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TEMPORAL BEHAVIOR OF NO_3 AND N_2O_5 IN THE STRATOSPHERE

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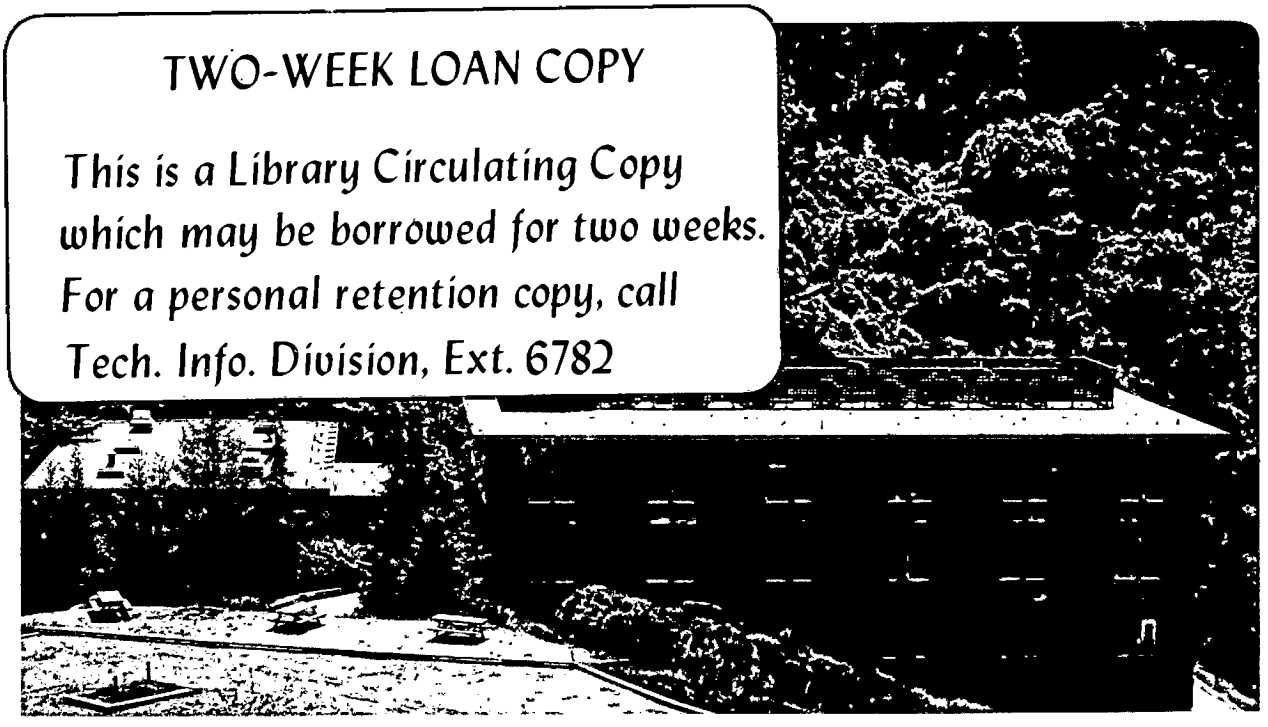

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Temporal Behavior of NO_3 and N_2O_5 in the Stratosphere

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ABSTRACT

The temporal behavior of NO_3 and N_2O_5 has been studied using recently determined laboratory kinetic data in a one-dimensional photochemical model. Comparison is made to previous laboratory and stratospheric modeling studies of this system. Theoretical considerations regarding the expected time behavior of these species and the pertinent reaction rate constants are discussed. Available experimental observations of NO_3 and N_2O_5 in the stratosphere are reasonably consistent with the results obtained.

Introduction

Recent observations of NO_3 and N_2O_5 in the stratosphere and laboratory kinetic and photochemical studies of N_2O_5 and NO_3 chemistry now allow examination of the understanding of that portion of the NO_x chemistry in the stratosphere. Model predictions of NO_3 and N_2O_5 mixing ratios and diurnal behavior using the earlier laboratory values conflict with direct observations of NO_3 and upper limits placed on N_2O_5 mixing ratios in the stratosphere. In this paper we discuss briefly the extrapolation of N_2O_5 thermal decomposition and recombination rate constants measured near room temperature to stratospheric conditions. These extrapolated values are then applied in a one-dimensional stratospheric model and the results are examined.

Chemistry of the NO_3-N_2O_5 System

The NO_x-O_3 system is in some ways unique in stratospheric chemistry. The NO_2 and NO_3 radicals, the intermediate N_2O_5, and O_3 are all long-lived with respect to the length of a day at stratospheric temperatures in the absence of photolyzing light. They thus exhibit significant rates of formation and destruction during the night. Model studies of the diurnal variations of NO_x and HO_x in the stratosphere were first discussed by Whitten and Turco (1974), who also emphasized that for species with substantial diurnal variation, models based on constant average solar illumination could give misleading steady state results.

