[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS, LINCOLN LABORATORY,[1] AND POLYTECHNIC INSTITUTE OF BROOKLYN]

Lanthanum Rhodium and Lanthanum Cobalt Oxides

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$LaRhO_3$ containing rhodium in the trivalent state has been prepared and studied by X-ray diffraction powder methods. Calculations based on the X-ray data show that $LaRhO_3$ has a distorted perovskite structure. It is orthorhombic, its space group is $D_{2h}(16)$Pbnm and there are four formula weights per unit cell. The lattice constants are a = 5.524 Å., b = 5.679 Å., c = 7.900 Å. $LaCoO_3$ belongs to space group $D_{3d}(5)\bar{3}$m with two formula weights per unit cell. The dimensions of the rhombohedral pseudocell are a = 7.64 Å., α = 90°42′. The dimensions of the primitive rhombohedral pseudo cell are a_p = 5.436 Å., α_p = 60°48′. The hexagonal form of this cell has the following dimensions: a = 5.424 Å., c = 13.068 Å.

Introduction

Recent papers by Geller[3-5] have indicated that many of the rare earth transition metal oxides crystallize as distorted perovskite structures which fall into one of two groups. Most of them belong to space group $D_{2h}(16)$Pbnm with four distorted perovskite units in the true crystallographic cell, the remainder belong to space group $D_{3d}(5)$-R$\bar{3}$m with two formula units per unit cell.

$LaCoO_3$ was first prepared by Askham, Fankuchen and Ward[6] and was represented as a deformed cube, *i.e.*, rhombohedral with a = 3.82 Å. and an interaxial angle of 90°42′. This investigation describes the preparation and crystal structure of $LaRhO_3$. A redetermination of the unit cell of $LaCoO_3$ has been made and the results compared with those obtained by previous investigations.

Experimental

Preparation of Lanthanum Rhodium Oxide.—Powdered rhodium metal is converted to rhodium(III) oxide by heating in air at 800° for 96 hours. Stoichiometric amounts of lanthanum oxide and rhodium(III) oxide needed to give lanthanum rhodium(III) oxide $LaRhO_3$ were ground together in an agate mortar. When the mixture appeared homogeneous, it was transferred to a platinum crucible. The sample was then placed in a furnace at 1100° for approximately 96 hours in an air atmosphere at the prevailing atmospheric pressure. During the heating period, the sample was removed three or four times, cooled and ground thoroughly in an agate mortar. X-Ray diffraction patterns were taken of the sample in a 114.7-mm. Debye–Scherrer camera, using iron radiation with a manganese filter.

Chemical Analysis of Lanthanum Rhodium Oxide.—A sample of the oxide was weighed, transferred to a platinum boat and heated in a stream of hydrogen at 800° until constant weight was obtained. The reduced sample, which contained rhodium metal and lanthanum oxide was treated with 25 ml. of 6 *N* hydrochloric acid and heated at the boiling point for 15 minutes in order to extract the lanthanum present. A saturated ammonium oxalate solution was added to the filtrate until precipitation was complete. The lanthanum oxalate precipitate was collected in a Selas crucible and ignited to lanthanum oxide.

TABLE I

ANALYSIS OF $LaRhO_3$

	Rh		La		Density		Mol./ unit
	Theor.	Obsd.	Theor.	Obsd.	Obsd.	Calcd.	cell
$LaRhO_3$	35.71	35.98	47.93	48.40	7.66	7.77	4

Density of samples was determined by the use of 10-ml. pycnometers, with water as the pycnometric liquid. Analytical results and density data are summarized in Table I.

Preparation of Lanthanum Cobalt Oxide.—Stoichiometric amounts of lanthanum oxide and cobalt carbonate were mixed thoroughly. The samples were then transferred to a platinum boat and heated at 900° for 96 hours in air. X-Ray diffraction patterns were taken of the samples using iron radiation.

TABLE II

POWDER DIFFRACTION DATA FOR $LaRhO_3$

Indices	Int.	d/n	
		Obsd.	Calcd.
111	w	3.538	3.451
020	w	2.840	2.839
112	s	2.795	2.797
200	w	2.760	2.762
021	vw	2.679	2.672
113	w	2.194	2.192
004	m	1.979	1.975
221	w	1.920	1.920
114	vw	1.766	1.767
310	vw	1.749	1.752
132	w	1.633	1.631
024	w	1.622	1.622
312	m	1.603	1.601
204	m	1.603	1.607
231	vw	1.537	1.532
133	vw	1.483	1.481
224	wm	1.396	1.398
116	w	1.250	1.249

(Orthorhombic) a = 5.524 Å., b = 5.679 Å., c = 7.900 Å.

TABLE III

STRUCTURE OF $LaCoO_3$

hkl (rhombohedral)	Obsd.	Calcd.	Int.	*hkl* (hexagonal)
200	3.82	3.814	m	102
$20\bar{2}$	2.711	2.715	vs	110
220	2.679	2.682	vs	014
$22\bar{2}$	2.213	2.212	m	022
222	2.178	2.177	w	006
400	1.909	1.908	s	204
$40\bar{2}$	1.719	1.713	vvw	212
420	1.701	1.699	vvw	116
$42\bar{2}$	1.563	1.560	s	124
422	1.542	1.543	m	108
$40\bar{4}$	1.356	1.352	m	220
440	1.340	1.341	m	028
600	1.275	1.271	vvw	306
$60\bar{2}$	1.213	1.211	m	314
620	1.203	1.200	m	218
622	1.143	1.142	vw	20.10

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(4) S. Geller and E. A. Wood, *Acta Cryst.*, **9**, 563 (1956).

