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Production and trapping of gaseous dimeric ClO: The infrared spectrum of chlorine peroxide (ClOOCl) in solid argon

Bing-Ming Cheng and Yuan-Pern Lee

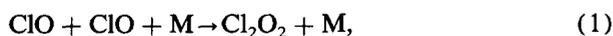
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The dimeric ClO has been generated in a gaseous discharge-flow system at 220 K and 10–30 Torr by reacting atomic Cl with O₃, ClOCl or OClO, and reacting atomic O with ClOCl or OClO, in a stream of Ar. The gas mixture in the flow tube was sampled through a pinhole and condensed on a CsI window maintained at 12 K. The infrared absorption spectrum of the matrix formed after 30–120 min deposition was then recorded. Absorption lines at 752.6, 649.8, and 647.6 cm⁻¹ have been assigned to ClOOCl, and previous assignments for dimeric ClO seem to be in error. The results are in excellent agreement with recent *ab initio* calculations. Under our experimental conditions, no other isomer of Cl₂O₂ was observed.

INTRODUCTION

The self-reaction of the ClO radical is very important in the theory of the catalytic chemical destruction of ozone, and was used to explain the large losses of ozone in the springtime Antarctic stratosphere reported in recent years.^{1,2} The formation and the photolysis of dimeric ClO are the key steps in the proposed catalytic cycle:



Recent findings of relatively high concentrations of ClO during the Antarctic spring suggested that the chemical destruction mechanism plays a very important role in the decrease in ozone concentration.^{3,4}

However, the structure and the spectroscopic properties of Cl₂O₂ have not been experimentally well established. Molina and Molina¹ mixed Cl atoms with O₃, ClOCl, or OClO in a gaseous flow system at 220–240 K and assigned the intense infrared (IR) absorption at 1225 and 1057 cm⁻¹ to ClOOCl. The absorption at 650 cm⁻¹ was attributed to a second form of the dimer, ClOClO. A broad ultraviolet (UV) absorption peaked near 270 nm was also attributed to ClOOCl. However, a recent study by UV spectroscopy reported a residual absorption maximum at 245 nm from photolysis of Cl₂/O₃/N₂ and Cl₂/Cl₂O/N₂ mixtures; this UV absorption was also ascribed to Cl₂O₂.² There have also been several studies of the matrix IR spectra of Cl₂O₂, and absorption peaks at 995, 986, 982, 945, and 936 cm⁻¹ have been tentatively attributed to different isomers of various ³⁵Cl- and ³⁷Cl-containing Cl₂O₂.^{5–8}

The structure of Cl₂O₂ is potentially important in atmospheric chemistry because the photochemistry and chemistry for each isomer of Cl₂O₂ may be very different. For example, there are two possible channels in the photolysis of the symmetric dimer ClOOCl:



and three for the asymmetric dimer ClOClO:



Reaction (6b) would participate directly in the catalytic cycle [reaction (2)] while reaction (7c) would form stable OClO which would be rapidly photolyzed in the atmosphere to yield O (+ ClO), leading to no net O₃ removal through the Cl₂O₂ cycle.

For the modeling of the proposed catalytic cycle, there is an urgent need to identify each Cl₂O₂ isomer under atmospheric conditions and to study the photochemistry and chemistry of each species.

We have coupled the discharge-flow technique, the matrix isolation technique, and IR spectroscopy to produce and characterize the dimer of ClO. Our results indicate that ClOOCl is the major dimeric form under our experimental conditions.

EXPERIMENTAL

Conventional matrix isolation techniques have employed either the codeposition method or *in situ* photolysis to produce radicals of interest, while the technique applied in this work utilized the discharge-flow method for their production. The advantage is that the latter method is known to provide excellent flexibility and accurate control of reactions, so that possible interfering reactions may be eliminated. On the other hand, the matrix isolation technique has proved superior for the trapping and preservation of reactive species. In this work, this technique may be regarded as a sampling method for the study of gaseous radical reactions. Although reaction may still occur in the matrix during or after deposition, it can be easily distinguished from any gaseous reaction by means of the variation of experimental conditions such as reaction time, pressure, and flow rates of reactants in the flow tube.

