extracts were washed with water, dried over anhydrous sodium sulfate, and evaporated. Crystallization of the residue from benzene–cyclohexane gave 66 mg. (74% yield) of 1,6-diphenyl-1,3,5-hexatriene, m.p. and m.m.p. 204–205°. The use of ceric ammonium nitrate instead of ferric chloride led to the rapid production of the theoretical amount of gas but apparently overoxidized the complex, since no hexatriene could be recovered from the reaction mixture.

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Pressure and Polymorphism in the Rare Earth Sesquioxides[1]

By James O. Sawyer, Bruce G. Hyde, and LeRoy Eyring

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Investigations of the temperature ranges of stability of the three polymorphs of the lanthanide sesquioxides, R_2O_3,[2,3] have been summarized in Figure 1.[4]

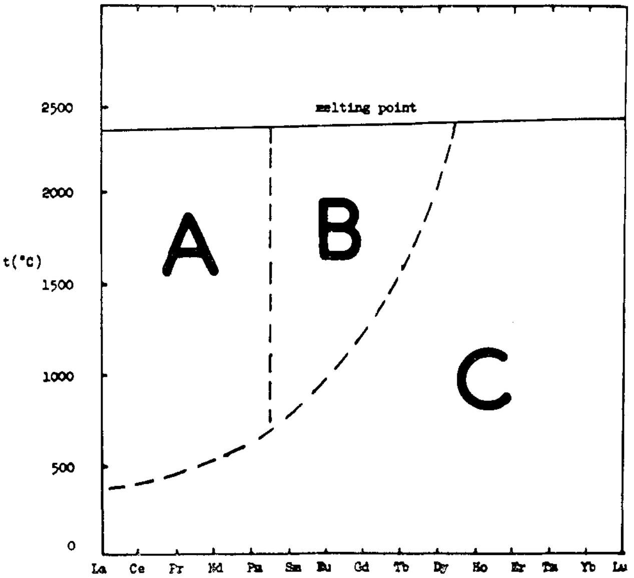

Figure 1.—Fields of stability for the polymorphic forms of M_2O_3: A, hexagonal; B, monoclinic; C, cubic.

The structures of each of the polymorphic forms are built up either from a single type of coordination polyhedron (MO_6 in the cubic C type and MO_7 in the hexagonal A form) or from a mixture of MO_6 and MO_7 polyhedra as in the monoclinic B form. The observed regions of stability of the various forms correlate well with the idea that it is the cation size (lanthanide contraction) and the temperature which determine the type of sesquioxide existing under ordinary conditions of pressure. For the different structures the densities are markedly different, with $\rho_A > \rho_B > \rho_C$: it therefore seemed possible that the transformation temperature for C → B and for B → A might be reduced by the application of high pressure. In particular, it might be possible to convert: (1) the B form of the sesquioxides of Sm through Dy to the A form; and (2) the C form sesquioxides of the heavy lanthanides (beyond Dy) and yttrium to the B form. We have, accordingly, investigated the effect of pressure on the following sesquioxides: B form: Sm_2O_3; C form: Pr_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3, and Y_2O_3; and A form: Pr_2O_3, Nd_2O_3.

Experimental

The starting materials all had a nominal purity of 99.9 + %: 1 to 2.5 g. of each oxide was dried by heating at 1000° for 24 hr. The phases were characterized by X-ray diffraction using a Guinier focusing camera. Each sample was tightly packed into a hole drilled in a steel cylinder. The open end of each cylinder was sealed by welding a steel rod into the hole—using a helium atmosphere and with the lower part of the cylinder in cold water. The cylinders were machined into cylindrical projectiles weighing 14.2 g. and then fired (at a velocity of ~1.5 km. sec.$^{-1}$) into a hole in a steel receiver.[5] When cool, the projectile was separated from the receiver, opened, and the contents examined in the Guinier camera. On the basis of observed changes of state in phosphorus and other materials in similar experiments, it is estimated[6] that the samples were subjected to a static pressure (during impact) of 10–20% of the theoretical, *i.e.*, $3 \pm 1 \times 10^5$ atm. Since there was no evidence that the steel projectiles had melted, the maximum temperature attained was presumably below ~1500°.

