[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WESTERN RESERVE UNIVERSITY]

Uranium Tetrafluoride[1]

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Although some reactions of the "Freons" at elevated temperatures have been studied,[5,6] the literature does not reveal any investigation of the reaction of these gases on uranium compounds. In attempting to find new methods for the preparation of uranium hexafluoride it was discovered that Freon 12 (difluorodichloromethane) reacts quantitatively with uranium trioxide at elevated temperatures to produce a dry uranium tetrafluoride of high purity. Methods for the preparation of this compound given in the literature[7] yield products containing water and hydrogen fluoride from which it is difficult to separate the uranium tetrafluoride without some decomposition.

The over-all equation for this reaction appears to be

$$2CF_2Cl_2 + UO_3 \xrightarrow{400°} UF_4 + CO_2 + COCl_2 + Cl_2$$

Experimental.—Freon (CF_2Cl_2) was passed at a rate of about one liter per hour from a cylinder 1 (Fig. 1), through a safety manometer 2, a sulfuric acid bubbler 3 and a phosphorus pentoxide tube 4 into a reaction tube 5 of Pyrex glass (2.4 × 38 cm.). The gases leaving the reaction tube passed through a tube 6, containing powdered antimony, and then into two mercury-sealed traps 7, 8, containing sodium hydroxide solution. The powdered uranium trioxide 10, was confined between glass wool stoppers 11, which were placed about 5-cm. from the ends of the reaction tube and occupied almost the whole cross section of this tube. The reaction tube was heated externally by an electric resistance furnace 9 and was controlled by a Leeds and Northrup recording controlling potentiometer.

Uranium trioxide in the reaction tube was first heated to 400°, and dry oxygen was passed over it for about one hour.

Shortly after the oxygen had been displaced by Freon 12 the uranium trioxide slowly turned green at the end at which the Freon entered. This reaction appears to begin at about 360–380°. The temperature was maintained at 400° in most of the experiments since the original objective was to obtain uranium hexafluoride, which appears to be less stable the higher the temperature. In some experiments temperatures much higher were used but with no apparent advantage save increased speed of the reaction. Uranium tetrafluoride appears to be thermally quite stable, and in one experiment appeared to begin to decompose only when a temperature of about 1100° was reached. The gaseous products were completely absorbed by the antimony and the sodium hydroxide. This indicated that all of the Freon reacted and was transformed into other gases, since Freon 12 would not have been absorbed.

During the period that the reaction was proceeding a relatively sharp borderline between the uranium tetrafluoride and the uranium trioxide was observed as it moved along the tube.

The gaseous products of the reaction were shown by analysis to be carbon dioxide, phosgene and chlorine in the proportions required by the above equation. The yield of uranium tetrafluoride is practically quantitative.

Analysis.—It was found that uranium tetrafluoride prepared by this procedure could be brought quantitatively into solution by fine-grinding a weighed sample of about 0.1 g., contacting the powder with 15 or 20 ml. of concentrated sodium hydroxide solution and boiling for five or ten minutes. This gave a dark residue (probably $UO_2 \cdot XH_2O$) which was dissolved by sulfuric acid. The uranium analysis was carried out according to the volumetric method of Lundell and Knowles.[8,9]

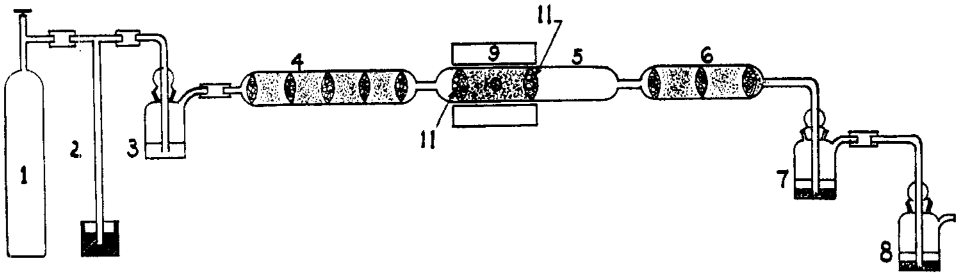

Fig. 1.

Samples of uranium tetrafluoride taken from the middle of the reaction tubes of separate experiments gave for uranium 75.51, 75.74; average 75.63; calculated 75.80%.

In order to determine the fluorine content, weighed samples of about 0.25 g. were finely powdered and fused with 0.7 g. of pure silica and a mixture of potassium and sodium carbonates. The solidified melt was dissolved and the fluoride content determined according to a modification of the lead chlorofluoride methods of Specht[10] and Hoffman and Lundell.[11] The fluorine content was found to be: 24.18, 24.22%; average 24.20%; calculated 24.197%.

Freon 11 (fluorotrichloromethane) appears to react similarly to Freon 12 yielding pure dry uranium tetra-

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[1] This investigation was carried out at Western Reserve University during the academic year, 1940–1941. Analytical results were completed at the University of Wisconsin immediately thereafter.

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[5] O. Ruff and R. Keim, *Z. anorg. Chem.*, **201**, 245 (1931).

[6] A. L. Henne, THIS JOURNAL, **60**, 2275 (1938).

