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Properties of Dichlorine Hexaoxide in the Gas Phase and in Low-Temperature Matrices

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The IR spectrum of matrix-isolated dichlorine hexaoxide shows that there are two inequivalent chlorine atoms in the molecule and that it is best described as the mixed anhydride of chloric and perchloric acids. Of 18 fundamental vibrations, 16 were observed and many of them were assigned. $O_3ClOClO_2$ exhibits a broad UV absorption at 268 nm (ϵ_{max} = 3000 $dm^3\ mol^{-1}\ cm^{-1}$) in the gas phase. It is decomposed on photolysis in an Ar matrix to $ClOClO_3$ and O_2. The kinetics of formation and decomposition of $O_3ClOClO_2$ in the gas phase were also investigated. The rate of formation depends strongly on the concentration of ClO_2 and O_3. Cl_2O_6 does not dissociate into ClO_3 radicals, and the primary stable decomposition products are ClO_2, $ClOClO_3$, and O_2.

Dichlorine hexaoxide, Cl_2O_6, was first described in 1843 by Millon, but its structural, spectroscopic, and chemical properties remain controversial.[2–6] An ionic structure, $[ClO_2^+][ClO_4^-]$, was deduced from the reactivity.[2] This formulation matches a proposal for the structure of solid Cl_2O_6 made on the basis of investigations of vibrational spectra at low temperatures.[3] A recent X-ray crystallographic analysis confirmed the structure and provided structural parameters.[7] Preliminary investigations of gaseous Cl_2O_6 by FTIR spectroscopy were consistent with a $O_3ClOClO_2$ structure and showed that it decomposes into ClO_2, $ClOClO_3$, O_2, and $HClO_4$ in a few minutes.[8]

Since IR bands are broadened by their rotational envelopes in the gas phase, individual vibrations cannot be resolved when they are close together. It therefore seemed advisable to record the IR spectrum of matrix-isolated Cl_2O_6 to obtain confirmation of our results. Although some matrix-isolation experiments on Cl_2O_6 have already been reported,[5] the spectra could not be interpreted reliably because of the presence of extra bands due to decomposition and hydrolysis products.

Because of the potential significance of Cl_2O_6 in stratospheric chemistry,[6] we have also recorded its UV/vis spectrum and have investigated its photochemistry in matrices and the kinetics of its formation and decomposition in the gaseous state.

Experimental Section

Caution! Chlorine oxides are potentially explosive, especially in the presence of organic materials. Pure ozone also has a tendency to explode spontaneously. It is important to take appropriate safety precautions when these compounds are handled and to carry out reactions only in millimolar quantities.

Synthesis of Cl_2O_6. Cl_2O_6 was synthesized and purified on a preparative scale by the method described previously.[7] Alternatively, it was made in situ in an IR cell by mixing equimolar proportions of ClO_2 and O_3.

Ozone was made in an ozonizer (Model 301, Sander, Eltze, FGR) and condensed in a Pyrex trap cooled by liquid oxygen. Oxygen dissolved in the ozone was pumped away at 77 K.

Recording of Spectra. The IR spectra of gaseous and matrix-isolated Cl_2O_6 were recorded in the range 4000–200 cm^{-1} with a resolution of 4, 1, and 0.5 cm^{-1} by using two FTIR spectrometers: Nicolet MXS, Bruker IFS-113v. The UV/vis spectra were measured between 190 and 670 nm with a Perkin-Elmer Model 402 spectrometer in a glass cell of 100-mm path length equipped with Suprasil windows.

