SOLVOLYTIC DISPROPORTIONATION OF NON-STOICHIOMETRIC OXIDES OF PRASEODYMIUM AND TERBIUM*

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Abstract—The solvolytic disproportionation of non-stoichiometric PrO_x and TbO_x in acid solutions to produce higher oxides has been investigated. Some new non-stoichiometric phases have been reported. A number of interesting features of the non-stoichiometric rare earth oxides have been discussed and the need for a satisfactory structural model has been pointed out.

THERE has been considerable interest in recent years in the study of non-stoichiometric rare earth oxides, particularly those of praseodymium.⁽¹⁻³⁾ The phase equilibria in the praseodymium-oxygen system have been investigated in detail and several well-defined phases of narrow composition range have been reported.^(3,4) An interesting result from the studies on the phase equilibria of the praseodymium oxide system is the coexistence of a homologous series^(2,5) of the formula $2Pr_2O_3 \cdot mPrO_2$ (0 < m < 8) or $Pr_nO_{2n-2}(4 < n < 12)$. Such a series reminds one of the MAGNELI structures in the molybdenum-oxygen, tungsten-oxygen and titanium-oxygen systems.^(6,7)

An early study of the solubility of praseodymia, Pr_6O_{11} , in acids was made by PRANDTL and HÜTTNER⁽⁸⁾ who found that a residue of Pr_4O_8 ·H₂O remained in acid solution. EVRING§ had observed that old samples of Pr_6O_{11} exposed to the atmosphere showed small traces of PrO_2 . Normally, PrO_2 is made by the treatment of the lower oxides of praseodymium with oxygen at a high pressure and temperature⁽⁹⁻¹¹⁾ and TbO₂ is made by the treatment of the lower oxides with atomic oxygen.⁽¹²⁾ It was

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therefore considered important to investigate the quantitative solvolytic behaviour of non-stoichiometric praseodymium and terbium oxides in acid solutions. If the dioxides of praseodymium and terbium were to remain as residues in acid solutions, the situation would be similar to the leaching of PbO from Pb_3O_4 in dilute nitric acid leaving a residue of $PbO_2^{(13)}$ or that of MnO from Mn_2O_3 leaving a residue of $MnO_2^{(13)}$.

EXPERIMENTAL

Praseodymium oxide, $\Pr_{e}O_{11}$, (Lindsay, 99.99% Pure) ignited to constant weight was used for these studies. Determination of active oxygen (Pr IV) by iodimetry as well as by use of arsenic (III) as reducing agent,⁽¹⁴⁾ confirmed that the composition was exactly $\Pr_{0_{1:E1}}$ (or $\Pr_{e}O_{11}$). The X-ray powder pattern when indexed on the basis of an f.c.c. lattice gave a lattice constant of 5.468 \pm 0.002 Å which agrees with the literature value.⁽¹⁾ A sample of $\Pr_{0_{1:72}}$ was made according to the procedure of KUNTZ and EYRING⁽¹⁵⁾ by heating $\Pr_{e}O_{11}$ in vacuum for 2 hr at 490°C and the composition was verified by active oxygen analysis.⁽¹⁴⁾ This oxide was rhombohedral as reported by EYRING and HOLMBERG.⁽¹⁾ An authentic sample of \Pr_{02} was made by heating $\Pr_{e}O_{11}$ in oxygen at 5 atm and at 360°C for 3 days. The lattice constant of this fluorite structure was 5.393 \pm 0.001 Å. Lindsay 99.9% pure terbium oxide was ignited in air to constant weight and its composition was found to be TbO_{1.81} by active oxygen estimation. The lattice constant of the oxide was 5.295 \pm 0.01 Å when the important lines were indexed on the basis of a cubic lattice; to be exact this phase should be considered as triclinic⁽¹⁾ with the angles showing very small deviations from 90°.

