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AN ANALYSIS OF THE AMMONIUM CHLORIDE ROUTE TO ANHYDROUS RARE-EARTH METAL CHLORIDES

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ABSTRACT

The ammonium chloride route to anhydrous rare-earth metal trichlorides, $RECl_3$, is a two-step procedure consisting in, firstly, the (dry or wet) synthesis of a complex chloride, $(NH_4)_3RECl_6$ ($t \approx 220^oC$) and, secondly, its decomposition either directly (small RE, $t \approx 425^oC$) or via the intermediates $(NH_4)_2RECl_5$ (large RE, $t \approx 385^oC$) and $NH_4RE_2Cl_7$ (medium-size RE), respectively.

INTRODUCTION

Rare-earth metal trihalides, especially the chlorides $RECl_3$, belong to the more important and extensively used compounds of the rare earths. They serve as starting materials not only for the production of metals, but also for many other chemical processes. However, the preparation of samples of very high purity has proven to be difficult. By far the most likely impurity one has to fight against is oxygen. This is because the oxychlorides REOCl are readily formed by reactions such as:

(1) $RECl_3 + H_2O = REOCl + 2\ HCl$

(2) $2\ RECl_3 + O_2 = 2\ REOCl + 2\ Cl_2$

(3) $RECl_3 + RE_2O_3 = 3\ REOCl$

(4) $6\ RECl_3 + 3\ SiO_2 = 6\ REOCl + 3\ SiCl_4$

Of these, reaction (1) has to be taken into account even at ambient temperature when trichlorides are exposed to moist air.

The methods used for the preparation of the anhydrous rare-earth trichlorides may be divided into three groups (see for example [1-3]):

A Direct chlorination of the metals with elemental chlorine or hydrogen chloride [4] as chlorinating agents.

B Conversion of the rare-earth sesquioxides using both a chlorinating and a reducing agent, for example chlorine and carbon, or preferably a compound containing both in one molecule such as $COCl_2$, $SOCl_2$, or S_2Cl_2.

C Dehydration of the hydrates of the rare-earth trichlorides using for example hydrogen chloride to prevent hydrolysis, i.e. the production of REOCl.

Ammonium chloride has been used as a reactant in both groups B [5,6] and C [7,8]. This route is very effective and inexpensive, especially when used on rather large scales. However, it needs careful control of the reaction conditions to achieve up to 99.8% conversion of the oxide [6] (variant 1) or hydrate (variant 2) to the anhydrous chloride.

Variant 1, essentially a one-batch synthesis [5], was said to follow equation (5):

$$(5) \qquad RE_2O_3 + 6\ NH_4Cl = 2\ RECl_3 + 3\ H_2O + 6\ NH_3$$

The role of the large excess of NH_4Cl that has always been, and has to be, used (at least twice the theoretical amount following equation (5), i.e. 12 NH_4Cl) was attributed to the 'acidic' nature of NH_4Cl [6], which should serve through the facile dissociation to HCl and NH_3 as a local HCl reservoir [7], thereby converting RE_2O_3 through a simple acid-base reaction to $RECl_3$ and preventing hydrolysis of the $RECl_3$ already formed.

However, no really sufficient explanation for the necessary 2.0 to 2.5 molar excess of NH_4Cl was given and also not for the observation that almost no NH_4Cl sublimes off at the reaction temperature (180 - 360°C) although the vapor pressure of NH_4Cl equals the atmospheric pressure at 340°C [9]. This is even at 250°C and an ambient pressure of 1 atm about 50 Torrs. In a flow system within 20 hrs time (a usual reaction time), there should considerable amounts of NH_4Cl be driven off.

Additionally, in view of the phases formed in the alkali metal chloride (ACl)/rare-earth metal trichloride ($RECl_3$) systems [10-12], it seems rather unlikely that NH_4Cl and $RECl_3$ could coexist as a plain mixture even at temperatures around 250 - 300°C, as was suggested. Also, as the sesquioxides RE_2O_3 and the oxychlorides REOCl are very stable compounds, a simple conversion of RE_2O_3 directly to $RECl_3$ seems to be thermodynamically unfavorable.

Therefore, an x-ray effort has been undertaken to follow the reaction pathway of the ammonium chloride route directly.

