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Kinetics of the Oxidation of Thiourea by Vanadium(V) in Perchlorate Media

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The redox reaction between vanadium(V) and thiourea has been investigated at 25 °C over the hydrogen ion concentration range $[H^+]$ = *0.2–1.40* M, *using a modified stopped-flow system. Several pathways have been identified and the existence has been established of intermediate complexes formed within the time of mixing. Two mol of thiourea are consumed per mol of oxidant, the vanadium(IV) product being considered to be a 1:1 thiourea complex. The reactions are too slow for positive identification of radical intermediates by flow e.s.r. methods. Both one- and two-electron transfer pathways are proposed and similarities in the reaction scheme with that of the corresponding chromium(VI) reaction are discussed.*

Introduction

The redox reactions of vanadium(V) with a variety of reagents have been well documented previously [1–3]. Many organic substrates require two equivalents of oxidant for reaction to a stable product. In such reactions a two step process involving formation of vanadium(IV) and a radical is preferred [1, 3] to a two electron transfer to vanadium(III). In a study of the oxidation of ascorbic acid [4] in an excess of vanadium(V), both kinetic and spectrophotometric evidence has been presented for intermediate complex formation. A transient species was also identified [5] in the reaction with thiomalic acid.

The oxidations of thiourea and its derivatives by metal ions have recently been examined. In the reaction with chromium(VI) [6], evidence has been provided for an inner-sphere route with the formation of a sulphur-bonded chromate ester. With Mn(III) [7] and Co(III) [8] as oxidants, however, although the reaction rates are consistent with a substitution-controlled inner-sphere redox mechanism, no direct evidence was available for any transient complexes. In order to extend the investigation to other oxo-ions, the reaction with vanadium(V) has been examined.

Experimental

Vanadium(V) solutions were prepared by dissolving ammonium metavanadate (Hopkin and Williams, A. R.) in aqueous perchloric acid. Thiourea (Hopkin and Williams) was twice recrystallised from 1:1 ethanol–water mixtures and purity of >99.8% confirmed by elemental analysis. Vanadium(IV) perchlorate solutions were prepared as follows: to a solution of vanadium(IV) sulphate, concentrated ammonium hydroxide was added dropwise until precipitation was complete. The dark blue–grey precipitate was digested for several hours, filtered, washed repeatedly with distilled water and then dried. A portion of the solid was dissolved in ~0.2 *M* $HClO_4$ and the resulting blue solution was analysed spectrophotometrically at λ = 750 nm (ϵ = 15.9 M^{-1} cm^{-1}) [9]. The preparation and standardisation of other reagent solutions has been described previously [6]. Solutions of thiourea were prepared immediately before use.

Stoichiometry

The stoichiometry of the reaction was determined in spectrophotometric titrations. After mixing solutions of vanadium(V) and thiourea, the residual oxidant concentration was monitored at wavelengths where there was little or no absorbance from vanadium(IV) or the organic products. In this way it was found that 1.95 ± 0.05 mol of thiourea react per mol of vanadium(V).

In a second analysis in excess of ligand, (the experimental conditions for kinetic runs) solutions after reaction were transferred to a cation exchange column. Since the thiourea is not protonated in moderately acidic media (<2 *M*), the unreacted substrate may thus be eluted without retention and monitored using a silver-ion titration in basic media [10]. A known excess of Ag(I) was added to the thiourea solution and after removal of the Ag_2S formed, the remaining Ag^+ ion was titrated with ammonium thiocyanate using Fe(III) as indicator. Repeated determinations indicated that 2.2 ± 0.1 mol of thiourea reacted per mol of oxidant.

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Kinetic Measurements

The rate of disappearance of vanadium(V) in the presence of an excess (>20fold) of thiourea was monitored on a modified stopped-flow apparatus described previously [11]. In some experiments where the formation of vanadium(IV) was examined (λ = 760 nm) identical rate constants were obtained. Measurements over the range $[H^+]$ = 0.20–1.40 *M* at I = 1.50 *M* were made at 25.0 °C. Each kinetic run was repeated at least twice, the agreement in all cases being ±3%.

Attempts to characterise the free radicals formed in the oxidation using a flow e.s.r. technique were unsuccessful owing to the slow rate of reaction. The formation of radicals was demonstrated by experiments with acrylonitrile. When ~0.02 *M* vanadium(V) was reacted with ~0.05 *M* thiourea in ~0.3 *M* $HClO_4$ in the presence of 5% v/v acrylonitrile, a cloudy suspension formed within a few minutes. Blank experiments with either vanadium(V) or thiourea excluded gave no detectable polymerisation. While these experiments do not serve to identify free radicals unambiguously, they do indicate that the reaction proceeds with the production of species capable of polymerisation initiation.