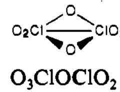
Cl_2O_6 was manipulated in the gas phase by using the apparatus described previously.[8]

Table I. Observed Frequencies of $O_3{}^{35}ClO^{35}ClO_2$ (A), $O_3{}^{35}ClO^{37}ClO_2$ (B), $O_3{}^{37}ClO^{35}ClO_2$ (C), and $O_3{}^{37}ClO^{37}ClO_2$ (D) in Ne and Ar Matrices (cm^{-1})

gas phase[a]	Ne matrix	Ar matrix	approx descrpn of mode			
	1284.1	1278.1	ν_{12}	a″	$\nu_{as}(ClO_3)$	A
	1282.6	1276.1		a″	$\nu_{as}(ClO_3)$	B
	1274.5	1270.7		a″	$\nu_{as}(ClO_3)$	C
	1269.3	1263.7		a″	$\nu_{as}(ClO_3)$	D
	1267.7	1261.7			?	
1265.0	1263.1		ν_{13}	a″	$\nu_{as}(ClO_2)$	A
	1257.7			a″	$\nu_{as}(ClO_2)$	C
	1251.3			a″	$\nu_{as}(ClO_2)$	B
	1249.5	1245.9	ν_1	a′	$\nu_{as}(ClO_3)$	A
	1248.2	1242.6[b]		a′	$\nu_{as}(ClO_3)$	B
	1245.6		ν_{13}	a″	$\nu_{as}(ClO_2)$	D
	1235.1	1231.9	ν_1	a′	$\nu_{as}(ClO_3)$	C
	1233.8	1228.5[b]		a′	$\nu_{as}(ClO_3)$	D
	1087.1	1084.7[b]			?	
1080.0	1082.3	1081.5[b]	ν_2	a′	$\nu_s(ClO_2)$	A, C
	1075.7	1074.9[b]		a′	$\nu_s(ClO_2)$	B, D
	1026.3	1026.0[b]	ν_3	a′	$\nu_s(ClO_3)$	A, B
1024.0	1023.7	1023.6[b]		a′	$\nu_s(ClO_3)$	C, D
	693.0	695.7	ν_4	a′	$\nu(O_3Cl{-}O)$	A
691.0	692.0	695.0		a′	$\nu(O_3Cl{-}O)$	B
	687.7	690.7		a′	$\nu(O_3Cl{-}O)$	C
	687.0	690.0		a′	$\nu(O_3Cl{-}O)$	D
629.0	625.2	624.0[b]	ν_5	a′	$\nu(O_2Cl{-}O)$	A, C
	621.0[b]	619.5[b]		a′	$\nu(O_2Cl{-}O)$	B, D
	585.5	585.9[b]	ν_{14}	a″	$\delta_{as}(ClO_3)$	A, B
579.0	582.8	583.0[b]		a″	$\delta_{as}(ClO_3)$	C, D
	578.2	580.0[b]	ν_6	a′	$\delta_{as}(ClO_3)$	
544.0	543.6	542.5	ν_7	a′	$\delta(ClO_2)$	A, C
	540.2	539.1		a′	$\delta(ClO_2)$	B, D
	486.6[b]	486.0[b]	ν_8	a′	$\delta_s(ClO_3)$	
		374.6	$\nu_{15/9}$	a″/a′	$\rho(ClO_2)$	
		371.2	$\nu_{16/10}$	a″/a′	$\rho(ClO_3)$	
		238.0	ν_{11}	a′	$\delta(ClOCl)$	

[a] Data from ref 8. [b] These bands showed matrix splittings.

Table II. Possible Structures of Cl_2O_6

structure	symm	no. of IR-active terminal ClO vib	no. of equiv Cl atoms
$OClOOClO_3$	C_1	4	0
$O_2ClOOClO_2$	C_2	4	2
	D_{2h}	2	2
$O_3ClOClO_2$	C_s	5	0
O_3ClClO_3	D_{3d}	2	2

Details of the matrix-isolation apparatus are given elsewhere.[10] The matrix was obtained in a manner similar to that used in ref 5 but under conditions in which decomposition and the presence of any moisture was avoided as far as possible. A gas stream of Ne or Ar was passed over

