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Nonaqueous Chemistry of Uranium Pentafluoride

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Following a report that uranium pentafluoride forms stable solutions in acetonitrile, we have investigated the remarkable behavior of β-UF_5 in a wide variety of coordinating and noncoordinating nonaqueous solvents. Nitriles, dimethyl sulfoxide, and dimethylformamide dissolve up to 0.3 g of UF_5/mL at 25 °C to form stable U(V) solutions containing UF_6^- anions and solvated UF_4^+ cations. Salts of the type $[UF_4L_x][UF_6]$ have been isolated from these solutions. Alcohols appear to form metastable solutions of U(V) from which mixed alkoxide–fluorides precipitate. Hydrocarbons, ethers, ketones, and amines are chemically attacked by β-UF_5, whereas fluorocarbons, SO_2, and CS_2 fail to react. A convenient method is also given for producing UF_6^- salts with a variety of cations. Solutions and isolated solids were characterized by elemental analysis and electronic, infrared, Raman, and EPR spectra.

Introduction

The physicochemical properties of transition-metal and actinide fluorides continue to be of great research interest.[2-4] However, comparatively little work in this area has been directed toward the behavior of actinide fluorides in organic solvents.[5-8] This deficiency is probably due in part to the rapid degradation of many organic substances by high-valent metal fluorides, by the difficulty in solubilizing the highly bridged, polymeric structures normally adopted by low-valent metal fluorides, and by the lack of convenient syntheses for intermediate valent metal fluorides. Accordingly, we were intrigued by a recent report that uranium hexafluoride has a finite lifetime in acetonitrile at ambient temperature and that the highly polymeric material β-UF_5 dissolves in acetonitrile to form stable U(V) solutions.[7,8] These reports, and our recent development of a convenient multigram synthesis of β-UF_5,[9] inspired us to investigate the behavior of β-UF_5 in a wide range of organic solvents. Our findings with more than 30 nonaqueous systems (Table I) are reported in this paper.

Table I. Behavior of UF_5 in Nonaqueous Systems

insoluble	soluble	reacts	decomposes	fails to react[a]
$CFCl_3$	CH_3CN	CH_3CH_2OH	C_6H_6	$Hg(C_6F_5)_2$
C_6F_6	C_6H_5CN	CH_3OH	ether	p-$(CN)_2C_6H_4$
HF (dry)	DMF	C_6F_5OH	tetrahydrofuran	
SO_2	Me_2SO	DME	p-dioxane	
CF_3COCl		CCl_4 (slow)	pyridine	
CF_3CO_2H		$SiCl_4$ (slow)	heptane	
CS_2		$SOCl_2$	acetone	
hexafluoroacetylacetone		C_3F_7I (slow)	18-crown-6	
C_5F_5N			$C_6F_5NH_2$	
			$C_6H_5NO_2$	
			CH_3NO_2 (slow)	

[a] In acetonitrile solution.

Experimental Section

Instrumentation. All reactions were carried out by using high-vacuum methods or an inert atmosphere of high-purity nitrogen. Transfer and handling of the air-sensitive materials were facilitated by the use of Schlenk techniques or a Vacuum Atmospheres HE-493 inert atmosphere glovebox having an oxygen- and moisture-free nitrogen atmosphere. A Cary 14 spectrometer was used for UV-visible–near-infrared studies and a Perkin-Elmer 521 spectrometer was used for infrared spectra. Raman spectra were recorded on a Cary 82 laser spectrometer using an exciting line of 15449.4 cm^{-1}. Solid-state electronic and infrared spectra were obtained as Nujol or fluorocarbon mulls between KBr plates. For Raman measurements, the solid samples were sealed in glass capillaries.

Carbon, hydrogen, and nitrogen elemental analyses and molecular weight determinations were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. Uranium and fluorine were determined as previously described.[9,10] Conductivities were measured in an inert atmosphere glovebox by using a Yellow Springs Instrument Co. YSI 3400 platinum black conductivity cell and a Barnstead PM 70CB conductivity bridge. EPR spectra were taken on a Varian V-4500 spectrometer with 100-kHz field modulation. The magnetic field was determined by using a Bruker BNM-12 tracking magnetometer and the microwave frequency was obtained with a Hewlett-Packard 5248-L electronic counter which employed a 5257A transfer oscillator.

The g values were measured at the zero of the first-derivative curve and the effects of small asymmetries in the broad (1000–1400 G) resonances reported here were neglected for the purposes of the present study. The g values are assumed to be negative; this assumption is based on the work of Hutchinson and Weinstock[11] on f^1 systems.

Materials. Uranium pentafluoride (β-form) and uranium pentaethoxide were prepared by a previously described method.[9] Sodium uranium hexaethoxide was synthesized via the reaction of $U(OC_2H_5)_5$ with $NaOC_2H_5$ by a literature procedure.[12] The alkali halides, NaF, KBr, and KF, were dried in vacuo at approximately 200 °C prior to placement in the drybox. The ammonium salt $[C_6H_5(CH_3)_3N]F$ was prepared by anion exchange of the iodide salt on Bio-Rad AG1-X2 resin with anhydrous methanol as the eluting agent. Bis(triphenylphosphin)iminium fluoride was prepared from $[(Ph_3P)_2N]Cl$ as previously described.[13]

Dried and degassed solvents were used in all reactions and solubility studies. Ethanol and methanol were dried over magnesium turnings and distilled prior to use. Dimethylformamide (DMF) was dried over BaO prior to vacuum distillation. Dimethyl sulfoxide (Me_2SO) was dried over KOH and vacuum distilled from BaO. Acetonitrile was refluxed over CaH_2 and distilled prior to use. Nitromethane, nitrobenzene, and benzonitrile were dried over phosphorus pentoxide prior to distillation. The following solvents were dried and purified as described in ref 14: carbon disulfide, carbon tetrachloride, tetrahydrofuran (THF), benzene, dimethoxyethane (DME), diethyl ether, heptane, pyridine, acetone, dioxane, and Freon 11 ($CFCl_3$). Other organic and inorganic materials were purified by high-vacuum transfer or recrystallization.