X-ray powder patterns were taken on a GE unit or a Reich-Seifert unit employing filtered Cu or Mo radiation. In the X-ray determination of the lattice constants of cubic substances, absorption correction was applied in relevant cases using the Nelson-Riley function. Thermogravimetric analysis was carried out emplying a balance described earlier.⁽¹⁶⁾ Differential thermal analysis was carried out with an apparatus⁽¹⁷⁾ similar to that described by NORTON.⁽¹⁸⁾

The procedure for studying the solvolysis was as follows. About 300 mg of the non-stoichiometric oxide was added to a known quantity of the acid contained in a stopped flask and maintained at a particular temperature and for a fixed period with frequent agitation. At the end of the period, the residue was washed with acid of the same concentration as used in the experiment and several times with water. The residue was dried to constant weight at 110°C and analysed for active oxygen.⁽¹⁴⁾ The quantity of oxide dissolved in the acid was determined by drying and ignition to the stable non-stoichiometric oxide. The kinetics of solvolysis were studied by first equilibrating stoppered flasks containing a known amount of acid in a thermostat and then adding Pr_6O_{11} . The flasks were frequently agitated and at the end of the required period, an aliquot portion of the acid was pipetted out into a crucible and the amount dissolved determined by drying and ignition to Pr_6O_{11} .

RESULTS

Solvolysis of non-stoichiometric praseodymium oxides

The results of the solvolysis of Pr_6O_{11} ($PrO_{1.83}$) in different acid solutions are presented in Table 1. The residue was found to be PrO_2 by active oxygen analysis in almost all cases except when acetic acid concentration was very high. The residue of PrO_2 was finely divided, but crystalline, as shown by the X-ray powder patterns.

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Conc. of acid	Amount dissolved as Pr ₆ O ₁₁	Residue (wt.%)	Active oxygen in residue (%)	Composition of the residue: x in PrO _x	Lattice constant from X-ray data (Å)
0.01 or			4.63	2.00	$5\cdot393\pm0\cdot002$
1.6 N HAc	32.1	63·8	4.63	2.00	5.393 ± 0.002
4 N HAc	32.2	63.5	4.62	1.98	5.394 ± 0.004
8 N HAc	32.9	63.8	4.63	2.00	5.393 ± 0.004
12 N HAc	32.5	63.6	4.62	1.98	5.399 ± 0.004
16 N HAc			3.64	1.92	5.430 ± 0.006
Glacial HAc	2.7	96.4	3.52	1.88	5.465 ± 0.004

TABLE 1.—LEACHING OF PrO1.83 BY ACIDS*

* When acetic acid solutions were employed the period was 5 days; in the case of HCl solutions the period was 2 hr, Temp. was $25 \pm 2^{\circ}$ C.

In order to verify the applicability of this method of leaching out Pr^{3+} in acid solutions to the other non-stoichiometric oxides, $PrO_{1.72}$ was prepared. It is known from studies of phase equilibria⁽³⁾ that this composition is the best defined nonstoichiometric oxide of praseodymium other than $PrO_{1.83}$. In the case of $PrO_{1.72}$ also, the residue from 8N acetic acid leaching was found to be PrO_2 .

The PrO₂ obtained by leaching of PrO_{1.83} gave good sharp X-ray patterns. A well crystallized single phase alone was present. It is not likely that any minor phase was present and the iodometric estimation of active oxygen agreed closely with the composition PrO_2 . The X-ray lines fitted a fluorite lattice and the lattice constants of the various samples correspond closely to the literature value⁽¹⁾ (5.393 \pm 0.001 Å). The PrO₂ obtained from solvolysis was subjected to thermogravimetric (TGA) and differential thermal analysis (DTA). The TGA curve showed that it starts losing weight from 110°C till about 320°C when more rapid weight loss occurrs. The loss below 320°C is due to moisture and chemisorbed acetate as pointed out by CLIFFORD et al.⁽¹⁹⁾ and the rapid weight loss occurring between 320 and 400°C corresponds to the reaction; $PrO_2 \rightarrow PrO_{1.83}$. The residue from TGA was found to be Pr_6O_{11} by X-ray powder diffraction and chemical analysis. The authentic sample of PrO₂ prepared from Pr₆O₁₁ by treatment with oxygen under high pressure showed oxygen loss between 360 and 420°C. The DTA curve of PrO₂ from solvolysis showed a small endothermic peak at 400°C due to decomposition to Pr₆O₁₁. The slow decomposition due to chemisorbed acetate noticed in TGA was not observed in the DTA.