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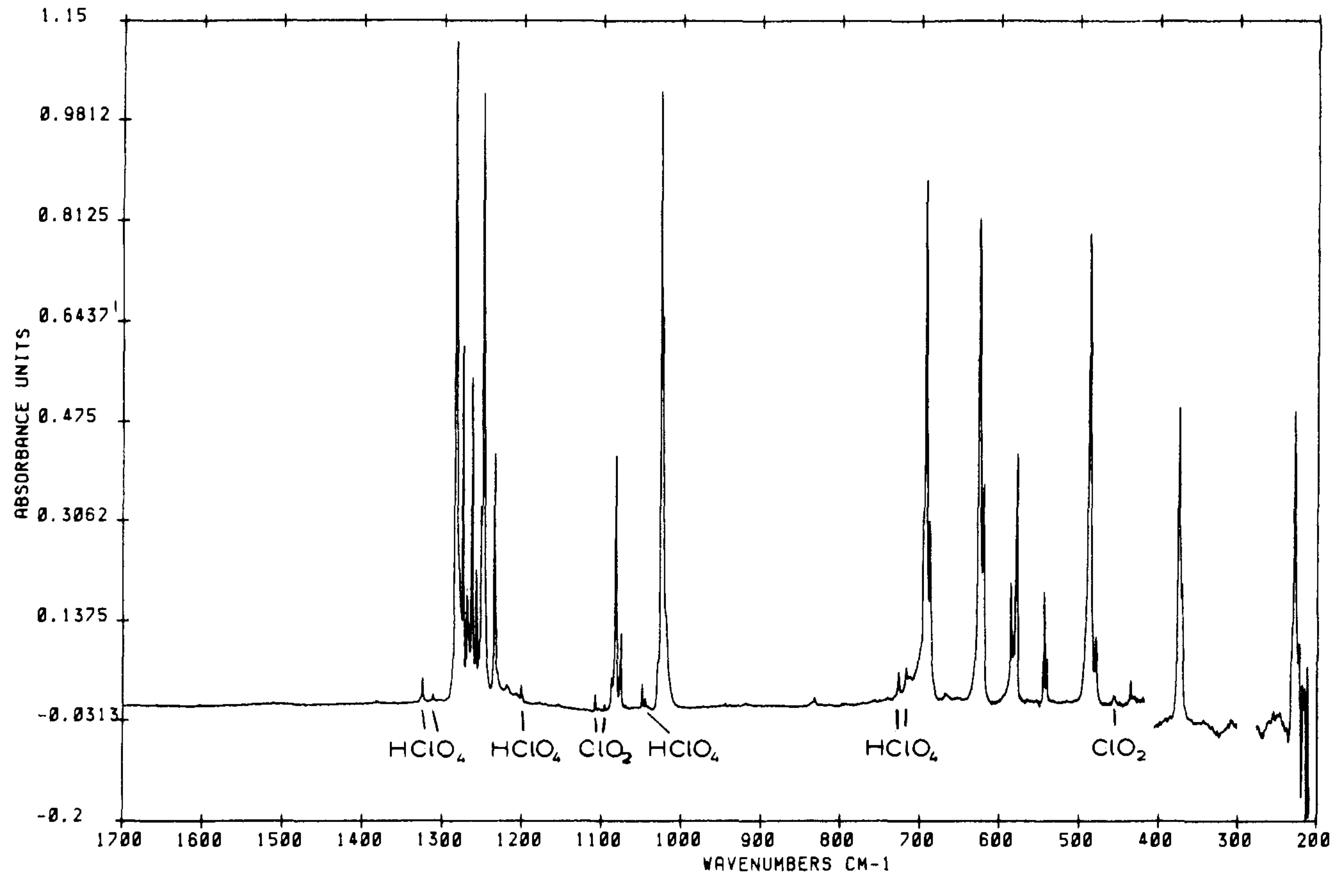


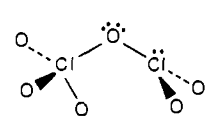
Figure 1. IR spectrum of Cl_2O_6 isolated in Ne matrix.

a very pure sample of Cl_2O_6 at 230 K, and the resulting gas mixture was condensed immediately onto a metal mirror at 4.5 K (Ne) or 16 K (Ar). Spectra were recorded on the Bruker IFS-113v via a reflection accessory.

Results and Discussion

Infrared Spectrum of Matrix-Isolated Cl_2O_6. A typical IR spectrum of matrix-isolated Cl_2O_6 is shown in Figure 1, and some spectral regions are shown under sufficient expansion in Figure 2 that the different $^{35/37}Cl$ isotopomers can be recognized. The experimental frequencies are listed in Table I.

