Matrix-Isolation-Infrared and Laser Raman Spectroscopic Study of the Gas-Phase Reactions of Chlorine Atoms and Ozone

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The products of the gas-phase reactions of chlorine atoms and ozone have been studied by infrared and Raman matrix isolation techniques. The primary products of the reaction of Cl atoms with excess ozone are ClOO and OClO, produced in a nearly 1:1 ratio. As the ozone (or chlorine) concentration is decreased, the primary products observed become ClOO and ClOO* (a conformational isomer of ClOO). The reactions of Cl atoms and ${}^{18}O_2/{}^{16}O_3$ mixtures, coupled with the ozone concentration variation studies, are employed to suggest possible mechanisms for the formation of the products.

Introduction

The gas-phase mechanism for the reaction between chlorine atoms and ozone has received much attention recently because of the proposed^{1,2} catalytic destruction of ozone by chlorine. The chlorine is transported to the stratosphere from the troposphere by freons (CF_xCl_y) ,³ which may be photolytically dissociated into *n* Cl atoms and CF_xCl_{y-n} fragments. The free chlorine atoms may deplete ozone by the well-known "ClO cycle":

$$Cl + O_3 \rightarrow ClO + O_2$$
 (1)

$$ClO + O \rightarrow Cl + O_2 \tag{2}$$

$$O_3 + O \rightarrow 2O_2 \tag{3}$$

Any reaction which may affect the ClO cycle by removing Cl or ClO is of potential importance since removal of Cl or ClO would lower the net ozone depletion. For example, the OClO cycle²

$$ClO + O_3 \rightarrow OClO + O_2 \tag{4}$$

$$OCIO + O \rightarrow CIO + O_2 \tag{5}$$

$$O_3 + O \rightarrow 2O_2 \tag{3}$$

will lower the net ozone destruction because a fraction of the total available ClO is diverted to OClO and (5) is two orders of magnitude slower than (2). However, the "OClO cycle" is considered to be unimportant because photodissociation of OClO (to yield ClO + O) is probably faster than (5). In any event, a knowledge of the products of the reactions of chlorine atoms and ozone is important to the determination of the possible mechanisms for the reactions which may affect the Cl and ClO concentrations.⁴

We have attempted⁵ to study the gas-phase, low-pressure (≤ 1 torr) reaction between Cl and O₃ by trapping the products in an argon matrix at 10 K, and characterizing the products by their infrared and/or Raman spectra. Several sets of experiments were attempted: (1) the reaction of Cl₂/Ar (1:25) mixtures with excess O₃; (2) the reaction of Cl₂/Ar (1:25) mixtures with O₃/Ar (1:10, 1:20, 1:40, 1:50, and 1:100) mixtures; (3) the reaction of Cl₂/Ar (1:20 to 1:100) mixtures with O₃/Ar (1:20) mixtures; and (4) the reaction of Cl₂/Ar (1:25) mixtures with ¹⁸O₂/¹⁶O₃ (1:10) mixtures. All reactions were carried out in the gas phase. Our results were correlated with kinetic rate data in order to suggest possible reaction mechanisms for the

formation of the observed products. Our method has the advantage over some methods usually employed in kinetic rate studies (e.g., mass spectrometry) in that we are able to easily observe molecular isomers.

Experimental Section

For the infrared studies, the products of the Cl_2/Ar and ozone reactions were deposited on a CsI window held at 10 K by an Air Products cryotip and helium refrigerator (Model SCS-202). A silver mirror was employed in the Raman experiments. A gas-flow kinetic cell was attached to a port of the rotatable cryotip.

The system was thoroughly cleaned prior to each experiment, and background spectra of the cleaned evacuated system were taken prior to each experiment. The greatest impurity, water, showed an IR absorbance typically in the range log $(I_0/I) = 0.021-0.035$.

