LIST OF PUBLICATIONS:

ACCEPTED:

1  Kinetics of oxidation of antimony(III) by vanadium(V) in aqueous hydrochloric acid medium.

2  Kinetics and mechanism of ruthenium(III) catalyzed oxidation of dimethyl formamide by periodate in aqueous alkaline medium.

3  Mechanism of vanadium(V) oxidation of thallium(I) in aqueous acetic acid medium: A kinetic study.

4  A mechanistic study of osmium(VIII) catalyzed oxidation of manganate by periodate in aqueous alkaline medium.

5  Kinetics of oxidation of thallium(I) by permanganate in aqueous hydrochloric acid medium using stopped flow technique.
ABSTRACTED:

1 Uncatalyzed and palladium(II) catalyzed oxidation of allyl alcohol by periodate in aqueous alkaline medium.

COMMUNICATED:

1 Ruthenium(III) catalyzed oxidation of hexacyanoferrate(II) by periodate in aqueous alkaline medium.

2 Ruthenium(III)/Osmium(VIII) catalyzed oxidation of thiocyanate by periodate in aqueous alkaline medium

3 A kinetic study of oxidation of vanadium(IV) by permanganate in aqueous sulphuric acid medium by stopped flow technique.
4 Osmium(VIII) catalyzed hexacyanoferrate(III) oxidation of antimony(III) in aqueous alkaline medium and Analysis of osmium(VIII) in micro amounts by a kinetic method. 
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5 Ru(III) / Os(VIII) / Ru(III)+Os(VIII) catalyzed oxidation of allyl alcohol by periodate in aqueous alkaline medium. 

6 A mechanistic study of oxidation of chromium(III) by permanganate in aqueous alkaline medium using stopped flow technique. 

7 Kinetics of oxidation of thallium(I) by permanganate in aqueous sulphuric acid medium using stopped flow technique. 

8 Uncatalyzed and palladium(II) catalyzed oxidation of allyl alcohol by periodate in aqueous alkaline medium. 
Kinetics of Oxidation of Antimony(III) by Vanadium(V) in Aqueous Hydrochloric Acid Media

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The oxidation of antimony(III) by vanadium(V) has been studied in aqueous hydrochloric acid media at 25°C. It follows the rate law (i) where \( K_1 \) and \( K_2 \) are the respective equilibrium constants of the reactions (ii) and (iii) and \( k \) is the rate constant of the slow step of the reaction. The data suggest

\[
\text{Rate} = \frac{d[V^V]}{dt} = \frac{AK_2[V(OH)^+][SbCl_4^-]}{1 + K_1[H^+][Cl^-]} (1)
\]

\[
[V(OH)]^{2+} + \text{H}_2\text{O} \rightleftharpoons [V(OH)]^{2+} + \text{H}^+ + \text{Cl}^-
\]

\[
[SbCl_4^-] \rightarrow [SbCl_4^-] + \text{Cl}^-
\]

The interaction of the active species [SbCl_4^-] and [V(OH)]^{2+} in the rate-limiting step followed by the formation of products in a subsequent fast step.

Owing to the importance of antimony(III) compounds as medicaments,1 antimony(III) oxidations have received much attention in recent years. The reactions of antimony(III) with various oxidants like manganese(II), hexacyanoferrate(III), cerium(IV) and bromate have been studied. Antimony(III) forms various chloride complexes in hydrochloric acid and different workers have suggested different active species, the nature of which is not well understood.

Vanadium(V) is an efficient oxidant in acidic media and various studies involving it have been reported, e.g. the oxidation of organic compounds like \( \alpha \)-hydroxy acids, aldehydes, ketones and alcohols has been reported by Waters and Littler.4,5 Its oxidation of inorganic compounds like hydrazine, tin(II), arsenic(III), titanium(III) and iodide has also been studied.6,7

The difference in the reduction potentials of the couples \( V^V-V^IV \) and \( Sb^V-Sb^VI \) (1.0 and 0.58 V respectively) in acidic media makes feasible the oxidation of antimony(III) by vanadium(V). Since this is a non-complementary reaction, it is of interest whether it proceeds through the formation of intermediate species like antimony(V) or a complex. Herein we report the results of a study of this oxidation in hydrochloric acid media.