Results and Discussion

Spectrophotometric and ion exchange measurements establish that the overall reaction may be written as

$$V(V) + 2(NH_2)_2CS \longrightarrow V(IV)(NH_2)_2CS + \tfrac{1}{2}N_4H_6C_2S_2 + H^+$$

Although the disulphide was not isolated owing to analytical difficulties, it has, however, been shown to be virtually the only product in the Ce(IV) [12], Mn(III) [7] and Co(III) [8] oxidations when the organic substrate is present in large excess. Also, an indirect confirmation of production of formamidine disulphide was given by its ready decomposition to sulphur in acidic media.

Since two moles of thiourea are involved in the overall reaction, and vanadium(V) is undergoing an overall one-electron reduction, it is reasonable to assume that the product vanadium(IV) has one mole of substrate coordinated. This is substantiated by the observation of an increase of ~10% in optical density (λ = 750 nm) when the reaction mixture was compared to one containing only vanadium(IV). (Figure 1) A complex of 1:1 composition is formed between vanadium(IV) and SCN^- with spectrum similar to that of vanadium(IV) and the interaction may be similar to that with the thiourea.

Preliminary kinetic measurements at λ = 360 nm indicated the formation of a complex vanadium(V) and thiourea within the time of mixing. Absorbance changes at the wavelengths monitored were not sufficiently large to enable determinations of the equilibrium constant to be made. First order kinetic plots were observed over 80–90% reaction when both decrease of vanadium(V) and formation of vanadium(IV) were monitored. No effect of oxygen was observed as de-gassed reactant solutions gave identical results.

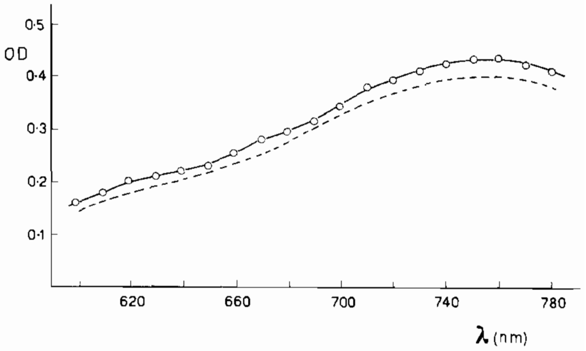


Figure 1. Comparison of spectra of reaction products of [V(V)] = 2.5 × 10^{-2} *M* + [thiourea] = 0.25 *M* in 1.0 *M* $[H^+]$ with that of a vanadium(IV) or ion of identical metal ion concentration.

The general kinetic features are that at the lower acidities studied, $[H^+] < 0.40$ *M* the order of reaction with respect of thiourea is two. However, as the acidity is increased, the order changes suggesting the involvement of an additional mole of substrate in the overall reaction. Also, at lower acidity the reaction order in $[H^+]$ is between 1 and 2 whereas above $[H^+]$ = 0.8 *M* a second order dependence is observed. The data are consistent with the following reaction scheme:

$$VO_2^+ + H_3\overset{+}{O} + L \overset{K_1}{\rightleftharpoons} V(OH)_3L^{2+} \qquad (1)$$

$$V(OH)_3L + H_3\overset{+}{O} + L \overset{K_2}{\rightleftharpoons} V(OH)_2L_2^{3+} + 2H_2O \qquad (2)$$

$$V(OH)_3L^{2+} + L \xrightarrow{k_1} V(IV)L + L' \qquad (3)$$

$$V(OH)_2L_2^{3+} \xrightarrow{k_2} V(III) + L_2^1 \qquad (4)$$

$$V(OH)_2L_2^{3+} + L \xrightarrow{k_3} V(III)L + L_2^1 \qquad (5)$$

$$V(III) + V(V) \xrightarrow{\text{fast}} 2V(IV) \qquad (6)$$

$$V(IV) + L \overset{\text{fast}}{\rightleftharpoons} V(IV)L \qquad (7)$$

$$2L^1 \xrightarrow{\text{fast}} L_2^1 \qquad (8)$$

where L represents thiourea, L′ the radical formed on oxidation and L_2^1 the corresponding disulphide. For this mechanism assuming equilibria K_1 and K_2 are rapidly established, the rate equation (9) may be derived.

$$\frac{-d[V(V)]}{dt} = (k_1K_1[H^+][L]^2 + k_2K_2K_1[H^+]^2[L]^2 + k_3K_2K_1[H^+]^2[L]^3)[V(V)] \qquad (9)$$

and under conditions of excess ligand the observed first order constant may be expressed in the form

$$k_{obs} = \frac{\{k_1K_1[H^+] + k_2K_1K_2[H^+]^2 + k_3K_1K_2[H^+]^2[L]\}[L]^2}{1 + K_1[H^+][L] + K_1K_2[H^+]^2[L]^2} \qquad (10)$$

