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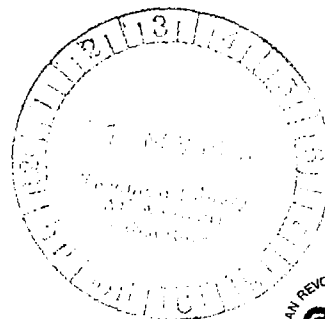


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PRODUCTS OF THE REACTION OF CHLORINE ATOMS AND OZONE

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16. ABSTRACT Preliminary matrix-isolation infrared spectroscopic studies of the gas-phase reaction of chlorine atoms and ozone are reported. The major product of the reaction is found to be the symmetric OCIO radical, while very little of the asymmetric ClOO radical is produced. It is also found that the presence of O ₂ enhances the OCIO production and that ClOO is the primary product in the reaction of Cl atoms and pure O ₂ . The radical ClO is also observed for the first time in a gas-phase reaction of Cl and O ₃ . A mechanism for these observations is proposed.					
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TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. PROCEDURE	1
III. RESULTS	1
IV. SUMMARY	8
REFERENCES	9

LIST OF ILLUSTRATIONS

Figure	Title	Page
1.	The IR spectrum of the reaction of Cl atoms and ozone . .	2
2.	The IR spectrum of the reaction of Cl atoms and oxygen	3
3.	The IR spectrum of the reaction of Cl atoms and an O ₃ /O ₂ mixture (1:10)	4
4.	The IR spectrum of the reaction of Cl atoms and an O ₃ /O ₂ mixture (1:20)	5
5.	The IR spectrum of the reaction of Cl atoms and an O ₃ /O ₂ mixture (1:60)	6

I. INTRODUCTION

Recently there has been much interest in the effect of catalytic cycles in stratospheric ozone chemistry [1-4]. The chlorine oxide (Cl_xO_y) cycle has been investigated to some extent, usually by postulating reaction mechanisms based upon reactions that these oxides are known to undergo and kinetics rate data (e.g., see Reference 4). However, while various mechanisms have been proposed, there is no firm experimental evidence that any of the proposed reaction intermediates are actually formed in the gas phase reaction of chlorine atoms and ozone. In our matrix isolation experiments, we are able to "trap" transient species on an argon matrix at 10° K and identify these species from their infrared spectra.

II. PROCEDURE

Our procedure was to pre-make ozone by discharging pure O_2 (Linde 99.99 percent) at low pressure with a Tesla coil. The O_3 was then trapped in liquid nitrogen. The ozone was then pumped on for 0.5 hr to remove any oxygen. Our experiments included the reaction of Cl atoms with pure O_3 , the reaction of Cl atoms with pure O_2 , and the reaction of Cl atoms with O_3/O_2 mixtures of ratios 1:10, 1:20, and 1:60. Chlorine atoms were produced by microwave discharge of a 50:1 mixture of Ar and Cl_2 (Linde 99.99 percent). The Cl atoms and the O_3/O_2 mixtures were allowed to react (in the gas phase) in a kinetic cell of our design before deposition on a CsI cold window.

III. RESULTS

The results of our experiments are as follows. In Figure 1 we give the infrared spectrum of the reaction of Cl atoms and pure O_3 . The absorption at 1100 cm^{-1} is due to symmetrical OCIO [5]. There is no evidence for the production of ClOO ; however, the absorption at 850 cm^{-1} is assigned to the ClO radical [6]. The absorptions at 1300 cm^{-1} , 1245 cm^{-1} , and 800 cm^{-1} to 740 cm^{-1} are tentatively assigned to higher chlorine oxides (ClO_x) and are presently under investigation. In Figure 2 we give the infrared spectrum of chlorine atoms and pure O_2 . There is an absorption at 1100 cm^{-1} due to OCIO , and the strong absorption at 1441 cm^{-1} indicates the presence of ClOO [5].

