

Hexacyanoferrate(III) oxidation of antimony(III) in aqueous acetic acid

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The rate of hexacyanoferrate(III) oxidation of antimony(III) in 50% aq. acetic acid (v/v) in the presence of H^+ and Cl^- ions is considerably accelerated with increase in $[H^+]$ and $[Cl^-]$ as well as increase in acetic acid content of the medium. The experimental results indicate that the reaction occurs mainly between $H_2Fe(CN)_6^-$ and $SbCl_4^-$.

The oxidation potentials of $hcFe(II)/hcFe(III)$ ($hcFe$ stands for hexacyanoferrate) and $Sb(III)/Sb(V)$ in dilute acid¹ undergo changes with increase in $[H^+]$ and $[Cl^-]$ and also with decrease in the dielectric constant of the reaction medium². Such changes permit a titrimetric estimation² of $Sb(III)$ with $hcFe(III)$ in 40% acetic acid in the presence of 5.0 mol dm^{-3} HCl. The importance of the less polar medium is evident from the fact that a fast $hcFe(III)-Sb(III)$ reaction is possible only in presence of $\sim 10 \text{ mol dm}^{-3}$ HCl in aqueous medium³. In view of such effects, we were interested in the title reaction and the results of our studies in 50% acetic acid in the presence of $1.40-2.50 \text{ mol dm}^{-3}$ HCl are reported herein.

Materials and Methods

Reagent grade chemicals and doubly distilled water were used throughout. Stock solution of $hcFe(III)$ (BDH) in water was standardised iodometrically. The $Sb(III)$ solution was obtained by dissolving Sb_2O_3 (Sisco) in 3.0 mol dm^{-3} HCl and standardised by titration⁴ with $KBrO_3$ (BDH). No perceptible hydrolysis of $Sb(III)$ occurred on keeping for several days. Acetic acid was purified by the standard procedure. Perchloric acid (E. Merck) was used to vary $[H^+]$ while LiCl was used to vary $[Cl^-]$. The ionic strength (I) was maintained with $NaClO_4$ at 2.60 mol dm^{-3} in most cases. The $Sb(V)$ solution was freshly prepared by the oxidation of $Sb(III)$ solution with $KBrO_3$ solution. Acidity function (H_0) under reaction conditions was measured⁵ spectrophotometrically using *p*-nitroaniline. The validity of such acid solutions to the H_0 scale was also shown⁶. Bausch and Lomb 2000 spectrophotometer was employed to follow the kinetics and to measure the acidity function (H_0). However a few UV

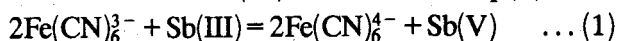
spectra were recorded on a Hitachi 150-20 spectrophotometer.

Kinetic measurements in 50% aq. acetic acid (v/v) were carried out at $27 \pm 0.05^\circ$ at $I = 2.60 \text{ mol dm}^{-3}$. Reactions were initiated by mixing previously thermostated solutions of $hcFe(III)$ and $Sb(III)$ which also contained the required $[H^+]$ and $[Cl^-]$. Kinetics were followed by measuring the absorbance of $hcFe(III)$ at 420 nm in the reaction mixture as a function of time. The application of Beer's law under the reaction conditions had earlier been verified between 1.0×10^{-4} and $8.0 \times 10^{-4} \text{ mol dm}^{-3}$ of $hcFe(III)$ ($\epsilon = 1183 \pm 1\%$). The second order rate constants, k_{expl} , were obtained from plots of $1/(a-x)$ versus time, the reaction being studied under conditions of equivalent concentrations of reactants. Second order plots of almost all runs were linear upto about 95% and k_{expl} was reproducible within $\pm 5\%$.