The principles of the discharge-flow technique have been described previously.^{9,10} In this study, the jacketed Pyrex flow tube is 17 mm inside diameter (i.d.), and is fitted inside with 15 mm i.d. Teflon tubing to reduce possible sur-

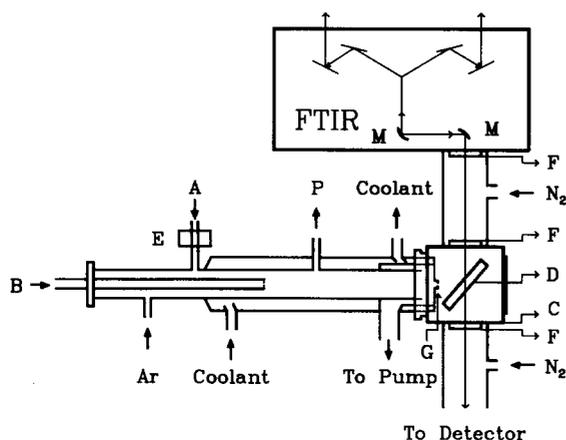


FIG. 1. Experimental setup of the discharge-flow/matrix-isolation/Fourier transform infrared system. A: atomic reactant inlet; B: movable inlet for molecular reactant; C: cryogenic system; D: CsI target (12 K); E: microwave discharge; F: KBr window; G: Teflon pinhole; M: mirror; P: pressure meter.

face reactions. A movable injector of size 10 mm outside diameter (o.d.) permitted adjustment for the optimal reaction distance (time). The temperature of the reaction zone was controlled by temperature-regulating fluids (methanol or water) circulating through the jacket, and monitored with copper-constantan thermocouples at the inlet and the outlet. The reaction pressure was measured with an MKS Baratron manometer at approximately the midpoint of the reaction zone. The gaseous flow rates were monitored by mass flow transducers.

As shown in Fig. 1, the atomic reactant (Cl or O) was generated in a microwave discharge and carried by a small proportion of He or Ar into the flow tube. The molecular reactant (O_3 , ClOCl, or OCIO) was carried by Ar into the flow tube through a movable inlet. Most of the Ar carrier gas was introduced into the tube through a side arm upstream from the inlet of the atomic reactant. The discharge-flow tube was attached to a matrix isolation system which was located at the rear port of a Bomem DA3.002 FTIR spectrometer. The matrix support was a 1.2 in. diameter CsI window maintained at 12 K by an Air-Products model DE-208L closed-cycle cryogenic system which has a cooling power of 5 W at 15 K. The cold window was rotatable in vacuum and could face either the flow tube (for deposition) or the IR beam (for detection).

A differential pumping scheme was employed to maintain the pressure of the cryosystem below 10^{-4} Torr while that in the flow tube was 10–30 Torr. A Teflon cap with a small pinhole (diameter ranging from ~ 30 to $300 \mu\text{m}$) was fitted at the end of the flow tube to allow sampling of the gas mixture into the chamber of the matrix isolation system. Most of the gas in the flow tube was pumped away by a mechanical pump, leaving only about 0.1% to pass through the pinhole to deposit onto the cold CsI window. The distance between the pinhole and the CsI window was about 1.5 cm.

The period of matrix deposition ranged from 30 to 120 min. After each period of deposition the IR absorption spec-

trum was recorded, using a KBr beam splitter and a wide-range Hg/Cd/Te detector cooled with liquid N_2 . Spectra were measured at a resolution 0.5 cm^{-1} in the range $500\text{--}2500 \text{ cm}^{-1}$, and usually 400 scans were taken.

ClO radicals were generated by the reaction of atomic chlorine with O_3 , ClOCl or OCIO, or the reaction of atomic oxygen with ClOCl or OCIO:



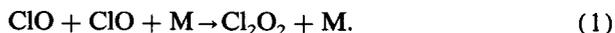
At room temperature the rate constants for these reactions are 1.2×10^{-11} , 9.8×10^{-11} , 5.9×10^{-11} , 3.5×10^{-12} , and $5.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively.¹¹

Typical experimental conditions were as follows: total flow rate: $F_T = 10\text{--}20 \text{ STP cm}^3 \text{ s}^{-1}$; reactant flow rates: F_{Cl_2} or $F_{\text{O}_2} = 10\text{--}50$, $F_{\text{O}_3} = 30\text{--}100$ or $F_{\text{Cl}_2} = 30\text{--}100$ (or $10\text{--}50$) for ClOCl (or OCIO) production (all in $10^{-3} \text{ STP cm}^3 \text{ s}^{-1}$); average gas velocity $\bar{v} = 200\text{--}450 \text{ cm s}^{-1}$; reaction distance $\approx 35 \text{ cm}$; total pressure $P_T = 10\text{--}30 \text{ Torr}$; and temperature $T = 220\text{--}300 \text{ K}$.