Several experiments were performed at different O_3/O_2 concentrations (1:10, 1:20, 1:60, Figs. 3, 4, and 5, respectively). All experiments,

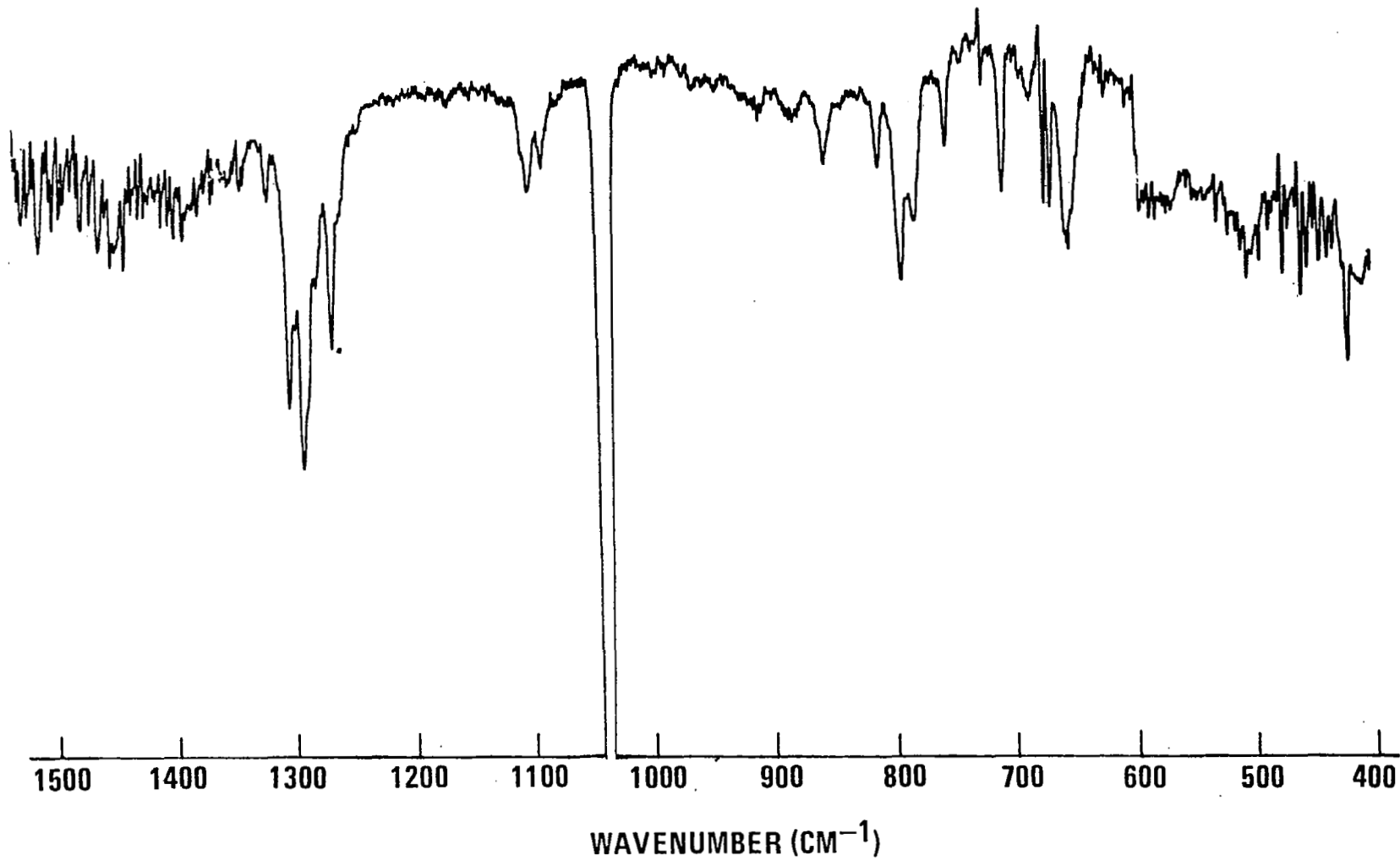


Figure 1. The IR spectrum of the reaction of Cl atoms and ozone.