Experimental

Materials.—All the chemicals used were of reagent grade. Doubly distilled water was used throughout. The stock solution of vanadium(V) was prepared by dissolving a known weight of \( \text{NH}_4\text{VO}_3 \) (Reidel) in 0.5 mol dm\(^{-3}\) HCl and standardized with \( \text{KBrO}_3 \) in the presence of 4.0 mol dm\(^{-3}\) HCl, using methyl orange as indicator. No perceptible hydrolysis of antimony(III) occurred on keeping it for several days. The vanadium(V) solution was made by dissolving a known amount of \( \text{VO}(_2\text{O})\text{H}_2\text{O} \) (Sisco) in water. The antimony(V) solution was prepared by dissolving a known amount of \( \text{V}_2\text{O}_5 \) (Reidel) in 4.0 mol dm\(^{-3}\) HCl and its concentration ascertained with KBrO3.

Materials.—All the chemicals used were of reagent grade. Doubly distilled water was used throughout. The stock solution of vanadium(V) was prepared by dissolving a known weight of \( \text{NH}_4\text{VO}_3 \) (Reidel) in 0.5 mol dm\(^{-3}\) HCl and standardized with \( \text{KBrO}_3 \) in the presence of 4.0 mol dm\(^{-3}\) HCl, using methyl orange as indicator. No perceptible hydrolysis of antimony(III) occurred on keeping it for several days. The vanadium(V) solution was made by dissolving a known amount of \( \text{VO}(_2\text{O})\text{H}_2\text{O} \) (Sisco) in water. The antimony(V) solution was prepared by dissolving a known weight of \( \text{Sb}_2\text{O}_3 \) (Bayer) in 4.0 mol dm\(^{-3}\) HCl and its concentration ascertained with KBrO3.

Results

Stoichiometry.—Several mixtures of different concentrations were allowed to react in 2.0 mol dm\(^{-3}\) HCl at an ionic strength of 3.0 mol dm\(^{-3}\) and analysed after 24 h at 25.0 ± 0.1°C. The vanadium(V) was estimated by the method mentioned earlier,6 antimony(III) by the standard method.7 The product vanadium(V) was analysed spectrophotometrically using a Hitachi 150-20 spectrophotometer at 745 nm (\( e = 20 \text{ dm} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1} \pm 1\% \)). The results are shown in Table 1 and indicate a 2:1 consumption ratio of oxidant to reductant [Equation (1)].

\[
2V^V + Sb^VI \rightleftharpoons 2V^IV + Sb^V
\]

Oxidation of Hydrochloric Acid by Vanadium(V). In addition to the vanadium(V) antimony(III) redox reaction, there might also be the possibility of a marginal oxidation of hydrochloric acid in the medium. At 25.0 ± 0.1°C and at higher temperatures with vanadium(V) and hydrochloric acid of concentrations 2.0 × 10\(^{-3}\) and 4.0 mol dm\(^{-3}\) respectively it was
found that no oxidation of hydrochloric acid occurred. Hence, no correction for such oxidation was made.

**Air Oxidation.**—Air oxidation did not occur to any significant extent under the conditions of the present study at 25 °C and for the duration of the vanadium(v)-antimony(III) reaction as found from runs in the presence and absence of air.

**Reaction Order.**—The reaction orders were determined from the slopes of plots of log (initial rate) versus log (concentration). The order with respect to [\(Vv\)] was unity in the concentration range 2.0 \(\times\) 10^{-3}-2.0 \(\times\) 10^{-2} mol dm^{-3} (Table 2) at constant concentration of antimony(III), hydrochloric acid and ionic strength of 3.0 \(\times\) 10^{-2}, 2.0 and 3.0 mol dm^{-3} respectively. This order was also confirmed by the linearity of plots of log (\(Vv\)) versus time to \(\geq 80\%\) completion of reaction, as well as the constant values of the rate constants for different concentrations of vanadium(III).

Under similar reaction conditions and with a constant vanadium(III) concentration of 5.0 \(\times\) 10^{-3} mol dm^{-3}, the antimony(III) concentration was varied between 0.01 and 0.1 mol dm^{-3}, which yielded an order of unity with respect to [\(Sb^{III}\)] (Table 2).

