falling into one of two categories: (a) decomposition of a substance by two or more processes of different order, (b) decomposition of a substance followed by reaction of this substance with one or more of the reaction products. Fortunately, it is possible to distinguish between these two types from the behavior of $\log(dP_T/dt)_{t=0}$ with $\log P_0$. For type (b), the function is linear, while for type (a) it is non-linear.

For the purpose of illustrating the method, let us consider the following sequence of reactions (Type b):

$$A \longrightarrow r_1B + C \text{ (first order)} \qquad (22)$$
$$A + C \longrightarrow r_2D \quad \text{(second order)}$$

which can be described in terms of the following differential equations

$$dP_A/dt = -k_1P_A \qquad (23)$$
$$dP_B/dt = r_1k_1P_A \qquad (24)$$
$$dP_C/dt = k_1P_A - k_2P_AP_C \qquad (25)$$
$$dP_D/dt = r_2k_2P_AP_C \qquad (26)$$

When $t = 0$, $P_A = P_0$ and $P_C = 0$, therefore equations 23 through 26 can be evaluated for $t = 0$ and summed to give

$$(dP_T/dt)_{t=0} = r_1k_1P_0 \qquad (27)$$

Differentiation of equations 23 through 26 and evaluation of the results for $t = 0$ followed by summation of the resulting equations leads to the result

$$(d^2P_T/dt^2)_{t=0} = -k_1P_0[r_1k_1 - (r_2 - 2)k_2P_0] \qquad (28)$$

It can be seen from equations 27 and 28 that the ratio of the second derivative to the first derivative is a linear function of the initial pressure. This relationship provides a method for determining whether or not the assumed mechanism is applicable to the reaction being studied.

The same procedure can be applied to any reaction where the initial conditions are known. The initial rates of change of the components of the system can always be expressed in terms of these initial pressures, therefore the sum of the initial rates of change, $(dP_T/dt)_{t=0}$, can be evaluated. Since higher derivatives can always be expressed in terms of the initial pressures and previously evaluated derivatives, the procedure can be extended to as many terms as desired. Reconciliation of a particular reaction with an assumed paradigm is effected by comparing the behavior of the experimentally determined initial values of the derivatives with the behavior of the expressions for these derivatives obtained from the paradigm.

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STORRS, CONN.

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

The Preparation of UClF$_3$[1]

BY ALBERT W. SAVAGE, JR.

RECEIVED AUGUST 12, 1955

A mixed halide of tetravalent uranium was prepared by five different methods. Microscopic examination and X-ray studies conclusively demonstrated that the principal product in each case was the same compound. Analytical and X-ray evidence indicated that the correct formula for the compound is UClF$_3$.

Summary of Previous Work

The reaction between uranyl fluoride and carbon tetrachloride was first studied by Gates, Andrews, Block and Young.[2] They reported investigation of both liquid phase (at 130° in a sealed tube under pressure) and vapor phase (at 450°) reactions and found the latter to be the more convenient. Their analysis of the reaction product showed a U/F/Cl ratio of 1:2:1.63, and they assumed the material to be UCl$_2$F$_2$. They further reported that this compound disproportionated on heating, forming UCl$_4$ and UF$_4$, the UCl$_4$ being removed by distillation.

In another experiment Gregory heated a mixture of equimolar quantities of UCl$_4$ and UF$_4$ at 600° in a quartz tube under an atmosphere of helium for 15 hours.[2] At the conclusion of this period the charge was a homogeneous mass except for a very small amount of sublimate. Heating to 500° completely melted the charge. He concluded that an addition compound was formed which had a melting point around 460°, and decomposed only very slowly at temperatures as high as 600°. The lack of any trace of fluorine in the distillate was "in agreement with the observation that UF$_2$Cl$_2$, if formed, would disproportionate on heating."

All attempts to reproduce these experiments in this Laboratory have resulted instead in the formation of UClF$_3$. This compound was first prepared by reaction of chlorine gas with UF$_3$ at 315°[2] at the Ames Laboratories.

Apparatus and Materials

Except as otherwise noted, all reactions between solids and gases were carried out by placing the solid in a small platinum or porcelain boat (about 4″ long and 1/2″ wide), which was then placed in a Pyrex tube 20″ long and 1 1/4″ in diameter. This tube was equipped with a stopcock at each end and lay horizontally in a cylindrical furnace 13″ long so that both ends of the Pyrex tube extended beyond the furnace, allowing any volatile uranium compounds formed to condense on these colder surfaces. Temperatures were measured by means of a thermocouple lying under the Pyrex tube. One end of the tube was connected by means of a three-way T-bore stopcock to a helium supply and to a 5-liter, 3-necked flask equipped with an electric

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[1] Work done under the auspices of the Atomic Energy Commission.