[7] "Gmelin's Handbuch anorgan. Chemie," 8th edition, System No. 55, p. 120.

[8] G. E. F. Lundell and H. B. Knowles, THIS JOURNAL, **47**, 2643 (1925).

[9] G. E. F. Lundell and H. B. Knowles, *ibid.*, 2637 (1925).

[10] F. Specht, *Z. anorg. allgem. Chem.*, **231**, 181 (1937).

[11] J. I. Hoffman and G. E. F. Lundell, *Bur. Standards J. Research*, **3**, 589 (1929).

fluoride but twice as much Freon 11 is required compared with Freon 12 thus making it less attractive as a method of synthesis. At 400° $CFCl_3$ presumably reacts with uranium trioxide according to the equation

$$4CFCl_3 + UO_3 \xrightarrow{400^\circ} UF_4 + 3COCl_2 + CCl_4 + Cl_2$$

This reaction appears to begin at 350–360°.

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Summary

Difluorodichloromethane reacts quantitatively with uranium trioxide to produce pure anhydrous uranium tetrafluoride at elevated temperatures. Monofluorotrichloromethane reacts similarly but its use has the disadvantage of needing twice as much as in the case of Freon 12.

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(12) The publication of this paper was delayed for war-time security reasons.—*The Editor.*

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1037]

The Crystal Structure of Methylammonium Chloride

BY EDWARD W. HUGHES[1] AND WILLIAM N. LIPSCOMB

Values of the carbon–nitrogen single-bond distance in various compounds are of special interest because of the occurrence of this bond in amino acids, proteins and related substances. Numerous electron diffraction studies[2] of gas molecules have yielded values of about 1.47 Å., which are consistent with the usual table of covalent radii.[3] On the other hand, distances ranging from 1.39 to 1.49 Å. have recently been reported in X-ray crystal structure investigations of compounds containing tetracovalent nitrogen.[2] Because of these many different values it was thought desirable to investigate the carbon–nitrogen distance in a simple crystal in which a minimum number of parameters needed determination; methylammonium chloride appeared to be such a crystal.

Methylammonium chloride crystallizes in the tetragonal system.[4] A determination of its crystal structure has been reported by Hendricks.[5] The smallest unit of structure which he found compatible with his data had the dimensions a = 4.28 Å. (obtained from powder data) and c = 5.13 Å. (obtained from oscillation photographs); this unit contains one molecule of CH_3NH_3Cl. The atomic positions were Cl^- at 000, N at $\frac{1}{2}\frac{1}{2}z_1$, and C at $\frac{1}{2}\frac{1}{2}z_2$, with the most probable values of the parameters given as $z_1 = 0.24$ and $z_2 = 0.50$.

When the present investigation was begun it was thought necessary only to refine the above parameter values, but it soon became evident that the structure proposed by Hendricks is incorrect. The value of a_0 was found to be larger by $\sqrt{2}$ and its direction to be at 45° to that given by him; hence the unit cell actually contains two molecules of CH_3NH_3Cl.

The Unit Cell and Space Group.—The material used for this investigation was Eastman Kodak Co. Red Label Grade methylamine hydrochloride. Suitable crystals were grown from aqueous solutions by allowing the water to evaporate slowly. A needle-like specimen approximately 0.2 mm. in thickness and 1.5 mm. in length was selected for the single-crystal photographs. Early experiments indicated that the compound is somewhat deliquescent; hence the crystal which was selected was dipped in a mixture of paraffin wax and vaseline. This mixture not only provided a film which protected the crystal from the atmosphere but was also found suitable for attaching the crystal to a quartz fiber mounted on the goniometer head. The crystal was oriented by means of preliminary oscillation photographs or Laue photographs.

The dimensions of the unit cell were determined approximately from layer-line separations and more accurately from the equatorial reflections on oscillation photographs taken with filtered CuKα radiation. Oscillations about the a, c and [110] axes gave the values a_0 = 6.04 Å. and c_0 = 5.05 Å. with probable errors of 0.01 Å. These dimensions of the unit cell together with the observed density value,[5] 1.23 g./cc., require two molecules of CH_3NH_3Cl per unit cell. The calculated value of the density, 1.216 g./cc., is in satisfactory agreement with the observed value. A set of powder photographs was taken with filtered CuKα radiation by means of the multiple-film technique.[6] These photographs were successfully indexed on the new unit cell.

The only systematic extinction which occurs on

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(1) Noyes Fellow.

(2) A partial list of values obtained for this distance in various compounds is given in Table V.

(3) L. Pauling, "The Nature of the Chemical Bond," second edition, Cornell University Press, Ithaca, N. Y., 1940, p. 164. The value 1.465 Å. is given by the slightly modified values of covalent radii proposed by V. Schomaker and D. P. Stevenson, THIS JOURNAL, **63**, 37 (1941).

(4) P. Groth, "Chemische Krystallographie," Vol. I, Wilhelm Engelmann, Leipzig, 1906, p. 168.

(5) S. B. Hendricks, *Z. Krist.*, **67**, 106 (1928).

(6) J. J. deLange, J. M. Robertson, and I. Woodward, *Proc. Roy. Soc.* (London), **A171**, 398 (1939).