The Preparation and Vaporization Thermodynamics of Diytterbium Monoxide Monocarbide.   On the Existence of Ytterbium Monoxide

BY JOHN M. HASCHKE[1a] AND HARRY A. EICK[1b]

Diytterbium monoxide monocarbide (fcc, $a = 4.857 \pm 0.002$ Å), prepared by reaction of stoichiometric mixtures of sesquioxide, metal, and graphite in sealed tantalum ampoules, was found to vaporize according to the reaction

$$6Yb_2OC(s) \longrightarrow 2Yb_2O_3(s) + 3YbC_2(s) + 5Yb(g)$$
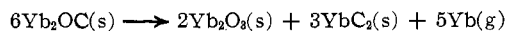
The equilibrium vapor pressure has been measured by a target collection Knudsen effusion technique in the temperature range 1120–1397°K. For the vaporization reaction $\Delta H°_{1259} = 264.5 \pm 3.6$ kcal/gfw and $\Delta S°_{1259} = 104.7 \pm 2.9$ eu. The heat capacity of the oxide carbide has been estimated, and second- and third-law results are presented. For $Yb_2OC(s)$, $\Delta H_f°_{298} = -169.0 \pm 4.5$ kcal/gfw, $\Delta G_f°_{298} = 163.3 \pm 4.5$ kcal/gfw, and $S°_{298} = 34.9 \pm 4.6$ eu. Experimental results and thermodynamic calculations indicate that diytterbium monoxide monocarbide is the phase previously reported to be ytterbium monoxide.

Introduction

During an investigation of the ytterbium–carbon system,[2] a face-centered cubic (fcc) phase was observed in a sample of the composition $YbC_{1.25+y}$ which had become contaminated by oxygen. The lattice parameter of this oxidized phase was identical with that reported for ytterbium monoxide by Achard and Tsoucaris.[3] Since other investigators have been unable to prepare this monoxide either by lithium hydride reduction of ytterbium oxide bromide[4] or oxide chloride,[5] by careful oxidation of the metal,[4] or by matrix stabilization in alkaline earth oxides,[4] the appearance of a product which exhibited cubic symmetry was of particular interest. Preparative and vaporization experiments were initiated to characterize this cubic phase.

Experimental Section

Preparations.—Three preparatory procedures were utilized. The first involved reaction of calcined ytterbium sesquioxide (99.9% rare earth content, Michigan Chemical Corp., St. Louis, Mich.) with ytterbium metal (99.9%; impurities: Ca, Mg, and Cu all <0.01%, Research Chemicals, Phoenix, Ariz.) and vacuum degassed CP graphite (Fisher Scientific Co., Pittsburgh, Pa.) mixed according to

$$(1 - x)Ln_2O_3 + (1 + 2x)Ln + 3xC \longrightarrow 3LnO_{1-x}C_x \quad (1)$$
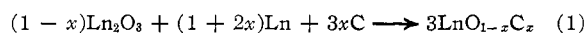
Mixtures with $x = 0$ and $0.25 \leq x \leq 0.50$ were sealed in previously outgassed 6.35-mm o.d. seamless tantalum ampoules by arc welding in argon. The ampoules were heated by induction in a 10^{-5}–10^{-6} Torr pressure at 1100–1300° for 3–4 hr. Product homogeneity was enhanced and reaction time decreased if the sesquioxide and graphite were thoroughly mixed. In one experiment, increments of ytterbium metal and graphite were successively allowed to react with the product from an $x = 0.25$ mixture until a crystallographically pure cubic phase was obtained.

In the second preparative procedure, which was similar to that described by Achard and Tsoucaris,[3] a mixture of ytterbium

sesquioxide and 30–40 wt % graphite was pressed into pellets and heated by induction to 1300° in an open graphite crucible until evolution of noncondensable gases had subsided. The product which effused from the cell was condensed on the water-cooled walls of the quartz vacuum system.

