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## ABSTRACT

## POLAR OZONE WORKSHOP

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## CHEMISTRY OF THE ClO DIMER AT LOW TEMPERATURES

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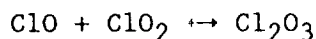
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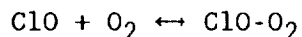
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The unique conditions of low temperature and high observed ClO concentrations in the Antarctic stratosphere have focussed attention on the possible role of ClO dimers in the photochemistry of that region, particularly as related to ozone depletion. Compared to other aspects of stratospheric chlorine chemistry, very little is known about the formation, structure, thermal decomposition, photochemistry, and chemical reactivity of the dimer. Other possible complexes of ClO, such as



and



are also very uncertain with regard to their importance under laboratory and atmospheric conditions.

We have conducted a series of experiments on the chlorine-catalyzed photo-decomposition of O<sub>3</sub> both in the gas phase and in inert solvents such as CF<sub>4</sub> and CO<sub>2</sub> in the temperature range of about 190 - 225 K. The liquid medium was chosen in order to minimize possible surface loss of long-lived ClO dimer, and to aid in the stabilization of transient excited intermediates. The mechanism of dimer formation was as follows:

- (1)  $\text{Cl}_2 + h\nu \rightarrow \text{Cl} + \text{Cl}$
- (2)  $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$
- (3)  $\text{ClO} + \text{ClO} \rightarrow \text{Cl}_2\text{O}_2$

The experiments were done in cooled low temperature cells, with irradiation from an Osram high pressure mercury arc, filtered to remove radiation below 325nm. Spectral analysis was by means of a Cary Model 2200 UV spectrometer.

The principal objectives were (1) to determine the lifetime of the dimer as a function of temperature, (2) to observe spectral changes in the mixture which could be attributed to dimer or related products, and (3) to observe chemical or photochemical reactions of the dimer.

## RESULTS

Gas Phase: A transient absorption spectrum attributed to symmetric ClO dimer was obtained in experiments at 200-220K. (Figure 1). Two methods were used to obtain the spectra: (1) Following partial photodecomposition of the O<sub>3</sub>, spectra were recorded and residual absorptions due to O<sub>3</sub>, Cl<sub>2</sub>, and the empty cell were successively subtracted. (2) After photolysis, a difference spectrum was taken before and after standing for a period of 10-30 minutes. The spectral change on standing corresponded to the same absorption as that obtained by method 1, indicating that the dimer was unstable on a time period of a few minutes. The proposed mechanism for dimer loss is discussed below.

Liquid Phase: These experiments provided further evidence of dimer instability at quite low temperatures. In liquid CO<sub>2</sub> near 225K, photolysis produced a rapid O<sub>3</sub> loss as expected from reactions 1 and 2, but no measurable Cl<sub>2</sub> loss corresponding to dimer formation by reaction 3. Computer simulations, assuming a long dimer lifetime with respect to thermal decomposition, indicated that measurable Cl<sub>2</sub> loss should have been observed. There is evidence that the dimer loss can be explained by the bimolecular self-reaction,



Experiments at and below 200K in liquid CF<sub>4</sub> contrasted sharply with the above experiments in liquid CO<sub>2</sub>, showing clear evidence of substantial product formation. The observed products included OClO and a material tentatively identified as Cl<sub>2</sub>O<sub>3</sub>. Spectral changes occurring in the mixtures on standing indicate that dark reactions are also important in the overall process. We consider that the onset of OClO formation follows from the appearance of the asymmetric dimer, ClOClO, as a stable product in the liquid medium. Since these products were not observed in gas phase experiments at the same temperature, it is probable that efficient quenching of the ClOClO reaction intermediate is necessary to prevent isomerization to the more stable ClOOCl structure.



Production of OClO can be accounted for by the reaction:



## MAJOR CONCLUSIONS

A spectral feature peaking near 245 nm, similar to that previously reported by R. A. Cox and co-workers, is attributed to the symmetric dimer ClOCl.

The dimer ClOCl undergoes a bimolecular self-reaction which can become the dominant loss mechanism at low temperatures.

The asymmetric dimer ClOClO, Although present as an excited intermediate in the ClO + ClO reaction, is difficult to stabilize and would not be expected to be produced under the low pressure conditions prevailing in the atmosphere.

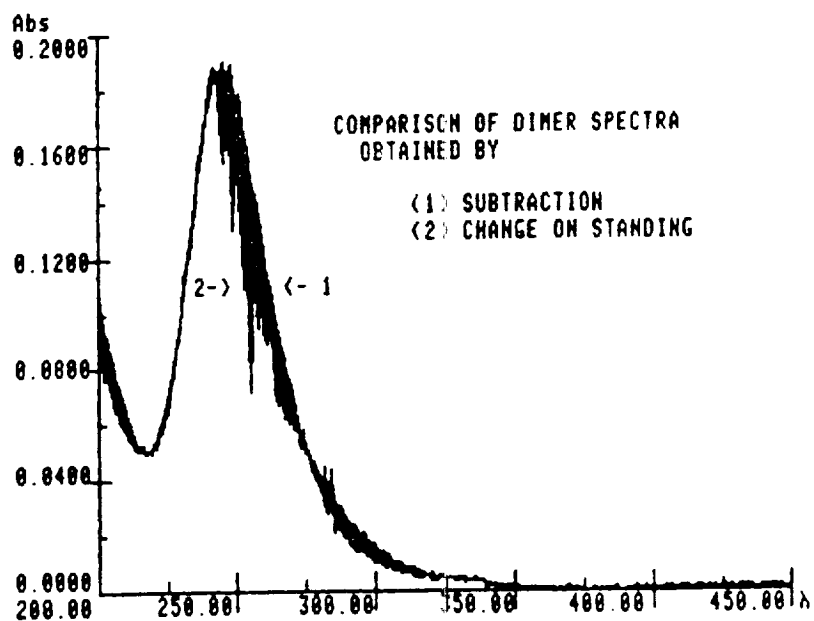


Figure 1.