ligands is extremely inert and once formed in concentrated HCl does not decompose in more dilute acids to yield the former species.

Preliminary results show that $Mo_2(HPO_4)_4^{2-}$ undergoes substitution in aqueous H_2SO_4. Single crystals of a $Mo_2(SO_4)_4^{2-}$ salt have not been obtained yet.

Registry No. I (n = 4), 75365-58-1; II, 75365-59-2; $[Mo_2]^{4+}$, 11083-49-1; $Cs_3Mo_2Cl_9$, 29013-02-3; $K_3Mo_2(SO_4)_4$, 63311-41-1; $(pyH)_3[Mo_2(HPO_4)_4Cl]$, 71597-13-2.

Contribution from the Chemical Technology Division,
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Gas-Phase Properties of Bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)(trimethyl phosphato)dioxouranium(VI)

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Compounds of the type $UO_2(HFA)_2X$, where HFA represents the 1,1,1,5,5,5-hexafluoropentane-2,4-dionato ion and X represents a neutral ligand such as trimethyl phosphate (TMP) or triphenylphosphine oxide (TPPO), have been known for some years[1,2] and, because of their volatility, have been recommended for the gas chromatographic determination of uranium.[3] The crystal structures of the two isomorphs[4,5] and some thermochemical properties[6] of $UO_2(HFA)_2TMP$ have been reported, while more recent studies have described the preparation,[7] crystal structure,[8] and gas-phase properties and dimerization equilibria[9] of anhydrous $UO_2(HFA)_2$.

The demonstration of the existence of $UO_2(HFA)_2$ in the gas phase suggests that compounds such as $UO_2(HFA)_2TMP$ might exist in the gas phase as partly or wholly dissociated molecules (eq 1), and the present work was undertaken to

$$UO_2(HFA)_2TMP \rightleftharpoons UO_2(HFA)_2 + TMP \qquad (1)$$

explore the possibility of this reaction. It might be noted that recent work by Kaldor et al.[10,11] has shown that laser irradiation under molecular beam conditions of the compound $UO_2(HFA)_2THF$ (THF = tetrahydrofuran) at a laser frequency corresponding to the ν_3 absorption of the uranyl group leads to the dissociation of the molecule to form free THF and, presumably, monomeric $UO_2(HFA)_2$.

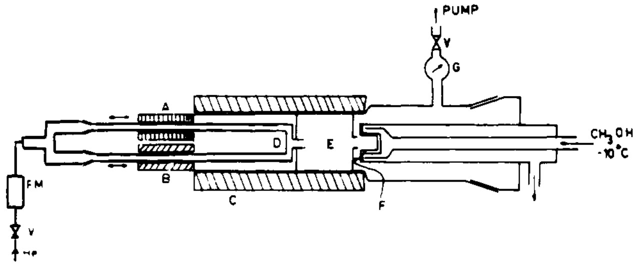

Figure 1. Apparatus to measure the gas-phase neutral ligand exchange: U, needle valve; FM, flow meter, calibrated for helium; A and B, tube furnaces movable horizontally; C, fixed tube furnace; D, mixing chamber; E, reaction chamber; F, cold finger insert; G, pressure gauge.

Table I. Summary of Vapor Pressure Measurements (log [P (Pa)] = $A - 1000B/K$)

compd	temp range, K	A	B	ΔH, kJ mol^{-1}
$UO_2(HFA)_2TMP$	365-414 (melt)	11.6 ± 0.1	4.0 ± 0.1	76 ± 2
$UO_2(HFA)_2TPPO$	406-442 (melt)	12.1 ± 0.5	5.2 ± 0.2	99 ± 4

Table II. Results of Test of Separation Procedure

input material, mg		duration of sublimation of $UO_2(HFA)_2$-TMP, h	recovered material			
			TMP		TPPO	
TMP (0.713% ^{235}U)	TPPO (0.408% ^{235}U)		wt, mg	% ^{235}U	wt, mg	% ^{235}U
36.4	46.3	2	34.8	0.709	45.2	0.410
52.3	30.4	4	51.0	0.714	28.7	0.409

Experimental Section

$UO_2(HFA)_2TMP$ and $UO_2(HFA)_2TPPO$ containing uranium of both natural (0.713% uranium-235) and depleted (0.408% uranium-235) isotopic content were prepared as described previously,[6] the diethyl ether being replaced by the stoichiometric quantity of the neutral ligand in the preparation. All compounds were purified by at least four successive sublimations.