RESULTS AND DISCUSSION

The main result from these investigations is: the ammonium chloride route consists in two steps, of which the first is the synthesis of a complex chloride, at least with sufficient NH_4Cl offered this is exclusively $(NH_4)_3RECl_6$. This step is independent on the size of the RE(III) ion. The reaction starts at about 220°C, the 180°C phase transition of NH_4Cl (CsCl → NaCl type) is always observed on 'dynamic' Simon-Guinier x-ray pat-

terns, before the reaction takes place. The reaction therefore follows, firstly, equation (6), which makes it clear at a glance why twice the theoretical amount of NH_4Cl with respect to equation (5) is needed. Obviously, NH_4Cl is consumed so readily at these temperatures that no considerable amounts of NH_4Cl are sublimed off.

(6) $$12\ NH_4Cl + RE_2O_3 = 2\ (NH_4)_3RECl_6 + 6\ NH_3 + 3\ H_2O$$

$(NH_4)_3YCl_6$ for example (prepared by the so-called variant 2a as outlined in the Experimental Section) undergoes phase transitions at about 100 (I ⇄ II) and 360°C (II ⇄ III). Modifications II and III are identical with those observed when starting with RE_2O_3 and NH_4Cl (variant 1, Fig. 1). $(NH_4)_3YCl_6$-III crystallizes cubic face-centered with a= 1110 pm at 380°C. This lattice constant obtained from the uncorrected high-temperature pattern is an approximate value because quenching to room temperature is not possible and a Guinier pattern at 380°C could not be obtained because of the narrow stability range of the phase (360 - 380°C) and the decomposition of $(NH_4)_3YCl_6$ which is completed at that temperature during the period of time which is necessary to obtain the x-ray pattern. However, from a comparison of the molar volume of $(NH_4)_3YCl_6$-III (205.9 $cm^3 mol^{-1}$) and that observed for $NH_4Y_2Cl_7$ (175.9), one derives a molar volume for NH_4Cl of 47.2 $cm^3 mol^{-1}$, in fairly good agreement with the value observed for the NaCl-type modification of NH_4Cl at 200°C (43.3).

In general, compound formation in the $ACl/RECl_3$ (A= K,Rb,Cs and NH_4^+ as well) systems is limited to the formula types ARE_2Cl_7, $A_3RE_2Cl_9$, A_2RECl_5, and A_3RECl_6 [10-12], of which the first and the last are the most stable in this series. Their occurence in a particular system (say $CsCl/ErCl_3$) is mainly governed by size/volume effects of the constituents. Coordination numbers of the trivalent rare earths are 6 (octahedron, A_3RECl_6, $A_3RE_2Cl_9$, partly A_2RECl_5), 7 (monocapped trigonal prism, ARE_2Cl_7, partly A_2RECl_5), and 8 (ARE_2Cl_7), respectively. The present knowledge of the crystal structures of the former three compound types is rather extensive as compared with the A_3RECl_6 type compounds. Here phase transitions occur frequently (for example three transitions in the 25 - 500°C range for K_3ScCl_6) which make crystal growth and structure determination almost impossible. On the other hand, the highest-temperature modification (stable below the melting point) crystallizes in most cases cubic face-centered (elpasolite (K_2NaAlF_6) or $(NH_4)_3FeF_6$ type) and is therefore easily detected. Roughly, the lower-temperature modifications arise from distortions due to octahedral tilting and upon further cooling from the apparent inability to maintain the high-temperature structural arrangement that is based on a 1:3 (A:Cl) close-packing of spheres. The A:Cl ratio of 1.5:3 in A_3RECl_6 makes arrangements similar to those observed in In_3InCl_6 [13] necessary. Fortunately, the crystal chemistry of complex ammonium chlorides is very similar to that of the analogous rubidium and, to a lesser extent, potassium chlorides. Therefore, with the experiences made for A_3RECl_6 compounds with A= K,Rb one is able to follow the reaction pathways and to, at least, identify the compounds formed.