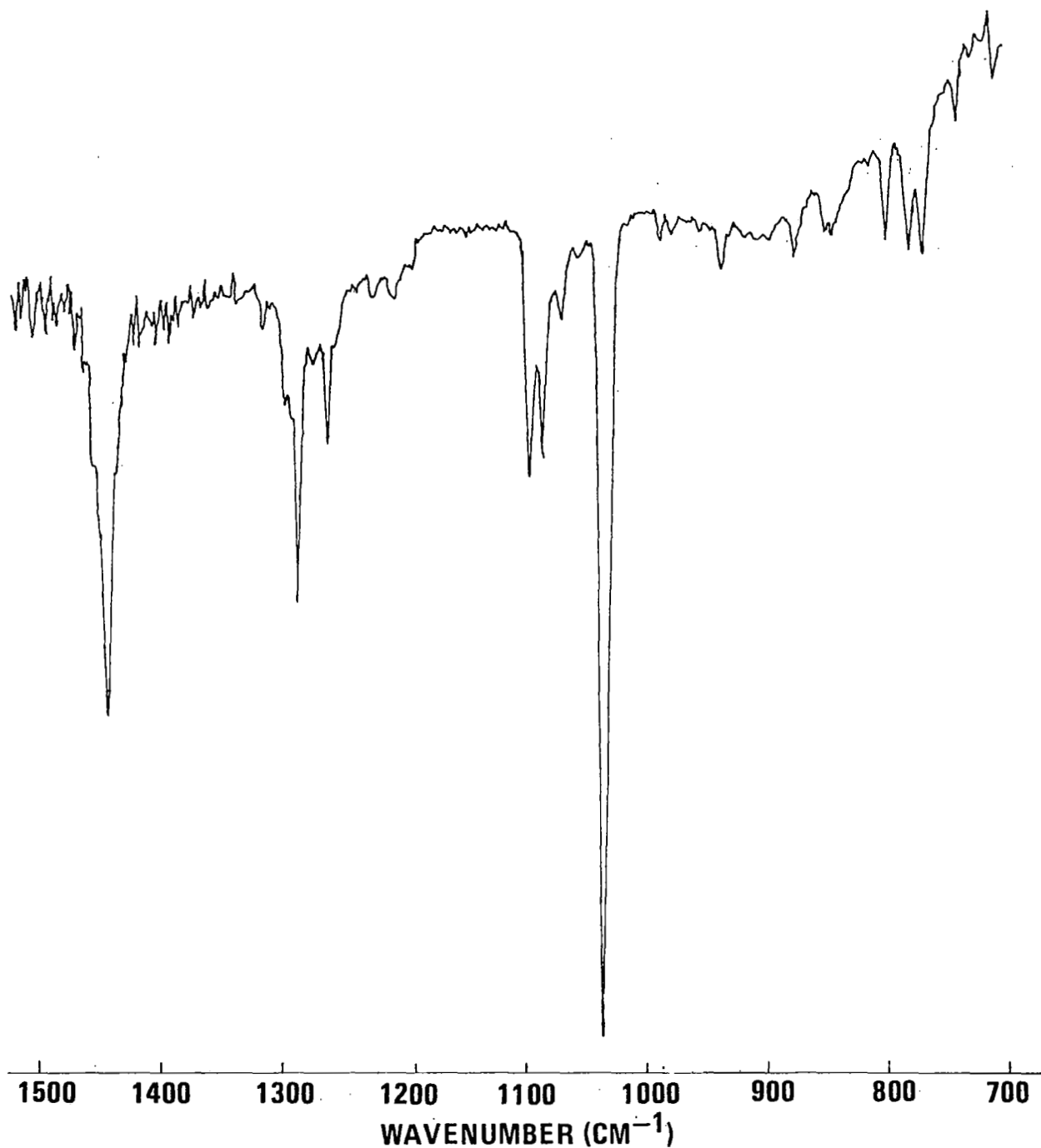


Figure 2. The IR spectrum of the reaction of Cl atoms and oxygen. The ozone absorptions observed at 1050 and 700 cm^{-1} are due to the reaction of excited argon and oxygen. We observed production of O_3 when argon was discharged and then allowed to react with pure O_2 atoms. The mechanism appears to be
$$\text{Ar}^* + \text{O}_2 \rightarrow \text{Ar} + 2\text{O}, \text{ and } 2\text{O} + 2\text{O}_2 \rightarrow 2\text{O}_3.$$