Quantities of initially added products, antimony(III) and vanadium(IV), in the ranges 5.0 \(\times\) 10^{-3}-5.0 \(\times\) 10^{-2} and 1.0 \(\times\) 10^{-3}-1.0 \(\times\) 10^{-2} mol dm^{-3} respectively, other conditions and reactant concentrations being kept constant, did not affect the vanadium(IV)-antimony(III) reaction significantly.

**Effect of H^+.**—The effect of varying [H^+] between 1.0 and 5.0 mol dm^{-3} at an ionic strength of 5.5 mol dm^{-3}, keeping other conditions, reactant concentrations and [\(Cl^-\)] (2.0 mol dm^{-3}) constant, was the rate of reaction increased with increasing [H^+] and the order found was less than unity (Table 2). To vary [H^+], HClO_4 was used. While varying [H^+], to maintain [\(Cl^-\)] at 2.0 mol dm^{-3}, 2.0 mol dm^{-3} HCl was added initially to the reaction mixture. At higher concentrations of H^+, HClO_4 was used as the source of H^+ and NaClO_4 to maintain the ionic strength. At lower [H^+], the [\(Cl^-\)] was maintained by using NaCl.

**Effect of Cl^-.**—The effect of [\(Cl^-\)] on the first-order rate constant \(k'\) was studied in the range 1.0-5.0 mol dm^{-3} [\(Cl^-\)], other conditions, reactant concentrations and [\(H^+\)] (2.0 mol dm^{-3}) being constant. Perchloric acid was used to maintain [H^+] and sodium chloride was used to vary [\(Cl^-\)]. Interestingly, the rate of reaction decreased with increasing [\(Cl^-\)] and the order found was a negative fraction \((-0.7)\) (Table 2) which led us to think of chloride complexes of antimony(III). There was no evidence for vanadium(IV)-chloride complexes and this possibility was also ruled out elsewhere.9

Antimony(III) forms several chloride complexes of general formula [\(SbCl_3\)\(^{n-}\) \((n = 1-6)\) with cumulative stability constants \(B_1\) to \(B_6\) having the values \(1.8 \times 10^3\), \(3.1 \times 10^3\), \(1.5 \times 10^5\), \(5.3 \times 10^4\), \(5.2 \times 10^4\), 1.3 \(\times\) 10^4 respectively at 25 °C in solutions of hydrochloric acid in the concentration range 0.2-4.0 mol dm^{-3}. Approximate concentrations of antimony(III)-chloride complexes containing one to six chlorides have been calculated10 and are shown in Table 3. The concentrations of SbCl_3 and [\(SbCl_4\)\(^-\)] show a decreasing trend with increasing [\(Cl^-\)], as does \(k'\), while the other complexes either decrease systematically or increase continuously with [\(Cl^-\)] (Table 3). In particular, the variation of [\(SbCl_4\)\(^-\)] with [\(Cl^-\)] is strikingly similar to that of log \(k'\) versus [\(Cl^-\)]. Lower acid concentrations than those used in the present study were not possible due to the precipitation of antimony(III).

Rates of reaction with 28 different sets of concentrations of antimony(III), vanadium(IV), \([H^+]\) and \([Cl^-]\) at constant ionic strength were found to obey the rate law (2) as shown in Fig. 1.

\[
\text{Rate} = k'[\text{Sb}^{III}]\times[V^+]\times[H^+][Cl^-]^{0.7} \tag{2}
\]

**Effect of Ionic Strength and Solvent Polarity.**—The ionic strength of the reaction solution was varied between 2.5 and 5.5 mol dm^{-3} with sodium perchlorate at constant oxidant, reductant, hydrogen-ion and chloride concentrations of 5.0 \(\times\) 10^{-3}, 3.0 \(\times\) 10^{-2}, 2.0 and 2.0 mol dm^{-3} respectively. The rate constant increased with increasing ionic strength and a plot of log (rate constant) versus \(I\) was linear with a positive slope.

