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

$$\text{Rate} = -\frac{d[V^V]}{dt} = \frac{kK_1K_2[VO_2^+][Sb^{III}][H_3O^+]}{(1 + K_1[H_3O^+])(K_2 + [Cl^-])} \qquad \text{(i)}$$

reactions (ii) and (iii) and k is the rate constant of the slow step of the reaction. The data suggest

$$[VO_2]^+ + H_3O^+ \rightleftharpoons [V(OH)_3]^{2+} \qquad \text{(ii)}$$

$$[SbCl_5]^{2-} \rightleftharpoons [SbCl_4]^- + Cl^- \qquad \text{(iii)}$$

the interaction of the active species $[SbCl_4]^-$ and $[V(OH)_3]^{2+}$ in the rate-limiting stage 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[2] like manganese(III), hexacyanoferrate(III), cerium(IV) and bromate have been studied. Antimony(III) forms various chloride complexes in hydrochloric acid and different workers[3] 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 α-hydroxy acids, aldehydes, ketones and alcohols has been reported by Waters and Littler.[4a] Its oxidation of inorganic compounds like hydrazine, tin(II), iron(II), arsenic(III), titanium(III) and iodide has also been studied.[4b]

The difference in the reduction potentials[5] of the couples V^V–V^{IV} and Sb^V–Sb^{III} (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(IV) 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 NH_4VO_3 (Reidel) in 0.5 mol dm^{-3} HCl and standardised[6] with $[NH_4]_2SO_4{\cdot}FeSO_4{\cdot}6H_2O$ (AR) solution using barium diphenylamine sulfonate as indicator. The antimony(III) solution was prepared by dissolving a known amount of Sb_2O_3 (Bayer) in 4.0 mol dm^{-3} HCl and its concentration ascertained[7] with $KBrO_3$ 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(IV) solution was made by dissolving a known amount of $VO(SO_4){\cdot}H_2O$ (Sisco) in water. The antimony(V) solution was prepared by dissolving $KSb(OH)_6{\cdot}0.5H_2O$ (BDH) in 0.5 mol dm^{-3} HCl. Sodium perchlorate and HCl were used to maintain the ionic strength and the required acidity respectively, $HClO_4$ and NaCl to study the effect of H^+ and Cl^- respectively.

Kinetic Procedure.—Runs were followed under conditions where antimony(III) was present in nearly a ten-fold excess over vanadium(V) at a constant temperature of 25.0 ± 0.1 °C. The reaction was initiated by mixing previously thermostatted solutions of vanadium(V) and antimony(III), which also contained the required amounts of HCl and $NaClO_4$. Aliquots of the reaction mixture were pipetted out at regular intervals and titrated against $[NH_4]_2SO_4{\cdot}FeSO_4{\cdot}6H_2O$ solution in the presence of acid.

The pseudo-first-order rate constants were obtained from plots of log $[V^V]$ *versus* time. Initial rates were calculated by the plane-mirror method.[8] Kinetic runs were followed to about three half-lives of the reaction in most cases and were reproducible within ±4%.

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(IV) was analysed spectrophotometrically using a Hitachi 150–20 spectrophotometer at 745 nm (ε = 20 dm^3 mol^{-1} cm^{-1} ± 1%). The results are shown in Table 1 and indicate a 2:1 consumption ratio of oxidant to reductant [equation (1)].

$$2V^V + Sb^{III} \longrightarrow 2V^{IV} + Sb^V \qquad (1)$$

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^{-2} 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 [V^V] was unity in the concentration range 2.0×10^{-3}–2.0×10^{-2} mol dm^{-3} (Table 2) at constant concentration of antimony(III), hydrochloric acid and ionic strength of 3.0×10^{-2}, 2.0 and 3.0 mol dm^{-3} respectively. This order was also confirmed by the linearity of plots of log [V^V] *versus* time to $\geqslant 80\%$ completion of reaction, as well as the constant values of the rate constants for different concentrations of vanadium(v).

Under similar reaction conditions and with a constant vanadium(v) concentration of 5.0×10^{-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(v) and vanadium(IV), in the ranges 5.0×10^{-3}–5.0×10^{-2} and 1.0×10^{-4}–1.0×10^{-3} mol dm^{-3} respectively, other conditions and reactant concentrations being kept constant, did not affect the vanadium(v)–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 studied. 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 attained by using NaCl.

