Effect of Nitric Oxide on Photochemical Ozone Formation in Mixtures of Air With Molecular Chlorine and With Trichlorofluoromethane

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APRIL 1978
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AND WITH TRICHLOROFLUOROMETHANE
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SUMMARY

An experimental and theoretical study was made of ozone ($O_3$) formation in air containing either molecular chlorine ($Cl_2$) and nitric oxide (NO) or trichlorofluoromethane (CFC$_3$) and NO. The purpose of this work was to study the NOx and ClOx mechanisms for $O_3$ destruction. Similar mechanisms have been proposed for $O_3$ destruction in the stratosphere by NO and CFC$_3$. Mixtures of these gases in air were photolyzed at room temperature and atmospheric pressure by ultraviolet, simulated solar radiation. Concentration-against-time profiles of $O_3$, NO, and NO$_2$ were measured. A temporary rise in $O_3$ concentration was observed for both Cl$_2$-NO-air and CFC$_3$-NO-air mixtures. Ozone concentration then decreased and, in the case of CFC$_3$-NO-air, stayed close to zero during the entire 3- to 4-hour reaction. A chemical mechanism that satisfactorily explains the experimental results was developed with the aid of a general chemical kinetics computer code. Computations show that the experimental $O_3$ concentration behavior is explained by the formation and subsequent destruction of chlorine nitrate (ClONO$_2$).

The gas-phase part of the chemical mechanism was used to compute $O_3$ formation in CFC$_3$-NO-air mixtures at stratospheric temperatures, pressures, and compositions. There was a large reduction in the steady-state $O_3$ concentrations for these mixtures as compared with pure air. These computations did not use a complete stratospheric model, since transport phenomena were not included. They were performed to show the effect of the laboratory-derived chemical mechanism when it is applied at stratospheric conditions. The computations indicate that ClONO$_2$ will probably not be a major factor in preventing $O_3$ destruction in the stratosphere.
INTRODUCTION

Two previous reports (refs. 1 and 2) describe the effect of various pollutants on ozone \((O_3)\) formation when air is photolyzed in a laboratory experiment. This work was done to obtain a better understanding of the chemistry of \(O_3\) destruction. Chemical mechanisms involved in stratospheric \(O_3\) destruction by these pollutants are similar to those in the laboratory simulations. The species studied were nitric oxide (NO) and one of the chlorofluoromethanes, trichlorofluoromethane (CFCl\(_3\)). The controversy over the extent of stratospheric \(O_3\) depletion by these pollutants is well known (refs. 3 to 7). In reference 2, we showed that NO had only a temporary effect in delaying \(O_3\) formation when air was photolyzed by simulated solar radiation in a static reaction chamber. Although 1 to 2 ppm of NO delayed \(O_3\) formation at first, the \(O_3\) concentration rose after a short delay (20 to 100 min) to the value it would have attained for pure-air photolysis. On the other hand, 1 to 100 ppm of CFCl\(_3\) had a permanent destructive effect on \(O_3\) formation in a similar experiment (ref. 1). The \(O_3\) concentration either leveled off at a value lower than that for pure air or went through a maximum and decreased toward zero.

Recently, there has been discussion about the interaction of the NO\(_x\) and ClO\(_x\) destruction mechanisms for \(O_3\) (ref. 8). By reacting with each other, the NO\(_x\) and ClO\(_x\) species may be partly removed, thus lessening the \(O_3\) destruction. Therefore, we extended our previous work to the photolysis of mixtures of NO and CFCl\(_3\) in air. In order to study a simpler but very similar chemical system, we also photolyzed mixtures of Cl\(_2\) and NO in air.

Ozone formation was measured in Cl\(_2\)-NO-air and CFCl\(_3\)-NO-air mixtures in a static reaction chamber. The mixtures were irradiated with ultraviolet simulated solar radiation to find out whether the two \(O_3\) destruction mechanisms reinforce each other or interfere with each other. Concentration profiles of NO and NO\(_2\) were also measured. All experiments were performed at atmospheric pressure and room temperature (298 K). A chemical mechanism to help in understanding the experimental results was developed by performing theoretical computations. These kinetic computations, which attempted to match the observed \(O_3\), NO, and NO\(_2\) concentration profiles, were performed with an improved version of the general kinetics computer code of Bittker and Scullin (ref. 9).

