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The Reactions of Uranium Hexafluoride with Hydrogen Sulfide and with Carbon Disulfide[1]

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Uranium hexafluoride reacts with hydrogen sulfide at 25° to produce uranium tetrafluoride, sulfur tetrafluoride, and hydrogen fluoride. Uranium hexafluoride reacts with carbon disulfide vapor at 25° to produce uranium tetrafluoride, sulfur tetrafluoride, bistrifluoromethyl disulfide [$(CF_3)_2S_2$], and bistrifluoromethyl trisulfide [$(CF_3)_2S_3$], and at elevated temperatures the reaction also produces sulfur hexafluoride and tetrafluoromethane, CF_4. When uranium hexafluoride vapor reacts with carbon disulfide vapor at 25° in the presence of helium as a diluent, the favored perfluoroalkyl product is bistrifluoromethyl trisulfide. Uranium hexafluoride is compared with other metal fluorides with respect to their reactions with carbon disulfide.

Introduction

Ruff reported[2] that uranium hexafluoride reacts with carbon disulfide to produce uranium tetrafluoride and a gaseous product which was not identified, although it was later suggested that it was sulfur tetrafluoride.[3] Ruff did not identify the carbon compounds produced in the reaction.

Carbon disulfide reacts with various other fluorinating agents to produce a variety of compounds of carbon, sulfur, and fluorine. Identification of the carbon compounds formed in the reaction with carbon disulfide offers a means of comparing uranium hexafluoride with other fluorinating agents.

Uranium hexafluoride often acts as an oxidizing agent, being reduced to the tetrafluoride.[3,4] One exception is the hydrolysis producing uranyl fluoride, UO_2F_2.[5] The reaction between uranium hexafluoride and hydrogen sulfide was studied to determine whether it is an analog of hydrolysis, producing thiouranyl fluoride, US_2F_2 (a compound which has not yet been prepared), or whether it is a simple reduction.

Experimental

Materials.—Reagent grade carbon disulfide and a purified grade of hydrogen sulfide gas were each dried over powdered phosphorus pentoxide. Uranium hexafluoride was obtained from Oak Ridge National Laboratory. Sodium fluoride was prepared by the decomposition of sodium bifluoride pellets at 400°. Helium was dried by passage through molecular sieves.

Apparatus.—Manifolds were constructed of nickel tubing and Hoke Monel diaphragm valves No. 413 and 411 using silver-soldered joints and Teflon-gasketed flare connections. Reaction vessels were constructed from bulbs of Pyrex or nickel, which were joined in pairs by a valve. One bulb of each pair was fitted with a flare connection.

The absorption spectra of gases were observed in cylindrical nickel cells equipped with silver chloride or quartz windows for measurements in the infrared or ultraviolet region, respectively. Absorption measurements were made with a Beckman IR-4 spectrophotometer in the infrared and a Cary Model 11 spectrophotometer in the ultraviolet region.

Procedures.—Gas phase reactions were carried out by filling one bulb of each pair with uranium hexafluoride and the other bulb with either carbon disulfide or hydrogen sulfide. A reaction was initiated by opening the valve connecting the bulbs and allowing the reactants to mix by expansion or diffusion at 25°. In some cases a larger quantity of uranium hexafluoride was condensed into the same bulb with carbon disulfide or hydrogen sulfide. This resulted in an uncontrolled reaction in which the reaction vessel became quite hot. Uranium hexafluoride and hydrogen sulfide vapors were also mixed in a tubular nickel flow reactor positioned in an electric furnace.

After the reactions reached completion, the gaseous reaction mixture was expanded into the evacuated optical cell for spectral measurements. The reaction vessels were finally flushed with helium and transferred to a drybox where they were opened, and samples of the solid products of the reaction were loaded into capillary tubes for X-ray analysis.