Results

The starting materials were sufficiently well-crystallized to give sharp diffraction patterns; whereas, after firing, all the powder patterns were composed of broad diffuse lines, with a rapid decrease in line intensity with increasing Bragg angle. Two transformations only were observed: C-type Pr_2O_3 was completely converted to the A modification and C-type Ho_2O_3 partly (~20%) converted to the B form. This latter conversion has not been reported previously: heating the C form of holmia at atmospheric pressure and up to its melting point has failed to effect it.[4] We therefore attribute the present observation to the effect of high pressure.

The identification of B form Ho_2O_3 follows from the fact that the powder pattern of the sample could be indexed completely as a two-phase mixture of: (1) a b.c.c. phase with $a_0 = 10.610 \pm 0.008$ Å. and (2) monoclinic phase, isostructural with the other B form sesquioxides and having the lattice parameters: $a_0 = 13.90 \pm 0.05$, $b_0 = 3.505 \pm 0.005$, $c_0 = 8.630 \pm 0.008$ Å., $\beta = 100.2 \pm 0.1°$.

In an attempt to improve the line quality of the film, a portion of the sample was annealed at 417° for 4 days. All lines due to the B form disappeared: the C form pattern sharpened considerably. The latter suggests that (at this low annealing temperature) the process is one of relief of microstrain produced in the original crystallites during impact, rather than an increase in crystallite size. Annealing at 715° for 3 days gave a monophasic, perfectly crystalline sample of C form

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(1) Work supported by the U. S. Atomic Energy Commission.

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(5) We are indebted to Dr. A. L. deLisle of Scottsdale, Ariz., for preparing and firing the projectiles, using techniques which he has developed.

(6) A. L. deLisle, private communication.

Ho_2O_3, with $a_0 = 10.606 \pm 0.001$ Å. This may be compared with the literature[2] value of $a_0 = 10.6065$ Å. A portion of yttria recovered from a projectile was also annealed (at 1055° for 2 days). A similar marked improvement in the line profile of the X-ray pattern for this (single phase) material was observed. The derived lattice constant was $a_0 = 10.604 \pm 0.001$ Å. (*cf.* literature[2] value, $a_0 = 10.6021$ Å.).

Although the ionic radii[4] of Ho^{3+} and Y^{3+} are approximately the same (0.91 Å.), no C → B conversion was observed in the case of Y_2O_3. However, the fact that the lattice parameter of C-type yttria is slightly smaller than that of holmia (10.6021 Å. as compared with 10.6065 Å.) suggests that $r_{Y^{3+}}$ is slightly less than $r_{Ho^{3+}}$ and that the pressure achieved during impact was insufficient to effect the conversion in the oxide with the smaller cation.

The absence of a B → A conversion in the case of Sm_2O_3 is presumably to be explained in the same way.

CONTRIBUTION FROM THE WM. A. NOYES LABORATORY,
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Preparation and Spectral Properties of Some Alcohol Complexes of Nickel(II)

BY V. IMHOF[1] AND RUSSELL S. DRAGO

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We have in the past reported on the preparation, stoichiometry, and electronic spectra of several transition metal ion complexes of nonaqueous solvents.[2,3] It was of interest to extend these studies to alcohols and to locate these materials in the spectrochemical series.

Alcohols are fairly common solvents and although a large number of complexes of polyhydric alcohols are known[4] those of the simple alcohols with transition metals have not been well characterized. There is some evidence for the existence of complexes in solution[5] and Quagliano and his co-workers[6] report the separation of hexaethanolnickel(II) perchlorate but do not present an elemental analysis or characterize it further.