The chemistry of NO\(_x\) and ClO\(_x\) systems has been studied for many years. The NO\(_x\) cycle for \(O_3\) destruction is shown in the following set of reactions\(^1\):

\(^1\)Numbering of reactions corresponds to the complete list in table I.
\[
\begin{align*}
k_{14} & \quad \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \\
k_{15} & \quad \text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2 \\
k_{16} & \quad \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \\
J_{17} & \quad \text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}
\end{align*}
\] (XIV)

(XV)

(XVI)

(XVII)

The net result of reactions (XIV) and (XV) is the destruction of odd oxygen, \( \text{O} + \text{O}_3 \rightarrow 2 \text{O}_2 \). When a chlorofluoromethane such as \( \text{CFCl}_3 \) is subjected to ultraviolet radiation, it dissociates into Cl atoms. The resulting Cl atoms start the ClO\(_x\) cycle for odd oxygen destruction:

\[
\begin{align*}
k_1 & \quad \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \\
k_2 & \quad \text{O} + \text{ClO} \rightarrow \text{Cl} + \text{O}_2 \\
J_5 & \quad \text{ClO} + \text{hv} \rightarrow \text{Cl} + \text{O}
\end{align*}
\] (I)

(II)

(V)

The net result of reactions (I) and (II) is also \( \text{O} + \text{O}_3 \rightarrow 2 \text{O}_2 \). When both chlorine compounds and NO are present in a reacting system, the following reaction can occur:

\[
k_{21} \quad \text{NO} + \text{ClO} \rightarrow \text{Cl} + \text{NO}_2
\] (XXI)

Although this reaction ties up NO, it also produces Cl. So it is not obvious whether it will interfere with or aid in the O\(_3\) depletion process. In addition, the formation of chlorine nitrate (ClONO\(_2\)) by the recombination of ClO and NO\(_2\) has been well established (refs. 10 and 11):

\[
k_{22} \quad \text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M}
\] (XXII)
If ClONO₂ is very stable, O₃ destruction would be decreased by the tieing up of ClO and NO₂. However, ClONO₂ is readily photolyzed by ultraviolet radiation, either in the laboratory or in the stratosphere, as follows (ref. 12):

\[ \text{ClONO}_2 + \text{hv} \rightarrow \text{ClO} + \text{NO}_2 \]  

(XXIII)

Computations by Eggleton, Cox, and Derwent (ref. 13) indicate that ClONO₂ has a quite high concentration in the stratosphere and thus that it might be a significant sink for Cl atoms. However, later computations by Rowland, Spencer and Molina (ref. 11) show much smaller ClONO₂ stratospheric concentrations. Obviously, the results of such computations depend partly on having an accurate chemical reaction mechanism.

In this experiment, we studied the chemical system used for the stratospheric work, but at nonstratospheric conditions. The pressure and temperature are higher and there are walls, which can affect the reaction kinetics.

The chemical mechanism that was developed to explain the laboratory results was then used in a computation at stratospheric conditions by eliminating the wall reactions. This latter computation does not use a complete stratospheric model since radiative heat transfer and mass transport are not included, just as they were not included in the reaction chamber computations. It indicates the expected results of a static gas-phase reaction at altitude conditions. The same chemical mechanism could show quite different trends in species formation for widely different conditions of temperature, pressure, and initial composition. It is therefore important to determine whether our mechanism predicts the same effect on O₃ formation at low temperature and pressure that was observed and computed at reaction chamber conditions. The results of computations to check on this point are presented.

**APPARATUS AND PROCEDURE**

The reaction chamber used for this work was used in our previous work (refs. 1 and 2). It is a 650-liter stainless steel tank with about 85 percent of the inner walls lined with Teflon sheets. This surface reduces heterogeneous reactions involving O₃ and other free radicals. Ultraviolet simulated solar radiation with wavelengths as low as 200 nanometers was obtained from a high-pressure xenon arc lamp. Commercially available gases were used as sources of NO and "ultrapure" air. The Cl₂ and CFCl₃ were distilled twice in the laboratory before use. The "ultrapure" air contained less than 0.1 part per million (ppm) of methane and 1 to 2 ppm of water.

We measured profiles of O₃, NO, and NO₂ concentrations as a function of time when various mixtures of the pollutants in air were irradiated in the reaction chamber.
All experiments were performed at room temperature (298 K) and atmospheric pressure.

