oxidizing radicals. From an ESR point of view, the 4,6-DHP's are easier to study due to their higher symmetry as compared to the uracils.

Acknowledgment. We thank Dr. J. Wroblewski for the synthesis of 5-methyl-4,6-dihydroxy- and 4,5,6-trihydroxypyrimidine. H.M.N. is very grateful to the Deutscher Akademischer Austauschdienst, the Max-Planck-Gesellschaft, and the Instituto Nacional de Investigacao Científica for supporting three short-term visits to Mülheim.

Registry No. 1c ($R_1 = R_2 = H$), 105163-90-4; 1c ($R_1 = R_2 = H$), 105163-91-5; 1c ($R_1 = Me$, $\tilde{R}_2 = H$), 105163-92-6; 1c ($R_1 = H$, $R_2 = H$) Me), 105163-93-7; OH, 3352-57-6; O⁻, 14337-01-0; SO₄⁻, 12143-45-2; Br2-, 12595-70-9; 4,6-DHP, 1193-24-4; 2-Me-4,6-DHP, 1194-22-5; 5-Me-4,6-DHP, 18337-63-8; 4,6-DHP radical anion, 105163-94-8; 2-Me-4,6-DHP radical anion, 105163-95-9; 5-Me-4,6-DHP radical anion, 105163-96-0; 4,6-DHP radical, 105163-97-1; 2-Me-4,6-DHP radical, 105163-98-2; uracil radical anion, 105163-99-3; 5-Me-uracil radical anion, 105164-00-9; 6-Me-uracil radical anion, 105164-01-0; uracil radical, 51446-22-1; 5-Me-uracil radical, 63031-49-2; 6-Me-uracil radical, 63221-84-1; 4,5,6-trihydroxypyrimidine radical anion, 105164-02-1; 4,5,6-trihydroxypyrimidine radical dianion, 105182-67-0; 4,5,6-trihydroxy-2-methylpyrimidine radical anion, 105164-03-2; 4,5,6-trihydroxy-2-methylpyrimidine radical dianion, 105164-04-3; 4,6-DHP-2ylmethyl radical dianion, 105164-05-4; 4,6-DHP-5-ylmethyl radical dianion, 105164-06-5; 4,6-DHP anion, 14341-11-8; 2-Me-4,6-DHP anion, 105164-07-6; 5-Me-4,6-DHP anion, 105164-08-7.

Production of Cl₂O₂ from the Self-Reaction of the CIO Radical

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The species Cl₂O₂ has been generated in a gaseous flow system at 220-240 K by reacting Cl atoms with one of three different ClO precursors: O₃, Cl₂O, or OClO. The infrared spectra of the reactive mixture indicate that at least two different dimers are produced: a predominant form with bands centered at 1225 and 1057 cm⁻¹ attributed to ClOOCI, and a second form with a band at 650 cm⁻¹ attributed to ClOCIO. The UV spectrum of the predominant form shows a maximum absorption cross section of $\sim 6.5 \times 10^{-18}$ cm²/molecule around 270 nm, with a wing extending beyond 300 nm. The implications of these results for the chemistry of the stratosphere are discussed.

Introduction

The self-reaction of the ClO radical has been the subject of numerous kinetic investigations, which have been reviewed on several occasions.^{1,2} The different studies have shown that the reaction exhibits second-order kinetic behavior with respect to the CIO concentration, but they have yielded conflicting results in terms of the relative importance of the various reactive pathways:

$$ClO + ClO \rightarrow Cl_2 + O_2 \tag{1}$$

$$\rightarrow$$
 Cl + ClOO (2)

$$\rightarrow$$
 Cl + OClO (3)

$$ClO + ClO + M \rightarrow Cl_2O_2 + M$$
 (4)

Evidence for the formation of a dimer, as in reaction 4, comes from the studies of Cox and co-workers^{3,4} and of Basco and Hunt,⁵ who observed a transient spectrum in the ultraviolet attributed to Cl₂O₂.