The relative permittivity (\(\epsilon_r\)) effect was studied by varying the acetic acid content in the reaction mixture with all other conditions constant. Attempts to measure the relative...
Table 3  Effect of [Cl\textsuperscript-] on the antimony(m) species* and rate constants for the oxidation of Sb\textsuperscript{III} by V\textsuperscript{V} in HCl medium at 25 °C; [V\textsuperscript{V}] = 5.0 \times 10\textsuperscript{-3}, [Sb\textsuperscript{III}] = 3.0 \times 10\textsuperscript{-3}, [H\textsuperscript{+}] = 2.0, [Cl\textsuperscript{-}] = 2.0, \textit{I} = 3.0 mol dm\textsuperscript{-3}

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* a\textsubscript{1}, a\textsubscript{2}, a\textsubscript{3}, a\textsubscript{4}, a\textsubscript{5}, a\textsubscript{6} are the fractions of total Sb\textsuperscript{III} represented by the species Sb\textsubscript{0}, [SbCl\textsubscript{2}]\textsuperscript{2+}, [SbCl\textsubscript{3}]\textsuperscript{+}, SbCl\textsubscript{3}, [SbCl\textsubscript{4}]\textsuperscript{3-} and [SbCl\textsubscript{5}]\textsuperscript{2-} respectively. Error ± 4%.

Discussion

The oxidation of antimony(m) by vanadium(v) was found to be slow in HClO\textsubscript{4} and H\textsubscript{2}SO\textsubscript{4} media and also limited by the solubility of antimony(m) in these media. However, it can be conveniently studied in hydrochloric acid media. Although antimony(m) and (v) compounds undergo hydrolysis in H\textsubscript{2}SO\textsubscript{4},\textsuperscript{12} in the present case, because of the high concentration of HCl, hydrolysis of antimony(m) was ruled out.\textsuperscript{13}

Since the reaction was studied in strong HCl, the possibility of the formation of chloride complexes with vanadium(v) is precluded.\textsuperscript{9} Interestingly, antimony(m), is widely believed\textsuperscript{3} to give several chloride complexes in HCl. Fridman et al.\textsuperscript{14} have shown from absorption data that [SbCl\textsubscript{4}]\textsuperscript{3-} and [SbCl\textsubscript{5}]\textsuperscript{2-} are only formed in strong acid solutions. The decrease in k' with increase in [Cl\textsuperscript{-}] can be attributed to the formation of [SbCl\textsubscript{4}]\textsuperscript{3-} from [SbCl\textsubscript{5}]\textsuperscript{2-} species. The kinetic results are consistent with the main active species of antimony(m) in HCl being [SbCl\textsubscript{5}]\textsuperscript{2-} (Scheme 1), the variation of log k' and a\textsubscript{4} versus [Cl\textsuperscript{-}] \{a\textsubscript{4} being the fraction of antimony(m) existing as [SbCl\textsubscript{5}]\textsuperscript{2-}\} showing greater similarity (Table 3) than is possible with any other antimony(m) chloride complexes. Polaro- graphic,\textsuperscript{15} spectral\textsuperscript{16} and solubility studies\textsuperscript{16} also support this.

Vanadium(v) Species in Aqueous Acid Solution.---As evidenced by the literature, vanadium(v) is known to exist\textsuperscript{17} as [VO\textsubscript{2}\textsuperscript{+}]\textsuperscript{3+} in aqueous acid solutions. Further, the fractional order in [H\textsuperscript{+}] indicates probably that protonated species of vanadium(v) are present as active species. Vanadium(v) is known to form protonated species\textsuperscript{17,18} in acidic media as follows (equation (3)).

$$[\text{VO}_2]^\text{+} + \text{H}_2\text{O}^\text{+} \rightarrow \text{[VO(OH)\textsubscript{2}]^3+}$$

(3)

The results suggest that [SbCl\textsubscript{5}]\textsuperscript{2-} reacts with [VO(OH)\textsubscript{2}]\textsuperscript{3+} in a slow step followed by a rapid step to give the products. The order of less than unity in [H\textsuperscript{+}] may be understood in terms of the predominant vanadium(v) species, [VO(OH)\textsubscript{2}]\textsuperscript{3+}, formed in a pre-equilibrium involving vanadium(v) species and H\textsuperscript{+}. In accordance with the generally well accepted principle of non-complementary oxidations taking place in sequences of one-electron steps, a mechanism like that in Scheme 1 may be envisaged.