In this work six different types of mixtures were irradiated:

1. Pure air
2. Air + Cl₂
3. Air + CFCl₃
4. Air + NO
5. Air + Cl₂ + NO
6. Air + CFCl₃ + NO

The experiments were divided into two series. Series A involves Cl₂, NO, and air; series B involves CFCl₃, NO, and air. The two series of experiments were performed several months apart, but each series was run over a period of about 3 weeks. During the series A experiments, runs were made with Cl₂-air, NO-air, and Cl₂-NO-air mixtures. In addition, runs with pure air were performed at the beginning and end of the complete series. This procedure gave a self-consistent set of results for comparison purposes. The pure-air runs also "calibrated" the chamber and helped insure that chamber characteristics such as surface activity and light source intensity did not change significantly over the time interval for the complete series A. For these same reasons, the series B experiments included runs with pure air, CFCl₃ + air, NO + air, and CFCl₃ + NO + air.

EXPERIMENTAL RESULTS

Cl₂-NO-Air System

Two different mixtures of Cl₂ and NO in air were irradiated in the reaction chamber. Mixture 1 contained 2-ppm Cl₂ and 2-ppm NO, while mixture 2 contained 4-ppm Cl₂ and 2-ppm NO. Two mixtures of Cl₂ with air and a mixture of NO with air were photolyzed very close to the time of the NO-Cl₂ experiments in order to obtain data to use as a reference. As in our previous work, pure air was photolyzed before and after this complete series of experiments in order to obtain reference O₃ formation profiles.

Figure 1 shows measured profiles of O₃, NO, and NO₂ concentrations as a function of time for the two Cl₂-NO-air mixtures. For mixture 1 (fig. 1(a)), O₃ was formed more slowly than in pure air, but then the O₃ concentration rose steadily. The O₃ concentration leveled off after about 240 minutes of reaction. The O₃ profile is significantly different for mixture 2 (fig. 1(b)). After the same delay noted for mixture 1, the O₃ concentration rose to a maximum value of 25 parts per hundred million (pphm) at 70 minutes and then decreased. There is a hint of this effect in figure 1 also. It reached a minimum and then increased steadily after that. Both mixtures show similar
trends in the NO and NO₂ concentration profiles. The NO was rapidly consumed and NO₂ was formed. For both mixtures the NO₂ concentration reached a maximum and then decreased. However, the rate of decrease was much faster for mixture 2 than for mixture 1, which had the smaller amount of Cl₂ present at the start. These profiles are compared in more detail later in this section.

Figure 2 shows a comparison of O₃ concentration profiles for pure air, air + Cl₂, air + NO, and air + Cl₂ + NO. In figure 2(a), initial concentrations of Cl₂ and NO are each 2 ppm. The NO-air mixture showed the longest O₃ formation delay, as compared with pure air. The slightly shorter delay until the first detection of O₃ for the NO-Cl₂-air mixture (mixture 1) indicates that NO destruction of O₃ was counteracted slightly by the combined mixture. For all pollutant mixtures the destruction of O₃ was only temporary. In figure 2(b), initial concentrations of Cl₂ and NO are 4 ppm and 2 ppm, respectively. In this case the Cl₂-air mixture showed an O₃ formation delay longer than that of the NO-air mixture. However, after 130 minutes, the two O₃ curves almost coincide. The O₃ formation curve for the NO-Cl₂-air mixture (mixture 2) shows the temporary early rise already noted. However, the effective delay for this mixture was much longer than for either pollutant separately. Mixture 2 temporarily impeded O₃ destruction but then the NOₓ and ClOₓ mechanisms reinforced each other. The reason for the temporary rise in O₃ concentration is discussed in the section DISCUSSION AND CONCLUDING REMARKS.

The effect of added Cl₂ on the NO and NO₂ profiles is shown in figure 3. Increasing Cl₂ concentration from 0 to 4 ppm steadily accelerated the consumption of NO, as shown in figure 3(a). Figure 3(b) shows that this Cl₂ addition not only accelerated NO₂ formation, but also accelerated its destruction after its concentration reached a maximum. This was probably due to the increasing importance of reactions XXI and XXII as Cl₂ concentration increased.

CFCl₃-NO-Air System

One mixture of CFCl₃ with NO in air was photolyzed in this work. The concentration of O₃ as a function of time for 12-ppm CFCl₃ plus 1.5-ppm NO in air is shown in figure 4. Trichlorofluoromethane is much more difficult to photolyze than Cl₂. Therefore, a relatively large amount had to be used so that a strong effect on O₃ formation would be observed in a practical laboratory time. Also shown in figure 4 are a pure-air reference curve, a curve for 16-ppm CFCl₃ in air, and one for 1.3-ppm NO in air. The latter curves were obtained at the same time as the one for the NO-CFC₁₃ mixture.

