Oxidation of Low Valent Sulphur Compounds with Lead Tetraacetate: Part II — Potentiometric Determination of Pb(IV) Acetate by Reduction with Thiosulphate or Metabisulphite

K. A. IDRISS, I. M.issa & M. S. EL-MELIGY
Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

Received 1 March 1975; accepted 28 April 1975

Lead tetraacetate is reduced quantitatively by thiosulphate or metabisulphite solution. As little as 0·14 mg of Pb(IV) can be estimated by potentiometric titration in glacial acetic acid medium. The titration proceeds fast and the end point is marked by a large potential jump. The oxidation products when S₃O₅²⁻ is used as titrant, have been identified as di- and tetrathionates, whereas sulphate is the end product in titrations using S₅O₆²⁻.

Materials and Methods

Lead tetraacetate was prepared and standardized as given before.

Sodium thiosulphate and metabisulphite solutions were prepared from the Analar product and standardized according to recommended procedures.

Other reagents were of analytical grade (E. Merck or BDH). Doubly distilled water was used for the preparation of solutions.

Platinum electrode in combination with SCE was used for e.m.f. measurements on a direct reading millivoltmeter. The titrations were performed at room temperature (≈ 22°C).

Results and Discussion

Owing to the instability of thiosulphate and metabisulphite in acid solutions the direct titration of these reducing agents with Pb(IV) acetate cannot be carried out successfully. The titration was performed in the presence of acetate buffer, and to pH of the titration medium being adjusted by the addition of the appropriate amounts of 1M NaOH throughout the titration process. The results obtained, however, were not reliable due to the complexity of the oxidation products. In addition, the end point was highly affected by the slight changes in the acidity of the medium. The reaction became very sluggish near the end point. These drawbacks restricted the scope of the method to the titration of Pb(IV) acetate only with the reducing material.

Titration of Pb(IV) acetate with thiosulphate — On titrating amounts of Pb(IV) acetate ranging from 0·28-140 mg with S₃O₅²⁻ solution the curves obtained are characterized by a single large inflection which amounts to 100 mV/0·02 ml of titrant. The reaction proceeds very fast at the start but near the end point it becomes less rapid and needs ≈ 2 min to attain equilibrium. From the amount of thiosulphate consumed at the equivalence point it is concluded that S₃O₅²⁻ is oxidized according to the overall reaction:

\[
7 \text{Pb}^{4+} + 9 \text{S}_3\text{O}_5^{2-} + 3\text{H}_2\text{O} \rightarrow 7\text{Pb}^{2+} + \text{S}_2\text{O}_3^{2-} + 4\text{S}_4\text{O}_6^{2-} + 6\text{H}^+ 
\]

The formal values of the equilibrium constant (\(K\)) and the extent of completion (\(\alpha\)) for reaction (I) are to \(1 \times 10^{19}\) and \(1 \times 10^{19}\) respectively indicating the quantitative nature of the reaction.

The formation of di- and tetrathionate as a result of the oxidation process was confirmed by recording the spectra of the titrated solution both prior to and at the equivalence point. The solution exhibited in each case two absorption bands at 242 nm and 318 nm characteristic of \(\text{S}_2\text{O}_3^{2-}\) and \(\text{S}_4\text{O}_6^{2-}\) anions respectively.

The formation of dithionate was also confirmed as follows:

At the end point in a series of titrations at different concentrations of Pb(IV) acetate, the Pb(II) produced was precipitated out as lead sulphate by adding dilute sulphuric acid. The dithionate in the filtrate was then determined according to Murthy by treating the filtrate with alkaline permanganate which destroys tetrathionate. The excess permanganate was then removed by boiling with manganous sulphate, the solution filtered and the dithionate in the filtrate oxidized with standard dichromate in acid medium. The excess dichromate was back titrated iodometrically.

