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THERMAL DECOMPOSITION OF OXALATES OF LANTHANUM AND THORIUM IN VACUUM

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ABSTRACT

Thermal decomposition of hydrated oxalates of lanthanum and thorium has been studied in vacuum in two ways: (*a*) heating the same sample to higher temperatures progressively and collecting the gaseous product in the specified temperature range and analysing and (*b*) taking different samples each time heated to the predetermined temperature, collecting the gaseous product as well as the solid residue ahd analysing them. The gaseous product contained carbon monoxide and carbon dioxide. The residue contained any undecomposed oxalate, basic carbonate of the metal or its oxide and elemental carbon. A mechanism for the decomposition is suggested on the basis of the intermediate formation of a metallic carbonate.

The results obtained by thermogravimetry, provided information concerning the stages of decomposition of hydrated oxalate of lanthanum and thorium.[1] Differential thermal analysis furnished data about the energetics involved in the process corresponding to different stages of decomposition.[2] It was not possible to analyse the products of decomposition at different stages by the above mentioned methods. It would be helpful to picture the mechanism of this reaction if such informatian could be procured. Investigations on the thermal decomposition of these oxalates in vacuum could provide the necessary data. The results of such a study are represented in this paper.

Experimental procedure. Decomposition studies were carried out in a vacuum manifold described earlier[3] consisting of an evacuating pump connected to a gas measuring unit provided with a manometer and a Topler pump. The Topler pump was necessary to collect the gaseous products obtained during thermal decomposition.

A weighed amount of the sample of hydrated oxalate was taken in a decomposition tube between plugs of pyrex glass wool and then attached to the vacuum assembly. The system was evacuated and then the sample was gradually heated in a tubular furnace to the desired temperature and maintained at that temperature with the help of a sunvic regulator for a specified period. Any water vapour produced during the thermal treatment of the hydrated samples was taken by the phosphorus pentoxide. Whenever gaseous products were obtained, the heating of the sample was continued at the desired temperature till the evolution of the gas practically ceased. The evolved gases were collected over mercury with the help of Topler pump and measured. This analysis of gaseous products showed that it was a mixture of carbon dioxide and carbon monoxide. The two gases were estimated by Hempel's method. The carbon dioxide was absorbed by caustic potash and the carbon monoxide fraction was absorbed by a freshly prepared solution of ammoniacal cuprous chloride.

When the decomposition of the oxalate sample was over, heating was stopped and the specimen tube containing the solid residue was sealed and weighed. Any undecomposed oxalate, carbonate and the metallic content in the sample were determined following the standard methods of analysis. Elemental carbon present in the residue was oxidised to carbon dioxide by heating the sample in oxygen and estimated after absorbing it with ascarite.[3]

RESULTS

Decomposition of lanthanum oxalate. Results of successive heat treatment of the same sample of the hydrated lanthanum oxalate are presented in Table I.

TABLE I

Thermal decomposition of Lanthanium Oxalate Decahydrate in vacuum
Weight of the sample taken = 278.2 mg.

Temp. of Thermal Treatment °C	Duration of heating in hours	Total vol. of the gas evolved at N.T.P. ml.	Vol. of CO at N.T.P. ml.	Vol. of CO_2 at N.T.P. mm.	Melecular formula of the residue
250	24	......	......	......	$La_2C_6O_{12}$
320	22	5.13	2.49	2.64	$La_2C_{5.4}O_{11.1}$
350	61	10.31	3.01	7.30	$La_2C_{4.2}O_{9.1}$
450	72	11.13	0.47	10.66	$La_2C_{2.9}O_{6.5}$
580	72	8.03	1.42	6.61	$La_2C_{1.99}O_{4.84}$

It can be seen from the Table that the oxalate did not decompose at 250°C even after heating for 24 hours. The decomposition set in at 320°C and it was rather slow. Only 5.13 ml of the gaseous product containing equal volumes of carbon monoxide and carbon dioxide was collected over a period of 22 hours. Nearly twice this amount of gas (10.31) was collected over a period of next 61 hours when the temperature of sample was raised to 350°C. The carbon dioxide content in the gaseous product was more than twice the carbon monoxide content. The temperature of the sample was later on maintained at 450°C for 72 hours. 11.13 ml of gas containing very little carbon monoxide was obtained. The decomposition became practically complete when the sample was heated at 580°C for 72 hours. Out of the 8 ml of the gas collected during this interval only 1.4 ml was found to be carbon monoxide.