$$[\text{VO}_2]^\text{+} + \text{H}_2\text{O}^\text{+} \underset{k\textsubscript{1}}{\overset{k\textsubscript{1}}{\rightleftharpoons}} \text{[VO(OH)\textsubscript{2}]^3+}$$

$$\text{[SbCl\textsubscript{5}]^2-} \overset{k\textsubscript{2}}{\underset{\text{slow}}{\rightleftharpoons}} \text{[SbCl\textsubscript{5}]^2-} + \text{Cl}^-$$

$$\text{[VO(OH)\textsubscript{2}]^3+} + \text{SbCl\textsubscript{5}]^2-} \rightarrow \text{[VO(OH)\textsubscript{2}]^3+} + \text{SbCl\textsubscript{5}]^2-} + \text{H}_2\text{O}$$

$$\text{[V(OH)]^2+} + \text{SbCl\textsubscript{5}]^2-} \rightarrow \text{[V(OH)]^2+} + \text{SbCl\textsubscript{5}]^2-} + \text{H}_2\text{O}$$

Scheme 1
Although no experimental evidence for the formation of antimony(rv) as an intermediate was obtained, such a species was observed in earlier studies. Scheme 1 leads to the rate law (4), which incorporates all the observed orders. Strictly the denominator on the right-hand side must also have a factor of too small for this to affect the rate significantly. The mechanism must be linear, which is verified in Fig. 2. The slope and intercept of such plots lead to the values of 

\[ \frac{kK_1K_2[Sb^{IV}][H_2O^+]}{K_x + K_y[H_2O^+] + [Cl^-] + K_z[Cl^-][H_2O^+]^2} \]  

(4)

denominator on the right-hand side must also have a factor of the type \(1 + K_1[VCl_2]^{-} \) but the vanadium(v) concentration is too small for this to affect the rate significantly. The mechanism in Scheme 1 and the rate law (4) may be verified by rearranging it in the form (5) where \( k' \) is the pseudo-first-order rate constant.

\[ \frac{d[V^{IV}]}{dt} = k' = \frac{kK_1K_2[Sb^{IV}][H_2O^+]}{K_x + K_y[H_2O^+] + [Cl^-] + K_z[Cl^-][H_2O^+]^2} \]  

(5)

Plots of \( [Sb^{IV}] / [V^{IV}] \) versus \( 1/[H_2O^+] \) and \( [Cl^-] \) are expected to be linear, which is verified in Fig. 2. The slope and intercept of such plots lead to the values of \( K_1, K_2 \) and \( k \) at 25 °C as 1.13 ± 0.02 dm³ mol⁻¹, 1.07 ± 0.01 mol dm⁻³ and 7.6 x 10⁻³ ± 3.0 x 10⁻³ dm³ mol⁻¹ s⁻¹ respectively. The value of \( K_2 \) (equilibrium constant) is in good agreement with that reported earlier. These values were utilised to calculate rate constants under several experimental conditions from equation (5). These are given in Table 2 along with the experimental values; there is reasonable agreement between them. However, marginal deviations occurred at higher acid concentrations which may be due to the possible existence of other oxidant species, in addition to \([V(OH)_2]^{+}\). The reaction is accelerated in media of low polarity which can be qualitatively explained by the involvement of oppositely charged ions. However, the decrease in rate with decreasing ionic strength is not easy to interpret. This might be due to the various ionic reactions shown in Scheme 1. The marked sensitivity shown by the reaction towards cations may be attributed to the occurrence of ion pairing. The rate is enhanced in the presence of \( Li^+ \) and \( K^+ \). This could be accounted for by the addition of a cation to the negatively charged species, such as \([SbCl_4]^-\), which thus favours the reaction. A relatively high value of the entropy of activation and much lower rate constants may be considered as powerful tools for the predictions of reactivity. In the mechanism proposed the co-ordination shells of the metal ions remain intact during the electron transfer. This would indicate that the oxidation of antimony(III) by vanadium(v) in HCl occurs through an outer-sphere mechanism, and is supported by earlier work.²⁰

References

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