PREPARATION OF ANHYDROUS LANTHANON HALIDES

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CONTENTS

I. Introduction 503
II. Preparation of Anhydrous Lanthanon Chlorides 504
  A. Dehydration of Lanthanon Chloride Hydrates 504
  B. Conversion of Oxides to Chlorides 505
  C. Some Miscellaneous Methods 507
III. Preparation of Anhydrous Lanthanon Bromides 507
  A. Dehydration of the Lanthanon Bromide Hydrates 507
  B. Conversion of the Oxides to Bromides 508
  C. Some Miscellaneous Methods 508
IV. Preparation of Anhydrous Lanthanon Iodides 508
  A. Dehydration of Lanthanon Iodide Hydrates 508
  B. Conversion of Oxides to Iodides 509
  C. Some Miscellaneous Methods 509
V. Preparation of Anhydrous Lanthanon Fluorides 509
  A. Dehydration of Lanthanon Fluoride Hydrates 509
  B. Conversion of Oxides to Fluorides 509
VI. References 510

I. INTRODUCTION

Among the most important compounds of elements in general and lanthanons in particular are the anhydrous halides, especially the chlorides. The chlorides are used widely for the production of metals both by electrolytic and metallothermic methods. They are the starting materials from which many other anhydrous compounds, especially the divalent lanthanon compounds, are prepared. Normally, anhydrous chlorides are used for studying thermochemical properties of the lanthanons and for studying their reactions in nonaqueous solutions. Although most of the methods for preparing the anhydrous lanthanon halides have been known since the beginning of this century, investigators still experience difficulty in preparing these compounds in pure form (28, 74). Also some investigators appear not to know of the existence of some of the earliest methods (74).

Pure aqueous solutions of lanthanon halides are prepared readily. The lanthanon halides which separate from these solutions usually retain 6 to 7 moles of water after the unbound water has been removed. Most of the water can be removed by careful dehydration below 100° but it is difficult to remove the last mole of water without decomposing the halide to some extent.

Normally, one would expect to prepare anhydrous metal halides by the reaction between metal and halogen or hydrogen halide either at room or elevated temperatures. Indeed, these were among the earliest methods applied in the preparation of anhydrous halides (5, 37, 60). These methods are limited by the lack of availability of most metals in pure form, which nearly always was true in earlier times. Indeed, it is the chlorides which usually serve as starting materials in the preparation of the metals.

Besides the metals, the most likely starting materials for the preparation of anhydrous halides are the oxides, because of all metallic compounds these are most likely to be readily available in the pure state. In addition, many metals occur naturally in the form of their oxides and most oxygen salts of metals can be decomposed thermally to produce oxides. Though some investigators claim to have prepared anhydrous chlorides by the direct reaction between the oxides and hydrogen chloride, other investigators (69) have been unable to do so. Since oxides are thermodynamically among the most stable compounds of the metals, one does not expect chlorine or hydrogen chloride to react directly with oxides to produce anhydrous chlorides. Considerable energy is required to decompose lanthanon oxides to produce the metal (91).

$$La_2O_3 \rightarrow 2La + 3/2O_2 \quad \Delta H = 428.5 \text{ kcal.} \qquad (1)$$

This is considerably more heat than is required to decompose aluminum oxide (399.0 kcal.).

Even when the thermodynamic energy balance favors such reactions, one does not get pure chlorides but,

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especially with lanthanon oxides, oxychlorides in accordance with equations 2 and 3.

$$Ln_2O_3 + Cl_2 \rightleftarrows 2LnOCl + {}^1/_2O_2 \qquad (2)$$

$$Ln_2O_3 + 2HCl \rightleftarrows 2LnOCl + H_2O \qquad (3)$$

Ln for lanthanon, the generic name for rare earth metals.

The energy balance for the preparation of anhydrous bromides and iodides by the above method would be expected to be even less favorable.

