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Rare Earth Metal–Metal Halide Systems. XVIII. Holmium–Holmium(III) Chloride System. Holmium in the Divalent State

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The phase study of the system $\text{HoCl}_3\text{--Ho}$ is reported. The only reduced chloride formed therein, $\text{HoCl}_{2.14\pm 0.01}$, melts incongruently at $551 (\pm 1)^\circ$, only slightly higher than the temperature of the system eutectic, 543° (at 17.1% Ho). The limited stability of this phase and the apparent absence of any reduced bromide or iodide of holmium is interpreted and generalized in terms of systematics expected for the phase relationships. The formation of a reduced holmium chloride phase is in good accord with expectations from Born–Haber calculations.

Introduction

In addition to the well-known divopositive states of Sm, Eu, and Yb those of Nd(II),^{1,2} Dy(II),^{3–5} and Tm(II)^{6,7} have been characterized in the form of the dihalides.⁸ Studies of the rare earth metal–metal halide systems have also revealed the existence of many intermediate phases with average oxidation states between II and III, and some of these seem to be derived from the parent dihalide structure.^{1,6,7,9} Marked variations in the stability of reduced dihalides of the rare earths have been shown to follow closely the variations in the third ionization potentials and the parallel trends in the negative of the sublimation energies of the metals, and the thermodynamic stabilities of the dihalides may be predicted quite well from Born–Haber cycle calculations.¹⁰

In the case of holmium a borderline stability situation is encountered. Both the third ionization energy and the sublimation energy for holmium are only slightly different from those of dysprosium, and cycle calculations¹⁰ predict that $\text{HoCl}_2(\text{s})$ should be somewhat less stable than DyCl_2 , with $\Delta G^\circ_{298} = -1 \pm 7$ kcal/mol for the disproportionation to metal and trichloride. The relatively large uncertainty thus leaves it unclear whether holmium phases corresponding to any of the known phases DyCl_2 , $\text{DyCl}_{2.11}$, DyBr_2 , and DyI_2 might exist. However, comparison of the $\text{DyCl}_3\text{--Dy}$ phase results with single analysis of the metal-saturated melt obtained in the course of a conductivity study of the $\text{HoCl}_3\text{--Ho}$ system¹¹ gives further caution regarding any prediction since the limiting reduction of the melt decreases from 32 mol % Dy in DyCl_3 to 18.5% Ho in HoCl_3 at 800° . Furthermore, an earlier study of the $\text{HoI}_3\text{--Ho}$ system clearly established the absence of any reduced iodide phase despite a substantial metal solubility, 26% at 1000° and 25% at the eutectic (746°).⁴ The purpose of the present study was to establish whether any reduced holmium chloride exists.

Experimental Section

The techniques and precautions utilized were similar to those described before.^{4,9,12} The pure metal was readily available at Ames Laboratory, and analysis of the arc-melted material showed the following impurities, in ppm: O, 58; C, 16; Cr, 10; Fe, 7; Cu, 95; Ag, 20; Ta, 10; Se, 8; Y, 10; La, 20; Dy, 50; Er, 6; Tm, 9; in the group H, Cl, Ca, V, Mn, Pr, Nd, Gd, Tb, Yb, between 2 and 5 each; K, Ti, Co, Ni, Zn, Ge, Lu, below 1 ppm each; N, Sm, Eu, W, not detectable. Holmium trichloride was prepared by reaction of the metal with electronic grade HCl at 560° and was twice sublimed in a tantalum container under high vacuum. As before, all handling of materials was carried out in a drybox flushed with purified nitrogen, and thermal analysis and equilibration experiments were carried out in sealed tantalum apparatus. The thermocouples were calibrated against the melting points of NaCl (800°) and NaI (660.1°),¹³ and the results obtained should be accurate within $\pm 1.0^\circ$ considering all other uncertainties.

