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

Rare Earth Nickel Oxides

BY AARON WOLD,[2] BENJAMIN POST AND EPHRAIM BANKS

RECEIVED APRIL 17, 1957

$LaNiO_3$, containing nickel in the trivalent state was prepared and its structure studied by X-ray diffraction methods. The dimensions of the rhombohedral pseudocell are $a = 7.676 \pm 0.002$ Å., $\alpha = 90°43'$. The dimensions of the primitive rhombohedral cell are $\alpha_p = 60°49'$, $a = 5.461$ Å. The hexagonal form of this cell has the following dimensions, $a = 5.456$ Å., $c = 13.122$ Å. Neodymium oxide reacts with nickel(II) oxide, in the presence of sodium carbonate, to form a single phase whose composition may vary between $Nd_{1.67}Ni^{+2}{}_{0.72}Ni^{+3}{}_{0.41}O_{3.84}$ and $Nd_{1.75}Ni^{+2}{}_{0.57}Ni^{+3}{}_{0.43}O_{3.84}$. An increase in the ratio Nd:Ni results in the formation of more trivalent nickel. With the exception of one very weak line at $2\theta = 31.2°$, all the lines of the X-ray diffraction patterns out to $2\theta = 75°$ could be indexed satisfactorily on the basis of a monoclinic unit cell with $a = 3.92$ Å., $b = 6.16$ Å., $c = 3.77$ Å. and $\beta = 92.4°$. Samarium, gadolinium and yttrium oxides do not appear to form stable compounds with nickel(II) oxide under the conditions used to form the other rare earth nickel oxides. The product of reaction between lanthanum oxide, samarium oxide and nickel(II) oxide, in the mole ratio 1:1:4, was a new phase, which seemed to be isomorphous with the phase obtained from the reaction of mixtures having compositions between $2NiO \cdot 1.5Nd_2O_3$ and $2NiO \cdot 1.75Nd_2O_3$. Mixtures having a 1:1 ratio of La:Nd showed the presence of the lanthanum nickel oxide and neodymium nickel oxide phases. At other ratios of La:Nd, X-ray data indicate extensive solubility of $LaNiO_3$ and neodymium nickel oxide.

Introduction

Several preparations of rare earth-transition metal oxides of the type ABO_3, in which the transition metal employed was iron, manganese, vanadium, chromium and cobalt[3-7] have been reported. In these compounds, A represents a trivalent rare earth ion which is coördinated to twelve oxygens to form a distorted perovskite structure. Recently Geller[8-10] has indicated that these compounds fall into one of two groups. Most of them are isostructural with $GdFeO_3$ and belong to space group $D_{2h}(16)$–Pbnm with four distorted perovskite units in the true crystallographic cell, or they belong to space group $D_{3d}(5)$–$R\bar{3}m$ with two formula units per unit cell.

Experimental

Preparation of Rare Earth Nickel Oxides.—Stoichiometric amounts of rare earth and nickel(II) oxides, needed to give a rare earth nickel oxide $RNiO_3$ or mixed rare earth nickel oxide $(R)_x(R')_{(1-x)}NiO_3$ type compound, were ground together in an agate mortar with sodium carbonate. The weight of sodium carbonate used was equal to the total weight of rare earth oxide. When the mixture appeared homogeneous, it was transferred to a gold crucible. Gold was found to be the best reaction vessel available. The sample was then placed in a furnace at 800° for approximately 72 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. When samples were prepared at higher temperature (1300°) platinum crucibles were used and the heating period was shortened to 48 hours.

After the heating period the sample was removed from the furnace, extracted with hot water, and filtered with number 50 Whatman paper. The sample was then dried at 100° and X-ray diffraction patterns were taken, using a Philips powder camera and either copper or iron radiation.