As is evident from the data included in Table 1, the titration of Pb(IV) acetate with \(\text{S}_3\text{O}_5^{2-}\) can be used as an analytical method for the microdetermination of amounts as small as 0·13 mg of Pb(IV).
Titrations of Pb(IV) acetate with sulphite — The potentiometric titration curves obtained by titrating varying amounts of lead tetraacetate with $S_{2}O_{3}^{2-}$, are characterized by two inflections. The first of these occurs much later than the one corresponding to Pb(III) step (Fig. 1). It may be attributed to the formation of a mixed acetate complex $[2Pb^{2+} . Pb^{4+}](Ac)_{5}$ by the interaction of $Pb^{2+}$ and the remainder of $Pb^{4+}$ in solution.

The reaction at the first inflection is expected to proceed in accordance with Eq. (2):

$$3Pb(Ac)_{4} + S_{2}O_{3}^{2-} + 3H_{2}O \rightarrow [2Pb(Ac)_{2}Pb(Ac)_{4}] + 2SO_{4}^{2-} + 4HAc + 2H^{+} \quad \text{... (2)}$$

The intermediate reduction product seems to be further reduced to divalent lead at the second inflection according to Eq. (4), which can be used in the quantitative determination of Pb(IV).

$$2Pb(Ac)_{4} + S_{2}O_{3}^{2-} + 3H_{2}O + 2H^{+} \rightarrow 2SO_{4}^{2-} + 2Pb^{2+} + 8HAc \quad \text{... (4)}$$

The values of the equilibrium constant $(K)$ and degree of completion $(\alpha)$ for this reaction, as obtained from the titration curves are $1.4 \times 10^{27}$ and $1.2 \times 10^{9}$ respectively.

Amounts of Pb(IV) up to 50 mg can be titrated with $S_{2}O_{3}^{2-}$ in glacial acetic acid medium with reasonable accuracy. At higher concentrations of Pb(IV) the second end point which corresponds to the completion of the reduction process occurs earlier than the expected value due to the incomplete decomposition of the mixed complex formed at the first inflection.

The data given in Table 2 show that the method can be applied for the microdetermination of amounts as small as 0.14 mg of Pb(IV). The inflection at the second end point which is used in the quantitative determination of lead(IV) decreases as the concentration of Pb(Ac)$_{4}$ solution increases. The reaction is very rapid at the early stages of the titration but becomes less rapid as the second end point is approached needing $\sim 2$ min for the establishment of equilibrium.

Oxidation of low valent sulphur compounds usually ends up into sulphate ion when the oxidation is carried out with alkaline permanganate, except in the oxidation of sulphone in the presence of telluric acid when dithionate is obtained as oxidation product. In oxidation in acid medium the formation of dithionate is frequently encountered with sulphide, sulphite and thiosulphate.
**Table 2 — Results Obtained for the Potentiometric Titration of Pb(IV) Acetate with S\textsubscript{2}O\textsubscript{8}^-**

(The titrations were performed in 50 ml glacial acetic acid)

<table>
<thead>
<tr>
<th>Amount of Pb(Ac)\textsubscript{4} \textsubscript{4+} tiritated</th>
<th>End point* (mg of Pb(IV))</th>
<th>Error Inflection at end point* (mV/0.02 ml of titrant)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ml</td>
<td>mg</td>
<td>Theor.</td>
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| TITRATION OF 4.88 × 10^(-5) M Pb(IV) ACETATE WITH 4.07 × 10^(-4) M S\textsubscript{2}O\textsubscript{8}^- |
|---|---|---|
| 3 | 32.45 | 15.164 | 0.9 | 0.9 | Nil | 18 |
| 5 | 54.09 | 25.276 | 1.5 | 1.49 | 0.66 | 15 |
| 8 | 86.55 | 40.445 | 2.4 | 2.38 | 0.83 | 12 |
| 10 | 108.18 | 50.552 | 3.0 | 2.98 | 0.66 | 12 |
| 15 | 162.27 | 75.828 | 4.5 | 4.28 | 0.88 | 10 |