Results

Stoichiometry

Stoichiometric studies were carried out using six different sets of concentrations of reactants ($[Sb(III)] \geq [hcFe(III)]$) at constant $[H^+]$ and $[Cl^-]$ (2.50 mol dm^{-3}) and $I = 2.60 \text{ mol dm}^{-3}$. After 24 hr, $hcFe(III)$ was estimated spectrophotometrically at 420 nm and unreacted $Sb(III)$ was estimated by titration with bromate where small quantities of iron did not interfere⁴. After the completion of the reaction $Sb(V)$ was estimated iodometrically, the $hcFe(III)$ having completely reacted. The results indicated that two moles of $hcFe(III)$ reacted with one mole of $Sb(III)$ in accord with Eq. (1).



Reaction order

In 50% acetic acid, modest $[H^+]$ and $[Cl^-]$ were

Table 1 – Effect of variation of concentrations of oxidant, reductant and products on the hcFe(III)-Sb(III) reaction in 50% aqueous acetic acid at 27°C

[HCl] = 2.5 mol dm ⁻³ ; I = 2.6 mol dm ⁻³				
[hcFe(III)] × 10 ⁴ (mol dm ⁻³)	[Sb(III)] × 10 ⁴ (mol dm ⁻³)	[hcFe(II)] × 10 ⁴ (mol dm ⁻³)	[Sb(V)] × 10 ⁴ (mol dm ⁻³)	<i>k</i> _{expl} (mol ⁻¹ dm ³ s ⁻¹)
5.0	1.0	—	—	18.5
5.0	2.5	—	—	19.1
5.0	4.0	—	—	28.2
5.0	6.0	—	—	33.9
5.0	8.0	—	—	36.4
5.0	10	—	—	43.9
1.0	4.0	—	—	26.3
2.0	4.0	—	—	28.4
4.0	4.0	—	—	25.5
6.0	4.0	—	—	27.5
8.0	4.0	—	—	24.2
10.0	4.0	—	—	24.2
5.0	2.5	2.0	—	19.1
5.0	2.5	4.0	—	19.3
5.0	2.5	6.0	—	19.3
5.0	2.5	8.0	—	19.3
5.0	2.5	10	—	19.2
5.0	2.5	—	2.0	19.1
5.0	2.5	—	4.0	19.2
5.0	2.5	—	6.0	20.0
5.0	2.5	—	8.0	19.8
5.0	2.5	—	10	20.0

required to facilitate the hcFe(III)-Sb(III) reaction. At high [H⁺] and [Cl⁻] ([HCl] ~ 5 mol dm⁻³), the reaction was instantaneous. The orders in [reactant] were therefore found at two acidities, viz. 1.40 and 2.50 mol dm⁻³ of dissolved [H⁺] at fixed I = 2.60 mol dm⁻³. All other things being constant, the order in hcFe(III), between 1.0 × 10⁻⁴ and 1.0 × 10⁻³ mol dm⁻³ of hcFe(III), was ~ 1 at both acidities; the order in Sb(III), in the same range of concentrations, was 1.1 and 0.91 respectively at higher and lower acidities. Furthermore, at the higher acidity, *k*_{expl} increased with increase in [Sb(III)], while change in [hcFe(III)] under similar conditions did not affect *k*_{expl}. Initially added products, hcFe(II) and Sb(V), did not cause appreciable change in *k*_{expl} (Table 1).

Effect of varying of [Cl⁻]

The effect of varying [Cl⁻] on *k*_{expl} was studied under conditions as above. At both acidities, *k*_{expl} increased between [Cl⁻] of 0.10 and ~ 1.0 mol dm⁻³ and, thereafter, it decreased upto [Cl⁻] = 2.5 mol dm⁻³. The orders in [Cl⁻], in the ascending and descending ranges, found from log-log plots were +0.56 and -1.1 ([H⁺] = 2.50 mol dm⁻³) and +0.54 and -2.1 ([H⁺] = 1.4 mol dm⁻³).