Chemical Analysis of Lanthanum Nickel Oxide and Neodymium Nickel Oxide.—A sample of the oxide was weighed into a 250-ml. beaker. About 25 ml. of 6 *N* hydrochloric acid solution was added and the flask was heated on a hot plate until all the material had dissolved. The beaker was cooled and the green solution neutralized (slightly to the acid side) with dilute ammonium hydroxide. A saturated ammonium oxalate solution was added until complete precipitation occurred. The precipitate was allowed to settle overnight. The precipitate was collected in a Selas crucible and ignited to the rare earth oxide.

Twenty-five ml. of a mixture of 1:3 concentrated nitric and hydrochloric acids was added to the nickel solution and then heated to dryness in order to destroy the excess oxalate. The precipitate was dissolved in 50 ml. of water to which a few ml. of 6 *N* hydrochloric acid was added, and the solution diluted to 150 ml. A 20% solution of sodium hydroxide was added, the precipitate filtered, washed thoroughly and redissolved in a minimum amount of hydrochloric acid. The solution was diluted to 150 ml., made alkaline with ammonium hydroxide and the nickel was precipitated and weighed as nickel dimethylglyoxime. The oxygen content was determined by difference. Determination of the valence was made by dissolving a sample of 6 *N* hydrochloric acid containing an excess of potassium iodide, and titrating the liberated iodine with standardized thiosulfate solution. Solutions containing 500 parts per million of dissolved sample were analyzed for sodium by flame photometric procedures. Density of samples was determined by the use of standard 5-ml. or 10-ml. glass pycnometers, using water as the pycnometric liquid. Analytical results and density data are summarized in Table I.

Results and Discussion

Nickel oxide reacts with lanthanum oxide at 800° to form a lanthanum nickel oxide, with a perovskite-like structure. The employment of a sodium carbonate flux in the preparation makes it possible to use lower temperatures, and results in clearer X-ray patterns. Solutions containing 500 p.p.m. of dissolved lanthanum nickel oxide analyzed for 3 p.p.m. of sodium. Table II summarizes the *d*-values obtained from the X-ray patterns for $LaNiO_3$. Calculations based on X-ray data show that $LaNiO_3$ belongs to space group D3d(5)–$R\bar{3}m$ with two formula weights per unit cell. The dimensions of the rhombohedral pseudocell are $a = 7.676$ Å., $\alpha = 90°43'$. The dimensions of the primitive rhombohedral cell are 5.461 Å., $\alpha_p = 60°49'$. The hexagonal form of this cell has the following dimensions: $a = 5.456$ Å., $c = 13.122$ Å. Determination of the number of "mole-

---

(1) The research in this document was supported jointly by the Army, Navy and Air Force under contract with the Massachusetts Institute of Technology.

(2) Address all inquiries c/o Lincoln Laboratory, Lexington, Massachusetts.

(3) H. Forestier and G. Guiot-Guillain, *Compt. rend.*, **230**, 1844 (1950).

(4) G. Guiot-Guillain, *ibid.*, **232**, 1832 (1952).

(5) I. Naray-Szabo, *Naturwiss.*, **31**, 203 (1943).

(6) G. H. Jonker and J. H. van Santen, *Physica*, **16**, 337 (1950).

(7) R. Ward and A. Wold, THIS JOURNAL, **76**, 1029 (1954).

(8) S. Geller, *J. Chem. Phys.*, **24**, 1236 (1956).

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

(10) S. Geller, private communication.

TABLE I

ANALYSIS OF $LaNiO_3$, $Nd_{1.67}Ni^{+2}_{0.72}Ni^{+3}_{0.41}O_{3.84}$, $Nd_{1.75}Ni^{+2}_{0.57}Ni^{+3}_{0.43}O_{3.84}$

	Ni theor.	Ni obsd.	R.E. theor.	R.E. obsd.	Valence obsd.	Density obsd.	No. mol. / unit cell
$LaNiO_3$	23.89	23.54	56.56	57.93	2.99	6.96	4
$Nd_{1.67}Ni^{+2}_{0.72}Ni^{+3}_{0.41}O_{3.84}$	17.79	16.61	65.56	64.70	2.36	7.08	1
$Nd_{1.75}Ni^{+2}_{0.57}Ni^{+3}_{0.43}O_{3.84}$	15.75	14.95	67.76	67.70	2.43	7.10	1

cules" per unit cell, and chemical analysis, indicate that the formula is $LaNiO_3$.