The residues from glacial and 16 N acetic acids gave lower active oxygen contents than PrO_2 and compositions are in the region of $PrO_{1.90}$ (Table 1). This composition is not known to be a stable phase.^(3,20) The X-ray powder patterns of these residues yielded lattice constants which are in between those of Pr_6O_{11} and PrO_2 . It is possible that these are mixtures of Pr_6O_{11} and PrO_2 ; the proportion should be Pr_6O_{11} : $2PrO_2$ to give $PrO_{1.88}$. Whether these are unique phases occurring in the miscibility range of $PrO_{1.83}$ to PrO_2 is difficult to ascertain from the present study.

It can be seen from Table 1 that the residue in dilute acetic acid (~ 64 per cent) is roughly the same in all cases. If Pr_6O_{11} were to be written as $2Pr_2O_3 \cdot 8PrO_2$ according

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to the homologous series, and if all the Pr_2O_3 went into solution, the residue of PrO_2 would be 67.7 per cent. In fact the quantity dissolved was about 33 per cent. The agreement in the percentage of the PrO_2 residue is not very good due to incomplete recovery caused by the fine particle size. These results seem to establish the quantitative nature of the separation of PrO_2 from Pr_6O_{11} in dilute acetic acid solution and are in accordance with the stoichiometry demanded by the homologous series. Apparently PrO_2 is insoluble in acetic acid solutions as was confirmed with the authentic sample.

When Pr_6O_{11} was hydrolysed by boiling water for 24 hr the residue consisted of PrO_2 and $Pr(OH)_3$. All the lines in the X-ray pattern of the residue could be fitted into lattices of either PrO_2 or $Pr(OH)_3$.

$$Pr_6O_{11} + 3H_2O \rightarrow 2Pr(OH)_3 + 4PrO_2$$

These results agree with those of BRAUER and PFEIFFER.⁽²¹⁾

Solvolysis of non-stoichiometric terbium oxides

It was found that terbia was nearly insoluble in acetic acid of any concentration at room temperature (20–30°C). Various concentrations of hydrochloric acid were therefore employed and the results are presented in Table 2. Decinormal hydrochloric acid was found to be useful in obtaining TbO₂ from TbO_{1.81}. Boiling TbO_{1.81} with a 1:1 acetic and hydrochloric acid mixture also gives TbO₂ as residue.⁽²²⁾ Unlike Pr_6O_{11} , the residue obtained does not exactly conform to that expected from the formulation according to the homologous series. The amount of residue also varies with time. It is possible that TbO₂ dissolves sufficiently in 0.1 N HCl solution. The composition of TbO_{1.83} (Tb₆O₁₁) obtained in one of the experiments has not been clearly defined in the literature and it is likely that this is the analog of Pr_6O_{11} . The ratio of the cell edges of Tb₆O₁₁ and Pr_6O_{11} is nearly the same as the ratio of the cell edges of Tb₂O₃(C) and $Pr_2O_3(C)$.

Medium	Residue (%)	Active oxygen (%)	Composition of the residue x in TbO-	Lattice constant from X-ray data (Å)
8 N HAc (5 days)	99.0	2.39-2.56	1.78-1.80	
0.01 N HCl	92 ·0	2.47-2.64	1·79-1·81	5.29 \pm 0.01
0·1 N HCl (8 hr)		2.81	1.83	5.26 ± 0.01
0.1 N HCl (24 hr or 5 days)	29.4	4.00-4.19	1.98-2.00	$\textbf{5.200} \pm \textbf{0.001}$
1.0 N hydrochloric acid	0-0			

TABLE 2.—SOLVOLYSIS OF TERBIUM OXIDE, TbO_{1.81}

The residue of TbO₂ obtained from 0.1 N hydrochloric acid was bright red in colour and gave a good X-ray powder pattern. The data fit a f.c.c. cell fairly well and lines from the back reflection region which were resolved into α_1 and α_2 components gave a lattice constant of 5.219 \pm 0.0005 Å. An examination of the pattern

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failed to reveal any splitting or broadening of the lines due to a possible distortion of the cubic cell. TbO₂ looses oxygen to give TbO_{1.8} around 340° C.