All but the initial X-ray data on powdered reduced samples were secured with a 100-mm Guinier camera (IRDAB, Stockholm); the samples were sealed in small poly(vinyl chloride) envelopes in the

drybox and maintained under vacuum except for the time necessary for mounting. For identification purposes, the stronger 55% of the diffractions of $\text{HoCl}_{2.14}$ at $d > 1.98 \text{ \AA}$ are as follows, in Å with relative intensities in parentheses: 6.50 (4), 4.84 (8), 3.96 (10), 3.544 (6), 3.46 (6), 3.305 (6), 3.15 (6), 2.982 (6), 2.88 (6), 2.84 (4), 2.81 (6), 2.746 (6), 2.739 (4), 2.658 (6), 2.473 (8), 2.418 (6), 2.410 (6), 2.386 (8), 2.283 (6), 2.276 (7), 2.222 (8), 2.216 (4), 2.116 (5), 2.080 (8), 2.071 (4), 2.011 (8), 2.003 (6). The HoCl_3 pattern obtained agreed very well with that calculated from the reported lattice constants and the fractional coordinates for the atoms determined for YCl_3 .¹⁴

Analysis Samples. Samples taken for analysis in the drybox were placed in 20-ml vials sealed with "pop top" polyethylene caps. After being weighed in air on an analytical balance, they were placed separately in a larger container which was evacuated whereupon the cap popped off. Ethanol, then water, and then acetic acid were admitted through the container stopcock to oxidize and dissolve the sample without loss of HCl. If the acetic acid is added too late, a cloudy yellow solution is obtained from precipitation of hydrolysis products, and this can be cleared only with extended heating with stronger acid. Analyses utilized complexometric titration with arsenazo indicator for holmium and precipitation with silver for chloride.¹

Results and Discussion

The pertinent portion of the phase diagram determined for the $\text{HoCl}_3\text{--Ho}$ system is shown in Figure 1. A limiting reduction value of 20.7% Ho obtained at 1000° is not shown.

The melting point of HoCl_3 found, 721.5° , compares well with the literature value of 720° .¹⁵ In accord with the reduction properties of many rare earth metal trihalides the magnitude of the freezing point depression of HoCl_3 by added metal is quite consistent with the formation of an ideal solution of HoCl_2 therein, the cryoscopic number of 3.0 new ions per metal atom dissolved being obtained from the experimental data with the aid of the heat of fusion determined calorimetrically.¹⁶ The system shows supercooling as large as 30° for the eutectic halt, particularly on the metal-rich side of the eutectic composition, perhaps because only a small amount of $\text{HoCl}_{2.14}$ provides nucleation and even that often after appreciable supercooling below its melting point. Location of the correct eutectic and $\text{HoCl}_{2.14}$ peritectic temperatures was aided by extended isothermal equilibrations in the $540\text{--}550^\circ$ range followed by observation of the delay, if any, in the cooling which followed power shutoff. A close-lying transition provides an effective internal heater in the system and hence gives a very significant delay in the achievement of normal cooling rates.

The principal feature in the system is the formation of the slightly stable phase $\text{HoCl}_{2.14\pm 0.01}$ (28.7 ± 0.3 mol%) which melts at 551° , compared with the system eutectic at $17.1 \pm 0.2\%$ and 543° . The initial cooling data did not clearly resolve the two halts and it was only after particular care was taken in securing data shown for the sample at 24.5% that the phase relationships became clear. The small interval between 543 and 551° which is available for effective production of the reduced phase by equilibration of salt with excess metal together with the appreciable incongruity of the formation