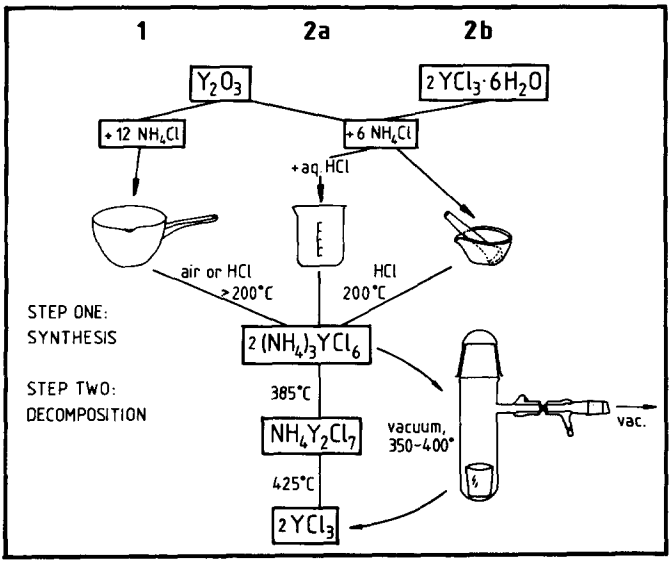


FIG. 1

A sketch of the variants and reaction pathways of the ammonium chloride route to anhydrous yttrium chloride

Step two of the ammonium chloride route is the decomposition of $(NH_4)_3RECl_6$ to (at last) $RECl_3$, which starts at around 385°C under the conditions used here (see Experimental Section). For large RE cations, $(NH_4)_2RECl_5$ compounds (RE= La-Eu) were observed as intermediates, which further decompose at around 425°C to yield $RECl_3$.

(7) $2\ (NH_4)_3RECl_6 = 2\ NH_4Cl + 2\ (NH_4)_2RECl_5$

(8) $2\ (NH_4)_2RECl_5 = 4\ NH_4Cl + 2\ RECl_3$

Medium-sized RE cations (RE= Gd-Yb,Y) lead to $NH_4RE_2Cl_7$ as intermediates, see Fig. 1.

(9) $2\ (NH_4)_3RECl_6 = 5\ NH_4Cl + NH_4RE_2Cl_7$

(10) $NH_4RE_2Cl_7 = NH_4Cl + 2\ RECl_3$

$(NH_4)_3RECl_6$ compounds with small RE cations (RE= Lu,Sc) decompose without the formation of an intermediate.

(11) $2\ (NH_4)_3RECl_6 = 6\ NH_4Cl + 2\ RECl_3$

Equation (5) is therefore only a net equation which corresponds to the initial and final states of the route and is obtained by summation of equations (6,7,8), or (6,9,10), or (6,11).

As examples for $(NH_4)_2RECl_5$ and $NH_4RE_2Cl_7$ type compounds and for identification purposes, the crystallographic properties of $(NH_4)_2PrCl_5$ and $NH_4Y_2Cl_7$ are summarized in Tables 1 and 2, respectively.

Rare-earth trichlorides that were obtained by this route had rather broad x-ray lines attesting to the high activity of the

TABLE 1

Crystallographic Data of $(NH_4)_2PrCl_5$
(Simon-Guinier camera, Cu-K-α_1 radiation, calibration with low-quartz; lattice constants were calculated with 37 reflections, the first 20 lines are given below)

a = 1308.0(1) pm

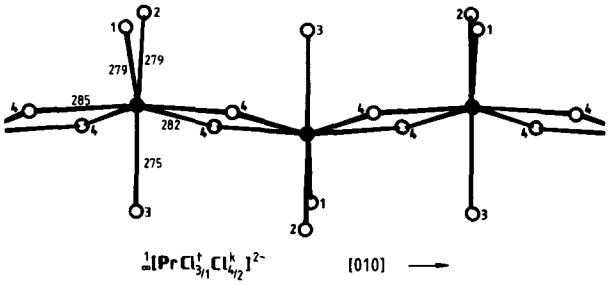
b = 886.87(7) pm

c = 818.0(1) pm

V_m = 142.86(3) $cm^3 mol^{-1}$

Pnma, Z = 4, isotypic with K_2PrCl_5 [14]

The $[PrCl_5]^{2-}$ chain along [010]



