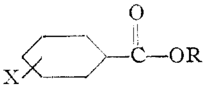
TABLE I

BENZOIC ACID ESTERS



R	X	R. I., $n^{25}D$	M. p., °C.	B. p., °C.	Mm.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Chlorine Calcd.	Chlorine Found
o-Allylphenyl	Hydrogen	1.5675		118	0.5	$C_{16}H_{14}O_2$	80.65	80.87	5.92	5.97		
o-Allylphenyl	*p*-Chloro	1.5789		149	1	$C_{16}H_{13}ClO_2$					13.49	12.98
2-Allyl-6-*s*-butylphenyl	Hydrogen	1.5497		161–162	2	$C_{20}H_{22}O_2$	81.59	81.63	7.53	7.48		
o-*s*-Butylphenyl	*p*-Chloro	1.5610		145–146	1.4	$C_{17}H_{17}ClO_2$					12.28	12.47
p-*s*-Butylphenyl[a]	*p*-Chloro		54–55			$C_{17}H_{17}ClO_2$					12.28	12.35
m-Tolyl[a]	*m*-Chloro		51–52			$C_{14}H_{11}ClO_2$					14.38	14.40
m-Tolyl[a]	*p*-Chloro		95–96			$C_{14}H_{11}ClO_2$					14.38	14.25
p-Tolyl[a]	*p*-Chloro		99–100			$C_{14}H_{11}ClO_2$					14.38	14.35
2,4,5-Trichlorophenyl[a]	*p*-Chloro		152.5–155			$C_{13}H_6Cl_4O_2$					42.21	42.09

[a] Recrystallized from methanol.

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Oxidation of Some Rare Earth Oxides with Ozone

BY SHERMAN RABIDEAU[1] AND GEORGE GLOCKLER

The possible oxidation states of the lanthanide series of elements has evoked considerable interest, not only for the bearing this information may have upon the placement of these elements in a periodic arrangement, but also because of the chemical relationship to the actinides. A valence greater than four has not been established for praseodymium, and it appears that the trivalent state is the maximum for neodymium, samarium and gadolinium.

Gruen and Katz[2] have reported that the oxidation of the sesquioxide of praseodymium to the dioxide occurs with the use of atomic oxygen at a reduced pressure and at elevated temperatures, but no change in the compound Pr_6O_{11} was found under similar conditions. Also with regard to the oxides of neodymium, samarium and gadolinium, atomic oxygen was apparently without effect.

In an attempt to produce the maximum oxidation state for praseodymium, neodymium, samarium, and gadolinium, the dry oxides were subjected to the action of ozone at room temperature and at atmospheric pressure.

Experimental.—The rare earth oxides were obtained from the collection of Professor L. Rolla and the purity was stated to be greater than 99.9%. The sesquioxide of praseodymium was obtained by reduction of the higher oxides in a stream of hydrogen at 950°. The compound Pr_6O_{11} was prepared by ignition in air. The ozone was produced with the use of three Berthollet tubes connected in series as described by Greenwood[3] with the exception that ground glass standard taper joints were used to join the tubes instead of mercury seals. The oxygen was prepared from the reaction of distilled water with C.P. sodium peroxide to avoid the interference from the nitrogen present in U.S.P. tank oxygen. Rather large weight increases in the rare earth oxides were noted when tank oxygen was used in the ozonizer. By sealing some of the gadolinium oxide exposed to ozone prepared from commercial oxygen into a tube connected to a vacuum line and then heating the sample, brown fumes were evolved which attacked the mercury in the McLeod gage. This weight increase was not observed when purified oxygen was used in the ozonizer. The oxygen was dried with concentrated sulfuric acid, solid potassium hydroxide, and barium oxide before entering the ozonizer. The ozone concentration produced by a silent electrical discharge was approximately 9% by weight.

Only in the case of the oxides of praseodymium was an oxidation by ozone observed. Both the sesquioxide and the higher oxide, Pr_6O_{11}, reacted with ozone to form the dioxide. In Table I are given the results of the oxidations of the two oxides of praseodymium with ozone.

TABLE I

OXIDATION OF PRASEODYMIUM OXIDES WITH OZONE

Oxide	Wt. of oxide, g.	Reaction time, hr.	Wt. gain on oxidation, g.	Wt. loss on reduction, g.	Moles O_2 gained/mole oxide	PrO_2, %
Pr_2O_3	2.3644	13	0.0936	0.0936	0.409	81.6
Pr_6O_{11}	2.5442	6.5	.0283	.1071	.355	89.5

The weight loss of the oxidation product was determined by reduction of the rare earth to the sesquioxide in a stream of purified hydrogen at a temperature of 950°. Indicative of a reaction were the change in color, the evolution of heat upon exposure to ozone, and the increase in weight. The green sesquioxide of praseodymium rapidly became cocoa-brown in color, and became black after a reaction period of several hours. Further evidence of the oxidation of the praseodymium oxides by ozone was obtained from an observed decrease in the paramagnetic susceptibility.

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[1] Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

[2] D. M. Gruen and J. J. Katz, A. E. C. D. 1892, March, 1948.

[3] F. L. Greenwood, *Ind. Eng. Chem., Anal. Ed.*, **17**, 446 (1945).

The Conductivity Measurements of the Aqueous Solutions from the Sulfates of Bivalent Metal and Titanium

BY S. R. PATEL

The compounds $RSO_4 \cdot Ti(SO_4)_2$ described previously[1] are hydrolyzed, by boiling with distilled water, according to the expression

$$RSO_4 \cdot Ti(SO_4)_2 + 4H_2O \longrightarrow Ti(OH)_4 + RSO_4 + 2H_2SO_4$$

The electric conductivity of the solutions so obtained has been measured and compared with that of similar solutions containing the calculated quantity of the bivalent metallic sulfate and sulfuric acid.

The general procedure and the data obtained for the compound $ZnSO_4 \cdot Ti(SO_4)_2$ taken for illustration are given below.

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[1] Mehta and Patel, THIS JOURNAL, **72**, 224 (1950).