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THERMOGRAVIMETRY OF THE ANALYTICAL PRECIPITATES $M_2Pb[Co(NO_2)_6]$ AND $MPb[Co(NO_2)_6]$

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ABSTRACT

Thermogravimetric studies are reported for analytical precipitates of the types $MPb[Co(NO_2)_6]$ and $M_2Pb[Co(NO_2)_6]$, where M represents the univalent cations NH_4^+, K^+, Rb^+, Cs^+, and Tl^+. Compounds of the latter series are consistently more stable to higher temperatures. For either series increasing the radius of M increases thermal stability. Decomposition to temperatures approaching 500 °C involves some four separate processes.

INTRODUCTION

The univalent cations NH_4^+, K^+, Rb^+, Cs^+, and Tl^+ have often been precipitated with lead(II) as hexanitrocobaltate(II) or hexanitrocobaltate(III) compounds. Qualitative and quantitative procedures have been reported, on micro or macro scale, with the majority of applications for potassium[1]. Methods have made use of compounds chiefly from the hexanitrocobaltate(II) series[2–7,12], but also from the hexanitrocobaltate(III) series[8–12]. The precipitates have generally been used as separation forms, with the final determinations by non-gravimetric means. There has been little attention to weighing them directly.

The magnetic properties[12–14], the crystal structure[12,14], and certain other properties[14] of several of these compounds have been described, but their behaviors during heating have not been examined. The purpose of this study was to note the thermogravimetric features of interest, including the upper temperature limits for drying, the composition of thermally degraded precipitates, processes of decomposition, and any relation of the preparation procedures to suitability of the compounds for analytical purposes. The relative stabilities of the compounds of the two series were to be noted.

EXPERIMENTAL

Preparation methods

The compounds of each series may be prepared in similar ways, except that the solutions must be neutral or slightly basic when the hexanitrocobaltate(II) compounds are formed. Acetic acid is added in the preparation of the hexanitrocobaltate(III) compounds, as it makes possible the oxidation of Co(II) to Co(III) by nitrite[1,10]. A procedure similar to that of Cuttica[2] was used for the hexanitrocobaltate(II) compounds, while that of Sergeenko[1,8] was used for the other series. In the formulas given, M represents the univalent cations NH_4^+, K^+, Rb^+, Cs^+, and Tl^+.

$M_2Pb[Co(NO_2)_6]$. MNO_2 solutions containing about 5 g in 100 ml were obtained from M_2SO_4 and $Ba(NO_2)_2$ (City Chemical Co., N.Y.). To each MNO_2 solution was added 10 ml of a solution containing 3 g $Co(NO_3)_2 \cdot 6H_2O$ and 5 g $Pb(NO_3)_2$ in 80 ml water. Both solutions were deaerated before mixing to decrease any possibility of Co(II) oxidation. In the preparation of the NH_4^+ compound, the NH_4NO_2 solution was kept ice cold and used soon after removal of $BaSO_4$.

$MPb[Co(NO_2)_6]$. A reagent mixture containing 22 g $NaNO_2$, 3 g $Co(NO_3)_2 \cdot 6H_2O$ and 5 g $Pb(NO_3)_2$ in 80 ml water was acidified with 5 ml glacial acetic acid, allowed to stand and decanted. To 50 ml of solutions containing one gram quantities of MNO_3 was added 10 ml portions of the reagent.

Precipitates formed immediately, and after 30 minutes they were filtered on paper using suction, and were washed with 5% MNO_2 or $NaNO_2$ solution, water, acetone and ether, then air-dried at room temperature. Small amounts of white basic lead nitrite were precipitated with the hexanitrocobalate(II) compounds, but they were removed by the washing procedure.

The air-dried compounds were chemically stable for several weeks at room temperature, but they did contain small amounts of water. Samples used in the thermal studies were stored at room temperature in a desiccator over P_2O_5 for 12 hours or more, and this removed the remaining moisture.

Completeness of washing

For precipitates of the hexanitrocobaltate(II) series, thermograms obtained in subsequent work indicated directly the sufficiency or completeness of washing, since the basic lead nitrite impurity produced a shoulder on the initial break and flattened the "peak" portion of the curve.