For CFCl₃ alone, the O₃ concentration rose immediately but soon reached a maximum and then decreased toward zero. This behavior is also reported in reference 1.
The effect of CFCl₃ on O₃ formation was slower than the effect of Cl₂ because CFCl₃ photolyzes much more slowly than Cl₂. Once O₃ destruction began, the effect of CFCl₃ was more permanent than the effect of Cl₂. The reason is that all the Cl₂ was rapidly photolyzed, while only a small fraction of the CFCl₃ was photolyzed during the total reaction time. The NO-air mixture delayed O₃ formation for about 120 minutes, but it then rose slowly and steadily. This delay is slightly longer than the 100-minute delay reported in reference 2 for a similar NO-air mixture. When the NO-CFCl₃ mixture was photolyzed, O₃ formation was delayed about 60 minutes. The O₃ concentration then rose but reached a maximum and then decreased sharply toward zero. Again, the interaction of the NOₓ and ClOₓ mechanisms to reduce O₃ destruction was only temporary.

Concentrations of NO and NO₂ as a function of time for the CFCl₃-NO-air mixture are presented in figure 5. They show the typical rapid conversion of NO to NO₂ and the subsequent loss of NO₂ that was observed previously (ref. 2).

**COMPARISON OF EXPERIMENTAL AND THEORETICAL RESULTS**

As in our previous work, chemical modeling computations were performed in order to explain the experimental results and to get a better understanding of the complex chemical mechanism involved.

**Cl₂-NO-Air System**

The NOₓ chemical reaction mechanism of reference 2 was combined with the ClOₓ mechanism of reference 1 to give the main part of the chemical model used for these computations. In addition, the reactions involving NOₓ and ClOₓ interactions (reactions XXI to XXIII) were added. Two other reactions of ClONO₂ are also included:

\[
\begin{align*}
\text{(XXIV)} & \\
O + \text{ClONO}_2 & \rightarrow \text{ClO} + \text{NO}_3 \\
\text{(XXV)} & \\
\text{Cl} + \text{ClONO}_2 & \rightarrow \text{Cl}_2 + \text{NO}_3
\end{align*}
\]

The complete list of reactions used and their rate constants are given in table I. The rate constant for O₂ photolysis

\[
\begin{align*}
\text{(VII)} & \\
O_2 + h\nu & \rightarrow O + O
\end{align*}
\]
was determined for each series of experiments. This was done by performing computations to match the experimental \( \text{O}_3 \)-against-time profiles for pure air, which were taken before and after each series of experiments. The initial slope of this reference \( \text{O}_3 \) profile was determined primarily by \( J_7 \). The value \( J_7 = 2.5 \times 10^{-9} \text{ sec}^{-1} \) was used for these \( \text{Cl}_2 \)-NO computations. This value corresponds to the pure-air \( \text{O}_3 \) curve of figure 2.

Two simulated wall destruction reactions are also needed to explain the results, as in our previous work (refs. 1 and 2). These are wall destruction of \( \text{O}_3 \) and \( \text{Cl} \) and are written

\[
\begin{align*}
\text{O}_3 + k_D & \rightarrow \frac{3}{2}\text{O}_2 \\
\text{Cl} + k_{\text{Cl}} & \rightarrow \text{N}_2
\end{align*}
\]

The latter unbalanced reaction does not affect the mass balance of the system because the \( \text{Cl} \) concentration is always small and the ratio of \( \text{N}_2 \) concentration to \( \text{Cl} \) concentration is quite high. An approximate value of \( k_D \) was obtained by matching the pure-air reference curve. However, \( k_D \) was adjusted slightly to match the \( \text{O}_3 \) curves in the presence of pollutants. The value \( k_D = 8 \times 10^{-4} \text{ sec}^{-1} \) was used for these \( \text{Cl}_2 \)-NO-air computations. The justification for invoking \( \text{Cl} \) wall destruction is discussed fully in reference 1. A constant value of \( k_{\text{Cl}} \) was used in that work in the presence of a few ppm of \( \text{Cl}_2 \). The value \( k_{\text{Cl}} = 3.5 \text{ sec}^{-1} \) used in the present computations is about one-tenth of the value used for \( \text{Cl}_2 \)-air mixtures in reference 1. This difference is due to small changes in wall surface characteristics and relatively high sensitivity of \( \text{Cl} \) wall destruction reactions to wall conditions.