$4\theta_{obs}/^\circ$	I_{obs}	I_{cal}	d_{cal}/pm	h k l
25.49	vst	100	693.51	1 0 1
27.02	st	59	653.98	2 0 0
29.39	m	22	601.27	0 1 1
40.04	st	29	443.43	0 2 0
40.04		17	442.62	2 1 1
46.27	w	10	384.74	3 0 1
47.59	m	23	373.59	1 2 1
48.49	w	14	367.02	2 2 0
49.79	w	10	357.27	1 1 2
51.31	vw	9	346.75	2 0 2
53.20*		12	334.85	2 2 1
54.49	w	11	326.99	4 0 0
58.81	w	17	303.63	4 0 1
59.40	vw	7	300.63	0 2 2
59.87	vw	10	298.28	3 0 2
60.95	m	18	292.99	1 2 2
62.22	m	17	287.26	4 1 1
63.25	w	13	282.72	3 1 2
64.29	w	13	278.02	0 3 1
65.53	m	29	273.15	2 2 2

*this value is calculated since the line obviously coincides with the 4θ = 53.28 line of low-quartz used for calibration

materials. These are for many practical applications sufficiently pure: they are free of any extra x-ray lines based on a Guinier level and dissolve completely in diluted hydrochloric acid solutions without cloudiness. If one follows the dry variant 1 (Fig. 1) starting with RE_2O_3 and 12 NH_4Cl, the reaction conditions have to be observed very accurately (see [6]) to prevent (or revoke) the formation of oxyhalide, REOCl. In this perspective, it is much easier to use variant 2a, although this is a two-step procedure and therefore more laborious at first sight. The advantage is, however, that as soon as one has prepared the

TABLE 2

Crystallographic Data of $NH_4Y_2Cl_7$
(Simon-Guinier camera, Cu-K-α_1 radiation, calibration with low-quartz; lattice constants were calculated with 42 reflections, the first 20 lines are given below)

a = 1287.9(2) pm

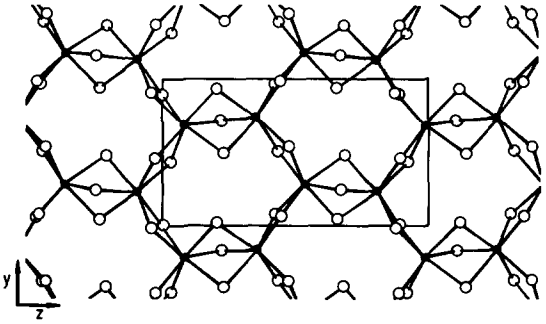
b = 692.5(1) pm

c = 1264.4(4) pm

V_m = 168.86(4) $cm^3 mol^{-1}$

Pnma, Z = 4, isotypic with $RbDy_2Cl_7$ [15]

The $[Y_2Cl_7]^-$ layer: view onto (100)



$4\theta_{obs}/^o$	I_{obs}	I_{cal}	d_{cal}/pm	h	k	l
27.49	vst	100	643.70	2	0	0
29.20	st	67	606.19	0	1	1
31.20	vw	7	567.56	1	0	2
32.24	vw	17	549.36	1	1	1
39.30	vw	2	451.39	2	0	2
40.15	st	45	441.93	2	1	1
43.70	vw	3	406.42	3	0	1
49.45	w	5	359.77	0	1	3
50.80	vw	2	350.36	3	1	1
51.30	m	41	347.00	1	1	3
57.20	w	11	311.85	4	0	1
58.50	w	11	305.06	2	2	0
58.80	vw	2	303.54	0	2	2
59.36	vw	5	300.74	3	0	3
60.26	w	9	296.35	2	2	1
61.20	vw	2	291.90	4	1	0
64.82	m	41	276.00	3	1	3
65.15	w	11	274.64	2	2	2
67.60	vw	1	264.96	4	1	2
68.45	m	13	261.77	1	2	3

pure and dry complex chloride $(NH_4)_3RECl_6$, the formation of oxyhalide during decomposition should be prevented (theoretically) completely in a rather simple apparatus as shown in Fig. 1. The YCl_3 obtained in this way could be used without further purification for the synthesis of e.g. InY_2Cl_7 [16] and is certainly sufficiently pure to serve for thermoanalytical purposes.

If the trichlorides are to be further used in reactions where the oxygen content is crucial, e.g. in the synthesis of the more reduced rare-earth chlorides, one or even more distillation or sublimation steps of the 'crude' product in a full-tantalum apparatus will be necessary subsequently. On the other hand, these purification steps always have as a consequence the recrystalli-

zation of the formerly poorly crystallized material. This also lowers the activity of the trichloride which might be fatal in view of reactions with very slow kinetics.

