Some Reactions of Uranium Chloride Pentafluoride†

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The molecule UF_5Cl has been isolated, together with an excess of UF_6, in a solid matrix of Ar, N_2, or CO and characterised by its i.r. spectrum. Under these conditions it dissociates under the action of radiation having wavelengths close to 500 nm to give UF_5; $OCCl^{\bullet}$ and OCClF are also formed on photolysis in a solid CO matrix, whereas a species believed to be U_2F_{11} is formed on photolysis in a solid N_2 matrix. CCl_3F solutions of fluoride-rich mixtures of uranium(VI) chloride fluorides have been shown to function as chlorinating, fluorinating, or chlorofluorinating reagents in their reactions with various unsaturated molecules at temperatures low enough to preclude thermal decomposition of the mixed halides (< -60 °C).

In a recent paper[1] we described the preparation and characterisation of mixtures of uranium(VI) chloride fluorides, UF_nCl_{6-n} ($n = 1$—5), in Freon solutions at temperatures below *ca.* -60 °C, and presented mass spectral evidence for the existence of UF_5Cl molecules in the vapour above solid fluoride-rich mixtures of these species. The results of these and other[2-4] studies confirm that the chloride fluorides are intermediates in the reduction of UF_6 by molecular chlorides like $SiMe_3Cl$.

The first direct evidence for the formation of the species UF_nCl_{6-n} was gained from the i.r. spectra of mixtures of UF_6 and $TiCl_4$, HCl, or BCl_3 in liquid xenon held at temperatures below -60 °C.[2] Here we report the i.r. spectrum of uranium(VI) chloride pentafluoride, UF_5Cl, trapped in the presence of an excess of UF_6 by co-condensing the vapour above a solid mixture of UF_5Cl and UF_6 with an excess of argon, nitrogen, or carbon monoxide on a CsI window held at *ca.* 12 K. We have exploited the spectrum to monitor the photodissociation of the UF_5Cl molecule on exposure to radiation having wavelengths near 500 nm. Photolysis of a solid N_2 matrix gives rise to new i.r. bands attributable to UF_5 and to a novel species we believe to be U_2F_{11}. Photolysis of a solid CO matrix results in the formation of not only UF_5 and the radical $OCCl^{\bullet}$, but also OCClF derived presumably from a photolytically initiated reaction between UF_6 and $OCCl^{\bullet}$.

This paper describes also some experiments designed to elicit the response of Freon solutions of fluoride-rich mixtures of uranium(VI) chloride fluorides to the following substrates: (*i*) NO_2, (*ii*) SO_2, (*iii*) PF_3, and (*iv*) C_2F_4. For this purpose it was necessary to maintain the reaction mixtures at temperatures low enough to forestall thermal decomposition of the species UF_nCl_{6-n} (< -60 °C). Our experiments show that, according to the nature of the substrate, the mixtures can function as chlorinating, fluorinating, or chlorofluorinating agents, being significantly more reactive than UF_6 in comparable circumstances.

Experimental

Apparatus.—The apparatus and techniques used in this laboratory for the preparation and manipulation of samples containing uranium(VI) chloride fluorides[1] and for the performance of matrix-isolation experiments[5] have been described elsewhere. Gaseous samples were admitted to the matrix-isolation apparatus *via* a Teflon-FEP inlet tube to impinge on a CsI window cooled typically to *ca.* 12 K by means of a Displex closed-cycle refrigerator (Air Products, model CS 202). The cold window was enclosed in a shroud maintained at a pressure less than 10^{-7} Torr. Temperatures were measured with a chromel *vs.* iron-doped gold thermocouple or with a hydrogen vapour bulb.

The i.r. spectra of the matrix deposits were measured with a Perkin-Elmer model 580A spectrophotometer affording a resolution and accuracy not exceeding 0.5 cm^{-1}. I.r. spectra of vapours or solid products were recorded either with this instrument or with a Pye-Unicam model SP 2000 spectrophotometer (resolution and accuracy not exceeding 2 cm^{-1}).

Mass spectroscopic measurements were carried out with a V.G. Micromass 12B mass spectrometer operating with an electron beam of 70 eV and an accelerating voltage of 3.0 kV, the vapour sample being admitted *via* a nozzle at room temperature. The spectra were calibrated with reference to peaks due to air or 'L'-grade perfluorokerosene.

Photolysis of matrix samples was achieved with the output from a Hanovia Uvitron source (a high-pressure Hg arc rated at 100 W). This was operated in conjunction with a 4-cm quartz cell containing water to act as a heat filter. A Balzer interference filter was used to remove u.v. radiation with wavelengths < 375 nm; in tandem with an acidified aqueous solution of $NiSO_4$, this transmitted visible radiation with wavelengths confined mainly to the range 430—600 nm.

Chemicals.—The purification of UF_6, $SiMe_3Cl$, and CCl_3F has been described previously.[1] Commercial samples of NO (Matheson), NO_2 (B. D. H.), SO_2 (B. D. H.), PF_3 (Strem Chemicals), and C_2F_4 (Matheson) were each purified prior to use by fractional condensation *in vacuo* and the i.r. spectrum was measured to check the purity. The matrix gases Ar, N_2, and CO were used as supplied by B.O.C. (grade 'X').

Procedure for studying the Reactions of Freon Solutions containing UF_6 *and* UF_5Cl.—In a typical experiment, approximately 70 mg (0.2 mmol) of UF_6 and the required amount of $SiMe_3Cl$, each measured tensimetrically, were co-condensed at -196 °C with *ca.* 5 cm^3 of liquid CCl_3F in a conditioned FEP reaction vessel. After this mixture had been allowed to equilibrate at -63 °C, typically over a period of 2 h, it was cooled back to -196 °C and an aliquot of the chosen reagent, also measured tensimetrically, was co-condensed with the frozen solution. The reaction mixture was then warmed up to -63 °C and shaken periodically. With the completion of any reaction, those components of the reaction mixture volatile at -63 °C were removed and fractionated *in vacuo*. Each fraction was identified by the i.r. spectrum of its vapour; in some cases this was supplemented by n.m.r. or mass spectroscopic and/or vapour-pressure measurements. The amount of each

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† *Non-S.I. units employed:* Torr ≈ 133 N m^{-2}, eV ≈ 1.60×10^{-19} J.