The reaction of excess uranium hexafluoride with hydrogen sulfide produced hydrogen fluoride, which was separated from the reaction mixture by its preferential absorption in a bed of sodium fluoride pellets at 100°. The excess uranium hexafluoride was taken up by uranium tetrafluoride formed in the reaction to yield a solid intermediate uranium fluoride as indicated below. It had been established previously that pure hydrogen fluoride could be absorbed by the bed of sodium fluoride at 100° and then quantitatively (99.48%) recovered by heating to 400°. It had been established also that pure sulfur tetrafluoride could be transferred back and forth through the bed of sodium fluoride pellets at 100° with 99.85% recovery. The mixture of reaction products, sulfur tetrafluoride and hydrogen fluoride, was vacuum-distilled back and forth through the bed of pellets. After the hydrogen fluoride was absorbed by the bed at 100°, the temperature was raised to 400° to liberate the hydrogen fluoride which was then condensed and weighed. The vapor density of the reaction product gases from which the hydrogen fluoride had been removed was 106 g. per g.m.v.; the formula weight of SF_4 is 108 g. per mole.

Total sulfur in the solid products was determined by initially pyrohydrolyzing the sample,[6] catching the distillate in alkaline peroxide, and removing the excess peroxide by boiling. The sulfate in the solution was then precipitated with 4-amino-4'-chlorodiphenyl hydrochloride, separated, and titrated with

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[1] (a) Work performed under the auspices of the U. S. Atomic Energy Commission; (b) operated by the University of Chicago under Contract No. W-31-109-eng-38.

[2] O. Ruff and A. Heinzelmann, *Z. anorg. allgem. Chem.*, **72**, 63 (1911).

[3] J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," Dover Publications, Inc., New York, N. Y., 1961, pp. 440–446.

[4] (a) N. P. Galkin, B. N. Sudarikov, and V. A. Zaitsev, *At. Energ.* (USSR), **10**, (2), 149 (1961); *Soviet J. At. Energy*, **10**, (2), 143 (1961); (b) I. V. Tananaev, N. S. Nikolaev, Yu. A. Luk'yanychev, and A. A. Opalovskii, *Usp. Khim.*, **30**, 1490 (1961); *Russ. Chem. Rev.*, **30**, (12), 654 (1961).

[5] N. Hodge, "Advances in Fluorine Chemistry," Vol. 2, M. Stacey, J. C. Tatlow, and A. G. Sharpe, Ed., Butterworth Publishers Ltd., London, 1961, pp. 138–182.

[6] J. C. Warf, W. D. Cline, and R. D. Tevebaugh, *Anal. Chem.*, **26**, 342 (1954).

sodium hydroxide as described by Belcher and Fildes.[7] Free sulfur in the solid products was determined by the method of Bartlett.[8]

Results

The Reaction of Uranium Hexafluoride with Hydrogen Sulfide.—When streams of uranium hexafluoride and hydrogen sulfide vapors were mixed in a flow reactor at 305°, the reactor temperature rose to 480° and then returned rapidly to 305°. The solid product formed in the tube was a mixture of yellowish green powder and dark green pieces. X-Ray analysis showed that the yellowish green powder was uranium tetrafluoride with a minor phase of sulfur. A chemical analysis showed that the powder contained 7% elemental sulfur. The dark green pieces were uranium tetrafluoride containing only 0.8% sulfur. The infrared spectrum of the gaseous effluent indicated that sulfur tetrafluoride was formed. Hydrogen fluoride, a relatively weak absorber in the infrared region, was not detected spectrophotometrically.

When uranium hexafluoride vapor and hydrogen sulfide vapor were mixed at 25° in glass apparatus, a finely divided solid was observed to form immediately. Conclusive X-ray analysis of the nearly amorphous solid was impossible, but the pattern of halos obtained suggested that it was uranium tetrafluoride. When the reaction was initiated by condensing hydrogen sulfide onto solid uranium hexafluoride and then warming to room temperature, the solid products were crystalline and could be definitely identified by X-ray analysis. When the reactants were mixed at 25° in a ratio of 0.56 mole of uranium hexafluoride per mole of hydrogen sulfide, the solid product was uranium tetrafluoride. When the reactants were mixed at 25° in the ratio of 3.57 moles of uranium hexafluoride per mole of hydrogen sulfide, the solid product was a mixture of uranium tetrafluoride and diuranium nonafluoride, U_2F_9. In this latter experiment, 92.6 mmoles of uranium hexafluoride was mixed with 25.9 mmoles of hydrogen sulfide, and 51.1 mmoles of hydrogen fluoride was produced. It was concluded from these data that one mole of hydrogen sulfide reacts with an excess of uranium hexafluoride to produce two moles of hydrogen fluoride.

