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

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Received 20 November 1988; revised 19 April 1989; rerevised and accepted 25 July 1989

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 H₂Fe(CN)₆ and SbCl₄⁻.

The oxidation potentials of hcFe(II)/hcFe(III) (hcFe stands for hexacyanoferrate) and Sb(III)/Sb(V) in dilute acid undergo changes with increase in [H⁺] and [Cl⁻] and also with decrease in the dielectric constant of the reaction medium. Such changes permit a titrimetric estimation of Sb(III) with hcFe(III) in 40% acetic acid in the presence of ~10 mol dm⁻³ HCl in aqueous medium. 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 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 Sb₂O₃ (Sisco) in 3.0 mol dm⁻³ HCl and standardised by titration with KBrO₃ (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 NaClO₄ at 2.60 mol dm⁻³ in most cases. The Sb(V) solution was freshly prepared by the oxidation of Sb(III) solution with KBrO₃ solution. Acidity function (Hₒ) under reaction conditions was measured spectrophotometrically using p-nitroaniline. The validity of such acid solutions to the Hₒ scale was also shown. Bausch and Lomb 2000 spectrophotometer was employed to follow the kinetics and to measure the acidity function (Hₒ). 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 ± 0.05° at 1 = 2.60 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 8.0×10⁻⁴ mol dm⁻³ of hcFe(III) (ε = 1183 ± 1%). The second order rate constants, kₑxp1, 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 kₑxp1 was reproducible within ±5%.

Results

Stoichiometry

Stoichiometric studies were carried out using six different sets of concentrations of reactants ([Sb(III)] ≫ [hcFe(III)] at constant [H⁺] and [Cl⁻] (2.50 mol dm⁻³) and 1 = 2.60 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 interfere. 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).

2Fe(CN)₆³⁻ + Sb(III) = 2Fe(CN)₆²⁻ + Sb(V) \ldots (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

<table>
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<tr>
<th>[hcFe(III)] x 10^4 (mol dm^-3)</th>
<th>[Sb(III)] x 10^4 (mol dm^-3)</th>
<th>[hcFe(II)] x 10^4 (mol dm^-3)</th>
<th>[Sb(V)] x 10^4 (mol dm^-3)</th>
<th>k_expl (mol^{-1} dm^3 s^{-1})</th>
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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 x 10^{-4} and 1.0 x 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 [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 up to [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 complexes of the general formula, SbCl_{3-n} (n = 1 to 6), with the cumulative stability constants, β₁ to β₆, having the values 1.8 x 10^2, 3.1 x 10^3, 1.5 x 10^4, 5.3 x 10^4, 5.2 x 10^4, 1.3 x 10^4, respectively at 25°C in solutions 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 calculated. 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-
The effect of increasing [HCl] on the UV spectrum of Sb(III) was examined. The extinction value at ~245 nm increased gradually with increase in [HCl] and reached a maximum value around [HCl] of ~5 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 $k_{\text{exp}}$ values and a plot of log $k_{\text{exp}}$ 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), $k_{\text{exp}}$ rapidly increased and the plot of log $k_{\text{exp}}$ versus $I/D$ was linear with positive slope.

**Discussion**

The $hcFe(III)$-Sb(III) reaction is instantaneous in ~10 mol dm$^{-3}$ HCl or in 50% acetic acid (v/v) in the presence of ~5 mol dm$^{-3}$ HCl. Although Sb(III) and Sb(V) undergo hydrolysis in H$_2$SO$_4$ medium$^9$, in the present case because of large concentrations of HCl, hydrolysis of Sb(III) was minimal$^{10}$. Even in the case of Sb(III)-Sb(V) exchange$^{11}$, the effect of varying [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 [hcFe(III)] at both acidities examined is expected, the departure of order from unity in [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. Polarographic$^{13}$, spectral$^{14}$ and solubility work$^{14}$ do support the formation of such chloride complexes of Sb(III). It was observed in the Sb(III)-Sb(V) exchange studies$^{11}$ that the UV spectrum remained unchanged at [HCl] > 6.0 mol dm$^{-3}$. In the present case also in solutions of 50% acetic acid, the molar absorptivity at ~245 nm of Sb(III) increased with increase in [HCl] but tended to be maximum near ~5 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$_4^-$.

Polarographic$^{13}$ and solubility work$^{14}$ 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 $k_{\text{exp}}$ with increase in [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 $k_{\text{exp}}$ versus [Cl$^-$] and $\alpha_4$ versus [Cl$^-$] ($\alpha_4$ being the fraction of 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 [SbCl$_3^-$] and [SbCl$_5^-$] and relative variation of $k_{\text{exp}}$ with [Cl$^-$], that, while SbCl$_3^-$ is rather inactive, SbCl$_5^-$ may be quite active. The fractional order of $\sim 0.5$ in the [Cl$^-$] range of 0.10 to 1.0 mol dm$^{-3}$ (at both acidities) and the higher orders of $\sim -1$ and $\sim -2.1$ (at the two acidities) found between [Cl$^-$] of $\sim 1.0$ and 2.50 mol dm$^{-3}$ probably arise because of the involvement of SbCl$_4^-$ in formation equilibria$^{14}$ of SbCl$_3$SbCl$_5^-$ and SbCl$_3^-$.

As stated earlier, oxidation reactions of Sb(III) are markedly affected by acidity changes. The order in acidity in the present case also is $\sim -2$. Both H$^+$ and Cl$^-$ cumulatively affect the reaction with the proviso that a minimum amount of H$^+$ ions ($\sim 1.0$ mol dm$^{-3}$) is necessary under the present reaction conditions, for [Cl$^-$] to be effective. If the [H$^+$] is too low, even large [Cl$^-$] do not have any substantial influence. At high [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 [Cl$^-$], does not affect the UV spectrum of Sb(III). On the other hand, hFe(III) is known to be protonated in acid solutions, and in view of the order of $\sim 2$ in [H$^+$] for the reaction, H$_2$Fe(CN)$_6^-$ may be the main oxidant species, although participation of H$_2$Fe(CN)$_6$ may also occur. The high [H$^+$], without which the reaction is rather slow, probably enables protonation of the oxidant to a considerable extent. With SbCl$_4$ and H$_2$Fe(CN)$_6^-$ as the main active species, the mechanism shown in Scheme 1 may be written. This mechanism satisfies the experimental data.

\[
\begin{align*}
\text{Sb}^{3+} + 4\text{Cl}^- & \rightleftharpoons \text{SbCl}_4^- \\
\text{Fe(CN)}_6^{3-} + 2\text{H}^+ & \rightleftharpoons \text{H}_2\text{Fe(CN)}_6 \\
\text{H}_2\text{Fe(CN)}_6^- + \text{SbCl}_4^- & \rightarrow \text{H}_2\text{Fe(CN)}_6^2^- + \text{SbCl}_4 \\
\text{H}_2\text{Fe(CN)}_6^- + \text{SbCl}_4^- & \rightarrow \text{H}_2\text{Fe(CN)}_6^2^- + \text{SbCl}_4
\end{align*}
\]

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 $\beta_3$ is negligible.

\[
\frac{-d[\text{Fe(CN)}_6^{3-}]}{dt} = \frac{k\beta_1[\text{Fe(CN)}_6^{3-}][\text{Sb}^{3+}][\text{Cl}^-][\text{h}_0]}{(1 + \beta_3[h_0 + \beta_2h_0])}
\]

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 an increase in $k_{\text{exp}}$ 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 $k_{\text{exp}}$.

References