$1 \gg K_1[H^+][L] + K_1K_2[H^+]^2[L]^2$ where the initial equilibrium constant values are low. Under conditions of high acidity where there is an observed $[H^+]^2$ dependence, the contribution from reaction (3) may be considered small and equation (10) reduces to the form

$$\frac{k_{obs}}{[H^+]^2[L]^2} = k_2K_2K_1 + k_3K_2K_1[L] \qquad (11)$$

The data are plotted in this manner in Fig. 2 from which values of $k_2K_2K_1 = 0.59\ M^{-1}\ s^{-1}$ and $k_3K_1K_2 = 2.6 \pm 0.14\ M^{-2}\ s^{-1}$ are derived. In the lower $[H^+]$ range and at low ligand concentrations, only reactions (3) and (4) contribute and a linear plot of $k_{obs}/[H^+][L]^2$ against $[H^+]$ was obtained from which values of $k_1K_1 = 0.30 \pm 0.04\ M^{-1}\ s^{-1}$ and $k_2K_1K_2 = 0.42 \pm 0.10\ M^{-1}\ s^{-1}$ were derived. The agreement in the values for $k_2K_1K_2$ is reasonable.

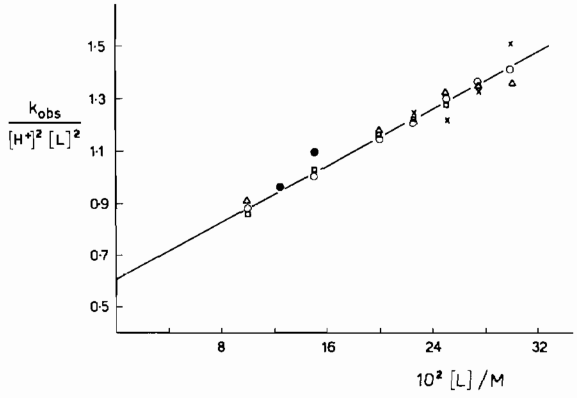
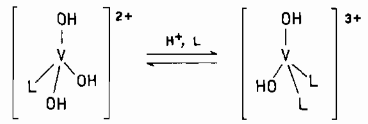


Figure 2. Plots of $k_{obs}/[H^+]^2[L]^2$ against [L] according to equation (11). ○, $[H^+] = 0.60\ M$; X, $[H^+] = 0.80\ M$; △, $[H^+] = 1.00$; □, $[H^+] = 1.25\ M$; ●, $[H^+] = 1.40\ M$.

Since plots of k_{obs} against $[H^+]^2$ pass through the origin at $[H^+] > 0.60\ M$ at constant [L] (equation (11)) it is suggested that VO_2^+ is a much weaker oxidising agent than $V(OH)_3^{2+}$. The role of the proton in reactions (1) and (2) may be to weaken the hydroxyl bond to the metal centre and so favour the formation (via H_2O elimination) of species of the type



(12)

The fact that in the lower hydrogen ion concentration range an intermediate order in $[H^+]$ between 1 and 2 is observed may be due to the incomplete establishment of equilibrium (12). The bis-coordinated complex in (12) may now act as a template for a two-electron transfer to the disulphide without the need for intermediate formation of vanadium(IV). This situation has been encountered previously in the corresponding reaction with Cr(VI) where a transition state of the type $[O_2CrL_2]^{\neq}$ is envisaged [6]. Also proton and ligand dependences similar to those observed in the present study have been identified in the reaction of vanadium(V) with iodide [13]. In such cases, the two electron reaction is followed by a rapid secondary electron transfer [14] with vanadium(V) to yield the observed vanadium(IV). It is of interest to note that in the case of ascorbic acid [4] where again a two-electron transfer is feasible, the rate of decomposition of the initial complex is sufficiently rapid that this (V(III) + V(V)) pathway is ruled out on the basis of reaction rate. Under the present conditions, however, both the formation of vanadium(IV) as a secondary process and the equilibration with ligand to yield the 1:1 vanadium(IV)–thiourea complex [15] would be rapid. It should be noted also that alternative reactions to (4) and (5) in which one-electron transfer is rate determining cannot be excluded since a similar kinetic analysis would result. It is unfortunate that the time scale of the reaction is such that e.s.r. techniques cannot readily be utilised in the identification of any radicals formed.

The observation that reactions (4) and (5) may proceed with direct formation of the disulphide is of interest in that the coordination sphere of the oxidant may provide the correct geometry for incipient S–S bond formation. A similar process for iron(III)–thiolate complexes [16] (where a unit change in the oxidation state of the metal is observed) is achieved by a rate-determining dimerisation with the formation of a Fe_2S_2 four-centre transition state. It thus appears that in many reactions involving thiols if the possibility exists where the formation of RS• may be eliminated by a multiple electron transfer then this route may be predominant.

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