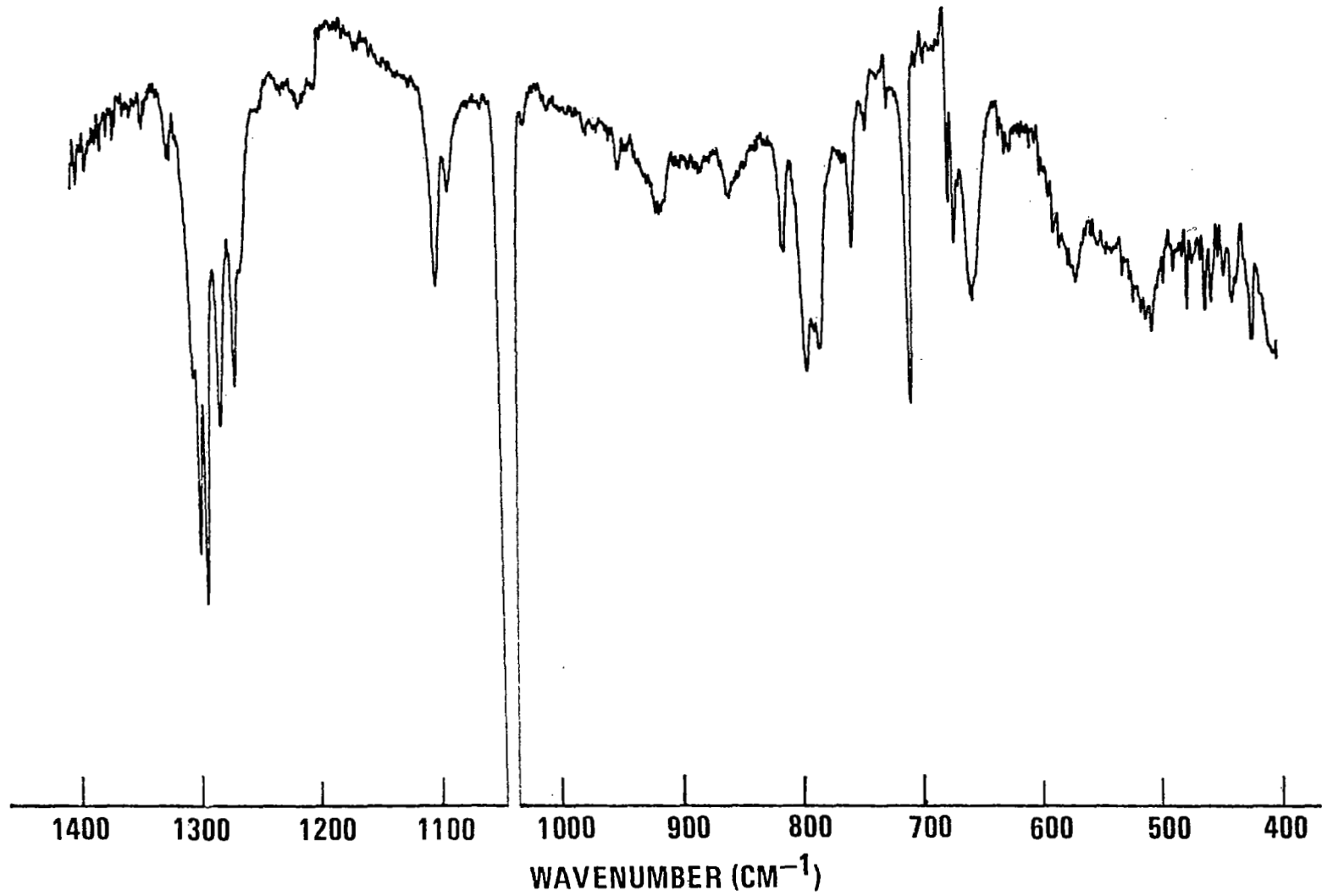