The equilibrium system of N_2O_5, NO_2 and NO_3 has been studied experimentally by Graham and Johnston (1978), who determined the temperature

$$N_2O_5 + M \xrightarrow{k_3} NO_2 + NO_3 + M$$

$$NO_2 + NO_3 + M \xrightarrow{k_2} N_2O_5 + M$$

dependence of the equilibrium constant, $K_{eq} = k_3/k_2$, between 289 and 329 K. Reaction 3, the thermal decomposition of N_2O_5, has been recently studied between 4 E14 and 2.78 E19 molecule cm^{-3} and 262 to 307 K (Connell and Johnston, 1979, where references are given to older studies of this reaction). Viggiano et al. (1979) have also reported thermal decomposition rate constants between 14 and 300 torr and 268 to 377 K. The recombination rate constant, k_2, is more difficult to determine directly, but can be readily inferred from the equilibrium constant and thermal decomposition rate constant.

The thermal decomposition of N_2O_5 is a standard example of a unimolecular reaction exhibiting a pressure dependent rate constant. At sufficiently low pressure the decomposition is bimolecular, since the rate determining step in the bond fission mechanism is energization of N_2O_5 molecules by collision. Conversely, at high pressure N_2O_5 is constantly being activated and deactivated by collision. The rate determining step for decomposition is the unimolecular process of the activated N_2O_5 actually falling apart. Between these extremes the order of the reaction is properly represented as neither first nor second order, but is in the 'fall-off' region. For the decomposition of N_2O_5 the fall-off region coincides with the range of stratospheric pressure. Use of a single bimolecular rate constant, as in the mechanism of Whitten and Turco (1974), will result in a significant overestimation of the rate constant in the lower stratosphere.

A better expression parameterizes the pressure dependence, as in the Hinshelwood mechanism (see e.g. Robinson and Holbrook, 1972) assumed in the diurnal model of Wuebbles and Chang (1975). An empirical

parameterized fit of intermediate pressure data, such as the data set provided over a wide temperature range by Viggiano et al. (1979), to the Hinshelwood form can provide an adequate temperature extrapolation formula. But fitting the Hinshelwood expression to experimental values of the high and low pressure limits of the decomposition constant will overestimate rate constants at intermediate pressure, since the true fall-off curve is shallower than that predicted by the simple two state hypothesis of Hinshelwood. We have earlier suggested a form (Connell and Johnston, 1979) which answers this theoretical objection by introducing an experimentally determined parameter to express the sharpness of the fall-off. This expression is applicable for temperature extrapolation at all pressures.

While the decomposition can be experimentally studied over the necessary pressure range, the small rate constants at low stratospheric temperature are difficult to measure. Application of laboratory data to atmospheric models then requires an extrapolation to lower temperature. Over a small range of 1/T the rate constant will follow the Arrhenius form, but over greater changes in temperature the activation energy becomes itself a function of temperature, as the distributions of all N_2O_5 molecules and those energized above the reaction barrier change in a complicated fashion. This effect appears as curvature in the Arrhenius plot and is evident in the case of N_2O_5 from the low pressure activation energy of 16 kcal/mole measured by Schott and Davidson (1958) at 500 K and the corresponding value of 19 kcal/mole measured at 300 K. First order theory predicts a linear dependence of activation energy on temperature and this form has been adopted to fit the present data with that of Schott and Davidson (1958).

The complete form used for extrapolation is

$$\frac{1}{k_{uni}} = \frac{1}{2}\left(\frac{1}{k_o'[M]} + \frac{1}{k_\infty}\right) + \frac{1}{2}\left[\left(\frac{1}{k_o'[M]} + \frac{1}{k_\infty}\right)^2 + \frac{22}{k_o'k_\infty[M]}\right]^{1/2} \qquad (1)$$

where $k_o' = 4.3 \times 10^{-3}\ (T/300)^{-8} \exp(-\ 12240/T)\ cm^3\ molecule^{-1}\ sec^{-1}$ and $k_\infty = 1.88 \times 10^{17} \exp(-\ 12550/T)\ sec^{-1}$. The best simple Arrhenius fit produces a 20% larger decomposition rate constant throughout the stratosphere. Use of the Hinshelwood form with the same high and low pressure limits introduces a maximum error of about 20% additional increase.