Table 1 Stoichiometry (mol dm^{-3}) of the V^V + Sb^{III} reaction at 25 °C, [HCl] = 2.0, I = 3.0 mol dm^{-3}

10^2[V^V] Taken	10^2[Sb^{III}] Taken	10^3[V^V] Remaining	10^3[Sb^{III}] Remaining	10^3[V^{IV}] Found
0.70	1.05	0.0	6.9	6.95
0.70	0.70	0.0	3.4	6.90
1.40	0.70	0.0	0.0	13.6
2.10	0.70	6.9	0.0	13.8
2.80	0.70	13.8	0.0	14.0

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 (−0.70) (Table 2) which led us to think of chloride complexes of antimony(III). There was no evidence for vanadium(v)–chloride complexes and this possibility was also ruled out elsewhere.[9]

Antimony(III) forms several chloride complexes[3] of general formula $[SbCl_n]^{3-n}$ (n = 1–6) with cumulative stability constants β_1 to β_6 having the values 1.8×10^2, 3.1×10^3, 1.5×10^4, 5.3×10^4, 5.2×10^4, 1.3×10^4 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 calculated[10] 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(v), [H$^+$] and [Cl$^-$] at constant ionic strength were found to obey the rate law (2) as shown in Fig. 1.

$$\text{Rate} = k[\text{Sb}^{\text{III}}][\text{V}^{\text{V}}][\text{H}^+]^{0.6}[\text{Cl}^-]^{-0.7} \qquad (2)$$

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 5.0×10^{-3}, 3.0×10^{-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* $I^{\frac{1}{2}}$ was linear with a positive slope.

The relative permittivity (ε_T) effect was studied by varying the acetic acid content in the reaction mixture with all other conditions constant. Attempts to measure the relative

Table 2 Effect of various species on the V^V + Sb^{III} reaction at 25 °C

(a) [HCl] = 2.0, I = 3.0 mol dm^{-3}

10^3[V^V]/ mol dm^{-3}	10^2[Sb^{III}]/ mol dm^{-3}	10^4 k'/s^{-1} Exptl.	10^4 k'/s^{-1} Calc.*
2.00	3.00	5.50	5.52
3.00	3.00	5.52	5.53
5.00	3.00	5.53	5.51
7.00	3.00	5.57	5.54
10.0	3.00	5.59	5.56
20.0	3.00	5.61	5.59
5.00	1.00	1.86	1.84
5.00	2.00	3.60	3.67
5.00	3.00	5.59	5.51
5.00	5.00	9.20	9.18
5.00	7.00	13.0	12.0
5.00	10.00	18.4	18.4

(b) [V^V] = 5.0×10^{-3}, [Sb^{III}] = 3.0×10^{-2}, I = 5.5 mol dm^{-3}

[H$^+$]/ mol dm^{-3}	[Cl$^-$]/ mol dm^{-3}	10^4 k'/s^{-1} Exptl.	10^4 k'/s^{-1} Calc.*
1.0	2.0	3.8	4.20
1.5	2.0	5.0	4.98
2.0	2.0	5.8	5.51
3.0	2.0	8.3	6.23
4.0	2.0	8.8	6.52
5.0	2.0	10.7	6.87
2.0	1.0	7.90	8.17
2.0	2.0	5.45	5.51
2.0	3.0	4.10	4.15
2.0	4.0	3.30	3.34
2.0	5.0	2.90	2.80

* Rate constants were calculated from equation (5) using K_1, K_2 and k as 1.13 ± 0.02 dm^3 mol^{-1}, 1.07 ± 0.01 mol dm^{-3} and $7.6 \times 10^{-2} \pm 3.0 \times 10^{-3}$ dm^3 mol^{-1} s^{-1} respectively. Error ±4%.

Table 3 Effect of [Cl$^-$] on the antimony(III) species* and rate constants for the oxidation of Sb^{III} by V^V in HCl medium at 25 °C; [V^V] = 5.0×10^{-3}, [Sb^{III}] = 3.0×10^{-2}, [H$^+$] = 2.0, I = 3.0 mol dm^{-3}

[Cl$^-$]/mol dm^{-3}	$10^7\alpha_0$	$10^5\alpha_1$	$10^3\alpha_2$	$10^3\alpha_3$	$10^3\alpha_4$	$10^2\alpha_5$	$10^2\alpha_6$	$10^4k'$/s^{-1}
1.0	73.56	132.4	22.8	110.4	39.99	38.25	9.56	7.9
2.0	2.800	10.36	3.56	34.5	24.99	47.86	23.93	5.45
3.0	0.773	2.019	1.04	15.10	15.99	47.07	35.31	4.10
4.0	0.0831	0.595	0.4	7.93	10.20	43.98	43.98	3.30
5.0	0.025	0.225	0.19	4.679	7.920	40.55	50.69	2.90

* α_0, α_1, α_2, α_3, α_4, α_5, α_6 are the fractions of total Sb^{III} represented by the species Sb$_f$, [SbCl]$^{2+}$, [SbCl$_2$]$^+$, SbCl$_3$, [SbCl$_4$]$^-$, [SbCl$_5$]$^{2-}$ and [SbCl$_6$]$^{3-}$ respectively. Error ±4%.