Solubility Studies. The behavior of β-UF_5 in the nonaqueous systems listed in Table I was investigated at 25 °C in the following manner. Between 0.2 and 0.5 g of β-UF_5 was weighed into a glass reaction tube in the drybox. The tube was transferred to a vacuum line and 3–25 g of the appropriate reagent was vacuum distilled onto the β-UF_5 at liquid N_2 temperature. The frozen mixture was allowed to warm slowly to room temperature. Liquids which could not be vacuum-transferred conveniently were added via syringe. In the case of nonvolatile solids (e.g., $Hg(C_6F_5)_2$), solutions of UF_5 and the reagent in acetonitrile were mixed directly at room temperature. The solubilities reported below were estimated from the near-infrared absorption spectra by utilizing the reported molar extinction coefficients for UF_6^- and the assumption of Beer's law.[15]

$[UF_4(Me_2SO)_3][UF_6]$. Uranium pentafluoride (2.06 g, 6.19 mmol) was weighed into a dry reaction tube fitted with a rubber septum. Dimethyl sulfoxide (25 mL) was introduced via syringe needle and the mixture was stirred to give an emerald green solution. The solution was stirred overnight and then heated under vacuum at 60 °C for 3 days to remove excess solvent. At this point the contents of the tube consisted of a light green powder weighing 2.76 g, corresponding to a weight gain of 34.0% (calcd 35.1% for $UF_5 \cdot 1.5Me_2SO$).

Anal. Calcd for $[UF_4(Me_2SO)_3][UF_6]$: U, 52.9; C, 8.00; H, 1.34. Found: U, 52.1; C, 8.23; H, 2.16.

$[UF_4(DMF)_3][UF_6]$. The reaction was carried out as described for the Me_2SO adduct. A yellow-green powder was obtained when the

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Table II. Infrared Spectra of UF_5 Reaction Products[a-c]

$[UF_4(Me_2SO)_3][UF_6]$	$[UF_4(DMF)_3][UF_6]$	$UF_5 \cdot CH_3CN$	$UF_5 \cdot xCH_3CN$	$UF_5 \cdot {}^3/_4C_6H_5CN$
	1650 vs, br	2330 vs	2327 vs	2265 vs
	1248 mw	2302 vs	2321 vs	2214 w, sh
1325 m, sh	1119 m	1114 w	2302 vs	1600 m, sh
1304 w, sh	1058 m	1034 s	2291 vs	1490 m, sh
1264 w, sh	941 ms	967 vs	2265 sh, w	1296 w
1000 vs, br	921 s	730 m	2245 sh, w	1203 w
957 vs, br	680 sh, s	597 vs	1110 w	1180 w
765 m	530 sh, s	580 vs	1030 m	1170 w
517 vs, br	521 vs	384 m	961 vs	1070 w
417 w	510 sh, s		942 sh	1028 w
	455 w		783 w	1000 w
	412 w		715 m	954 s
	397 w		573 s	842 s
	358 w		546 s	758 s
	300 w		525 s	682 s
			500 s	614 m
			388 s, br	563 vs
				546 vs
				487
				382

[a] Recorded on Nujol and/or fluorolube mulls. [b] Key: m = medium, sh = sharp, w = weak, vs = very strong, br = broad, s = strong, mw = medium weak. [c] Frequencies in wavenumbers.

reaction mixture was maintained under high vacuum for 5 days at room temperature.

Anal. Calcd for $[UF_4(DMF)_3][UF_6]$: U, 53.8; C, 12.21; H, 2.39; N, 4.75. Found: U, 52.1; C, 12.00; H, 2.40; N, 4.64.

$[UF_4(CH_3CN)_x][UF_6]$. A saturated solution, formed by the dissolution of 3.0 g (9.0 mmol) of β-UF_5 in ca. 10 mL of CH_3CN, was cooled to −20 °C and filtered to yield blue-green crystals. These crystals readily lost solvent to produce a green powder with the stoichiometry $UF_5 \cdot CH_3CN$ after several days in vacuo. The molecular weight (found 410, calcd 415) determined by vapor pressure osmometry is consistent with the formulation $[UF_4(CH_3CN)_4][UF_6]$ in acetonitrile solution. The estimated solubility of β-UF_5 in acetonitrile is 29 g/100 mL at 25 °C.

Anal. Calcd for $UF_5 \cdot CH_3CN$: U, 63.6; F, 25.4. Found: U, 64.2; F, 25.3.

$[UF_4(C_6H_5CN)_x][UF_6]$. Benzonitrile (~25 mL) was added to 1.0 g (3.00 mmol) of UF_5. The solvent was removed via high-vacuum pumping for 3 days, yielding a pale green powder with the stoichiometry $UF_5 \cdot 0.75C_6H_5CN$.