Table 1. Wavenumbers, relative intensities, and assignments of i.r. absorptions exhibited by a mixture of UF_6 and UF_5Cl isolated in an Ar, N_2, or CO matrix at *ca.* 12 K

Ar matrix		N_2 matrix		CO matrix		Assignment	
$\tilde{\nu}$/cm^{-1} [a]	Intensity [b]	$\tilde{\nu}$/cm^{-1} [a]	Intensity [b]	$\tilde{\nu}$/cm^{-1} [a]	Intensity [b]	Molecule	Mode
1 281	w	1 285	w	1 280	w	UF_6 [c]	$\nu_1 + \nu_3$ (T_{1u})
1 146	w	1 147	w	1 142	w	UF_6 [c]	$\nu_2 + \nu_3$ ($T_{1u} + T_{2u}$)
847	mw	844	mw	843	mw	UF_6 [c]	$\nu_1 + \nu_4$ (T_{1u})
817	vw	820	vw	818	vw	UF_6 [c]	$\nu_3 + \nu_5$ ($A_{2u} + E_u + T_{1u} + T_{2u}$)
673	w	679	w	677	w	UF_6 [c]	$\nu_2 + \nu_6$ ($T_{1u} + T_{2u}$)
d	*d*	649	s (60)	647	s (67)	UF_5Cl	$\nu_1(a_1)$ $\nu(U-F_{ax})$ [e]
655—585	vs (>100)	640—595	vs (>100)	640—595	vs (>100)	UF_6 [c] + UF_5Cl [f]	$\nu_3(t_{1u})$ $\nu_2(a_1)$ $\nu(U-F_{rad})$ [e]
564	m (19)	566	m (22)	563	m (27)	UF_5Cl	$\nu_8(e)$ $\nu(U-F_{rad})$ [e]
530	m (15)	531	mw (6)	528	mw (8)	$(UF_6)_n$ [f]	$\nu(U-F)$
342	m (11)	342	m (12)	341	m (14)	$UF_5{}^{35}Cl$	$\nu_3(a_1)$ $\nu(U-Cl)$
334	w (4)	334	w (4)	333	w (5)	$UF_5{}^{37}Cl$	$\nu_3(a_1)$ $\nu(U-Cl)$

[a] Error limits ±1 cm^{-1}. [b] Numbers refer to band areas (in arbitrary units) in absorbance plots. [c] See ref. 7 for comparison. [d] Obscured by the intense band at 655—585 cm^{-1} due to UF_6. [e] ax = axial, rad = radial. [f] See text.

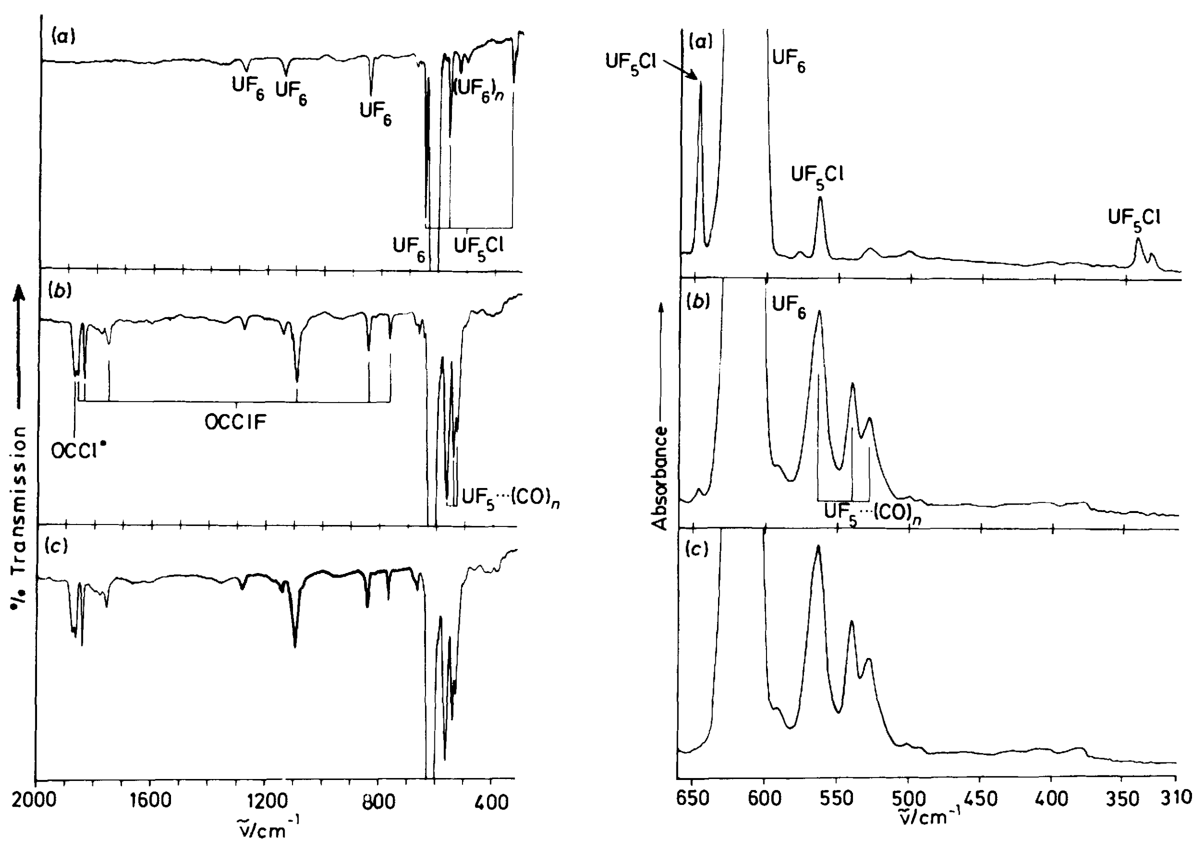


Figure 1. The regions 2 000—300 cm^{-1} and 660—310 cm^{-1} in the i.r. spectrum of a CO matrix containing UF_6 and UF_5Cl held at *ca.* 12 K: (*a*) after deposition; (*b*) after 5 min photolysis at λ ~ 500 nm; and (*c*) after a further 20 min photolysis at λ ~ 500 nm

volatile component was estimated tensimetrically, where possible, or by chemical analysis. The less volatile material was characterised by i.r. measurements augmented, in some cases, by chemical analysis.