A comparison of computed and experimental \( \text{O}_3 \) profiles for two mixtures of \( \text{Cl}_2 \) and NO is shown in figure 6. Each computed curve is the best of several trials in which a few of the reaction rate constants were varied within their experimental uncertainties. The largest variation was by a factor of 2. The curves were chosen by the authors on the basis of the general shape of the curve as well as the closeness of fit. There is semi-quantitative agreement between the experimental and computed curves for both mixtures. For 4-ppm \( \text{Cl}_2 \) (mixture 2) the computation reproduced the \( \text{O}_3 \) concentration maximum rather well and gave fair agreement with the rest of the experimental curve (fig. 6(b)). For 2-ppm \( \text{Cl}_2 \) (mixture 1) the computed \( \text{O}_3 \) curve still shows a maximum at about 65 minutes, but the experimental curve shows only a slight bending over at this point (fig. 6(a)). However, after the computed concentration begins to rise again, it follows the experimental curve fairly well. Concentration profile comparisons for NO
and NO2 with these same two mixtures are shown in figure 7. Again, the computed curves are in fairly good agreement with experiment, except for the NO2 profile of mixture 1. The computed curve decreases from its maximum much faster than the experimental curve.

These computations involved all the reactions and rate constants in table I, along with the simulated wall destruction reactions previously mentioned. The computations were repeated without the ClONO2 reactions. The results did not reproduce the shapes of the experimental curves and are not shown. Thus, the ClONO2 reactions are needed to explain the experimental results.

CFCl3-NO-Air System

In addition to the reactions already used, the following reactions (refs. 14 and 15) have been added for the photolysis of CFCl3:

\[ \text{CFCl}_3 + h\nu \rightarrow \text{CCl}_2 F + \text{Cl} \]  
\[ \text{CCl}_2 F + \text{O}_3 \rightarrow \text{CFCl}_2 O + \text{O}_2 \]  
\[ \text{CFCl}_2 O \rightarrow \text{CFOCl} + \text{Cl} \]  
\[ \text{CCl}_2 F + \text{O}_2 \rightarrow \text{CFCl}_2 O_2 \]

The photolytic formation of Cl atoms is the most important of these reactions. Because the decomposition of CFCl3 is quite complicated, this mechanism is probably not complete. It is, however, the best available at this time. The rate constants used for these reactions are those used in reference 1. The values are \( J_{26} = 1.3 \times 10^{-6} \), \( k_{27} = 5 \times 10^{12} \) cm³/mole sec, \( k_{28} = 1 \times 10^{-2} \) sec⁻¹, and \( k_{29} = 1 \times 10^{8} \) cm³/mole sec. The values of \( k_{27}, k_{28}, \) and \( k_{29} \) were estimated because no experimental values for these rate constants have been reported in the literature. As shown in reference 1, the computed results are quite insensitive to the values of these last three rate constants. The value \( J_7 = 1.2 \times 10^{-9} \) sec⁻¹ was used for the O₂ photolysis. This value corresponds to the pure-air O₃ curve shown in figure 4. The values \( k_D = 7.5 \times 10^{-4} \) sec⁻¹ and \( k_{Cl} = 0.1 \) sec⁻¹ were used for the O₃ and Cl wall destruction reactions in these CFCl₃-NO computations. Again, the value of \( k_{Cl} \) is about one-tenth of the value used for the CFCl₃ computations in reference 1.
Figure 8 shows experimental and computed O$_3$ against-time profiles for a mixture of 12-ppm CFCl$_3$ and 1.5-ppm NO. The overall agreement is good, with a very good reproduction of the observed maximum in O$_3$ concentration. Concentration profiles for NO and NO$_2$ are shown in figure 9 for this CFCl$_3$-NO mixture. The agreement between computed and observed profiles is quite good for both species. Our computations have been able to reproduce all measured profiles for this one CFCl$_3$-NO mixture.