Products of the microwave discharge employed to produce Cl atoms are known to react with the glass walls of kinetic cells; therefore, the cell was thoroughly cleaned with concentrated hydrofluoric acid prior to each experiment. Hydrofluoric acid also served to prevent recombination of chlorine atoms on the walls of the kinetic cell.

Chlorine gas (99.9% purity, Linde) was further purified by trap-to-trap distillation, in order to remove nitrogen.

Ozone was prepared by a "static method" whereby oxygen was discharged with a Tesla coil through a Pt wire vacuum sealed into a 12 in. \times 0.5 in. Pyrex tube, which was immersed in liquid nitrogen and filled with molecular sieves to stabilize the liquid ozone. The ozone condensed as a blue-purple liquid. Volatile impurities were removed by pumping on the liquid nitrogen-trapped ozone for 0.5 h.

Gas mixtures of Cl_2/Ar or O_3/Ar were prepared by standard manometric techniques. Chlorine atoms were produced by microwave discharge of flowing Cl_2/Ar mixtures.

Several experiments were performed to test for the presence of observable products in the $Cl_2 + O_3$, $Cl_2 + Ar^*$, $Cl_2/Ar^* + O_3$, or $Cl_2/Ar + O_3$ system (Ar* is excited argon ${}^{3}P_{1/2}$). In each of these experiments, no IR absorptions

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⁽¹⁾ R. J. Cicerone, R. S. Stolarski, and S. Walters, Science, 185, 1165 (1974).

 ⁽²⁾ R. S. Stolarski and R. J. Cicerone, Can. J. Chem., 52, 1569 (1974).
 (3) M. J. Molina and F. S. Rowland, Nature (London), 249, 812 (1974).

 ⁽³⁾ M. J. Molina and F. S. Rowland, Nature (London), 249, 812 (1974).
 (4) R. M. Stimpfle, R. A. Perry, and Carleton J. Howard, J. Chem. Phys., 71, 5183 (1979).

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⁽⁵⁾ The work presented in this publication is an extension of the initial work described by Amanda Cain, M.S. thesis, Atlanta University, 1977.



Figure 1. The IR spectrum of the products of the CI + excess of O_3 reaction.



Figure 2. The IR spectrum of the products of the CI + O_3 /Ar (1:20).

other than those due to ozone, and the trace impurities CO_2 and H_2O , were observed.

Results

The matrix-isolated products of the gas-phase reaction of Cl atoms with excess ozone is illustrated in Figure 1. The primary products of interest are OCIO (1105 and 940 cm⁻¹)⁶ and ClOO (1442 cm⁻¹).⁶ The shoulder to the 1105-cm⁻¹ absorption (1100 cm⁻¹) is due to the ν_1 fundamental of ozone,^{7,8} but there may be a contribution from O^{37} ClO.⁶ The ClO molecule (845 cm⁻¹)^{9,10} was not observed in the above experiments, and only once in approximately 50 total experiments was a significant absorption observed at 845 cm⁻¹.

Mixtures of Cl_2/Ar (1:25) were subjected to a microwave discharge and subsequently reacted with ${}^{16}O_3/Ar$ mixtures of ratios 1:10, 1:20, 1:40, 1:50, and 1:100 (Figures 2-4);

⁽⁷⁾ Leo Brewer and J. Ling-Fai Wang, J. Chem. Phys., 56, 759 (1972).
(8) M. Spoliti, S. Nunzainte, and B. Mariti, J. Chem. Phys., 59, 985 (1973).

 ⁽⁹⁾ N. Basco and R. D. Morse, J. Mol. Spectrosc., 45, 35 (1973).
 (10) F. K. Chi and L. Andrews, J. Phys. Chem., 77, 3062 (1973).

⁽⁶⁾ A. Arkell and I. Schwager, J. Am. Chem. Soc., 89, 5999 (1967).



Figure 3. The IR spectrum of the products of the CI + O_3 /Ar (1:50).