Results

Isolation of UF_5Cl *in a Solid* Ar, N_2, *or* CO *Matrix: Infrared Spectrum.*—A two-fold excess of UF_6 was co-condensed with $SiMe_3Cl$ and CCl_3F in an FEP reaction vessel and the mixture maintained at −63 °C for *ca.* 2 h to give UF_5Cl and unchanged UF_6 as the predominant solute species.[1] Material volatile at this temperature was then evaporated *in vacuo* through an FEP U-tube enclosed by two poly(tetrafluoroethylene) valves and held at −77 °C so as to trap UF_6 and UF_5Cl but not CCl_3F and $SiMe_3F$. When *ca.* 10 mg of a red solid condensate had collected, the U-tube was isolated and connected directly to the FEP inlet tube of the matrix-isolation apparatus.

Table 2. Wavenumbers and assignments of i.r. absorptions appearing after visible photolysis ($\lambda \sim 500$ nm) of a CO matrix containing UF_6 and UF_5Cl at *ca.* 12 K

Bands appearing after photolysis		Effect of continued photolysis[c]	Assignment		$\tilde{\nu}$/cm^{-1} reported previously
$\tilde{\nu}$/cm^{-1} [a]	Intensity[b]		Molecule	Mode	
1 873	ms	↓	$OCCl^{\bullet}$	$\nu_1(a')$	1 880/1 873[d]
1 862	ms	↑	OCClF	$\nu_1(a')$	1 876[e]
1 840	ms	↑	OCClF	$\nu_2 + \nu_3(a')$	1 847[e]
1 755	m,br	↑	OCClF	$\nu_2 + \nu_6(a'')$	1 752[e]
1 094	ms	↑	OCClF	$\nu_2(a')$	1 095[e]
767	m	↑	OCClF	$\nu_3(a')$	776[e]
664	w	↑	OCClF	$\nu_6(a'')$	667[e]
591	w,sh	?	$(OCCl^{\bullet})_n$?	?	590[d]
563	s (100)	↑	$\left\{\begin{array}{l}UF_5\cdots(CO)_n\\ +\ OCCl^{\bullet}\end{array}\right.$	ν(U–F) $\nu_2(a')$	568 (100)[f] 570[d]
540	ms (64)	↑	$UF_5\cdots(CO)_n$	ν(U–F)	543 (70)[f]
528	ms (48)	↑	$UF_5\cdots(CO)_n$	ν(U–F)	533 (50)[f]

[a] Error limits ± 1 cm^{-1}. [b] Numbers in parentheses give relative areas under bands. [c] ↓ Decays, ↑ grows. [d] CO matrix, ref. 14. [e] Gas phase, ref. 15. [f] CO matrix, ref. 7*a*.

The matrix gas was introduced to the apparatus by way of the U-tube. In a typical experiment with CO as the matrix gas, the U-tube was held at *ca.* -63 °C and deposition of the gas mixture took place for 30 min at a rate of *ca.* 2 mmol h^{-1}. As indicated in Figure 1 and Table 1, the i.r. spectrum of the condensate showed, in addition to the absorptions characteristic of solid CO,[6] bands at the following wavenumbers (cm^{-1}): 1 280w, 1 142w, 843mw, 818vw, 677w, 647s, 640—595vs, 563m, 528mw, and 341m/333w (s = strong, m = medium, w = weak, v = very). That the absorptions at 1 280, 1 142, 843, 818, 677, 640—595, and 528 cm^{-1} are associated with UF_6 was established unequivocally by carrying out experiments in which CO was co-deposited with UF_6 alone under conditions otherwise identical to those described above. The very intense band at 640—595 cm^{-1} originates in the fundamental ν_3, corresponding to the t_{1u} U–F stretching mode, of UF_6.[7] The weak band at 528 cm^{-1} seems to correspond to the e_g fundamental ν_2, which should be silent in i.r. absorption but has been observed in the Raman spectrum of UF_6 vapour at 534.1 cm^{-1}.[8] Bougon and Rigny[9] have reported that the i.r. spectrum of solid UF_6 includes two weak bands at 524 and 518 cm^{-1} which they have assigned to fundamentals related to ν_2 of the isolated UF_6 molecule made weakly active in i.r. absorption by the intermolecular interactions of the solid state. It appears therefore that the matrices formed in this study contained UF_6 in sufficiently high concentrations to afford appreciable yields of aggregates $(UF_6)_n$ which are presumed to be responsible for the weak band at 528 cm^{-1}.

Systematic studies based on several experiments showed that the three remaining bands, *viz.* at 647, 563, and 341/333 cm^{-1}, shared the same growth and decay patterns implying that they arose from but a single molecule. This molecule we believe to be UF_5Cl for three reasons. (*i*) The conditions of the experiments were selected to produce UF_6 and UF_5Cl as the only uranium(VI) halides present in appreciable concentrations. The possibility that the absorber is the solvent (CCl_3F), the co-product ($SiMe_3F$), or a decomposition or disproportionation product (*e.g.* UF_5, UF_4, or UCl_6) we can rule out by comparison with the *known* i.r. spectra of these species. (*ii*) The observed wavenumbers suggest that two of the bands (at 647 and 563 cm^{-1}) originate in the U–F stretching modes of a UF_n moiety and the third (at 341/333 cm^{-1}) in a U–Cl stretching mode. Furthermore, the bands occur at energies almost coincident with those of i.r. bands attributed previously to the molecule UF_5Cl as formed in liquid xenon solution,[2] an assignment supported by simplified normal-co-ordinate calculations. (*iii*) The two components making up the doublet at 341/333 cm^{-1} had intensities in the ratio $I(341):I(333) =$ *ca.* 3:1, corresponding to the relative natural abundances of the isotopes ^{35}Cl and ^{37}Cl. For an isolated diatomic U–Cl oscillator, the ^{35}Cl–^{37}Cl isotopic shift is calculated to be 8.1 cm^{-1}, in excellent agreement with the observed doublet separation of 8 ± 1 cm^{-1}. The intensity pattern, combined with the frequency shift, argues persuasively for the presence in the absorber of a single U–Cl bond.