From a knowledge of the amount of sample taken and the amounts of gaseous products evolved, it is possible to compute the composition of the residue left after each stage of thermal treatment and the information is presented in the last column. The final composition of the residue $La_2C_{1.99}O_{4.84}$ can be visualised as a mixture of the basic carbonate $La_2O_3.CO_2$ and elemental carbon. The presence of elemental carbon was inferred from the dark colour imparted to the residue. It may mentioned that a series of intermediate colours are observed during this process from yellow, reddish brown, to dark brown. Analysis of the final residue confirmed that there was elemental carbon associated with the basic carbonate. The formation of the basic carbonates ($La_2O_3 2CO_2$ and $La_2O_3CO_2$) during the decomposition of lanthanum oxalate has been observed during the thermogravimetric analysis of the sample and also reported by earlier workers.[4]

In order to get an idea about the carbonate and oxalate contents of the residue obtained at the end of each stage, fresh samples of the oxalate were taken and heated at a predetermined temperature till the evolution of gases was practically nil. Results of such a series of experiments are presented in Table II.

TABLE II

Thermal decomposition of lanthanum oxalate decahydrate samples in vacuum

Sl. No.	Weight of the sample taken mg.	Temp.° C	Duration of heating hr.	Vol. of CO ml. N.T.P.	Vol. of CO
1	2	3	4	5	6
1	576.8	300 – 320	144	9.15	12.62
2	639.6	360	72	15.32	39.84
3	591.0	450	85	15.92	49.94
4	759.2	600	48	19.47	75.21

TABLE II—*concld.*

Total Vol. of gas evolved ml. N.T.P.	Molecular formula of the residue	Vol. of CO_2 evolved carbonate ml.N.T.P.	Probable composition of the residue
7	8	9	10
21.77	$La_2 C_{4.78} O_{10.08}$	42.0	$La_2 (C_2 O_4)_{0.7} (CO_2)_{2.3} \cdot + 1\ 08\ C$
55.16	$La_2 C_{3.22} O_{7.22}$	38.7	$La_2 O_3 \cdot (CO_2)_{2.1} + 1{,}1C$
65.86	$La_2 C_{2.40} O_{5.68}$	18 68	$La_2 O_3 \cdot (CO_2)_{1.2} + 1.2C$
94.68	$La_2 C_{1.98} O_{4.78}$	16.49	$La_2 O_3 \cdot (CO_2)_{0\ 9} + 1.1C$

Decomposition of the oxalate was found to be incomplete even after heating the sample at 300-320°C for 144 hours. Analysis of the residue indicated that nearly 23% of the original oxalate remained undecomposed along with about 40% of the original carbon content as carbonate and about 10% elemental carbon. The decomposition was found to be rapid at 360°C. The residue contained very little oxalate. The carbonate content was lower than the earlier sample but the amount of elemental carbon increased. The gaseous product was rich in carbon dioxide. The carbon dioxide content became higher at higher temperatures (450°C and 600°C). The composition of the residue obtained at 450°C did not correspond to a definite basic carbonate. The solid left behind at 600°C was a mixture of elemental carbon and lanthanum basic carbonate, very nearly corresponding to $La_2CO_3CO_2$ which had undergone slight decomposition. The material value for carbon taken in the form of oxalate could be satisfactorily accounted in terms of the gaseous product and the residue containing elemental carbon and carbonate or oxalate.

THERMAL DECOMPOSITION OF THORIUM OXALATE

The products of thermal decomposition of thorium oxalate were slightly different. The final residue was predominently thorium oxide associated with elemental carbon. The results obtained when a sample was subjected to thermal treatment successively at different temperatures are presented in Table III.

The oxalate remained undecomposed even when the sample was heated at 230°C for about 12 hours. When the temperature was raised to 260°C and maintained at that temperature for 48 hours, about 10 ml of the gaseous product was collected and it contained almost equal amount of carbon monoxide and carbon dioxide. The extent of decomposition increased further

TABLE III

Thermal decomposition of thorium oxalate hexahydrate in vaccum
Weight of the sample taken=470.6 mg.

