the less substituted compounds and correlates directly with the difference of spectra in polar and non-polar solvents.

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Preparation and Properties of the Rare Earth Fluorides and Oxyfluorides

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Although fluorine and anhydrous hydrogen fluoride have been successfully used in the preparation of the rare earth fluorides, comparatively little work has been done on the fluorination of rare earth compounds with halogen fluorides. A recent qualitative study[1] has indicated that chlorine trifluoride and bromine trifluoride react with the rare earth oxides and oxalates and that the reaction seems to depend on the amount of moisture absorbed by the rare earth compound previous to fluorination. Since chlorine trifluoride is easily available and is comparatively easy to handle, it was decided to investigate its reactions with the rare earth oxides in greater detail.

Only the oxyfluorides of lanthanum,[2] yttrium,[2b] cerium[3] and holmium[4] are mentioned in the literature. Of these, the first two were prepared by a high temperature reaction between the corresponding oxide and fluoride,[2a,3] and the first by hydrolysis of the trifluoride.[2] Since the latter reaction appeared to present the simplest method of preparation, it was used to prepare other rare earth oxyfluorides.

Chemicals.—The rare earths were obtained as oxides from the A. D. Mackay, Inc., or from the Fairmont Chemical Co. They were guaranteed to be 99.8% pure. Whenever possible, the purity was checked by converting the oxides to the respective chlorides, and comparing the absorption spectra of their aqueous solutions with the data of Moeller and Brantley.[5] No impurities were observed in cases of lanthanum, cerium, praseodymium, neodymium, samarium and gadolinium. The available samples of other rare earth oxides were too small to permit an accurate analysis.

Chlorine trifluoride was obtained from the Harshaw Chemical Company in one pound cylinders. It was of technical grade, and probably contained some hydrogen fluoride and chlorine monofluoride as impurities.

Reactions of the Rare Earth Oxides with Chlorine Trifluoride.—The rare earth oxides in a platinum boat were heated in a muffle furnace at 800° for several hours and then quickly transferred to a nickel tube where they were allowed to cool in a current of dry nitrogen. After cooling to room temperature of approximately 25°, the oxides were rapidly weighed, reintroduced into the nickel tube and a slow stream of chlorine trifluoride was passed through the apparatus. After several minutes the chlorine trifluoride was shut off, the reaction tube was flushed with dry nitrogen, and the fluorinated sample was taken out and weighed. The increase in weight due to the conversion $M_2O_3 \rightarrow 2MF_3$, indicated that the reaction, if any, occurred within the first five minutes. No further change in the sample was observed even after passing chlorine trifluoride for one hour.

Only a slight increase in weight of the samples was no-

ticed in the reaction with lanthanum, cerium, praseodymium, neodymium and samarium oxides; on the other hand, gadolinium showed approximately 80% conversion to the fluoride. Dysprosium, erbium, thulium, ytterbium and lutetium oxides showed no increase in weight.

Since in all cases the reaction of chlorine trifluoride was, at least, incomplete, the effect of moisture was studied next. Several drops of water were added to each rare earth oxide sample before it was subjected to fluorination. After the reaction, the sample was weighed and then treated again with water and with chlorine trifluoride. In a few cases the treatment had to be repeated several times before a constant weight of the product could be obtained. The final results were generally reproducible to within 2–3%.

The lighter rare earth oxides, from lanthanum through samarium were, usually, completely fluorinated. The intermediate oxides (Eu_2O_3–Er_2O_3) showed only partial fluorination varying from 80% in the cases of gadolinium, to about 12% for erbium, while the higher oxides did not react at all. In the case of yttrium, the reaction was approximately 45% complete. These results were confirmed by the analysis of the reaction product whenever possible. Since the amount of the heavier rare earth oxides available for this investigation was of the order of magnitude of 10 mg., it was rather difficult to obtain accurate analytical results. The fact that the last members of the lanthanide series did not fluorinate was, however, checked by taking the X-ray powder diagrams of the material after fluorination. In all cases erbium, thulium, ytterbium and lutetium gave the known oxide pattern. The lighter elements on the other hand gave powder diagrams which checked with the known fluoride pattern.