To provide sufficient energy to prepare the chloride from the oxide, a reducing agent must be used in addition to the chlorinating agent. One of the earliest reducing agents was carbon which in combination with Cl_2 (84) or HCl (86) converts oxides smoothly into anhydrous chlorides in accordance with the equations 4 and 5.

$$Ln_2O_2 + 3Cl_2 + 3C \rightleftarrows 2LnCl_3 + 3CO \qquad (4)$$

$$Ln_2O_3 + 6HCl + 3C \rightleftarrows 2LnCl_3 + 3CO + 3H_2 \qquad (5)$$

When available, metal carbides can be converted directly to halides by their reaction with halogens or hydrogen halides at elevated temperatures (76, 77, 79, 80, 87). The reactions between lanthanon carbides and a halogen on a hydrogen halide occur in accordance with equations 6 and 7.

$$2LnC_2 + 3Cl_2 \rightleftarrows 2LnCl_3 + 4C \qquad (6)$$

$$LnC_2 + 3HBr \rightarrow LnBr_3 + 2C + {}^3/_2H_2 \qquad (7)$$

The reactions occur readily at dull red heat and theoretically the pure halides can be obtained. Actually pure carbides are no easier to obtain than pure metals so that the halides obtained by this method are usually less than 100 per cent pure.

Other binary metallic compounds of lanthanons such as the sulfides (78, 81, 82), nitrides, and hydrides (72) which have been used to prepare anhydrous lanthanon halides offer no special advantage since such compounds usually are not readily available in the pure form. A general method for preparing anhydrous halides from oxides was developed by Oersted (84) in 1824. It consisted in passing a stream of chlorine over a hot, intimate mixture of oxide and carbon. It has been stated (7) that no oxide can resist this method of chlorination. The method has been used successfully by several investigators. Although quite useful for the preparation of relatively volatile halides, the method is inconvenient for the preparation of relatively non-volatile halides because they remain contaminated with the excess carbon required to insure complete reaction. Also, the method is time consuming and not convenient for the preparation of small, laboratory quantities of pure anhydrous halides. To avoid carbon contamination, carbon monoxide was introduced (20, 21, 33, 72) as the reducing agent. Although some investigators obtained pure chlorides with this method, it has not been used widely. Hydrocarbons also have been used as reducing agents (26, 33).

The most popular method for the preparation of anhydrous lanthanon halides involves the use of volatile compounds which include both the reducing agent and the chlorinating agent in the same molecule. Among the first such compounds to be used were halides of carbon including CCl_4, $HCCl_3$, and $COCl_2$. Later halides of sulfur such as SCl_2, S_2Cl_2 and Cl_2, S_2Cl_2 alone, and $SOCl_2$ were used. Ammonium chloride also has been used for this purpose. Most of these reagents have produced pure anhydrous lanthanon chlorides. Their specific application will be discussed below in some detail.

Phosphorus(V) chloride has been used to convert heated oxides into their corresponding chlorides (97, 110) but the method has not proved very effective.

Instead of chlorinating the oxide directly, several methods have been developed which involve dehydration of the hydrated halides.

Many oxides, including those of the lanthanons, dissolve readily in dilute hydrochloric acid to produce solutions of the chloride. When these solutions are evaporated to dryness, definite hydrates remain. One might expect to be able to dehydrate these thermally to produce anhydrous halides; instead, one obtains oxyhalides in accordance with equation 8.

$$LnCl_3 \cdot 6H_2O \xrightarrow{\text{heat}} LnOCl + 2HCl + 5H_2O \qquad (8)$$

A variety of dehydration reagents have been used to prevent hydrolysis, among them are hydrogen halides, S_2Cl_2, $SOCl_2$, and ammonium halides. Most of these reagents have produced pure anhydrous halides. Their specific application will be discussed below.

Of the anhydrous lanthanon halides the chlorides have been the most studied. For this reason, it will be profitable to discuss their preparation in some detail. Only methods which have been shown to yield pure anhydrous chlorides conveniently will be discussed. Nothing more will be said about many of the methods mentioned above which produce impure chlorides. Some few miscellaneous methods not mentioned previously but which may prove convenient for the preparation of anhydrous chlorides under certain circumstances will be discussed. After consideration of the chlorides, methods for preparing anhydrous bromides, iodides, and fluorides will be taken up. Some of the methods for preparing anhydrous chlorides can be applied directly in the preparation of the other halide compounds.

