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a possible stratospheric sink
for ClO radicals and NO_x
with significant implication
for ozone depletion**

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May 1976

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CHLORINE NITRATE - A POSSIBLE STRATOSPHERIC SINK FOR ClO
RADICALS AND NO_x WITH SIGNIFICANT IMPLICATION FOR OZONE
DEPLETION

R.A. Cox, R.G. Derwent and A.E.J. Eggleton

ABSTRACT

Thermodynamic and kinetic data from the literature is used to show that chlorine nitrate could be formed in the stratosphere by the reaction $\text{ClO} + \text{NO}_2(+\text{M}) = \text{ClONO}_2$. The rates for formation and removal of chlorine nitrate in the stratosphere have been incorporated into a ten-layer one-dimensional photochemical-diffusion computer model of atmospheric chlorine chemistry. The calculations indicate a significant role for chlorine nitrate as a sink for ClO radicals and nitrogen oxides, NO_x , both of which play an important part in the destruction of stratospheric ozone. If future experimental measurements support the predicted rate constants then the ozone depletion expected from the release of chlorofluorocarbons 11 and 12 is considerably reduced.

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Table

- 1 Thermodynamic and kinetic data for the reactions of chlorine nitrate with stratospheric constituents

ILLUSTRATIONS

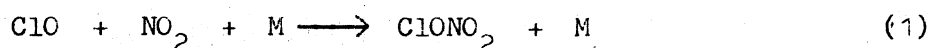
Figure

- 1 The fraction of free odd-chlorine species present as chlorine nitrate calculated using the 'high', 'medium' and 'low' formation rates for chlorine nitrate
- 2 The calculated depletion in the total ozone column resulting from the continued release of chlorofluoromethanes with and without the formation of chlorine nitrate at the 'high', 'medium' and 'low' rates.

1. Introduction

The hypothesis that the chlorofluoromethanes, CF_2Cl_2 and CFCl_3 , widely used as aerosol propellants, constitute a potential threat to the integrity of the earth's ozone shield, is currently of widespread concern. Predictions of the depletion of the ozone content of the stratosphere resulting from the release of chlorofluoromethanes are based mainly on one-dimensional photochemical-diffusion models of the atmosphere. Besides adequate representation of atmospheric dynamics the validity of such models depends on the inclusion of accurate photochemical and rate data for all reactions of importance. We show here that incorporation of predicted rate data for a compound not previously considered, chlorine nitrate, could radically change current estimates of ozone depletion resulting from the injection of chlorofluoromethanes into the stratosphere.

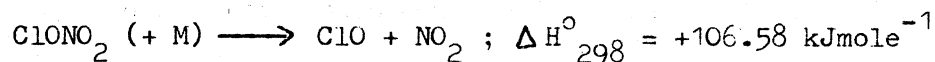
Some recent measurements by Lazrus et al.⁽¹⁾ of the distribution of hydrogen chloride in the stratosphere indicate marked seasonal variations. This is not predicted by current photochemical models of the chemistry of chlorine-containing trace gases, which indicate that hydrogen chloride is the major stratospheric reservoir of free chlorine species. The authors suggest that the measurements can be explained by the presence of an additional stratospheric constituent, chlorine nitrate, which is formed by the three-body combination of chlorine oxide radicals with nitrogen dioxide, (1)



Chlorine nitrate (B.pt 18°C) is a colourless gas which thermally decomposes above room temperature liberating nitrogen dioxide⁽²⁾. The previously reported absorption cross sections of chlorine nitrate in the ultra-violet region⁽³⁾ have recently been confirmed by Rowland et al.⁽⁴⁾ who have calculated the resulting photolysis rates as a function of altitude in the stratosphere.