The self-reaction of the ClO radical has been neglected in stratospheric modeling calculations due to the slow overall rate to yield final products (Cl or Cl₂, reactions 1-3).^{2,4} However, the rate of formation of the dimer (reaction 4) is likely to be considerably faster, especially at the higher pressures and lower temperatures prevailing in the lower stratosphere, and the reaction might be of importance depending on the subsequent fate of the dimer. In particular, the following cycle might play a role in the Antarctic stratosphere, where the total atmospheric ozone content in the spring has fallen remarkably over the past 10 years:^{6,7}

$$ClO + ClO \xrightarrow{M} Cl_2O_2$$
 (4)

$$Cl_2O_2 + h\nu \rightarrow Cl + ClOO$$
 (5)

$$ClOO \xrightarrow{M} Cl + O_2$$
 (6)

$$2(Cl + O_3 \rightarrow ClO + O_2) \tag{7}$$

net:
$$2O_3 \rightarrow 3O_2$$

In this paper we present the results of our studies of IR and UV spectroscopic characterization of the ClO dimer produced in reaction 4.

Experimental Section

The infrared analyses were obtained using a Teflon-coated absorption cell wrapped with a copper cooling coil and fitted with internal optics (57 cm long, 36 passes, 300 mL volume) interfaced to a Nicolet 7199A or a Nicolet 20SX Fourier-transform infrared (FTIR) spectrometer and a liquid N_2 cooled HgCdTe detector. Routine spectra were recorded at 1 cm⁻¹ resolution in order to achieve rapid data collection. The temperature inside the cell was controlled by circulating cooled methanol through the copper coil and monitored with copper-constantan thermocouples.

The ultraviolet spectra were recorded with a Cary 219 double beam spectrophotometer interfaced to a Nova 3 computer, and using a 50 cm long, 3.5 cm diameter jacketed quartz cell fitted with Suprasil windows and with folded optics giving an optical path length of 100 cm. Low-temperature spectra were recorded by pumping cooled methanol through the outer jacket.

Chlorine atoms were generated by flowing a 1-5% Cl₂/N₂ mixture (Matheson, Certified Standard) through a quartz capillary tube wrapped with Nichrome heating wire. The effluent gas was

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Figure 1. Infrared spectrum of ClO dimers at 238 K produced with Cl_2O as a ClO precursor.

mixed downstream with the other reactant gas (Cl₂O, OClO, NOCl, or NO₂) at about room temperature, before entering the cold absorption cells. Chlorine monoxide (Cl₂O) and chlorine dioxide (OClO) were prepared by passing Cl₂/N₂ mixtures through a column of freshly precipitated yellow HgO and NaClO₂ column, respectively. Ozone was generated by passing O₂ through a Welsbach T-408 ozonator and was collected on silica gel at 195 K. The concentration of OClO, Cl₂O, or O₃ in the flowing mixture was monitored continuously with a Perkin-Elmer 552 UV-visible spectrophotometer fitted with a 50-cm cell (with folded optics, giving an optical path of 100 cm), connected in series with the FTIR absorption cell. NO₂/N₂ mixtures (Matheson, Certified Standard), NO/N₂ mixtures (Matheson, Certified Standard), NO/N₂ (Matheson), and N₂ (Matheson, Prepurified) were used without further purification.

All experiments were carried out by flowing the gaseous mixture through the absorption cells, with a linear velocity of 50–500 cm s⁻¹. The flow rates were determined with Matheson 8160 mass flowmeters, or by measuring the pressure change in a given volume. Pressures were monitored before and after the absorption cells with a 0–1000 Torr MKS capacitance manometer.

Results and Discussion

ClO radicals were generated by the reaction of chlorine atoms with one of three different reactants:

$$Cl + O_3 \rightarrow ClO + O_2$$
 (7)

$$Cl + Cl_2O \rightarrow Cl_2 + ClO$$
 (8)

$$Cl + OClO \rightarrow ClO + ClO$$
 (9)

At room temperature the rate constants for these reactions are 9.8×10^{-11} , 5.9×10^{-11} , and 1.2×10^{-11} cm³ molecule⁻¹ s⁻¹, respectively,⁸ so that under the conditions of our experiment, essentially all the chlorine atoms were converted to ClO before entering the absorption cells. The residence time of the flowing mixture in these cells was in the 0.1–1-s range; the OClO, Cl₂O, and O₃ concentrations ranged between 5 and 500 mTorr, and the total pressure between 20 and 100 Torr, with N₂ as the carrier gas. Molecular chlorine was in the 100–500 mTorr range, with about 5% being thermally dissociated to produce atomic chlorine (as determined by titration with NOCl). For most experiments the temperature of the absorption cells was kept in the 220–240 K range; for some experiments it was ~298 K.