II. PREPARATION OF ANHYDROUS LANTHANON CHLORIDES

A. DEHYDRATION OF LANTHANON CHLORIDE HYDRATES

1. *Dehydration with HCl*

This is one of the oldest methods of preparing pure anhydrous lanthanon chlorides. It was perhaps used first by Matignon (63) and has been described adequately by this investigator and many others (23, 32, 49, 52, 64, 65, 68, 69, 98, 99). The method consists essentially in heating the hydrated chloride at 105° until sufficient water has been removed to form the monohydrate. Then the temperature is raised slowly to about 190°, where the monohydrate decomposes to the anhydrous salt. Usually the anhydrous salt is heated to 350° in a stream of HCl. All lanthanon chlorides can be prepared by this method although the preparation of the chlorides of higher atomic weight requires considerably more skill.

The method is rather tedious. The gases, HCl and N_2, which are used to displace the HCl, must be completely free of impurities, especially H_2O and O_2 which convert the chlorides to oxychlorides. Melting before complete dehydration absolutely must be avoided because oxychloride will be occluded in the melts and protected from further attack by HCl. Some investigators have avoided the deleterious effects of O_2, H_2O, and melting by either adding an auxiliary agent, NH_4Cl, to the chloride to be dehydrated (1, 35, 40, 82) or mixing an auxiliary agent (S_2Cl_2 or Cl_2) with the HCl (65, 68). The purity of the product can be tested by treating it with water. If pure, it dissolves with considerable hissing, due to the large quantity of heat evolved, and yields a water clear solution. The presence of the slightest bit of basic chloride will produce cloudiness in the solution. The dehydration time given by most investigators varies from a few hours to several days. Kremers (59) was able to reduce the dehydration time to a working day by operating at reduced pressure but Jantsch (48, 49) did not find it necessary to work under reduced pressure.

Although some investigators (32, 74) still experience difficulty obtaining pure anhydrous halides by dehydrating the hydrated salt in HCl, the validity of the method has been well established. It is the most widely used method for preparing anhydrous lanthanon halides for use in the chemical determination of the atomic weight of the lanthanons (3, 4, 27, 40, 41, 42, 43). Although the lighter lanthanons are dehydrated easily in a stream of HCl, pure anhydrous chlorides of the heavier lanthanons are more difficult to prepare by this method.

2. *Dehydration with Ammonium Chloride*

Although, as has been mentioned above, ammonium chloride has been used widely as an additional reagent in the dehydration of hydrated halides with HCl, only a few investigators (11, 22, 35, 38, 61) appear to have used it as the sole dehydrating reagent. Although some (22, 61) have failed to obtain good results with the method, others (11) found that it worked quite well. Probably one of the main objections to this method is that the yield is reduced by sublimation of some of the lanthanon chloride with NH_4Cl. Although the product can be retrieved, no loss whatsoever of the quite scarce lanthanon compounds could be tolerated in previous times. The author and his students (105) have prepared nearly all the anhydrous lanthanon chlorides by dehydrating a mixture of NH_4Cl and the hydrated lanthanon chloride *in vacuo*. With careful work the yields average around 90%.

The method consists in evaporating to dryness a solution containing ammonium chloride and the desired lanthanon chloride in a mole ratio of 6/1, heating the mixture slowly *in vacuo* to 200° to drive off the water, and finally raising the temperature to 300° to drive off the NH_4Cl. The final product is completely free of H_2O and NH_4Cl and dissolves in water to yield a perfectly clear solution. This is probably the only method which is capable of producing absolutely pure lanthanon halides in quantity.

3. *Dehydration with Other Reagents*

Except for HCl and NH_4Cl, few reagents appear to have been used in the dehydration of hydrated lanthanon chlorides though one would expect most reagents which decompose water (acid anhydrides, especially those containing chlorine) to be suitable. The author (104) has tried acetic anhydride and acetyl chloride without success. Watt (75, 109) using acetyl iodide failed to obtain pure SmI_3 by this method. One difficulty appears to be the tendency of the unwanted anion of the dehydrating reagent to exchange with the halide ion.