Antimony(III) forms several chloride complexes⁷ of the general formula, SbCl_n³⁻ⁿ (n = 1 to 6), with the cumulative stability constants, β₄ to β₉, having the values 1.8 × 10², 3.1 × 10³, 1.5 × 10⁴, 5.3 × 10⁴, 5.2 × 10⁴, 1.3 × 10⁴, respectively at 25° in solutions⁷ of [HCl] in the range 0.20 to 4.0 mol dm⁻³. Approximate concentrations of the Sb(III)-chloride complexes containing 1 to 6 chlorides were calculated⁸. The plots of concentrations of the different chloride complexes of Sb(III) versus [Cl⁻] and that of *k*_{expl} versus [Cl⁻] are shown in Fig. 1. The concentrations of SbCl₃ and SbCl₄⁻ show a rise followed by a decrease with [Cl⁻] as does *k*_{expl}, while the concentrations of the other complexes either decrease systematically or increase continuously with [Cl⁻]. In particular, variation of [SbCl₄⁻] with [Cl⁻] is strikingly similar to that of log *k*_{expl} versus [Cl⁻]. Only the variation of *k*_{expl} with [Cl⁻] at higher acidity is shown in Fig. 1, since at lower acidity the trend is similar to that at higher acidity.

Effect of varying [acid]

The effect of varying [H⁺] between 1.0 and 2.50 mol dm⁻³ was studied under identical conditions. Since [H⁺] does not reflect the true proto-

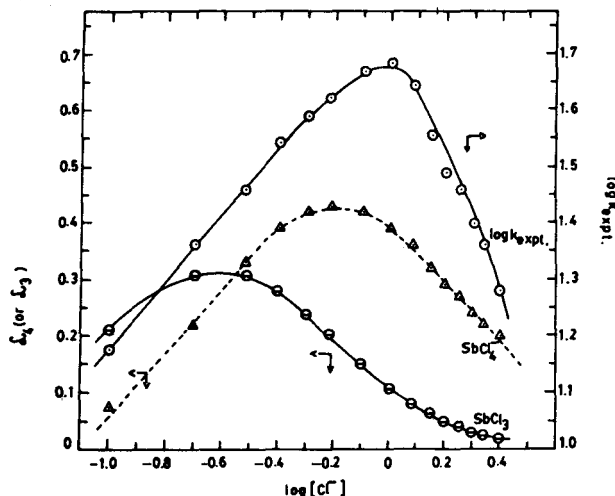


Fig. 1 - Plots of $\log k_{\text{expl}}$ versus $\log [\text{Cl}^-]$ ($-\circ-$) and α_4 (or α_3) versus $\log [\text{Cl}^-]$ ($-\Delta-$; $-\ominus-$) in 50% aqueous acetic acid containing HCl at 27°. $2[\text{Sb(III)}] = [\text{Fe(CN)}_6^{3-}] = 5.0 \times 10^{-4}$, $I = 2.6 \text{ mol dm}^{-3}$. $\alpha_0, \alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5$ and α_6 are fractions of the total Sb(III) existing as $\text{Sb}^{3+}, \text{SbCl}^{2+}, \text{SbCl}_2^+, \text{SbCl}_3, \text{SbCl}_4^-, \text{SbCl}_5^{2-}$ and SbCl_6^{3-} respectively. $\alpha_0, \alpha_1, \alpha_2$ which systematically decrease, and α_5 and α_6 which systematically increase, with increasing $[\text{Cl}^-]$ are not shown

nating power of the solutions at high acidities used in the reaction especially in media of low polarity, the order in acidity was found to be 1.9 from log-log plots of initial rates versus acidity function⁵, h_0 ($H_0 = \log h_0$). Although the reaction became rather slow below $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$, the order in the $[\text{H}^+]$ range of 0.60 to 1.0 mol dm^{-3} was obtained as ~ 2 from log-log plots of initial rates versus $[\text{H}^+]$. This latter result supports the order found in h_0 at higher acidities. As the acid solutions become more dilute, the $p\text{H}$ and H_0 approach each other. Thus the agreement between the orders determined in the two $[\text{H}^+]$ ranges may be taken as reflecting, as nearly as possible, the actual property of these solutions.