The UF_5Cl molecule is expected to belong to the C_{4v} point group (in keeping with its ^{19}F n.m.r. spectrum[1]) so that three ($2a_1 + e$) of the four ($2a_1 + b_1 + e$) should, like the unique U–Cl stretching fundamental (a_1), be active in i.r. absorption. In the region 500—700 cm^{-1} characteristic of U–F stretching modes, the CO matrix showed only two bands distinguishable from the features associated with UF_6 or $(UF_6)_n$. Detailed vibrational assignments have been proposed for the analogous molecules SF_5Cl,[10] SeF_5Cl,[11] TeF_5Cl,[12] and WF_5Cl,[13] in each case on the basis of both i.r. and Raman measurements. The U–F stretching fundamentals of matrix-isolated UF_5Cl have been assigned by analogy with the corresponding modes of WF_5Cl.[13] Hence we associate the i.r. absorption at highest frequency (647 cm^{-1}) with the a_1 mode ν_1 approximating to the stretching vibration of the unique U–F bond *trans* to the U–Cl bond; the absorption at 563 cm^{-1} we identify with the e mode ν_8 approximating to the antisymmetric stretching motion of the (more-or-less) square-planar UF_4 unit. On the evidence of the vibrational properties of WF_5Cl[13] and approximate normal-co-ordinate calculations,[2] the second a_1 mode ν_2, approximating to the symmetric stretching motion of the UF_4 unit, is expected to occur near 620 cm^{-1}, and thus to be almost coincident with ν_3 of UF_6. So it is reasonable to infer that the corresponding i.r. absorption of UF_5Cl is hidden by the intense absorption at 640—595 cm^{-1} due to UF_6. There can be little doubt about the identification of the doublet at 341/333 cm^{-1} with the a_1 fundamental ν_3 approximating to the U–Cl stretching vibration. No features attributable to deformation modes of the matrix-isolated UF_5Cl molecule were detected either for want of intensity or because they occur at wavenumbers < 200 cm^{-1}, *i.e.* outside the range of the spectrometer used.

Solid argon or nitrogen matrices containing UF_6 and UF_5Cl, prepared by similar methods, displayed i.r. spectra akin to that of the CO matrix. The spectroscopic results summarised in Table 1 show that the wavenumbers of the absorptions due to the trapped molecules do not vary significantly from one matrix to another.

Photolysis of UF_5Cl *isolated in a* CO *Matrix*.—Photolysis of a solid CO matrix containing UF_5Cl and UF_6 with visible radiation at wavelengths between 430 and 600 nm for 5 min caused the i.r. bands associated with UF_5Cl virtually to disappear and to be replaced by three new bands in the U–F stretching region (at 563, 540, and 528 cm^{-1}). In addition, the spectrum revealed the growth of bands at the following wavenumbers: 1 873, 1 862, 1 840, 1 755, 1 094, 767, 664, and 591 cm^{-1}. The relevant spectroscopic details are listed in Table 2, the region of the spectrum between 660 and 310 cm^{-1} being illustrated in Figure 1.

Continued photolysis under the same conditions for a further 20 min gave rise to new i.r. features. All traces of UF_5Cl had now disappeared to the accompaniment of a modest growth in the intensities of all but one of the bands which had developed during the initial period of photolysis. The one exception was the band at 1 873 cm^{-1}, the intensity of which decreased somewhat. Exposure of the matrix to the full emission of the Hg arc for a further 5 min also caused a modest growth in the intensities of all the new bands, with the exception of that at 1 873 cm^{-1} which decayed proportionately.

The absorptions at 563, 540, and 528 cm^{-1} which developed on photolysis in this experiment grew at the same rate and must therefore originate in a single molecule. The intensity pattern and wavenumbers of the bands, allied to the conditions of the experiment, suggest that they represent U–F stretching fundamentals of the fragment UF_5 under the perturbing influence of one or more CO molecules. We base this identification on the i.r. spectrum reported previously[7a] for UF_5 as formed by u.v. photolysis of UF_6 isolated in a CO matrix [ν(U–F) 568, 543, and 533 cm^{-1} with an intensity pattern similar to the one we observed].

The i.r. band at 1 873 cm^{-1} must be ascribed to the radical OCCl$^•$, a view supported by previous studies of this species trapped in a CO matrix.[14] The assignment is confirmed, moreover, by the way in which the band decays on continued photolysis of the matrix. The bands at 1 862, 1 840, 1 755, 1 094, 767, and 664 cm^{-1}, which continue to grow at the expense of the band due to OCCl$^•$, we attribute to the molecule OCClF on the basis of the i.r. spectrum reported for the gaseous molecule.[15]

If the sole photochemical reaction involving a uranium compound was the simple photodissociation (1), then the only

$$UF_5Cl \xrightarrow[\text{CO matrix}]{h\nu,\ \lambda\ \sim\ 500\ \text{nm}} UF_5 + Cl^• \qquad (1)$$

new species to be formed, in addition to UF_5, would be products of the ensuing reactions between chlorine atoms and CO molecules, *e.g.* OCCl$^•$ and $OCCl_2$.[14] The radical OCCl$^•$ is certainly formed, but so is OCClF whose presence implies an additional reaction involving a uranium fluoride. The increase in the matrix concentrations of UF_5 and OCClF with the decrease in that of OCCl$^•$ brought about by visible photolysis, even when most, if not all, the UF_5Cl has been exhausted, leads us to believe that the OCCl$^•$ radicals are reacting with a fluorine atom source to give OCClF and UF_5. The fluorine atom source is clearly not UF_5Cl or UF_5 and there is no spectroscopic evidence for the formation of lower uranium fluorides (*e.g.* UF_4 which is characterised by an intense i.r. band at 499 cm^{-1} [7,16]). The only other possible precursor is therefore UF_6. UF_6 molecules isolated alone in a CO matrix are unlikely to be photolabile with respect to visible radiation. This we conclude since the i.r. spectrum of the photolysed matrix gave no hint of species such as OCF$^•$ and OCF_2.[17] Furthermore, the u.v.–visible spectrum of UF_6 isolated in a CO matrix is unlikely to differ significantly from that of UF_6 isolated in an N_2 matrix, and we have shown that prolonged exposure of an N_2 matrix containing UF_6 to visible radiation produced no detectable change in the i.r. spectrum. Accordingly we conclude that UF_6 must be activated by OCCl$^•$ radicals causing photodissociation under the action of visible radiation with the production of UF_5 and OCClF, equation (2). It appears that such photodissociation

$$UF_6 + OCCl^• \xrightarrow[\text{CO matrix}]{h\nu,\ \lambda\ \sim\ 500\ \text{nm}} UF_5 + OCClF \qquad (2)$$

of UF_6 requires some form of co-ordination to the OCCl$^•$ radical since the i.r. spectrum was devoid of any features associated with the products of reactions involving fluorine atoms, *e.g.* OCF$^•$ and OCF_2. The formation of OCClF from OCCl$^•$, which is unlikely under the conditions of our experiment to have migrated far from the site of dissociation of the UF_5Cl argues that the immediate environment of the UF_5Cl molecule in the initial deposit commonly included a UF_6 molecule. On the other hand, the failure to detect $OCCl_2$[14] amongst the photolysis products argues that the UF_5Cl molecules were well isolated from one another, thereby minimising the opportunity for reaction (3).