TABLE II

STRUCTURE OF $LaNiO_3$

hkl Rhomb. indices	*d*, obsd.	*d*, calcd.	Int.	*hkl* hex. indices
100	3.835	3.839	s	101
$10\bar{1}$	2.728	2.719	vs	110
110	2.697	2.696	vs	012
$11\bar{1}$	2.222	2.219	m	021
111	2.187	2.187	w	003
200	1.919	1.920	s	202
$20\bar{1}$	1.721	1.721	vw	211
210	1.706	1.706	vw	113
$21\bar{1}$	1.578	1.574	s	122
211	1.548	1.548	m	104
$20\bar{2}$	1.364	1.361	m	220
220	1.349	1.347	m	024
300	1.279	1.280	vvw	303
$30\bar{1}$	1.218	1.215	s	312
310	1.210	1.207	s	214
311	1.153	1.149	vvw	205

When mixtures of neodymium oxide and nickel oxide, in a mole ratio of 1:1, were treated by the same procedure used to prepare $LaNiO_3$, a compound of markedly different structure was formed, in addition to excess NiO (Table III). A single phase forms whose composition may vary between $Nd_{1.67}Ni^{+2}_{0.72}Ni^{+3}_{0.41}O_{3.84}$ and $Nd_{1.75}Ni^{+2}_{0.57}Ni^{+3}_{0.43}O_{3.84}$. An increase in the ratio Nd:Ni results in the formation of more trivalent nickel. Solutions containing 500 p.p.m. of dissolved neodymium nickel oxide analyzed for 4 p.p.m. of sodium. X-Ray diffraction patterns of this phase were taken with filtered iron radiation. The patterns were rather poor; lines were generally broad and low in intensity. Samples of both compositions $Nd_{1.67}Ni^{+2}_{0.72}Ni^{+3}_{0.41}O_{3.84}$ and $Nd_{1.75}Ni^{+2}_{0.57}Ni^{+3}_{0.43}O_{3.84}$ gave essentially the same pattern, although a very slight shift of the lines was observed. With the exception of one very weak line at $2\theta = 31.2°$, all the lines of these patterns out to $2\theta = 75°$ could be indexed satisfactorily on the basis of a monoclinic unit cell with $a = 3.92$ Å., $b = 6.16$ Å., $c = 3.77$ Å. and $\beta = 92.4°$. Calculations based on an observed density of 7.1 and a cell volume of 90.8 Å.,^{3} result in a cell weight of 388 which is within 4% of the formula weights of both compositions. The neodymium nickel oxide phase contains 1 molecule per unit cell. The cell chosen was the smallest one consistent with the experimental data (Table III).

When mixtures of lanthanum oxide and neodymium oxide were heated with nickel oxide, in such proportions that the number of gram atoms of nickel was equal to the total number of gram atoms of lanthanum plus neodymium, the products only showed the presence of two phases, identified as lanthanum nickel oxide and neodymium nickel oxide, in the case of the sample having a 1:1 ratio of La:Nd (Table IV). Samples of lower lanthanum content showed only the lines of neodymium nickel oxide, while samples of higher lanthanum content showed only the deformed perovskite pattern of lanthanum nickel oxide. This seems to indicate extensive intersolubility of lanthanum nickel oxide and neodymium nickel oxide, although not much change in spacing is observed.