Ultraviolet spectra

The effects of varying $[\text{H}^+]$, $[\text{Sb(III)}]$ and $[\text{HCl}]$ on the absorption spectrum of Sb(III) (λ_{max} at 245 nm) were also studied. The UV spectrum of Sb(III) solutions containing fixed $[\text{Cl}^-]$ of 3.0 mol dm^{-3} did not show any change at different $[\text{H}^+]$ in the range of 1.0-3.0 mol dm^{-3} . At fixed $[\text{HCl}]$ of 1.0 mol dm^{-3} , the absorption spectra of Sb(III) solution containing $[\text{Sb(III)}]$ of $0.25 \times 10^{-3}, 0.5 \times 10^{-3}, 0.75 \times 10^{-3}$ and $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ showed that the molar absorptivity (ϵ) of the band at 245 nm decreased with increase in $[\text{Sb(III)}]$ indicating that the fraction of the absorbing species increased with decrease in $[\text{Sb(III)}]$. Finally, the effect of increasing $[\text{HCl}]$ on the UV spectra of

Sb(III) was examined. The ϵ value at $\sim 245 \text{ nm}$ increased gradually with increase in $[\text{HCl}]$ and reached a maximum value around $[\text{HCl}]$ of $\sim 5 \text{ mol dm}^{-3}$.

Effect of varying ionic strength and dielectric constant

Variation of ionic strength (I) between 2.0 and 2.80 mol dm^{-3} with sodium perchlorate lead to different k_{expl} values and a plot of $\log k_{\text{expl}}$ versus $I^{1/2}$ was linear with positive slope. As the acetic acid content in the reaction medium increased from 30 to 55% (v/v), k_{expl} rapidly increased and the plot of $\log k_{\text{expl}}$ versus $1/D$ was linear with positive slope.

Discussion

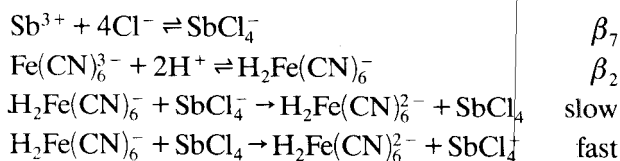
The hcFe(III)-Sb(III) reaction is instantaneous in $\sim 10 \text{ mol dm}^{-3}$ HCl or in 50% acetic acid (v/v) in the presence of $\sim 5 \text{ mol dm}^{-3}$ HCl. Although Sb(III) and Sb(V) undergo hydrolysis in H_2SO_4 medium⁹, in the present case because of large concentrations of HCl, hydrolysis of Sb(III) was minimal¹⁰. Even in the case of Sb(III)-Sb(V) exchange¹¹, the effect of varying $[\text{HCl}]$ was large and the effect was not explained as was the case with other oxidation reactions of Sb(III) which were largely influenced by acidity^{9,11,12}.

While the order of around unity in $[\text{hcFe(III)}]$ at both acidities examined is expected, the departure of order from unity in $[\text{Sb(III)}]$ at the two acidities probably arises because of the formation of several chloride complexes of Sb(III) in such solutions. Presumably, the formation of active Sb(III) species is facile at higher acidity than that at lower acidity. Polarographic¹³, spectral¹⁴ and solubility work¹⁴ do support the formation of such chloride complexes of Sb(III). It was observed in the Sb(III)-Sb(V) exchange studies¹¹ that the UV spectrum remained unchanged at $[\text{HCl}] \geq 6.0 \text{ mol dm}^{-3}$. In the present case also in solutions of 50% acetic acid, the molar absorptivity at $\sim 245 \text{ nm}$ of Sb(III) increased with increase in $[\text{HCl}]$ but tended to be maximum near $\sim 5 \text{ mol dm}^{-3}$ HCl. The limiting absorption has almost been reached under such conditions and, as given under Results, the principle species appears to be SbCl_4^- . Polarographic¹³ and solubility work¹⁴ have also shown the latter species as the main Sb(III) species in such solutions. This would, no doubt, explain the departure of the order of the reaction in Sb(III) from unity but it is more difficult to rationalise the increase of k_{expl} with increase in $[\text{Sb(III)}]$.