One can distinguish the five possible structures for the Cl_2O_6 molecule (Table II) by the number of IR-active terminal ClO vibrations in the spectral range 1300–1000 cm^{-1} and the number of equivalent Cl atoms. By comparison of these theoretical numbers with the observed spectral features, the only possible structure for Cl_2O_6 is $O_3ClOClO_2$. The minimum-energy conformation of $O_3ClOClO_2$ based on VSEPR arguments is



Since this gives the Cl_2O_6 molecule C_s symmetry, the 18 fundamental vibrations are all IR-active; 11 of them belong to the a′ representation and the remaining 7 to a″. Because of the ^{35}Cl:^{37}Cl natural abundance ratio of 1:0.32, the four possible isotopomers $O_3{}^{35}ClO^{35}ClO_2$ (A), $O_3{}^{35}ClO^{37}ClO_2$ (B), $O_3{}^{37}ClO^{35}ClO_2$ (C), and $O_3{}^{37}ClO^{37}ClO_2$ (D) are distributed in the ratio of 1:0.32:0.32:0.1. It follows that 72 bands are expected in principle. All four isotopomers could indeed be detected (see Figure 2) for those vibrations involving substantial motion of the chlorine atoms.

Assignment. The assignments proposed in Table I were made on the basis of comparisons between the band positions, relative intensities, and isotopic shifts observed for ClO_2F and ClO_3F (Table III).

Table III. Fundamental Vibrational Frequencies and $^{35/37}Cl$ Isotopic Shifts of $FClO_2$[a] and $FClO_3$[b]

$F^{35}ClO_2$ freq, cm^{-1}	^{35}Cl–^{37}Cl isotopic shift, cm^{-1}	approx descrpn of mode	$F^{35}ClO_3$ freq, cm^{-1}	^{35}Cl–^{37}Cl isotopic shift, cm^{-1}	approx descrpn of mode
1271.4	12.8	$\nu_{as}(ClO_2)$	1315.0	15.80	$\nu_{as}(ClO_3)$
1105.8	7.4	$\nu_s(ClO_2)$	1063.0	3.05	$\nu_s(ClO_3)$
630.2	8.6	$\nu(ClF)$	717.0	10.00	$\nu(ClF)$
546.5	3.5	$\delta(ClO_2)$	591.0	3.09	$\delta_{as}(ClO_3)$
401.6		$\delta_s(FClO)$	550.0	0.89	$\delta_s(ClO_3)$
367.0		$\delta_{as}(FClO)$	405.0	0.17	$\rho(ClF)$

[a] Data from ref 11. [b] Data from ref 12.

The spectrum is particularly complicated in the region of the asymmetric stretching modes of the ClO_2 and ClO_3 groups (1300–1200 cm^{-1}). There are at least 12 bands that may be arranged into three groups of four in accordance with the expected $^{35/37}Cl$ isotope pattern and a $^{35/37}Cl$ isotope shift of 12–15 cm^{-1}. Several alternative ways exist for assigning the three groups of bands to the $\nu_{as}(ClO_2)$ (a″), $\nu_{as}(ClO_3)$ (a′), and $\nu_{as}(ClO_3)$ (a″) vibrations. Only the most likely will be discussed here.

The lowest frequency group of bands shows the expected intensity pattern of 1:0.32:0.32:0.1 for a molecule with two inequivalent chlorine atoms. The $^{35/37}Cl$ isotope shift of about 15 cm^{-1} clearly indicates an a′ or a″ component of a $\nu_{as}(ClO_3)$ vibration. The second a″ or a′ component of the $\nu_{as}(ClO_3)$ vibration of the isotopomers A and B should have the same intensity as the first. It is clearly recognizable and is separated by 34 cm^{-1} (split by the C_s symmetry). The frequency separation is, therefore, substantially larger than in $ClOClO_3$ (16 cm^{-1}).[14] This splitting could be caused by a greater distortion of the ClO_3 group or by more pronounced coupling between the $\nu_{as}(ClO_2)$ (a″) and the $\nu_{as}(ClO_3)$ (a″) vibrations. In cases of strong coupling we should