Figure 4. The IR spectrum of the products of the Cl + O_3/Ar (1:100).

consistent sample sizes were employed in each experiment. Again the primary products are ClOO and OClO. An absorption (961 cm⁻¹) attributable to Cl₂O (ClClO)^{11,12} is also observed, but previous studies¹¹⁻¹³ indicate that this molecule is probably formed on the matrix by photolysis from the infrared glower. Figures 2-4 show that as the ozone concentration decreases, there is a systematic decrease in the concentration of OClO produced (relative to the concentration of ClOO produced). More quantitatively, the ratios of the integrated intensities of the ClOO (1442-cm⁻¹ absorption) to the OClO (1105-cm⁻¹ absorption) increase significantly in going from the pure O_3 experiment to the $O_3/Ar = 1:50$ experiment (Figure 5). A comparison of (ClOO)/(OClO) ($\bullet-\bullet$) and (ClOO + ClOO*)/OClO (X-X) ratios (Figure 5) indicates that both curves follow the same pattern. Thus, we cannot explain the decrease in the (ClOO)/(OClO) ratio in the O₃/Ar (1:100) experiment by the presence of the alternate form of ClOO (ClOO*). Recent theoretical calculations¹⁴ suggest that ClOO* may be a low-lying electronically excited species rather than a structural isomer. Thus, if the theoretical predictions are valid, the ClOO and ClOO* molecules may have different electronic distributions, and the absorption coefficients for the two species may be different. In any event, the data points corresponding only to the ClOO integrated intensity show exactly the same trend as those corre-

⁽¹¹⁾ M. M. Rochkind and G. C. Pimentel, J. Chem. Phys., 46, 4481 (1967).

 ⁽¹²⁾ W. Alcock and Pimentel, J. Chem. Phys., 48, 2373 (1968).
 (13) Subhash Bhatia and J. H. Hall, Jr., Inorg. Chem., 20, 629 (1981).

⁽¹⁴⁾ J. L. Gole, J. Phys. Chem., 84, 1333 (1980).



Figure 5. A plot of relative integrated intensities for CIOO/OCIO (\bullet), O₃/OCIO (\blacktriangle), O₃/OCIO (\blacktriangle), O₃/OCIO (\blacksquare), and (CIOO + CIOO*)/OCIO (×).

sponding to the ClOO + ClOO* integrated intensities. In each case, integrated intensities were obtained from three different weighings of each absorption and checked by using a planimeter. The average errors in weighing were 5.4% for the ClOO intensities, 8.2% for the OClO intensities, 3.1% for the O₃ intensities, and 21.3% for the ClOO* intensities. As might be expected, the greatest error occurs in weighing the O₃/Ar = 1:100 data points, since the intensities of the absorptions are quite weak. Therefore, one must be careful when interpreting the O₃/Ar = 1:100 experiment. In the O₃/Ar = 1:100 experiment, the ClOO/ OClO ratio decreases to around 0.48, and there is a meaningful increase in the absorption at 1415 cm⁻¹. This latter absorption has been previously assigned to an intermediate form of the ClOO radical (ClOO*).⁶



The ClOO* molecule is proposed to be a structural isomer of ClOO. Conformational isomerism as a direct result of the restricted rotation in a rigid matrix was first observed by Pimentel.¹⁵

A comparison of Figures 1 and 4 shows that the 1415cm⁻¹ absorption increases relative to the 1442-cm⁻¹ absorption, as the ozone concentration is decreased. The 1415-cm⁻¹ (ClOO*) absorption is one-tenth the intensity of the 1442-cm⁻¹ (ClOO) absorption in the $O_3/Ar = 1:10$ experiment, and nearly twice the intensity of the 1442-cm⁻¹ absorption in the 1:50 experiment. However, in the 1:100 experiment, the (ClOO + ClOO*)/OClO ratio decreases to $\simeq 1.3$. We cannot explain the decrease in the ClOO/ OClO ratio in this experiment entirely to the presense of the alternate form of ClOO (ClOO*), and this decrease may just be a manifestation of the error in obtaining the integrated intensities. It is clear, however, that while the productions of ClOO and OClO are nearly equivalent in the pure O_3 experiments, there is significantly more ClOO produced in the $O_3/Ar = 1:50$ experiment.