The evidence for the formation of SbCl_4^- as the principle Sb(III) species is well supported by the

kinetic results. The fact that $\log k_{\text{expl}}$ versus $[\text{Cl}^-]$ and α_4 versus $[\text{Cl}^-]$ (α_4 being the fraction of $[\text{Sb(III)}]$ existing as SbCl_4^-) show greater similarity (Fig. 1), than is possible with other Sb(III)-chloride complexes, indicates that this is the main active form of Sb(III) in the reaction. It is also possible, in view of the comparative changes in $[\text{SbCl}_5^{2-}]$ and $[\text{SbCl}_6^{3-}]$ and relative variation of k_{expl} with $[\text{Cl}^-]$, that, while SbCl_5^{2-} is rather inactive, SbCl_6^{3-} may be quite active. The fractional order of ~ 0.5 in the $[\text{Cl}^-]$ range of 0.10 to 1.0 mol dm⁻³ (at both acidities) and the higher orders of -1 and -2.1 (at the two acidities) found between $[\text{Cl}^-]$ of ~ 1.0 and 2.50 mol dm⁻³ probably arise because of the involvement of SbCl_4^- in formation equilibria¹⁴ of $\text{SbCl}_3, \text{SbCl}_5^{2-}$ and SbCl_6^{3-} .

As stated earlier, oxidation reactions of Sb(III) are markedly affected by acidity changes. The order in acidity in the present case also is ~ 2 . Both H^+ and Cl^- cumulatively affect the reaction with the proviso that a minimum amount of H^+ ions (~ 1.0 mol dm⁻³) is necessary under the present reaction conditions, for $[\text{Cl}^-]$ to be effective. If the $[\text{H}^+]$ is too low, even large $[\text{Cl}^-]$ do not have any substantial influence. At high $[\text{H}^+]$ used, SbCl_4^- has been shown to be the main active species. The possibility of protonation of such negatively charged Sb(III) species is ruled out on the basis that the partial substitution of LiCl for HCl, at fixed $[\text{Cl}^-]$, does not affect the UV spectrum of Sb(III). On the other hand, hcFe(III) is known to be protonated in acid solutions, and in view of the order of ~ 2 in $[\text{H}^+]$ for the reaction, $\text{H}_2\text{Fe(CN)}_6^-$ may be the main oxidant species, although participation of $\text{H}_3\text{Fe(CN)}_6$ may also occur. The high $[\text{H}^+]$, without which the reaction is rather slow, probably enables protonation of the oxidant to a considerable extent. With SbCl_4^- and $\text{H}_2\text{Fe(CN)}_6^-$ as the main active species, the mechanism shown in Scheme 1 may be written. This mechanism satisfies the experimental data.



Scheme 1

No evidence for the formation of Sb(IV) is available but the experimental data rule out a single

two-equivalent step. Scheme 1 leads to the rate law (2) where it has been assumed that β_3 is negligible.

$$\begin{aligned} -\frac{d[\text{Fe(CN)}_6^{3-}]}{dt} &= \frac{k\beta_2\beta_7[\text{Fe(CN)}_6^{3-}][\text{Sb}^{3+}][\text{Cl}^-]^4 h_0^2}{(1 + \beta_1 h_0 + \beta_2 2h_0^2)} \times \\ &\quad (1 + \beta_4[\text{Cl}^-] + \beta_5[\text{Cl}^-]^2 + \beta_6[\text{Cl}^-]^3 \\ &\quad + \beta_7[\text{Cl}^-]^4 + \beta_8[\text{Cl}^-]^5 \\ &\quad + \beta_9[\text{Cl}^-]^6)^{-1} \quad \dots (2) \end{aligned}$$

In Eq. (2), h_0 is used in view of the order determination with respect to h_0 .

Lastly, the substantially positive effect of ionic strength of the reaction points to a reaction between ions of like charge. However, increasing acetic acid content in the reaction medium leading to increase in k_{expl} is contrary to the expectation of slower reaction between like ions in media of lower dielectric constant. Perhaps, this effect is countered substantially by the formation of active reactant species to a greater extent in lower dielectric media, leading to a net increase in k_{expl} .

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