The gas-phase neutral-ligand-exchange experiments were carried out with the apparatus shown in Figure 1, the gas-phase concentrations of the TMP and TPPO complexes being controlled by the temperatures of furnaces A and B. The temperature of furnace C was controlled at 250 °C, and the helium carrier-gas pressure was 2.7 kPa for all runs. The residence time was controlled by the carrier-gas flow rate and by the volume of the reaction chamber.

In a typical experiment, samples of the two compounds were placed in glass boats at positions A and B, the carrier-gas pressure was established at the desired flow rate, and furnace C was heated to 250 °C. Furnaces A and B were then heated to the required temperature and moved into position. The compounds were volatilized, mixed in the mixing chamber D, allowed to flow through the reaction chamber E, and condensed as a solid on the cold finger insert F. At the end of the run, the cold finger insert together with the deposited compounds was removed and weighed, the TMP complex selectively sublimed off at 80 °C, the cold finger insert reweighed, the TPPO complex sublimed off at 150 °C, and the empty cold finger insert reweighed. From the above, the total quantities of the TMP and TPPO complexes which passed through the reaction chamber in a given time could be obtained, and the average gas-phase concentrations of the TMP and TPPO complex could be calculated. Samples of the sublimed TMP and TPPO complexes were then converted to $UO_2(NO_3)_2$ and analyzed for their uranium-235 content with a Metropolitan-Vickers MS5 mass spectrometer.

The vapor pressure measurements and the determination of the equilibrium constant for reaction 1 were carried out with the apparatus and experimental procedures described in detail elsewhere.[9]

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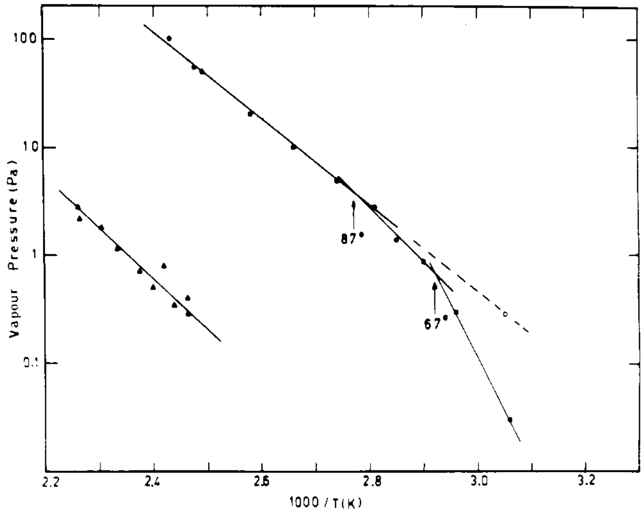

Figure 2. Vapor pressure–temperature curves of $UO_2(HFA)_2TMP$ and $UO_2(HFA)_2TPPO$: ●, $UO_2(HFA)_2TMP$ (solid and liquid sample); ○, supercooled liquid; ▲, $UO_2(HFA)_2TPPO$.

Results

(a) Vapor Pressure Measurements. The results of these measurements are illustrated in Figure 2, and, not unexpectedly, the vapor pressure of the TPPO complex was very much less than that of the TMP complex.

The two inflection points (at 68 and 87 °C) observed in the vapor pressure vs. temperature curve of $UO_2(HFA)_2TMP$ appear to reflect the phase transition and melting point reported previously.[6] It was also observed that, on cooling molten $UO_2(HFA)_2TMP$, a supercooled liquid was frequently formed, and this form of the compound has a significantly higher vapor pressure than observed for the crystalline solid at the same temperature.

The results of the least-squares analysis of the above vapor pressure data in terms of the expression log $[P\ (\mathrm{Pa})] = A - B/K$, and the derived thermodynamic parameters for the various phase transitions are summarized in Table I.

(b) Ligand-Exchange Experiments. The vapor pressure data suggested that $UO_2(HFA)_2TMP$ and $UO_2(HFA)_2TPPO$ could be separated by fractional sublimation without melting either compound, the vapor pressure of the two components differing by a factor of ~100 at 80 °C. To confirm this expectation, we mixed $UO_2(HFA)_2TMP$ (50 mg, 0.713% uranium-235) with $UO_2(HFA)_2TPPO$ (50 mg, 0.408% uranium-235), and the mixture was placed in a conventional sublimation apparatus, and the components separated by fractional sublimation as described above. Samples of the recovered materials were analyzed for their uranium-235 content, and the results obtained (Table II) showed that no changes in the isotopic composition of the TMP and TPPO complexes occurred in the course of the separation procedure.