It was complained that the conversion rates of RE_2O_3 to $RECl_3$ are sometimes fairly low. $RECl_3$ was said to be 'swept away' with the excess NH_4Cl during the sublimation step of the dry route. As this is indeed the NH_4Cl that is produced during decomposition of $(NH_4)_3RECl_6$, it seems rather likely that this 'sweeping' away is in fact the formation of gas complexes such as NH_4RECl_4. Analogous complexes $ARECl_4$ are well-known in the gas state with A= K,Rb,Cs (see for example [17]).

Another problem is whether the reaction of RE_2O_3 with NH_4Cl in the dry route is a solid-solid or a solid-gas reaction which would then make use of the facile dissociation of NH_4Cl to NH_3 and HCl. The dependence upon the flow rate of dried air [6] was interpreted in favor of a solid-gas reaction. Our x-ray investigations show that the synthesis of $(NH_4)_3RECl_6$ can take place without any flow system which, on the other hand, certainly supports the removal of water that would otherwise promote the REOCl formation via reaction (1). Although this does not rule out the possibility that NH_4Cl may react only after dissociation to NH_3 and HCl, it is certainly clear that both components (NH_3 and HCl) are mandatory to achieve the conversion of RE_2O_3 to, finally, $RECl_3$, and it is not simply the acid HCl that reacts with the base RE_2O_3. Obviously, it is most important for the ready success of the (dry) ammonium chloride route that the complex chloride $(NH_4)_3RECl_6$ is formed completely (which consumes up to 20 hours) and that this is decomposed slowly (to diminish the 'sweeping away' of $RECl_3$ through gas complexes) and controlled to yield a high (overall) conversion rate.

EXPERIMENTAL SECTION

The experimental details of the (dry) ammonium chloride route have been described [5] and the reaction conditions investigated extensively [6]. As was mentioned in the previous section, the use of variant 2a is emphasized to prevent or disregard the formation of the most likely impurity, REOCl. As an example, the synthesis and decomposition of $(NH_4)_3YCl_6$ is described below. This synthesis follows a general procedure for ternary rare-earth halides that has been described recently [18].

Step 1: Synthesis of $(NH_4)_3YCl_6$

Approximately 50 mL of conc. hydrochloric acid are added to one mmole of Y_2O_3. A clear solution is obtained after some minutes of boiling. 6 mmoles (optionally more) of NH_4Cl are then added and the clear solution is evaporated slowly to dryness. Care should be taken to avoid any spattering, or sublimation of NH_4Cl. The residue is transferred to a corundum boat and inserted into a glass tube in the center of a tubular furnace. A slow stream of dried HCl (dried with conc. H_2SO_4 or a dry-ice trap) is then added and the temperature raised slowly to about 200°C and allowed to sit overnight. $(NH_4)_3YCl_6$ is obtained as a white deliquescent powder which should not be exposed to moist air.

Step 2: Decomposition of $(NH_4)_3YCl_6$

$(NH_4)_3YCl_6$ is transferred to a platinum crucible under dry conditions. The crucible is inserted into a glass tube, which is fused to a condenser, cooled with water (see Fig. 1), and this is joined to a trap cooled with dry-ice or liquid nitrogen. While evacuating, the temperature is raised slowly to 350 - 400°C. A few hours are usually sufficient to ensure complete decomposition to YCl_3.

$(NH_4)_2RECl_5$ and $NH_4RE_2Cl_7$ compounds are analogously obtained via step 1 with appropriate amounts of NH_4Cl and RE_2O_3 (NH_4:RE = 2:1 in the former and 1:2 in the latter case). Decomposition of these compounds via step 2, too, results in the formation of $RECl_3$.

For x-ray investigations either the pure complex chlorides obtained via step 1 or, to elucidate the reaction pathways of the dry route, mixtures of NH_4Cl and RE_2O_3 (12:1 molar ratios) were filled in quartz capillaries of 0.2 mm o.d. under dry Ar. These were then inserted into a Simon-Guinier camera (FR 553, Enraf-Nonius, Delft/Netherlands) equipped for high-temperature exposures. Typical heating rates were 10 degrees per hour, typical film speeds 2 mm/hr.

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