The nighttime chemistry of the NO_x species is dominated by the reactions

$$NO_2 + O_3 \xrightarrow{k_1} NO_3 + O_2$$

$$NO_2 + NO_3 + M \xrightarrow{k_2} N_2O_5 + M$$

$$N_2O_5 + M \xrightarrow{k_3} NO_2 + NO_3 + M \quad .$$

Nitric oxide present at sunset is rapidly oxidized to NO_2 by ozone. During the day NO_3 and N_2O_5 mixing ratios are depressed by large photolytic decomposition rates and will increase during the night at the expense of NO_2, which is initially present in much higher concentration. The daytime steady state level of NO_3 is given by the production rate of reaction 1 divided by the photolytic rate constant. At night, over much of the stratosphere, NO_3 relaxes to a larger steady state value, for which the j value is replaced in the denominator by $k_2[NO_2][M]$. If the concentrations of NO_2 and N_2O_5 are considered constant during this rapid increase, the time dependence of NO_3 is approximately given by

$$[NO_3]_t = \left(k_1[O_3]/k_2[M]\right) - C\ \exp\left(-\ k_2[NO_2][M]t\right) \quad , \tag{2}$$

where the preexponential factor is the difference of nighttime and daytime steady state concentrations. Correspondingly, if NO_3 is considered to be in steady state, the time dependences of $[NO_2]$ and $[N_2O_5]$ are, respectively,

$$[NO_2]_t = [NO_2]_{sunset}\ \exp\left(-\ 2k_1[O_3]t\right)$$

and

$$[N_2O_5]_t = [N_2O_5]_{sunset} + \frac{[NO_2]_{sunset}}{2}\left[1 - \exp\left(-\ 2k_1[O_3]t\right)\right] \quad .$$

The time constant for NO_3 relaxation, $1/k_2[NO_2][M]$, is, however, greater than an hour above 35 km (in the region of the NO_3 maximum) so that assumptions of constant NO_2 and N_2O_5 concentration are not valid at all altitudes.

Within the limitations of the NO_3 steady state assumption, the NO_2 column will decrease exponentially through the night with a half time of around sixteen hours, averaged over the NO_2 distribution. The N_2O_5 increases on the same time scale by mass balance. The NO_3 steady state concentration is

$$[NO_3]_{ss} = \left(k_1[O_3]/k_2[M]\right) + K_{eq}[N_2O_5]/[NO_2] \tag{3}$$

The first term in Eq. 3 has a weak temperature dependent contribution from the activation energy of reaction 1 and inverse pressure dependence from reaction 2. The second term has a much stronger temperature dependence from the ΔH of the thermal dissociation of N_2O_5. At lower

colder altitudes, between 15 and 30 km, the NO_3 will recover rapidly, (on the order of an hour), from daytime levels to the steady state amount given by the first term in Eq. 2. Above 35 km the initial increase will be somewhat slower, as $[NO_2]$ and [M] both decrease with increasing altitude. The NO_3 at higher altitude will also exhibit an increase throughout the night, since the second term in Eq. 2 becomes significant. The increase will be related to the changing ratio of $[N_2O_5]$ to $[NO_2]$ and the increase in the equilibrium constant. The time dependence of this term is

$$[NO_3]_t = k_1[O_3]/k_2[M] + K_{eq}\left[\left(\left.\frac{[N_2O_5]}{[NO_2]}\right|_{sunset} + 1/2\right)e^{2k_1[O_3]t} - 1/2\right]$$

Below 30 km, NO_3 will be constant after a short period after sunset, while the N_2O_5 will increase on a time scale comparable to that of the NO_2 decrease. Above 35 km the NO_3 and N_2O_5 will increase together as the higher temperatures favor the product side of the N_2O_5 dissociation equilibrium.

Model Description

We have studied this behavior using a one dimensional photochemical model. The model, originally obtained from Lawrence Livermore Laboratory, has been modified to include the additional species necessary. Twenty species are treated as time dependent and are solved for numerically with the Gear method: $O(^3P)$, O_3, NO, NO_2, N_2O, HNO_3, NO_3, N_2O_5, $ClONO_2$, Cl, ClO, HCl, CF_2Cl_2, $CFCl_3$, OH, HOO, H_2O_2, H_2O, CO and CH_4. Two ppb of total chlorine is prescribed in the form of CF_2Cl_2 and $CFCl_3$ in place of natural sources such as methyl chloride. The $O(^1D)$, N and H are

calculated from the respective steady state expressions. The rate constants employed are given in Table 1. The one dimensional eddy diffusion coefficient is that of Stewart and Hoffert (1975). The standard mid-latitude atmosphere of the U.S. Standard Atmosphere Supplements, 1966, is used. The model has been described in more detail by Chang (1974).

The model was run for thirty years using a half intensity constant sun. Diurnal calculations with 100 second time steps and the corresponding continuously varying solar zenith angle were then carried out for four model days. Although a quasi-steady state is achieved, it should be noted that a much longer integration time would be necessary to obtain a true diurnal steady state with respect to both chemistry and transport over the entire atmosphere. Above 30 km the photochemistry is rapid and our calculations in this region should reflect the actual steady state solution. Wuebbles and Chang (1975) have demonstrated the numerical stability of the Gear method in treating this problem.

