |
|---|---|
| 5   | 5.66  |
| 10  | 5.72  |
| 25  | 5.64  |
| 40  | 5.63  |
| 50  | 5.67  |
| 10 <sup>3</sup> [CH <sub>3</sub> COO <sup>-</sup> ] |   |
| 5   | 5.63  |
| 10  | 5.66  |
| 25  | 5.72  |
| 40  | 5.64  |
| 50  | 5.67  |
| 10 <sup>3</sup> [K <sup>+</sup> ]                   |   |
| 5   | 5.61  |
| 10  | 5.65  |
| 25  | 5.64  |
| 40  | 5.66  |
| 50  | 5.63  |
| 10 <sup>3</sup> [Mg <sup>2+</sup> ]                 |   |

|    |      |
|----|------|
| 5  | 5.64 |
| 10 | 5.68 |
| 25 | 5.70 |
| 40 | 5.66 |
| 50 | 5.63 |

#### Reaction Mechanism

Considering the stoichiometry, acid dependence, effect of ionic strength and effect of added anions and cations, the following mechanism is proposed for the reaction



$$\text{Rate} = -d[\text{V(V)}] = k_1[\text{VO}_2\text{-SPh}][\text{H}^+]^2 + k_3[\text{PhS-VO}_3][\text{PhSH}] \quad 17$$

Following steady state approximation (SSA) and taking recourse to equations (9)-(11), it is deduced that

$$[\text{VO}_2\text{-SPh}] = \frac{K_4[\text{VO}_2^+][\text{PhSH}]}{[\text{H}^+]} \quad 18$$

Also

$$[\text{VO}_2^+] = K_3[\text{H}_3\text{VO}_4][\text{H}^+] \quad 19$$

$$[\text{H}_3\text{VO}_4] = K_2[\text{H}_2\text{VO}_4^-][\text{H}^+] \quad 20$$

and

$$[\text{H}_2\text{VO}_4^-] = K_1[\text{NH}_4\text{VO}_4] \quad 21$$

substituting equations (21) into (20) gives

$$[\text{H}_3\text{VO}_4] = K_2K_1[\text{NH}_4\text{VO}_4][\text{H}^+] \quad 22$$

And substituting equation (22) into (19) gives

$$[\text{VO}_2^+] = K_3K_4K_2K_1[\text{NH}_4\text{VO}_4][\text{PhSH}][\text{H}^+] \quad 23$$

In line with SSA

$$[\text{PhS-VO}_3] = k_2[\text{PhS}^*][\text{H}_2\text{VO}_4^-] \quad 24$$

$$[\text{H}_2\text{VO}_4^-] = K_1[\text{H}^+][\text{NH}_4\text{VO}_3] \quad 25$$

and

$$[\text{PhS}^*] = k_1K_4K_2K_1[\text{NH}_4\text{VO}_3][\text{H}^+]^2 \quad 26$$

Substituting equations (26) into (24) gives that

$$[\text{PhS-VO}_3] = k_2K_1K_2K_3K_4[\text{NH}_4\text{VO}_3][\text{H}^+] \quad 27$$

Substituting equations (23) and (27) into (17) gives

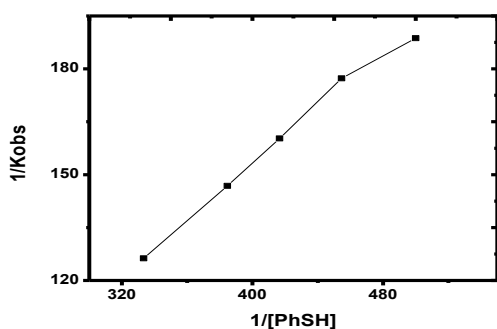
$$\text{Rate} = k_1K_1K_2K_3K_4[\text{NH}_4\text{VO}_3][\text{PhSH}][\text{H}^+]^2 + k_2k_3K_1K_2K_3K_4[\text{NH}_4\text{VO}_3][\text{PhS}][\text{H}^+]^2 = \{k_1 + k_2k_3K_1K_2K_3K_4[\text{NH}_4\text{VO}_3][\text{PhS}]\}[\text{H}^+]^2$$

$$k_2k_3\}K_1K_2K_3K_4 [NH_4VO_3][PhSH] [H^+]^2$$

Equation (28) is similar to equation (3) where  
 $m = \{k_1 + k_2k_3\} K_1K_2K_3K_4$   
 $= 0.70 \text{ mol}^2 \text{ dm}^{-6} \text{ s}^{-1}$

Formation of free radicals of the form PhS\* is a common feature of redox reaction of thiols and was confirmed by positive free radicals scavenging by acrylamide in the reaction mixture is excess methanol [13,11,8,9].

Equations (13) and (15) are the rate determining steps and involve decay of the intermediates. In each of the reactions, anion-neutral molecule or cation-neutral molecule is interacting thereby ruling out primary salt effect. These rate determining steps involve intramolecular electron transfer and decomposition of the precursor complex thereby inferring inner-sphere electron transfer path.



**Figure 3** Michaelis-Menten-type plot of  $1/K_{obs}$  versus  $1/[PhSH]$

Michaelis-Menten-type plot of  $1/k_{obs}$  versus  $1/[PhSH]$  (Figure 3) was linear with intercept at the  $1/k_{obs}$  axis. This corroborates operation of inner-sphere electron transfer reaction.

### Conclusion

This study was undertaken to investigate the kinetics of the reduction of V(V) by thiophenol and a reaction mechanism has been proposed. The rate law is determined as

$$-d[V(V)]/dt = \frac{\{k_1+k_2k_3\}K_1K_2K_3K_4 [NH_4VO_3][PhSH][H^+]^2}{[NH_4VO_3][PhSH][H^+]^2}$$

The formation of blue coloured complex  $[VO_2-SPh]$ , and increase of rate constants with increasing  $[H^+]$  is in accord with the proposed mechanism of the reaction.

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