Application to Stratospheric Conditions

This work has shown that CFCl$_3$ and NO together permanently inhibit O$_3$ formation in laboratory experiments. However, these conditions are much different from stratospheric temperatures, pressures, and concentrations. As in our previous work, we wanted to determine the effect on O$_3$ formation shown by our mechanism at stratospheric conditions, assuming that the same gas-phase chemical model applies. Therefore, we computed O$_3$ formation time profiles and steady-state concentrations for several pollutant mixtures at stratospheric conditions. Measurements of NO and CFCl$_3$ concentrations at altitudes of 20 to 30 kilometers, obtained from references 16 and 17, are listed in table II. These concentrations are $10^3$ to $10^5$ times smaller than the reaction chamber concentrations in our experiments. Also given in this table is the value of $J_7$, the O$_2$ photolysis rate constant used for each of the three altitudes listed. These $J_7$ values were taken from reference 18. For each altitude condition the reaction mechanism, without any wall destruction reactions, was used to compute O$_3$ concentration against time out to the steady-state condition. We assumed, for each altitude condition, that air containing the tabulated amounts of NO and CFCl$_3$ was irradiated until a steady-state O$_3$ concentration was reached. These steady-state O$_3$ concentrations are given in table II along with the corresponding O$_3$ concentration that was computed for the irradiation of pure air. The last column in this table shows the percentage of reduction in the pure-air O$_3$ concentration in the presence of the pollutants. Clearly, this computation shows a very large O$_3$ reduction at altitude conditions due to the presence of CFCl$_3$ and NO.

Figure 10 shows the results of computations that compare the effect of each pollutant separately with that of the combined mixture. The computations are for 25-kilometer-altitude conditions. Figure 10(a) shows results for the atmospheric NO and CFCl$_3$ concentrations given in table II. In this case, CFCl$_3$ alone gives the smallest reduction (20 percent) in the steady-state O$_3$ concentration. Nitric oxide alone gives about the same O$_3$ reduction ($\sim$ 50 percent) as the mixture of the two pollutants. Figure 10(b) shows the results of a similar computation, but with the pollutant concentrations both made 100 times the present measured values. These high concentrations could possibly be reached in the stratosphere if emissions continue unchecked. The
results now show a steady-state O₃ concentration reduction of more than 95 percent for all three pollutant mixtures. In this case, NO alone gives the smallest reduction, but the differences among the mixtures are rather trivial.

These computations do not give values for actual O₃ reduction in the stratosphere. The chemical model used is only one part of a complete atmospheric model. Indeed, the inclusion of transport phenomena in the computation does make the computed reductions of O₃ much smaller (e.g., ref. 19). The computations were performed to show that the chemical mechanism that explains O₃ destruction in our experiments also predicts O₃ destruction at stratospheric conditions.

DISCUSSION AND CONCLUDING REMARKS

In this work we have compared the effects of different pollutant mixtures on O₃ formation during the photolysis of air. In our laboratory experiments we have studied O₃ formation in the presence of small amounts of molecular chlorine (Cl₂) alone, small amounts of trichlorofluoromethane (CFCCl₂) alone, and mixtures of these compounds with nitric oxide (NO). Apparent interaction between the NOₓ and ClOₓ destruction cycles for O₃ was observed. For Cl₂-NO mixture 1 (2-ppm Cl₂ and 2-ppm NO), O₃ destruction was more than for 2-ppm Cl₂ alone but only slightly less than for 2-ppm NO alone. For mixture 2 (4-ppm Cl₂ and 2-ppm NO) the situation was more complicated. At first, O₃ destruction was less than for either 4-ppm Cl₂ alone or 2-ppm NO alone. Ozone concentration rose but then reached a maximum value and decreased. The strikingly different behavior of these two Cl₂-NO mixtures is only partially explained by our reaction mechanism. For mixture 2, the computations show the observed O₃ maximum quite nicely. The O₃ peak occurs at the same time as a computed peak in the ClONO₂ concentration. This indicates that formation of ClONO₂ at first prevents O₃ destruction as it ties up both NO and the chlorine species. However, after about 60 minutes of reaction time, ClONO₂ starts to be destroyed, releasing ClOₓ species, and O₃ destruction increases. For mixture 1, computations predict the same temporary tie-up of the ozone-destroying species by ClONO₂. However, this was not observed experimentally. There was no maximum in the O₃ concentration early in the reaction, only a very slight leveling off for a short time. It is not very likely that ClONO₂ would be more stable in this experiment than when the higher amount of Cl₂ is present. The discrepancy may be due to a combination of such factors as (1) an incomplete reaction mechanism and (2) additional surface effects.

The CFCCl₂-NO mixture also temporarily stopped O₃ destruction, but at a later reaction time. The CFCCl₂ alone, NO alone, and the mixture of both had about the same strong destructive effect on O₃ in air. The computations reproduced the O₃, NO, and
NO\textsubscript{2} profiles quite well for the one mixture studied, although this might not be the case for different mixtures of CFCl\textsubscript{3} and NO.