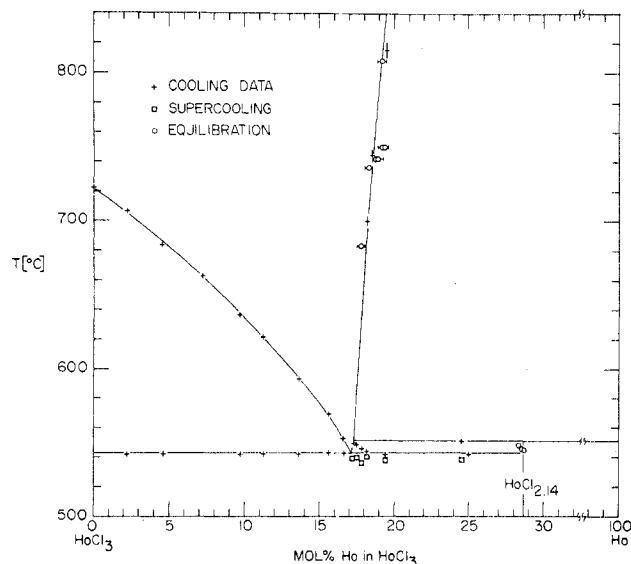


Figure 1. The HoCl_3 –Ho phase diagram: +, thermal analysis data on cooling; \square , cooling data exhibiting supercooling but still usable; \circ , data from equilibration at temperature with excess metal followed by quenching and analysis.

reaction caused some difficulty in achieving and hence identifying the pure reduction product. Consistent formation of the indicated $\text{HoCl}_{2.14}$ composition rather than the possible dichloride or some other phase was achieved after extended equilibrations in the 545–548° region, the most extreme of which spanned 16–19 days and utilized packets of holmium foil of varying size so that the initial weight ratio of metal to trichloride varied from 0.55 to 7.3. The analytical data for three products so synthesized are 68.12, 68.40, 68.47% Ho; 31.47, 31.44, —% Cl; Cl/Ho = 2.15, 2.138, —, respectively.

A preliminary and incorrect notice^{9,17} that the product phase in this system was HoCl_2 was based on Debye–Scherrer patterns of reduction mixtures in the neighborhood of $\text{HoCl}_{2.2}$ which were available at that time. Although the pattern extracted for the reduced product can be indexed fairly well on an orthorhombic cell ($a = 13.20$ (1), $b = 7.08$ (1), $c = 9.911$ (5) Å), quite analogous to the SrI_2 -type structure¹⁸ known for the dichlorides of dysprosium, thulium, and ytterbium,^{3,6} the higher resolution Guinier data of the pure phase made it clear that the structure is not so simple, there being at least 20 extra lines. There was no evidence in the X-ray data for more than one phase or for a range of composition. The pattern of $\text{HoCl}_{2.14}$ is quite similar to but not identical with that for a thulium chloride phase of similar composition. Presumably a superstructure arrangement occurs comparable to that found for $\text{TmCl}_{2.16}$ where the layered arrangement derives naturally (and, in form, plausibly¹⁹) from the layered structure of the TmCl_2 parent phase.⁷ The Debye–Scherrer data available for $\text{DyCl}_{2.11}$ ³ are too poor for a good comparison. This aspect should probably be reinvestigated as the dysprosium chloride system is quite possibly more complex in this region than first thought.

Although the HoBr_3 –Ho system phase study is not complete, the limiting reduction therein is approximately 24 mol % Ho at 950°, and X-ray examinations of the products of extended equilibrations give no evidence for the formation of a reduced holmium bromide.²⁰ Similarly, an earlier study made it clear that no reduced holmium iodide phase was stable in spite of the very appreciable reduction of the liquid triiodide by excess metal (26%).⁴ In this context the existence of only a lower chloride of holmium is somewhat surprising since reduced saline bromides and iodides are generally expected to be thermodynamically more stable than the corresponding chlorides because of lattice energy regularities.²¹ However

the nonexistence of a reduced iodide and bromide can be satisfactorily explained in terms of predictable or plausible phase relationships deriving from expectations for (a) the stability and melting point of the reduced halides and (b) the relative position of the MX_3 liquidus curves based on the enthalpies of fusion and, especially, the melting points of the trihalides.