Temp. °C	Duration of heating hrs.	Total Vol. of gas evolved ml. N.T.P.	Vol. of CO ml. N.T.P.	Vol. of CO_2 ml. N.T.P.	Ratio CO/CO_2	Molecular formula
230	12	......	......	......	......	ThC_4O_8
260	48	10.17	4.46	5.88	0.799	$ThC_{3.5}O_{7.24}$
300	117	29.51	16.60	12.91	1.286	$ThC_{2.06}O_{5.16}$
350	70	10.07	2.88	7.19	0.401	$ThC_{1.57}O_{4.31}$
600	34	20.15	1.92	18.23	0.105	$ThC_{0.53}O_{2.22}$

at 300°C evolving 29.51 ml of gaseous product over a period of 117 hours. The carbon monoxide content was less and it decreased considerably when the sample was maintained at 380°C and then at 600°C. The composition of the residue computed from the analysis of the gaseous products is given in the last column. The final residue was dark grey in colour and contained thorium dioxide associated with a little amount of elemental carbon. The presence of thoria was confirmed by X-ray diffraction patterns.

In order to have an idea of the nature of the residue obtained at different stages of decomposition corresponding to different temperatures, fresh samples of the oxalate were taken and heated to predetermined temperature till the decomposition was practically complete. The residue was analysed for its oxalate, carbonate and elemental carbon contents by standard methods. The results of such a series of experiments are given in Table IV.

TABLE IV

Thermal decomposition of thorium oxalate hexahydrate samples in vacuum

Sl. No.	Weight of the sample taken mg.	Temp.°C	Duration of heating hr.	Vol. of gases evolved ml. N.T.P	Vol. of CO ml. N.T.P.	Vol. of CO_2 ml. N.T.P.
1	597.2	269	165	29.57	14.06	15.51
2	689.0	300	141	75.17	33.12	42.05
3	1031.8	350	190	148.88	54.78	94.10
4	819.0	600	209	128.2	47.16	81.04

TABLE IV—*concld.*

Vol. of CO_2 as carbonate ml. N.T.P.	% of original oxalate with the residue	Molecular Formula	Composition of the residue
3.26	58.03	$Th\,C_{2.86}\,O_{6.26}$	$Th(C_2O_4)_{1.16}\,(CO_2)_{0.063}\,O_{1.49} + 0.48C$
4.47	23.73	$Th\,C_{1.49}\,O_{4.08}$	$Th(C_2O_4)_{0.47}\,(CO_2)_{0.075}\,O_{2.05} + 0.47C$
2.02	5.54	$Th\,C_{0.68}\,O_{2.57}$	$Th(C_2O_4)_{0.11}\,(CO_2)_{0.022}\,O_{2.09} + 0.44C$
......	......	$Th\,C_{0.39}\,O_{2.11}$	$Th\,O_2 + C_{0.39}\,O_{0.11}$

Nearly 58% of the original thorium oxalate remained undecomposed when the sample was heated at 260°C for 165 hours. Only a small quantity of carbonate was found along with thoria in the residue. The oxalate contents in the residue left at 300°C and 350°C decreased to 25% and 5% of its original value. Destruction of the oxalate became complete when the sample was heated at 600°C and there was no carborate in the residue. The X-ray diffraction pattern of the residue correspond to $Th\,O_2$. The residue was dark grey in colour indicating the presence of elemental carbon along with thorium oxide. The material balance for carbon was calculated on the basis of analysis and it was found to be satisfactory. It is of interest to note that the formation of carbonate is not pronounced as in the case of the decomposition of oxalates of lanthanum and cerium. The maximum amount found in this case was only 0.075 mole per mole of thorium oxalate. This confirms the observations reported by earlier workers.[5,6]

DISCUSSION

Thermal behaviour of metal oxalates has engaged the interest of several workers right from the early days of chemistry. Decomposition of an oxalate is an irreversible process and requires the breaking of the bonds in the metal-oxygen-carbon system. It has been observed that metal-oxygen thermochemical bond energies determine the nature of the products.[7] As already mentioned earlier, carbon monoxide, carbon dioxide, elemental carbon, metal carbonate, metal oxide and sometimes free metal are among the products of decomposition reaction.

Alkali metal oxalates give carbon monoxide and the corresponding carbonate which remains stable even beyond 800°C. Oxalates of the alkaline earth metals give rise to carbonates and carbon monoxide only during the first stage of decomposition in the range 400—510°C and their carbonates eventually give the corresponding oxide beyond 800°C and above.

