of electrolysis rates on current density has been demonstrated previously.[16] The incubation period is inversely proportional to the current density as expected if the amount of base generated is proportional to the current–time product.

Figure 8 shows that the precipitation is second order with respect to Tm concentration. This dependence can be pictured as a reaction in which two lanthanon polymer fragments combine with electrosolvolytically-formed base to form a bridged polymer which precipitates.

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The Reaction of Rare Earth Oxides with a High Temperature Form of Rhodium(III) Oxide

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Lanthanum rhodium oxide and neodymium rhodium oxide, containing rhodium in the trivalent state, have been prepared and possess distorted perovskite structures. They are orthorhombic and probably belong to space group D_{2h}^{16} Pbnm. The lattice constants are a = 5.524 Å., b = 5.679 Å., c = 7.900 Å. for $LaRhO_3$ and a = 5.402 Å., b = 5.772 Å., c = 7.816 Å. for $NdRhO_3$. The distinguishing feature of this distortion is that $a < c/\sqrt{2} < b$, indicating that it is probably due to a size effect only. This is in contrast to the distortion observed for $LaMnO_3$ ($c/\sqrt{2} < a < b$) that is caused by both an electronic ordering (Jahn–Teller) and size effects. Neither samarium oxide nor yttrium oxide form a simple perovskite when allowed to react with rhodium(III) oxide under the same conditions used to prepare neodymium rhodium oxide. This implies that the maximum distortion possible due to size effects is of the type where $a < c/\sqrt{2} < b$ and can be distinguished from the distortion caused by electron ordering. This paper also reports the existence of two forms of rhodium oxide, a hexagonal low temperature form with the corundum structure and a high temperature form apparently related to the perovskites. The low temperature form transforms to the high temperature form above 750°.

Introduction

Lanthanum rhodium oxide, $LaRhO_3$, containing rhodium in the trivalent state, has been prepared and reported[3] to have a distorted perovskite structure. It is orthorhombic and belongs to space group D_{2h}^{16} Pbnm with four distorted perovskite units in the true crystallographic cell. The lattice constants are a = 5.524 Å., b = 5.679 Å., c = 7.900 Å. The investigation described in this paper is an attempt to prepare the other rare earth rhodium oxides. Neodymium rhodium oxide possesses a greater distortion than lanthanum rhodium oxide, although for both compounds $a < c/\sqrt{2} < b$. Goodenough[4] has referred to perovskites with this type of distortion by the symbol O, and these compounds are distinguished from the orthorhombic perovskites labeled O′ where $c/\sqrt{2} < a < b$ (*e.g.*, $LaMnO_3$). Samarium and yttrium oxides do not form perovskites of either the O or O′ type structure under the same conditions used to prepare neodymium rhodium oxide. Samarium oxide reacts with rhodium oxide to form an unknown phase, and yttrium oxide does not appear to react with rhodium oxide at all.

This paper also reports the existence of two forms of rhodium oxide. A hexagonal low temperature form was prepared by decomposition of hydrated rhodium oxide at 700° and corresponded to the cell dimensions given by Zachariasen.[5] In addition a high temperature form of rhodium oxide exists when rhodium metal is converted directly to the sesquioxide at 1000°. The hexagonal rhodium oxide transforms to the high temperature form above 750°.

Experimental

Preparation of Hexagonal Rhodium Oxide.—Finely powdered (325 mesh) spectroscopic grade rhodium metal is fused with potassium hydrogen sulfate in a porcelain crucible. After prolonged fusion the contents of the crucible are extracted with boiling water and filtered. A sodium hydroxide solution is added slowly to the filtrate until precipitation of the hydrated rhodium oxide is complete. The precipitate is filtered, carefully washed, and air dried. The oxide is then transferred to a porcelain crucible and heated in air at 700°. The resulting low temperature form of Rh_2O_3 was measured on a Norelco diffractometer using copper Kα radiation. The hexagonal values obtained were a = 5.108 Å. and c = 13.81 Å. The oxide was analyzed for rhodium by reduction in a stream of hydrogen at 800° until constant weight was obtained. The formula corresponded to Rh_2O_3.

Preparation of High Temperature Rh_2O_3.—Finely divided

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[1] Operated with support from the U. S. Army, Navy, and Air Force.

[2] Brown University, Providence, R. I.

[3] A. Wold, B. Post, and E. Banks, *J. Am. Chem. Soc.*, **79**, 6365 (1957).

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(325 mesh) rhodium metal was heated at 1000° in air until constant weight was obtained. The resulting weight gain indicated a composition of $Rh_2O_{2.996}$. The powder diffraction data for this form of Rh_2O_3 taken with copper Kα radiation are reported in Table I.