For a test of neutral ligand exchange in the liquid phase, $UO_2(HFA)_2TMP$ (41.5 mg, 0.713% uranium-235) and $UO_2(HFA)_2TPPO$ (45.5 mg, 0.408% uranium-235) were sealed in an evacuated tube and heated to 160 °C for 2 h. Under these conditions the two compounds formed a mutually miscible melt although, of course, some gaseous material was also present. At the end of the period, the tube was opened, the TMP and TPPO complexes were separated by sublimation, and the TMP complex was found to contain 0.56% uranium-235. For complete exchange, 0.57% uranium-235 would have been expected.

The results of the gas-phase exchange experiments are summarized in Table III, and as shown by the identical uranium-235 content of the TMP and TPPO complexes recovered after passage through the reaction chamber, a very rapid neutral-ligand-exchange reaction had occurred.

Table III. Summary of Ligand-Exchange Experiments

		av concn, M			recovered material % ^{235}U	
run	duration of run, h	UO_2-$(HFA)_2$-TMP[a]	UO_2-$(HFA)_2$-TPPO[b]	av residence time, s	TMP	TPPO
1	0.50	3.8×10^{-6}	1.6×10^{-6}	20	0.605	0.610
2	3.2	1.2×10^{-6}	1.1×10^{-6}	13	0.555	0.553
3	4.2	9.1×10^{-7}	8.1×10^{-7}	13	0.562	0.562
4	5.6	1.8×10^{-6}	2.1×10^{-7}	4	0.699	0.699
5	4.0	5.6×10^{-7}	9.4×10^{-7}	4	0.511	0.504

[a] 0.713% ^{235}U. [b] 0.408% ^{235}U. [c] At 250 °C.

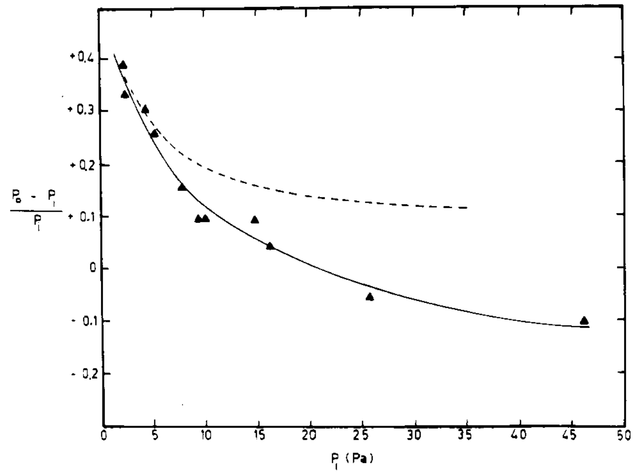

Figure 3. Plot of $(P_o - P_i)/P_i$ (the degree of dissociation) against P_i for $UO_2(HFA)_2TMP$ at 209 °C: solid line, calculated dependence using values of K_1 and K_2 summarized in Table IV; broken line, calculated dependence, assuming the presence of reaction 1 only with $K_1 = 0.50\ \mathrm{Pa}^{-1}$; solid triangles, experimental points.

(c) Determination of the Equilibrium Constant for Reaction 1. The experimentally determined pressures (P_o) measured for various samples sizes of $UO_2(HFA)_2TMP$ at 225, 209, 190, and 175 °C are summarized in Table IV. Comparison of the observed pressure with the pressure (P_i) expected if the compound behaved as an ideal gas indicates that a significant dissociation of $UO_2(HFA)_2TMP$ occurred.

For a simple reversible dissociation such as that represented by eq 1, the equilibrium constant K_1 will be given by the expression

$$K_1 = \alpha^2 P_o[1 - \alpha^2]^{-1} \qquad (2)$$

where α, the degree of dissociation, is given by

$$\alpha = [P_o - P_i]P_i^{-1} \qquad (3)$$

It follows from Le Chatelier's principle and from the definition of K_1, that, at constant temperature and volume, α should decrease with increasing sample size but K_1 should remain constant. However, examination of the data in Table IV and Figure 3 shows that this simple model cannot apply to the present system since, although dissociation is indicated at low values of P_i ($P_o > P_i$), K_1 decreases consistently with increasing sample size, and α becomes negative ($P_o < P_i$) at high pressures at 205, 190, and 175 °C.