Heap (33) claims to have obtained good results by treating the hydrated chlorides with either $COCl_2$ or CO and Cl_2. Matignon and Bourion (70, 106) prepared anhydrous $EuCl_3$ and other anhydrous chlorides by drying the hydrated salt at 100° and dehydrating it further in a stream of S_2Cl_2 and Cl_2 by raising the temperature slowly but avoiding fusion. Freeman and Smith (28) prepared anhydrous chlorides of most of the lanthanons by refluxing the hydrated chlorides with thionyl chloride. The process is reported to be rapid for the lighter lanthanons but to require up to 110 hours for the heavier ones. The method has not proved especially satisfactory in the hands of the author.

B. CONVERSION OF OXIDES TO CHLORIDES

1. *With Sulfur Monochloride and Chlorine or Sulfur Monochloride Alone*

The use of S_2Cl_2 and Cl_2 to chlorinate lanthanon oxides appears to have been developed first by Matignon and Bourion (70). The optimum conditions since have been investigated thoroughly by these (8, 9, 68) and other workers (57, 58, 107). The method appears to be applicable to oxides in general (6, 7, 8, 9, 71, 72, 83). In addition, sulfates and carbonates (7, 69, 70) and, indeed, any oxygen salt (71) appears to be convertible to the anhydrous chloride with S_2Cl_2 and Cl_2. The method has been used successfully to open up lanthanon (36) and other ores (8). Pure $EuCl_3$ cannot be prepared by this method (7, 9, 106), probably because of the reducing action of the chlorinating reagent. However, Bourion (106) succeeded in using this method to prepare $EuCl_3$ from the hydrated chloride.

The general procedure for carrying out the reaction consists in passing a completely dry current of Cl_2 through S_2Cl_2 and passing the mixture over the heated oxide. For the lanthanon oxides the temperature is raised to around 400° in 1.5 hours and heated up to 700 or 800° in 4 to 5 hours. Fusion must be avoided until the oxide is converted completely. Reaction occurs in accordance with equation 9.

$$4Ln_2O_3 + 3S_2Cl_2 + 9Cl_2 \leftrightarrows 8LnCl_3 + 6SO_2 \qquad (9)$$

Sulfur monochloride and chlorine are highly energetic chlorinating reagents. The energy which they release on reacting with oxides often is sufficient to cause melting, which facilitates occlusion of particles of oxide which are protected from further reaction with the chlorinating reagents. For this reason, some anhydrous chlorides are not obtained absolutely pure. Bourion (8) avoided this difficulty by omitting Cl_2 and using S_2Cl_2 alone as the chlorinating reagent. The chlorinating reaction occurs in accordance with equation 10.

$$4Ln_2O_2 + 12S_2Cl_2 \leftrightarrows 8LnCl_3 + 6SO_2 + 18S \qquad (10)$$

The lanthanon oxides are heated in a current of S_2Cl_2 for 2–3 hours during which the temperature is raised from 250–500° or higher if necessary.

2. With Thionyl Chloride

Bourion and Darzens (17) were the first to have used $SOCl_2$ to convert lanthanon oxides to chlorides. The use of $SOCl_2$ to convert oxides to chlorides is of general applicability. The reaction is postulated to occur in accordance with equation 11.

$$Ln_2O_3 + 3SOCl_2 \leftrightarrows 2LnCl_3 + 3SO_2 \qquad (11)$$

However, it is certain that other reactions occur because above 440° $SOCl_2$ dissociates according to equation 12

$$4SOCl_2 \leftrightarrows 2SO_2 + 3Cl_2 + S_2Cl_2 \qquad (12)$$

to yield two good chlorinating compounds. The above authors felt that $SOCl_2$ offered no essential chlorinating advantage over S_2Cl_2 and Cl_2. Bourion and Darzens heated the oxides in a stream of $SOCl_2$ but North and Hagmon (83) obtained chlorides by heating $SOCl_2$ and the oxides in a sealed tube. However, Hecht and Jander (34) pointed out that $SOCl_2$, in addition to acting as a chlorinating reagent, also could react as an oxidizing reagent, producing S_2Cl_2, and as a reducing reagent, producing SO_2Cl_2. They were unable to obtain pure lanthanon halides with its use. Stubblefield, Machlan, and Eyring (102) designed a very convenient semimicro apparatus for preparing small samples of very pure $SmCl_3$ and $YbCl_3$ by chlorinating the oxide with $SOCl_2$. They report that $EuCl_3$ obtained when $SOCl_2$ reacts with Eu_2O_3 contained sulfide impurity.