It is seen from the above results that the ease of fluorination decreases with increasing atomic number of the rare earth series. The last members do not undergo any appreciable reaction under the described conditions. This behavior is not surprising since the relative basicity of the oxides decreases in going from lanthanum to lutetium.[6] Although many various reactions have been used in order to establish the sequence of basicities,[7] and the relative sequence is not always the same, it is interesting to note that, on the basis of theoretical considerations, von Hevesy predicted that the basicity of yttrium is intermediate between that of dysprosium and holmium, and the next element, erbium, should be less basic than holmium.[8] The reactivity of yttrium oxide toward chlorine trifluoride is indeed less than that of dysprosium oxide but considerably greater than that of erbium oxide.

Since the rare earth fluorides are insoluble in dilute acids, while the oxides are readily soluble, it is possible that the differences in their reactivities toward chlorine trifluoride may be utilized in the initial stages of the rare earth separation.

Rare Earth Fluorides.—The rare earth fluorides are insoluble in water and in dilute acids either at room temperature, or on boiling. They are slightly soluble in hot concentrated acids and are readily soluble in 0.5 M solution of aluminum nitrate, and in 0.1 M solution of the disodium salt of ethylenediamine tetraacetic acid, provided, in the latter case, that the solution is neutral or basic.

(1) A. I. Popov and G. Glockler, THIS JOURNAL, **74**, 1357 (1952).
(2) (a) W. Klemm and H. A. Klein, Z. anorg. Chem., **248**, 167 (1941); (b) W. H. Zachariasen, Acta Cryst., **2**, 288 (1949); (c) ibid., **4**, 231 (1951).
(3) W. Finkelnburg and A. Stein, J. Chem. Phys., **18**, 1296 (1950).
(4) A. Zalkin and D. H. Templeton, THIS JOURNAL, **75**, 2453 (1953).
(5) T. Moeller and L. C. Brantley, Anal. Chem., **21**, 1325 (1949).
(6) T. Moeller and H. E. Kremers, Chem. Revs., **37**, 97 (1945).
(7) Ref. 6, p. 130.
(8) G. von Hevesy, Z. anorg. allgem. Chem., **147**, 217 (1925).

The ease of solubility depends to a large extent upon the method of preparation of the fluorides. When they are freshly precipitated from aqueous solutions, they are much more soluble than the anhydrous material, which is, in turn, more soluble than the fluorides which were heated at several hundred degrees.

Oxyfluorides.—When the rare earth fluorides are heated in a muffle furnace to approximately 800°, they slowly lose weight. If this loss in weight is plotted against heating time, the curve shows two definite breaks. Figure 1 illustrates this in the case of neodymium fluoride.
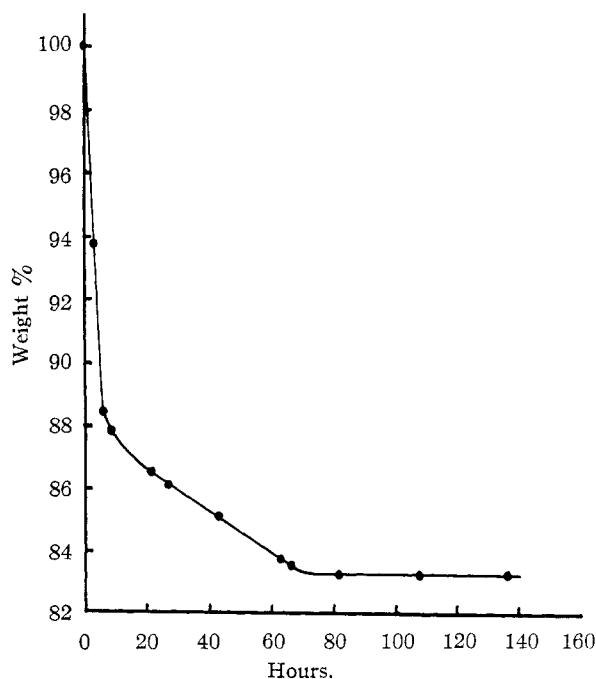

Fig. 1.—Hydrolysis of NdF$_3$ in air at 800°.

