TABLE I

PARAHYDROGEN CONVERSION BY PLATINUM OXIDE IN
D_2O AND H_2O

Each flask contained 5.0 mg. of PtO_2, 46.4 mg. of Na_2HPO_4, 57.4 mg. of KH_2PO_4 and 5.0 ml. of either D_2O or H_2O; the final buffer concentration was 0.15 M and the pH 6.6. The experimental details of this experiment are similar to those described in reference 6.

Time (min.)	Relative parahydrogen concentration[a] in D_2O	in H_2O
0	100	100
32	101	75
61	110	60
92	107	33
123	110	25
154	111	15
185	105	13

[a] The relative parahydrogen concentration, P, is defined as $P = \dfrac{(P_t - P_\infty)}{(P_0 - P_\infty)} 100$, where P_0, P_t and P_∞ are the percentages of parahydrogen at $t = 0$, t and at equilibrium, respectively.

mation is five times more rapid than D_2 formation with *Proteus vulgaris* and equal to the rate of D_2 formation with *Desulfovibrio desulfuricans*.[8] In the enzyme case, the formation of HD in greater quantities than D_2 and the absence of parahydrogen conversion in D_2O was taken as evidence for the heterolytic split of the hydrogen molecule with
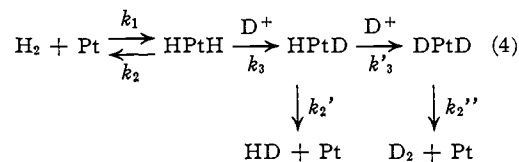
(8) A. I. Krasna, E. Riklis and D. Rittenberg, *J. Biol. Chem.*, **235**, 2717 (1960).

the formation of an enzyme hydride,[6] *i.e.*

$$E + H_2 \rightleftharpoons EH^- + H^+ \quad (3)$$
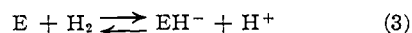
If the hydrogen molecule were split homolytically, only D_2 would be formed and very little HD.

Clearly, the activation of hydrogen by platinum is not due to a heterolytic split of the hydrogen molecule since D_2 is the predominant species. The mechanism of the platinum activation of hydrogen is probably an essentially homolytic one and can be represented by the equations

$$H_2 + Pt \underset{k_2}{\overset{k_1}{\rightleftharpoons}} HPtH \xrightarrow{D^+}{k_3} HPtD \xrightarrow{D^+}{k'_3} DPtD \quad (4)$$

$$\downarrow k_2' \qquad \downarrow k_2''$$

$$HD + Pt \qquad D_2 + Pt$$

The hydrogen atoms on the platinum in the species HPtH are probably present in the ionic form as protons[4] which exchange rapidly with the deuterons of the D_2O. The exchange of HPtD and DPtD with H^+ is negligible in a system containing 100% D_2O. The data presented suggest that k_3 and k_3' are much greater than k_2, k_2' and k_2''. This explains the large amount of D_2 formed, the small amount of HD and the absence of parahydrogen conversion in D_2O. This last fact by itself demonstrates that k_3 is very much larger than k_2. The formation of HD might be due to reaction 2 even though it is not rapid enough to bring about equilibrium.

Fluorine 18 Exchange between Uranium Hexafluoride and Metal Fluorides[1]

BY IRVING SHEFT, HERBERT H. HYMAN, RICHARD M. ADAMS AND JOSEPH J. KATZ

RECEIVED JULY 5, 1960

Uranium hexafluoride has been reported to form a compound 3 $NaF \cdot UF_6$ with sodium fluoride. The fluorine exchange between UF_6 and NaF was undertaken to further investigate the nature of this addition compound. With the radioactive fluorine F^{18} in either the NaF or UF_6, exchange experiments indicate complete exchange for a compound of the composition 2 $NaF \cdot UF_6$. In some experiments with more than one mole of UF_6 for three moles of NaF all the UF_6 was absorbed, and the extent of exchange indicated the compound 2 $NaF \cdot UF_6$ was formed. Essentially no exchange occurs when gaseous UF_6 is passed through NaF^{18} at temperatures above which the solid addition compound forms. No compound was formed, and essentially no exchange occurred, between UF_6 and LiF, KF, ZrF_4 and AgF. No compound was identified in the case of CaF_2, but a significant amount of exchange was noted.