The patterns of non-stoichiometric praseodymium and terbium oxides as well as the dioxides contained many lines other than those belonging to the unit cells already described. It was possible to index some of these lines on the basis of a unit cell of the C-type sesquioxides. In the case of TbO₂ the extra lines were fitted into a b.c.c. lattice with a cube edge of 10.73 ± 0.03 Å. The cell dimension agrees with the literature value⁽¹⁾ of 10.7281 ± 0.0005 Å for C-Tb₂O₃.

Kinetics of solvolyis of Pr_6O_{11}

Rates of dissolution of Pr_6O_{11} in 8 N acetic acid solution were found to follow the first-order rate law with an energy of activation of 4 to 5 kcal. This value of the energy of activation could be reproduced although the values of the rate constants varied from sample to sample. For one sample, the rate constants were $1\cdot 20 \times 10^{-3}$ and $1\cdot 58 \times 10^{-3}$ min⁻¹ at 29 and 40°C respectively, while for another sample the values were $2\cdot 9 \times 10^{-4}$ and $3\cdot 5 \times 10^{-4}$ min⁻¹ at 40° and 50°C respectively. The low value of the energy of activation is significant and together with the first-order dependence of the reaction, it indicates that the process is akin to a simple dissolution. An attempt to study the rate of dissolution of a 1:4 mixture of Pr_2O_3 and PrO_2 (corresponds to Pr_6O_{11}) was unsuccessful since the dissolution of Pr_2O_3 and PrO_2 mixed in the proper proportions to form $PrO_{1\cdot71}$ and $PrO_{1\cdot833}$ showed only lines belonging to Pr_2O_3 and PrO_2 .

In order to examine the nature of the intermediate products, samples of residues from solvolysis at 40°C were separated after intervals of 15 min and 1 hr and their powder patterns were taken. The pattern of the 1 hr sample turned out to be that of PrO₂ ($a = 5.400 \pm 0.005$ Å) with several additional lines which belonged neither to a fluorite type lattice nor to Pr(OH)₃. The pattern of the specimen after 15 and 25 min showed larger d-spacings and the fluorite lines could be accounted for by cells with lattice constants of 5.460 \pm 0.005 and 5.435 \pm 0.003 Å respectively. While even these patterns did not show any Pr₆O₁₁ lines, they showed the same additional lines as the 1-hr specimen. The absence of Pr₆O₁₁ lines after only 15 min of solvolysis is surprising. A fluorite cell with a = 5.435 Å which is between the size of the Pr_6O_{11} and PrO_2 cells could mean a solid solution. Using a smooth curve obtained by plotting the unit cell lengths of all the cubic and rhombohedral phases of praseodymium oxides from the literature⁽¹⁾ vs. the composition (pseudo cell dimensions were used where necessary), it was found that a = 5.435 Å corresponds to a composition of $PrO_{1.92}$. A similar composition with about the same lattice constant was also obtained by solvolysis of $Pr_{6}O_{11}$ with 16 N acetic acid (Table 1). A miscibility gap is known to exist between Pr₆O₁₁ and PrO₂ and how such a uniphasic composition in this region could result is not clear; but it is possible that in the medium of a solution of praseodymium ions, such solid solutions could form. This would also explain the absence of Pr₆O₁₁ lines and is a strong argument in favour of solid solution formation.

DISCUSSION

The formation of MnO_2 and PbO_2 by the action of acids on the mixed valence oxides Mn_2O_3 and Pb_3O_4 respectively is well known.⁽¹³⁾ Pb_3O_4 consists of metal ions

in non-equivalent positions⁽²³⁾ and if these correspond to different valence states, those in the lower valence state (being the more basic) are preferentially attacked by acids; the crystalline sub-particles that are left behind would then rearrange into a stable structure. In the non-stoichiometric oxides of praseodymium, however, the Pr^{3+} and Pr^{4+} ions are supposed to be crystallographically indistinguishable.⁽²⁴⁾ It is, therefore, difficult to offer an unified explanation for the solvolysis of non-stoichiometric rare earth oxides and the mixed valence oxides of lead and manganese, based on the existing knowledge of the crystallography of these systems. Several interesting features of these non-stoichiometric oxides are apparent.