2. Thermochemical and kinetic data for chlorine nitrate

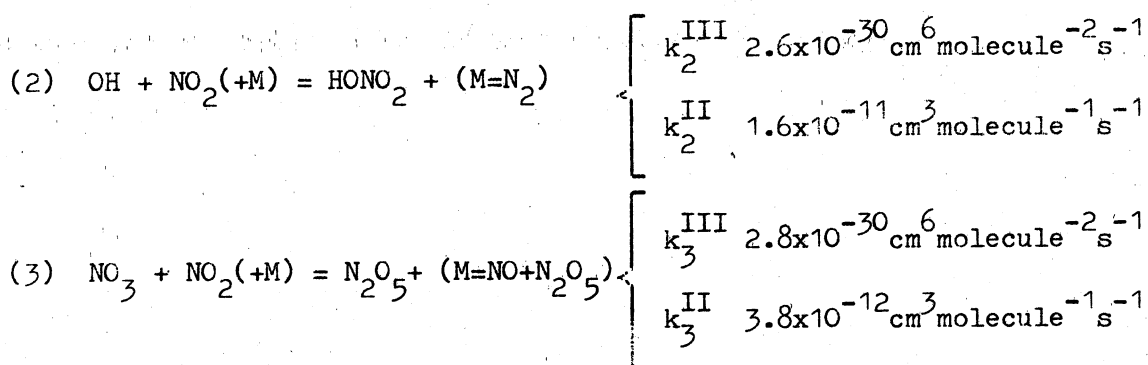
The previously determined standard enthalpy of formation of chlorine nitrate⁽⁵⁾, allows an evaluation of the enthalpy change for the reverse reaction (-1), viz.



If it is assumed that the activation energy for the recombination reaction (1) is close to zero, ΔH_{298}° can be equated to $\Delta H_{298}^\circ (\text{ClO}-\text{NO}_2)$. Furthermore, the

activation energy for dissociation of chlorine nitrate, E_{-1} , is equal to $H^{\circ}(\text{ClO}-\text{NO}_2)$ at 0°K , i.e. $+102.18 \text{ kJ mol}^{-1}$. Assuming a normal pre-exponential factor for unimolecular decomposition of small molecules, viz. $A_{-1} \approx 10^{14} \text{ s}^{-1}$, the high pressure limiting dissociation rate constant is given by $k_{-1}^{\infty} = 10^{14} \exp(-12480/T)$, s^{-1} . The thermal decomposition rate calculated using this expression is significantly lower than the photolysis rate in the lower and middle stratosphere, but may become comparable in the warmer atmospheric regions of the lower troposphere and upper stratosphere.

The experimental value of ΔH_{298}° for reaction (1) can be combined with available standard entropy data⁽⁶⁾ to calculate the equilibrium constant, K , which in turn allows k_1^{II} to be evaluated, since $k_1^{\text{II}} = K k_1^{\infty}$. Here k_1^{II} refers to the effective bimolecular rate constant for reaction (1) at the high pressure limit. The value obtained is $k_1^{\text{II}} = 3.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is independent of temperature according to our assumption that $E_1 = 0$. This value is similar in magnitude to those for corresponding additions of other oxygen-containing radicals to NO_2 which have been measured experimentally.⁽⁷⁾



Here k^{III} refers to the third order rate constants at the low pressure limit. Under atmospheric conditions, both of the above reactions are in the pressure dependent region between third and second order kinetics⁽⁷⁾, where extrapolation is difficult. Therefore, experimental determinations over a range of pressures and temperatures, with $\text{M} = \text{Air}$, are required to define precisely the rate constants k_1 , k_2 and k_3 at each altitude. Such data have only recently become available for the $\text{OH} + \text{NO}_2$ reaction (2)⁽⁸⁾ and it will take some time to gather the corresponding data for $\text{ClO} + \text{NO}_2$, (1)

3. Model calculations of the distribution of stratospheric chlorine

In order to investigate the possible role of chlorine nitrate in the stratosphere we have incorporated its formation and removal into our ten-layer one-dimensional photochemical-diffusion model of atmospheric chlorine

chemistry⁽⁹⁾. In the absence of any available measurements of k_1 , we have used the corresponding k_2 data⁽⁷⁾ for the reaction $\text{OH} + \text{NO}_2$ which, as shown above, is a reasonable analogue. We have termed these rate constants 'high' values, and carried out computations with k_1 values $1/10$ and $1/100$ of the values of k_2 giving 'medium' and 'low' values. Photochemical and thermal destruction rates were incorporated as described above.