TABLE I
X-RAY DIFFRACTION DATA FOR Rh_2O_3 (HIGH TEMPERATURE FORM)

$a = 5.149$ Å. $b = 5.436$ Å. $c = 14.688$ Å.

Orthorhombic indices	d calcd.	d obsd.	I/I_0
004	3.672	3.68	15
111	3.622	3.623	11
020	2.718	2.722	31
021	2.672	2.673	4
114	2.619	2.623	100
200	2.574	2.574	39
023	2.376	2.378	2
024	2.184	2.188	6
204	2.108	2.106	4
220	1.869	1.869	27
008	1.836	1.836	10
223	1.746	1.747	6
131	1.697	1.698	9
132	1.664	1.665	7
224	1.665		
118	1.647	1.649	10
134	1.549	1.549	8
028	1.521	1.522	4
314	1.494	1.495	33
235	1.322	1.326	2
137	1.325		
307	1.328		
228	1.309	1.310	6
043	1.309		
400	1.287	1.286	4
331	1.241	1.242	1
00·12	1.224	1.222	4
240	1.201	1.202	2
414	1.185	1.187	2
242	1.186		
046	1.188		
334	1.179	1.180	3
243	1.167	1.168	2
420	1.163	1.163	6
422	1.149	1.148	2
423	1.132	1.132	2
147	1.114	1.114	2
13·10	1.114		
424	1.109	1.106	2
246	1.079	1.079	2
152	1.053	1.054	4
342	1.054		
408	1.054		

Neodymium Rhodium Oxide.—Stoichiometric amounts of neodymium oxide and rhodium(III) oxide (high temperature form) needed to give neodymium rhodium(III) oxide $NdRhO_3$ were ground together in an agate mortar. When the mixture appeared homogeneous, it was transferred to a platinum boat and heated in a tube furnace under a stream of oxygen at 1100° for 96 hr. During the heating period, the sample was removed three times, cooled, and ground thoroughly in an agate mortar. X-Ray diffraction patterns were taken using iron $K\alpha_1$ radiation ($\lambda = 1.93597$ Å.).

Chemical Analysis of Neodymium 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 neodymium oxide, was treated with 25 ml. of 6 N hydrochloric acid and heated at the boiling point for 15 min. in order to extract the neodymium present. The pH of the filtrate was adjusted with NH_4OH to the point where neodymium hydroxide began to precipitate. A saturated ammonium oxalate solution was added to the filtrate until precipitation was complete. The neodymium oxalate precipitate was collected in a Selas crucible and ignited to neodymium oxide. The formula obtained from the analytical results corresponded to $NdRhO_3$.

Attempted Preparation of Samarium and Yttrium Rhodium Oxides.—The procedure for the preparation of neodymium rhodium oxide was applied to prepare samarium and yttrium rhodium oxides. X-Ray analysis showed the presence of an unidentified phase for the samarium oxide–rhodium oxide reaction product and a lack of reaction between yttrium oxide and rhodium oxide.

Results and Discussion

A low temperature form of rhodium oxide was prepared by precipitating a hydrated rhodium oxide and heating it in air at 700°. This form was hexagonal with $a = 5.108$ Å., $c = 13.81$ Å. This corresponds to the oxide reported by Zachariasen[5] ($a = 5.09$ Å., $c = 13.74$ Å.). If the hexagonal rhodium oxide is heated above 750°, it transforms to another form of rhodium oxide, whose powder pattern is given in Table II.

TABLE II
$NdRhO_3$ sample 81d
Orthorhombic; space group Pbnm
Unit cell: $a = 5.402$ Å., $b = 5.772$ Å., $c = 7.816$ Å.

hkl	d calcd.	d obsd.	I/I_0
111	3.521	3.533	m−
020	2.886	2.886	m
112	2.776	2.777	s
200	2.701	2.701	m
211	2.335	2.334	w
113	2.173	2.169	w
220	1.972	1.978	m
004	1.954	1.954	m
023	1.934	1.930	w−
221	1.912	1.913	w
130	1.812	1.817	w
131	1.766	1.768	w+
132	1.644	1.643	m−
024	1.618	1.620	m−
204	1.583	1.583	w
312	1.573	1.576	m
231	1.536	1.532	w−
303	1.481	1.487	w
224	1.388	1.388	m−
042	1.354	1.353	w
400	1.351		
125	1.332	1.328	w
411	1.297	1.297	w
043	1.262	1.258	w
241	1.256		
332	1.246	1.246	w−
116	1.237	1.235	w+
420	1.223	1.225	w
225	1.225		
421	1.208	1.211	w
305	1.180	1.182	w−
413	1.174	1.175	w
243	1.144	1.143	vw
340	1.126	1.129	vw
430	1.105	1.107	vw
235	1.107		
511	1.052		vw
316	1.038	1.056	w+
424	1.037		