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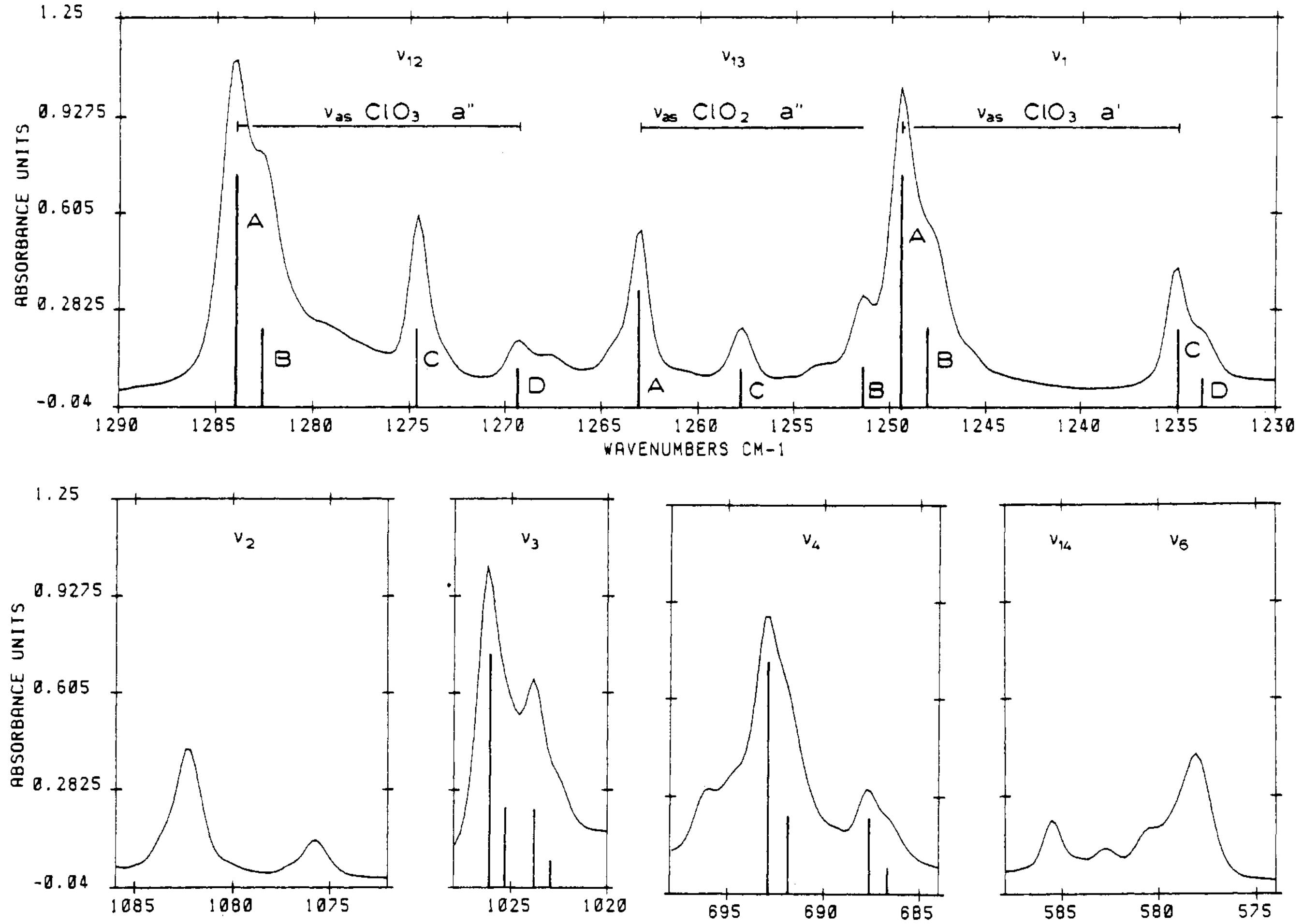