It is interesting to note that Arkell and Schwager (AS)⁶ observed the ClOO* molecule in a rigid matrix at ≤ 4 K. with warmup to >5 K resulting in conversion to ClOO. Our matrix was approximately 10 K, and we, therefore, should not have observed ClOO*, according to the results of AS. However, AS employed $Cl_2/O_2/Ar$ matrices of 1:1:40 and 1:4:40, while our matrix $(\tilde{C}l_2/Ar = 1:25; O_3/Ar)$ = 1:100) provides for significantly better isolation (as evidenced by the sharpness of the absorption bands). This difference may explain the appearance of ClOO* in our 10 K experiments. Although conformational isomerism is surely in part a result of restricted rotation in low-temperature (4 K) matrices, it is very reasonable to assume that matrix dilution should also play a significant part in the isolation of conformational isomers. The fact that the 1415-cm⁻¹ absorption is present, but weak, in our experiments where isolation is not as great $(O_3/Ar = 1:10, 1:20,$ 1:40, and 1:50) is also evidence that the increased intensity of the ClOO* absorption may be a result of the enhanced isolation in the $O_3/Ar = 1:100$ experiment.

The Cl_2/Ar ratios were also varied from 1:20 to 1:100 while the O_3/Ar ratio was held constant at 1:20. The results were consistent with the experiments in which the O_3/Ar ratios were varied, with the exception that the production of OCIO was even less. Again, at high matrix to radical ratios the ClOO* molecule was observed at 1415 cm⁻¹.

The microwave discharge of Cl_2/Ar mixtures always produced excited argon (Ar*), which reacted with molecular oxygen to produce $O(^{1}D)$, which subsequently reacted with molecular oxygen to produce ozone. This process is very efficient and, consequently, we were unable to study the reactions of Cl atoms and pure O_2 . Therefore, several experiments were repeated with oxygen-18 in order to determine if the ClOO molecule is produced from the direct reaction with oxygen

$$Cl + O_2 + M \rightarrow ClOO + M$$
 (6)

or from some chlorine oxide produced in the initial reaction between Cl and O₃. A 10:1 ${}^{16}O_3/{}^{18}O_2$ mixture was allowed to react with the microwave discharged Cl₂/Ar mixture. The Cl-¹⁸O-¹⁸O isotopic shift (84 cm⁻¹ to lower frequency) is well-known. Absolutely no absorptions due to Cl-18O-¹⁸O were observed (Figure 6). However, the $Cl^{-16}O^{-16}O$ radical is evident at 1442 cm^{-1} , as is ${}^{16}\text{O}-\text{Cl}-{}^{16}\text{O}$ at 1105, 945, and 450 cm⁻¹. Additional bands occur at 1550 cm⁻¹ due to α -¹⁶O₂, 1447 cm⁻¹ due to ¹⁸O₂, and 1110, 1040, and $700~{\rm cm^{-1}}$ due to ${\rm ^{16}O_3}.$ The absorptions at 1021 and 900 ${\rm cm^{-1}}$ are due to various forms of isotopic O_3 (primarily ¹⁶O-¹⁶O-¹⁸O). Based on the study of AS, the isotopic spacings for ClOO* are nearly identical with ClOO. Keeping that in mind, we should observe the $Cl^{18}O^{18}O^*$ species at 1335 cm⁻¹. We have not observed any absorption bands in the 1300-1400-cm⁻¹ region. The region $1200-1300 \text{ cm}^{-1}$ shows three absorptions (1292, 1270, and 1210 cm⁻¹) of various intensity in each experiment performed. These (1292, 1270, and 1210 cm⁻¹) absorptions are strongest in both the pure O_3 and ${}^{16}O_3/{}^{18}O_2$ 10:1 experiments. We, as well as AS, were unable to assign these peaks to any chlorine oxides. We conclude that reaction 6 does not occur in our system and that the isomers of ClO_2 are products of initial reaction between chlorine atoms and ozone.