In Fig.1 we show the fraction of free odd-chlorine species (Cl , ClO , HCl and ClONO_2) present as chlorine nitrate for typical present-day atmospheric concentrations of chlorofluorocarbons and other chlorine compounds. Our results are similar to those given by Rowland et al.⁽⁴⁾ and show a maximum in the mole fraction of chlorine nitrate at about 30 km which could approach a value of unity if the 'high' values assumed for k_1 turn out to be correct. Even with the lower k_1 values significant amounts of ClONO_2 should be present. These calculations were carried out for constant solar irradiance at 30°N but the fraction of chlorine present as ClONO_2 is expected to show diurnal and seasonal variations since the photolytic lifetime of ClONO_2 varies from a few hours at 45 km to a few tens of hours at 15 km. The magnitude of the seasonal variability of stratospheric HCl concentrations observed by Lazrus et al.⁽¹⁾ is consistent with the formation of ClONO_2 and would indicate k_1 values close to 'medium' rate constant chosen in our calculations.

4. Ozone depletion due to chlorofluorocarbons

The inclusion of the formation and destruction of ClONO_2 affects the steady state concentrations of ClO and NO_2 , both of which play an important role in the destruction of stratospheric ozone. We have, therefore, recalculated the ozone depletion expected from continued global release of chlorofluorocarbons 11 and 12 (CFCl_3 and CF_2Cl_2) at 1973 production rates. The results with chlorine nitrate included are shown in Fig.2, together with our earlier calculations without ClONO_2 . We observe that the predicted ozone depletion for the 'medium' rate constant is substantially less than that found in the absence of ClONO_2 and the 'high' rate constant even produces a significant increase in ozone concentration. This result differs from that obtained using a less complete modelling technique by Rowland et al.⁽⁴⁾ who concluded that inclusion of ClONO_2 reduced the ozone depletion by a factor of 0.7 at most. This difference is almost certainly due to the effect of chlorine nitrate formation on the NO and NO_2 concentrations in the lower stratosphere, which was not considered in their paper.

5. Other possible sinks for chlorine nitrate

These tentative conclusions depend not only on correct prediction of the range of k_1 values but also on the absence of other significant stratospheric sinks for ClONO_2 . Some other possible sink reactions are given in Table 1, together with the lower limits of their rate constant which would be required to give a 10% contribution to the chlorine nitrate destruction rate at 25-30 km, as deduced from our calculations. Of those considered only the reaction with $\text{O}(^3\text{P})$ appears to be of possible consequence. By analogy with the rapid reaction of $\text{O}(^3\text{P})$ with the Cl-O bond in ClOCl (chlorine monoxide)⁽¹³⁾ the reaction of $\text{O}(^3\text{P})$ with ClONO_2 may be sufficiently fast to provide a significant sink process.

Experimental investigations of these potentially important reactions and further atmospheric measurements are clearly required before a full understanding of the effects of chlorine species on ozone depletion can be achieved.

Acknowledgement

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TABLE 1 Thermodynamic and kinetic data for the reactions of chlorine nitrate with stratospheric constituents.

Reaction	ΔH_{298}° kJ mol ⁻¹	Chemical kinetic Data, cm ³ molecule ⁻¹ s ⁻¹	
		Estimated Rate Constant	Rate Constant to give 10% removal
$\text{Cl} + \text{NO}_3\text{Cl} \longrightarrow \text{Cl}_2 + \text{NO}_3$	-78	$\leq 10^{-12(7)*}$	>collision rate
$\text{ClO} + \text{NO}_3\text{Cl} \longrightarrow \text{NO}_2 + \text{O}_2 + \text{Cl}_2$	-120	$< 10^{-16}$	7.3×10^{-13}
$\text{NO} + \text{NO}_3\text{Cl} \longrightarrow \text{NOCl} + \text{NO}_3$	+ 7	$\sim 10^{-21(4)}$	1.4×10^{-15}
$\text{NO}_2 + \text{NO}_3\text{Cl} \longrightarrow \text{NO}_2\text{Cl} + \text{NO}_3$	+ 24	$\leq 10^{-24}$	6.3×10^{-16}
$\text{HCl} + \text{NO}_3\text{Cl} \longrightarrow \text{Cl}_2 + \text{HNO}_3$	-68	$> 5 \times 10^{-20(4)}$	1.0×10^{-14}
$\text{O}(^3\text{P}) + \text{NO}_3\text{Cl} \longrightarrow \text{ClO} + \text{NO}_3$	-104	$< 1.5 \times 10^{-11(13)*}$	1.4×10^{-13}
$\text{O}(^1\text{D}) + \text{NO}_3\text{Cl} \longrightarrow \text{ClO} + \text{NO}_3$	-1142	$\sim 10^{-11}$	>collision rate