Conclusions

The first order rate constant for thermal decomposition of N_2O_5, derived from Eq. 1, applied to the standard atmosphere is shown in Figure 1 as a function of altitude for both the simple Arrhenius and the T^n temperature extrapolation schemes. The differences are within the extrapolated error of the experimental data. Both curves are below the previous values used by atmospheric modelers. The late night vertical distributions derived from the model are shown in Figure 2.

The NO_3 total column abundance above 15 km, (Figure 3), increases rapidly after sunset for about three hours and then more slowly as a result of the long term exponential changes in NO_2 and N_2O_5 concentrations. The detailed behavior at individual altitudes for NO_3 and N_2O_5 is shown

in Figure 4. The early evening NO_3 increase slows at both extremes of stratospheric altitude, representing the decrease in $[NO_2]$, [M], or both factors. The slower increase from the second term in Eq. 2 increases in significance with increasing altitude, as noted above.

Experimental measurements imply a pre-dawn mixing ratio of 3 ppb above 30 km for N_2O_5 [Evans et al. (1978)], and a twilight upper limit of 2×10^8 molecule cm^{-3} in the 25-30 km region [King et al. (1976)]. These values, smaller than those predicted with the previously suggested rate constants for N_2O_5 chemistry, are in reasonable agreement with the present study.

The total column behavior of NO_3 reflects primarily the temporal behavior in the upper stratosphere around the concentration maximum. The NO_3 total column abundance increases by about 20% during the night after the initial rapid increase. At the altitude of the NO_3 maximum the time constant for this initial increase is on the order of two hours, somewhat longer than observations by Noxon (1978) would indicate. These observations showed no increase, within the 30% experimental error, in the total column abundance of 1×10^{14} molecule cm^{-2} from 40 minutes after sunset to the late night.

The sensitivity of the model results to certain input parameters should be mentioned. Small variations in the assumed temperature profile will produce large changes in the dissociation rate constant and the equilibrium constant. A decrease in stratospheric temperature will suppress the nighttime increase of NO_3. The formation of NO_3 is also dependent on the ozone profile through the linear dependence in the steady state expression. Sensitivity to NO_2 abundance is however weak. Changes in NO_2 affect mostly the time scale of the initial increase

after sunset. This is a consequence of the similar dependence of NO_3 production and destruction rates in the stratosphere on NO_2.

The application of these recently determined rate constants and the somewhat more involved treatment of their pressure and temperature dependence produces reasonable consistency with the available stratospheric observations of NO_3 and N_2O_5. The role of these species in global NO_x chemistry may be significant, particularly during the polar night. Further stratospheric observations are required to examine this behavior in detail.

Acknowledgment

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Table 1. List of Reactions

Reaction Rates [rate constants taken from Hampson and Garvin (1977) except as noted].

$O + O_2 + M \rightarrow O_3 + M$	$1.07 \cdot 10^{-34}\ e^{(510/T)}$	
$O_3 + O \rightarrow 2\ O_2$	$1.9 \cdot 10^{-11}\ e^{(-2300/T)}$	
$O_3 + NO \rightarrow NO_2 + O_2$	$2.1 \cdot 10^{-12}\ e^{(-1450/T)}$	
$N_2O + O(^1D) \rightarrow N_2 + O_2$	$5.5 \cdot 10^{-11}$	
$N_2O + O(^1D) \rightarrow 2\ NO$	$5.5 \cdot 10^{-11}$	
$N + O_2 \rightarrow NO + O$	$5.5 \cdot 10^{-12}\ e^{(-3220/T)}$	
$N + NO \rightarrow N_2 + O$	$8.2 \cdot 10^{-11}\ e^{(-410/T)}$	
$N + NO_2 \rightarrow 2\ NO$	$6.0 \cdot 10^{-12}$	
$H_2O + O(^1D) \rightarrow 2\ OH$	$2.3 \cdot 10^{-10}$	
$CH_4 + O(^1D) \rightarrow OH + 2\ HO_2 + CO$	$1.3 \cdot 10^{-10}$	
$OH + O_3 \rightarrow O_2 + HO_2$	$1.5 \cdot 10^{-12}\ e^{(-1000/T)}$	
$O(^3P) + OH \rightarrow H + O_2$	$1.0 \cdot 10^{-10}\ e^{(-250/T)}$	
$HO_2 + O_3 \rightarrow OH + 2\ O_2$	$1.4 \cdot 10^{-14}\ e^{(-590/T)}$	Howard (1978)
$O(^3P) + HO_2 \rightarrow OH + O_2$	$1.0 \cdot 10^{-10}\ e^{(-250/T)}$	
$H + O_2 + M \rightarrow HO_2 + M$	$2.08 \cdot 10^{-32}\ e^{(290/T)}$	
$H + O_3 \rightarrow OH + O_2$	$1.42 \cdot 10^{-10}\ e^{(-478/T)}$	
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$3.9 \cdot 10^{-14}\ e^{(1245/T)}$	Cox (1978)
$OH + HO_2 \rightarrow H_2O + O_2$	$5.0 \cdot 10^{-11}$	
$OH + NO_2 + M \rightarrow HNO_3 + M$	$4.10^{-12} \cdot M/(1.12 \cdot 10^{18} + M)$	
$OH + HNO_3 \rightarrow H_2O + NO_3$	$8.0 \cdot 10^{-14}$	
$OH + H_2O_2 \rightarrow HO_2 + H_2O$	$1.0 \cdot 10^{-11}\ e^{(-750/T)}$	
$N_2 + O(^1D) + M \rightarrow N_2O + M$	$3.5 \cdot 10^{-37}$	
$N + NO_2 \rightarrow N_2O + O(^3P)$	$2.0 \cdot 10^{-11}\ e^{(-800/T)}$	
$NO + O(^3P) + M \rightarrow NO_2 + M$	$1.55 \cdot 10^{-32}\ e^{(584/T)}$	
$NO + HO_2 \rightarrow NO_2 + OH$	$3.3 \cdot 10^{-12}\ e^{(254/T)}$	Howard (1978)
$H_2 + O(^1D) \rightarrow OH + H$	$2.7 \cdot 10^{-10}$	