Introduction

Sodium fluoride has been used for many years to absorb hydrogen fluoride from uranium hexafluoride. Small amounts of uranium were often found trapped on the sodium fluoride. In 1946 Martin and Albers[2] reported the formation of stable complexes between uranium hexafluoride and a number of inorganic fluorides. Further work,[3-6] primarily with the sodium fluoride complex, indi-

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) H. Martin and A. Albers, *Naturwissenschaften*, **33**, 370 (1946).

(3) H. Martin, A. Albers and H. P. Dust, *Z. anorg. u. allgem. Chem.*, **265**, 128 (1951).

(4) R. E. Worthington, United Kingdom Atomic Energy Authority, IGR-R/CA 200 (1957).

(5) G. I. Cathers, M. R. Bennett and R. L. Jolley, "Formation and Decomposition Reactions of the Complex $UF_6 \cdot 3NaF$," Paper presented at the A.C.S. meeting, Spring 1957.

cated its composition to be 3 $NaF \cdot UF_6$. A study of the exchange of fluorine between uranium hexafluoride and some of these inorganic fluorides was inaugurated in hopes of learning more about the nature of those complexes which were formed. Rapid exchange between fluorine atoms is good evidence for the introduction of fluorine atoms into the nearest neighbor coordination sphere of the uranium atom, while absence of such exchange can be taken as evidence that the uranium hexafluoride was incorporated mechanically into the metal fluoride. The use of radioactive F^{18} as a tracer for fluoride ion exchange is well established both in this Laboratory and elsewhere. The preparation, properties and some general considerations in the

(6) F. E. Massoth and W. E. Hensel, Jr., *J. Phys. Chem.*, **62**, 479 (1958).

use of this 110 minute positron-emitting nuclide have been reviewed by Bernstein and Katz[7] and Adams, Sheft and Katz.[8]

Experimental

Radioactivity Measurements.—The F^{18} for these experiments was prepared by the irradiation of fluorides with fast neutrons. The nuclear reaction is F^{19} (n, 2n)F^{18}. The fast neutrons were produced in the Argonne 60-inch cyclotron by a (d, n) reaction on a beryllium target. (Other targets were occasionally used when efficient scheduling of cyclotron time suggested such multiple use, but with the lower fast neutron flux resulting from such substitutions, somewhat longer exposure was required to obtain a useable concentration of F^{18} in the fluoride being bombarded.)

Fluorine-18 decays by positron emission, and the radiation detected is the annihilation gamma resulting from collision of the positron with electrons in the surrounding material. A sodium iodide scintillation crystal, photomultiplier and single channel analyzer were used to detect the radiation. The scintillation crystal contained a cylindrical well 3.8 cm. deep and 1.6 cm. in diameter in which a counting tube containing the sample could be inserted. These sample tubes were made of glass and attached to the vacuum line, where the manipulations were actually carried out, by means of flexible Kel-F tubing. Vacuum-tight Kel-F to glass seals were constructed by molding the end of the Kel-F tubing around the glass. The vacuum line employed was a metal and Kel-F assembly of the type used in this Laboratory for work with reactive fluorine compounds.[9]

Materials.—The uranium hexafluoride was tank material available at the laboratory. A small amount of hydrogen fluoride impurity was effectively removed by trap-to-trap distillation at $-78°$, pumping off residual vapor after each condensation.

Zirconium tetrafluoride was supplied by General Chemical Co. and used without further purification. All other fluorides were readily available reagent grade chemicals used without further purification.