The latter result is consistent either with an improbably large van der Waals correction or, more likely, with concurrent dissociation and association equilibria, coupled with the dimerization of $UO_2(HFA)_2$.[9] It will be noted that the dissociation of $UO_2(HFA)_2TMP$ coupled only with the dimerization of $UO_2(HFA)_2$ will not, under any circumstances, result in $P_o < P_i$.

Accordingly, the data were analyzed in terms of the simultaneous equilibria shown in Scheme I, which represent the

Table IV. Summary of Pressure Measurements on $UO_2(HFA)_2TMP$

temp, °C	P_i, Pa	P_o, Pa	$(P_o - P_i)/P_i$ (α)	K_1,[a] Pa	K_1,[b] Pa	K_2,[b] $Pa^{-1/2}$	$100(P_o - P_i)/P_o$[c]
225	2.00	3.11	0.555	1.38	1.68 ± 0.15	0.38 ± 0.06	2.57
	3.62	4.79	0.323	0.56			1.67
	4.28	5.38	0.257	0.38			2.97
	7.17	8.10	0.129	0.14			1.23
	7.15	8.26	0.155	0.20			0.97
	8.88	9.57	0.078	0.06			0.63
	13.71	14.00	0.021	0.006			5.00
209	2.26	3.14	0.389	0.56	0.50 ± 0.05	0.13 ± 0.02	1.20
	2.43	3.24	0.333	0.41			1.85
	4.18	5.44	0.301	0.54			2.57
	5.25	6.63	0.262	0.49			2.40
	7.68	8.87	0.155	0.22			1.13
	9.39	10.30	0.097	0.097			3.49
	9.96	10.91	0.094	0.097			2.75
	14.70	16.09	0.095	0.14			2.50
	16.09	16.79	0.043	0.03			0.36
	25.10	24.39	−0.051				2.34
	46.20	41.70	−0.097				2.50
190	0.82	1.05	0.280	0.09	0.14 ± 0.02	0.16 ± 0.02	2.80
	0.86	1.15	0.337	0.15			2.00
	1.21	1.58	0.305	0.16			3.26
	1.64	2.03	0.238	0.12			1.50
	4.54	5.10	0.123	0.08			0.34
	5.29	5.63	0.064	0.02			0.02
	6.74	7.05	0.046	0.01			0.17
	8.83	8.00	−0.094				0.95
	9.72	9.05	−0.068				5.22
	15.11	14.31	−0.052				2.35
	17.29	15.80	−0.085				0.70
	18.45	17.75	−0.040				6.86
	20.63	27.35	−0.077				7.11
175	1.32	1.53	0.159	0.039	0.050 ± 0.008	0.14 ± 0.02	2.61
	2.21	2.49	0.126	0.040			0.40
	3.73	3.96	0.062	0.015			0.75
	4.25	4.36	0.026	0.003			2.75
	6.43	6.28	−0.023				3.19
	8.15	7.63	−0.063				4.06
	11.70	10.67	−0.088				1.96
	12.90	12.55	−0.027				5.65
	14.18	13.47	−0.051				4.60

[a] Value calculated from eq 2, i.e., assuming only a simple dissociation reaction. [b] Values obtained by analysis of the data in terms of eq 8. [c] Percent difference between observed pressure (P_o) and that calculated with values of K_1 and K_2 in columns 6 and 7.

simplest possible reaction sequence.