The He (99.9995%), Ar (99.999%), O_2 (99.97%), and Cl_2 (99.98%) were used without purification. Ozone was generated by passing O_2 through a Welsbach T-408 ozonator and was collected on silica gel at 195 K. Chlorine monoxide (ClOCl) and chlorine dioxide (OCIO) were prepared on line by passing a Cl_2/Ar mixture through a column of yellow HgO and $NaClO_2$, respectively. An ozone meter that utilized the absorption by O_3 of light of 254 nm was used to determine the concentration of ozone.

RESULTS AND DISCUSSION

The kinetic studies of the self-reaction of the ClO radical have been reviewed in several papers.^{11–13} At room temperature the bimolecular channels compete with the termolecular (dimer formation) channel, while at low temperature and high pressure the termolecular channel dominates.



The recommended rate constants¹¹ $k_{12} = 8.0 \times 10^{-13} \exp(-1250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_1 = 4.0 \times 10^{-32} (T/300)^{-2} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ imply that at a pressure of 20 Torr, the branching ratio of the termolecular channels increases from $\sim 70\%$ at 300 K to $\sim 95\%$ at 220 K. This change can be illustrated in Fig. 2 in which the matrix IR spectra of the products of the $\text{Cl} + \text{O}_3$ reaction carried out in a discharge-flow system under similar experimental conditions except at different temperatures are contrasted. The reaction at 300 K gave a spectrum (trace A) with substantial absorption due to the reactant O_3 (703, 1040, and 1102 cm^{-1})¹⁴ and products OCIO (1086–1108 cm^{-1} , multiplet)^{15,16} and ClO (849.0 and 841.8 cm^{-1}).¹⁷ New peaks at

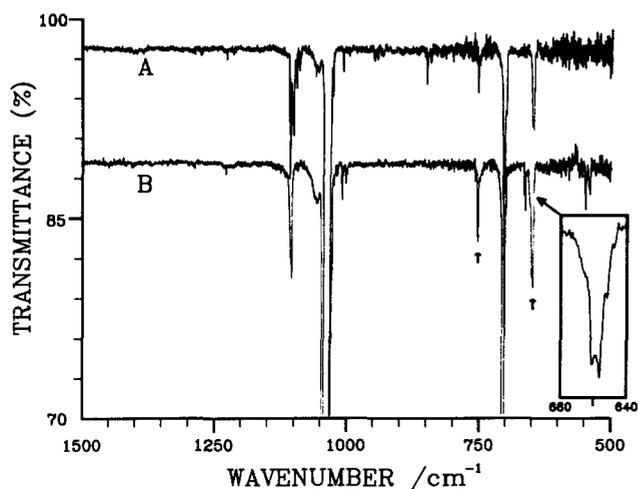


FIG. 2. Infrared spectra of the products (in solid Ar) of the reaction $\text{Cl} + \text{O}_3$ at 20 Torr. A: $T = 300$ K; B: $T = 220$ K. The peaks near 648 cm^{-1} are expanded in the inset box. The absorptions due to ClOCl are indicated by arrows.

752.6 , 649.9 , and 647.7 cm^{-1} have been observed with the latter two mutually overlapping. These peaks correspond to the *C* and *D* bands near 740 and 653 cm^{-1} reported by Molina and Molina.¹ When the flow tube was cooled to 220 K (trace B), the absorption due to OCIO and ClO disappeared and the three new peaks in the range 540 – 753 cm^{-1} increased in intensity. The CO_2 absorption¹⁸ at 662.0 cm^{-1} and two new peaks at 547.1 and 539.7 cm^{-1} showed up.