Analyses.—Residues were dissolved and analyzed for uranium and other metal content by established procedures. Analyses were performed by the Analytical Group under the direction of R. Bane. We gratefully acknowledge their coöperation.

Experimental Procedure

For most of the experiments the following procedure was employed. The fluoride being studied was irradiated in a standard sample holder to generate a reasonable amount of F^{18} tracer. The fluoride was transferred to the glass counting tube, the tube attached to the vacuum line and evacuated and the tube and sample thoroughly dried in a furnace at 350° for about an hour. The sample was placed in the counter and the half-life measured to insure the absence of radiochemical impurities. A calibrated volume was filled with uranium hexafluoride gas, the pressure measured with a Booth–Cromer gauge, and the uranium hexafluoride condensed onto the non-volatile fluoride in the counting tube. The stopcock on the sample tube was shut and the tube warmed to aid complex formation. The sample tube was then allowed to cool to room temperature, replaced in the counter and its radioactivity measured. Any material volatile at room temperature was then distilled away. When finely divided sodium fluoride was treated with UF_6 by this procedure, at least one mole of UF_6 was retained for every three moles of sodium fluoride. For most of the other non-volatile fluorides, the UF_6 was recovered essentially intact at this step. Whatever the results of this preliminary evacuation, the sample was then heated to 350°. At this temperature the complex with NaF has a vapor pressure of several hundred mm. of Hg, and any UF_6 remaining and volatile at this temperature is separated from the original fluoride. The UF_6 was then condensed in a second counting tube. This tube contained nonradioactive sodium fluoride to bind the UF_6 as a solid in order to obtain the same counting geometry in both counting tubes.

Some additional experiments were performed with sodium fluoride using a modified procedure. Sodium fluoride containing radioactive F^{18} was placed in a tube maintained at 350°, and uranium hexafluoride preheated to 350° was passed through the sodium fluoride. No solid complex is formed under these conditions. After a predetermined number of passes, the uranium hexafluoride was condensed onto nonradioactive sodium fluoride in a counting tube. In two experiments F^{18} activity was introduced into uranium hexafluoride by exchange with F^{18} containing sodium fluoride. In one experiment the uranium hexafluoride containing F^{18} tracer was then allowed to react with fresh sodium fluoride. No unbound uranium hexafluoride was found, and after the complex was decomposed by heating at 350° the F^{18} activity was measured in both the recovered uranium hexafluoride and the residual sodium fluoride fractions. In the other experiment the labeled uranium hexafluoride was allowed to react with silver fluoride. In this case no compound was formed and essentially no exchange of F^{18} was observed.

Results and Discussion

The Sodium Fluoride–Uranium Hexafluoride Complex.—No significant exchange was observed in experiments in which hot uranium hexafluoride was passed through hot sodium fluoride. It is therefore reasonable that in those experiments resulting in extensive fluorine exchange, the formation of a solid compound of uranium hexafluoride and the metal fluoride occurs.

The amount of exchange may be expressed in several ways. The per cent exchange can be calculated by simply comparing the final activity in the recovered uranium hexafluoride to that which would result from a statistical distribution of F^{18} among all the fluorine atoms present. However, since it appears that exchange takes place only between fluorine atoms involved in compound formation, it seems more meaningful to assume complete exchange only between the UF_6 fluorine atoms and those fluorine atoms in sodium fluoride which become part of the compound and no exchange involving the excess sodium fluoride. Assuming exchange under these restrictions, the number of fluorine atoms associated with each uranium atom in the complex can be calculated:
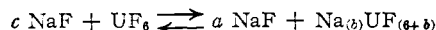
Let n be the number of moles of UF_6 recovered after exchange

cn the total number of moles of NaF.

bn the number of moles of NaF combined with the UF_6 during the exchange.

an the number of moles of excess NaF.