[2] J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," National Nuclear Energy Series, Division VIII, Vol. 5, McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p. 541.

heating mantle. This flask served as a CCl_4 reservoir, through which helium gas could be bubbled. The three-way stopcock was connected to the helium supply by a rubber tube and two silica-gel filled traps immersed in liquid nitrogen to dry the helium. Between the traps and the stopcock a T connection allowed some of the helium to flow through a tube with a ground-glass inter-joint through one of the necks of the CCl_4 reservoir and down below the liquid surface. The third neck of the flask contained a tube leading also below the liquid surface to produce a pressure relief. All joints were ground glass standard taper and were lubricated with a Dow Corning silicone grease.

The deliquescent nature of both UCl_4 and $UClF_3$ made the use of a good dry-box imperative. The one used was made of stainless steel with lucite windows and neoprene gloves, the windows being sealed with zinc chromate tape. The box was equipped with a device for measuring the dew point, and no exposures of UCl_4 or $UClF_3$ were made unless the dew point was below −30°. The dryness was maintained by circulating the air over trays of magnesium perchlorate. The box was also equipped with a helium inlet and an exhaust line so that an inert atmosphere could be produced.

The reagent grade CCl_4 used was further protected from moisture by the use of anhydrous $CaCl_2$ in the reservoir. The UO_2F_2 was prepared by treating UO_3 with an excess of aqueous hydrofluoric acid in a platinum container, followed by evaporation on a steam-bath and subsequent drying in air at 250° for four hours. The uranium metal used in the preparation of UF_3 was obtained by degreasing turnings in trichloroethene and acetone, followed by cleaning with hot nitric acid. Only the brightest turnings were selected. Other materials used were reagent grade stock items.

Experimental

I. **Preparation from UO_2F_2 and CCl_4.**—The most convenient and most reliable method of preparation involved the reaction of carbon tetrachloride vapors with uranyl fluoride at 420°. This reaction was carried out in the Pyrex tube by first heating the partially dried UO_2F_2 in a helium atmosphere at 200–250° for about one hour to drive off all remaining moisture, the entire system having previously been thoroughly flushed with helium to expel any air. The temperature was then raised to 420°, and the helium flow was diverted through the CCl_4 reservoir. At the same time heat was applied to the CCl_4 so as to bring it to its boiling point. The color of the UO_2F_2 began to change at once from a lemon yellow to a brilliant yellow-green, and then to a mixture of brown and emerald green. Within a period of from 10 to 15 minutes this sequence of color changes was completed. The CCl_4 vapor flow was then cut off, and the tube and contents were allowed to digest for an hour or two at 420–450°. This digestion usually removed a good portion of the brown material from the boat to the walls of the tube by sublimation. Upon examination the brown material was found to be UCl_4. The green residue could be further purified by vacuum sublimation at 550–560°. However, this process tended to produce some UF_4 as evidenced by microscopic examination. The principal product of the reaction, as discussed below, was $UClF_3$.

II. **Preparation from UO_2F_2 and $CCl_3{\cdot}CCl{:}CCl_2$.**—In principle this second method of preparation was very similar to the first, the reducing and chlorinating agent being changed from carbon tetrachloride to hexachloropropene. In practice the reaction occurs at a much lower temperature, permitting the use of a liquid phase reaction at atmospheric pressure. The hexachloropropene containing uranyl fluoride was refluxed. When the temperature of the liquid reached 118° a greenish color began to appear in the suspended solid. The temperature was slowly raised to 175°. The reflux condenser was then converted to an ordinary distillation apparatus, and some of the trichloroacrylyl chloride, $CCl_2{=}CCl{-}COCl$, formed as the main organic by-product, was distilled off. The reaction vessel was allowed to cool in a dry-box. The suspension was filtered, and the residue was washed with CCl_4 and dried. Despite the presence of some moisture in the dry-box the product was observed to contain a large proportion of $UClF_3$.

III. **Preparation from UF_4 and UCl_4.**—In order to produce a more reactive UF_4 the hydrate $2UF_4{\cdot}5H_2O$ was first prepared and then dehydrated. The hydrate was prepared by digesting anhydrous UF_4 in 1% aqueous HF solution for three days. The light green feathery crystals were easily collected on a sintered glass filter funnel, washed and dried in the open air. Analysis and microscopic examination revealed the product to be quite pure $2UF_4{\cdot}5H_2O$. A portion of this hydrate was then heated in a platinum boat in a nickel reactor tube for 4 hours in a stream of H_2 and HF gases. This produced an anhydrous product of large specific surface.