Anal. Calcd for $UF_5 \cdot 0.75C_6H_5CN$: U, 58.0; C, 15.36; H, 0.92; N, 2.56. Found: U, 59.5; C, 15.55; H, 0.94; N, 2.19.

$Na[UF_6]$. Uranium pentafluoride (2.00 g, 6.00 mmol) and NaF (0.252 g, 6.00 mmol) were combined in a 250-mL flask. Acetonitrile (ca. 150 mL) was then vacuum transferred into the flask, and the contents were allowed to warm to room temperature. With stirring of the mixture, the NaF gradually dissolved over a period of 12 h. The reaction mixture was then Schlenk filtered and cooled to −20 °C, yielding blue-green crystals. The crystals lost solvent in vacuo to yield a pale blue powder. In subsequent preparations the filtrate was taken to dryness directly, yielding primarily the rhombohedral form of $NaUF_6$ (as determined by X-ray powder diffraction).[2]

$K[UF_6]$. The reaction was carried out in a manner analogous to that for $NaUF_6$.

$[C_6H_5N(CH_3)_3][UF_6]$. To a stirred solution of UF_5 (5.23 g, 15.7 mmol) in ca. 150 mL of CH_3CN was added via syringe a solution of $[C_6H_5N(CH_3)_3]F$ in 6 mL of CH_3CN (2.68 M, 16.1 mmol). A turquoise precipitate of $[C_6H_5N(CH_3)_3]UF_6$ separated immediately, and the slurry was stirred overnight at room temperature. The precipitate was then Schlenk-filtered from the yellow supernatant. The resultant solid was stable under N_2 when moist with solvent but decomposed to a golden brown, sticky solid under high vacuum. Similar results were observed for $[(C_2H_5)_4N]F$ and other anhydrous tetraalkylammonium fluorides.[15,16]

$[(C_6H_5)_3PNP(C_6H_5)_3][UF_6]$. To a stirred solution of UF_5 (0.50 g, 1.50 mmol) in 50 mL of CH_3CN was added a solution of 0.84 g (1.51 mmol) of [PPN]F in 50 mL of CH_3CN. Stirring was continued overnight and the solvent was removed in vacuo to yield a stable, light blue-green powder.

Anal. Calcd for $[(C_6H_5)_3PNP(C_6H_5)_3][UF_6]$: C, 48.51; H, 3.40; N, 1.57. Found: C, 47.99; H, 3.55; N, 1.46.

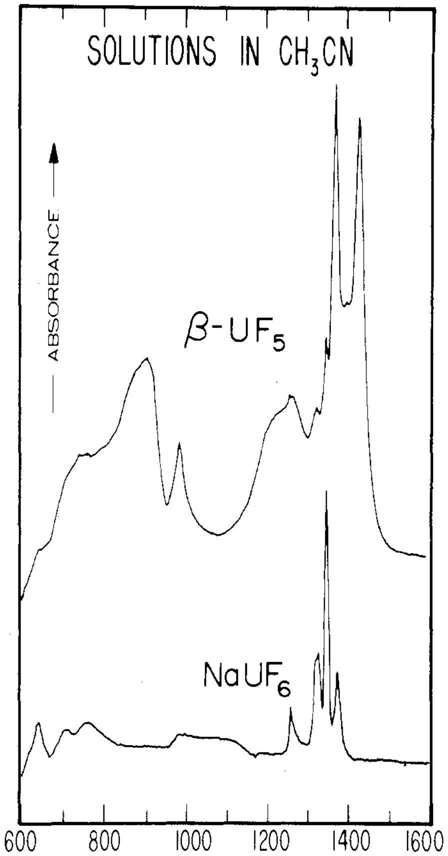

Figure 1. Electronic spectra of β-UF_5 and $NaUF_6$ in acetonitrile, showing the Γ_7–$\Gamma_{7'}$ transition characteristic of the UF_6^- anion.

Spectral Studies. The infrared and Raman and EPR spectra for the above compounds are listed in Tables II and III, respectively. Electronic spectra are tabulated in the supplementary material and appear in Figures 1 and 2.

Discussion

The behavior of β-UF_5 in more than 30 nonaqueous systems is summarized in Table I. The reactions were carried out by directly combining the reagents and stirring them at room temperature, followed by filtration and/or high-vacuum removal of the solvent. Solids and solutions were characterized

Table III. Table of *g* Values of the U(V) Species Studied by EPR

sample	$\|g\|$	sample	$\|g\|$
α-UF_5	0.892	UF_5–ethanol[c]	0.71
$NaUF_6$	0.71	β-UF_5 in Me_2SO[c]	0.76
KUF_6[a]	0.703	$Na[U(OC_2H_5)_6]$[b]	0.76
$[UF_4(Me_2SO)_3][UF_6]$	0.68	$[UF_4(CH_3C{\equiv}N)_x]UF_6]$[a]	0.70
$[UF_4(DMF)_3][UF_6]$	0.67	$[Bu_4N][UCl_6]$	1.10
UF_5–methanol[c]	0.73	UCl_5·TCAC	1.14

[a] In $CH_3C{\equiv}N$ solution. [b] In EtOH solution. [c] Line widths for the UF_5 species were 1100–1400 G. No **g** tensor anisotropy was resolved.