The exchange reaction may be written

$$c \text{ NaF} + UF_6 \rightleftharpoons a \text{ NaF} + Na_{(b)}UF_{(6+b)}$$

Let f be the total amount[10] of F^{18} in the UF_6 recovered after exchange.

i the total amount[10] of F^{18} in the NaF before exchange (if the UF_6 contained all the original F^{18}, this number is zero).

r the total amount[10] of F^{18} in the NaF after exchange (if the NaF contained all the original F^{18} then $r = i - f$).

After exchange, the specific activity of the fluorine participating in the exchange will be $f/6n$. The total activity in the sodium fluoride after exchange r will be the sum of the activity in the fraction which did not participate and that which formed a compound.

$$r = \frac{a \, n \, i}{c \, n} + \frac{b \, n \, f}{6 \, n}$$

(7) R. B. Bernstein and J. J. Katz, *Nucleonics*, **11**, 46 (1953).

(8) R. M. Adams, I. Sheft and J. J. Katz. Second U. N. Conference on the Peaceful Uses of Atomic Energy, **20**, 219 (1958).

(9) I. Sheft and J. J. Katz, *Anal. Chem.*, **29**, 1322 (1957).

(10) In counts/min. corrected for decay.

TABLE I

F[18] EXCHANGE BETWEEN UF$_6$ AND NaF

NaF (moles × 10^{-3})	Uranium (moles × 10^{-3})			F[18] Total counts/min., found after exchange, corr. for decay		Formula calcd. from exchange
	Added initially as UF$_6$	Recovered as UF$_6$	Found on NaF after exchange	NaF	UF$_6$	
11.52	3.35	2.94	0.42	33,000	21,700	Na$_{2.10}$UF$_{8.10}$
11.09	3.36	2.46	.69	33,200	16,800	Na$_{2.03}$UF$_{8.03}$
10.22	4.47	4.44	.09	14,500	23,300	Na$_{1.87}$UF$_{7.87}$
10.0^a	3.26	2.58	.68	28,200	68,300	Na$_{2.02}$UF$_{8.02}$

^{a} The F[18] was added with the UF$_6$; the residual NaF activity was corrected for the UF$_6$ remaining after the separation.

TABLE II

F[18] EXCHANGE BETWEEN UF$_6$ AND METAL FLUORIDES

Metal fluoride	Amount (moles × 10^{-3})	Uranium (moles × 10^{-3})			F[18] Total counts/min., found after exchange, corr. for decay		Exchange %^{a}
		Added initially as UF$_6$	Recovered as UF$_6$	Found on metal fluoride after exchange	Metal fluoride	UF$_6$	
NaF^b	10.0	3.66	3.44	0.08	6,800	410	8
LiF	10.0	2.59	2.54	.14	158,000	1,409	1.5
KF	9.65	4.50	3.51	.93	13,800	790	8
CaF$_2$	11.85	3.96	3.80	.12	35,500	3,300	16
ZrF$_4$	8.91	3.47	3.28	.15	41,500	250	1
AgF^c	13.93	4.18	3.98	.16	2,900^c	295,000	2.6

^{a} Calculated assuming 100% exchange requires statistical distribution of F[18] among all fluorine atoms present. ^{b} NaF and UF$_6$ were contacted at 350°; the UF$_6$ was passed through an NaF bed ten times. ^{c} The F[18] was initially in the UF$_6$ fraction; the residual AgF activity is corrected for the fluorine contained in the uranium hexafluoride residue found with the non-volatile fraction.

Rearranging and solving for b

$$b = \frac{c(i - r)}{i - cf/6}$$

A different hypothesis is also consistent with the data shown in Table I. Identical numerical results are obtained if the complex formed is assumed to contain one molecule of UF$_6$ combined with three molecules of NaF but in such a way that only three of the six fluorine atoms of the uranium hexafluoride are available for exchange with the NaF. In this case there will be $3n$ moles of NaF participating in the exchange with n moles of UF$_6$.