The infrared spectra of the reaction mixtures indicated that sulfur tetrafluoride was also produced in the reaction of uranium hexafluoride with hydrogen sulfide at 25°.

The Reaction of Uranium Hexafluoride with Carbon Disulfide.—When uranium hexafluoride vapor and carbon disulfide vapor were mixed in a 5:1 ratio in glass equipment at 25°, a bright green solid immediately formed and slowly turned dark brown. X-Ray powder analysis showed the major solid phase to be diuranium nonafluoride, containing minor phases of β-uranium pentafluoride and uranium tetrafluoride. The solid contained 1.7% total sulfur and 0.3% free sulfur. Spectrophotometric measurements showed that carbon disulfide had been completely consumed. When the gas phase reaction was carried out at 25° in nickel equipment with 0.370 mole of uranium hexafluoride per mole of carbon disulfide, the solid product was uranium tetrafluoride, containing 0.2% total sulfur and less than 5×10^{-2}% free sulfur. In this case the gas phase contained residual carbon disulfide. In both cases the reaction mixture contained other gases identified by the experiments described below.

When excess carbon disulfide was condensed onto 94.5 g. of uranium hexafluoride in a nickel bulb and allowed to react at 25°, an exothermic reaction resulted which produced a complex gaseous mixture. The infrared spectra of the mixture showed the presence of sulfur hexafluoride, sulfur tetrafluoride, carbon disulfide, tetrafluoromethane (CF_4), and thionyl fluoride (SOF_2). The thionyl fluoride presumably resulted from the reaction of sulfur tetrafluoride with traces of moisture or oxides. Bistrifluoromethyl disulfide, $(CF_3)_2S_2$, was one of the principal organic products, and bistrifluoromethyl trisulfide, $(CF_3)_2S_3$, possibly was present. The infrared absorption maxima of these two trifluoromethyl sulfides are quite similar.[9–11] However, the absorption peak at 1133 cm.$^{-1}$ in the spectrum of bistrifluoromethyl disulfide is useful in distinguishing it from bistrifluoromethyl trisulfide. The positions of the absorption maxima of the two compounds are quite close in the ultraviolet region also.[9] All of the reaction mixtures had an absorption peak at a wave length of 235–236 mμ, which was further evidence that the trifluoromethyl sulfides were products of the reaction.

When the reaction was carried out in the gas phase in nickel equipment with smaller quantities (1.02 g. of uranium hexafluoride), the temperature of the reaction vessel was easily kept at 25°, and the gaseous reaction mixture was less complex. The principal infrared absorption maxima of the mixture were those of the trifluoromethyl sulfides and carbon disulfide. Sulfur tetrafluoride and thionyl fluoride were formed in smaller concentration than in the case where the reaction temperature was uncontrolled. Since there is a significant difference in the boiling points of the two trifluoromethyl sulfides,[10,12] simple distillation of the reaction products resulted in a partial separation which was sufficient to demonstrate that both compounds were present. In the infrared absorption of the fraction of the reaction mixture volatile at −78°, the spectrum of bistrifluoromethyl disulfide was predominant. In the infrared absorption of the fraction of the gaseous products nonvolatile at −78°, the spectrum of bistrifluoromethyl trisulfide was predominant.

When uranium hexafluoride and carbon disulfide were each diluted with helium, and mixed in the gas phase, only bistrifluoromethyl trisulfide, carbon disulfide, and

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[9] R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 3219 (1953).

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a relatively small amount of thionyl fluoride were present as gaseous components. The infrared absorption of the fraction of the reaction mixture volatile at −78° also showed clearly the spectrum of bistrifluoromethyl trisulfide. The absorption peak of bistrifluoromethyl disulfide at 1133 cm.$^{-1}$ was not definitely resolved. Either the disulfide was absent or it was present in a small quantity relative to the trisulfide. Dilution of the reactants with helium favors the formation of bistrifluoromethyl trisulfide.

Discussion

The solid product of the reaction between uranium hexafluoride and either hydrogen sulfide or carbon disulfide is uranium tetrafluoride when excess sulfide is used. It is a mixture of uranium tetrafluoride and diuranium nonafluoride, or a mixture of diuranium nonafluoride and β-uranium pentafluoride, when excess uranium hexafluoride is used.