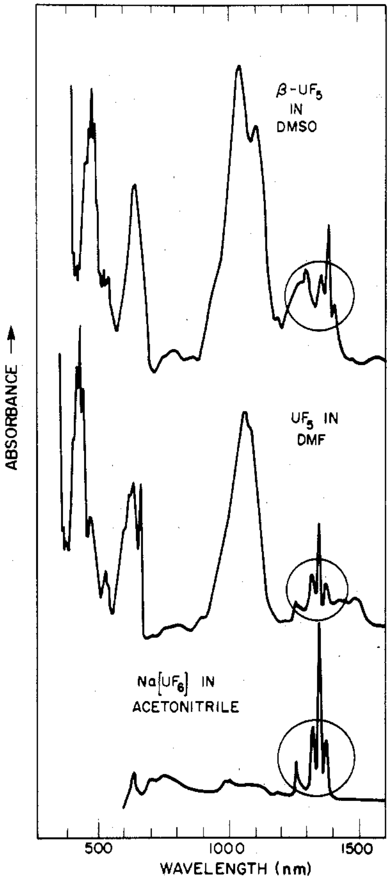

Figure 2. Electronic spectrum of β-UF_5 in Me_2SO and DMF solutions. The circle encloses the Γ_7–$\Gamma_{7'}$ transition of the UF_6^- anion.

by a combination of elemental analysis, electronic, IR, Raman, and EPR spectra. In the following sections we will discuss the different classes of reactions individually and then conclude with some generalities pertaining to the reactions of UF_5 with organic materials.

Nitriles. Berry and co-workers[8] reported that uranium pentafluoride forms a stable solution in acetonitrile, from which a neutral 1:1 monomeric adduct can be isolated. We have found the solubility of UF_5 in acetonitrile at 25 °C to be at least 0.29 g of UF_5/mL. The solutions hydrolyze readily to give UF_4 solid and uranyl solutions but are stable in the absence of air for at least several months without significant decomposition. Removal of solvent from the solution yields an unstable solvate which, on prolonged high-vacuum pumping, yields a pale blue-green solid analyzing for UF_5·CH_3CN. In the solid state this 1:1 compound is stable at 110 °C for short periods of time and decomposes at 150 °C, leaving a brown residue.

In contrast to the earlier formulation of the 1:1 compound as a neutral monomeric adduct, we favor the salt formulation $[UF_4(CH_3CN)_x][UF_6]$ in acetonitrile solution, on the basis of the following observations: (1) UF_5 in acetonitrile has a molar conductance (140 and 170 Ω^{-1} cm^2 mol^{-1} at 2.2×10^{-3} and 1.3×10^{-3} M concentrations, based on UF_6^-) indicative of a 1:1 conductor.[17] (2) In the UV–visible–near-IR spectrum, sharp bands are observed at 1323 and 1351 nm, corresponding to components of the Γ_7–$\Gamma_{7'}$ transition which is highly characteristic of the UF_6^- anion (see Figure 1).[15] Much stronger, broader bands overlap this region and also occur near 1250 and 833 nm; these absorptions are assigned to a less symmetric solvated UF_4^+ cation. (3) A broad (~1100 G) single-line EPR signal is observed in frozen acetonitrile solution at $|g| = 0.759$. This *g* value is in the region characteristic of the octahedral UF_6^- anion.[18] The solid-state electronic spectrum of UF_5·CH_3CN resembles that of the acetonitrile solution and, hence, a salt formulation probably applies for the isolated 1:1 compound as well as the solution. However, an EPR signal is not observed for solid UF_5·CH_3CN. At present we are unable to say whether this effect is due to relaxation caused by distortion of UF_6^- in the less highly solvated environment[19] or whether a significantly different structure is present in the solid.

The infrared spectra of both the 1:1 solvate and the unstable higher solvate in the 2300-cm^{-1} region are listed in Table II. (The actual spectra appear in the supplementary material.) A pattern of four strong bands is observed for the more highly solvated form, but only two strong bands remain when the material is vacuum dried to a composition consistent with the formula UF_5·CH_3CN. The bands above 2300 cm^{-1} are assigned to combination modes involving methyl deformation and C–C stretching, and the bands at or below 2300 cm^{-1} are assigned to the C–N stretching mode, in accordance with previously assigned transition-metal nitrile spectra.[20] The shift of the C–N stretching frequency to higher energy (from 2257 cm^{-1} in liquid CH_3CN) is quite general for nitriles coordinated to transition metals via the nitrogen.[20] Weak absorptions at 2240, 2260, and 2410 cm^{-1} are assignable to other combination bands.

With the exception of strong absorption in the 500–600-cm^{-1} region, other observed infrared bands for $[UF_4(CH_3CN)_x][UF_6]$ are attributable to coordinated acetonitrile. In UF_6^- salts such as $NaUF_6$, the asymmetric U–F stretching mode occurs at 520–526 cm^{-1},[15] and indeed we observe strong absorption in this region for the higher solvate, in agreement with Berry's band at 530 cm^{-1}.[8] Other strong absorptions at 500, 546, and 573 cm^{-1}, not readily assignable to ligand vibrations, are attributed to U–F vibrations of the solvated cation. The 1:1 complex lacks an absorption band near 525 cm^{-1} but strong bands do occur at 580 and 597 cm^{-1}. Coupled with the absence of an EPR signal, the infrared data are contrary to the presence of an octahedral UF_6^- anion in the 1:1 complex. Berry et al. reported the Raman spectrum of their 1:1 "adduct" to be identical in solution and in the solid state with bands at 602 and 611 cm^{-1}, in the range expected for U–F vibrations. For the 1:1 solid we find a strong Raman band at 593 cm^{-1} assignable to a ν_{U-F} vibration and weaker bands at 2314, 2303, 2787, and 2286 cm^{-1} ascribable to coordinated acetonitrile.