An equimolar mixture of this UF_4 and anhydrous UCl_4 was prepared in a dry-box and sealed under an argon atmosphere in a small quartz tube. The tube was then heated to 600° and finally allowed to cool slowly. On examination it was found to contain about 80–90% $UClF_3$, the balance being $UOCl_2$, formed no doubt from the reaction of UCl_4 with some moisture inadvertently introduced.

IV. **Preparation by the Action of Chlorine Gas on UF_3.**—In order to establish further identity of the mixed halide as $UClF_3$, the latter was prepared by an established method.[2] UF_3 was first prepared by heating a stoichiometric mixture of uranium tetrafluoride and uranium metal turnings in a hydrogen atmosphere at 1050°. The product contained three phases: UF_3 (about 60% by volume), which was observed under the microscope as deep reddish violet crystals with a refractive index *ca.* 1.74, very low birefringence and a U(III) adsorption spectrum; UF_4 (about 25% by volume); and UO_2 (about 15% by volume). This mixture was then treated with chlorine gas at 350–380° for two hours. Powder X-ray diffraction patterns of the product proved conclusively that the major constituent was identical to the mixed uranous halide produced by the action of CCl_4 on UO_2F_2. This identity was also indicated by the adsorption spectra of the two products, and by the observable optical properties of the very fine-grained material produced by the action of the chlorine gas on UF_3 as compared with those of the CCl_4–UO_2F_2 product. The other constituents of the resultant mixture were some unreacted UF_3 and UF_4.

V. **Preparation from UF_4 and CCl_4.**—In order to determine whether UCl_2F_2 might not first be forming and subsequently be disproportionating into $UClF_3$ and UCl_4 in the reaction of UO_2F_2 with CCl_4, the early stages of this reaction were investigated. The process was interrupted at the first color change from yellow to a yellow-green, and a sample was examined under the microscope. The sample contained a few small, well-formed crystals of $UClF_3$. The bulk of the sample consisted of very fine-grained aggregates with mean refringence variable around 1.64. The aggregates were composed of UO_2F_2, UO_2Cl_2, UF_4, and at least one other unidentified constituent. The presence of UF_4 as the only compound of tetravalent uranium was indicated by the absorption spectrum of the aggregates and by the powder X-ray diffraction pattern.

This surprising appearance of UF_4 in the early stages of the reaction, coupled with its later disappearance, led to the belief that it might be the material from which the $UClF_3$ was formed. Accordingly a portion of the dehydrated (reactive, fine-grained) UF_4 was treated with CCl_4 vapors at 420° exactly as the UO_2F_2 had been, with special care being taken that no oxygen or moisture could get in to convert the UF_4 to UO_2F_2. Microscopic examination of the product revealed it to be a mixture of $UClF_3$, UCl_4 and UF_4, predominantly $UClF_3$.

Results and Conclusions

In all five preparations the principal product was the same brilliant emerald green salt with an optic angle of −80°, refractive indices of 1.725, 1.745 and 1.755, the mean refringence being 1.74. Single crystal X-ray studies indicate this compound to be orthorhombic with unit cell dimensions a_0 = 8.673 Å., b_0 = 8.690 Å., c_0 = 8.663 Å., and hence a cell volume of 652.9 Å.[3] The similarity of the three dimensions might easily account for the confusion with a "cubic structure with a_1 = 8.64 Å." as previously reported.[2]

The space group is either Cmca or Aba2. Symmetry of these two possible groups permits a cell content of 4 or 8 molecules but not 6. A rough density determination on an impure sample gave a value of 5.9 g./cc., which favors the cell content $8(UClF_3)$. This would give a molar refractivity of 19.8 cm.^{3}. The molar refractivity of UF_4 and UCl_4

are 15.5 and 38.6 $cm.^3$, respectively. On this basis we would expect the refractivity of UCl_2F_2 to be somewhere near the mean of these values, or 27 $cm.^3$. Therefore the formula $UClF_3$ fits the observed refractivity much better than does UCl_2F_2.

A portion of the material weighing 448.7 mg. and containing (by microscopic estimation) at least 95% of this mixed halide, the balance being entirely UCl_4, was analyzed for total U, F and Cl. The material was not found to be readily water soluble, but was dissolved in a strong, aqueous solution of NaOH to which H_2O_2 was added. Aliquot portions of this solution were checked for uranium content by a standard ceric titration, for fluorine by a triphenyl tin precipitation, and for chloride by a silver chloride gravimetric method. The results gave 371 mg. of U, 91 mg. of F, and 47.9 mg. of Cl, or 70.6% U, 20.3% F, and 10.7% Cl (a total of 101.6%). Table I compares these results with the theoretical values for the formulas indicated.