Figure 2. IR spectrum of Cl_2O_6 isolated in Ne matrix in the regions of ν_1, ν_2, ν_3, ν_4, ν_6, ν_{12}, ν_{13}, and ν_{14} in expanded scale. The four isotopomers $O_3{}^{35}ClO^{35}ClO_2$ (A), $O_3{}^{35}ClO^{37}ClO_2$ (B), $O_3{}^{37}ClO^{35}ClO_2$ (C), and $O_3{}^{37}ClO^{37}ClO_2$ (D) are indicated.

expect an irregular isotope pattern in the higher frequency component. The frequency of the isotopomer C is indeed strongly shifted, since the difference in frequency between $\nu_{as}(ClO_3)$ (a″) and $\nu_{as}(ClO_2)$ (a″) is particularly small. In this way we may assign the bands in the order

$$\nu_{as}(ClO_3)\ (a'') > \nu_{as}(ClO_2)\ (a'') > \nu_{as}(ClO_3)\ (a')$$

Two bands are observed in the region of the symmetric stretching modes of the ClO_2 and ClO_3 groups (1100–1000 cm^{-1}). The resolution is no longer sufficient to distinguish isotopomers B and D because of the weak coupling between $\nu_s(ClO_2)$ and $\nu_s(ClO_3)$. (At the maximum possible vibrational coupling, as exists between $\nu_s(ClO_3)$ of the ClO_3 groups in Cl_2O_7, we were able to observe a 1:0.64:0.1 intensity pattern at ca. 1062 cm^{-1}.) The comparison with the band positions and isotope shifts of ClO_3F and ClO_2F leads directly to the conclusion that $\nu_s(ClO_2) > \nu_s(ClO_3)$.

The bands at 691 and 629 cm^{-1} should correspond to the missing stretching modes of a′ symmetry. The ionic resonance form $[ClO_2{}^+][ClO_4{}^-]$ should make a significant contribution to the bonding of $O_3ClOClO_2$, so that we can anticipate that the O_2Cl–O bond will be weak. Consequently, the bands at 629 and 961 cm^{-1} should show the characteristics of O_2Cl–O and O_3Cl–O vibrations, respectively. However, the isotope pattern indicates that the vibrations are strongly mixed.

Apart from the ClO_3 and ClO_2 torsional modes, there remains the correct number of bands for the 11 deformation modes of Cl_2O_6. However, the assignment is not always clear because the bending modes are strongly coupled to one another.

The splitting pattern of the band at ca. 580 cm^{-1} is very complicated, indicating that there are two overlapping bands here. The band positions and isotopic shifts suggest by comparison with ClO_3F that these peaks correspond to the $\delta_{as}(ClO_3)$ vibration, split by the C_s symmetry. Similarly, the band at ca. 540 cm^{-1} can be described as a ClO_2 deformation on the basis of its position and isotope pattern. We assign the intense band at 490 cm^{-1} to the umbrella mode and the lowest energy band at 238 cm^{-1} as the skeletal deformation. The remaining rocking modes of the ClO_3 and ClO_2 groups are observed in the expected region.

In all, we have recorded 16 out of the 18 IR-active fundamentals of Cl_2O_6 and proposed a partial assignment. From a few of the bands it was clear that Cl_2O_6 consists of four isotopomers. There is, therefore, no longer any doubt that its molecular structure corresponds to the $O_3ClOClO_2$ formulation.

There was no indication in any of the numerous experiments that we performed that Cl_2O_6 dissociates to ClO_3 radicals, as has been postulated frequently in earlier work. Even when Cl_2O_6 was subjected to flash pyrolysis (150 °C; tube l = 100 mm, o.d. = 6 mm) immediately before matrix isolation, we could only detect ClO_2 and $HClO_4$. The other possible hydrolysis product, $HClO_3$, was not observed.