Attempts to observe the high-resolution ^{19}F spectrum of β-UF_5 in acetonitrile were unsuccessful. Wide-line NMR experiments revealed a single broad ^{19}F resonance 1100 ppm downfield from Teflon with a line width at maximum derivative of 1200 ppm. Similar results were obtained with β-UF_5 in ethanol. The large line widths, attributable to lifetime broadening due to the paramagnetic f^1 ion, preclude structure assignment by ^{19}F NMR.[21]

The solubility and stability of UF_5 in benzonitrile are somewhat less than in acetonitrile. The electronic absorption spectrum of the pale, blue-green solution closely matches that of the acetonitrile solution, demonstrating that similar UF_6^-

and $UF_4L_x^+$ species are present in both solutions. The solid residue remaining after high-vacuum pumping for several days analyzes for $UF_5(C_6H_5CN)_{0.75}$ and fails to give an EPR signal. The solid-state infrared spectrum contains a C–N stretch at 2265 cm^{-1} as well as a U–F stretching mode at 546 cm^{-1}. Hence, as for acetonitrile, the isolated adduct appears not to contain a symmetric UF_6^- anion.

Dimethyl Sulfoxide. β-UF_5 dissolves in dimethyl sulfoxide (Me_2SO), solubility about 0.3 g/mL (20 °C), to form emerald green solutions which are stable for at least several months. The solutions are moderately air sensitive and hydrolyze readily to give UF_4 precipitates and uranyl solutions. An electronic absorption spectrum of the UF_5/Me_2SO solution (Figure 2 and Table II) contains the triplet characteristic of UF_6^- centered at 7410 cm^{-1}, as well as much stronger and broader bands at about 10 000, 16 800, and 23 000 cm^{-1} which we attribute to solvated UF_4^+ cations. The molar conductivity of a 5.4×10^{-3} M solution was found to be 40 Ω^{-1} cm^2 mol^{-1}, well within the range for a 1:1 conductor.[17] When excess solvent is removed via high vacuum for several days, a green solid analyzing for $UF_5 \cdot 1.5Me_2SO$ remains. The electronic spectrum of a fluorocarbon mull of the solid matches closely that of the solution. The spectrum remains unchanged when the solid is dissolved in acetonitrile, showing that a large excess of acetonitrile will not displace the coordinated Me_2SO ligands. Broad, single-line EPR spectra were observed for both solid $UF_5 \cdot 1.5Me_2SO$ ($|g| = 0.68$) and solutions of β-UF_5 in Me_2SO ($|g| = 0.76$). The conductivity, analytical, and spectral data are consistent with the autoionization of β-UF_5 with Me_2SO, to give $[UF_4(Me_2SO)_3][UF_6]$ in solution and in the solid state.

The infrared spectrum of $[UF_4(Me_2SO)_3][UF_6]$ in a Nujol mull (Table II) contains strong bands at 1000 and 957 cm^{-1}, attributable to S–O stretching and CH_3 rocking vibrations, respectively.[22-24] The downward shift of ν_{SO} upon complexation (from the value 1060 cm^{-1} in pure Me_2SO) is an indication of ligation through oxygen. The values for the complex agree satisfactorily with ranges 940–960 cm^{-1} for ν_{SO} and 910–1035 cm^{-1} for δ_{CH_3} observed in actinide tetrachloride complexes with Me_2SO.[22-24] A very strong, broad absorption is centered at 517 cm^{-1} assignable to a U–F stretching mode. This band is consistent with a UF_6^- anion, with U–F stretching modes of the solvated cation lying unresolved within the absorption envelope.

Dimethylformamide. The properties of UF_5 with dimethylformamide (DMF) very closely parallel the results with Me_2SO. A molar conductance for a 4.5×10^{-3} M solution of 53 Ω^{-1} cm^2 mol^{-1} shows the substance to be a 1:1 conductor in DMF.[17] The electronic spectrum (Figure 2) contains the characteristic Γ_7–$\Gamma_{7'}$ triplet at 7407 cm^{-1} demonstrating the presence of UF_6^-. Other electronic bands, closely resembling those found in the Me_2SO complex, indicate the structure of the solvated cation to be very similar to that in the Me_2SO complex.

When excess solvent is removed via high vacuum, a green solid is obtained whose analysis is consistent with the formulation $[UF_4(DMF)_3][UF_6]$. This solid exhibits a strong, broad carbonyl stretching frequency centered at 1650 cm^{-1}, showing the presence of coordinated carbonyl groups. Other infrared bands assignable to coordinated DMF occur at lower energy. A very strong band is centered at 521 cm^{-1}, with strong shoulders at 510 and 530 cm^{-1}, assignable to U–F stretches of the UF_6^- anion and a solvated UF_4 cation. A puzzle, however, is the appearance of a strong band at 920 cm^{-1} with a shoulder at 940 cm^{-1}, in a region which should be free of DMF and uranium fluoride vibrations. The band is in the correct range for a uranyl stretch,[25] but the anhydrous/air-free conditions for the synthesis and constant appearance of the band through several preparations disfavor a uranyl formulation. In the nitrile and Me_2SO solutions this region is obscured by ligand bands, so the presence of this band in other compounds could not be checked. Consistent with the presence of UF_6^- in the solid, a single, broad EPR resonance is observed at $|g| = 0.67$. As for the acetonitrile solution and the Me_2SO solid and solution, EPR signals were not found for the cation.