Intermediate uranium fluorides are formed by contacting uranium tetrafluoride with uranium hexafluoride vapor[13] so that even if the primary product is uranium tetrafluoride, it would react with excess uranium hexafluoride to form intermediate uranium fluorides. Although the results do not definitely establish the stoichiometry of the reaction between uranium hexafluoride and hydrogen sulfide at 25°, it is probably represented by the equation

$$3UF_6 + H_2S \rightarrow 3UF_4 + SF_4 + 2HF$$

The disproportionation of sulfur tetrafluoride takes place at 500°,[14] and it is probably the source of elemental sulfur in the reaction between uranium hexafluoride and hydrogen sulfide in which the temperature rose to 480°.

The reactions of several other fluorinating agents with carbon disulfide have been reported. The main product of the reaction of mercury difluoride with carbon disulfide at temperatures above 300° is bistrifluoromethyl disulfide.[15] Cobalt trifluoride reacts with carbon disulfide at 200–250° to produce trifluoromethylsulfur pentafluoride, CF_3SF_5, sulfur hexafluoride, and sulfur tetrafluoride.[16] Iodine pentafluoride reacts with carbon disulfide at 60–200° to produce bistrifluoromethyl disulfide, bistrifluoromethyl trisulfide, and sulfur tetrafluoride, and at the higher end of this temperature range, also tetrafluoromethane.[9] In the electrochemical fluorination of carbon disulfide in anhydrous hydrogen fluoride, the main product is trifluoromethylsulfur pentafluoride, and small amounts of difluoromethylenebis-(sulfur trifluoride), $CF_2(SF_3)_2$, are also produced.[17] Fluorine gas and carbon disulfide, both diluted with nitrogen, react at 40° to produce tetrafluoromethane, sulfur hexafluoride, thiocarbonyl fluoride (CSF_2), sulfur tetrafluoride, trifluoromethylsulfur pentafluoride, trifluoromethylsulfur trifluoride (CF_3SF_3), disulfur decafluoride (S_2F_{10}), difluoromethylene-(sulfur trifluoride)-(sulfur pentafluoride) ($SF_3CF_2SF_5$), and difluoromethylenebis-(sulfur pentafluoride) ($CF_2(SF_5)_2$).[18]

It has been suggested that the reactivity of uranium hexafluoride as a fluorinating agent is of the same order as cobalt trifluoride and fluorine[19]; however, uranium hexafluoride reacts with carbon disulfide to form the same products as iodine pentafluoride and mercury difluoride, both of which are weak fluorinating agents.[9,20] Cobalt trifluoride, traditionally classified as a strong fluorinating agent, is the only one of the inorganic fluorides studied which reacts with carbon disulfide to form CF_3SF_5 as the main product.

Haszeldine and Kidd[9] proposed that the reaction of carbon disulfide with iodine pentafluoride involves the intermediate formation of trifluoromethylthio radicals, $CF_3S\cdot$. Cobalt trifluoride, mercury difluoride, uranium hexafluoride, and iodine pentafluoride all react, under the appropriate conditions, with carbon disulfide to yield, as the predominant perfluoroalkyl product, a molecule formed by cleavage of one carbon–sulfur bond per carbon disulfide molecule, *e.g.*, CF_3SF_5, CF_3SSCF_3, CF_3SSSCF_3. This observation suggests that, in spite of differences in their electronic and structural configurations, cobalt trifluoride, mercury difluoride, uranium hexafluoride, and iodine pentafluoride all react with carbon disulfide to form $CF_3S\cdot$ radicals in a preliminary step. Two subsequent reaction paths are then offered to explain the difference in the type of final products formed by the action of inorganic fluorides on carbon disulfide. One hypothesis is that the combination of trifluoromethylthio radicals to form CF_3SSCF_3 and the fluorination of trifluoromethylthio radicals to form CF_3SF_5 are competing reactions, with the radical combination occurring only with weak fluorinating agents, and the formation of CF_3SF_5 occurring only with strong fluorinating agents. The alternate hypothesis is that the radical combination step takes place to form CF_3SSCF_3 in the presence of both weak and strong fluorinating agents, but that a strong agent carries the reaction further by splitting the S–S bond and fluorinating the fragments to CF_3SF_5. The feasibility of the latter hypothesis is supported by the fact[12] that both CS_2 and CF_3SSCF_3 react with cobalt trifluoride to form CF_3SF_5.