$$UF_5Cl + OCCl^• \xrightarrow{h\nu} UF_5 + OCCl_2 \qquad (3)$$

Photolysis of UF_5Cl *isolated in an* N_2 *Matrix*.—In order better to understand the photochemistry of mixtures of UF_5Cl and UF_6 trapped in a solid N_2 matrix, we investigated first the effects of photolysing an N_2 matrix containing UF_6 alone (N_2:UF_6 = *ca.* 250:1). The i.r. spectrum of the initial deposit showed an intense sharp singlet at 622 cm^{-1} with a much weaker satellite at 612 cm^{-1} (assumed to arise from UF_6 molecules in a different matrix site). The effects of broad-band u.v. photolysis and subsequent annealing we found to be analogous to those reported previously for UF_6 isolated in an Ar matrix.[7] Photolysis resulted in the appearance and growth of new bands at 647, 581, and 552 cm^{-1} attributable to the molecule UF_5; prolonged photolysis caused about 80% conversion of UF_6 to UF_5. On the other hand, UF_6 was regenerated from UF_5 when the matrix was allowed to soften by warming to *ca.* 24 K for 10 min. On the basis of the number and relative intensities of the i.r. bands observed, the UF_5 molecule isolated in an N_2 matrix appears to be a square-based pyramid with C_{4v} symmetry. The relative intensities of the bands lead to an estimate of 100 ± 3.5° for the angle subtended by the radial and axial U–F bonds. This may be compared with an angle of 101° estimated on the basis of similar calculations for UF_5 held in an Ar matrix.[7d]

Figure 2 illustrates the i.r. spectrum of a solid N_2 matrix containing both UF_5Cl and UF_6 and the effect of exposing the matrix to radiation with wavelengths near 500 nm. Hence it is apparent that photolysis brought about the depletion of the matrix of UF_5Cl, as attested by the marked decrease in the intensity of the doublet at 342/334 cm^{-1}. By contrast, the intensities of the bands near 648 and 566 cm^{-1} actually *increased* slightly and at the same time new bands appeared at 588, 581, 575, 555, 546, and 450 cm^{-1} (see Table 3). The bands near 648 and 566 cm^{-1} must therefore be common to both UF_5Cl and a new species produced on photolysis. With due allowance for the contribution of UF_5Cl (estimated by reference to the behaviour of the band near 340 cm^{-1}), the intensities of these bands were found to increase in step with those of the other new bands which appeared and grew on photolysis.

Several experiments were performed to determine the effect of changing the concentrations of the guest molecules in the matrix. After exhaustive photolysis with radiation having $\lambda \sim$ 500 nm, the bands at 648, 588, 575, 566, 546, and 450 cm^{-1} invariably maintained the same relative intensities, as did the two bands at 581 and 555 cm^{-1}. However, the results of different experiments showed that the two sets of bands did not maintain the same relative intensities with respect to each other, and they must therefore arise from two different absorbers.

The bands at 581 and 555 cm^{-1} we identify with a UF_5

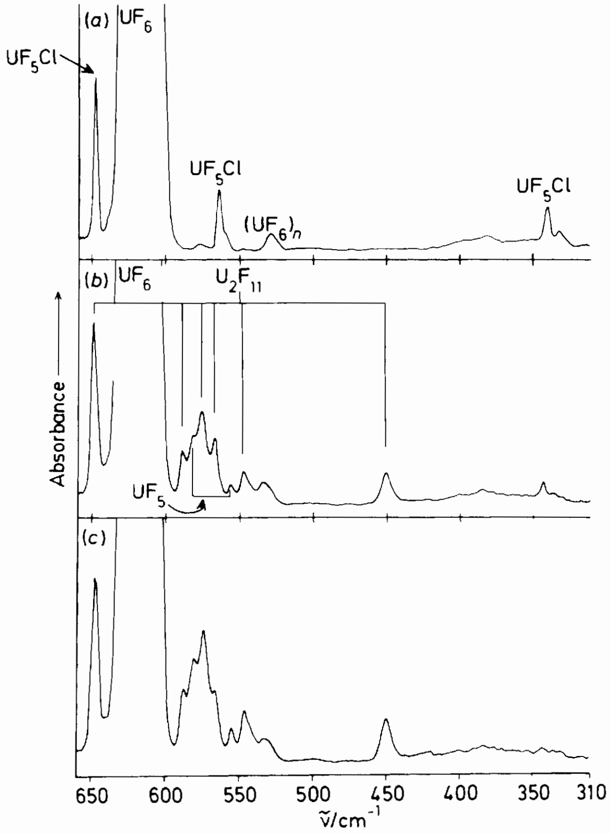
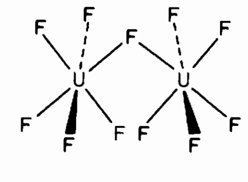


Figure 2. The region 660—310 cm^{-1} in the i.r. spectrum of an N_2 matrix containing UF_6 and UF_5Cl held at *ca.* 12 K: (*a*) after deposition; (*b*) after 21 min photolysis at $\lambda \sim 500$ nm; and (*c*) after a further 60 min photolysis at $\lambda \sim 500$ nm

molecule in a matrix cage composed exclusively of N_2 molecules. Comparison with the results of earlier studies[7] supports this assignment and suggests that the third i.r.-active U–F stretching fundamental should occur at 647 cm^{-1}. The photolysed matrix did indeed exhibit a band here (see above) but, with an intensity about an order of magnitude greater than would be expected, it must be presumed to originate mainly in another product.