Alcohols. β-UF_5 has excellent solubility in ethanol at 25 °C, forming green solutions which are stable without noticeable change for several hours. After 1 day, however, a considerable quantity of green, insoluble residue with variable elemental analysis forms. The electronic spectrum of a freshly prepared solution of β-UF_5 in ethanol (see the supplementary material) reveals the characteristic Γ_7–$\Gamma_{7'}$ transition near 7400 cm^{-1} indicative of UF_6^-, as well as broader transitions assigned to a solvated UF_4^+ cation. When volatiles are quickly removed from a fresh solution, an impure green solid is obtained which gives an EPR signal at $|g| = 0.71$.

The behavior of UF_5 in methanol is similar to that in ethanol, except that decomposition occurs more rapidly. The EPR of a rapidly prepared solid sample gives several weak signals in the $|g| = 0.73$ region.

Our results with UF_5–alcohol solutions contrast with studies showing NbF_5 to form stable solutions of NbF_6^- in ethanol.[26] We believe, without conclusive evidence, that the insoluble mixtures obtained from UF_5–alcohol solutions are probably mixed uranium(V) fluoroalkoxides. We deliberately attempted to prepare a mixed fluoroalkoxide by directly reacting β-UF_5 and $U(OC_2H_5)_5$ in 1:1 molar ratio in acetonitrile. A yellow, insoluble powder, analyzing approximately for $UF_3(OC_2H_5)_2$, was obtained. A material with the same composition and appearance was obtained from the reaction of $U(OC_2H_5)_5$ with either a 3:1 or very large excess of liquid HF. The insolubility of this presumably polymeric material has thus far hindered attempts at further characterization. No reaction was observed between pure $U(OC_2H_5)_5$ and NaF.

Nitro Compounds. Uranium pentafluoride dissolves in nitromethane to give a light blue-green solution. Although decomposition begins immediately, as evidenced by the deposition of a flocculent yellow-green precipitate, the characteristic blue-green solution is still present over a period of several days. The electronic spectrum (in the supplementary material) of UF_5 in nitromethane most closely resembles that of 1,2-dimethoxyethane and acetonitrile. A strong doublet occurs near 7300 cm^{-1} and overlies bands attributable to the Γ_7–$\Gamma_{7'}$ transitions of UF_6^-.

Uranium pentafluoride also has considerable solubility in nitrobenzene. However, decomposition is so rapid that a brown solution is formed almost immediately. An absorption near 7300 cm^{-1} resembling that of CH_3NO_2 solutions is observed in addition to strong bands at 8800 cm^{-1} and above 12 000 cm^{-1}, apparently due to decomposition products. No attempts were made to isolate a solid product from nitromethane or nitrobenzene.

Dimethoxyethane. β-UF_5 dissolves in dimethoxyethane (DME) to give solutions which are stable for approximately 1 day before noticeable decomposition occurs, yielding uncharacterized green residues. The solution electronic spectrum resembles that of ethanol solutions of UF_5. A shoulder at 1350 nm on the intense band at 1371 nm (assigned to a solvated UF_4^+ cation) is consistent with the presence of UF_6^-. No attempts were made to isolate a pure compound.

Reaction of β-UF_5 with Other Materials. The interaction of β-UF_5 with a wide variety of other organic materials was found to give either no reaction or decomposition. Liquids which do not react with β-UF_5 or dissolve β-UF_5 within a few days include C_6F_6, $CFCl_3$, CF_3CO_2H, CF_3COCl, SO_2, hexafluoroacetylacetone, and CS_2. No reaction was observed between an acetonitrile solution of UF_5 and SO_2, *p*-tetrafluoroquinone, *p*-dicyanobenzene, or bis(pentafluorophenyl)mercury. The compounds CCl_4, $SiCl_4$, and C_3F_7I react only very slowly (days) with UF_5 to give dark colored solutions. Carbon tetrachloride was previously reported to react with UF_5 to give UCl_6 and UF_4,[2] which would account for the observed color changes with the latter compounds, but in the present case other decomposition products are formed and further characterization was not attempted. Benzene, heptane, tetrahydrofuran, pyridine, acetone, dioxane, and pentafluoroaniline are rapidly attacked by β-UF_5 with reduction of the uranium.

