Perowskite-Type Oxides of Cobalt, Chromium and Vanadium with Some Rare Earth Elements

BY AARON WOLD AND ROLAND WARD

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In the course of an investigation of ternary oxides of the transition metals, the preparation of compounds containing trivalent rare earth ions and having perowskite-like structures was undertaken. Compounds of this type usually conform to the formula ABO_3 when A is a large cation and B a smaller cation—in this case the transition metal. The compounds $LaMnO_3$ and $LaFeO_3$ with this structure were prepared by Naray-Szabo,[1] and Askham[2] showed that $LaCoO_3$ has also the perowskite structure but slightly distorted to the rhombohedral form. The relative ionic radii of the A and B cations appears to be a limiting factor in the adoption of this structure and we were interested to discover the effect of the decreasing size of the rare earth ions on the formation of such compounds and on the degree of distortion of the cobalt compounds in particular. This paper describes the results obtained with the available rare earth ions in combination with vanadium, chromium and cobalt.

Experimental

Rare Earth–Cobalt–Oxides.—Mixtures of cobalt(II) carbonate and rare earth oxides or mixtures of the nitrates when heated in air at 900° give compounds similar to $LaCoO_3$. The purest compounds (as indicated by the X-ray patterns of the products) were obtained by using an excess of rare earth oxide or nitrate, by heating for long periods and by occasional regrinding of the samples. The unreacted rare earth oxide was removed from the product by prolonged extraction with boiling, almost saturated ammonium chloride solution followed by washing with warm ammonium chloride solution and then with water.

In this way compounds of cobalt with neodymium, praseodymium and samarium were obtained. The products were black powders like lanthanum cobalt oxide. From the X-ray data summarized in Table I, it is obvious that these compounds are essentially similar to $LaCoO_3$ in structure and can be assigned the formula $ACo(III)O_3$. The oxidation state of the cobalt was not otherwise determined since only very small samples were available.

The cerium compound with cobalt was not obtained because of the tendency for cerium to oxidize to the tetravalent state under the conditions of the preparation.

TABLE I

COMPARISON OF PRINCIPAL d/n VALUES[a] OF $LaCoO_3$, $PrCoO_3$, $NdCoO_3$, $SmCoO_3$

Reflec. Plane	Intensity	$LaCoO_3$	$PrCoO_3$	$NdCoO_3$	$SmCoO_3$
100	m.	3.82	3.78	3.77	3.75
110	v.s.	2.711	2.67	2.67	2.65
110	v.s.	2.679	. . .	2.64	. . .
111	m.	2.313	. . .	. . .	. . .
111	w.	2.178	2.178	2.172	2.163
200	s.	1.909	1.890	1.884	1.876
211	s.	1.563	. . .	. . .	. . .
211	m.	1.542	1.543	1.540	1.538
220	m.	1.356	1.356(w)	. . .	. . .
220	m.	1.340	1.335	1.333	1.326
310	m.	1.213	1.196	1.193	1.186
310	m.	1.203	1.179	1.179	. . .

[a] 57.3 mm. Philips camera was used to obtain these X-ray data.

Rare Earth–Vanadium–Oxygen Compounds.—Vanadium sesquioxide was used as the starting material and in this case it was necessary to prevent the oxidation of the vanadium. This was accomplished by heating pressed pellets of intimately mixed rare earth oxide and vanadium sesquioxide in silica glass capsules at 1200° under vacuum. Under these conditions the lanthanum, neodymium, praseodymium and samarium compounds were obtained. In addition, it was possible to prepare cerium(III) vanadium(III) oxide by heating cerium(III) oxalate and vanadium sesquioxide *in vacuo* at 1200°. The X-ray patterns indicate that these compounds are cubic perowskites with unit cell edge ranging from 3.91 ± 0.01 Å. for lanthanum vanadium oxide to 3.87 ± 0.03 Å. for samarium vanadium oxide.

Rare Earth–Chromium–Oxygen Compounds.—These compounds were prepared by heating intimate mixtures of chromium(III) oxide and rare earth oxide in air at 900°. X-Ray diffraction powder diagrams of the products indicate cubic perowskite patterns; if distortion from the cubic lattice occurs, it must be quite small.

Table II summarizes the unit cell dimensions for the various rare earth transition metal oxygen compounds prepared.