Sources of thermodynamic data:

Clyne, McKenney and Watson⁽¹⁰⁾

Ray and Ogg⁽¹¹⁾

Calvert and Pitts⁽¹²⁾

*Estimates based on analogous reactions with chlorine monoxide, Cl₂O

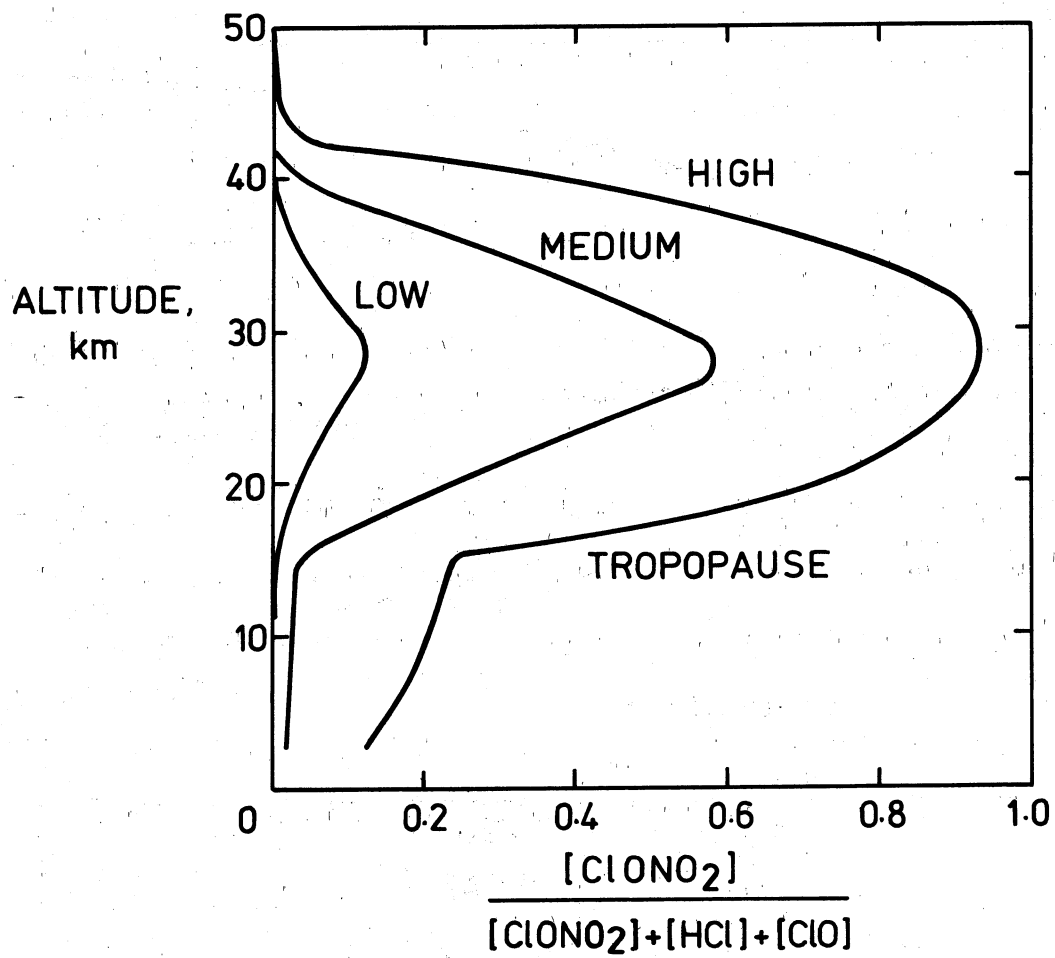


FIG. 1.