From the intensity variation under various experimental conditions it was concluded that the 752.6 , 649.9 , and 647.7 cm^{-1} lines belonged to one species and those at 547.1 and 539.7 cm^{-1} to another. The latter were readily assigned to $^{35}\text{Cl}^{35}\text{Cl}$ and $^{35}\text{Cl}^{37}\text{Cl}$, respectively. The theoretical ratio 1.014 for the harmonic vibrational frequencies of $^{35}\text{Cl}^{35}\text{Cl}/^{35}\text{Cl}^{37}\text{Cl}$ is well within the uncertainties of the experimental value 1.013 ± 0.002 . The intensity ratio was approximately $3:2$. The $^{37}\text{Cl}^{37}\text{Cl}$ absorption, expected near 532 cm^{-1} , was observed too weakly for definite identification. The observed wave numbers are also very close to previously reported values 549.2 and 554.3 cm^{-1} for Cl_2 in solid argon¹⁹ and in the gas phase,²⁰ respectively. The perturber which activates the Cl_2 IR absorption is probably O_3 because identical peaks were also observed from a matrix deposited with a stream of argon containing Cl_2 and O_3 at low temperature. It is worth noting that the Cl_2 absorption was greatly enhanced as the temperature of the flow tube was decreased, indicating the ease of complex formation at low temperature.

With regard to the reaction kinetics of the ClO self-reactions, the peaks at 752.6 , 649.9 , and 647.7 cm^{-1} are most likely due to Cl_2O_2 . Complication may however result from secondary reactions in the $\text{Cl} + \text{O}_3$ system, although care has been taken to minimize possible interfering reactions in the flow system. Further experiments using different ClO sources have therefore been carried out. Shown in Fig. 3, traces A and B, are IR absorption spectra in the 500 – 1500 cm^{-1} region of the matrix-isolated samples from the reac-

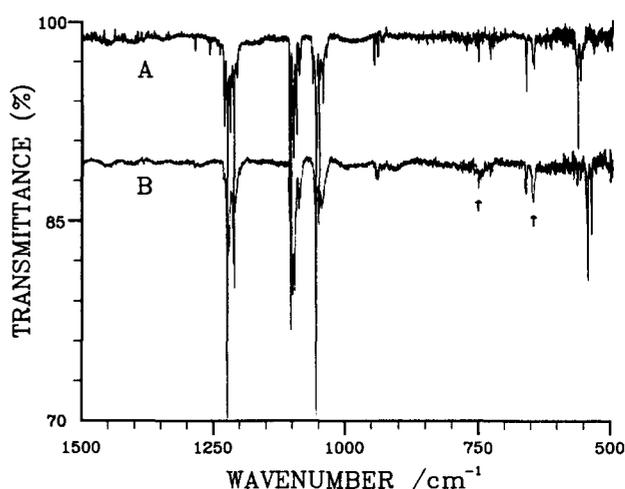


FIG. 3. Infrared spectra from the reactions at 20 Torr and 220 K. A: $\text{O} + \text{OCIO}$ reaction; B: $\text{Cl} + \text{OCIO}$ reaction. The absorptions due to ClOCl are indicated by arrows.

tions $\text{O} + \text{OCIO}$ and $\text{Cl} + \text{OCIO}$, respectively. The reactant OCIO displayed complex multiplets peaked near 1106 and 947 cm^{-1} .^{15,16} The reaction of $\text{Cl} + \text{OCIO}$ produced peaks at 752.5 , 649.4 , 647.5 , 545.8 , 538.4 , and 530.8 cm^{-1} along with intense complex absorption multiplets peaked near 1226 and 1058 cm^{-1} . The peaks at 545.8 , 538.4 , and 530.8 cm^{-1} with intensity ratios of approximately $9:6:1$ were assigned to $^{35}\text{Cl}^{35}\text{Cl}$, $^{35}\text{Cl}^{37}\text{Cl}$, and $^{37}\text{Cl}^{37}\text{Cl}$, respectively, in a slightly different matrix environment from that in the $\text{Cl} + \text{O}_3$ study. The complex groups near 1226 and 1058 cm^{-1} correspond to the *A* and *B* bands reported near 1225 and 1057 cm^{-1} by Molina and Molina.¹ The assignments of these peaks are discussed later.