Thermal analysis

Thermogravimetric studies of each compound were conducted using a Cahn RG Electrobalance and the Cahn #2006 "Little Gem" TGA accessory stand and furnace[15]. Samples ranging between 1.5 and 6 mg were weighed using the 10 mg range of the balance. Sensitivity was increased to one or two mg full-scale deflection during a run. Calibration of mass or mass change read-out on a time-base ten inch recorder was verified periodically with National Bureau of Standards Class M weights. Chart speed on the recorder was one inch per three minutes, and each run was continued for 24 minutes.

Samples were heated in air under static conditions in open aluminium cups sitting in a platinum pan suspended from the balance arm by nichrome wire. Room temperature was generally about 25 °C and the relative humidity was about 15 to 30%. The heating chamber was a 10 mm borosilicate glass tube (Corning 9880), and the pan within the chamber was near the center of the furnace. The furnace was controlled in a manner similar to that described by the manufacturer, using a Superior Electric Type 116 Powerstat. A time-temperature response curve was obtained using a Chromel–Alumel thermocouple positioned about one cm below the pan. The curve was fairly linear to about 350 °C and the upper limit of about 500 °C. The heating rate was about 25° per minute in the lower part of the range. Temperature reproducability at a given time during successive runs was within five degrees.

Identification of products

Products of the thermal decomposition reactions were identified by qualitative tests including observed colors of the oxides of lead, solubility tests for oxides of cobalt, nitrite decolorization of permanganate, and the brown-ring test for nitrate. In 1 *M* HCl cobalt(II) oxide is soluble, Co(III) oxide slightly soluble, and Co_3O_4 insoluble. Cobalt(III) oxide dissolved rapidly in acidic KI solution with release of I_2. Hyponitrites, thallium(III) compounds and lead(IV) compounds other than Pb_3O_4 were not detected in the residues.

Volatile products of thermal decomposition were not identified for all samples. A white sublimate from the NH_4^+ compounds appeared on cool portions of the hang-down tube, and was apparently NH_4NO_2. The deposit disappeared as the temperature increased. In one experiment, a sample of $K_2Pb[Co(NO_2)_6]$ was heated in a stream of nitrogen and the evolved oxides of nitrogen were identified by the infrared absorption peaks in the range 1800 to 1900 cm^{-1} for NO and 1250 to 1280 cm^{-1} for NO_2[16].

RESULTS AND DISCUSSION

The TG curves for all compounds of the study are reproduced in Figs. 1 and 2. Since the behaviors were somewhat similar, they are being discussed together.

Table I lists the temperature limits of the initial plateaus. At this limit the samples had lost no more than 0.1% of their masses. No other plateau that may have analytical significance had appeared for any of the compounds until the temperature had approached the upper limit of the heating program. The observed values of net per cent mass lost represent values read from the curves at 450 °C, except that for the cesium and thallium hexanitrocobaltates(II) the last one per cent or so was lost very slowly while the samples were held at the upper temperature limit for an additional five to ten minutes.

Four sequential but slightly overlapping processes are characteristic of the decomposition:

1. Conversion of the hexanitro-anion to oxides of nitrogen and oxides of cobalt plus nitrite equivalent to M^+ content, nitrate equivalent to part of the Pb(II) content, and with the remaining lead having been converted to lead(II) oxide.

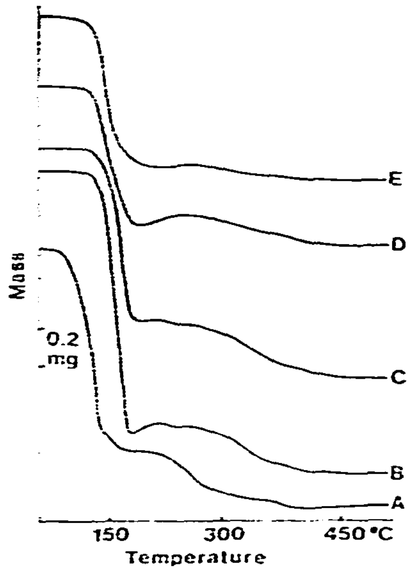

Fig. 1. Thermogravimetric curves for lead(II) hexanitrocobaltate(III) compounds: A, $NH_4Pb[Co(NO_2)_6]$, B, $KPb[Co(NO_2)_6]$, C, $RbPb[Co(NO_2)_6]$, D, $CsPb[Co(NO_2)_6]$, and E, $TlPb[Co(NO_2)_6]$.