Reactions with Fluoride Salts. We have found the solvent system UF_5/acetonitrile to be a very convenient medium for synthesis of various U(V) compounds. Berry et al. previously formed UF_6^- solutions by mixing TlF and UF_5 in acetonitrile but did not report isolated products.[8] Sodium fluoride reacts readily with UF_5 in acetonitrile to afford a solvated crystalline material which, on vacuum drying, yields $NaUF_6$ (primarily the rhombohedral form, by X-ray powder diffraction). The electronic spectrum of $NaUF_6$ in acetonitrile is identical with that reported for $[AsPh_4][UF_6]$.[15] Likewise, bis(triphenylphosphin)iminium fluoride, abbreviated [PPN]F, reacts cleanly with UF_5 in acetronitrile to give $[PPN][UF_6]$. Quaternary ammonium fluorides (e.g., $[C_6H_5N(CH_3)_3]F$) also react immediately to form a crystalline precipitate, but on vacuum drying the solid decomposes. This behavior is similar to that previously observed for $[N(C_2H_5)_4]F$.[16]

Electronic Spectra. The electronic spectra of β-UF_5 in Me_2SO, DMF, and acetonitrile are presented in Figures 1 and 2 (spectra in benzonitrile, ethanol, nitromethane, and DME appear in the supplementary material). The spectra are highly similar in that all contain features (notably the Γ_7–$\Gamma_{7'}$ triplet) characteristic of the UF_6^- anion. Other bands are also present which are attributable to solvated U(V) cations. A dominant spectral feature in each case is a strong, fairly broad pattern (usually resolved into a doublet) at about 7000–9055 cm^{-1}. A second medium, broad band also occurs at about 9300–16 700 cm^{-1}, and other medium intensity bands occur at higher energy. The pattern of bands strongly suggests that similar cation geometries are present in various solutions. On the basis of the shifts of the band near 7000–9500 cm^{-1}, a spectrochemical series $Me_2SO \geq DMF > CH_3NO_2 \geq DME > EtOH > CH_3CN$ is observed. Due to the similarity of mull and solution spectra for the DMF, Me_2SO, and nitrile compounds, similar solution and solid-state structures are indicated.

EPR Studies. Very few EPR studies have been reported on U(V) systems. This has been due in part to a paucity of available uranium(V) compounds and to the belief that relaxation effects preclude the observation of an EPR signal except for complexes of extremely high symmetry.[19] However, in the present study we have found EPR to be a very useful technique for identifying UF_6^- in a variety of environments.

Solid $NaUF_6$ at liquid-nitrogen temperature gives an EPR signal at $|g| = 0.71$, in agreement with earlier measurements for UF_6^-. Solid KUF_6, in which uranium has eightfold coordination,[2] gives no EPR spectrum at liquid-nitrogen temperature. However, a frozen acetonitrile solution of KUF_6 does give a broad asymmetric resonance at $|g| = 0.71$ and the solution electronic spectrum is characteristic of UF_6^-, providing strong evidence for the existence of octahedral UF_6^- anions in acetonitrile solution. The solids $[UF_4(L)_3][UF_6]$, where L = Me_2SO and DMF, as well as residues remaining when methanol and ethanol solutions are taken to dryness, also give EPR signals in the same region, again consistent with the presence of UF_6^- salts.

We have also observed EPR signals for two U(V) compounds which do not contain UF_6^- (Table III). α-UF_5 has a structure bridged by fluorines, consisting of linear chains of UF_6 octahedra, with D_{4h} symmetry at uranium and U–F(terminal) = 1.994 (8) Å and U–F(bridging) = 2.235 (1) Å.[1,27] An asymmetric EPR resonance at $|g| = 0.892$ is observed for this complex. On the basis of stoichiometry and electronic spectrum the salt $Na[U(OC_2H_5)_6]$ appears to have an octahedral geometry, yet the pure solid does not give an EPR signal at liquid-nitrogen temperature. However, ethanol solutions of $Na[U(OC_2H_5)_6]$ do give an EPR signal at $|g| = 0.76$. We attribute this result to solvation of the Na cation, which in the pure solid may be accomplished by bridging ethoxide groups and consequent distortion of the octahedral symmetry around uranium. The $|g|$ value and the electronic spectrum indicate the ligand field strength of ethoxide toward uranium(V) to be very similar to, but slightly weaker than, fluoride.

We failed to observe EPR signals for solid $UF_5 \cdot CH_3CN$, $UF_5 \cdot {}^3/_2CH_3CN$, U_2F_9, β-UF_5, and $U(OC_2H_5)_5$ at temperatures as low as −150 °C. Solutions of $U(OC_2H_5)_5$ in pyridine and THF also failed to give EPR signals.

Conclusion

In the assessment of the reactivity of UF_5 with a wide range of organic materials, it is clear that nitrile, Me_2SO, and DMF solutions of UF_5 have considerable stability. From our results it appears that hydrocarbons which do not contain coordinating groups are degraded by UF_5. Ethers also apparently are not sufficiently good donors to prevent attack. The unreactivity of fluorocarbons suggests that the primary point of attack of hydrocarbons is at C–H bonds, and it further appears that aromatic C–H bonds are attacked more rapidly than aliphatic C–H bonds. These reactivity patterns suggest that an area of potential promise is the use of UF_5, perhaps in acetonitrile solution, as a reagent toward a variety of organic materials.