The reaction of $\text{O} + \text{OCIO}$ produced similar peaks to those observed from the $\text{Cl} + \text{OCIO}$ reaction except that the Cl_2 triplet (530 – 546 cm^{-1}) was absent and new peaks at 1285.8 , 1258.7 , 1240.0 , 730.9 , 565.7 , and 559.7 cm^{-1} were observed. The peak at 1285.8 cm^{-1} and a weak line at 775.7 cm^{-1} coincided with those reported for ClONO_2 ,²¹ and the peak at 1240 cm^{-1} was due to HOCl .²² The rest of the new lines are probably due to ClO_3 produced from the association reaction $\text{O} + \text{OCIO}$ and will be discussed in a separate publication.¹⁶

The matrix IR spectra from the reactions $\text{O} + \text{ClOCl}$ and $\text{Cl} + \text{ClOCl}$ are shown in Fig. 4, traces A and B, respectively. In the reaction $\text{Cl} + \text{ClOCl}$, peaks at 1340.3 , 1307.5 , 1271.6 , 964.6 , 677.0 , and 638.7 cm^{-1} along with their corresponding weaker ones for the ^{37}Cl -containing species were due to the reactant ClOCl.²³ Absorptions at 752.4 , 650.0 , and 647.5 cm^{-1} (partially overlapped by the ClOCl absorption at 638.7 cm^{-1}) were also observed. The Cl_2 absorptions at 545.8 , 538.4 , and 530.8 cm^{-1} were also present. In addition, HOCl lines were observed at 1239.9 and 728.9 cm^{-1} , and for CO_2 at 662 cm^{-1} .

In the reaction $\text{O} + \text{ClOCl}$, the absorption intensities due to Cl_2 were greatly reduced, compared with those from the $\text{Cl} + \text{ClOCl}$ reaction. In Fig. 4, trace A, the absorptions due to ClOCl reactant were also reduced because of the ex-

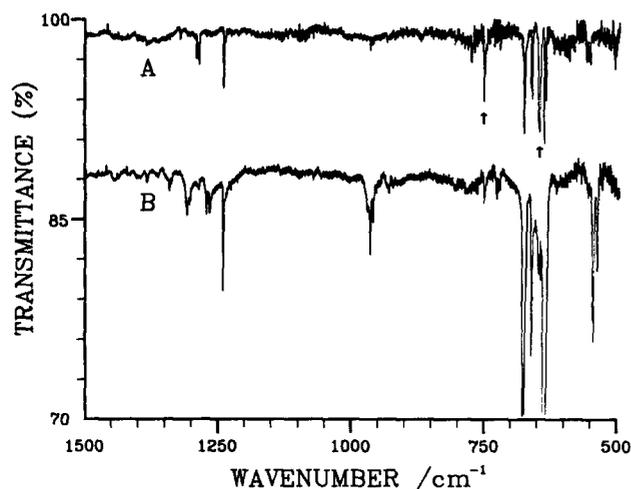


FIG. 4. Infrared spectra from the reactions at 20 Torr and 220 K. A: O + ClOCl reaction; B: Cl + ClOCl reaction. The absorptions due to ClOOCI are indicated by arrows.

cessive atomic oxygen employed. However, the peaks at 752.6, 649.7, and 647.6 cm^{-1} were enhanced. The impurity peaks due to ClONO₂ at 1285.8, 807.6, and 776.0 cm^{-1} , to HOCl at 1239.9 cm^{-1} and to HNO₃²⁴ at 1321.1 cm^{-1} were also present.

The observed wave numbers of the absorption peaks produced from the above five reactions at 220 K are summarized in Table I. All five reactions are known to generate ClO. Peaks at 752.6, 649.8, and 647.6 cm^{-1} were observed in all five cases at low temperature and high pressure. Thus, it is reasonable to assign these peaks to Cl₂O₂. Recent *ab initio* calculations by McGrath and coworkers²⁵ have identified three stable isomers on the Cl₂O₂ potential surface. The highest-level calculations (MP2/6-31 + G(3d)//MP2/6-31G*) showed that the straight-chain symmetric isomer ClOOCI and the branched species ClClO₂ are of comparable stability, with the straight-chain asymmetric isomer ClOClO some 11 kcal mol⁻¹ higher in energy. The IR vibrational wave numbers and their corresponding intensities have also been predicted for each species. Among them, the lines with intensities higher than 0.1 D² amu⁻¹ are at 765, 679, and 633 cm^{-1} for ClOOCI, at 1351, 1190, 490, 359, and 196 cm^{-1} for ClClO₂, and at 1275, 328, 324, 178, and 55 cm^{-1} for ClOClO. Our observed absorption frequencies at 752.6, 649.8, and 647.6 cm^{-1} fit surprisingly well with the predicted values for ClOOCI. The deviation of the theoretical prediction less than 5% from experimental values is also consistent with those derived for the related molecules HOCl, ClOCl, OClO, HOOH, and FClO₂ from similar calculations.^{25,26} Furthermore, the ratio ~ 0.24 for the integrated

