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"A" REPORT

Charles A. Kraus, Brown University

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PRELIMINARY INVESTIGATION EMPLOYING A ROTATING KILN FOR THE
PREPARATION OF RF_4 BY REACTION OF RO_3 AND "FREON-114"
($C_2F_4Cl_2$) AT ELEVATED TEMPERATURES

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A. ABSTRACT

RF_4 may be prepared successfully by passing dichlorotetrafluoroethane ("Freon-114") over R oxides at temperatures ranging between 675° and 700°C . With RO_3 made from RO_4 , the reaction is rapid and conversion to RF_4 is essentially quantitative. Under the conditions of these experiments, only a very small quantity of material is carried out of the reaction chamber (by volatilization or dusting), which is rotated during the course of the reaction. The bulk density of the products averages slightly greater than 2.5 g./cc.

The reaction vessel was made of graphite. Neither silica nor metals are suitable as materials for construction because they are attacked by the "Freon" at elevated temperatures. CaF_2 ware is unaffected by the "Freon" and could be employed in the process.

B. TECHNICAL REPORT

In previous investigations of the preparation of RF_4 by reaction of R oxides and "Freon-114", the reaction was carried out in graphite or CaF_2 boats, contained in "Pyrex" glass or "Vycor" tubes. (Report No. BT-35, CC-1717 (A-1096)). Fluorination was not always complete under these conditions, since a layer of RF_4 appeared to form over the oxide, preventing diffusion of "Freon" into the interior of the mass. Since it seemed that agitation would facilitate the reaction, a rotating kiln type of reactor was constructed, in which the reacting mass could be kept in motion so as to continuously expose a fresh surface to the action of the "Freon" vapor.

The selection of a material from which to construct the reactor offered a considerable problem. Both metal and silica are attacked by the "Freon" at elevated temperatures. Metals are badly corroded and carbon is produced by cracking of the "Freon"; silica likewise is corroded and both oily and solid cracking products are formed. Only two materials appeared unaffected, graphite and CaF_2 . Since CaF_2 ware was not readily available, the reactor was made of graphite. The latter material might prove potentially disadvantageous in certain instances, since there is danger that the product might become contaminated with carbon. It appears that the danger would be lessened on continued use, since a thin surface layer of RF_4 is formed on the walls of the reactor.

1. Reactor Design. A sketch of the reactor employed in the present investigation is given in Figure I. As may be seen from the figure, the rotating device is contained in a silica tube which, in turn, is provided with a graphite liner to protect the silica from the action of the "Freon" vapor. The reaction chamber

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Figure 1.

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is the enlarged center portion of a graphite tube extending the length of the apparatus, which could readily be disassembled for filling with oxide and for removing the product. The tube is supported at one end in a metal bearing, which permits free rotation, and at the other end by a drive shaft mounted in a gas-tight (and vacuum-tight) stuffing box. The system is closed at either end with vacuum-tight metal flanges, one portion of which is securely attached to the silica tube. "Freon" is admitted to the graphite tube through the bearing, as shown in the sketch; two vent holes are drilled through the walls of the graphite tube near the exhaust end to permit the gaseous by-products and excess "Freon" to escape. A source of dry N_2 and vacuum are attached to the "Freon" line. The reactor tube is rotated at approximately 6 R.P.M.

During reaction, the ends of the silica tube were cooled with H_2O (from points a and b outward to the flanges) to keep the temperature below a value which would damage the rubber employed as gasket material between the flanges.

Temperatures were measured with thermocouples both within the reaction chamber and between the furnace cover and the quartz containing tube. The thermocouple within the reaction chamber was shielded by a thin-walled quartz tube. Quartz proved rather unsatisfactory as a shield since the end of the tube exposed to the action of hot "Freon" was corroded through completely after ten experiments. A thin-walled tube of graphite would have proved more suitable as a shield.

A split-tube furnace was employed for heating.