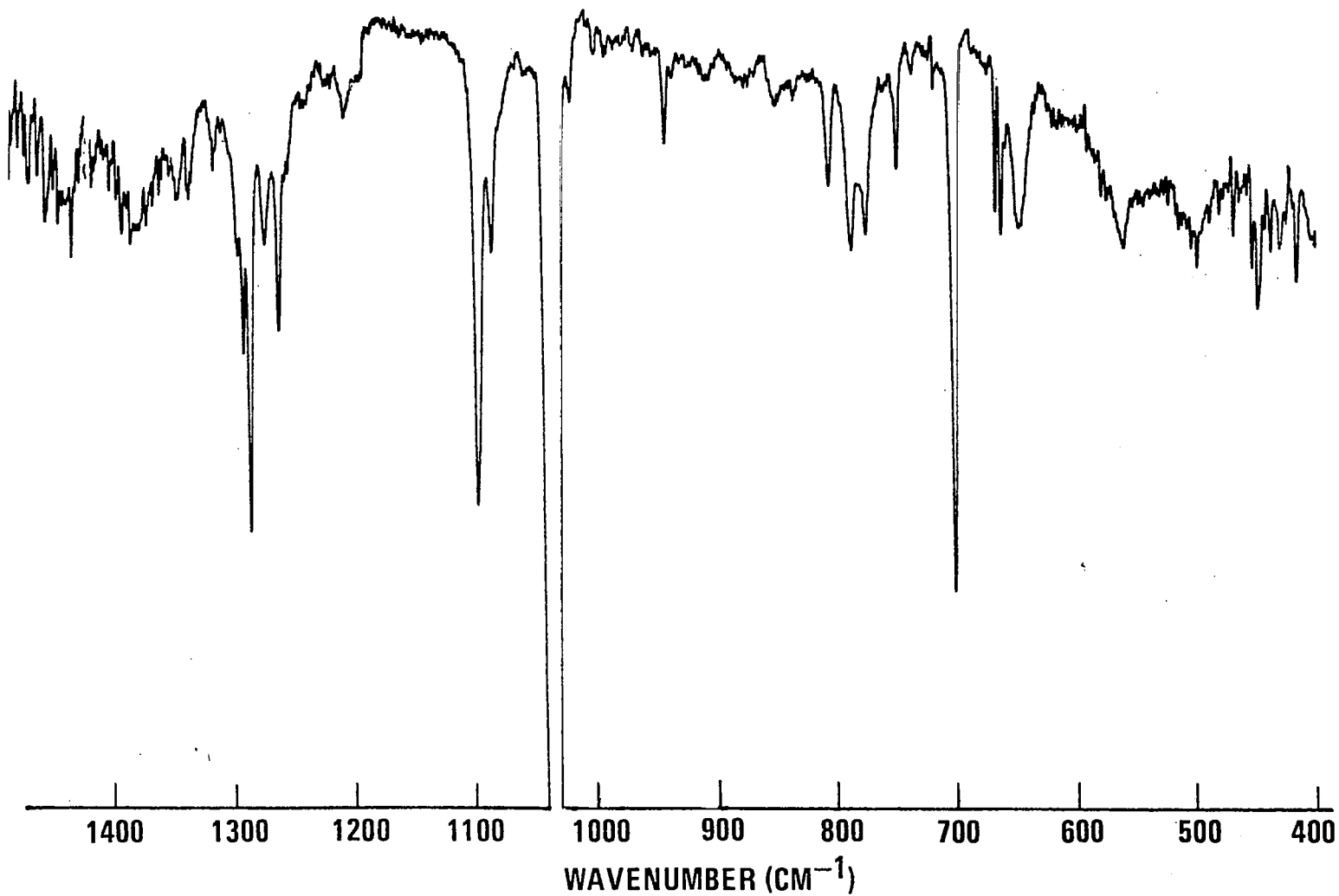