3. With Carbon Tetrachloride

Chlorination of oxides with CCl_4 to produce anhydrous chlorides is one of the oldest methods for making these compounds. Demarçay (19) appears to be the first investigator to have demonstrated the feasibility of the method. He reported reaction to take place below red heat, 400–500°, and to occur in accordance with equations 13 and 14.

$$Ln_2O_3 + 3CCl_4 \rightleftarrows 2LnCl_3 + 3Cl_2 + 3CO \qquad (13)$$

$$Ln_2O_3 + 3CCl_4 \rightleftarrows 2LnCl_3 + 3COCl_2 \qquad (14)$$

At the temperature of reaction CCl_4 is catalytically decomposed to some extent in accordance with equation 15.

$$2CCl_4 \rightleftarrows C_2Cl_6 + Cl_2 \qquad (15)$$

H. Quantin (92, 93) showed that, in addition to oxides, carbonates, sulfates, phosphates, and silicates could be chlorinated with CCl_4 and he and other investigators (47) showed that it could be used to open up several minerals. Though CCl_4 is nearly a universal chlorinating reagent, it does not convert all oxides (73) and only converts some of them to the oxychloride stage (18). The use of chlorine as a supporting gas increases the chlorinating power of CCl_4.

The most extensive study of the reaction between oxides and CCl_4 was conducted by Camboulive (12). He passed CCl_4 vapor over the heated oxides. He recognized the onset of reactions by incandescence, evolution of $COCl_2$, changed appearance of product, or appearance of chlorine. The temperature of reaction varied with the nature of the oxide but usually was between 215 and 580°. The efficacy of the method for preparing halides of the heavier lanthanons has been proved by Miller (74) and Stubblefield (101) has obtained very pure $EuCl_3$ by chlorinating Eu_2O_3 with CCl_4.

Though one would expect other chlorinated hydrocarbons to be good chlorinating reagents, few appear to have been tried. Methyl chloride can produce chlorination; Renz (95) used $CHCl_3$ to prepare anhydrous chlorides; on the other hand Meyer (73) did not find $CHCl_3$ suitable for preparing these compounds.

4. With Phosgene

Phosgene, perhaps because of its poisonous nature, has been little used as a chlorinating reagent. However, Chauvenet (14) found that below 650° it converts many oxides to their anhydrous chlorides in accordance with equation 16.

$$Ln_2O_3 + 3COCl_2 \rightleftarrows 2LnCl_3 + 3CO_2 \quad (16)$$

The transitional metal oxides often produce oxychlorides but lanthanon oxides yield pure chlorides.

5. *With Ammonium Chloride*

Hopkins, *et al.* (46), developed the method of heating an intimate mixture of a lanthanon oxide with twice the theoretical quantity of NH_4Cl to produce the anhydrous lanthanon chloride in accordance with equation 17.

$$Ln_2O_3 + 6NH_4Cl \rightleftarrows 2LnCl_3 + 3H_2O + 6NH_3 \quad (17)$$

Excess NH_4Cl is sublimed away *in vacuo*. The method has been described in some detail by various investigators (11, 45, 94). It produces anhydrous chlorides in around 90% yield and 98% purity. Though quite efficient for producing anhydrous chlorides in quantity, it is unsatisfactory for producing materials of the highest purity.

C. SOME MISCELLANEOUS METHODS

Compounds of the lanthanons with weakly acidic anions (acetates, oxalates, benzoates, acetylacetonates, *etc.*) are readily prepared. Indeed, some of these (acetates and benzoates) can be obtained in the anhydrous state relatively easily. One would expect the strong acid, HCl, to convert such compounds into their anhydrous chlorides with the elimination of the weak, volatile acid. Such reactions have not been used widely, however, probably because usually they do not yield pure products. The most common difficulty is that the halide produced forms a low melting eutectic with the original salt and the melt is quite resistant to further attack by HCl. Another frequent difficulty is that at a temperature where the exchange reaction is appreciable the organic anion is already beginning to decompose to produce carbonaceous materials.