TABLE II

UNIT CELL DIMENSIONS FOR RARE EARTH TRANSITION METAL OXIDES

Compound	Å.	Compound	Å.
$LaCoO_3$	3.82 ± 0.01[a]	$NdVO_3$	3.89 ± 0.03
$PrCoO_3$	3.78 ± .01	$SmVO_3$	3.89 ± .03
$NdCoO_3$	3.77 ± .01	$LaCrO_3$	3.90 ± .03
$SmCoO_3$	3.75 ± .01	$CeCrO_3$	3.89 ± .03
$LaVO_3$	3.91 ± .01[b]	$PrCrO_3$	3.89 ± .03
$CeVO_3$	3.90 ± .03	$NdCrO_3$	3.89 ± .03
$PrVO_3$	3.89 ± .03	$SmCrO_3$	3.86 ± .03

[a] 57.3 mm. Philips camera was used. [b] 35.0 mm. Picker camera was used.

Discussion

The data given in Table I indicate clearly that with the cobalt compounds, the rhombohedral distortion of the cubic perowskite structure diminishes with decreasing size of the rare earth cation and becomes cubic with samarium. With the corresponding chromium and vanadium compounds, on the other hand, all of the structures are cubic. The radii of the B cations in these compounds are very nearly the same. Naray-Szabo[3] gives 0.65 Å. for V^{+3} and 0.62 Å. for Cr^{+3}. The value for the radius of Co^{+3} must be nearly the same as the latter. The following radii (Å.) are assigned[3] to the rare earth ions. La(1.26), Ce(1.18), Pr(1.16) Nd(1.15), Sm(1.13) upon the basis of $O^{-2} = 1.32$. Using these values to calculate the tolerance factor, t, in the equation $R_A + R_O = t\sqrt{2}(R_B + R_O)$, we find the range to extend from 0.895 to 0.94 for the cobalt and chromium compounds and from 0.88 to 0.925 for the vanadium compounds. It is difficult to see why this modest variation in t should give rise to a quite pronounced distortion with the cobalt series and have no effect at all in the others. The phenomenon appears to indicate that with the vanadium and chromium compounds we have a quite rigid framework of the BO_6 octahedra, while with the cobalt compounds the structure is more dependent upon packing.

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(1) S. Naray-Szabo, *Naturwissenschaften*, **31**, 203 (1943).

(2) F. Askham, I. Fankuchen and R. Ward, THIS JOURNAL, **72**, 3799 (1950).

(3) S. Naray-Szabo, *Müegyetemi-Közelemënyck-Hungary*, **1**, 30 (1947).

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CHEMICAL LABORATORIES
UNIVERSITY OF CONNECTICUT
STORR, CONN.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE COLLEGE]

Steric Effects of the *t*-Butyl Group in Organosilicon Compounds[1]

BY LEO H. SOMMER AND LESLIE J. TYLER

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Steric effects of the *t*-butyl group have made possible the synthesis of a new class of organosilicon compounds, *dialkyldiaminosilanes*. Silanediols containing a *t*-butyl group are extremely resistant toward condensation in comparison with ordinary dialkylsilanediols.

Previously,[2] we reported the synthesis of *t*-butyltrichlorosilane, *t*-butyltrimethylsilane and di-*t*-butyldichlorosilane, as comprising the first examples of *t*-alkylorganosilicon compounds. These substances were prepared through the use of *t*-butyllithium, it having been shown that *t*-alkyl Grignard reagents fail to give *t*-alkylorganosilicon compounds with a variety of starting materials under a wide range of conditions.

In extension of our previous synthesis of di-*t*-butyldichlorosilane, we have now prepared three additional dialkyldichlorosilanes containing a *t*-butyl group, by the general reaction

$$t\text{-BuLi} + RSiCl_3 \longrightarrow t\text{-BuRSiCl}_2$$

where R is methyl, phenyl and *n*-hexadecyl. In sharp contrast to the reaction of *t*-butyllithium with *t*-butyltrichlorosilane which gave a 59% yield of di-*t*-butyldichlorosilane after four days at 70°,[2,3] the present reactions proceeded smoothly at reflux temperature (37°), required only three or four hours for completion and gave yields of about 70%.

