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

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

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).

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

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

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

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),

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

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

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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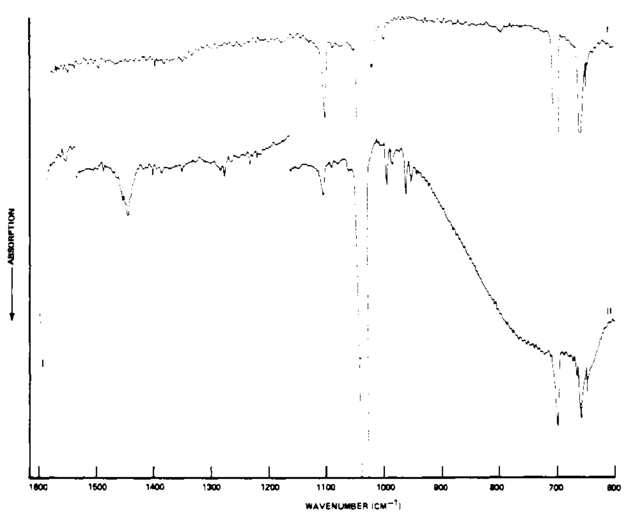


Figure 1. Infrared spectrum of the $Cl_2/O_3/Ar$ matrix prior to photolysis (I) and after 5 h of photolysis with $\lambda > 3300$ Å (II). In I, the only absorptions are due to ozone (1110, 1040, and 700 cm^{-1}). In II, the 1440-cm^{-1} absorption is ClOO, the 952- and 961-cm^{-1} absorptions are ClClO, and the 995-, 989-, and 983-cm^{-1} absorptions are due to $(ClO)_2$. The absorption near 1600 cm^{-1} is α-O_2.

Table I

ν, cm^{-1}	designation	time lapse,[a] h
961.3, 952.9	Cl-Cl-O (Cl-O stretch)	≃1
995.6, 989.4, 983.2	$(ClO)_2$ (Cl-O stretch)	≃2
1444	ClOO (O-O stretch)	≃4

[a] Between the start of photolysis and appearance.

photolysis of $Cl_2/O_3/Ar$ and $Cl_2/O_2/Ar$ mixtures.

Chlorine (Matheson, research grade) was further purified by trap to trap distillation to remove nitrogen. Chlorine/argon (1:50) mixtures were prepared by standard manometric techniques. Typically 2 mmol of Cl_2/Ar and 0.15 mmol of ozone (or oxygen) were simultaneously deposited onto a CsI window held at 10 K by an Air Products CS-202 refrigerator. A 1000-W Oriel mercury lamp, with water and glass filters ($\lambda > 3300$ Å), was employed for matrix photolysis. Spectral observations (4000–200 cm^{-1}) were made with a Beckman 4250X infrared spectrometer, with a frequency accuracy better than 1.5 cm^{-1} in the 1500–700-cm^{-1} region.

Figure 1 contrasts the prephotolysis and postphotolysis spectra of the region of interest (650–1500 cm^{-1}). The ClClO doublet at 961 and 953 cm^{-1}[3] was the first absorption to appear (after 1 h of photolysis). The ClOCl molecule was not observed. Further irradiation of the sample produced, after ≃2 h, a doublet at 995 cm^{-1}, indicating the presence of the ClO dimer.[3] After ≃5 h of photolysis, the ClOO molecule was observed (1444 cm^{-1}, see Table I).[2b]

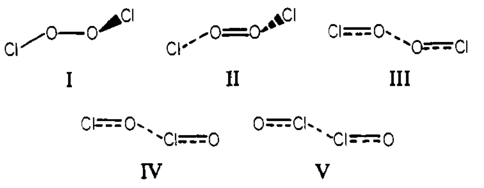
Warming the sample to ≃15 K resulted in an increase in the 995-cm^{-1} absorption (ClO dimer) and a decrease in the 961-cm^{-1} absorption (ClClO). There was a complete loss in intensity of the 1444-cm^{-1} absorption (ClOO) upon warming the sample to 40 K, and the ClOO absorption did not reappear upon recooling the sample, consistent with the expected $ClOO \xrightarrow{\Delta} Cl + O_2$ reaction.

The formation of ClClO is best explained by the mechanism

$$O_3 + h\nu \rightarrow O_2 + O \qquad (1)$$

$$Cl_2 + O \rightarrow Cl_2O \qquad (2)$$

The Cl_2O molecule may further react with oxygen atoms to give the observed ClO dimer,[3,4] $(ClO)_2$. The ClO molecule (850 cm^{-1}) was not observed in our experiments, and the dimerization of ClO in a 10 K matrix is unlikely. The structure of the ClO dimer absorbing at 995 cm^{-1} may be inferred from the possible photolysis mechanisms. In $Cl_2O/O_3/Ar$ photolysis experiments,[2a] the 995-cm^{-1} band is very intense, and Chi and Andrews[2a] suggest that the structure is Cl═O···Cl═O (I), while Pimental et al.[3,4] have proposed five different structures (I–V). If the ClO dimer is formed



by the reaction of ClClO and a migrating oxygen, then structures I–III require a (photolytic) intramolecular rearrangement in order to impose the two oxygen atoms between the two chlorine atoms. Structures IV and V require only the capture of migrating oxygen atom. However, the present growth data (Table I) suggests that the 995-cm^{-1} absorber is formed from the 962-cm^{-1} absorber which suggests that the 995-cm^{-1} band is due to structure V. Electronic structure calculations of the geometrical orientation of the ClO dimer are very desirable, inasmuch as they would provide information on the relative stabilities of the structures I–V.

The appearance of the ClOO molecule may be due to the direct reaction of ClO and O atoms, by the reaction of ClO and O atoms to produce OClO which undergoes intramolecular photochemical rearrangement to ClOO[2b] or by scission of a Cl=O bond in structure IV to produce OClO which subsequently rearranges to give ClOO. The photolytic conversion of OClO to ClOO is complete,[2b] and thus the OClO molecule should not be observed in our experiments.

The in situ photolysis of $Cl_2/O_2/Ar$ matrices for 5 h, under conditions identical with the $Cl_2/O_3/Ar$ photolysis, produced no chlorine oxides, consistent with published data.[2b] Thus, the direct reaction of Cl and O_2 to produce ClOO is conclusively ruled out.

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Registry No. Cl_2, 7782-50-5; O_3, 10028-15-6; ClClO, 7791-21-1; $(ClO)_2$, 12292-23-8; ClOO, 17376-09-9.

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Lanthanum and Neodymium Diiodide Hydride Phases and Their Hydrogen Dissociation Pressures

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Recently, lower halides of several early transition and lanthanide metals and thorium have been found to absorb hy-