The growth pattern of the bands at 648, 588, 575, 566, 546, and 450 cm^{-1} suggests that they all belong to a common species. The band at 648 cm^{-1} is remarkably close in energy to the $U–F_{ax}$ stretching fundamental in each of the molecules UF_5Cl and UF_5, whereas the four bands between 588 and 546 cm^{-1} all lie within the region characteristic of the stretching fundamentals associated with the radial UF_4 units of the same molecules. We attach particular significance to the appearance of a broader band at 450 cm^{-1}, an energy much lower than that for the stretching of any terminal U–F bonds in monomeric UF_6,[7,8] UF_5,[7] or UF_4[16] isolated in matrices, and yet much higher than that of any UF_x bending modes in the same species. The most plausible explanation is that the band arises from the stretching vibration of a U–F–U bridge. There is support for this assignment from two sources. (*a*) Vibrational features occurring in the range 390—480 cm^{-1} have been assigned to the stretching of U–F–U bridges in the polymeric solids α- and β-UF_5,[18–20] OUF_4,[21] and UF_4,[22,23] whose crystal structures have been established. (*b*) The i.r. spectrum we observed has much in common with that of a discrete molecular species containing two heavy metal atoms linked by a single fluorine bridge. Although no matrix-isolated M_2F_{11} molecules have been reported previously, the structure of the crystalline compound $BrF_5{\cdot}2SbF_5$ determined by *X*-ray diffraction[24] consists of discrete $Sb_2F_{11}^-$ anions which are coupled by only relatively weak fluorine bridges to the BrF_4^+ cations. An i.r. band of this solid at 488 cm^{-1} has been assigned[25] to a stretching vibration of the Sb–F–Sb skeleton (solid $CsSb_2F_{11}$ exhibits a band at 480 cm^{-1} which has been assigned similarly[26]), while bands at 690, 655, 645, 568, and 540 cm^{-1} are thought to correspond to stretching vibrations of the terminal SbF_5 moieties. The anion $Sb_2F_{11}^-$ therefore has i.r. bands which are the same in number, as well as relative intensity and disposition, as the new species formed on visible photolysis of an N_2 matrix containing UF_5Cl and UF_6. Hence, we believe that this new species is most plausibly formulated as U_2F_{11} comprising two UF_5 units linked through a single bridging fluorine atom, as in (**1**). We remark that the existence of such a species has been postulated earlier[27] to account for the increased transport of gaseous UF_5 in the presence of UF_6. U_2F_{11} is formed presumably in the N_2 matrix by the interaction of a UF_5 fragment, produced by the photodissociation of UF_5Cl, with a UF_6 molecule in a neighbouring site. If there is no such UF_6 molecule in the matrix cage, the photoproduct is UF_5 and not U_2F_{11}. The proportions of UF_5 and U_2F_{11} reflect therefore the composition and concentration of the matrix initially deposited.



(**1**)

The number of i.r. bands attributable to the stretching of terminal bonds in U_2F_{11} seems to obviate any structure with higher than C_{4v} symmetry; on these grounds, for example, we can discount D_{4h} or D_{4d} models, each with a linear, symmetrical U–F–U bridge linking the two square-pyramidal UF_5 units. The energy of the stretching vibration of the U–F–U bridge is consistent with a symmetrical more than an unsymmetrical bridge characterised by two markedly different U–F distances. In the circumstances we favour a structure such as (**1**) with a single angular but symmetrical U–F–U bridge; certainly this is the structure known to be adopted by the following molecular ions in crystalline derivatives: $Sb_2F_{11}^-$,[24] $Xe_2F_{11}^+$,[28] and $Nb_2F_{11}^-$.[29]

Reactions of Freon Solutions containing UF_5Cl *and* UF_6 *at Low Temperatures.*—As reported previously,[1] Freon solutions containing uranium(VI) chloride fluorides with mean U:Cl ratios of 1:1 or 1:2 decompose at temperatures above *ca.* −60 °C to form elemental chlorine and either β-UF_5 or UF_4 respectively. Admission of NO to a uranium(VI) chloride fluoride solution at −70 °C has also been shown to afford NOCl and either β-UF_5 or UF_4.[1] Uranium hexafluoride reacts with NO_2 in the gas phase to give the nitronium salt NO_2^+-UF_6^-.[30] In a second attempt to fix UF_5Cl in the form of the corresponding hexahalogenouranate(V) anion, we admitted NO_2 to a Freon solution initially containing UF_6 and $SiMe_3Cl$ to give the proportions U:Cl:NO_2 = *ca.* 2:1:1. The solution was rapidly decolourised at −63 °C with the precipitation of a pale green solid shown by its elemental analysis and i.r. spectrum[18] to be β-UF_5. The volatile products included approximately 1 mol of NO_2Cl (identified by its i.r. spectrum[31]) for every mol of NO_2 taken. Hence we conclude that reaction (4) takes place in these conditions.

Table 3. Wavenumbers and assignments of i.r. absorptions appearing after visible photolysis ($\lambda \sim 500$ nm) of an N_2 matrix containing UF_6 and UF_5Cl at *ca.* 12 K

Bands appearing after photolysis		Assignment		ṽ/cm⁻¹ for UF_5 isolated in			
ṽ/cm⁻¹ [a]	Intensity	Molecule	Mode [b]	N_2 matrix [c]	Ne matrix [d]	Ar matrix [c,d]	CO matrix [c,d]
648	s	U_2F_{11} $+ UF_5$	$\nu(U-F_{term})$ $\nu(U-F)$	647w	649	646w	564s
588	m	U_2F_{11}	$\nu(U-F_{term})$				
581	m	UF_5	$\nu(U-F)$	581s	593	584s	540m
575	ms	U_2F_{11}	$\nu(U-F_{term})$				
566	m	U_2F_{11}	$\nu(U-F_{term})$				
555	mw	UF_5	$\nu(U-F)$	552m	572	561m	528m
546	m	U_2F_{11}	$\nu(U-F_{term})$				
450	m,br	U_2F_{11}	$\nu(U-F_{br}-U)$				

[a] Error limits ±1 cm⁻¹. [b] term = Terminal, br = bridging. [c] This work. UF_5 prepared by u.v. photolysis of a matrix containing UF_6. [d] See ref. 7.

$$UF_5Cl + NO_2 \xrightarrow[UF_6]{-63\ ^\circ C,\ CCl_3F} \beta\text{-}UF_5 + NO_2Cl \quad (4)$$

In view of the apparent capacity of UF_5Cl to bring about oxidative chlorination of NO and NO_2, we investigated the interaction of Freon solutions containing UF_5Cl with a number of unsaturated reagents susceptible to two-electron oxidation processes, *viz.* SO_2, PF_3, and C_2F_4.

Uranium hexafluoride reacts when heated with SO_2 to give SO_2F_2 and lower-valent uranium fluorides.[32] However, there was no sign of any reaction when SO_2 was admitted to a CCl_3F solution containing UF_5Cl even after prolonged contact at − 63 °C (typically for periods up to 40 h). Unchanged SO_2 was recovered quantitatively in each case.