The UF$_6$ fraction after exchange will contain 1/2 of the fluorine participating in exchange. If the hypothesis of complete exchange of fluorine atoms in Na$_2$UF$_8$ is employed, the UF$_6$ fraction after exchange will contain 3/4 of the fluorine participating in exchange. If the specific activity before exchange is j, the specific activity in the UF$_6$ fraction after exchange will be $3 \times 1/2j$ in the first case and $2 \times 3/4j$ in the second case. Thus the two situations cannot be distinguished by these exchange observations.

In spite of support in the literature for the existence of 3NaF·UF$_6$, the hypothesis of partial exchange of fluorine from UF$_6$ is less likely in our opinion than the formation of the Na$_2$UF$_8$ compound with complete exchange. We have not found a suitable model for the 3NaF·UF$_6$ complex which makes such partial exchange plausible. As supporting evidence for the stability of a 2NaF·UF$_6$ complex, we find that mixtures of NaF and UF$_6$ with UF$_6$ in excess of a 3NaF·UF$_6$ ratio have a very low partial pressure of UF$_6$ either at room temperature or at the sublimation point of UF$_6$. Indeed, for the third experiment tabulated in Table I, the NaF/UF$_6$ ratio is 2.30. In spite of the low NaF/UF$_6$ ratio the UF$_6$ vapor pressure remained low. Ninety eight per cent. of the uranium

hexafluoride was recovered by heating at 350° indicating the retention of the UF$_6$ on the NaF as recoverable UF$_6$. In the absence of such recovery, a low UF$_6$ vapor pressure may be attributed to reaction of the UF$_6$ to form a non-volatile species by reduction or hydrolysis.

Our experience in obtaining preparations with UF$_6$ in excess of the 3NaF·UF$_6$ formula is similar to that reported by earlier workers and by Cathers, Bennett and Jolley in particular.[5] A preliminary examination of the vapor pressure of the NaF–UF$_6$ system indicates a somewhat higher UF$_6$ partial pressure in the range of composition between 3NaF·UF$_6$ and 2NaF·UF$_6$ than in mixtures of lower UF$_6$ content. Above 2NaF·UF$_6$, the observed partial pressure of UF$_6$ rises sharply. These observations may account for the usual emphasis on the 3NaF·UF$_6$ compound as reported in the literature.

The uranium hexafluoride can be recovered from the complex by heating at 350°. Recoveries of UF$_6$ up to 98% of the initial UF$_6$ were observed, but as is shown in Table I, up to 20% of the uranium can be retained with the sodium fluoride in a given experiment. This does not appear to represent decomposition of the complex to yield fluorine and a uranium fluoride with lower oxidation number but rather reaction with container materials such as is common with reactive fluorides at elevated temperatures.

X-Ray investigation of the sodium fluoride–uranium hexafluoride has shown the existence of a structure unrelated to that of either of the starting materials. As yet, however, no satisfactory description of the lattice has been achieved.

Other Complexes.—Martin, Albers and Dust also reported the formation of complexes between UF$_6$ and KF, AgF and RbF. In the present research fluorine exchange experiments were carried out be-

tween UF_6 and LiF, KF, CaF_2, ZrF_4 and AgF. In no case was any physical evidence of compound formation observed. The UF_6 did not appear to react with the fluoride and could be recovered at room temperature. The exchange values in Table II are calculated assuming complete exchange involving a statistical distribution of F^{18} among all the fluorine atoms. Data on the exchange between UF_6 gas at high temperatures and NaF are included for comparison. Essentially no exchange is observed to occur between UF_6 and LiF, ZrF_4 and AgF. The relatively large amount of uranium rendered permanently non-volatile by KF is probably due to reaction of the UF_6 with potassium hydroxide or oxide formed during the drying of the KF. In an experiment using a prefluorinated sample of KF, 90% of the UF_6 was recovered. Martin, Albers and Dust observed compound formation to the extent of $3KF \cdot 2UF_6$ after prolonged contact of the reactants at $67°$. The observations on KF in Table II therefore are not necessarily

directly contradictory with the results reported by Martin, Albers and Dust. However, the difficulty of preventing attack on the container over a period of many days, especially if any initial hydroxide is present, and the qualitative differences observed by Martin, et al., between the behavior of NaF and KF suggest that compound formation between UF_6 and KF has not been adequately established.