(1) The X-ray analysis of the quenched samples of the various non-stoichiometric praseodymium and terbium oxides does not seem to be satisfactory; for example, several extra lines are found in the patterns, which cannot be assigned to the main phase.^(2,5) These extra lines are not due to an impurity of sesquioxide, but are likely to arise from the disordered nature of these oxides. An X-ray pattern of an intimate mixture of Pr_2O_3 and PrO_2 in the proportion 1:4 (giving a composition of Pr_6O_{11}) was not identical to the pattern of Pr_6O_{11} and clearly showed the distinct lines of both the components.

(2) An examination of the thermodynamic data⁽²⁵⁻²⁷⁾ on the oxides of praseodymium and terbium oxides has shown that the heat of formation of the non-stoichiometric oxides is equal to the sum of the heats of formation of the stoichiometric oxides taken in proper proportion (following the homologous series $2Pr_2O_3 \cdot m PrO_2$). This is similar to the linearity of thermodynamic data in the stoichiometric range found by ARIYA and MOROZOWA⁽²⁸⁾ in the Ti-O system.

Composition	ΔH ^o 298.16 kcal/g atom of Pr, observed	$\Delta H^{\circ}_{$198.16}$ kcal/g atom of Pr, derived from the values of C—Pr ₂ O ₃ and PrO ₂	
PrO _{1.83}	-227.6 ± 0.8 -224.0 + 0.9	-228·1 -224·6*	

* Value calculated for PrO_{1.714}

This striking additivity of the heats of formation following the homologous series can only mean that energetically, there is little or no difference between a nonstoichiometric rare earth oxide and a corresponding mixture of the stoichiometric oxides.

(3) Recent studies on the phase equilibria in the praseodymium-oxygen system have shown very large hysteresis effects,⁽²⁹⁾ particularly in the monophasic regions. Observation of hysteresis effects may mean that one is not dealing with true equilibrium systems and throws some doubt on the X-ray analysis of quenched samples.

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(4) From the available thermodynamic data^(3.30) it is found that the entropy change, ΔS° , for the formation of $PrO_{1.714}$ from Pr_2O_3 is considerably higher than the normal differential molar standard entropy change for such oxidation reactions. The higher value for ΔS° would also indicate that one may not be dealing with an equilibrium situation. However, assuming a random distribution of 4 moles of Pr^{3+} , 3 moles of Pr^{4+} , 2 moles of vacancies and 12 moles of O^{2-} in $PrO_{1.714}$ ($2Pr_2O_3 \cdot 3PrO_2$), one can account for a major portion of the discrepancies in ΔS° .

(5) Preliminary ESR studies have indicated that the signals for the ions in the non-stoichiometric and stoichiometric oxides are not different and magnetic susceptibilities⁽³¹⁾ of non-stoichiometric praseodymium oxides can be interpreted in terms of the additive susceptibilities of Pr_2O_3 and PrO_2 in suitable proportions.

From the discussion above, it becomes clear that the structures of the nonstoichiometric praseodymium and terbium oxides need clarification. The crystallography of these systems should account for the number of extra weak lines in the X-ray pattern, the additivity of heats of formation, the ready separation of the dioxides in acid solutions and the existence of the homologous series. A plausible model seems to be one involving a "string" as the structural entity (analogous to the shear plane of $Ti_n O_{2n-1}^{(6)}$ generating a series of LnO_{2n-2} from the parent LnO_2 .⁽³²⁾ In this model, cubic Ln₂O₃ can be pictured as containing non-intersecting linear strings of LnO_6 octahedra (LnO_6V_2 cubes where V stands for oxygen ion vacancy) arranged in four directions. $LnO_{1.71}$ (or Ln_7O_{12}) consists of parallel infinite strings of RO_6V_2 cubes surrounded by sheaths of 7 co-ordinated cations. The composition of the phase is determined by the concentration of strings and the symmetry by the geometrical arrangement in the (111) directions. Thus, any non-stoichiometric phase Ln_2O_{2n-2} or $LnO_{2(1-1/n)}$ will consist of 1/n-th of the cations in the string with each of them having RO_6V_2 co-ordination. This model seems to be able to explain most of the unusual features of non-stoichiometric rare earth oxides described earlier.

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