Attempts to effect the synthesis of tri-*t*-butylchlorosilane from *t*-butyllithium and di-*t*-butyldichlorosilane even at an elevated temperature of 160° met with failure.[2,4]

We turn now to a consideration of the products obtained by ammonolysis and hydrolysis of the above four *t*-butyldichlorosilanes, substances whose properties show in striking fashion the profound influence exerted by the *t*-butyl group in inhibiting intermolecular condensation of difunctional silanes.

It has long been known that the silicon–chlorine bond reacts readily with ammonia. The reaction of trialkylchlorosilanes with liquid ammonia gives excellent yields of the corresponding trialkylaminosilane, except in the reaction of trimethylchlorosilane which gives the dimer, $Me_3SiNHSiMe_3$, hexamethyldisilazane.[5] Further, ordinary dialkyldichlorosilanes, such as dimethyl- and diethyldichlorosilane react readily with ammonia, but yield no dialkyldiaminosilanes, $R_2Si(NH_2)_2$. Instead, cyclic trisilazanes and tetrasilazanes, $(R_2SiNH)_3$ and $(R_2SiNH)_4$ are formed exclusively.[6] In the present work ammonolysis of di-*n*-butyldichlorosilane likewise gave no di-*n*-butyldiaminosilane. The product was the cyclic trimer, hexa-*n*-butylcyclotrisilazane. It is evident that in such reactions an unstable diaminosilane is formed which immediately gives intermolecular condensation with elimination of ammonia and formation of Si–NH–Si linkages.

The formation of di-*t*-butyldiaminosilane in excellent yield from the reaction of the dichlorosilane with liquid ammonia is in striking contrast to the above.

$$(t\text{-Bu})_2SiCl_2 + 4NH_3 \longrightarrow (t\text{-Bu})_2Si(NH_2)_2 + 2NH_4Cl$$

Di-*t*-butyldiaminosilane is a clear, water-white liquid with an unpleasant ammoniacal odor; *it can be distilled at atmospheric pressure (190°) without decomposition.*

Subsequent to the synthesis of di-*t*-butyldiaminosilane, which provided the first example of a dialkyldiaminosilane,[7] it was found that *t*-butylmethyl-, *t*-butylphenyl- and *t*-butyl-*n*-hexadecyldichlorosilane, could readily be converted to the corresponding dialkyldiaminosilanes. Thus, the presence of even a single *t*-butyl group on silicon permits the formation of a variety of stable dialkyldiaminosilanes.

Dialkylsilanediols, $R_2Si(OH)_2$, *e.g.*, diethyl-, di-*n*-propyl- and di-*n*-butylsilanediol have been prepared by carefully controlled hydrolysis of the corresponding dichlorosilanes,[8] while hydrolysis of the difluorosilanes has given diisopropyl-, diisobutyl- and dicyclohexylsilanediol.[9] The three dialkylsilanediols containing primary alkyl groups are obtained as white solids that melt in the vicinity of

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[1] Paper 38 in a series on organosilicon chemistry; for 37 see THIS JOURNAL, "New Intramolecular Rearrangements of α-Chloroalkylsilanes" Sommer, *et al.*, in press. Taken from the Ph.D. thesis of L. J. Tyler, The Pennsylvania State College, 1948.

[2] L. J. Tyler, L. H. Sommer and F. C. Whitmore, THIS JOURNAL, **69**, 981 (1947); *ibid.*, **70**, 2876 (1948).

[3] This temperature was obtained by removing a large portion of the pentane by distillation.

[4] In this connection it is of some interest to note that triisopropylchlorosilane, but not tetraisopropylsilane, has been synthesized by reaction of isopropyllithium with silicon tetrachloride; H. Gilman and R. N. Clark, THIS JOURNAL, **69**, 1499 (1947).

[5] R. O. Sauer and R. H. Hasek, *ibid.*, **68**, 241 (1946).

[6] S. D. Brewer and C. P. Haber, *ibid.*, **70**, 3888 (1948).

[7] Prior to this work the synthesis of organosilicate compounds of the type $(RO)_2Si(NH_2)_2$ was reported; these compounds have no carbon–silicon linkages and hence are not classed as organosilicon compounds; C. S. Miner, Jr., *et al.*, *Ind. Eng. Chem.*, **39**, 1368 (1947).

[8] P. D. George, L. H. Sommer and F. C. Whitmore, THIS JOURNAL, **75**, 1585 (1953).

[9] C. Eaborn, *J. Chem. Soc.*, 2840 (1952).