The phase was produced also by heating for 9 hr at 900–1000° a mixture containing a 3:1 ratio of $YbC_{1.25+y}$ ($y = 0.14$)[2] and Yb_2O_3 confined in a sealed tantalum ampoule. All reaction products were manipulated in a glove box whose recirculated argon atmosphere was purified by an oxygen (BASAF catalyst, Badische Anilin und Soda Fabrik, A.G.) and water (activated alumina and phosphorus pentoxide) removal system.

The preparation of an analogous europium phase was attempted *via* reaction 1. Europium sesquioxide (99.9% lanthanide content; spectrographic analysis: 0.05% La_2O_3, 0.01% Nd_2O_3, other lanthanides below detectable limits, 0.02% Zn; American Potash and Chemical Corp., West Chicago, Ill.), europium metal (99.9 %, Michigan Chemical Corp., St. Louis, Mich.), and graphite were combined for $x = 0.25$ and $x = 0.50$.

Analyses.—The reaction products were analyzed for metal and carbon content by conversion to the sesquioxide and carbon dioxide in a microanalytical system. Samples (0.2–0.3 g) were weighed into quartz boats in the glove box, transferred to the analysis line in argon-filled polyethylene bags, and ignited at 850–950° in a stream of high-purity oxygen. A cupric oxide-ceria catalyst was employed for conversion of carbon monoxide to the dioxide, which was determined gravimetrically by collection on Ascarite. The metal content was determined from the sesquioxide residue and oxygen content was obtained by difference. Whenever possible, triplicate analyses were made. Some weighed samples were treated with 1.0 M HCl and the residue, which was identified as the sesquioxide by X-ray diffraction, was determined gravimetrically. Errors reported represent the standard deviations of the measurements.

X-Ray Methods.—X-Ray powder diffraction patterns of the polycrystalline samples were obtained as described previously.[5]

Vaporization.—The vaporization mode of the cubic phase was characterized by a combination of X-ray examination, weight loss studies, analytical procedures, and mass spectrometric measurements. A weighed sample of the cubic phase was heated by induction to constant weight at 1050° in a thoroughly outgassed molybdenum effusion cell. The solid residue which resulted, as well as those which came from all vaporization experiments, were examined by X-ray powder diffraction. Chemical analysis of the weight loss residue for free carbon was effected by heating the sample in 6 M HCl and then determining the graphite gravimetrically. A sample containing a mixture of $YbC_{1.25+y}$, cubic phase, and YbC_2 was vaporized from a molyb-

(1) (a) Abstracted in part from the Ph.D. dissertation of J. M. H., submitted to the Graduate College of Michigan State University. (b) To whom correspondence should be addressed.
(2) J. M. Haschke and H. A. Eick, *J. Am. Chem. Soc.*, **92**, 1526 (1970).
(3) J. C. Achard and G. Tsoucaris, *Compt. Rend.*, **246**, 285 (1958).
(4) G. Brauer, H. Baernighausen, and N. Schultz, *Z. Anorg. Allgem. Chem.*, **356**, 46 (1967).
(5) J. M. Haschke, unpublished data.

denum cell at 925–950° in 1-hr increments, with examination of the residue by X-ray diffraction after each heating. The vapor species originating from an identical mixture were examined in a Bendix time-of-flight mass spectrometer (Model 12-107) with a 25-eV ionizing electron beam.

Target collection Knudsen effusion measurements were made as described previously.[6] Molybdenum effusion cells of the asymmetric (blackbody hole) and symmetric (identical optical and sample cavities) designs[7] with orifice areas of 8.5×10^{-4} (runs 3 and 4), 42.2×10^{-4} (runs 1 and 2), and 62.2×10^{-4} cm² (run 5) were employed. The effusion cells were charged with 0.25–0.40 g of the cubic phase, 0.05–0.1 g of freshly prepared YbC_2,[8] and 0.05–0.10 g of Yb_2O_3. The pressure measurements, which were made at successively increasing and decreasing temperatures in the range 847–1197°, were conducted to 50% sample depletion. During the measurements, residual pressures in the vacuum system were maintained at 10^{-5}–10^{-6} Torr. Procedures utilized for temperature measurement and for collection and analysis of the effusate were similar to those described previously[7] with the exception that the maximum sensitivity of the fluorescence spectrometer for the ytterbium L$\bar{\alpha}$ was attained by the procedure of Neff.[9] The consistency of the analytical results with previous measurements for ytterbium was confirmed by a redetermination of the equilibrium vapor pressure of ytterbium dicarbide.[8]