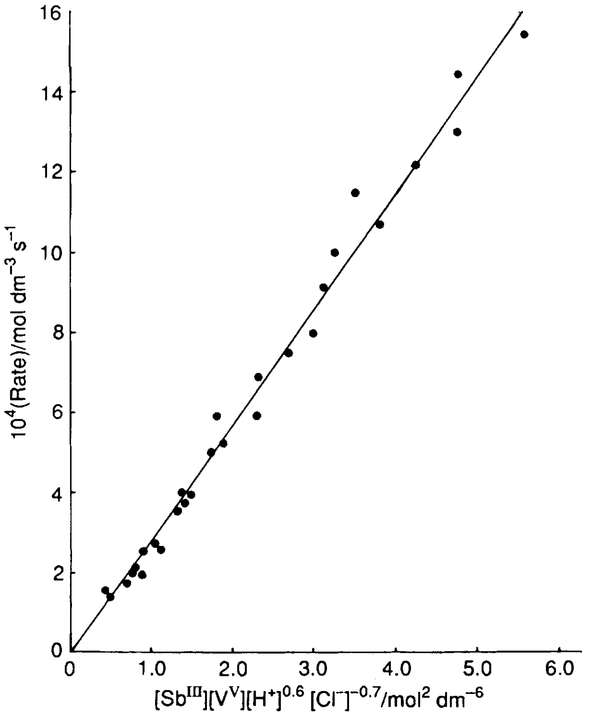

Fig. 1 Plot of the rate of the V^V + Sb^{III} reaction *vs.* the product of reactant concentrations at 25 °C, [HCl] = 2.0, I = 3.0 mol dm^{-3}

permittivity of the medium failed. However, it was computed from the values for the pure liquids as in earlier work.[11] There was no reaction of the solvent with the oxidant under the experimental conditions used. The rate constant increased with decreasing relative permittivity of the medium. A plot of log (rate constant) *versus* $1/\varepsilon_T$ was linear with a positive slope.

Effect of Added Ions.—The effect of added cations and anions on the reaction rate was studied at constant ionic strength (3.0 mol dm^{-3}) maintained by sodium perchlorate. When sodium ions were replaced by lithium ions (lithium perchlorate) the rate increased significantly, while on replacement of sodium by potassium ions (potassium perchlorate) the rate increased only marginally. Similar replacement of perchlorate by sulfate (Na_2SO_4) and nitrate ions ($NaNO_3$) did not affect the reaction rate.

Effect of Temperature.—The activation parameters were calculated by using the values of the rate constants (k) of the slow step of Scheme 1, obtained from the intercepts of plots of [Sb^{III}]/k' *versus* [Cl$^-$] at four different temperatures. The values of k were found to be 7.6×10^{-2}, 11.0×10^{-2}, 15.0×10^{-2} and 21.0×10^{-2} dm^3 mol^{-1} s^{-1} at 25, 30, 35 and 40 °C respectively, thus leading to $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values of 50.0 ± 2 kJ mol^{-1} and −94.0 ± 4 J K^{-1} mol^{-1}.

$$[VO_2]^+ + H_3O^+ \overset{K_1}{\rightleftharpoons} [V(OH)_3]^{2+}$$

$$[SbCl_5]^{2-} \overset{K_2}{\rightleftharpoons} [SbCl_4]^- + Cl^-$$

$$[V(OH)_3]^{2+} + [SbCl_4]^- \xrightarrow[\text{slow}]{k} [HVO_2]^+ + SbCl_4 + H_2O$$

$$[V^V(OH)_3]^{2+} + Sb^{IV}Cl_4 \xrightarrow{\text{fast}} [HV^{IV}O_2]^+ + [Sb^VCl_4]^+ + H_2O$$

Scheme 1

Discussion

The oxidation of antimony(III) by vanadium(V) was found to be slow in $HClO_4$ and H_2SO_4 media and also limited by the solubility of antimony(III) in these media. However, it can be conveniently studied in hydrochloric acid media. Although antimony-(III) and -(V) compounds undergo hydrolysis in H_2SO_4,[12] in the present case, because of the high concentration of HCl, hydrolysis of antimony(III) was ruled out.[13]