Reaction Mechanisms

A knowledge of any products of the reaction of Cl and O_3 is desirable since, in principle, any products may raise or lower the net ozone depletion by altering the Cl or ClO availability in reactions 1 and 2. Any reaction mechanism proposed for our system must be consistent with kinetic

⁽¹⁵⁾ G. C. Pimentel, J. Am. Chem. Soc., 80, 62 (1958).



Figure 6. The IR spectrum of the products of the reaction of CI atoms with ${}^{16}O_3/{}^{18}O_2$ (10:1).



Figure 7. The Raman spectrum of the products of the reaction of CI atoms and pure O3.

rate data.¹⁶ The measurements of the rate of reaction 1 ($\simeq 10^{-12}$ cm³ molecule⁻¹ s⁻¹) indicate that it is a significant reaction in chlorine oxide chemistry. Once ClO is produced, there are many reactions that it may undergo. For example, OClO and ClOO may be produced by several reactions, each involving ClO, and each having not too different rates.

$$ClO + O_3 \rightarrow OClO + O_2$$
 (4)

$$ClO + O_3 \rightarrow ClOO + O_2 \tag{7}$$

$$ClO + ClO \rightarrow OClO + Cl$$
 (8)

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

In addition, OClO is photolytically converted to ClOO. If both ClOO and OClO are produced by the same mechanisms (either (4) and (7) or (8) and (9)), lowering the ozone concentration should affect both isomers similarly. The concentrations of both species may decrease, but the ratio of the concentrations should remain constant. However, in the ozone dilution experiments, the OClO production was affected more than the ClOO production. This result indicates that ClOO and OClO are produced via different reactions, and that the production of OClO is enhanced by high ozone concentrations. This system is difficult to analyze numerically because of the many possible reactions of ClO, the uncertainty of the OClO decomposition reactions, and because rate constants for reactions 7, 8, and 9 are not known accurately. However, we venture to suggest reactions 1 and 4 for the production of OClO, and reactions 1 and 9 for the production of ClOO. At O₃ dilution ratios greater than or equal to $O_3/Ar = 1:100$, the ClOO and ClOO* absorptions were too weak to obtain meaningful integrated intensities. It is clear, however, that the ClOO/OClO ratios change as the O₃ concentration is varied, implying that ClOO and OClO are produced by different reactions. The reactions we have proposed appear to be the most logical.

⁽¹⁶⁾ R. T. Watson, J. Phys. Chem. Ref. Data, 6, 871 (1977), provides an excellent critical review of rate-constant data for the reactions of chlorine oxides.

⁽¹⁷⁾ F. K. Chi and L. Andrews, J. Mol. Spectrosc., 52, 82 (1974).

Finally, the rates for reactions 8 and 9 are not known with accuracy, and the partitioning between the channels is uncertain, but the best values are $\simeq 10^{-14}$ at room temperature. Clearly, more accurate values are necessary if these reactions are significant reaction channels for ClO.

Raman Studies

Several experiments were repeated and the samples were deposited onto a silver mirror in order to study the Raman spectra of the products. A SPEX Ramalog 6 laser Raman spectrometer with visible-ultraviolet optics was employed for spectra observation (2000–150 cm^{-1}). The 4800-Å line from a CR-6 5 W argon ion laser was employed for excitation. A typical spectrum $(Cl_2/Ar (1:25) + pure O_3)$ is given in Figure 7. The Raman spectra adds little to our previous interpretations; however, the OClO symmetric stretch (940 cm⁻¹), Cl_2 (540 cm⁻¹), O_2 (1550 cm⁻¹), and O_3 (1090, 1030 cm⁻¹) are observed.