The conductivity and EPR, electronic, and infrared spectra show that those organic materials which dissolve β-UF_5 to form stable or metastable solutions do so by autoionization of UF_5 to form UF_6^- anions and solvated UF_4^+ cations. We have observed no exceptions to this rule and, together with related observations on U(IV) halides, suggest that autoionization is a very general feature of nonaqueous actinide chemistry.[24,28] It is interesting to contrast this behavior with that of niobium and tantalum pentafluorides. TaF_5 and NbF_5 form *neutral* 1:1 adducts with acetonitrile, in contrast to ionic species with UF_5.[29–31] NbF_5 and TaF_5 have been shown by conductance and NMR measurements to form 1:2 adducts with Me_2SO and DMF which are reported to contain $[MF_4L_4][MF_6]$.[24–26,28–32] Both UF_5 and NbF_5 rapidly decompose acetone and nitrobenzene. However, 2:1 pyridine and tetrahydrothiophene adducts and neutral 1:1 adducts with dimethyl sulfide and diethyl ether were isolated with NbF_5. It appears, therefore, that the chemistry of TaF_5 and NbF_5 with organic materials in some ways resembles that of UF_5 but that UF_5 is more reactive and has a greater proclivity for autoionization. Our results indicate that an extensive U(V) chemistry awaits exploration by capitalizing on these reactivity trends in selected nonaqueous solvents.

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Registry No. UF_5, 13775-07-0; $[UF_4(Me_2SO)_3][UF_6]$, 71032-31-0; $[UF_4(DMF)_3][UF_6]$, 71032-33-2; $[UF_4(CH_3CN)_2][UF_6]$, 71032-35-4;

$Na[UF_6]$, 18918-89-3; $K[UF_6]$, 18918-88-2; $[C_6H_5N(CH_3)_3][UF_6]$, 71032-36-5; $[(C_6H_5)_3PNP(C_6H_5)_3][UF_6]$, 71032-37-6; $Na[U(OC_2H_5)_6]$, 71032-38-7; $[Bu_4N][UCl_6]$, 30723-72-9; UCl_5, 13470-21-8.

Supplementary Material Available: The infrared spectra of $UF_5 \cdot CH_3CN$ and $UF_5(CH_3CN)_x$ and the near-infrared visible spectra of UF_5 in DME, ethanol, and nitromethane and a table of near-infrared visible absorption frequencies for $Na[UF_6]$ and for UF_5 in acetonitrile, benzonitrile, Me_2SO, DMF, CH_3NO_2, DME, and ethanol (4 pages). Ordering information is given on any current masthead page.

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Mechanism of the Reaction between Vanadium(III) Ions and *p*-Aminosalicylic Acid

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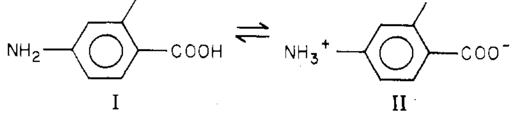
The kinetics of the vanadium(III)–*p*-aminosalicylic acid (H_2L_T) system have been investigated at 25 °C and an ionic strength of 1 M, by use of the stopped-flow technique. Rate constants for the reaction between V^{3+} and HL^- and H_3L^+ have been measured, and limits for the rate constants involving the proton-ambiguous, nonpolar H_2L and zwitterion $H_2L^{\pm}$ have been estimated. The dependence of the rate constant on the basicity of the ligand confirms the associative mechanism suggested earlier. An additional argument in favor of this mechanism is provided by the value of k_{HL^-}, 7×10^3 M^{-1} s^{-1}, which is higher than would be compatible with the alternative, dissociative, reaction path.

Introduction

We have recently[1] studied the kinetics of the complex formation between V^{3+} and salicylic acid. Our results tended to confirm the associative mechanism suggested by previous authors.[2-4] A further investigation of the kinetics of reactions involving V^{3+} seemed, however, desirable. Again[5] with the aim of comparing ligands which have identical reactive sites and differ only in their basic strength, we chose *p*-aminosalicylic acid.

The system investigated exhibits some special features since, like all amino acids, our ligand in its neutral form may be assumed to exist partly as a nonpolar molecule H_2L (I) and partly as a zwitterion $H_2L^{\pm}$ (II). This creates a new kind of proton ambiguity.



I II

We shall write H_2L_T when we do not wish to differentiate between the two forms. Clearly, $[H_2L_T] = [H_2L] + [H_2L^{\pm}]$.

Experimental Section

The *p*-aminosalicylic acid used was from Aldrich Chemical Co. ("analyzed"). Stock solutions in excess sodium hydroxide were stored under refrigeration for not more than a few days and were checked spectrophotometrically for possible decarboxylation.[7] Solutions of V(III) were prepared as described previously.[1]

The kinetic results were again[1] obtained by the stopped-flow technique; all the experimental methods were those described in our previous paper.[1] The temperature was 25 °C throughout, and the ionic strength was 1 M.

The concentrations of the cation, *a*, ranged between 2×10^{-3} and 3×10^{-2} M and were in excess over those of the ligand, *b*, which ranged between 10^{-4} and 7.5×10^{-4} M. All experiments were carried out at a wavelength of 325 nm, where the difference in absorption between the complex and the sum of the absorptions of *p*-aminosalicylic acid and of V(III) solutions, at the same concentration and pH, was at its maximum.[1]

Results

Equilibrium Constants. We again[1,5] define an apparent, $[H^+]$-dependent, formation constant of our complex, namely

$$K_{app} = \frac{[\text{complex}]}{[\text{V(III)}]([H_3L^+] + [H_2L_T] + [HL^-])} = \{[\text{complex}]K_{H1}K_{H2}[H^+]\}/\{[V^{3+}][HL^-](K_{H1}K_{H2} + K_{H1}[H^+] + [H^+]^2)(K_{OH} + [H^+])\} \quad \text{(I)}$$

where K_{H1} and K_{H2} are the dissociation constants of H_3L^+ and of H_2L_T, respectively, and K_{OH} is the hydrolysis constant of V^{3+}.

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