UV/Vis Spectrum and Photochemical Behavior of Cl_2O_6. Dichlorine hexaoxide is deep red in the solid state and black in the liquid phase. Details of its UV/vis spectrum have been published previously,[13] but considering our present study, we suspect that these authors recorded the spectrum of mixtures of Cl_2, $ClOClO_3$, and $HClO_4$. In order to record the UV spectrum of Cl_2O_6, we followed the reaction of ClO_2 and O_3 simultaneously in IR and UV cuvettes. Under appropriate conditions this reaction generates Cl_2O_6 quantitatively. The spectrum recorded in this way showed an unstructured band at λ_{max} = 268 nm ($\epsilon_{max} \approx 3000$ dm^3 mol^{-1} cm^{-1}) with a full width at half-height of ca. 120 nm, so the absorption stretched into the visible region. It could be assigned as an intervalence charge-transfer band.

On photolysis in an argon matrix with radiation of wavelength $\lambda > 400$, $\lambda > 320$, and $\lambda > 250$ nm, Cl_2O_6 underwent dissociation to O_2 and $ClOClO_3$ as the only products. The rate of reaction increased with shorter wavelength photolysis, as a consequence of the higher extinction. The IR bands of $ClOClO_3$ generated photochemically agree excellently with those given in ref 14.

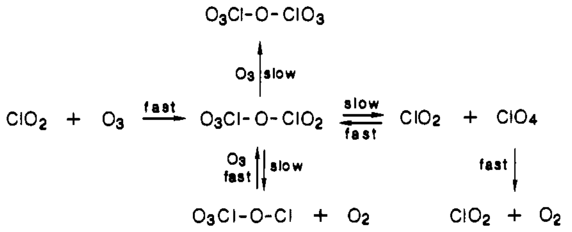
Mechanism of Formation and Decomposition of Cl_2O_6. In order to characterize the chemical behavior of Cl_2O_6 in more detail, we have followed both the formation and the decomposition in a gas cell using FTIR spectroscopy. Appropriate quantities of the reagents were allowed to stream into the evacuated cell at room temperature. Spectra were then recorded immediately.

Investigations of the formation of Cl_2O_6 from pure ClO_2 and O_3 in equimolar ratios showed that the rate of reaction was dependent on the partial pressures of both reagents and that the reaction proceeds according to the stoichiometry

$$2ClO_2 + 2O_3 \rightarrow Cl_2O_6 + 2O_2$$

At room temperature the reaction of 4 mbar of ClO_2 and 4 mbar of O_3 is complete in about 15 s, with 2 mbar of each reagent in about 60 s, and with 0.5 mbar of each in about 10 min. Excess of either ClO_2 or O_3 accelerates the reaction. No reaction intermediates, e.g. ClO_3 or Cl_2O_5, could be detected. Excess ClO_2 does not react with Cl_2O_6 after the reaction, but it strongly reduces the rate of decomposition. Excess O_3 inhibits the decomposition of Cl_2O_6 and also oxidizes it slowly (in 30–60 min) to Cl_2O_7. The simplest method of preparing pure gaseous Cl_2O_6 is, therefore, to mix stoichiometric quantities of ClO_2 and O_3 at 25 °C without exceeding the vapor pressure of 2 mbar for Cl_2O_6.

In contrast to its behavior in the liquid and solid states, Cl_2O_6 is very short-lived in the gas phase. Its half-life in completely dry, well-conditioned glassware is about 8 min with a starting pressure of 1 mbar at room temperature. ClO_2, $ClOClO_3$, and O_2 were detected as decomposition products. No bands of the possible radical intermediates, ClO_3 and ClO_4, could be detected in the IR spectra during the decomposition, so their partial pressures must be less than about 0.05 mbar. In the presence of traces of moisture or organic matter, $HClO_4$ was also formed. Addition of gaseous H_2, Cl_2, or Cl_2O_7 to Cl_2O_6 had no influence on the decomposition products, but the rate of decomposition was reduced slightly. These observations suggest that the decomposition is surface-catalyzed. In conclusion, the reactivity of Cl_2O_6 can be summarized by the following scheme:



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Registry No. Cl_2O_6, 12442-63-6; Cl_2O, 10049-04-4; O_3, 10028-15-6; Ar, 7440-37-1; Ne, 7440-01-9; ^{35}Cl, 13981-72-1; ^{37}Cl, 13981-73-2.