Summary

The extensive study of the gas-phase reactions of chlorine atoms and ozone indicates that, under laboratory conditions, the primary products are ClOO, ClOO*, and OClO with ClOO and OClO produced in nearly equivalent quantities when O_3 is in excess. The mechanisms for the production of these species are proposed as follows:

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + ClO \rightarrow ClOO + Cl$$

$$ClO + O_2 \rightarrow OClO + Cl$$

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Equilibrium Thermodynamics of the Glass Transition

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The equilibrium thermodynamics of the glass transition is carefully formulated by using the concept of order parameters in a very general sense. Attention is focused on the behavior of the Jacobian matrix of second derivatives of the Gibbs free energy when various assumptions about the behavior of the order parameters at the transition are made. This formulation clarifies the assumptions made by various authors in their derivations of the Ehrenfest relation for the glass transition. The question of the proper formalism for a statistical mechanical theory of the glass transition is also discussed in some detail.

I. Introduction

Several years ago DiMarzio¹ raised a controversy concerning the application of the Ehrenfest (or Prigogine-Defay) relation to the thermodynamics of the glass transition. This relationship among certain discontinuities in the various second derivatives of the Gibbs free energy comes mainly from the work of Davies and Jones,² who extended earlier work of Ehrenfest³ and Prigogine and Defay.⁴ Davies and Jones assumed that the thermodynamic properties of the system depend on a number of thermodynamic order parameters which vary so as to maintain equilibrium above the glass transition but are frozen at constant values below the transition. From these assumptions they claimed that

$$R = \Delta\beta \Delta C_p / [TV(\Delta\alpha)^2] \ge 1 \tag{1}$$

where the Δ represents the discontinuity in a given property as measured above and below the glass transition. The three thermodynamic properties in eq 1 are the coefficient of thermal expansion, α , the isothermal compressibility, β , and the constant-pressure heat capacity, C_p . The equality holds if only one order parameter is needed to describe the system. If more than one parameter is necessary, the relationship becomes a strict inequality. The

sense of the inequality is determined from stability considerations.

The Davies and Jones derivation of eq 1 is usually characterized as being based on the principles of nonequilibrium thermodynamics. Although Davies and Jones did use nonequilibrium thermodynamics to derive equations describing relaxation processes near the glass transition, their derivation of eq 1 is based only upon a particular choice for the form of the differential of the thermodynamic internal energy and the general properties of partial derivatives. The time dependence of the order parameters is never used. Therefore, the Davies-Jones derivation must be considered as based on the equilibrium properties of a particular energy surface.

DiMarzio, however, was able to show that under what he claimed to be the same assumptions made by Davies and Jones the equality must always hold in eq 1 no matter how many order parameters are involved. He then concluded that, if experimentally one finds an inequality, the concept of order parameters is not applicable to the glass transition. Since DiMarzio's mathematical analysis is correct and the experimental data suggest that the inequality holds in most cases, several authors have attempted to rescue the concept of order parameters by examining and questioning the assumptions on which his argument rests. Goldstein⁵ and Gupta and Moynihan⁶ have offered

E. A. DiMarzio, J. Appl. Phys., 45, 4143 (1974).
 R. O. Davies and G. O. Jones, Adv. Phys., 2, 370 (1953).
 P. Ehrenfest, Leiden Comm. Suppl., 756 (1933); see also H. Callen, "Thermodynamics", Wiley, New York, 1960. (4) I. Prigogine and R. Defay, "Chemical Thermodynamics", Long-

mans, Green and Co, New York, 1954, Chapter 19.

⁽⁵⁾ M. Goldstein, J. Appl. Phys., 46, 4153 (1975); Macromolecules, 10, 1407 (1977)

⁽⁶⁾ P. K. Gupta and C. T. Moynihan, J. Chem. Phys, 65, 4136 (1976).