Figure 3. The IR spectrum of the reaction of Cl atoms and an O₃/O₂ mixture (1:10).



51

Figure 4. The IR spectrum of the reaction of Cl atoms and an O₃/O₂ mixture (1:20).

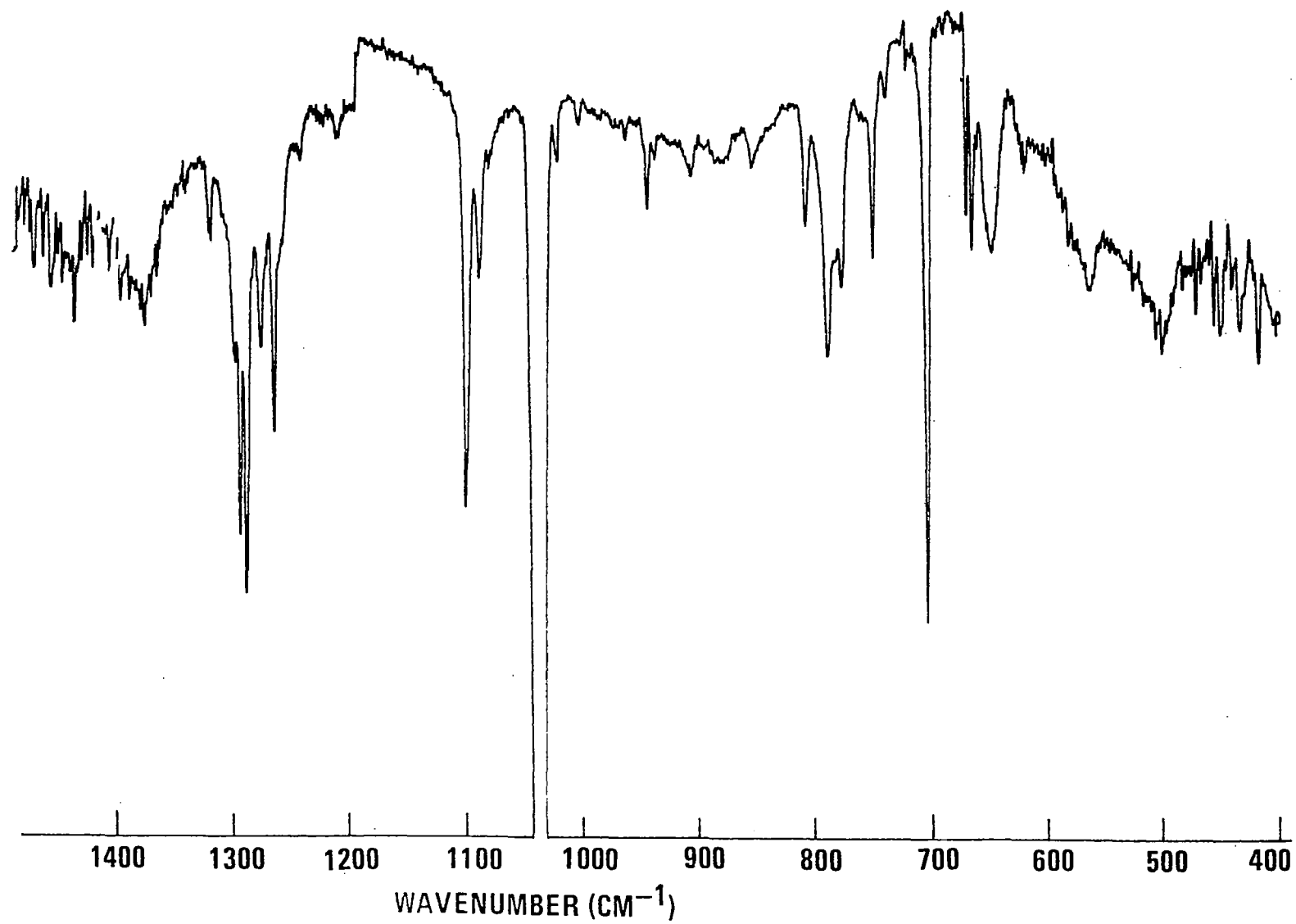
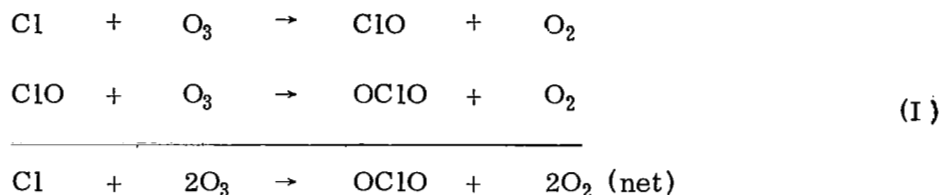