The high temperature form was indexed from powder diffraction charts on the basis of an orthorhombic unit cell with a = 5.149 Å., b = 5.436 Å., c = 14.688 Å. If finely divided rhodium powder is heated in air above 600°, it converts to the high temperature form directly. The optimum temperature for the formation of Rh_2O_3 is 1000°. However, above 1100° Rh_2O_3 decomposes to the metal.

Goldschmidt[5] has shown that the perovskite-type structure is stable only if a tolerance factor, t, defined by $(r_A + r_O) = t\sqrt{2}(r_B + r_O)$, has an approximate range of $0.8 < t < 1$. The values for r_A, r_B, and r_O are the Goldschmidt radii of the respective ions. Megaw[6] has tabulated the tolerance factor of a large number of perovskites and found that if $0.8 < t < 0.9$, a cooperative buckling and enlargement of the unit cell occurs. The values of t are given for several rare earth rhodium oxides in Table III. These values are based on the rare earth radii reported by Templeton and Dauben[7] and a radius of 0.69 for trivalent rhodium (coordination number six). The decrease in the value for t as one proceeds from lanthanum to neodymium is accompanied by greater difficulty in the preparation of the rare earth rhodium oxide. Neodymium rhodium oxide does not form unless the oxides are allowed to react in an oxygen atmosphere at 1100°. Neodymium rhodium oxide also possesses a greater distortion than lanthanum rhodium oxide, although for both compounds $a < c/\sqrt{2} < b$ (O structure). Calculations based on X-ray data and comparison with $GdFeO_3$[8] show that $NdRhO_3$ probably belongs to the space group D_{2h}^{16} Pbnm, with four formula weights per unit cell. The lattice constants are a = 5.402 Å., b = 5.772 Å., c = 7.816 Å. Attempts to prepare samarium and yttrium rhodium oxides were unsuccessful, and it can be seen from Table III that formation of these compounds necessitates a further decrease in the value of t. It is apparent that for the radii chosen a minimum value of t (0.810) is reached for $NdRhO_3$. A further decrease in t results in the lack of formation of a perovskite structure. Since both lanthanum and neodymium rhodium oxides possess the O structure, it can be concluded that the only factor to be considered for the formation of rare earth rhodium perovskites is the ionic size effect. The lack of formation of an O′ structure ($c/\sqrt{2} < a < b$) indicates that this type of distortion must be caused by a superposition of electron-ordering as was suggested by Goodenough.[4]

TABLE III

VALUES OF t FOR $MRhO_3$

Compound	t
$LaRhO_3$	0.832
$NdRhO_3$	.810
$SmRhO_3$	.800
$YRhO_3$	.785

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Decomposition of Nitrosyl Disulfonate Ion in Mildly Alkaline Solution[1]

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Decomposition of nitrosyl disulfonate ion between 25 and 90° in the pH range 6 to 11 gives the products found by Divers and Haga in amounts now found quantitatively and a still unrecognized anion, probably divalent with N/S = 1.0. The stoichiometry and kinetics were consistent with two decomposition paths involving initial rupture of the radical anion into the free radicals SO_3^- (k_1) and NO (k_2), respectively. These are also proposed as the reactions which initiate the material chain process in acid solution. Assuming the reactions actually to be S_N2 involving water, the rate constants for color disappearance could be expressed by $k_1 = (kT/h)\exp(1 - (32900/RT) + (18.8/R))$ and $k_2 = (kT/h)\exp(1 - (29800/RT) + (9.5/R))$ independent of pH and initial concentration and subject to only a secondary salt effect. Rates of nitrite ion formation and liberation of acid were proportional to the rate of color disappearance.

While a certain amount was learned concerning the behavior of nitrous acid as a chain carrier during previous observation of nitrosyl disulfonate ion decomposition in acid solution, the reaction had such complexity that no conclusion could be reached concerning the initiating reaction. In the pH range 6–11 the reaction is much slower,[3] and the inventory of products[4] made long ago lent encouragement that suitable observations of alkaline solutions might indicate the initiating reactions. Since our last paper other such experiments

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[1] Paper VI of a series in which the most recent is J. C. M. Li and D. M. Ritter, *J. Am. Chem. Soc.*, **75**, 5831 (1953).

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