The author (103) has been unable to transform acetates completely into chlorides by treatment with HCl at the temperature of boiling of benzene. When HCl is passed over the heated benzoates, fusion and charring occur. Careful and patient work might establish suitable conditions for performing such reactions. When a suspension of lanthanon acetylacetonate in ether is treated with HCl it adds to the compound to produce $Ln(C_5H_8O_2)_3 \cdot 3HCl$. When heated *in vacuo*, the compound dissociates mainly into acetylacetone and $LaCl_3$, but before a temperature is reached where conversion is complete charring occurs and considerable insoluble matter is formed.

Lanthanon trichlorides are soluble in various organic solvents (alcohol, acetone, dimethylformamide). One might expect to use such solvents to extract the anhydrous halides from their mixtures with other materials. However, these solvents never can be removed completely from the products. Two methods which are reported to lead to the transformation of weakly acidic lanthanon salts into pure anhydrous chlorides are discussed below.

1. *Reaction between HCl and Lanthanon Benzoates Suspended in Ether*

Braumann and Takvarian (10) reported the preparation of the anhydrous chlorides of La, Nd, and Sm by passing HCl into a suspension of the benzoates in ether. This procedure has not worked well in the hands of the author (103). Although chlorides were obtained with assay values of at least 99%, they dissolved in water with little or no hissing and the resulting solution always contained a little cloudiness. No report was found of this method having been applied to the preparation of anhydrous lanthanon bromides. It cannot be applied without modification to the preparation of the iodides because HI reacts with ether to produce ethyl iodide.

2. *Reaction between Hydrated Lanthanon Oxalates and HCl*

Robinson (96) reports obtaining pure $CeCl_3$ by the reaction of HCl on the oxalate. Harmon and Wichers (31) give directions for preparing anhydrous UBr_3 and PuF_3 by the reaction between the respective oxalates and hydrohalides. They claim the method to be a general one for converting oxalates of the lanthanons and actinons to anhydrous halides.

III. PREPARATION OF ANHYDROUS LANTHANON BROMIDES

Far fewer methods have been perfected for preparing anhydrous lanthanon bromides than exist for the preparation of the chlorides. One does not expect the bromides to have been as well studied as the chlorides because there is much less need for the bromides as reagents; chloride can nearly always be substituted for bromide. Also fewer compounds which can serve as convenient reagents for preparing bromides exist than are available for preparing chlorides. Usually the primary reasons for preparing lanthanon bromides is to study their fundamental properties. The method applied most frequently for the preparation of anhydrous lanthanon bromides will be discussed below.

A. DEHYDRATION OF THE LANTHANON BROMIDE HYDRATES

1. *Dehydration with HBr*

Although some investigators (32, 90) have been able to prepare pure anhydrous bromides by heating the hydrated salt in a stream of pure dry HBr, others (24, 54) have not succeeded in doing so, especially for the heavier lanthanons. It is quite likely that the difficulty of the method lies in the inability to obtain pure HBr absolutely free of H_2O and O_2. In most cases, the anhydrous bromide could be obtained smoothly by heating the hydrated bromide, equilibrated with NH_4Br, in a stream of pure, anhydrous HBr (24, 25, 50, 54). The temperature is raised slowly to 250°, where most of the water is expelled, after which the sample is heated slowly to 600°, where the NH_4Br is sublimed away completely.

2. *Dehydration with Ammonium Bromide*

Above, mention has been made of the use of NH_4Br as an auxiliary reagent in the dehydration of the hydrated lanthanon bromide with HBr. Ephraim (25) was able to volatilize the NH_4Br in a stream of N_2 and Jantsch (50, 54) obtained good results in one trial for $YbBr_3$ by pumping away first the H_2O and later NH_4Br *in vacuo* at 350°. He did not pursue the method, because of loss of some of the material which he could not recover. The author (104) has been able to prepare practically pure bromides of La, Eu, Sm, and Yb by equilibrating the hydrated bromide with NH_4Br and subsequently subliming away the water and ammonium bromide *in vacuo*.