TABLE III

X-RAY POWDER DATA FOR $Nd_{1.67}Ni^{+2}_{0.72}Ni^{+3}_{0.41}O_{3.84}$ AND $Nd_{1.75}Ni^{+2}_{0.57}Ni^{+3}_{0.43}O_{3.84}$

	$\sin^2\theta$		
d	Obsd.	Calcd.	*hk*
3.600	0.0723	....	..
3.080	.0988	0.0988	020
2.777	.1215	.1213	$10\bar{1}$
2.665	.1320	.1320	101
2.062	.2204	.2203	$12\bar{1}$
2.052	.2226	.2223	030
2.016	.2306	.2306	121
1.885	.2637	.2640	002
1.671	.3356	.3350	102
1.657	.3413	.3420	220
1.628	.3535	.3546	131
1.610	.3613	.3597 .3628	112 023

TABLE IV

COMPARISON OF *d*-VALUES BETWEEN THE PRODUCT FORMED BY TREATING 50 MOLE % Sm_2O_3 AND 50 MOLE % La_2O_3 WITH NiO AND $Nd_{1.75}Ni^{+2}_{0.57}Ni^{+3}_{0.43}O_{3.84}$

50% Sm	$Nd_{1.75}Ni^{+2}_{0.57}Ni^{+3}_{0.43}O_{3.84}$
3.60 m	3.60 wm
3.09 w	3.08 w
2.76 s	2.78 s
2.66 s	2.67 s
2.06 w	2.06 m 2.05 m
2.01 w	2.02 m
1.89 m	1.89 s
1.66 w	1.67 w 1.66 w
1.62 vw	1.63 w
1.59 vw	1.61 s

Attempts were made to prepare a samarium nickel oxide by the same method used to prepare lanthanum and neodymium nickel oxides. Gray products were formed and the results indicate that most of the product of the reaction at 800° is unreacted nickel oxide and samarium oxide. There are several lines which are not attributed to these compounds, but which are caused by the formation of a high temperature form of samarium oxide.

When a series of mixed lanthanum–samarium–nickel oxides were prepared, it was observed that 0 to 30% substitution of samarium for lanthanum caused no marked effect, except for a decrease in lattice constant. At 50% samarium a new phase is formed which is similar to that of neodymium nickel oxide in structure. Table IV indicates this similarity in structure between the two phases; the X-ray pattern for the lanthanum samarium nickel oxide was taken with copper radiation using a 114 mm. Philips powder camera. The pattern for the neodymium nickel oxide was taken with iron radiation using a Norelco G.P. Diffractometer. Lines were resolved with the diffractometer that were not observed on the films taken of the same material. At 70% samarium the pattern is practically identical with that of the 50% composition. The 50% phase can accommodate appreciable substitution of samarium for lanthanum with little apparent change in structure. However, when 85% samarium is reached, the X-ray pattern indicates that most of the product is samarium oxide and nickel oxide.

In the investigation of gadolinium and yttrium nickel oxides, it has been found that gadolinium or yttrium nickel oxides do not form under the conditions used to prepare $LaNiO_3$. Reaction products prepared at 800°, with a sodium carbonate flux, contain only lines of unreacted gadolinium and nickel oxides or yttrium and nickel oxides. When the per cent. substitution of Gd for La is varied from 0 to 100 mole %, the only compounds formed are gadolinium oxide, nickel oxide and lanthanum nickel oxide.

Acknowledgment.—The authors wish to express their appreciation for the financial support given by Research Corporation and the National Science Foundation to Hofstra College where this work was initiated. They also wish to acknowledge the assistance given this study by R. Mazelsky, L. Vogt, A. Craig and L. J. Bailin.

LEXINGTON, MASS.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, DREXEL INSTITUTE OF TECHNOLOGY]

Reactions of Triethyltin Hydride with Inorganic Halides and Oxides

BY HERBERT H. ANDERSON

RECEIVED MARCH 6, 1957

Triethyltin iodide and lithium aluminum hydride react in diethyl ether to yield new liquid triethyltin hydride, b.p. 146°. Triethyltin hydride reduces certain halides and oxides of at least 13 transitional elements and 7 regular group elements either to a lower oxidation state or sometimes to the free element. Some vigorous reactions require gradual addition of a slight deficiency of the inorganic halide in converting triethyltin hydride into a triethyltin halide without forming any diethyltin dihalide. Three different explanations for the 25 reactions in Table I appear possible; heats of formation or free energies per equivalent of available halogen or oxygen in the compounds, also the ionization potentials of the elements, also, although they are not exactly comparable, oxidation potentials in aqueous solution. This paper merely presents the three explanations for the reactions, without lengthy evaluation of the advantages and disadvantages, also theoretical limitations, of each explanation.