Electrical Properties.—The resistivity of a sintered sample of the cubic phase was measured; a single crystal of tellurium ($\rho = 2 \times 10^5$ μohms/cm) served as reference material.
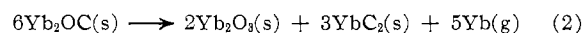
Results

All three preparatory procedures produced a charcoal gray cubic phase, but only the first method in the one experiment described in detail yielded a pure product. Reaction 1 produced a mixture of the cubic material and the sesquioxide for all mixtures with $x < 0.50$. At the $x = 0.50$ composition, a very faint X-ray diffraction pattern of the sesquioxide was observed in addition to that of the fcc phase. The insoluble residue which remained when an $x = 0.50$ product was treated with 1.0 M HCl indicated 1.02 ± 0.05 wt % Yb_2O_3. For $x = 0$ (no carbon), no evidence of reaction or formation of the cubic phase was observed. Successive additions of metal and graphite to the $x = 0.25$ stoichiometry produced a crystallographically pure cubic phase. X-Ray diffraction patterns of the material which condensed on the walls of the vacuum system during graphite reduction of the sesquioxide were diffuse but were indicative of a mixture of Yb_2O_3 (major component) and cubic phase. The reaction of $YbC_{1.25+y}(s)$ and $Yb_2O_3(s)$ yielded a mixture of the cubic phase, Yb_2O_3, and YbC_2.

Chemical analysis of pure samples and those with known oxide contamination indicated the following results for the cubic phase. *Anal.* Calcd for Yb_2OC: Yb, 92.51; C, 3.21. Found: Yb, 92.71 ± 0.09; C, 3.00 ± 0.09 [$YbO_{0.50\pm0.01}C_{0.47\pm0.01}$]. The lattice parameter observed for this phase, which hereafter is called Yb_2OC, was $a = 4.857 \pm 0.002$ Å.

Reaction 1 did not proceed when europium was substituted for ytterbium. The products of this latter reaction were reddish brown europium monoxide, which was easily separated from other products, an unidentified metal carbide, and free metal. *Anal.* Calcd for

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EuO: Eu, 90.47; O, 9.53. Found: Eu, 90.29; O, 9.71. The lattice parameter is $a = 5.140 \pm 0.002$ Å.

Combination of X-ray, weight loss, analytical, and mass spectrometric results indicates that in the 800–1100° temperature range diytterbium monoxide monocarbide vaporizes according to

$$6Yb_2OC(s) \longrightarrow 2Yb_2O_3(s) + 3YbC_2(s) + 5Yb(g) \quad (2)$$

X-Ray powder diffraction patterns of the solid residues which resulted after vaporization of pure monoxide monocarbide indicated the presence of Yb_2OC, Yb_2O_3, and YbC_2.

The only species observed in the mass spectrum of the effusate was Yb^+. Neither an oxygen- nor a carbon-containing entity could be found.