Reaction Rates

$OH + OH \rightarrow H_2O + O(^3P)$	$1.0 \cdot 10^{-11}\ e^{(-550/T)}$	
$N + O_3 \rightarrow NO + O_2$	$5.0 \cdot 10^{-12}\ e^{(-650/T)}$	
$NO_2 + O_3 \rightarrow NO_3 + O_2$	$1.23 \cdot 10^{-13}\ e^{(-2470/T)}$	
$OH + CH_4 \rightarrow H_2O + CO + 2\ HO_2$	$2.36 \cdot 10^{-12}\ e^{(-1710/T)}$	
$OH + OH + M \rightarrow H_2O_2 + M$	$1.25 \cdot 10^{-32}\ e^{(900/T)}$	
$O(^3P) + H_2O_2 \rightarrow OH + HO_2$	$2.75 \cdot 10^{-12}\ e^{(-2125/T)}$	
$Cl + O_3 \rightarrow ClO + O_2$	$2.7 \cdot 10^{-11}\ e^{(-257/T)}$	
$ClO + O(^3P) \rightarrow Cl + O_2$	$7.7 \cdot 10^{-11}\ e^{(-130/T)}$	
$ClO + NO \rightarrow Cl + NO_2$	$2.2 \cdot 10^{-11}$	
$Cl + CH_4 \rightarrow HCl + CO + 2\ HO_2$	$7.3 \cdot 10^{-12}\ e^{(-1260/T)}$	
$Cl + H_2 \rightarrow HCl + H$	$4.9 \cdot 10^{-11}\ e^{(-2340/T)}$	
$Cl + HO_2 \rightarrow HCl + O_2$	$3.0 \cdot 10^{-11}$	
$HCl + OH \rightarrow Cl + H_2O$	$3.0 \cdot 10^{-12}\ e^{(-425/T)}$	
$HCl + O \rightarrow Cl + OH$	$1.14 \cdot 10^{-11}\ e^{(-3370/T)}$	
$ClO + NO_2 + M \rightarrow ClONO_2 + M$	$3.3 \cdot 10^{-23} \cdot T^{-3.34} / (1 + 8.7 \cdot 10^{-9} \cdot T^{-.6} \cdot M^{.5})$	
$ClONO_2 + O \rightarrow ClO + NO_3$	$4.5 \cdot 10^{-12}\ e^{(-840/T)}$	
$CF_2Cl_2 + O(^1D) \rightarrow Cl + ClO$	$2.0 \cdot 10^{-10}$	
$CFCl_3 + O(^1D) \rightarrow 2\ Cl + ClO$	$2.0 \cdot 10^{-10}$	
$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$		Connell and Johnston (1979)
$N_2O_5 \rightarrow NO_2 + NO_3$		
$NO + NO_3 \rightarrow 2\ NO_2$	$1.87 \cdot 10^{-11}$	
$NO_2 + NO_3 \rightarrow NO + O_2 + NO_2$	$2.5 \cdot 10^{-14}\ e^{(-1127/T)}$	
$NO_3 + O \rightarrow NO_2 + O_2$	$1.0 \cdot 10^{-11}$	
$NO_3 + NO_3 \rightarrow 2\ NO_2 + O_2$	$8.5 \cdot 10^{-13}\ e^{(-2450/T)}$	
$CO + OH \rightarrow CO_2 + H$	$1.4 \cdot 10^{-13} + 7.33 \cdot 10^{-33} \cdot M$	Chan *et al*. (1977)
$Cl + HNO_3 \rightarrow HCl + NO_3$	$1.0 \cdot 10^{-11}\ e^{(-2170/T)}$	