First, the composition of the melt in equilibrium with excess metal, e.g., 18% Ho or 54 mol % HoCl_2 in HoCl_3 , Figure 1, is a good measure of the relative reducibility of the different rare earth trihalides which is free from the complications of different product structures. Trends in these relatively temperature-independent reduction limits across the rare earth metal series are subject to straightforward interpretations in terms of simple thermodynamic quantities, especially as reflecting the major influence of the third ionization energy and heat of sublimation for the metal.^{4,9} It is also the activity of MCl_3 at this reduction limit which restricts the existence of a reduced phase, in the sense that a single reduced phase of given stoichiometry and structure has the degree of disproportionation (incongruity) required on melting and hence its melting point fixed by this reduction limit. The inverse relationship expected on this basis for incongruity vs. melting point is supported by the compositions of the equilibrium melts and the melting temperatures of the similar compositions $\text{HoCl}_{2.14}$, $\text{TmCl}_{2.11}$, and $\text{DyCl}_{2.11}$, viz., 17, 24 and 28 mol % metal and 551, 615, and 675°, respectively.

In the rare earth halide systems it appears very likely that the melting temperature of any reduced phase as well as the degree of reduction at the melting point must exceed the temperature and degree of reduction of the system eutectic in order for the phase to be stable.²² The inherent reduction limit discussed above determines the required melt composition relatively directly, but the temperature of the eutectic intersection is determined largely by the course of the MX_3 liquidus curve. It is probable that changes in the last are responsible for absence of any reduced holmium bromide or iodide phase. Although each liquidus curve would presumably be consistent with a common Ho^{2+} solute, these would be raised appreciably from chloride to iodide in response to an appreciable increase in the melting points of the trihalides, 721.5, 921,²⁰ and 1003°,⁴ respectively. A simultaneous increase in enthalpy of fusion, 7.3, 12.0 and ~ 14 kcal mol⁻¹, respectively (the last estimated from ΔS° for TbI_3),¹⁶ would accentuate the effect by lessening the magnitude of the freezing point depression by the Ho^{2+} solute for the two heavier and higher melting halides. Thus although the limiting reduction does increase appreciably from chloride to iodide, 17 to ~ 24 to 26 mol % holmium, there is no reason to expect that the melting point and stability of any reduced phase containing holmium(II) would rise nearly rapidly enough to overcome the sizable counterstability effects of both increasing melting point and increasing enthalpy of fusion of the trihalides. Indeed the melting points of the reduced components probably come down—compare a melting point of 659° for DyI_2 with 729° for DyCl_2 which melts slightly incongruently.

In terms of the foregoing the difference in melting and eutectic temperatures provides a convenient enumeration of the limited stability of a single reduction product such as $\text{HoCl}_{2.14}$. Among the smaller values known the 8° value found here for $\text{HoCl}_{2.14}$ compares with 13° for $\text{PrCl}_{2.31}$, 31° for DyI_2 , and, for different types of products, 6° for the metallic GdI_2 and 31° for Gd_2Cl_3 .⁹ In the heavy half of the series where one expects similar structures, holmium is the least reducible system to yield a chloride phase and, in fact, all of the others which form a reduced phase yield the dichloride— DyCl_2 , TmCl_2 , and YbCl_2 .²³

In order to make comparisons with expectations from

Born-Haber cycle calculations for holmium it must be presumed that there is little difference between HoCl_2 and the observed $\text{HoCl}_{2.14}$ lattice in free energy per equivalent of reduction. Within this limitation the present findings are in excellent accord with predictions, especially when the latter are updated in light of more recent fundamental data. In particular the estimates hinge on experimental values of the enthalpies of formation of some of the known dichlorides¹⁰ and a recent 2% change in the value for $\text{EuCl}_{2.24}$ is particularly significant. Taking this together with other small changes in fundamental data into account now yields calculated quantities which are in even better agreement with experimental observation; viz., $\Delta H^\circ_{298} \approx \Delta G^\circ_{298} = +1 \pm 6 \text{ kcal mol}^{-1}$ for the disproportionation of HoCl_2 , a value which is even more meaningful alongside the more firmly predicted relative stabilities of DyCl_2 and ErCl_2 , 6 ± 6 and $-6 \pm 6 \text{ kcal mol}^{-1}$, respectively.²⁵