Since the reaction was studied in strong HCl the possibility of the formation of chloride complexes with vanadium(V) is precluded.[9] Interestingly, antimony(III), is widely believed[3] to give several chloride complexes in HCl. Fridman *et al.*[14] have shown from absorption data that [SbCl$_4$]$^-$ and [SbCl$_5$]$^{2-}$ are only formed in strong acid solutions. The decrease in k' with increase in [Cl$^-$] can be attributed to the formation of [SbCl$_5$]$^{2-}$ from [SbCl$_4$]$^-$ species. The kinetic results are consistent with the main active species of antimony(III) in HCl being [SbCl$_4$]$^-$ (Scheme 1), the variation of log k' and α_4 *versus* [Cl$^-$] {α_4 being the fraction of antimony(III) existing as [SbCl$_4$]$^-$} showing greater similarity (Table 3) than is possible with any other antimony(III) chloride complexes. Polarographic,[15] spectral[16] and solubility studies[16] also support this.

Vanadium(V) *Species in Aqueous Acid Solution.*—As evidenced by the literature, vanadium(V) is known to exist[17] as [VO$_2$]$^+$ in aqueous acid solutions. Further, the fractional order in [H$^+$] indicates probably that protonated species of vanadium(V) are present as active species. Vanadium(V) is known to form protonated species[17,18] in acidic media as follows [equation (3)].

$$[VO_2]^+ + H_3O^+ \rightleftharpoons [V(OH)_3]^{2+} \qquad (3)$$

The results suggest that [SbCl$_4$]$^-$ reacts with [V(OH)$_3$]$^{2+}$ in a slow step followed by a rapid step to give the products. The order of less than unity in [H$^+$] may be understood in terms of the predominant vanadium(V) species, [V(OH)$_3$]$^{2+}$, formed in a pre-equilibrium involving vanadium(V) species and H$^+$. 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.

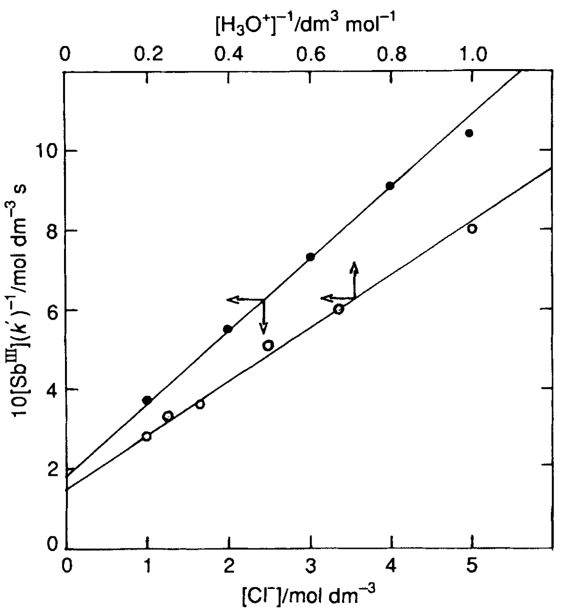

Fig. 2 Verification of equation (4); conditions as in Table 2

Although no experimental evidence for the formation of antimony(IV) as an intermediate was obtained, such a species was observed in earlier studies.[19] Scheme 1 leads to the rate law (4), which incorporates all the observed orders. Strictly the

$$-\frac{d[V^V]}{dt} = \frac{kK_1K_2[VO_2^+][Sb^{III}][H_3O^+]}{K_2 + K_1K_2[H_3O^+] + [Cl^-] + K_1[Cl^-][H_3O^+]} \quad (4)$$

denominator on the right-hand side must also have a factor of the type $1 + K_1[VO_2^+]$ 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.

$$\frac{\text{Rate}}{[V^V]} = k' = \frac{kK_1K_2[Sb^{III}][H_3O^+]}{K_2 + K_1K_2[H_3O^+] + [Cl^-] + K_1[Cl^-][H_3O^+]} \quad (5)$$

Plots of $[Sb^{III}]/k'$ *versus* $1/[H_3O^+]$ 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 dm^3 mol^{-1}, 1.07 ± 0.01 mol dm^{-3} and 7.6 ± 0.3 × 10^{-2} dm^3 mol^{-1} s^{-1} respectively. The value of K_2 (equilibrium constant) is in good agreement with that reported earlier.[10] 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 $[V(OH)_3]^{2+}$.

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 than found in similar redox reactions 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]

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Received 29*th March* 1995; *Paper* 5/01990G