Scheme I

reaction	partial pressure
$^1/_2[UO_2(HFA)_2TMP]_2$	x
$\uparrow\downarrow$ (K_2)	
$UO_2(HFA)_2TMP$	$P_i - 2x - 2z - y$
$\uparrow\downarrow$ (K_1)	
$UO_2(HFA)_2 + TMP$	y (each)
$\uparrow\downarrow$ (K_3)	
$^1/_2[UO_2(HFA)_2]_2$	z
	$P_o = P_i - x + y - z$

If in Scheme I P_i is the ideal pressure of $UO_2(HFA)_2TMP$ in the absence of any dissociation or association and y, x, and z are the partial pressures of $UO_2(HFA)_2$ (and TMP), $[UO_2(HFA)_2TMP]_2$, and $[UO_2(HFA)_2]_2$, respectively, then $P_i - 2x - y - 2z$ is the partial pressure of $UO_2(HFA)_2TMP$, and the total observed pressure (P_o) is given by eq 4, and the

$$P_o = \sum(\text{partial pressures}) = P_i - x + y - z \quad (4)$$

three equilibrium constants are respectively defined by (5)–(7)

$$K_1 = y^2[P_i - 2x - y - 2z]^{-1} \quad (5)$$

$$K_2 = x^{1/2}[P_i - 2x - y - 2z]^{-1} \quad (6)$$

$$K_3 = z^{1/2}[y]^{-1} \quad (7)$$

Eliminating x and z from eq 5–7 gives eq 8 for which it will

$$2y^4K_2^2 + y^2[K_1 + 2K_3^2K_1^2] + yK_1^2 - p_iK_1^2 = 0 \quad (8)$$

be noted that, if the dimerization of $UO_2(HFA)_2$ is excluded ($K_3 = 0$), eq 8 simplifies to eq 9.

$$2y^4K_2^2 + y^2K_1 + yK_1^2 - P_iK_1^2 = 0 \quad (9)$$

Equation 8 was solved numerically for y (and hence for x and z), in combination with a least-squares program which refined the initial estimates of K_1 and K_2 to values which best fitted the observed dependence of P_o on P_i (eq 5), the value of K_3 being obtained by extrapolation of published data.[9] Examination of the results obtained by the above procedure indicated that the inclusion of K_3 in eq 8 had no statistically significant effect on the values of K_1 and K_2. This observation is quite reasonable, since the dissociation of $UO_2(HFA)_2TMP$ is small, and K_3 also not large, the term $[2K_3^2K_1^2]$ in eq 8, will be small in comparison to K_1 at all temperatures and pressures. As shown by the solid line of Figure 3 and the percent differences between the observed and calculated pressures, the above model reproduces the experimental data quite well. Least-squares analysis of the temperature dependence of K_1 and K_2 in terms of the usual expression[12] leads to the ther-

Table V. Summary of the Effect of Temperature on the Dissociation and Dimerization Equilibrium Constants of $UO_2(HFA)_2TMP$

	K_1, Pa^{-1}		K_2, $Pa^{-1/2}$	
temp, °C	obsd	calcd[a]	obsd	calcd[a]
225	1.68 ± 0.15	1.58	0.38 ± 0.06	0.23
209	0.50 ± 0.05	0.55	0.15 ± 0.02	0.20
190	0.14 ± 0.02	0.14	0.16 ± 0.02	0.16
175	0.05 ± 0.008	0.04	0.14 ± 0.02	0.13
$\Delta H°$, kJ mol^{-1}	132 ± 6		2 ± 2	
$\Delta S°$, J K^{-1} mol^{-1}	174 ± 13		79 ± 46	

[a] See ref 12.

modynamic parameters summarized in Table V. While the values of K_2 display considerable scatter, reflecting the difficulty of accurately measuring second-order deviations from ideal-gas behavior, the above analysis led to values of 132 ± 6 kJ mol^{-1} and 174 ± 13 J K^{-1} mol^{-1} for $\Delta H°$ and $\Delta S°$ of reaction 1.

Discussion

The results obtained from the ligand-exchange experiments showed unambiguously that a rapid, thermally induced mechanism for the exchange of the neutral ligand (eq 1) is

$$^{235}UO_2(HFA)_2TMP + {}^{238}UO_2(HFA)TPPO \rightleftharpoons {}^{235}UO_2(HFA)_2TPPO + {}^{238}UO_2(HFA)_2TMP \quad (10)$$

operating in both the liquid and gaseous phases. Since complete exchange was obtained for contact times of only 4 s, it is apparent that the rate of reaction 10 is very rapid.

