

A STUDY OF THE CHEMICAL DEGRADATION OF ClONO₂ IN THE STRATOSPHERE

A. R. Ravishankara and D. D. Davis

Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Georgia 30332

G. Smith and G. Tesi

Department of Chemistry, University of Maryland, College Park, Maryland 20742

J. Spencer

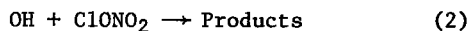
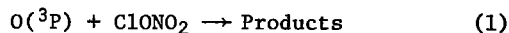
Chemistry Department, University of California, Irvine, California 92664

Abstract. The flash photolysis-resonance fluorescence technique has been utilized to measure the rate constants for the reactions of chlorine nitrate (ClONO₂) with two stratospheric radicals, O(³P) and OH. Both rate constants were measured at a pressure of 20 Torr and a temperature of 245 K. The reactions with their corresponding rate constant in units of cm⁻³ molecule⁻¹s⁻¹ are: O(³P) + ClONO₂ → Products, $k_1 = (2.0 \pm 0.2) \times 10^{-13}$; OH + ClONO₂ → Products, $k_2 = (3.7 \pm 0.2) \times 10^{-13}$.

The above results, coupled with the photolysis rate of ClONO₂, indicate that these chemical degradation pathways contribute less than 10% to the removal of ClONO₂ in the stratosphere.

INTRODUCTION

Recent modelling calculations by Crutzen (1976), McAfee and Crutzen (1976), Chang and Wuebbles (1976), and Molina (1976), have indicated that stratospheric chlorine nitrate (ClONO₂) might be of importance as a temporary sink for both chlorine and nitrogen oxides. If so, the impact of injected NO_x and/or chlorine on stratospheric ozone profiles could be significantly reduced. The effectiveness of this potential sink in altering model calculated stratospheric ozone profiles depends primarily on two factors: (1) the rate of formation, and (2) the rate of destruction of ClONO₂. The work to be reported here deals with the rate of destruction of ClONO₂ under stratospheric conditions. There are two possible modes of destruction of ClONO₂; viz, photolysis by sun light, and removal by chemical reactions. In the latter case, which will be the primary focus of this paper, likely reaction paths would involve the two free radical species O(³P) and OH, i.e.:



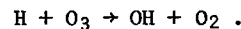
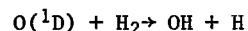
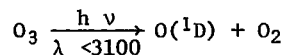
Presented in the following text will be recently measured gas kinetic data on Reactions (1) and (2). Rates of destruction via the above processes will then be compared with that resulting from direct photochemical decomposition.

Copyright 1977 by the American Geophysical Union.

EXPERIMENTAL

The flash photolysis-resonance fluorescence system used in this study has been described in detail in earlier publications (Davis et al., 1974, 1972). Hence, only a limited description of the system is presented here. In this investigation a pyrex cell with an internal volume of ~150 cm³ was used to examine both Reactions (1) and (2). The reaction mixture was maintained at 245 K by circulating methanol from a thermostated circulation bath through the outer jacket of the reaction cell. The temperature of the cell was monitored using an Iron-Constantan thermocouple.

O(³P) was produced by the vacuum UV photolysis of 150 m Torr of O₂. Since 20 Torr of Ar was used as the diluent gas in these experiments, all O(¹D) formed during the flash would have been quenched to O(³P) within a few microseconds after its formation. OH was produced by the photolysis of a mixture of 25 m Torr of O₃, 100 m Torr of H₂, and 20 Torr of Ar through the sequence of reactions:



OH produced in the last step would be excited; however, these radicals would be quenched to their ground state within a few microseconds. The change in concentration of O(³P) or OH was followed by the resonance fluorescence technique using either an EMR vacuum UV photomultiplier tube (1300Å), or an RCA 8850 tube (3095Å).

In carrying out experiments on both reactions, the gas handling system and the reaction cell were "conditioned" by filling them with chlorine nitrate at a low pressure (<30 m Torr) to remove any active spots on the glass surfaces. This procedure was carried out immediately prior to the direct introduction of a measured amount of chlorine nitrate into the reaction cell. In all experiments, the concentration of chlorine nitrate was in large excess (>10³) over the concentration of O(³P) or OH; hence, pseudo-first order kinetics prevailed.