TABLE I

	Wt. %		
	U	Cl	F
As found	70.6	10.7	20.3
UCl_2F_2	68.61	20.44	10.95
$UClF_3$	72.03	10.73	17.25

The fluorine analysis, being the most uncertain, was rechecked by a different method on a new sample taken from the same mixture. The basic solution was acidified, care being taken not to heat the acid solution and drive off any HF; and from 1 liter of solution 10-ml. aliquots were steam distilled by the method of Huckaboy, Welch and Metler[3] to separate the fluorine from the uranium. The distillate was then titrated against a standard thorium nitrate solution according to the method of Willard and Winter[4] using a zirconium nitrate–alizarin indicator, with sodium fluoride as the primary standard. The results of these titrations indicated 17–19% F and thus tended to confirm the formula as $UClF_3$.

From these results, it seems most likely that previous analyses of the suspected UCl_2F_2 were made on mixtures of $UClF_3$ and UCl_4 in such proportions that the overall composition had a U:F:Cl mole ratio of closer to 1:2:2.

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[3] W. B. Huckabay, E. T. Welch and A. V. Metler, *Anal. Chem.*, **19**, 154 (1947).

[4] H. H. Willard and O. B. Winter, *Ind. Eng. Chem., Anal. Ed.*, **5**, 7 (1933).

LOS ALAMOS, NEW MEXICO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

The Formation and Decomposition of Trichloromonogermane and Germanium Dichloride[1]

BY CHARLES W. MOULTON AND JOHN G. MILLER

RECEIVED OCTOBER 20, 1955

Various methods of preparing $GeHCl_3$ have been tested. The most efficient method appears to be the reaction of gaseous HCl with GeS and an improvement of this procedure has been obtained. Both $GeHCl_3$ and $GeCl_2$ have been found more unstable than indicated in the literature. $GeHCl_3$ is apparently highly ionized in acidic aqueous solutions even at high hydrogen ion concentrations. $GeCl_2$ has been prepared as residue of the low temperature distillation of $GeHCl_3$. The dichloride has been shown to decompose into polymeric subchlorides even at low temperatures. The results have been correlated with the observations of other workers.

In efforts to prepare trichloromonogermane, $GeHCl_3$, in a high state of purity, we have been surprised to find that this substance is even less stable than the literature would indicate.[2-4] Furthermore, it appears that the product of the dissociation of $GeHCl_3$, germanium chloride, when free of $GeHCl_3$ and HCl, decomposes readily at much lower temperatures than one would expect from earlier descriptions of this compound.[2,5,6]

Even at temperatures in the neighborhood of −30°, $GeHCl_3$ loses HCl readily and when the $GeHCl_3$ has been converted in this way to $GeCl_2$, the dichloride even at these low temperatures decomposes into subchlorides of the type formed by Schwarz and Baronetzky[7,8] at high temperatures by the cracking of $GeCl_4$.

The results of this study are of interest in relation to the recent findings of Schumb and Smyth[9] who showed how readily and similarly Ag_2O and O_2 react with $GeHCl_3$ to form $GeCl_2$, and who suggested that the silver oxide might act as a chemical acceptor for HCl in this reaction. Earlier, Brewer and Dennis[6] tried, with only partial success, to prepare $GeCl_2$ by chemical removal of HCl from $GeHCl_3$. They were able, however, to prepare $GeBr_2$ from $GeHBr_3$ on removal of HBr by physical means.

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[1] Taken from a dissertation submitted by Charles W. Moulton in partial fulfillment of the requirements for the Ph.D. degree, University of Pennsylvania, 1955.

[2] L. M. Dennis, W. R. Orndorff and D. L. Tabern, *J. Phys. Chem.*, **30**, 1049 (1926).

[3] A. Tchakirian, *Bull. soc. chim.*, [4] **51**, 846 (1932).

[4] P. Venkateswarlu, R. C. Mockler and W. Gordy, *J. Chem. Phys.*, **21**, 1713 (1953).

[5] L. M. Dennis and H. L. Hunter, THIS JOURNAL, **51**, 1151 (1929).

[6] F. M. Brewer and L. M. Dennis, *J. Phys. Chem.*, **31**, 1526 (1927).

[7] R. Schwarz and E. Baronetzky, *Naturwissenschaften*, **39**, 256 (1952).

[8] R. Schwarz and E. Baronetzky, *Z. anorg. allgem. Chem.*, **275**, 1 (1954).

[9] W. C. Schumb and D. M. Smyth, THIS JOURNAL, **77**, 3003 (1955).