Photolysis Reactions

$O_2 + h\nu \rightarrow 2\ O(^3P)$	Hudson and Mahle (1972)
$O_3 + h\nu \rightarrow O + O_2$	
$O_3 + h\nu \rightarrow O(^1D) + O_2$	
$NO_2 + h\nu \rightarrow NO + O$	
$N_2O + h\nu \rightarrow N_2 + O$	
$NO + h\nu \rightarrow N + O$	
$HNO_3 + h\nu \rightarrow OH + NO_2$	
$H_2O_2 + h\nu \rightarrow 2\ OH$	
$HCl + h\nu \rightarrow Cl + H$	
$ClONO_2 + h\nu \rightarrow ClO + NO_2$	
$CF_2Cl_2 + h\nu \rightarrow 2\ Cl$	
$CFCl_3 + h\nu \rightarrow 3\ Cl$	
$N_2O_5 + h\nu \rightarrow 2\ NO_2 + O$	Graham and Johnston (1978)
$NO_3 + h\nu \rightarrow NO_2 + O$	Graham and Johnston (1978)
$NO_3 + h\nu \rightarrow NO + O_2$	Graham and Johnston (1978)

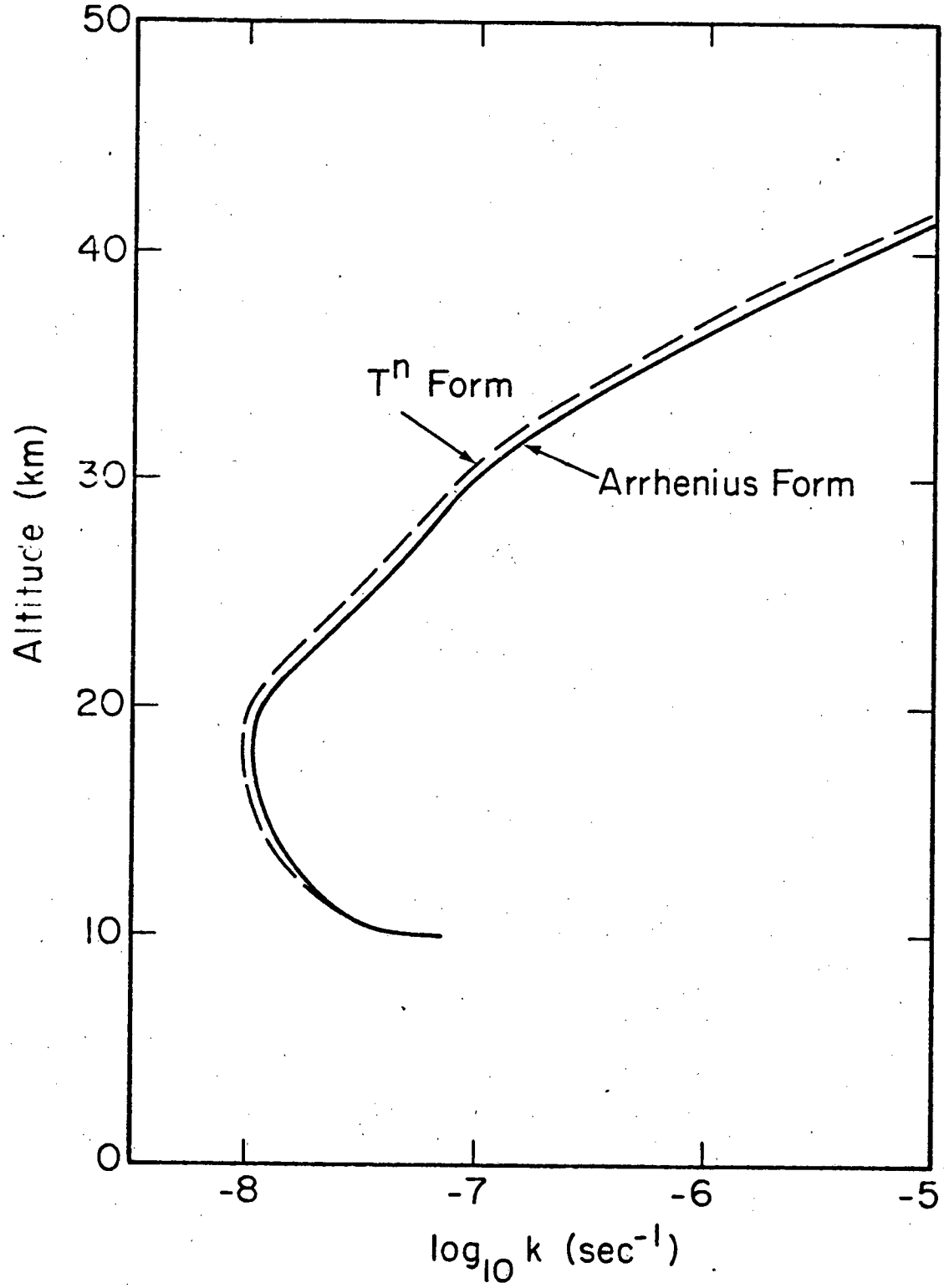
Figure Captions

Figure 1. Altitude profile of the rate constant k_3 in the model stratosphere.

Figure 2. Calculated distributions of NO_3, NO_2 and N_2O_5 before sunrise.

Figure 3. Calculated nocturnal behavior of the NO_3 and N_2O_5 stratospheric columns.

Figure 4. Calculated nocturnal behavior of NO_3 and N_2O_5 at selected altitudes.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40
30
20
10
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-6
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$\log_{10} k$ (sec^{-1})
T^n Form
Arrhenius Form

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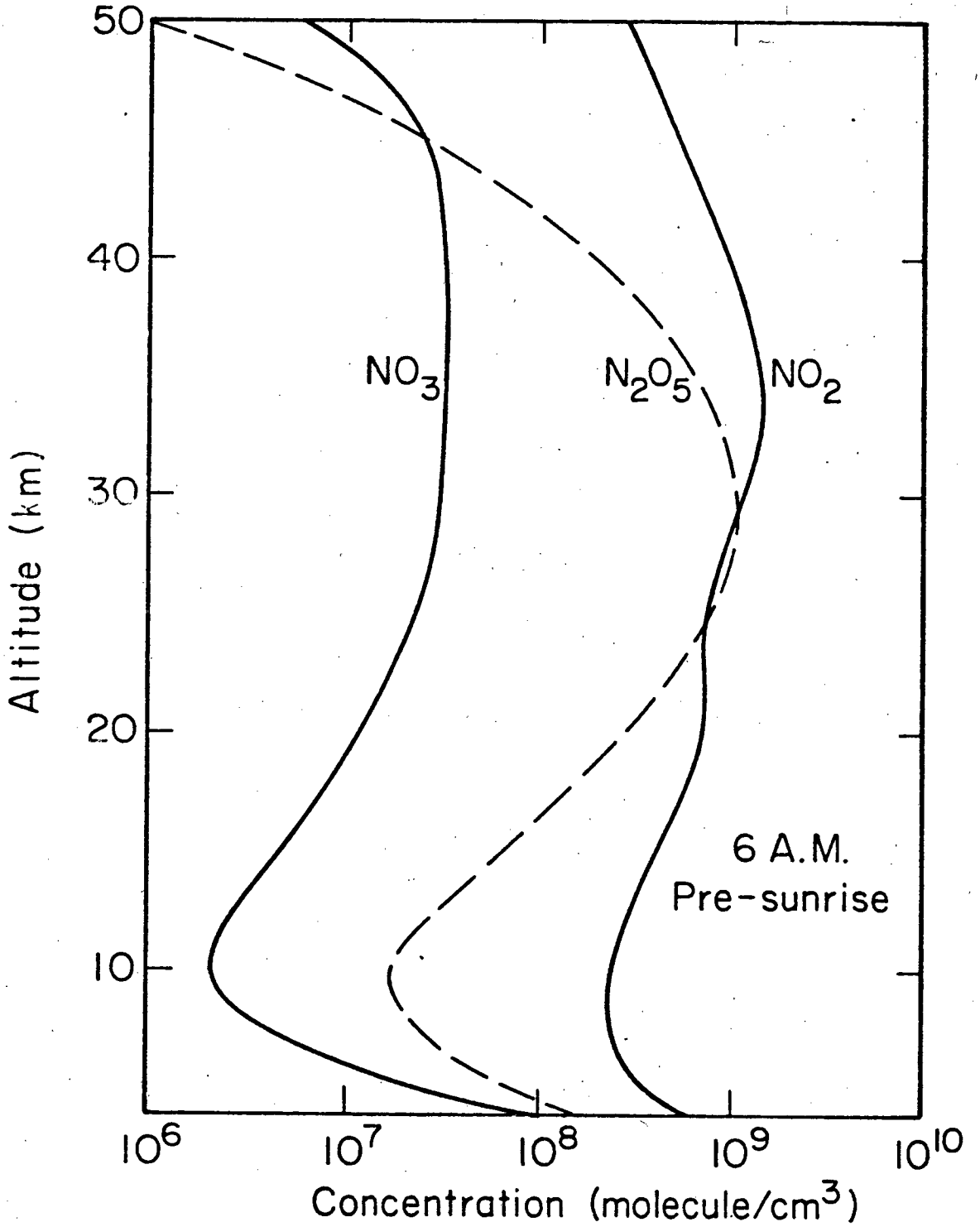