In addition to the absorption bands due to excess reactants, the infrared spectra contained in each case bands A, B, C, D, and



Figure 2. Infrared spectrum of ClO dimers at 238 K produced with O_3 as a ClO precursor.



Figure 3. Infrared spectrum of CIO dimers at 243 K produced with OCIO as a CIO precursor.



Figure 4. Same as Figure 3, after subtraction of the OCIO contribution.

E, centered at 1225, 1057, 740, 653, and 562 cm^{-1} , respectively. Within experimental error, the ratio of the peak absorbances of bands A and B remained constant with variations in reactant

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Figure 5. Ultraviolet spectrum of Cl_2O_2 at ~ 240 K. The solid line represents the average of 10 runs, and the shaded area plus or minus one standard deviation (this study); the solid circles are from ref 5.

concentrations, residence time, and total pressure. In contrast, the A to D absorbance ratio varied significantly. The weaker C and E bands appear to be correlated in strength with the A and B bands, but the experimental error was not sufficiently small to assign them to the same molecular species.

The intensities of all these bands increased as the temperature decreased, and they all disappeared in the presence of NO_2 , in which case the only product observed was ClONO₂. Typical product spectra are shown in Figures 1–4. In most cases the dominant product bands (in the absence of NO_2) were A and B.

These results indicate that two or more different species are formed in the reaction of ClO with itself. We conclude that these are isomeric forms of $(ClO)_2$, and the structures of two of these forms probably correspond to the two different intermediates required to explain the formation of the overall reaction products:

$$cio + cio = ciocci \qquad ci_2 + o_2$$

$$cio + cio = cioccio - ci + ciocio$$

$$cio + cio = cioccio - ci + ocio$$

The A and B bands are likely to correspond to Cl–O or to O–O stretches of the ClOOCl isomer, which is the predominant form; the D band might correspond to ClOClO. The experiments in which Cl_2O or O_3 were used as precursors showed a small amount of OClO being formed as a product, confirming earlier reports^{1–5} that the branching ratio for this channel is about 5%.

The experiments in which OCIO was used as a CIO precursor yielded the largest amount of products (due to the catalytic cycle consisting of reactions 2, 6, and 9). Besides the IR bands mentioned above, in some of these experiments weak bands were observed at 2440, 2270, and 2114 cm⁻¹, and these are clearly overtones or combinations of bands A and B. Furthermore, for some room temperature runs we observed a band at 1280 cm⁻¹ and a feature at 1025 m⁻¹ which appeared as a shoulder on the strong 1057-cm⁻¹ (B) band. These bands are probably due to a secondary reaction product such as a CIO–OCIO adduct (they are most likely the CIO₃ stretches of CIOCIO₂), even though the CIO + OCIO reaction is very slow.⁹

Figure 5 shows the ultraviolet spectrum of the flowing product mixture at ~240 K, with OCIO as a CIO precursor, after subtraction of the OCIO and Cl₂ absorptions. The spectrum represents an average of 10 runs; the standard deviation was ~15% around 270 nm, as shown in the figure. The banded structure between 280 and 300 nm is clearly due to residual CIO. For each run, the amount of Cl₂O₂ present was estimated by accounting for Cl₂ and OCIO in a material balance; the Cl₂ concentration was determined by its UV absorbance and the OCIO concentration both by its UV and by its IR absorbance. The IR spectrum of the same mixtures showed bands A and B prominently. The bands C, D, and E were also present, but much weaker. Hence, we attribute the UV spectrum to the dimer CIOOCl, the predominant form under most experimental conditions.