The carbon products of the reactions between carbon disulfide and the covalent fluorides discussed above are all formed by the cleavage of one or more carbon–sulfur bonds per carbon disulfide molecule. The main product of the gas phase reaction of plutonium hexafluoride

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with carbon disulfide[21] is tetrafluoromethane, also the result of cleavage of both carbon–sulfur bonds of the carbon disulfide molecule. It is only in the electrochemical fluorination of carbon disulfide in anhydrous hydrogen fluoride[17] and in the fluorination of carbon disulfide with nitrogen-diluted fluorine gas[18] that perfluoroalkyl molecules with both carbon–sulfur bonds intact are produced, *e.g.*, $CF_2(SF_5)_2$, $CF_2(SF_3)_2$, and $SF_3CF_2SF_5$.

In a comparison of the reactions of cobalt trifluoride and fluorine with ketones, Holub and Bigelow[22] found that the two fluorinating agents differed with respect to the type of compounds produced. The products of reaction with cobalt trifluoride were all formed by cleavage of the ketone molecule, whereas some of the products of reaction with fluorine were not formed by cleavage. In this respect the reaction of fluorinating agents with ketones is similar to the reaction of fluorinating agents with carbon disulfide. Holub and Bigelow[22] explained their results on the basis of a difference between the fluorination mechanisms of cobalt trifluoride and of fluorine. Although perfluoroalkyl molecules with both carbon–sulfur bonds intact are not the predominant products of the reaction of fluorine with carbon disulfide, their formation indicates that the mechanism of the fluorination of carbon disulfide with fluorine probably differs fundamentally from the mechanism of the fluorination of carbon disulfide with covalent fluorides.

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Ion-Exchange Studies in Concentrated Solutions. I. The Alkali Cations with a Sulfonic and a Carboxylic Acid Resin[1]

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An investigation of the cation-exchange behavior on Dowex-50W (sulfonic acid type) and Bio-Rex 70 (carboxylic acid type) resins of Na, Rb, and Cs tracers in 0.1 M to saturated solutions of $LiClO_4$, LiCl, $LiNO_3$, $LiC_2H_3O_2$, and of the corresponding acids and of CsCl on Dowex-50W, has been made. The exchange in dilute solutions is discussed in terms of the competition for solvation of the cation between water and the resin anionic groups. As the aqueous phase concentration rises, deviations from the simple mass-action law behavior occur; these deviations are explained in terms of the decreasing water activity, increasing cation–anion interactions in both the resin and aqueous phases, and resin invasion by nonexchange aqueous electrolyte. Individual differences among the various salts and acids are related to the different water activities and extent of anion–cation interactions present in the aqueous phase, and the variation of resin selectivity with the nature of the exchange group is treated in terms of the varying complexing ability for cations shown by the different resin anions.

Introduction

The selectivity of a moderately cross-linked sulfonic (strong) acid type cation-exchange resin for alkali and hydrogen ions in dilute aqueous solution is $Li^+ < H^+ < Na^+ < K^+ < Rb^+ < Cs^+$; a discussion of the various models which have been advanced to explain this order is given in a recent book by Helfferich.[2] It has been noted, however, that in concentrated solutions of strong acids, HCl,[3,4] HBr,[4] and $HClO_4$,[4] this order becomes reversed, and a reversal has been reported for 13 M LiCl[5,6] also. In the original discussion of the reversal of the elution order in concentrated HCl solutions[3] it was suggested that disruption of the solvation shell of the ions, that is, ion dehydration, was the principal reason for the inversion, with the invasion of the resin by nonexchange electrolyte, the shrinkage of the resin, and possible interaction with the chloride anions playing secondary roles.

In order to investigate more fully the effects of the water activity and of the nature of the anion on this reversal, a study of the distribution of sodium and cesium, and in some cases rubidium, tracers between a strong (sulfonic) acid resin and solutions of $HClO_4$, HNO_3, HCl, and $HC_2H_3O_2$, as well as of their corresponding lithium salts, and of CsCl, has been performed and is reported upon herein. During the course of this work, studies of the $HClO_4$[4] and of the LiCl[5] systems appeared in the literature, and the results are in general agreement with the present work, although we believe more definite conclusions can be drawn from the wider scope of this paper.

Another factor which influences the selectivity of the

(1) This work was supported by the U. S. Atomic Energy Commission.

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