B. CONVERSION OF THE OXIDES TO BROMIDES

1. *With Bromine and Carbon Monoxide*

Attempts have been made to prepare anhydrous lanthanon bromides by passing a mixture of carbon monoxide and bromine over the heated oxide (57), but without success. The most likely source of difficulty is the inability to prepare the reagents pure.

2. *With Ammonium Bromide*

Although no one appears to have reported the conversion of lanthanon oxide to the anhydrous bromides with NH_4Br, the ability of this reagent to do so scarcely can be doubted since it is well known that NH_4Cl (45, 46, 94) and NH_4I (44, 111) can produce chlorination and iodination.

C. SOME MISCELLANEOUS METHODS

1. *Reaction between Anhydrous Lanthanon Chlorides and Hydrogen Bromide*

This is one of the oldest methods for preparing anhydrous lanthanon bromides. It was used first by Matignon (66) and has been applied widely by this (67, 68) and other investigators (57). The procedure consists in heating the anhydrous chloride in a stream of pure dry HBr at 400 to 600° for 7–10 hours. Care must be exercised to prevent the chloride–bromide eutectic from melting which prevents complete conversion of the chloride. The process is very difficult to carry out because the last traces of chloride are removed extremely slowly and it is almost impossible to free HBr completely of impurities. If the reaction is continued long enough to convert the chloride completely, the bromide will be contaminated with oxybromide. In practice one usually stops when the chloride is about 96% converted so as to avoid oxygen contamination.

IV. PREPARATION OF ANHYDROUS LANTHANON IODIDES

Of the lanthanon halides the iodides are the most difficult to prepare. One reason is that iodine compounds of carbon and sulfur (analogous to chlorine and bromine compounds of these elements), which could be used as iodating reagents, are unknown. The principal iodating reagent is HI gas. However, because of its instability and the difficulty of preparing it pure, it is unsuitable for dehydrating hydrated lanthanon iodides. The most common method for preparing anhydrous lanthanon iodides is to pass HI over heated, anhydrous $LnCl_3$, a procedure which almost never produces absolutely pure anhydrous iodides. This method and others which are applied currently for the production of anhydrous iodide will be discussed in some detail below.

A. DEHYDRATION OF LANTHANON IODIDE HYDRATES

1. *Dehydration with HI*

Investigators (32, 49, 51) have been unable to prepare pure anhydrous lanthanon iodides by dehydrating the hydrated salt in a stream of anhydrous HI. Anhydrous iodides have been obtained by heating in a stream of HI and H_2 the hydrated iodide that has been equilibrated with ammonium iodide (39, 49, 51). Even this procedure, however, failed to produce pure anhydrous iodides for the heavier lanthanons (24, 25, 39, 52, 54).

2. *Dehydration with NH_4I in Vacuo*

Previous investigators appear not to have investigated this procedure. The author and his students (104) have prepared practically all the lanthanon iodides completely pure by this method. The method is believed to succeed because *in vacuo* the activity of the water vapor is too low to permit it to react with the NH_4I protected lanthanon iodide. The method cannot be used to prepare anhydrous triiodides of Sm and Eu because these compounds are reduced to diiodides (105). The method consists in dissolving the oxide in a solution of HI, adding 12 moles ammonium iodide per mole of oxide, and evaporating the mixture to dryness. The mixture then is transferred to a special apparatus and the temperature is raised slowly to 200° and held there until all the water has been expelled. Then the temperature is increased to 300–350° and held there until all the ammonium iodide has sublimed away.