TABLE I. Absorption wave numbers (cm^{-1}) in solid argon of the products of various reactions at 220 K and 20 Torr. The values in parentheses indicate absorption wave numbers for the corresponding ³⁷Cl-isotopic species. The corresponding values for the O + OClO and O + ClOCl reactions are not shown.

Cl + O ₃	Cl + OClO	O + OClO	Cl + ClOCl	O + ClOCl	Assignment
			1340.3		ClOCl 2ν ₃
				1321.1	HNO ₃
			1307.5		ClOCl ν ₁ + ν ₃
1285.9		1285.8		1285.8	ClONO ₂ ν ₂
			1271.6(1265.9)		ClOCl 2ν ₁
		1258.7			?
		1240.0			HOCl ν ₂
1226.2	1226.1 ^a	1226.1 ^a		1239.9	Cl ₂ O ₃ ^f
	1106.5 ^b	1106.5 ^b			OClO ν ₃
1102.4					O ₃ ν ₁
	1058.4 ^c	1058.4 ^c			Cl ₂ O ₃ ^f
1040 ^d					O ₃ ν ₃
			964.6(959.2)	964.7	ClOCl ν ₂ + ν ₃
	947.3 ^e	947.3 ^e			OClO ν ₁
				807.6	ClONO ₂ ν ₃
		775.7		776.0	ClONO ₂ ν ₄
752.6	752.5	752.6	752.4	752.6	ClOOCI
	730.9(725.8)	730.9			?
			728.9(722.6)		HOCl ν ₃
703.3					O ₃ ν ₂
			677.0(675.1)	677.0	ClOCl ν ₃
662.0	662.0	662.0	662.0	662.0	CO ₂ ν ₂
649.9	649.4	650.0	650.0	649.7	ClOOCI
647.7	647.5	647.6	647.5	647.6	ClOOCI
			638.7(635.7)	638.7	ClOCl ν ₁
	565.4(559.7)	565.7			?
				560.8	ClONO ₂ ν ₅
547.1(539.7)	545.8(538.4)		545.8(538.4)	547.2	Cl ₂

^a Multiplet: 1232.1, 1226.1, 1223.9, 1222.5, 1222.1, 1213.0, and 1210.7 cm^{-1} .

^b Multiplet: 1108.0, 1106.4, 1101.3, 1098.2, 1094.8, 1089.6, and 1086.5 cm^{-1} .

^c Multiplet: 1058.4, 1056.9, 1051.3, 1049.7, 1045.4, and 1044 cm^{-1} .

^d Multiplet: 1045 ~ 1020, 1016.3, 1006.1, and 998.8 cm^{-1} .

^e Multiplet: 948.1, 947.1, 944.1, 942.4, 941.0, and 935.0 cm^{-1} .

^f Tentative assignment.

intensity of the peak at 752.6 cm^{-1} to that of the doublet at 649.9 and 647.6 cm^{-1} is close to the predicted ratio $0.14/(0.45 + 0.30) = 0.19$. Therefore, the observed peaks at 752.6 , 649.9 , and 647.6 cm^{-1} are best attributed to ClOOCl. Roughly speaking, the 752.6 cm^{-1} peak is basically due to O–O stretching and the doublet at 649.9 and 647.6 cm^{-1} due to Cl–O stretching. The close spacing of the two Cl–O stretching frequencies is typical for symmetric peroxides.²⁷ The corresponding fundamentals of FOOF are separated by about 6 cm^{-1} .^{28,29} However, the possibility that the complex structure near 650 cm^{-1} is due to site perturbation cannot be ruled out. The absence of the ^{37}Cl counterpart of the 752.6 cm^{-1} peak near 746 cm^{-1} is also in agreement with the assignment as a O–O stretching rather than a Cl–O stretching. Spectra at higher resolution showed that there was a shoulder at 751.6 cm^{-1} which is best attributed to $^{37}\text{ClOO}^{35}\text{Cl}$. The shoulders at 646.0 and 645.0 cm^{-1} shown in the inset box of Fig. 2 are also likely due to $^{37}\text{ClOO}^{35}\text{Cl}$. The observed isotopic shifts are close to the estimations based on the geometry predicted from *ab initio* calculations.