Weight loss data collected from total vaporization experiments indicated 99.0% of the theoretical loss for reaction 3 and X-ray diffraction results confirmed that sesquioxide and graphite comprised the solid residue.

$$3Yb_2OC(s) \longrightarrow Yb_2O_3(s) + 3C(s) + 4Yb(g) \quad (3)$$
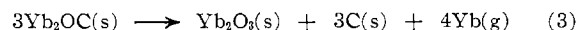
Reaction 3 is consistent with the continued vaporization of the YbC_2 product of reaction 2 to yield graphite and gaseous ytterbium.[9] The graphite was recovered completely in the gravimetric analysis of the solid residue. This recovery is consistent with the previous reports that graphite does not react with the Yb_2O_3 below 1300°.[3] These weight loss data indicate also that neither an oxygen- nor a carbon-containing species appears in the vapor and that $YbC_{1.25+y}$, Yb_2OC, and YbC_2 are in equilibrium with the gaseous ytterbium. The order of disappearance of these phases in the equilibrium vaporization of their mixtures indicates: $P_{Yb}(YbC_{1.25+y}) > P_{Yb}(Yb_2OC) > P_{Yb}(YbC_2)$. No evidence for crucible interaction was detected at low temperatures, but between 1100 and 1200° internal cell surfaces acquired a dull gray coating.

The log P_{Yb} vs. $1/T$ results of five independent vaporization experiments are presented in Figure 1. The linear least-squares equation (with its associated standard deviation) which describes data in the temperature range 1120–1397°K is

$2.303R \log P_{Yb}(atm) =$

$$[-(1.15_6 \pm 0.03_5) \times 10^4/T] + 4.5_8 \pm 0.2_8 \quad (4)$$

Over the 1355–1470°K temperature region, the apparent ytterbium partial pressure is described by

$2.303R \log P_{Yb}(atm) =$

$$[-(1.23_7 \pm 0.05_7) \times 10^4/T] + 5.7_5 \pm 0.4_0 \quad (5)$$

The three data points marked by asterisks in Figure 1 were not included in either data set. Although eq 4 describes the equilibrium pressure for reaction 2, the vaporization reaction at higher temperatures is unknown. The following thermodynamic data were calculated from eq 4 for reaction 2: $\Delta H°_{1259} = 264.5 \pm 3.6$ kcal/gfw and $\Delta S°_{1259} = 104.7 \pm 2.9$ eu.

High-temperature heat capacity equations for the oxide carbide and dicarbide were estimated by use of a Kopp's rule approximation scheme for binary (A_xB_y)
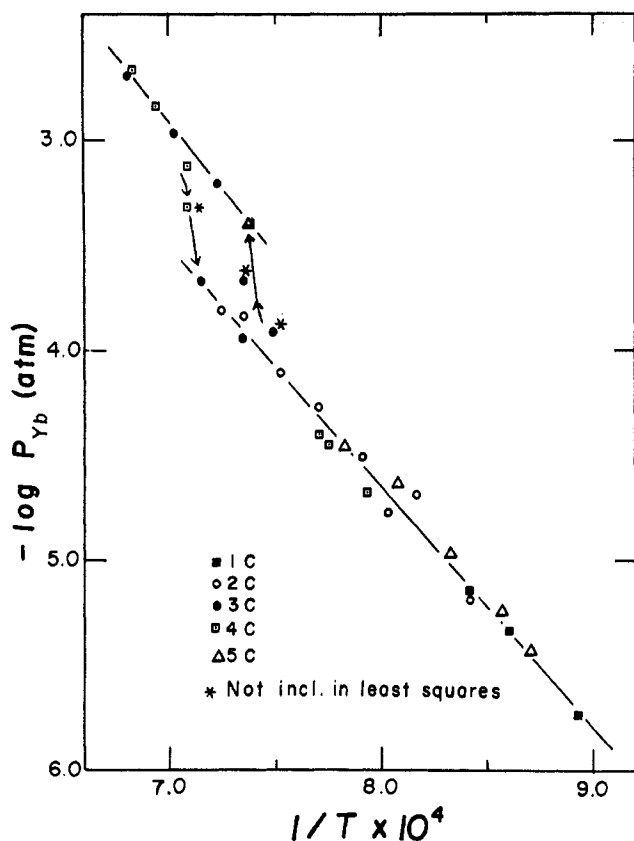
Figure 1.—The pressure of Yb(g) in equilibrium with Yb$_2$OC(s), Yb$_2$O$_3$(s), and YbC$_2$(s).