The situation with respect to calcium fluoride is different. Although no compound appeared to form, in agreement with the observations of Martin, Albers and Dust and over 96% of the UF_6 was recovered at room temperature, a substantial amount of exchange occurred. If the assumption is made that all the UF_6 has exchanged only once with the CaF_2, the F^{18} content of the UF_6 can be accounted for by the exchange of each mole of UF_6 with 2.3 moles of CaF_2.

The reasons for formation of complexes between UF_6 and some non-volatile metal fluorides but not others remain obscure.

The Photolysis of Acetone in a Perfluorinated Solvent at Several Temperatures[1]

BY RICHARD DOEPKER AND GILBERT J. MAINS

The photolysis of acetone in perfluorodimethylcyclobutane solutions has been studied in the 2537 Å. region at 2, 24 and 41°. Preliminary evidence is cited for self-quenching of acetone in solution. The ratio of the specific rate constants for hydrogen abstraction to recombination for methyl radicals was evaluated at each temperature and shown to be consistent with data obtained in other solvents and with a diffusion-controlled combination of methyl radicals. An apparent relationship between the material balance and the product quantum yields is noted and discussed.

Introduction

The photolysis of acetone in the vapor phase has been the subject of many careful studies[2] and is well understood at temperatures over $100°$. At lower temperatures complicating factors are evident[3-5] and the vapor phase photolysis is less certain. Liquid phase studies of the photolysis of acetone are generally limited to temperatures below $100°$ by the nature of the solvent, and, therefore, these investigations are theoretically as well as experimentally difficult. Early liquid phase studies[6,7] using pure acetone and acetone–hydrocarbon solutions demonstrated a very low quantum yield of gaseous products and indicated that reactions occurred between photo-excited acetone molecules and hydrogen-containing molecules in the liquid phase. A recent study[8] conducted in this laboratory using fluorocarbon solvents and acetone-d_6 showed the photolysis to proceed via a free radical

mechanism. A more recent study[9] of the photolysis of acetone in water solutions is in complete accord with a free radical interpretation.

The present study reports the results of the photolysis of dilute solutions of acetone in perfluorodimethylcyclobutane at several temperatures. It is expected that studies of ketone photolysis in low concentrations in inert solvents, such as those reported by Volman[9] and the present investigation, will contribute kinetic data for free radical reactions in the liquid phase and possibly give some insight into the effects of condensed media on the primary photochemical process.

Experimental

The solvent employed in this investigation was perfluorodimethylcyclobutane. While its purity has not been established, it is believed to consist of a mixture of cis- and trans-1,2-perfluorodimethylcyclobutane. The mass spectra of the vapor and liquid solvent indicated some fractionation in vaporization but failed to reveal more than very small possible traces of hydrogen in either fraction. The mass spectra were consistent with ions of the formula C_xF_y. Small side peaks which could arise from ions of the formula $C_xF_yH_z$ were attributable to C^{13} isotopes to within 1% of the isotope peak. The ultraviolet absorption spectrum showed the solvent to be optically transparent out to 2200 Å. Hence, the solvent was used without further purification. Viscosity measurements of perfluorodimethylcyclobutane were made over the temperature range 2–42° using an Ostwald viscometer.

(1) Based upon thesis research submitted by R. D. Doepker in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Carnegie Institute of Technology.

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(5) P. Ausloos and E. W. R. Steacie, Can. J. Chem., 33, 47 (1955).

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(7) P. E. Frankenburg and W. A. Noyes, Jr., THIS JOURNAL, 75, 2847 (1953).

(8) D. B. Peterson and G. J. Mains, ibid., 81, 3510 (1959).

(9) D. H. Volman and L. W. Swanson, ibid., 82, 4141 (1960).