Further evidence supports this assignment. As the pressure was increased from 10 to 30 Torr at 300 K, the ratio of the absorption intensity of the line at 752.6 (ClOOCl) to that at 849.0 (ClO) cm^{-1} increased from ~ 0.2 to ~ 2.5 . The enhancement of dimer formation at higher pressures could also be explained by the increased reaction rate for the termolecular channel and possibly the increased extent of cooling during expansion.

The observation of only ClOOCl in our experiments is also consistent with the theoretical prediction. Although ClClO_2 and ClOOCl are of comparable stability, a high barrier for the formation of ClClO_2 from $\text{ClO} + \text{ClO}$ is expected. The absence of ClOClO in our experiments is probably due to its high energy relative to ClOOCl.

The observed ClOOCl absorptions at 752 , 649 , and 647 cm^{-1} correspond to the *C* and *D* bands assigned to ClOClO by Molina and Molina.¹ The lines at around 1226 and 1058 cm^{-1} (corresponding to the *A* and *B* lines assigned to ClOOCl by Molina and Molina) were observed only when the concentration of OClO, used as the precursor of ClO, was relatively high. Thus, the most reasonable candidate for the *A* and *B* absorption bands is Cl_2O_3 , produced from the termolecular reaction of OClO with ClO. Similar absorptions at 1280 and 1015 cm^{-1} have been observed in the reaction of O_3 with liquid Cl_2 at 233 K and they were assigned to Cl_2O_3 .³⁰ However, further studies are needed for a definite assignment of these peaks. The presence of the *A* and *B* lines in all three reactions involving atomic Cl in the study by Molina and Molina might result from secondary reactions owing to the much higher radical concentrations employed.

Previous assignments for the matrix-isolated Cl_2O_2 in the $945\text{--}995\text{ cm}^{-1}$ region using *in situ* photolysis technique^{5–8} gave vibrational wave numbers smaller by more than 20% from those predicted in the *ab initio* calculation: 1190 cm^{-1} for ClClO_2 and 1275 cm^{-1} for ClOClO.²⁵ In our study, these peaks were not observed. Because both FOO and ClOO have relatively small values of wave numbers for the stretching fundamentals (585 and 407 cm^{-1} , respectively),^{15,28,31} and the two O–F stretching fundamentals of

FOOF are also near 620 and 614 cm^{-1} ,^{28,29} one might expect that the Cl–O stretching fundamentals of ClOOCl should occur at relatively low frequencies rather than in the $900\text{--}1000\text{ cm}^{-1}$ region. Thus, it is likely that previous assignments are erroneous. Further experiments are in progress to disclose the identity of this Cl–O containing species.¹⁶ A more recent matrix study on the products of the $\text{Cl} + \text{O}_3$ reaction was carried out by Carter and Andrews.¹⁷ The emphasis of their study was placed on the detection of ClO_3 , but no observable absorption for possible ClO_3 or Cl_2O_2 has been recorded. It was probably difficult for the dimer to form in the dual deposition arrangement used in their experiments. A similar study on the $\text{Cl} + \text{O}_3$ reaction by Bhatia and Hall produced only ClOO and OClO; the absence of ClO indicated severe problems with their experiments.³²

In conclusion, the dimeric ClO has been produced in a discharge–flow system at high pressure and low temperature from five different chemical reactions. The IR spectrum showed absorptions in solid argon at 752.6 , 649.9 , and 647.6 cm^{-1} which are assigned to ClOOCl, in excellent agreement with theoretical predictions. Under our experimental conditions, no other isomer of Cl_2O_2 was identified.

ACKNOWLEDGMENTS

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