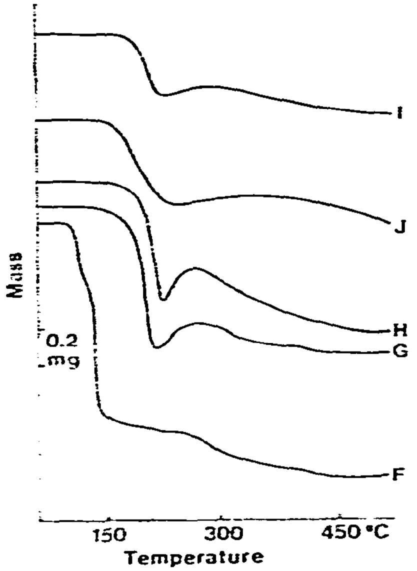

Fig. 2. Thermogravimetric curves for lead(II) hexanitrocobaltate(II) compounds: F, $(NH_4)_2Pb[Co(NO_2)_6]$, G, $K_2Pb[Co(NO_2)_6]$, H, $Rb_2Pb[Co(NO_2)_6]$, I, $Cs_2Pb[Co(NO_2)_6]$, and J, $Tl_2Pb[Co(NO_2)_6]$.

2. A gain of mass corresponding to conversion of remaining nitrite to nitrate by air oxidation.

3. Successive losses of mass in two stages as $Pb(NO_3)_2$ is converted to PbO and oxides of nitrogen.

TABLE 1

THERMOGRAVIMETRY OF $MPb[Co(NO_2)_6]$ AND $M_2Pb[Co(NO_2)_6]$ COMPOUNDS

Curve and compound	*Temp. limit initial plateau*[a] (°C)	*Observed net % mass lost*[a] (450 °C)	*Calculated % for assumed residue*
A $NH_4Pb[Co(NO_2)_6]$	60	45.9	45.9
B $KPb[Co(NO_2)_6]$	115	30.5	30.4
C $RbPb[Co(NO_2)_6]$	135	28.9	28.2
D $CsPb[Co(NO_2)_6]$	130	19.1	26.2
E $TlPb[Co(NO_2)_6]$	125	24.7	23.7
F $(NH_4)_2Pb[Co(NO_2)_6]$	102	46.3	47.6
G $K_2Pb[Co(NO_2)_6]$	160	18.0	18.4
H $Rb_2Pb[Co(NO_2)_6]$	190	16.1	16.1
I $Cs_2Pb[Co(NO_2)_6]$	200	15.1	14.2
J $Tl_2Pb[Co(NO_2)_6]$	130	18.4	12.1

[a] Averages from two or more thermograms for each compound; the average deviations were approximately ±5° for the temperature limits and ±0.7% for the mass losses.

4. A small increase in mass near the end of the range, beginning at about 450 °C, due to conversion of yellow PbO to red Pb_3O_4.

The hexanitrocobaltate(II) compounds are stable to higher temperatures than the hexanitrocobaltate(III) series. The lower temperature limit for the latter series is perhaps due to the occupancy of fewer cation sites in the crystal structure, which is cubic for both series[12,14]. An increase in decomposition temperature approximately corresponds to increasing size of the univalent cation for either series. There is no significant difference of the shapes of the curves in the region of the initial decomposition that can be related to the initial cobalt(II) or cobalt(III) content.

In residues removed at temperatures less than 275 °C both cobalt(II) oxide and cobalt(III) oxide could be identified, however as temperatures exceeded about 300 °C all cobalt went into the acid insoluble oxide Co_3O_4. The initial decomposition process was similar to that observed by Wendlandt and Southern[17] for sodium hexanitrocobaltate(III).