At −78 °C uranium hexafluoride oxidises PF_3 to PF_5 while itself being reduced to β-UF_5, although the reaction is incomplete even after 2 d.[33] We found that PF_3 reacted with a CCl_3F solution containing UF_5Cl (with the approximate proportions $U:Cl:PF_3 = 1:1:1$) in 4 h at −63 °C. More than 90% of the PF_3 was thus converted to PF_5 which was identified by its i.r. spectrum.[34] Judging by chemical analysis and i.r. spectroscopy, however, the products did not include PF_4Cl,[35] PF_3Cl_2,[34a] or Cl_2. The involatile dark green solid residue was shown, also by chemical and spectroscopic analysis, to be a mixture of uranium(IV) and uranium(V) halides UX_nY_{4-n} and UX_nY_{5-n} (where X = Cl, Y = F, and *n* = 0—2). Under comparable conditions UF_6 did not react to a measurable extent with PF_3, even after 8 h at −63 °C. Hence the reaction of UF_5Cl with PF_3 is appreciably more facile than that of UF_6.

Tetrafluoroethene also reacted with a CCl_3F solution containing UF_6 and UF_5Cl in *ca.* 30 min at −63 °C. From a mixture prepared to give the approximate proportions $C_2F_4:U:Cl = 1.1:2:1.1$ no C_2F_4 could be recovered. The major volatile product, accounting for 75% of the C_2F_4 originally taken, was shown to be CF_3CF_2Cl by the i.r.[36] and mass[37] spectra of its vapour and by vapour-pressure[38] measurements. The only other volatile product to be identified on the evidence of its i.r. spectrum[39] was CF_2ClCF_2Cl; this accounted for only *ca.* 7% of the C_2F_4 taken. The reaction gave rise also to an involatile green solid which proved to be a mixture of UF_4[23] and β-UF_5.[18] Hence the major reaction occurring in these conditions appears to be (5), accompanied by one or both of the secondary reactions (6) and (7). Since only about 80% of the C_2F_4 is accounted for in this way, we believe that there is also some competition from polymerisation involving, for example, $C_2F_4Cl^\bullet$ radicals. The polymerisation yields chlorofluorocarbons which, with volatilities and i.r. spectra similar to those of the solvent (CCl_3F), escaped detection.

$$UF_5Cl + CF_2{=}CF_2 \longrightarrow UF_4 + CF_3CF_2Cl \quad (5)$$

$$2UF_5Cl + CF_2{=}CF_2 \longrightarrow 2\beta\text{-}UF_5 + CF_2ClCF_2Cl \quad (6)$$

$$UF_4Cl_2 + CF_2{=}CF_2 \longrightarrow UF_4 + CF_2ClCF_2Cl \quad (7)$$

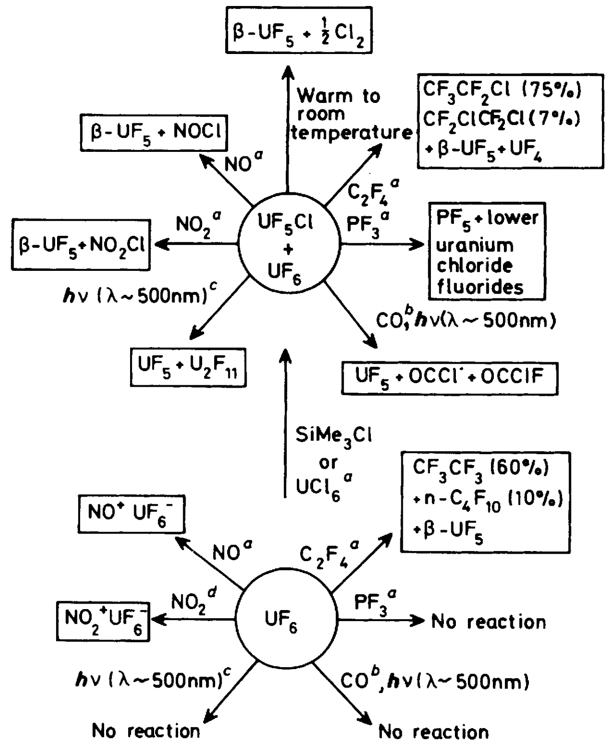
That polymerisation occurs to some extent is certainly indicated by experiments with UF_6 in place of the mixture of UF_6 and UF_5Cl. Hence we found that C_2F_4 reacted slowly with a four-fold excess of UF_6 in a CCl_3F solution at −63 °C. Even after 90 min the reaction was incomplete. In this case β-UF_5[18] was the sole uranium-containing product, whereas C_2F_6[40] was the principal volatile product, accounting for *ca.* 60% of the C_2F_4 consumed. In addition, however, the volatile products included n-C_4F_{10}, detected by its i.r. spectrum[41] and accounting for *ca.* 10% of the C_2F_4 consumed. No other fractions could be separated from the solvent by fractionation *in vacuo*, although the i.r. spectrum of the vapour exhibited some features characteristic of fluorocarbons other than CCl_3F. So we conclude (*i*) that C_2F_4 is quicker to react with UF_5Cl than with UF_6 under the conditions prevailing in these experiments, and (*ii*) that both reactions involve some polymerisation, *via* $C_2F_4X^\bullet$ fragments (X = F or Cl), as an alternative pathway to dihalogen addition.

Discussion

The results of the matrix experiments described here show that UF_5Cl is photolabile with respect to radiation of wavelengths near 500 nm. The formation of UF_5 in both CO and N_2 matrices and the trapping of the $Cl^\bullet$ atom as $OCCl^\bullet$ in the CO matrix indicate that the primary photoprocess is the dissociation of the U–Cl bond of UF_5Cl, equation (8). It appears therefore that the band observed at *ca.* 510 nm in the visible absorption spectrum of CCl_3F solutions of UF_5Cl[1] is the agency for this dissociation. UF_6 is immune to photodissociation under these conditions, in keeping with its transparency in the visible region.[42]

$$UF_5Cl \xrightarrow{h\nu,\ \lambda \sim 500\ nm} UF_5 + Cl^\bullet \quad (8)$$

The intensities of the i.r. bands imply that the matrices are appreciably richer in UF_6 than in UF_5Cl giving quite a high probability that UF_6 will be found in the matrix cage of a UF_5Cl molecule. This expectation is borne out by our finding that U_2F_{11} is formed on photolysis of an N_2 matrix and that OCClF is formed on photolysis of a CO matrix. Although $UF_6 \cdots UF_5Cl$ contacts play an important part in the observed photochemistry of the matrices, the UF_5Cl molecules are well



Scheme. Behaviour of UF_5Cl compared with that of UF_6 under comparable conditions: [a] CCl_3F solution at 210 K; [b] CO matrix at *ca.* 12 K; [c] N_2 matrix at *ca.* 12 K; [d] neat reagents at ambient temperatures

isolated from one another and $UF_5Cl \cdots UF_5Cl$ contacts play little or no part.