Some evidence for the formation of reduced holmium on irradiation of Ho_2O_3 and its limited stability in aqueous solutions has recently been noted.²⁶

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Registry No. HoCl_3 , 10138-62-2; Ho, 7440-60-0.

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Polyiodine Cations as Chlorometalate Salts. Synthesis and Nuclear Quadrupole Resonance Characterization of Triiodinium, Pentaiodinium, and Chlorodiiodinium Tetrachloroaluminates, I_3AlCl_4 , I_5AlCl_4 , and $\text{I}_2\text{ClAlCl}_4$

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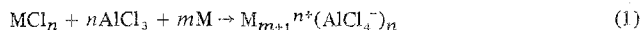
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Reactions of I_2 with $\text{ICl}-\text{AlCl}_3$ mixtures have been investigated by thermal, microscopic, and X-ray analysis. The system contains only the phases I_3AlCl_4 , I_5AlCl_4 , and $2\text{ICl}\cdot\text{AlCl}_3 (= \text{I}_2\text{ClAlCl}_4)$ which melt at 45, 50–50.5, and 53°, respectively. Comparable polyhalogen derivatives of the anions FeCl_4^- , HfCl_6^{2-} , and TaCl_6^- do not exist and neither do any compounds with compositions corresponding to I_4Cl^+ , I_3Cl_2^+ , I_2^+ , or Br_3^+ with AlCl_4^- or SbCl_6^- anions or the phase $\text{ICl}\cdot\text{TaCl}_5$. Unfavorable physical characteristics of the three new phases preclude many normal methods of characterization but the ^{35}Cl and ^{127}I nqr and ^{27}Al nmr spectra for these and the compound $\text{ICl}_2\text{AlCl}_4$ provide substantial information, indicating that the compounds contain normal "ionic" AlCl_4^- groups and therefore the cations I_3^+ , I_5^+ , I_2Cl^+ , and ICl_2^+ . A bonding angle of 97° is obtained from the observed ^{127}I data in I_3^+ ; I_2Cl^+ and ICl_2^+ appear closely analogous. Bond populations and atom charges inferred from the nqr data for these cations are given. Properties of chlorometalate anions which appear important for the stabilization of these cations are considered. The published estimation of the chloride ion affinity of $\text{FeCl}_3(\text{g})$ is corrected to a value of about 85 kcal/mol.

Introduction

The value of acidic conditions in the synthesis of salts which contain homopolyatomic cations has been demonstrated in several ways, for example with AlCl_3 through the general reactions



where the reduced cation stabilized by the large anion may be, among others, Cd_2^{2+} , Bi_5^{3+} , Te_4^{2+} , and Se_8^{2+} .^{1–5} The extension of this approach to the halogens that is reported in the present paper allows a comparable test of the stability of polyatomic cations for elements which are more noted for

polyanion formation. As might be expected, iodine provides the most stable cation examples as well *via* the general reaction

$$\text{ICl} + \text{AlCl}_3 + n\text{I}_2 \rightarrow \text{I}_{2n+1}\text{AlCl}_4 \quad (2)$$

Characterization of new phases by ^{35}Cl and ^{127}I nqr spectroscopy proves to be particularly helpful.

In general the identity and stability of the particular polyatomic cations achieved in such acidic systems must depend on not only the basicity or pCl of the anion formed but also to some extent on the size and charge on this group, but the relative importance of these factors appears complex and is not well understood.⁴ Notwithstanding, chloride ions disso-