Those metals whose basic character is not as pronounced as alkali or alkaline earth metal give rise to a basic carbonate when corresponding metal oxalates are decomposed by heating. Both carbon monoxide and carbon dioxide are given off during the decomposition. Lanthanum oxalate and a few other rare earth metal oxalates belong to this group. Observations made in the present investigation clearly indicate that elemental carbon is one of the products of decomposition of metal oxalate when the decomposition takes place in vacuum. However, presence of carbon has not been clearly indicated in the results reported by many earlier workers as there is no specific mention of elemental carbon among the products of decomposition.

It can be inferred that the basic character of a metal, which can be gauged in terms of ionic radii and ionization potential will determine the composition of the final residue with respect to metal, metal oxide or metal carbonate. Those metals with larger ionic radii and lower ionization potentials are highly basic in character as is the case with alkali metals. Such strongly basic oxides have the capacity to retain carbon dioxide and thus give rise to the formation of a carbonate when the oxalate is decomposed. The alkaline earth metals have slightly smaller ionic radii and also have a tendency to form stable carbonate which will decompose at elevated temperatures. Lanthanum, the first element in the rare earth group has an ionic radius of 1.06 Å(La^{3+}) which is very near to that of strontium (1.13 ÅSr^{2+}). Lanthanum oxide has been observed to be quite basic and it is reasonable to expect the formation of a carbonate or a basic carbonate when its oxalate is decomposed.

The basic carbonate decomposes at elavated temperatures to give the oxide La_2O_3. The other elements in the rare earth group are not as basic as lanthanum and it is quite probable that the carbonates are less stable in such cases. The same tendency may be expected in the case of those metals whose ionic radii are smaller and in consequence have less basic properties with the result even if the metal carbonate is formed it would decompose very easily. The presence of carbonate is found in the residue of the cerus oxalate after decomposition. The ionic radius of cerium is 1.03 Å for Ce^{3+} and O.92 Å for Ce^{+4}. In the case of thorium oxalate only a very small quantity of carbonate would be observed. The ionic radius of thorium lies between these above two values of cerium (O.99 Å for Th^{+4}). Here again thorium resembles cerium in its chemistry.[8] *

It is rather difficult to propose a mechanism for the decomposition of a metal oxalate which would satisfactorily account for all the products as

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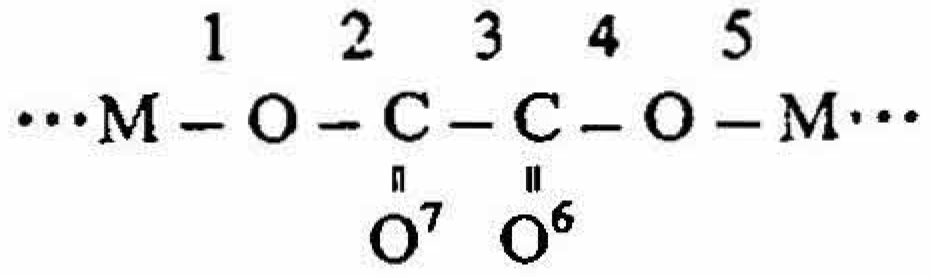
* The fact that thorium oxide is obtained at a comparatively low temperature is rather difficult to explain. Consideration of other parameters such as hydrogen bonding in the crystals of oxalate, etc., will become necessary to account for this behaviour.

mentioned above. According to one school of thought the oxalate decomposes first into metal and carbon dioxide. Subsequently the carbon dioxide is reduced by the metal giving rise to metal oxide and carbon monoxide. Part of the carbon dioxide may also be reduced to carbon.[9 10, 11].

In the case of highly reactive metals like sodium, potassium or calcium only half of carbon dioxide is reduced to carbon monoxide and the rest of the carbon dioxide combines with the highly reactive oxide giving rise to carbonate. In the case of iron and lead which are not so easily oxidised only a part of carbon dioxide is reduced and a mixture of metal and a lower oxide of the metal are produced. Thus the products obtained during thermal decomposition of metal oxalate are determined by the bond breakage in the triad carbon-oxygen-metal, followed by subsequent desorption or escape of the gaseous products from the decomposing mass. Under the strain of heat bonds can break at random, the probability (P) of any bond being broken follows Boltzmann relationship which can be expressed mathematically $P = Ae^{-E/RT}$ where A is a constant, R gas constant, T absolute temperature and E activation energy. Thus there exists a finite probability for any bond to break in the system say for example in the case of a divalent metal oxalate.



$$\cdots M \overset{1}{-} O \overset{2}{-} \underset{\underset{O^7}{\|}}{C} \overset{3}{-} \underset{\underset{O^6}{\|}}{C} \overset{4}{-} O \overset{5}{-} M \cdots$$

The function of free radicals may be expected when the bonds are broken by thermal treatment.