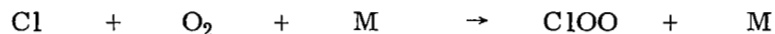
Figure 5. The IR spectrum of the reaction of Cl atoms and an O₃/O₂ mixture (1:60).

naturally, employed the same ozone concentrations, with successively increasing oxygen concentrations. Figure 3 represents the O_3/O_2 experiment of ratio 1:10. We see that the OCIO (100 and 940 cm^{-1}) [5] production is greatly enhanced when compared to that from the reaction of Cl and pure O_3 . The radical ClO (850 cm^{-1}) [6] is also present, together with ClO_x species. Note that no ClOO (1442 cm^{-1}) [5] is produced. The OCIO production increases in the O_3/O_2 , 1:20 experiment (Fig. 4), and the OCIO absorption for the 1:60 experiment (Fig. 5) is essentially the same for the 1:20 experiment.

That OCIO is produced via a ClO intermediate, we propose



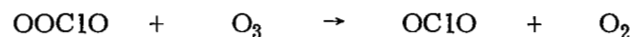
and that chlorine atoms react with O_2 and a third body to produce ClOO



However, the reaction mechanism involving the production enhancement of OCIO when O_2 is present is not as evident. The mechanism may involve an asymmetrical ClO_3 (OOCIO) intermediate, formed by the reaction of ClO and O_2

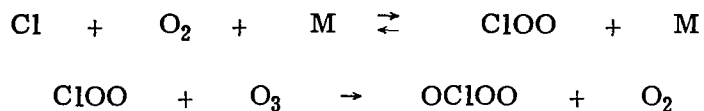


which can, in turn, react with O_3 to give OCIO



The net reaction is the same as for reaction scheme (I): $Cl + 2O_3 \rightarrow OCIO + 2O_2$.

Interestingly, Zahniser, Kaufman, and Anderson (ZKA) [7] propose that asymmetrical ClO_3 and not symmetrical ClO_3 may be a product of the $Cl + O_3$ reaction. The proposed mechanism is



Our results lead us to postulate asymmetrical ClO_3 in order to explain the oxygen enhancement of the OCIO production. Also, if the ZKA scheme were correct, it is plausible to assume that unless the second reaction were extremely fast, relative to the first, we should see some ClOO at all times in our experiments, but we do not.

IV. SUMMARY

The notable observations are: (1) the reaction of Cl atoms and O_3 produces primarily OCIO , (2) the reaction of Cl atoms and O_2 produces primarily ClOO , (3) oxygen enhances the production of OCIO in the $\text{Cl} + \text{O}_3$ reactions, and (4) the radical, ClO , is an intermediate in these gas phase reactions.

Attempts are now under way to identify and characterize the OOCIO radical as well as the ClO_x species which absorb in the regions 1300 cm^{-1} to 1245 cm^{-1} and 800 cm^{-1} to 740 cm^{-1} .

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