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Kinetic Study of the Dissociation of Sodium Cryptate(2,2,1)

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The rate of dissociation of sodium cryptate(2,2,1) ($NaCry^+$) has been measured at various temperatures and pressures in dimethyl sulfoxide (Me_2SO), *N,N*-dimethylformamide (DMF), and acetonitrile (MeCN) by using a high-pressure stopped-flow apparatus with conductometric detection. There are two reaction paths: an acid-independent path (k_{d1}), $CryNa^+ \rightarrow Cry + Na^+$, and an acid-dependent path (k_{d2}), $CryNa^+ + Hdca \rightarrow CryH^+ + Na^+ + dca^-$, where Hdca is dichloroacetic acid. Activation parameters are as follows: in Me_2SO, $k_{d1}/s^{-1} = (7.65 \pm 0.05) \times 10^{-1}$ (25 °C), $\Delta V_{d1}^{\ddagger}/cm^3\,mol^{-1} = 2.1 \pm 0.7$, $\Delta H_{d1}^{\ddagger}/kJ\,mol^{-1} = 70.4 \pm 0.8$, and $\Delta S_{d1}^{\ddagger}/J\,mol^{-1}\,K^{-1} = -11 \pm 3$; in DMF, $k_{d1}/s^{-1} = (3.37 \pm 0.03) \times 10^{-1}$ (25 °C), $k_{d2}/mol^{-1}\,kg\,s^{-1}$ (25 °C), $\Delta V_{d1}^{\ddagger}/cm^3\,mol^{-1} = 2.0 \pm 0.2$, $\Delta V_{d2}^{\ddagger}/cm^3\,mol^{-1} = -8.8 \pm 1.0$, $\Delta H_{d1}^{\ddagger}/kJ\,mol^{-1} = 73.0 \pm 0.9$, $\Delta H_{d2}^{\ddagger}/kJ\,mol^{-1} = 30 \pm 5$, $\Delta S_{d1}^{\ddagger}/J\,mol^{-1}\,K^{-1} = -9 \pm 3$, and $\Delta S_{d2}^{\ddagger}/J\,mol^{-1}\,K^{-1} = -140 \pm 20$; in MeCN, $k_{d2}/mol^{-1}\,kg\,s^{-1} = 73.5 \pm 0.5$, $\Delta V_{d2}^{\ddagger}/cm^3\,mol^{-1} = -16.0 \pm 0.8$, $\Delta H_{d2}^{\ddagger}/kJ\,mol^{-1} = 41.1 \pm 1.3$, and $\Delta S_{d2}^{\ddagger}/J\,mol^{-1}\,K^{-1} = -71 \pm 4$. The reaction volume for the formation of $NaCry^+$ in Me_2SO has also been measured dilatometrically: $\Delta V^{\circ} = 3.3 \pm 0.4\ cm^3\,mol^{-1}$. The reaction mechanism is discussed on the basis of these parameters.

Introduction

Cryptands as well as crown ethers form unusually stable complexes with metal cations, especially with alkali- and alkaline-earth-metal cations, which play an important role biologically. Thus, metal cryptates have been the subject of extensive study in the past two decades.

Kinetics for the formation and dissociation of cryptates has been fairly extensively studied, although more attention has been drawn to the thermodynamics of metal cryptates than to their kinetics.[1-11] However, no data of activation volumes for these reactions have been reported, partly because of little change in visible or ultraviolet spectra associated with formation of alkali- or alkaline-earth-metal cryptates and partly because of the lack of means to follow these reactions under high pressure.

We have developed a high-pressure stopped-flow apparatus with conductometric detection to follow such fast reactions under high pressure with no color change.

In this work, dissociation reaction 1 of sodium cryptate(2,2,1) has been followed conductometrically at various pressures up to 200 MPa with Me_2SO, DMF, and MeCN as solvents. Dichloroacetic acid (Hdca) was used as a scavenger for the dissociated cryptate. We selected these three solvents because of their very different basicities. This is apparently the first report both

$$NaCry^+ + Hdca \rightarrow Na^+ + CryH^+ + dca^- \qquad (1)$$

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