We have had considerable success in dehydrating aquo–metal complexes with 2,2-dimethoxypropane, which reacts with water according to eq. 1.

$$(CH_3O_2)_2C(CH_3)_2 + H_2O \longrightarrow (CH_3)_2C{=}O + 2CH_3OH \quad (1)$$

A whole series of complexes has been prepared by adding ligands to methanolic solutions of the dehydrated metal ion. It seemed that it should be possible to prepare a methanol complex from the solution which resulted after dehydration. This proved to be the case when the initial aquo complex was hexaaquonickel(II) perchlorate. By dehydrating with the ketal, 2,2-diethoxypropane, we were able to isolate the corresponding ethanol complex.

Experimental

The alcohol complexes are extremely hygroscopic. All manipulations, including the initial filtrations, were carried out in a dry atmosphere box in baked equipment. Microanalyses were accomplished with the use of closed pigs which were weighed, filled in the drybox, reweighed, and analyzed immediately.

Reagents.—2,2-Dimethoxypropane (Dow, technical grade) is contaminated with acetone, methanol, and 2-methoxy-1-propene. The vinyl ether must be removed because it polymerizes in the presence of the metal ion. The brown polymer precipitates with the alcohol complex and is difficult to remove because of the sensitivity of the complex. Purification can best be accomplished by fractionation at reduced pressure. The fraction boiling at 34° at 130 mm. was used here. 2,2-Diethoxypropane (Eastman, White Label) was used without further purification as was hexaaquonickel(II) perchlorate (G. F. Smith). The alcohols used as solvents were dried by stirring over 4A molecular sieve and distilling from Grignard grade magnesium.

Preparation of Hexamethanolnickel(II) Perchlorate.—One gram (2.73 mmoles) of hexaaquonickel(II) perchorate was dissolved in 5 ml. of methanol. To this solution 3.65 g. (32.8 mmoles) of dimethoxypropane (100% excess) was added. This solution was stirred under dry nitrogen for 10 hr. at 4°. Upon the addition of copious quantities of dry ether (about ten times the volume of the solution) the desired methanol complex separates as a pale yellow-green powder.

Anal. Calcd. for $[Ni(CH_3OH)_6][ClO_4]_2$: C, 16.01; H, 5.34; Ni, 13.06. Found: C, 15.96; H, 5.15; Ni, 13.44.

Preparation of Hexaethanolnickel(II) Perchlorate.—The preparation is identical with that of the methanol complex described above except that ethanol and diethoxypropane were substituted for methanol and dimethoxypropane.

Anal. Calcd. for $[Ni(CH_3CH_2OH)_6][ClO_4]_2$: C, 26.95; H, 6.74; Ni, 11.56. Found: C, 26.02; H, 6.91; Ni, 11.40.

Spectra.—Infrared spectra in the region 250 to 4000 cm.$^{-1}$ were obtained on a Perkin-Elmer Model 521 grating spectrophotometer. The spectra were obtained as Nujol mulls of the complexes between NaCl and CsBr plates. A stream of dry nitrogen was passed through the sample compartment during the scan time.

Spectra in the range 350 to 1400 mμ were obtained on a Cary Model 14M spectrophotometer. The complexes were examined as solutions in the appropriate alcohol in 1-cm. stoppered cells.

Results

Infrared Spectra.—The O–H stretching frequencies observed in the two alcohol complexes were compared with the free O–H frequencies of the appropriate alcohol in dilute solution in carbon tetrachloride (see Table I). The values for water in the aquo complex are included for reference. The spectra of the alcohol complexes show none of the characteristic absorptions of water and give no indication of perchlorate coordination. The metal–oxygen stretching frequencies appear to be in the range 600–700 cm.$^{-1}$ but the appearance of a perchlorate mode in that region makes identification difficult.

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(1) Abstracted from a thesis submitted by V. Imhof to the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1964.

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