The first break in the curve corresponds to weight loss of 11.4%, which agrees quite well with the theoretical loss of 10.9% calculated for the conversion of neodymium fluoride to the oxyfluoride. The total loss in weight after 80 hours is 16.7% as compared with 16.4% calculated for the conversion of the trifluoride to the sesquioxide. The X-ray powder diffraction pattern of the final product was identical to that of the original oxide. The product also gave a negative test for fluorine with zirconium alizarin solution.

Although the hydrolysis under normal atmospheric conditions and at 800° required some 80 hours for completion, the reaction proceeded much more rapidly when the rare earth fluoride was heated in streams of air or nitrogen, which were saturated with water vapor at room temperature.

The above reaction was subsequently used to prepare the oxyfluorides of lanthanum, neodymium, samarium, europium and gadolinium. When praseodymium and cerium trifluorides were hydrolyzed by moist air, a mixture of the oxyfluoride and the higher oxide (presumably Pr$_6$O$_{11}$) was obtained in the first case, and the dioxide, in the second. Hydrolysis in a current of moist nitrogen likewise

led to the formation of higher oxides probably due to traces of oxygen present in nitrogen. Good results were, however, obtained by carrying out the reaction in a stream of moist ammonia, or in moist hydrogen. Terbium oxyfluoride also was prepared by hydrolysis in moist hydrogen.

The rare earth oxyfluorides proved to be insoluble in dilute or concentrated acids at room temperature. They dissolved slowly in hot sulfuric or perchloric acids, and consequently the fluoride could be distilled off as fluorosilicic acid, and its amount was determined in the distillate. The distillation residue was then partially neutralized and the rare earth ion was precipitated by cupferron, and ignited to the oxide. Table I summarizes the analytical results.

Table I

Analysis of Rare Earth Oxyfluorides

| Oxy-fluoride	Color	Fluorine, % Found	Theor.	Rare earth, % Found	Theor.
CeOF	Black	9.59	10.85	80.01	79.00
LaOF	Gray-lilac	10.80	10.93	79.68	79.87
PrOF	Brown	10.26	10.80	80.68	80.10
NdOF	Purple	10.54	10.60	80.21	80.43
SmOF	Gray-green	10.00	10.25	81.77	81.13
SmOF	Gray-green	10.08	10.25	81.62	81.13
EuOF	White	...	(10.16)	...	(81.28)
GdOF	Yellow	9.75	9.90	82.03	81.76
TbOF	White	...	(9.78)	...	(81.98)

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Rate of Oxidation of Hydrogen Sulfide by Hydrogen Peroxide

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The rate of reaction of dilute aqueous solutions of hydrogen peroxide with hydrogen sulfide was studied in conjunction with another problem in which it was desired to minimize the disappearance of hydrogen peroxide in its aqueous solutions saturated with hydrogen sulfide. Since no quantitative data have been published on the rate of this reaction, the results may be of some general interest. The reaction proceeds according to equation 1

$$H_2S(aq) + H_2O_2 \longrightarrow 2H_2O + S \qquad (1)$$
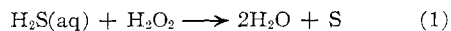
Earlier literature describes the reaction qualitatively,[1,2] the possibility of forming other products such as sulfate,[2] and the catalytic effect of iron salts.[3] No sulfate was detected in the products formed in the present studies.

Experimental

The reactor was essentially a thermostated inverted 500-cc. erlenmeyer flask. A fritted glass disc was sealed into the neck, through which hydrogen sulfide, saturated with water vapor, was continuously blown into the flask contents. The exhaust hydrogen sulfide passed through a reflux condenser sealed to the flat base of the flask (now the top of the

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