Our gas-phase chemical model indicates very little interaction between the ClO\textsubscript{X} and NO\textsubscript{X} reactions when applied to mixtures of NO and CFCl\textsubscript{3} at stratospheric conditions. Essentially no counteraction of O\textsubscript{3} destruction was observed for the individual pollutants. One purpose of these computations was to determine the ability of ClONO\textsubscript{2} formation to counteract O\textsubscript{3} destruction. The indication is that ClONO\textsubscript{2} is not a major sink for chlorine atoms at stratospheric conditions. This agrees with the computed results of reference 11.

In summary, we have shown that O\textsubscript{3} destruction by mixtures of Cl\textsubscript{2} or CFCl\textsubscript{3} with NO can be explained by a chemical mechanism involving the formation and destruction of ClONO\textsubscript{2}. The mechanism explains the important results of these experiments. Computations indicate that ClONO\textsubscript{2} is not an important factor in preventing O\textsubscript{3} destruction either at the experimental conditions or at stratospheric conditions.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, January 13, 1978,
198-10.

REFERENCES


### TABLE I. - REACTIONS IN ClO₅-NOₓ SYSTEM

<table>
<thead>
<tr>
<th>Number</th>
<th>Reaction</th>
<th>(k = AT^N \exp(-E_a/RT))</th>
<th>Reference</th>
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<tbody>
<tr>
<td>I</td>
<td>Cl + O₃ → ClO + O₂</td>
<td>(1.3 \times 10^{13})</td>
<td>0</td>
</tr>
<tr>
<td>II</td>
<td>O + ClO → Cl + O₂</td>
<td>(3 \times 10^{13})</td>
<td>0</td>
</tr>
<tr>
<td>III</td>
<td>Cl₂ + hν → 2 Cl</td>
<td>(5.8 \times 10^{-4})</td>
<td>0</td>
</tr>
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<td>IV</td>
<td>2 Cl + M → Cl₂ + M</td>
<td>(1.8 \times 10^{0})</td>
<td>2x10⁻³</td>
</tr>
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<td>V</td>
<td>ClO + hν → Cl + O₂</td>
<td>(5.6 \times 10^{12})</td>
<td>12970</td>
</tr>
<tr>
<td>VI</td>
<td>O₂ + Cl₂ → ClO₂ + Cl</td>
<td>3x10⁻³</td>
<td>5.55x10⁻³</td>
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<tr>
<td>VII</td>
<td>O₂ + hν → O + O₂</td>
<td>(3.8 \times 10^{13})</td>
<td>-4216</td>
</tr>
<tr>
<td>VIII</td>
<td>O₃ + hν → O + O₂</td>
<td>(1.1 \times 10^{13})</td>
<td>19120</td>
</tr>
<tr>
<td>IX</td>
<td>O₂ + O₂ → O₃ + O</td>
<td>(2 \times 10^{10})</td>
<td>0</td>
</tr>
<tr>
<td>X</td>
<td>NO + O₃ → NO₂ + O₂</td>
<td>(2 \times 10^{10})</td>
<td>0</td>
</tr>
<tr>
<td>XI</td>
<td>Cl₂ + ClO₂ → Cl₂ + Cl</td>
<td>(9.4 \times 10^{13})</td>
<td>0</td>
</tr>
<tr>
<td>XII</td>
<td>Cl₂ + ClO₂ → Cl₂ + M</td>
<td>(7.8 \times 10^{12})</td>
<td>8326</td>
</tr>
<tr>
<td>XIII</td>
<td>ClO₂ + hν → ClO₂ + Cl</td>
<td>(3.4 \times 10^{11})</td>
<td>9979</td>
</tr>
<tr>
<td>XIV</td>
<td>NO + ClO₂ → NO₂ + O₂</td>
<td>(1 \times 10^{13})</td>
<td>0</td>
</tr>
<tr>
<td>XV</td>
<td>NO₂ + O₃ → NO₃ + O₂</td>
<td>(1 \times 10^{10})</td>
<td>20500</td>
</tr>
<tr>
<td>XVI</td>
<td>NO₂ + hν → NO + O₂</td>
<td>(1 \times 10^{10})</td>
<td>0</td>
</tr>
<tr>
<td>XVII</td>
<td>NO₂ + hν → NO₂ + O</td>
<td>(1.3 \times 10^{12})</td>
<td>-1661</td>
</tr>
<tr>
<td>XVIII</td>
<td>NO₂ + NO₂ + M → NO₃ + O_2 + M</td>
<td>(1 \times 10^{10})</td>
<td>1x10⁻¹⁰</td>
</tr>
<tr>
<td>XIX</td>
<td>N₂O₅ + hν → NO₃ + NO₃</td>
<td>(7.7 \times 10^{10})</td>
<td>0</td>
</tr>
<tr>
<td>XX</td>
<td>NO + ClO → Cl + NO₂</td>
<td>(6.8 \times 10^{12})</td>
<td>-1661</td>
</tr>
<tr>
<td>XXI</td>
<td>ClO + NO₂ → Cl + NO₃</td>
<td>(1.6 \times 10^{15})</td>
<td>4.8x10⁻¹⁴</td>
</tr>
<tr>
<td>XXII</td>
<td>CINO₂ + hν → ClO + NO₂</td>
<td>(2 \times 10^{10})</td>
<td>6987</td>
</tr>
<tr>
<td>XXIII</td>
<td>ClO₂ + Cl + NO₂</td>
<td>(1 \times 10^{12})</td>
<td>5063</td>
</tr>
</tbody>
</table>