The most likely mechanism for this exchange is one which involves the predissociation of the neutral ligand, followed by random recombination reactions (eq 11–13).

$$^{235}UO_2(HFA)_2TMP \rightleftharpoons {}^{235}UO_2(HFA)_2 + TMP \quad (11)$$

$$^{238}UO_2(HFA)_2TPPO \rightleftharpoons {}^{238}UO_2(HFA)_2 + TPPO \quad (12)$$

$$^{235}UO_2(HFA)_2 + TPPO \rightleftharpoons {}^{235}UO_2(HFA)_2TPPO \quad (13)$$

This interpretation appears consistent with the results of the measurements of the equilibrium constant for eq 1, which show a significant degree of dissociation for low-pressure samples of $UO_2(HFA)_2TMP$ at temperatures in the range 175–225 °C, and would suggest that even in the gas phase these compounds can be regarded as Lewis base–Lewis acid adducts.

Comparison of the thermodynamic parameters obtained for reaction 1 with those obtained[9] for the dissociation of dimeric $UO_2(HFA)_2$ and $UO_2(THD)_2$ shows that the $\Delta H°$ values for all three reactions are comparable. Recent studies on the properties of the ν_3 vibration of the uranyl group in dimeric $UO_2(HFA)_2$ have shown[13] that dimerization in this molecule occurs by coordination of one uranyl oxygen into the coordination sphere of the other, thus giving an unsymmetrical dimeric molecule in which one uranyl oxygen atom acts as the neutral ligand for the adjacent uranyl group. If other factors such as steric effects can be neglected, the similar $\Delta H°$ values for these two reactions may indicate that a uranyl oxygen atom can function as a Lewis base which is nearly as effective as the strongly basic TMP molecule. It is therefore possible that bridging via uranyl oxygen atoms in polymeric uranyl complexes, particularly those formed under rigorously anhydrous conditions, may be more common than previously anticipated.

The identity of the $UO_2(HFA)_2TMP$ dimer is not clear, but obvious possibilities include a weakly hydrogen bonded form, or possibly one involving coordination via the uranyl oxygen, the carbonyl oxygen atoms, or the phosphate ester oxygen atoms. Although the uranyl β-diketone complexes generally exhibited a coordination number (excluding the uranyl oxygen atoms) of 5,[14] the UV–visible spectrum of $UO_2(HFA)_2TMP$ in dry hexane solution is markedly altered by the presence of small concentrations of free TMP,[15] suggesting the expansion of the coordination number of the uranyl ion. Dimerization could conceivably also occur via the sequence (14) and (15),

$$UO_2(HFA)_2TMP \rightleftharpoons UO_2(HFA)_2 + TMP \quad (14)$$

$$UO_2(HFA)_2 + UO_2(HFA)_2TMP \rightleftharpoons [UO_2(HFA)_2]_2TMP \quad (15)$$

although it cannot be the only mode of dimerization, since its presence in the system will not contribute to a difference between the calculated and observed pressures exerted by $UO_2(HFA)_2TMP$.

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Registry No. $UO_2(HFA)_2TMP$, 64708-00-5; $UO_2(HFA)_2TPPO$, 75701-20-1.

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(12) It should be noted that because the unit for pressure in the SI system is pascals and the standard state of a gas is defined as 0 °C and 101 325 Pa (1 atm), the right hand side of the expression $K_p = \exp(\Delta S°/R)\cdot\exp(-\Delta H°/RT)$ has to be multiplied by the term $(101\,325)^{\Delta n}$, where Δn is the change in the number of molecules in the reaction, to ensure that the values of $\Delta S°$ and $\Delta H°$ refer to the defined standard state; cf., e.g., J. P. Moore, "Physical Chemistry", 4th ed., Prentice-Hall, Englewood Cliffs, N.J., 1964, p 174.

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In Situ Photolysis of Chlorine/Ozone/Argon Matrices at 10 K

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The photolysis products of $Cl_2/O_2/Ar$, Cl_2/O_2, Cl_2O/N_2, Cl_2O/Ar, and $Cl_2/O_3/Ar$ matrices have been extensively studied by a number of investigators.[2-4] The in situ photolysis of $Cl_2/O_3/Ar$ matrices has been performed by Arkell and Schwager in 1967; however, to our knowledge this work has not been reported in the open literature.[2a] The reactions of chlorine atoms and ozone are of particular interest because of the stratospheric importance of the chlorine/ozone reaction mechanisms. The gas-phase reactions of chlorine and ozone, however, are very complicated because of the many reaction channels for ClO.[5-7] The in situ photolysis involves only the breaking of bonds, migration of oxygen atoms, and intramolecular rearrangements and is not nearly so complicated as gas-phase mechanisms. We report here, the results for the

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