Chlorine nitrate was purified by bulb-to-bulb distillation and its purity was checked by recording both its IR (Miller et al., 1967), and

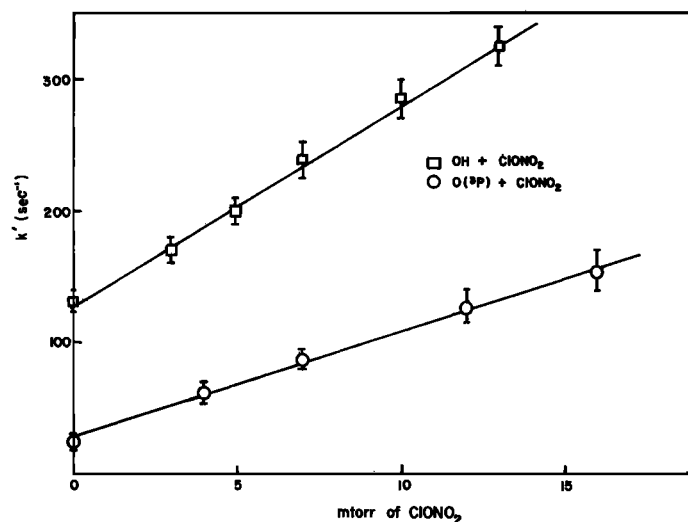


FIGURE 1

A plot of the pseudo-first order rate constant for the decay of OH [□], or O(³P) [○] as a function of ClONO₂ pressure at 245 K. The error bars in these plots show the total uncertainty observed in three to four independent measurements of the first order rate constant at a given ClONO₂ pressure.

UV spectrum. On the basis of these analyses, together with calculations of the O(³P) loss due to the reaction, O(³P) + NO₂ → NO + O₂ (Davis et al., 1973), the NO₂ impurity level was placed at less than .5%. It should be noted, however, that at 298 K there was evidence indicating that ClONO₂ decomposed in the glass reaction cell when allowed to stand for several minutes. This decomposition was evident from repeated measure-

ments of the rate constant k_1' , and finding steadily increasing k_1' values with an increase in the residence time. However, at 245 K there was no evidence for the decomposition of ClONO₂. For this reason, both reactions were studied at the reduced temperature of 245 K.

Ozone was prepared by passing O₂ through an ozonator. Before use, O₃ was purified by continuously pumping while at 195 K; its purity was checked by UV absorption spectroscopy. UHP grade Matheson H₂ and O₂, and UHP gold label Ar were used without further purification.

RESULTS AND DISCUSSION

The rate constants for both Reactions (1) and (2) were measured at 245 K simulating stratospheric temperatures. The pseudo-first order rate constants, k_1' and k_2' , for the disappearance of O(³P) and OH are shown as a function of the ClONO₂ pressure in Figure 1. Linear least square analyses of the data were carried out to obtain the bimolecular rate constants, k_{b1} . At 245 K, the k_{b1} values are

$$k_1 = (2.0 \pm .2) \times 10^{-13} \text{ cc molecule}^{-1} \text{ sec}^{-1}$$

and

$$k_2 = (3.7 \pm .2) \times 10^{-13} \text{ cc molecule}^{-1} \text{ sec}^{-1}.$$

For Reactions (1) and (2), the quoted errors are two standard deviations.

In the investigations of Reactions (1) and (2) the concentration of ClONO₂ (>10¹⁴ molecule cm⁻³) was typically a thousand times greater than that of either O(³P) (<<10¹¹ atom cm⁻³), or OH (<10¹¹ radical cm⁻³). Under these conditions, it can be calculated that secondary reactions should have

TABLE I

Altitude in km	a		a		(R ₁ +R ₂) x10 ⁵	Jx10 ⁵	(J+R ₁ +R ₂) x10 ⁵	% of (R ₁ +R ₂)
	Concentration of O(³ P) in atoms per cm ³ x10 ⁻⁸	b R x10 ⁻⁵	Concentration of OH in radicals per cm ³ x10 ⁻⁶	c R ₂ x10 ⁻⁶				
20	.02	0.04	1.1	.41	0.08	8.0	8.08	1%
25	.14	0.28	1.75	.65	0.35	9.2	9.55	4%
30	0.62	1.2	3.0	1.11	1.3	12.4	13.7	9.5%
35	2.4	4.8	6.3	2.3	5.0	20	25	20%
40	8	16	14	5.2	16.5	39	55.5	30%
45	22	44	16	5.7	44	70	114	39%
50	36	72	11	4.1	72	95	167	43%

a: Liu, et al. (1976)

b: R₁ = k₁ × [O(³P)]

c: R₂ = k₂ × [OH]

been negligible. Supporting evidence of this point of view was provided by carrying out several flash energy variation experiments, typically a factor of four, and finding that the pseudo-first order rate constants k_1 and k_2 were independent of the flash intensity. Since any secondary reaction would necessarily involve either the photofragments of ClONO₂ or products of Reactions (1) and (2), the decay rate of O(³P) or OH would be proportional to the square of the flash energy. As noted above, no such observation was recorded.