\(k\) has units of sec⁻¹ for photochemical reaction, cm³/mole sec for bimolecular reaction, and cm⁶/mole² sec for termolecular reaction. \(R = 8.3143\) J/mole K.

Value adjusted from value given in reference.

### TABLE II. - COMPUTED O₃ DEPLETION BY NO AND CFCl₃ IN AIR

### AT STRATOSPHERIC CONDITIONS

<table>
<thead>
<tr>
<th>Altitude, km</th>
<th>CFCl₃ concentration, parts per trillion</th>
<th>NO concentration, parts per billion</th>
<th>Rate constant, (J_7) sec⁻¹</th>
<th>(O_3) concentration in pure air, ppm</th>
<th>(O_3) concentration with pollutants, ppm</th>
<th>Reduction in (O_3), percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>50</td>
<td>0.27</td>
<td>(1 \times 10^{-13})</td>
<td>2.35</td>
<td>0.55</td>
<td>77</td>
</tr>
<tr>
<td>25</td>
<td>18</td>
<td>0.8</td>
<td>(1.3 \times 10^{-12})</td>
<td>4.90</td>
<td>2.36</td>
<td>52</td>
</tr>
<tr>
<td>30</td>
<td>9</td>
<td>2.6</td>
<td>(1 \times 10^{-11})</td>
<td>8.02</td>
<td>3.81</td>
<td>52</td>
</tr>
</tbody>
</table>
Figure 1. Concentration-time profiles for NO, NO\textsubscript{2}, and O\textsubscript{3} in air-C\textsubscript{2}NO mixtures.
Figure 2. - Ozone formation in airCl₂ and airCl₂-NO mixtures.
Figure 3. - Effect of adding Cl\textsubscript{2} on conversion of NO to NO\textsubscript{2} and consumption of NO\textsubscript{2}.
Nitric oxide initial concentration, 1.8 ppm.
Figure 4. - Formation of $O_3$ in air-CFC$_3$ and air-CFC$_3$-NO mixtures.

Figure 5. - Formation of NO and NO$_2$ in air + 12 ppm CFC$_3$ + 1.5 ppm NO.
Figure 6. - Comparison of experimental and computed ozone formation in air-Cl₂-NO mixtures.
Figure 7. - Comparison of experimental and computed NO and NO$_2$ formation in air-Cl$_2$-NO mixtures.

Figure 8. - Comparison of experimental and computed O$_3$ formation for air + 12 ppm CFC$_3$ + 1.5 ppm NO.
Figure 9. - Comparison of experimental and computed NO and NO₂ formation for air + 12 ppm CFC₁₃ + 1.5 ppm NO.
Figure 10. - Computed O3 formation at 25-kilometer-altitude conditions (temperature, 222 K; pressure, 0.0252 atmosphere).
Ozone formation in a reaction chamber at room temperature and atmospheric pressure has been studied for the photolysis of mixtures of NO with either Cl₂ or CFC₁₃ in air. Both Cl₂ + NO and CFC₁₃ + NO in air strongly inhibited O₃ formation during the entire 3- to 4-hour reaction. A chemical mechanism that explains the results is presented. An important part of this mechanism is the formation and destruction of chlorine nitrate (ClONO₂). Computations were performed with this same mechanism for CFC₁₃-NO-air mixtures at stratospheric temperatures, pressures, and concentrations. Results show large reductions in steady-state O₃ concentrations in these mixtures as compared with pure air. This work shows that ClONO₂ is not a significant sink for the O₃-destroying Cl atoms. It was not a major factor in preventing O₃ destruction in the laboratory experiments and probably will not be in the stratosphere either.
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