The fraction of free odd-chlorine species present as chlorine nitrate calculated using the 'high', 'medium' and 'low' formation rates for chlorine nitrate

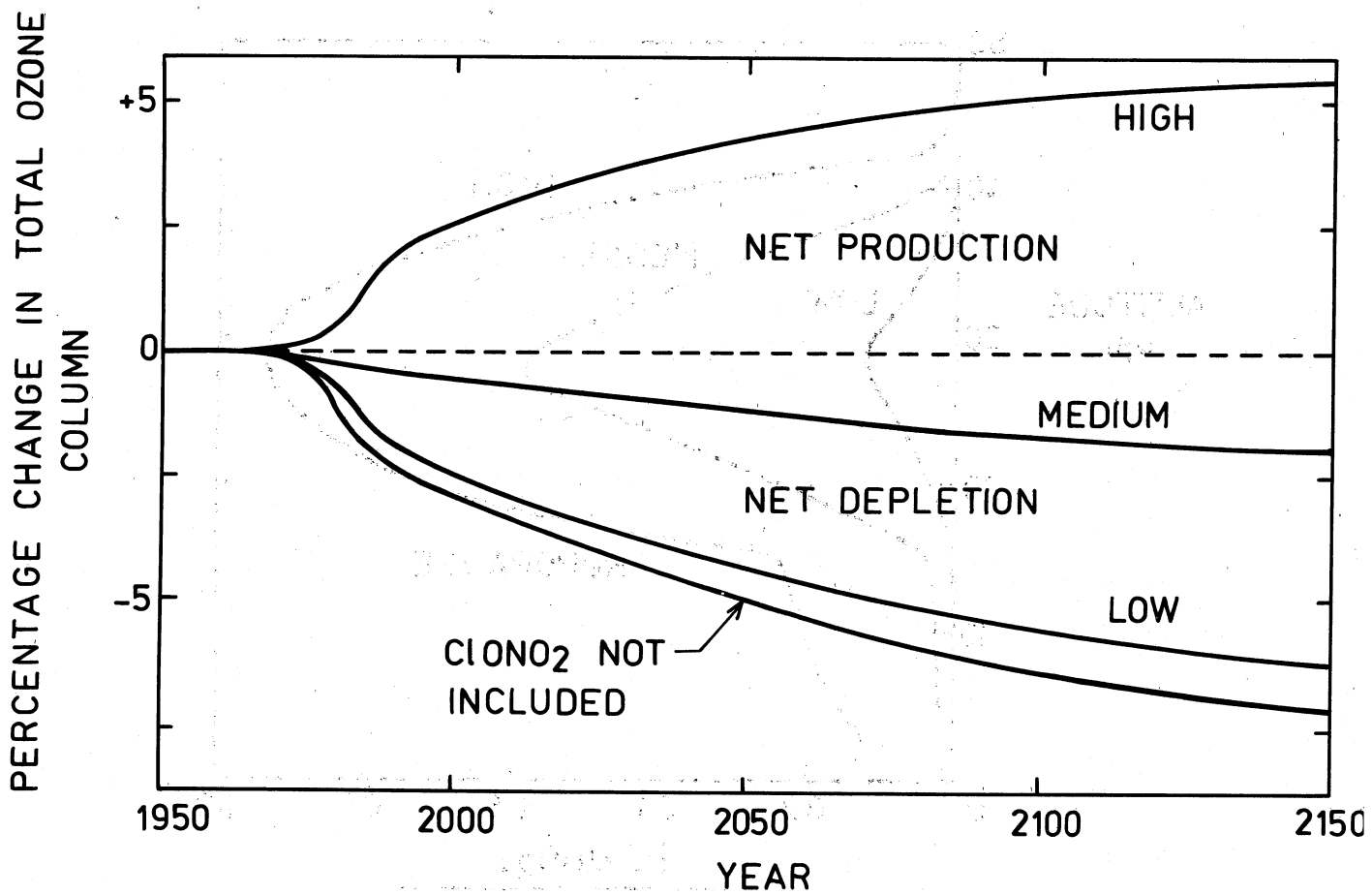


FIG. 2.

The calculated depletion in the total ozone column resulting from the continued release of chlorofluoromethanes with and without the formation of chlorine nitrate at the 'high', 'medium' and 'low' rates