of catalysts in each test. This was accomplished by suspending the catalysts in hardened cottonseed oil. In this form, the catalyst could be handled dry and weighed out accurately. The tests were made by adding a definite weight of the catalyst to a pressure bottle containing 50 g. of U.S.P. cottonseed oil. The bottle was attached to an Adams reductor and heated to 116 ± 1°. The bottle was evacuated and then the system was pressurized to 51 pounds per square inch and the reduction carried out in the usual manner. During the reduction the temperature was controlled between 116 and 120° by means of a jacket containing refluxing *n*-butanol. A record was kept of the pressure and time during the reduction.

Figure 1 shows aging curves for two samples of Raney nickel of the W-4[9] type. The activities shown are the initial rates of reductions carried out as described above.

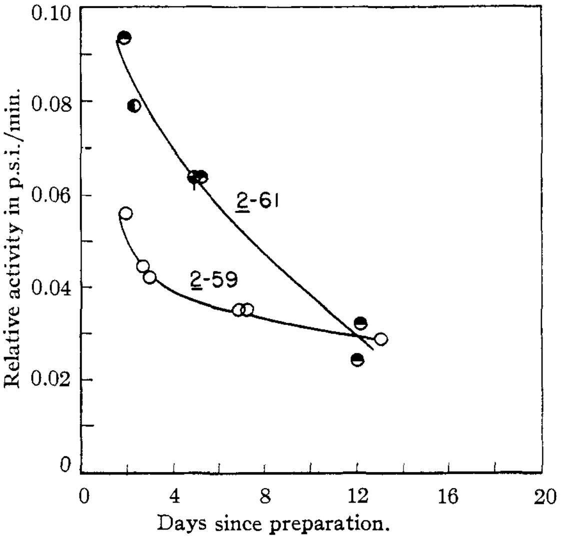

Fig. 1.—Aging of Raney nickel catalysts 2-59 and 2-61a.

The Oxygen Effect.—In order to determine what part oxygen plays in the loss of activity of this type of catalyst, another sample of W-4 Raney nickel was prepared. After the counter-current wash a small sample (about 10 g. of Ni) was removed and stored under distilled water, the bottle being kept completely filled. This sample was designated 2-69-a. The remainder of the catalyst was transferred to absolute alcohol by rinsing and decanting six times. At this point another sample was removed and stored in a bottle full of absolute ethanol as ordinarily recommended for the storage of Raney nickel. This sample was also about 10 g. and was called 2-69-b.

The remainder of the catalyst was covered with hardened cottonseed oil and warmed on the hot-plate 6 hours to remove most of the ethanol. The maximum temperature was 80°. This mixture was stirred rapidly while cooling to maintain a uniform dispersion of catalyst in oil. The solidified catalyst was broken into small particles and separated into five portions according to particle size as follows: 2-69-c larger than 4 mesh, 2-69-e (8–14 mesh), and 2-69-g (smaller than 20 mesh) were stored in air; 2-69-d (the 4–8 mesh portion) was stored in an atmosphere of nitrogen, air was rigorously excluded by a heavy layer of paraffin over the tightly closed tube; 2-69-f was from 14 to 20 mesh and was stored in an atmosphere of pure oxygen.

Tests run as soon as possible after the preparation of these catalysts showed about the same activity, as would be expected since they were all part of the same original preparation. Figure 2, however, shows that after 3 days there was already a definite difference in the catalysts stored in hardened cottonseed oil, the smaller particles losing their activity the fastest. At the end of 12 days the samples stored in alcohol, water and hardened cottonseed oil had approximately equal activities.

Comparisons were also made of catalysts 2-69-d (stored in nitrogen), 2-69-e (stored in air) and 2-69-f (stored in oxygen) 10 days after their preparation. These are given in Fig. 3. The sample stored in nitrogen retained its original activity whereas the sample stored in air was much less active. Storage in oxygen was even more harmful to the catalyst. This would indicate that the loss of activity of Raney nickel is either caused by the reaction of oxygen with the nickel or the loss of hydrogen from the catalyst (presumably in this case by reaction with oxygen to form water) or both.

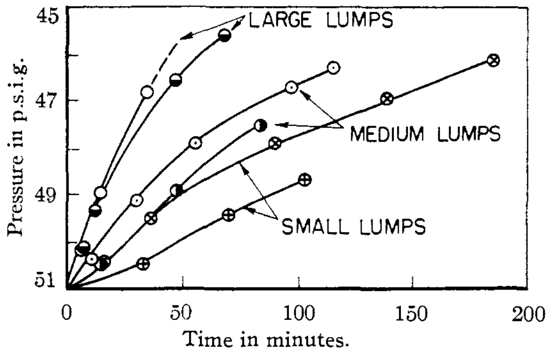

Fig. 2.—Reductions with Raney nickel 2-69; age 3 days.

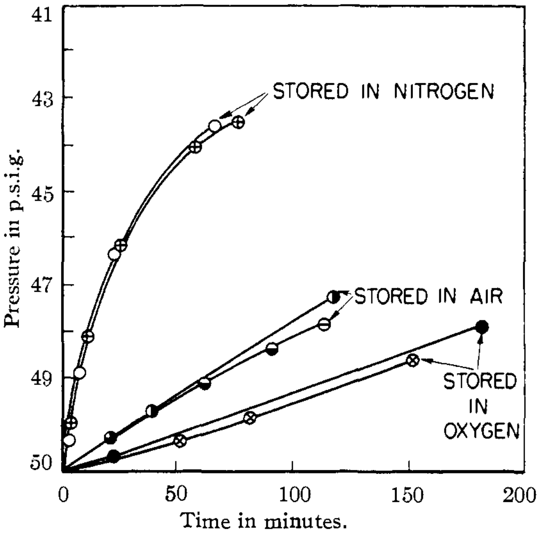

Fig. 3.—Effect of oxygen on Raney nickel 2-69; age 10 days.

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PURDUE RESEARCH FOUNDATION AND
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Esters of Benzoic and Chlorobenzoic Acids

BY EZRA MONROE AND CLARE R. HAND

The esters were prepared by the well known Schotten–Bauman reaction. The properties and analyses of the esters prepared are summarized in Table I. Yields are not reported since they would be based on single experiments and thus would not necessarily be representative of what may be obtained. These compounds have been tested against the two-spotted spider mite and Mexican bean beetle.[1]

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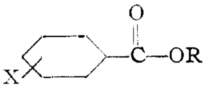
(9) Pavlic and Adkins, THIS JOURNAL, **68**, 1471 (1946).

(1) Kenaga, *J. Econ. Entomol.*, **42**, 999 (1949).

TABLE I

BENZOIC ACID ESTERS



R	X	R. I., $n^{75}D$	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.

DEPARTMENT OF CHEMISTRY
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IOWA CITY, IOWA
RECEIVED SEPTEMBER 5, 1950

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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).