and ternary (A$_x$B$_y$C$_z$) ionic solids of heavy elements expressed in the form[10,11]

$$C_p(\mathrm{A}_x\mathrm{B}_y\mathrm{C}_z) = (x/u)[C_p(\mathrm{A}_u\mathrm{B}_v)] + [((uy - vx)/2) + z](3R)$$

For these estimations $C_p(\mathrm{A}_u\mathrm{B}_v)$ was the experimentally determined heat capacity of Yb$_2$O$_3$, a binary solid which contained the same heavy element, A. Combination of these estimated enthalpy and entropy functions with those reported for ytterbium sesquioxide[12] and gaseous ytterbium[13] yielded $\Delta H^\circ{}_{298} = 274.3 \pm 4.1$ kcal/gfw and $\Delta S^\circ{}_{298} = 118.7 \pm 4.0$ eu. The reported error includes the experimental standard deviation and a possible error of $\pm 20\%$ in the estimated enthalpy and entropy corrections.

Third-law calculations were effected with free energy functions derived from published data[8,12-14] or estimated from approximated high-temperature heat capacity and entropy data for Yb$_2$OC. An entropy value of $S^\circ{}_{298} = 34.5$ eu was obtained for Yb$_2$OC(s) from the sum of lattice (26.2 eu) and magnetic (8.3 eu) contributions.[14] The third-law enthalpy of vaporization, $\Delta H^\circ{}_{298} = 273.2 \pm 2.6$ kcal/gfw, was temperature independent.

Combination of the second-law enthalpy observed for

reaction 2 with published enthalpies of formation[8,13,15] yielded for diytterbium monoxide monocarbide, $\Delta H_f{}^\circ{}_{298} = -169.0 \pm 4.5$ kcal/gfw. The free energy of vaporization (238.9 $\pm$ 4.1 kcal/gfw), the free energies of formation of the dicarbide[8] and gaseous ytterbium,[13] and that calculated for the sesquioxide (-412.7 kcal/gfw) from its enthalpy of formation[15] and entropy data[10] and the entropies of the elements[13,16] yielded $\Delta G_f{}^\circ{}_{298}$ (Yb$_2$OC) $= -163.3 \pm 4.5$ kcal/gfw. From use of published entropy data[8,13,14] and the second-law entropy change, $S^\circ{}_{298}$(Yb$_2$OC) $= 34.9 \pm 4.6$ eu.

The electrical resistivity of the oxide carbide was approximately 10^4 μohms/cm.

Discussion

Although preparation of several lanthanide monoxides in the condensed state has been reported, the existence of only europium monoxide has been verified.[4] Both our analytical and preparative results indicate that the ytterbium monoxide phase described by Achard and Tsoucaris[3] is actually an oxide carbide of trivalent ytterbium. Since the phase is observed only in the presence of carbon, our results are consistent with the failure of other preparative techniques. This conclusion is analogous to that reported recently for samarium oxide nitride,[17] a phase also originally thought to be the monoxide. The large size of the cubic lattice parameter was the major reason for assuming that the phase contained divalent ytterbium. However, this large interatomic distance probably arises from the random distribution of methanide ions in the lattice, and the ytterbium phase probably belongs to the same general class of cubic oxide carbides reported for the heavier lanthanides.[18]

A thermodynamic calculation was undertaken to determine at what temperatures ytterbium monoxide is stable with respect to disproportionation into the metal and the sesquioxide. For this calculation the enthalpy of formation of YbO was estimated by two methods. One procedure, which involved the thermodynamic data for EuO[7] and EuOBr[11] and the trend with lanthanide radius established by the lanthanide oxide chlorides,[19] gave an estimated $\Delta H_f{}^\circ{}_{298}$(YbO) $= -142$ kcal/gfw. The second method employed a modified Born–Haber cycle with thermodynamic and structural data for Eu[13,20] and EuO.[7] In the modified equation, $\Delta H_f{}^\circ$(YbO) was expressed as a function of the enthalpy of vaporization,[18] the ionization potential,[20] the divalent radius of ytterbium, and a constant term which was derived from the EuO data and included all steps common to both monoxides. The radius of Yb(II) (1.06 Å) was estimated from the Eu(II):Eu(III) radius ratio (1.17 Å/