| TITRATION OF 1.22 × 10^(-5) M Pb(IV) ACETATE WITH 3.81 × 10^(-4) M S\textsubscript{2}O\textsubscript{8}^- |
|---|---|---|
| 2 | 5.41 | 2.528 | 1.6 | 1.6 | Nil | 22 |
| 4 | 10.82 | 5.056 | 3.2 | 3.18 | 0.62 | 20 |
| 8 | 20.64 | 10.112 | 6.0 | 5.9 | 0.64 | 18 |
| 12 | 32.46 | 15.168 | 9.6 | 9.57 | 0.31 | 16 |

| TITRATION OF 1.4 × 10^(-5) M Pb(IV) ACETATE WITH 8.3 × 10^(-4) M S\textsubscript{2}O\textsubscript{8}^- |
|---|---|---|
| 1 | 0.31 | 9.145 | 0.42 | 0.42 | Nil | 25 |
| 2 | 0.62 | 0.290 | 0.84 | 0.85 | 1.19 | 22 |
| 5 | 1.55 | 0.725 | 2.1 | 2.12 | 0.95 | 20 |
| 10 | 3.1 | 1.450 | 4.2 | 4.20 | Nil | 20 |
| 15 | 4.65 | 2.175 | 6.3 | 6.26 | 0.63 | 18 |

*At the second reduction step.

Metabisulphite solution is found to be oxidized to sulphate with Br\textsubscript{2}, iodine, alkaline permanganate or acid permanganate in the presence of fluoride ions. Thiosulphate solution is oxidized to tetrathionate (S\textsubscript{2}O\textsubscript{4}^-) or sulphate ions with many oxidizing agents.

In the present investigation the oxidation of thiosulphate with lead tetraacetate initially leads to the formation of tetrathionate as an oxidation product while the oxidising agent is reduced to the intermediate reduction product [2Pb\textsuperscript{2+}.Pb\textsuperscript{4+}](Ac\textsubscript{8}) and divalent lead ions. The mixed acetate complex appears throughout the titration process as a slight white turbidity which vanishes completely within few seconds due to its reduction to divalent lead by tetrathionate present in solution. The tetrathionate, in turn, is partially oxidized to dithionate.

The reaction can be represented by Eq. (1): Eq. (1) is based on the two partial reactions (a) and (b)

\[
14 \text{Pb}^{2+} + 18 \text{S}_2 \text{O}_8^{2-} + 20 \text{OH}^- \rightarrow 4[2\text{Pb}^{2+}.\text{Pb}^{4+}](\text{Ac})_8 + 2 \text{Pb}^{2+} + 9 \text{S}_2 \text{O}_8^{4-} + 2 \text{H}_2 \text{O} + 2 \text{e}^- \quad \text{(a)}
\]

\[
4[2\text{Pb}^{2+}.\text{Pb}^{4+}](\text{Ac})_8 + \text{S}_2 \text{O}_8^{4-} + 6 \text{H}_2 \text{O} + 2 \text{e}^- = 12 \text{Pb}^{2+} + 2 \text{S}_2 \text{O}_8^{6-} + 8 \text{H}_2 \text{O} + 4 \text{H}^+ \quad \text{(b)}
\]

Reaction (b) seems to be very fast as evidenced by the rapid dissociation of the mixed acetate complex. Accordingly the formation of the latter is readily terminated and consequently only one inflection is exhibited in the titration curves of Pb(Ac)\textsubscript{4} with S\textsubscript{2}O\textsubscript{8}^-.

When lead tetraacetate is titrated with S\textsubscript{2}O\textsubscript{8}^- or HSO\textsubscript{4}^- (ref. 1) the intermediate acetate complex is stabilized in solution because of the absence of any reducing species in the titration medium. The reducing agents are oxidized in such cases to sulphate ions. The mixed acetate complex is only affected, i.e. converted to divalent lead, when the required amount of the reducing agent (titrant) is added to the attainment of the second end point. This fact reflects itself in the appearance of the second inflection.

References