One of the most puzzling features of our results is that the change of matrix host from N_2 to CO should provoke such a marked difference of photoproducts. The initial N_2 and CO matrices were prepared by the same method and had similar compositions, as verified by the near-identity of the i.r. spectra due to the guest species (see Table 1). It is not surprising that visible photolysis of a mixture of UF_5Cl and UF_6 should be more rapid with a CO host in view of the efficiency of CO as a halogen-atom scavenger.[43] What is surprising is that the uranium-containing product appears to be a mononuclear fragment UF_5 with a CO host but a mixture of UF_5 and the binuclear fragment U_2F_{11} with an N_2 host. The results suggest that, with respect to UF_5, the co-ordinating ability of potential ligands decreases in the order CO > UF_6 > N_2. That CO interacts strongly with UF_5 is apparent from the marked difference in the i.r. spectrum of UF_5 when CO replaces a noble gas or N_2 as the matrix host.[7a] Not only is the mean value of ν(U–F) reduced by 50—60 cm^{-1}, but the intensity pattern of the relevant i.r. absorptions is radically changed [with the feature highest in frequency now most intense, instead of being the *least* intense of the three features attributable to ν(U–F) fundamentals]. Indeed the i.r. spectrum suggests that the UF_5 moiety in a CO matrix conforms to neither C_{4v} nor D_{3h} symmetry. The perturbation produced by the CO may even proceed to the point of forming a compound such as UF_5CO. However, further experiments involving Ar or N_2 matrices doped with varying amounts of CO have failed to bring to light any i.r. absorption attributable to ν(C–O) of a co-ordinated CO molecule.

The relative weakness of the U–Cl bond appears to be a major factor in the enhanced reactivity of UF_5Cl compared with UF_6. We have reported previously[1] the decomposition of UF_5Cl [and other uranium(VI) chloride fluorides] at temperatures in excess of −60 °C and also the reaction with NO at −70 °C giving NOCl and β-UF_5. We have now shown that NO_2 is analogous to NO in its reaction with UF_5Cl (in CCl_3F solution in the presence of UF_6) resulting in the formation of NO_2Cl and β-UF_5 in accordance with equation (4). UF_6 is known to react with NO or NO_2 to form $NO^+UF_6^-$ or NO_2^+-UF_6^- respectively,[30,44] and we have shown, with NO for example, that the reaction is rapid in CCl_3F solution at −63 °C. Hence it is noteworthy that the reaction of NO or NO_2 with UF_5Cl to give NOCl or NO_2Cl respectively takes place even in the presence of an excess of UF_6; so long as the proportions NO:UF_5Cl or NO_2:UF_5Cl do not exceed 1:1, we found no traces of $NO^+UF_6^-$ or $NO_2^+UF_6^-$. Evidently chloride-transfer involving UF_5Cl is faster than the formal outer-sphere redox reaction which occurs between UF_6 and NO or NO_2.

By contrast, PF_3 is converted, not to a phosphorus(V) chloride fluoride like PF_4Cl, but to PF_5 by a CCl_3F solution containing mainly UF_5Cl at *ca.* −63 °C. We have found that PF_3 undergoes little reaction with UF_6 alone under similar conditions. Hence oxidation of phosphorus(III) to phosphorus(V) must be initiated by a species other than UF_6 present in the fluoride-rich solution of uranium(VI) chloride fluorides. We note too that the reaction between stoicheiometric amounts of UF_6 and PCl_3 results in a simple halogen exchange to give UCl_6 and PF_3;[45] with an excess of UF_6, the only phosphorus-containing products are PF_3 and PF_5. This indicates that halide exchange between the phosphorus and uranium centres is more rapid than the oxidation of phosphorus(III) to phosphorus(V). We suppose therefore that the reaction in the Freon solution at −63 °C proceeds in two stages: (*i*) oxidation of phosphorus(III) to phosphorus(V) by UF_5Cl to give an intermediate phosphorus(V) chloride fluoride; (*ii*) rapid halogen-exchange between this intermediate and fluoride-rich uranium species to give PF_5 as the sole oxidation product to be isolated.

The complication of halogen-exchange reactions can be alleviated by the choice of a substitutionally inert substrate like tetrafluoroethene, the oxidation products of which are unlikely to undergo halogen exchange in Freon solution at low temperatures. Tetrafluoroethene reacts incompletely with an excess of UF_6 in CCl_3F solution at −63 °C after 90 min with *ca.* 60% conversion to C_2F_6 and 10% conversion to n-C_4F_{10}, the remainder being converted to other unidentified fluorocarbons formed by polymerisation reactions. This may be compared with the complete reaction inside 30 min with UF_5Cl under similar conditions with *ca.* 75% conversion to CF_3CF_2Cl and 7% conversion to CF_2ClCF_2Cl. The speed of the reaction, combined with the absence from the products of C_2F_6 in detectable quantities, underlines the preference of the substrate to react selectively with UF_5Cl even in the presence of UF_6.

The Scheme summarises the reactions of UF_5Cl which we have charted on the basis of our matrix and solution experiments; it also shows how UF_6 behaves under similar conditions. The greater reactivity of UF_5Cl may be attributed partly to the polarity of the molecule, but mainly to the lability of the U–Cl bond.

Conclusions

The UF_5Cl molecule has been isolated, together with UF_6, in a solid Ar, N_2, or CO matrix and characterised by its i.r. spectrum. The molecule undergoes photodissociation under the action of visible radiation with wavelengths near 500 nm. The uranium-containing species thus generated in a CO matrix is $UF_5 \cdots (CO)_n$; those generated in an N_2 matrix are UF_5 and a novel species believed to be U_2F_{11}. That UF_5Cl is appreciably more reactive than UF_6 is shown by the response of Freon solutions containing both UF_5Cl and UF_6 to the reagents NO_2,

PF_3, and C_2F_4 at −63 °C, a temperature low enough to prevent thermal decomposition of the UF_5Cl. Our experiments show that NO_2 is oxidatively chlorinated to NO_2Cl, PF_3 is oxidatively fluorinated to PF_5 [probably *via* a phosphorus(v) chloride fluoride intermediate], and the major product of the reaction with C_2F_4 is CF_3CF_2Cl.

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