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0.95 Å)[11,21] and the Yb(III) radius (0.85 Å).[21] This Yb(II) value is close to the apparent metal radius (1.03 Å) calculated from the cubic lattice parameter of Yb_2OC. The results of the Born–Haber calculation gave $\Delta H_f{}^\circ{}_{298}(YbO) = -144$ kcal/gfw. Free energy changes for reaction 6 calculated at various temperatures from an average estimated enthalpy of formation (−143 kcal/gfw) and published[13] or estimated[11] free energy functions are $\Delta G^\circ{}_{298} = 8$ kcal/gfw, $\Delta G^\circ{}_{1000} =$

$$Yb(s, l, g) + Yb_2O_3(s) \longrightarrow 3YbO(s) \qquad (6)$$
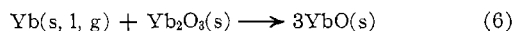
16 kcal/gfw, $\Delta G^\circ{}_{1400} = 21$ kcal/gfw, and $\Delta G^\circ{}_{2000} = 114$ kcal/gfw. The definite trend in these free energies indicates that it is impossible to prepare the monoxide at elevated temperatures and that only a low-temperature technique has any chance of success. Attempts to prepare ytterbium monoxide by reaction of oxygen with a liquid ammonia solution of the metal yielded a white product which contained an fcc phase ($a = 4.87$ Å) and the sesquioxide.[22]

The vaporization behavior of diytterbium monoxide monocarbide is unusual because of the sharp break in the vapor pressure curve. As is indicated by the arrows in Figure 1, the discontinuity has the appearance of a hysteresis loop, but the path is reversed from that of normal temperature effects. The break might mark the onset of a diffusion-controlled process which arises from the growth of a sesquioxide and dicarbide layer on the sample surface. It is interesting to note that the break is coincident with the $\alpha \rightarrow \beta$ transition of the sesquioxide at 1376°K ($1/T = 7.315$ deg⁻¹).[12] A diffusion-controlled process which might be significant at higher temperatures is the congruent vaporization of Yb_2OC to form gaseous ytterbium and carbon monoxide. The

existence of this competing vaporization mode would explain the results of Achard and Tsoucaris,[3] who condensed a mixture of metal and cubic phase upon revaporization of a sample from a tantalum crucible under vacuum. In addition, the presence of carbon monoxide in the vapor could give rise to crucible reaction at the higher temperatures.

The thermodynamic results are consistent with those anticipated for an oxide carbide. As the preliminary experiments had indicated, the equilibrium vapor pressure of the oxide carbide is greater than that of ytterbium dicarbide. Although no thermodynamic data are available for comparison, the enthalpy of formation of $YbO_{0.5}C_{0.5}$ (−84.5 kcal/gfw) should be similar to that of the lanthanide nitrides. The enthalpy of formation reported for LaN is −72.1 kcal/gfw.[23] The values obtained for $\Delta H_f{}^\circ{}_{298}$ and $S^\circ{}_{298}$ of Yb_2OC indicate that phase contains trivalent ytterbium.

The NaCl-type oxide carbides probably exist for all the lanthanides except europium. Such a phase has been observed previously for La, Nd, Gd, Ho, and Er.[18] The europium system was of particular interest because of the possibility of an $EuO–EuO_{0.5}C_{0.5}$ solid solution; however, the greater stability of the monoxide prevents formation of the oxide carbide. No evidence for variable composition was observed for Yb_2OC.

Our results indicate that the stability of divalent ytterbium is not nearly so great as that of europium and that the preparation of condensed ytterbium monoxide by a high-temperature technique is unlikely.

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