This paper is a continuation of an earlier paper on the reactions of triethylgermanium hydride with the salts of transitional elements and with organic haloacids such as CF_3COOH, CCl_3COOH, CBr_3COOH and CH_2ICOOH.[1] In this paper the subject is the reactions of $(C_2H_5)_3SnH$ with halides or oxides of transitional elements and elements in regular groups.

The preparation of $(CH_3)_3SnH$, b.p. 59°, from $(CH_3)_3SnCl$ and $LiAlH_4$[2] suggested the one-step preparation of new $(C_2H_5)_3SnH$ reported herein. There is little information on the reactions of alkyltin hydrides in the literature.

Experimental Results

Table I lists 25 reactions of $(C_2H_5)_3SnH$ with halides or oxides of 13 transitional elements and 7 elements in regular groups; these appear to be the first reactions of an alkyltin hydride with halides or oxides of elements in regular groups. A median yield of 88% in Table I is based upon the starting material present in the lesser amount. Some of these reactions, especially those with $SnCl_2$ or HgO, may prove of preparative value on a larger scale.

Gradual addition of the halide or HgO to a slight excess of $(C_2H_5)_3SnH$ is necessary to ensure formation of the monosubstitution product $2(C_2H_5)_3SnH + PdCl_2 \rightarrow 2(C_2H_5)_3SnCl + Pd + H_2$ rather than the disubstitution product $2(C_2H_5)_3SnH + 2PdCl_2 \rightarrow 2(C_2H_5)_2SnCl_2 + 2Pd + H_2 + C_4H_{10}$. Other experiments here show the related unpublished reaction $2(C_2H_5)_4Sn + PdCl_2 \rightarrow 2(C_2H_5)_3SnCl + Pd + C_4H_{10}$.

Certain compounds do not react with $(C_2H_5)_3SnH$ at a perceptible rate. No reaction is expected using $BaCl_2$ or TlCl—considering oxidation potentials, ionization potentials or heats of formation—and none occurs. Expected reactions with $KClO_3$ (reduction to KCl expected) or K_2CrO_4 do not occur, although CrO_2Cl_2 does react.

At 25° benzene solutions of $(C_2H_5)_3SnH$ react fairly rapidly with $PdCl_2$, $AsCl_3$, $HgBr_2$ and $SnCl_4$; an excess of the last compound yields $SnCl_2$ as an instantaneous white precipitate. However, K_2PtCl_6 does not react, even in one minute of reflux in benzene solution.

Discussion

Four previous publications are vitally related to an explanation of the probably partly ionic $(C_2H_5)_3Sn^{\delta+}H^{\delta-}$, which yields a definitely partly ionic chloride $(C_2H_5)_3Sn^{\delta+}Cl^{\delta-}$. Numerous reactions of $(CH_3)_2SnCl_2$ in aqueous solution suggest that $(CH_3)_2SnCl_2$ resembles $SnCl_2$ rather than $SnCl_4$; the ion $(CH_3)_2Sn^{+2}$ evidently resembles Sn^{+2}.[3] The fewer the number of halogen atoms in an ethyltin chloride molecule, the stronger the Sn–Cl bond

---

[1] H. H. Anderson, This Journal, **79**, 326 (1957).

[2] A. E. Finholt, *et al.*, *ibid.*, **69**, 2692 (1947).

[3] E. G. Rochow, *et al.*, *ibid.*, **75**, 3099 (1953).