Even in the case of univalent metal oxalate one could expect the formation of different radicals of the type $\dot{M}$, $M\dot{O}$ $MO\overset{\overset{O}{\|}}{C}$ which could variously combine in the following manner:

$$\dot{M} + \dot{M} \longrightarrow 2\ M \text{ metal}$$

$$\dot{M} + M\dot{O} \longrightarrow M_2O \text{ metal oxide}$$

$$M\dot{O} + M\dot{O} \longrightarrow M_2O_2 \text{ peroxide}$$

and

$$MO + MO\overset{\overset{O}{\|}}{C}O \longrightarrow M_2CO_3 \text{ carbonate}$$

apart from other unstable combinations. This idea may be extended to explain the decomposition of di, tri and tetra valent metal oxalates also.

However, in the metal oxalate chain one can see that the $M-O$ bonds 1 and 5 are similar and therefore can be expected to break at the same time.

Similarly bonds 2 and 4 are identical which might also break simultaneously. Such simultaneous breakages of identical bonds would give rise to the radicals $O\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}O$ and $\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{O}$. Combination of such radicals could result in the formation of a carbon-oxygen polymer. Significance of the postulate is discussed a little later.

A similar trend for the disruption of the bouds and formation of free radicals may be expected even in the case of di-, tri-and tetra valent metal oxalates. The formation of metal carbonate has been identified in both the cases of metal oxalate decomposition studies in the present investigations.

$$La_2(C_2O_4) \longrightarrow La_2(CO_3)_3 + 3\,O$$

and

$$Th(C_2O_4)_2 \longrightarrow Th\ (CO_3)_2 + 2\,CO$$

The dissociation of the carbonate will take place giving rise to either a basic carbonate (lanthanum) or oxide.

$$La_2(CO_3)_3 \dashrightarrow La_2O_3.2CO_2 + CO_2$$
$$\hookrightarrow La_2O_3\,CO_2 + CO_2$$
$$\hookrightarrow La_2O_3 + CO_2$$

and $Th(CO_3)_2 \rightarrow ThO_2 + 2\,CO_2$

It remains to explain the formation of elemental carbon which is invariably produced when a metal oxalate decomposes out of contact with air. As mentioned earlier, the free carbon may be found as a result of the reduction of carbon dioxide by the metal. A more satisfactory explanation that is generally offered is that the formation of free carbon during the decomposition of a metal oxalate is due to the dismutation of carbon monoxide.[12,13]

$$2\,CO \rightleftharpoons CO_2 + C$$

The results obtained in the present investigations clearly indicate the presence of elemental carbon even at low temperatures (about 250°C) but the colour of the residue became black (dark-grey) only after 400°C. During intermediate stages yellow to brown colours have been observed. It is likely that the free radicals formed especially $\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}$ and $O\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}O$, during the decomposition of the oxalate may combine in such a manner so as to gvie a polymer of carbon' and oxygen, which then deposits on the surface of the decomposed mass. The formation of coloured polymers of carbon suboxide has been observed by Brodie[14] by subjecting carbon monoxide to prolonged electric discharges. He has reported that carbon rich oxides, C_4O_3 is formed under these experimental conditions (and also such as C_8O_3 and $C_{12}O_9$) have also been observed by others.[15,16] This polymer can slowly evolve oxides of carbon leaving behind free carbon on the surface of the decomposed mass, a phenomenon very similar to charring.

It is thus extremely difficult to put forward a clear mechanism for the decomposition of the metal oxalate in general. Although the overall decomposition of the oxalate can be represented by the equation $\underset{\text{(solid)}}{A} \longrightarrow \underset{\text{(solid)}}{B} + \underset{\text{(gas)}}{C}$ suggesting the possibility of a first order reaction. However, it has been reported that the order of the reaction is very much different from the expectation even in the simple case of the decomposition of silver nitrate owing to the complicated process involved in it.[17]

It is necessary to provide additional experimental evidence in support of the postulations mentioned above. Further work is in progress.

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