Cox et al.⁴ concluded from their experiments that the (Cl-O)–(ClO) bond dissociation energy is about 17.6 kcal/mol, in good agreement with the 16.5 kcal/mol value given by Basco and Hunt.⁵ Based on these results, the lifetime against thermal decomposition at 243 K can be estimated to be at least 1 min. Thus, Cl_2O_2 should be quite stable in our IR and UV cells at the lower temperatures employed, while the lifetime is only ~13 ms at room temperature.⁴

Our UV cross section values for Cl_2O_2 do not agree well with those obtained by Basco and Hunt,⁵ as can be seen in Figure 5. Of the six values reported by these authors, two (at 277.4 and at 299.2 nm) are smaller than ours and the rest (at 232, 235.5, 240, and 251 nm) are larger; furthermore, no maximum is apparent in their spectrum. The reason for the discrepancy is not clear.

There are two earlier studies of IR spectra attributed to various $(ClO)_2$ species, obtained by matrix isolation techniques, which are different from the spectra we report here. Rochkind and Pimentel¹⁰ reported bands at 982 and 945 cm⁻¹, and Chi and Andrews¹¹ observed bands at 945, 986, and 995 cm⁻¹, with the last two bands assigned to Cl–O stretches in Cl–O–Cl–O produced in the matrix by reaction of O atoms with Cl₂O. The most likely reason for the discrepancy is the vastly different set of experimental conditions leading to different chemical species: photolysis of Cl₂O/O₃ mixture in a solid matrix at ~20 K, vs. chemical generation of ClO in the gas phase at 250–300 K in our work.

More recently, Loupec and Potier¹² investigated the products of the reaction of ozone with liquid Cl₂ at 233 K, obtaining infrared spectra with bands at 1210, 780, and 740 cm⁻¹, which they attributed to Cl–O–Cl–O. It is possible that several isomeric forms were present in their experiment. The 1210- and 740-cm⁻¹ bands correspond most likely to our A and C bands. In addition to the well-characterized bands of ClOClO₃, these authors also observed bands at 1280 and 1015 cm⁻¹, which they assigned to ClOClO₂. These two bands clearly correspond to the 1280- and 1025-cm⁻¹ bands which appeared in our Cl + OClO experiments.

Schell-Sorokin et al.13 carried out an IR study of the photolysis products of OCIO and reported a transient IR band of unknown origin at ~ 1232 cm⁻¹, which they speculate to be Cl₂O₃, formed by the reaction between CIO and OCIO. Clearly, their 1232-cm⁻¹ band is the same as our "A" band, which is observed also with Cl₂O or O₃ as ClO precursors, and hence it cannot be due to Cl₂O₃. These authors also describe qualitatively a transient broadband UV absorption spectrum originating at ~290 nm and extending to beyond ~ 230 nm. It could well correspond to our (ClO)₂ spectrum; however, their experimental conditions involved much higher reactant concentrations, presumably at room temperature or above, with production of ClOClO3 as a final product. More recently, Barton et al.14 monitored a UV product spectrum in the photolysis of OCIO, which they attributed to a mixture of ClO-ClO₃ and Cl₂O₂. Their results cannot be directly compared with ours, since the UV spectrum of ClOClO₃ is unknown; they did report a residual spectrum assigned to ClOClO₃, but only after subtracting the Cl₂O₂ contribution assuming the equilibrium constant and absorption cross section values given by Basco and Hunt.5

Possible photolysis channels for Cl_2O_2 include the following:

$$Cl_2O_2 + h\nu \rightarrow ClO + ClO \tag{10}$$

$$Cl_2O_2 + h\nu \rightarrow Cl + ClO_2$$
 (11)

By analogy with H_2O_2 , which photodissociates to yield OH radicals,¹⁵ one might expect reaction 10 to occur. However, the Cl_2O_2 UV spectrum extends to longer wavelengths compared to that of H_2O_2 , and absorption at these longer wavelengths is most likely

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due to transitions involving nonbonding electrons in the Cl atom. Near-UV photolysis of ClONO₂ breaks the Cl–O bond (rather than the stronger ClO–NO₂ bond)⁸, so that reaction 11 is certainly possible. In fact, Margitan¹⁶ found evidence for the occurrence of this channel: by premixing NO with OClO at 220 K in a flow system, he observed an enhancement in the primary product yield of Cl atoms upon photolysis of the mixture at 266 nm. He attributed this enhancement to the presence of Cl₂O₂, which was formed in addition to ClONO₂:

$$NO + OCIO \rightarrow NO_2 + CIO$$
$$CIO + NO_2 \xrightarrow{M} CIONO_2$$
$$CIO + CIO \xrightarrow{M} Cl_2O_2$$