2. Procedure. Oxide charges weighing between 40 and 60 g. were employed in the experiments. After the charge was introduced, the system was sealed, evacuated to remove air, filled with dry and purified N_2 and heated to $400^\circ C$. Nitrogen was passed through the system for 15 minutes at $400^\circ C$ to expel moisture. A stream of "Freon" (15 cc./sec.) was then substituted for the N_2 and the system was raised rapidly to the reaction temperature and held there for a specified time. After cooling, (with "Freon" running through during cooling) the apparatus was taken apart (only the flange at the drive shaft end was removed) and the product was examined. With a reaction time of 1.5 hours, the total time required for a complete run was approximately 4 hours.

3. Analysis of Product. The completeness of the reaction was gauged by the appearance of the product and by an analysis for total R. Nearly all the products tested were completely soluble in ammonium oxalate solution (which was not the case when the reaction was carried out in boats, l.c.), but since R_3Og was found to be soluble in this reagent, this test was not employed as a criterion of completeness of reaction. No analysis was made for fluorine, which should be done in a more critical study. Since this investigation was only exploratory, no attempt was made to determine whether the products were contaminated with carbon.

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4. Results of the Experiments. A few trial runs were first carried out to establish a temperature range within which the fluorination reaction would proceed properly. At too high a temperature, some cracking products were formed; at too low a temperature, the reaction was too slow. The optimum temperature range appeared to lie between 675° and 700°C (reactor couple temperature). In this range the products were uniformly green in color after 1 to 2 hours' heating and only the faintest trace of cracking products were found near the exhaust end of the system. The cracking probably was due primarily to the presence of the quartz thermocouple shield.

The results of a series of experiments on the fluorination reaction are presented in Table I. In the experiments recorded, the furnace temperature was varied between 775° and 860°C; both the furnace temperature and the reactor temperature, when measured, are given. Finely ground RO_3 (100F) was employed in Experiments Nos. F-31 and F-33; it will be noted that the density of the products was low (<1.9).

TABLE I

Summary of Experiments on Preparation of RF_4 in Rotating Graphite Reactor by Reaction of RO_3 and "Freon-114", $\text{C}_2\text{F}_4\text{Cl}_2$.

Exp. No.	Reaction Time Hours	Furnace Temp. °C	Reactor Temp. °C	% R in Product	Bulk Density Product
F-17	2.0	775	---	76.34	2.7
F-20	1.75	785	---	76.72	2.4
F-25	1.5	790	650	76.21	---
F-16	2.25	800	---	75.66	2.6
F-27	2.0	810	675	75.77	---
F-26	1.5	815	675	75.91	---
F-3	2.0	820	---	75.83	3.0
F-35	2.0	825	705	75.78	---
F-28	2.0	830	700	75.63	---
F-30	1.0	830	700	75.84	---
I-31*	1.0	830	690	75.73	<1.9
F-33*	1.0	830	700	75.78	<1.9
F-36	1.0	830	695	75.94	---
F-37**	2.0	830	695	75.64	---
F-32	1.25	835	695	75.71	1.9
F-21	2.0	835	---	75.98	2.5
F-4	2.0	850	---	75.69	2.8
F-7	2.0	850	---	75.74	2.7
F-22	1.5	860	---	75.80	2.6

* RO_3 , 100F

**Reactor charged with R_3O_8

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From the above table, it may be seen that, on the basis of the analysis for total R, the reaction was incomplete in the first three experiments, Nos. F-17, F-20 and F-25. The theoretical % R in RF_4 is 75.80%; higher values indicate the presence of oxygen. The average analysis for the products from reactions F-10 through F-22 was 75.78%, which is well within the limit of the analytical error for the R determination.

In reactions F-31 and F-33, finely ground RO_3 (100F) was employed. The density of the resulting product was <1.9 as compared with an average value of 2.58 g./cc. for the other products which were examined. These densities were somewhat lower than those obtained in reactions carried out in boats (l.c.).

A reaction temperature in the neighborhood of 700°C seems optimum for this reaction.

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