B. CONVERSION OF OXIDES TO IODIDES

1. *With Ammonium Iodide*

Young and Hastings (111) applied the method of Hopkins (46) for preparing anhydrous lanthanon chlorides to the preparation LaI_3. They heated 1.0 g. of La_2O_3 with an approximately 14 mole ratio of NH_4I at 350° and sublimed the excess NH_4I at 250° *in vacuo*. Their LaI_3 was about 90% pure. Later Hopkins and Taebel (44) established the experimental conditions for using NH_4I to convert the oxides of Ce, La, Pr, Sm, and Yb to their corresponding anhydrous iodides. They used a 60–120 molar excess of NH_4I and obtained iodides in 85–90% yield. Analysis of the iodides of La, Pr, and Nd showed them to be 95% pure. Some investigators (30) have obtained AcI_3 by heating a mixture of the oxide with NH_4I.

2. *With Aluminum Iodide*

Fried, Hagerman, and Zachariasen (29, 30) prepared iodides of Ac and Am by heating their oxides in an excess of AlI_3. Chaigneau (13) prepared iodides of Ce, La, Pr, Sm, and Yt in this manner. Instead of AlI_3 a mixture of Al and I_2 can be used. The method is inconvenient for the preparation of non-volatile iodides since it is difficult to separate them from the Al_2O_3 which is formed. Some of the lanthanon iodides sublime if heated above 1000°. Using a similar procedure, bromides can be prepared with $AlBr_3$.

C. SOME MISCELLANEOUS METHODS

1. *Reaction between Lanthanon Chlorides and Hydrogen Iodide*

This is the method which has been applied most generally for the preparation of anhydrous lanthanon iodides. It was reported first by Matignon (66) and since has been widely applied by him (67, 68) and other investigators (32, 49, 50, 54, 57). The procedure is similar to that which has been outlined above for the preparation of the bromides and suffers from the same deficiencies. Instead of pure HI, the more readily obtainable mixture of H_2 and HI normally is used. The transformation occurs at 400–600° and may take as long as 24 hours. Pure EuI_3 cannot be obtained by the method (39, 56) and extreme care is required to prepare pure SmI_3 and YbI_3 (39, 52, 68).

V. PREPARATION OF ANHYDROUS LANTHANON FLUORIDES

Unlike the other lanthanon halides, the fluorides are insoluble in water. One expects them to be prepared conveniently by precipitation from aqueous solution of the lanthanons with soluble fluorides. Though such precipitates are obtained readily, they usually are gelatinous and highly hydrated. In the course of dehydration, oxyfluorides often are formed. Currently used methods for making anhydrous lanthanon fluorides are discussed below.

A. DEHYDRATION OF LANTHANON FLUORIDE HYDRATES

The hydrated fluoride is usually precipitated from a solution of the appropriate lanthanon chloride solution (15, 16, 85, 100). When such a precipitate is dried directly, it usually is contaminated with a small amount of moisture (85). By digesting the mixture on a water-bath, Spedding and Daane (16) were able to obtain a granular precipitate which was dried *in vacuo* at 250° to a free flowing powder. Popov and Glockler (88) were able to prepare a crystalline, easily filterable lanthanon fluoride precipitate by slowly adding a 40% solution of Hf to a solution of lanthanon nitrate in 95% ethanol. They obtained the anhydrous salt directly. Staritzsky and Asprey (100) avoided oxyfluoride formation by heating the hydrated fluoride in a stream of HF.

Analogous to the other hydrated lanthanon halides, anhydrous lanthanon fluorides should be capable of preparation by precipitating the fluorides from lanthanon nitrate solutions with excess NH_4F and subliming the excess *in vacuo*.

B. CONVERSION OF OXIDES TO FLUORIDES

Von Wartenburg (108) prepared fluorides of Nd and Pr by heating the oxides in a stream of HF. Zalkin and Templeton (112) used the same procedure to prepare the fluorides of Sm, Eu, Yb, Dy, Ho, Er, Tb, and Lu. Glockler, Popov, and Knudson (88, 89) prepared anhydrous fluorides by heating moist lanthanon fluorides in a stream of ClF_3 at 800°. Complete conversion was achieved.

One sees from the above discussion that numerous methods have been developed for preparing anhydrous lanthanon halides. The ability of most of them to yield pure products is limited only by the skill of experimenter. However, a universal method which is easy to carry out, and which is capable of yielding products of the highest purity is dehydraion *in vacuo* of the hydrated salt equilibrated with the proper ammonium halide. This is probably the only method which can yield pure material in quantity.

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