Stratospheric Implications

In order to assess the potential role of Cl_2O_2 in the atmosphere, its rate of formation and of destruction needs to be estimated. The rate constant for the formation reaction

$$ClO + ClO + M \rightarrow Cl_2O_2 + M$$
 (4)

is not well established. Values reported in the literature (defined as $(-1/2[M][ClO]^2)(d[ClO]/dt))$ include ~5 × 10⁻³² cm⁶ molecule⁻² s⁻¹ (Johnston et al.,¹⁷ for M = O₂); 3 × 10⁻³² cm⁶ molecule⁻² s⁻¹ (Cox et al.,⁴ for M = O₂ + N₂); and 1.1 × 10⁻³² cm⁶ molecule⁻² s⁻¹ (Basco and Hunt,⁵ for M = O₂), all at 298 K; no lower temperature studies have been published yet, but the rate is expected to increase at lower temperature, as is the case with other radical recombination reactions.

The Cl_2O_2 photodissociation rate in the atmosphere can be estimated from the cross sections obtained in this work (see Figure 5); considering only photolysis beyond ~290 nm, the cross sections happen to be very similar to those of HOCl.^{8,18} The solar photolysis rate for HOCl is ~4 × 10⁻⁴ s^{-1,18} Hence, the Cl₂O₂ lifetime against solar photodissociation should be of the order of 1 h.

The chemistry of Cl_2O_2 is not important in the upper stratosphere, since ClO reacts predominantly with O atoms and with NO, rather than with itself, and in the lower stratosphere reaction with NO₂ to form ClONO₂ normaly dominates. However, under conditions of low NO_x abundance, high ClO abundance and low temperature, Cl_2O_2 could become considerably more important. Such conditions appear to occur in the Antarctic stratosphere where a striking decline in spring ozone abundances has been observed in recent years.^{6,7} Solomon et al.¹⁹ proposed the reaction

$$HCI + CIONO_2 \rightarrow Cl_2 + HNO_3$$
(12)

as the rate-limiting step to explain these observations. McElroy et al.²⁰ and Tung et al.²¹ proposed instead the following reactions as the rate limiting step:

$$CIO + BrO = Br + CI + O_2$$
(13)
Br + OCIO (14)

The rate constants for these reactions are quite large $(k_{13} \approx$ $k_{14} \approx 6.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).⁸ To explain the observed ozone decline, the BrO concentration would have to be around 20 ppt and the ClO concentration around 3 ppb,¹⁹ but no measurements of these species have been carried out yet over Antarctica. Assuming these concentration values, and assuming the rate constant for reaction 4 (the Cl₂O₂ formation reaction) to be in the $(1-5) \times 10^{-32}$ cm⁶ molecule⁻² s⁻¹ range (as discussed above), ClO would react with itself about as fast as with BrO. Furthermore, in the lower stratosphere over Antarctica the Cl_2O_2 photodissociation rate would be comparable, if not considerably faster than its thermal decomposition rate, due to the very low temperatures found at those latitudes (190-220 K). Hence, if our UV measurements are correct, and if the primary Cl_2O_2 photolysis products are Cl + ClOO, the cycle consisting of reactions 4-7 might indeed play a role in explaining the observed Antarctic ozone decline. Clearly, additional studies of the chemistry and photochemistry of Cl_2O_2 are needed to address this question.

Acknowledgment. We thank M. McElroy, S. Solomon, N. D. Sze, and R. S. Stolarski for providing us with their results prior to publication. The early part of this work was carried out while the authors were at the University of California, Irvine, and was supported by the National Science Foundation under Grant ATM-8106136. The research described was performed at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

Registry No. Cl, 22537-15-1; Cl₂O, 7791-21-1; OClO, 10049-04-4; NOCl, 2696-92-6; NO₂, 10102-44-0; O₃, 10028-15-6; ClOOCl, 12292-23-8; ClOClO, 105206-44-8; ClO, 14989-30-1.

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