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Results and Discussion

Rhodium oxide reacts with lanthanum oxide at 1100° to form a lanthanum rhodium oxide, with a perovskite-like structure. Table II summarizes the *d*-values obtained for $LaRhO_3$. Calculations based on X-ray data show that $LaRhO_3$ belongs to the space group $D_{2h}(16)Pbnm$ with four formula weights per unit cell. The lattice constants are $a = 5.524$ Å., $b = 5.679$ Å., $c = 7.900$ Å. Determination of the number of formula weights per unit cell, and chemical analysis, indicate that the formula is $LaRhO_3$.

Lanthanum oxide reacts with cobalt carbonate to form lanthanum cobalt oxide, with a perovskite-like structure. Table III summarizes the *d*-values obtained for $LaCoO_3$. $LaCoO_3$ belongs to space group $D_{3d}(5)R\bar{3}m$ with two formula weights per unit cell. The dimensions of the rhombohedral pseudo-cell are $a = 7.64$ Å., $\alpha = 90°42'$. The dimensions of the primitive rhombohedral cell are $a_p = 5.436$ Å., $\alpha_p = 60°48'$. The multiple primitive hexagonal cell in terms of which the rhombohedral cell may be described has the dimensions: $a = 5.424$ Å., $c = 13.068$ Å.

The unit cell reported by Askham, Fankuchen and Ward,[6] is based on a unit cell one-half the size of that given here. The larger cell is based on data obtained by Geller[3–5] from isostructural materials in which two very faint lines necessitated doubling of the indices. These lines did not appear on the films of lanthanum cobalt oxide. However, by step-counting using a Norelco Diffractometer, over the region where these lines should appear, the stronger of the two lines was detected and had an intensity of 25% above background.

[Contribution from Department of Chemistry and Enrico Fermi Institute of Nuclear Studies, University of Chicago]

C^{14} Hot Atom Chemistry of *n*-Pentane and Isopentane[1]

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Reactions of C^{14} atoms of velocities corresponding to energies up to 40,000 electron volts have been studied in liquid *n*-pentane and isopentane at about room temperature. C^{14} atoms were generated at the Argonne National Laboratory pile through the reaction of thermal neutrons in the $N^{14}(n,p)C^{14}$ process. Aniline was most often used as the source of nitrogen, but substitution of aliphatic amines for the aniline gave similar results indicating that the products were characteristic only of the hydrocarbon solvent. A wide variety of hydrocarbons was formed. Hexane and pentane isomers were identified. Hexane isomers predominate, yields of individual compounds being up to 12%. The type and yield of compounds formed from *n*-pentane differ from those formed from isopentane. A mechanism is proposed based on previously developed hot atom kinetic theory which assures very rapid reactions of produced radicals before general diffusion takes place allowing all possible reactions to occur. The evidence appears to favor our more specific theory.

I. Introduction

Interest in C^{14} hot atom chemistry has risen both for itself and as a possible short route to production of C^{14} tagged organic compounds. Several studies of organic systems have been undertaken, the first being that of Yankwich, Rollefson and Norris.[4] Anderson, Penna-Franca and Wolf[5] have studied the production of C^{14}-labeled benzoic acid from nicotinic acid finding most of the activity in the ring. Wolf, Redvanly and Anderson[6] have reported the yield of C^{14}-benzoic acid from the irradiation of a benzene–nickel cyanide clathrate compound to be 1.44% in disagreement with the 4.0% reported by Zifferero.[7] When the irradiation of acridine was carried out by Wolf and Anderson[8] they found the yield of acridine to be 3.5% and that of anthracene to be 0.2%. The fact that this ratio of yields is about that expected for random substitution of ring carbon and nitrogen by C^{14} led them to hypothesize that substitution was indeed random. An analysis for C^{14} by position in acetic acid produced from irradiated acetamide was carried out by Wolf, Gordon and Anderson.[9] Substitution was not random. In acetic acid produced by acid hydrolysis from neutron irradiated acetamide they found 63.1% of the C^{14} in the carbonyl position and 36.9% in the methyl position; for basic hydrolysis 60.9% in the carbonyl position and 39.1% in the methyl position. Propionamide was also isolated as a product of the irradiation of acetamide, and the propionic acid produced from it was similarly analyzed. Acid hydrolysis gave 21.0% in the carbonyl carbon, 26.8% in the methylene position and 52.9% in the methyl position. Basic hydrolysis gave 23.9% in the carbonyl position, 23.1% in the methylene position and 52.9% in the methyl carbon. Toluene produced from a mixture of benzene and 2-methylpyrazine showed 86.1% of the C^{14} in the methyl group and 13.9% in the benzene ring. In all of these cases the fraction of the total C^{14} generated accounted for was small and the questions of over-all mechanism and the general behavior of high velocity C^{14} atoms remained unelucidated.

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