In a study of the products of initial decomposition for $K_2Pb[Co(NO_2)_6]$, nitrogen(II) oxide was present in somewhat larger amount than nitrogen(IV) oxide and nitrogen(I) oxide was not found.

No nitrite could be found in the residues following step one for $(NH_4)_2Pb[Co(NO_2)_6]$ or $NH_4Pb[Co(NO_2)_6]$, and therefore lead(II) nitrite had not been formed or had been short-lived if ever present as an intermediate.

Process two begins at or preceeding the "valley" appearing on the thermograms. The air oxidation of MNO_2 to MNO_3 was apparently catalyzed by the cobalt oxides, since samples of MNO_2 alone were not air oxidized under similar conditions. The oxidation was accentuated for the $M_2Pb[Co(NO_2)_6]$ series, where twice as much mass gain than for the other series corresponds to the two M^+ present. Process two is missing for the compounds containing NH_4^+, since a loss of all NH_4^+ as NH_4NO_2 or other volatile material accompanied the initial process. For the $MPb[Co(NO_2)_6]$ series the MNO_2 to MNO_3 conversion overlaps the initial process considerably.

At the "peak" where process three begins, the residues contained mixtures of MNO_3, Co_3O_4, $Pb(NO_3)_2$ and β-PbO (yellow). No quantitative determinations of lead(II) oxide and lead(II) nitrate were made, but calculations indicate that a 1:1 ratio of the two compounds is in good agreement with the observed masses of the residues at that point; furthermore, the observed mass loss during process three is also in agreement with that calculated for conversion to PbO of one half mole of $Pb(NO_3)_2$ per mole of original compound.

The slow decline toward horizontal of step three is interrupted by one or more inflection points discernible on most thermograms. These points may be associated with the stable mixtures of lead(II) oxide and nitrate observed by Nichol[18]. Those portions of the TG curves due to processes three and four are quite similar to TG curves for lead nitrate.

The calculated per cent differences based on the stoichiometry of the conversions of steps one, two and three are the values given in the last column of Table 1. Lack of agreement with these generalizations will be noted for $CsPb[Co(NO_2)_6]$ and $Tl_2Pb[Co(NO_2)_6]$. The cesium compound was possibly of variable composition[12]. The behavior of the thallium compound may have been due to the presence of liquid thallium(I) nitrite which appeared during the initial stage of decomposition and which was oxidized to the nitrate very slowly. The liquid tended to creep, and a portion may have evaporated. Samons[19] has noted a similar thermal behavior for $Tl_3[Co(NO_2)_6]$. Perhaps because of the lower temperature of decomposition and smaller amount of thallium, $TlPb[Co(NO_2)_6]$ did not show this behavior.

SUMMARY AND CONCLUSIONS

When prepared, washed and air-dried as described above, compounds of the types $M_2Pb[Co(NO_2)_6]$ and $MPb[Co(NO_2)_6]$ may be dried further at 100°C without thermal decomposition. Exceptions are $(NH_4)_2Pb[Co(NO_2)_6]$, which may be dried at 80°C, and $NH_4Pb[Co(NO_2)_6]$ which may be dried at 40°C.

When the $M_2Pb[Co(NO_2)_6]$ compounds are heated in air to 450°C the residues have the general composition: $2MNO_3+PbO+\frac{1}{3}Co_3O_4$, where M represents K^+, Rb^+, Cs^+, and Tl^+. When M is NH_4^+ the final residue is PbO and $\frac{1}{3}Co_3O_4$.

Similarly, the residue when $MPb[Co(NO_2)_6]$ compounds are heated to 450°C is $MNO_3+PbO+\frac{1}{3}Co_3O_4$, and is $PbO+\frac{1}{3}Co_3O_4$ when M is NH_4^+.

For the compounds of both series the conversion of the PbO to Pb_3O_4 was evident in residues heated beyond 450°C. For quantitative analysis applications it would appear difficult to rely upon ignition in the vicinity of 400°C. The plateau between the temperature where the last of the lead nitrate is converted to PbO and where PbO is converted to Pb_3O_4 is limited.

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