Table I lists the relative chemical degradation rates (R_1 and R_2) as a function of altitude resulting from Reactions (1) and (2). The destruction of ClONO₂ through its reaction with Cl(²P_{3/2}) has not been included in the quoted total chemical degradation rate because: (1) the rate constant for the reaction of Cl(²P_{3/2}) with ClONO₂ is only $\sim 1 \times 10^{-13}$ cm molecule⁻¹s⁻¹ according to preliminary results obtained in our laboratory, and (2) the concentration of Cl(²P_{3/2}) at mid-stratospheric altitudes is very much lower than that of either OH or O(³P). Along with the chemical degradation rates, we have listed the photochemical destruction rate (J), as well as the total degradation rate of ClONO₂ ($R_1 + R_2 + J$). As can be seen from the Table, chemical processes (1) and (2) contribute less than 10% to the total rate of ClONO₂ destruction at altitudes less than 30 Km. Since the concentration of ClONO₂ is calculated to be near its maximum around 25 Km and drops off very significantly at higher altitudes, it must be concluded that the photochemical decomposition of ClONO₂ in the stratosphere is by far the most important degradation path for this molecule. It is possible that the contribution of the chemical degradation rate to the total destruction of ClONO₂ could be different from our calculations since, (a) the concentration of OH radicals in the stratosphere is still not well known, and (b) radicals other than OH, O(³P), or Cl(²P_{3/2}) could also degrade ClONO₂ to a significant degree. However, we do not expect our basic conclusion, that photolysis is the dominant mode, to change.

Acknowledgements. D. D. Davis would like to acknowledge the financial support of this work by

the National Aeronautics and Space Administration. G. Tesi was on sabbatical leave from the National Science Foundation during this project.

References

- Chang, J. and D. Wuebbles, "An Analysis of Coupled Chemical Kinetics and Transport Models of the Stratosphere", Intl. Ozone Symposium, Dresden, E. Germany, August 1976.
- Crutzen, P.J., Review of Atmospheric Chlorine Chemistry, Intl. Ozone Symposium, Dresden, E. Germany, August 1976.
- Davis, D.D., R.E. Huie, J.T. Herron, M.J. Kurylo, and W. Braun, "Absolute Rate Constant for the Reaction of Atomic Oxygen with Ethylene Over the Temperature Range 232-500 K", *J. Chem. Phys.*, **56**, p.4868 (1972).
- Davis, D.D., J. Herron, and J. Huie, "Absolute Rate Constant for the Reaction O(³P) + NO₂ → NO + O₂ Over the Temperature Range 230-339 K", *J. Chem. Phys.*, **58**, p.530 (1973).
- Davis, D.D., S. Fischer, and R. Schiff, "Flash Photolysis Resonance Fluorescence Kinetics Study: Temperature Dependence of the Reactions OH + CO → CO₂ + H, and OH + CH₄ → H₂O + CH₃", *J. Chem. Phys.*, **61**, p.2213 (1974).
- Liu, S.C., T.M. Donahue, R. Cicerone, and W.L. Chameides, "Effects of Water Vapor on the Destruction of Ozone in the Stratosphere Perturbed by Cl_x or NO_x Pollutants", *J. Geophys. Res.*, **81**, pp.3111-3118 (1976).
- McAfee, J. and P.J. Crutzen, Modelling Stratospheric Photochemistry and Kinetics, The 12th Informal Conference on Photochemistry, NBS, U.S. Department of Commerce, June 28 - July 1, 1976.
- Miller, R.H., D.L. Bernitt, and I.C. Hisatsune, "Infrared Spectra of Isotopic Halogen Nitrates", *Spectrochimica Acta*, **23A**, p.223 (1967).
- Molina, M.J., Atmospheric Chemistry of Chlorofluorocarbons, The 12th Informal Conference on Photochemistry, NBS, U.S. Department of Commerce, June 28 - July 1, 1976.

(Received November 3, 1976;
accepted November 18, 1976.)