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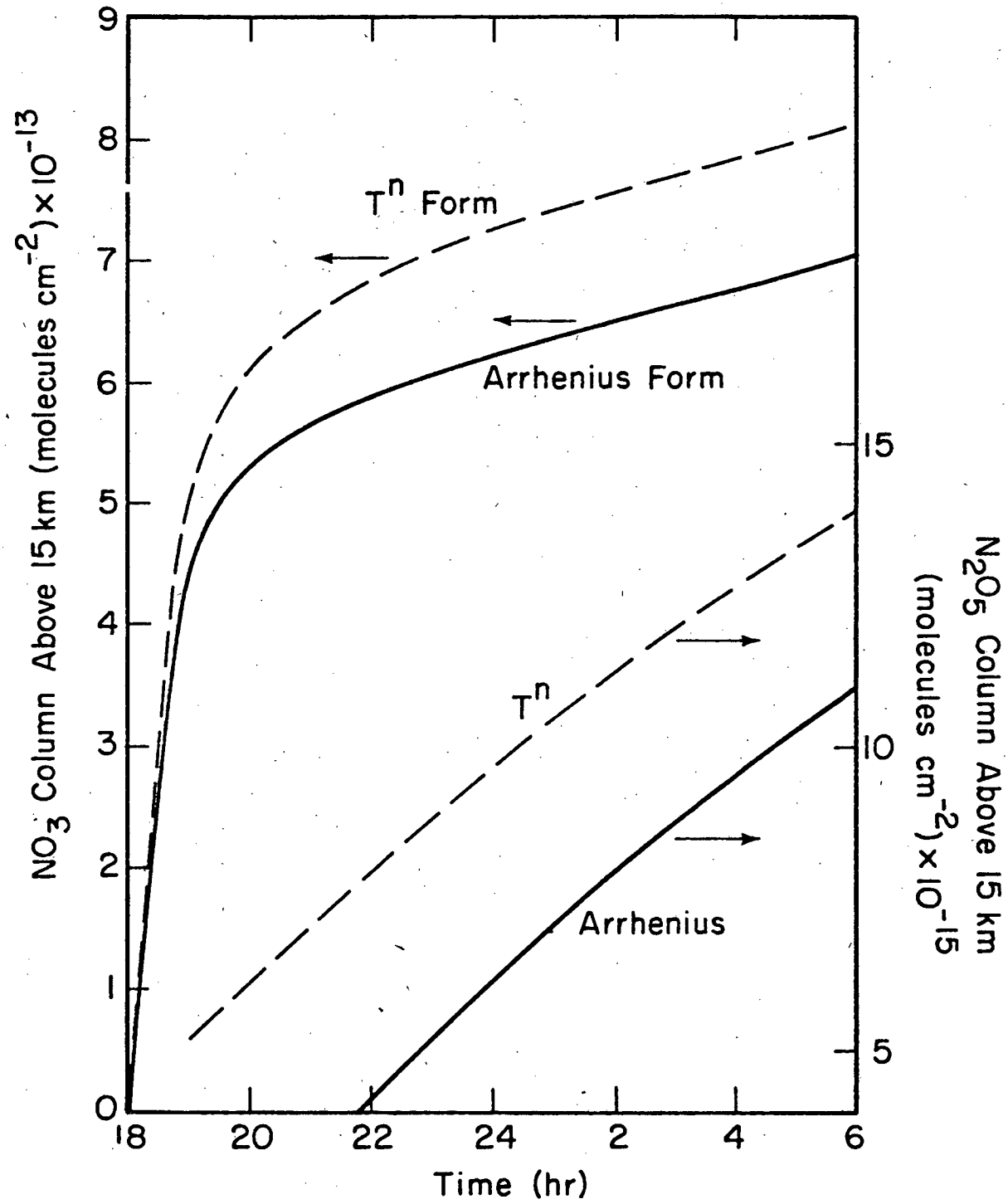
NO_3 Column Above 15 km (molecules cm^{-2}) $\times 10^{-13}$
N_2O_5 Column Above 15 km (molecules cm^{-2}) $\times 10^{-15}$
Time (hr)
T^n Form
Arrhenius Form
T^n
Arrhenius
0
1
2
3
4
5
6
7
8
9
5
10
15
18
20
22
24
2
4
6

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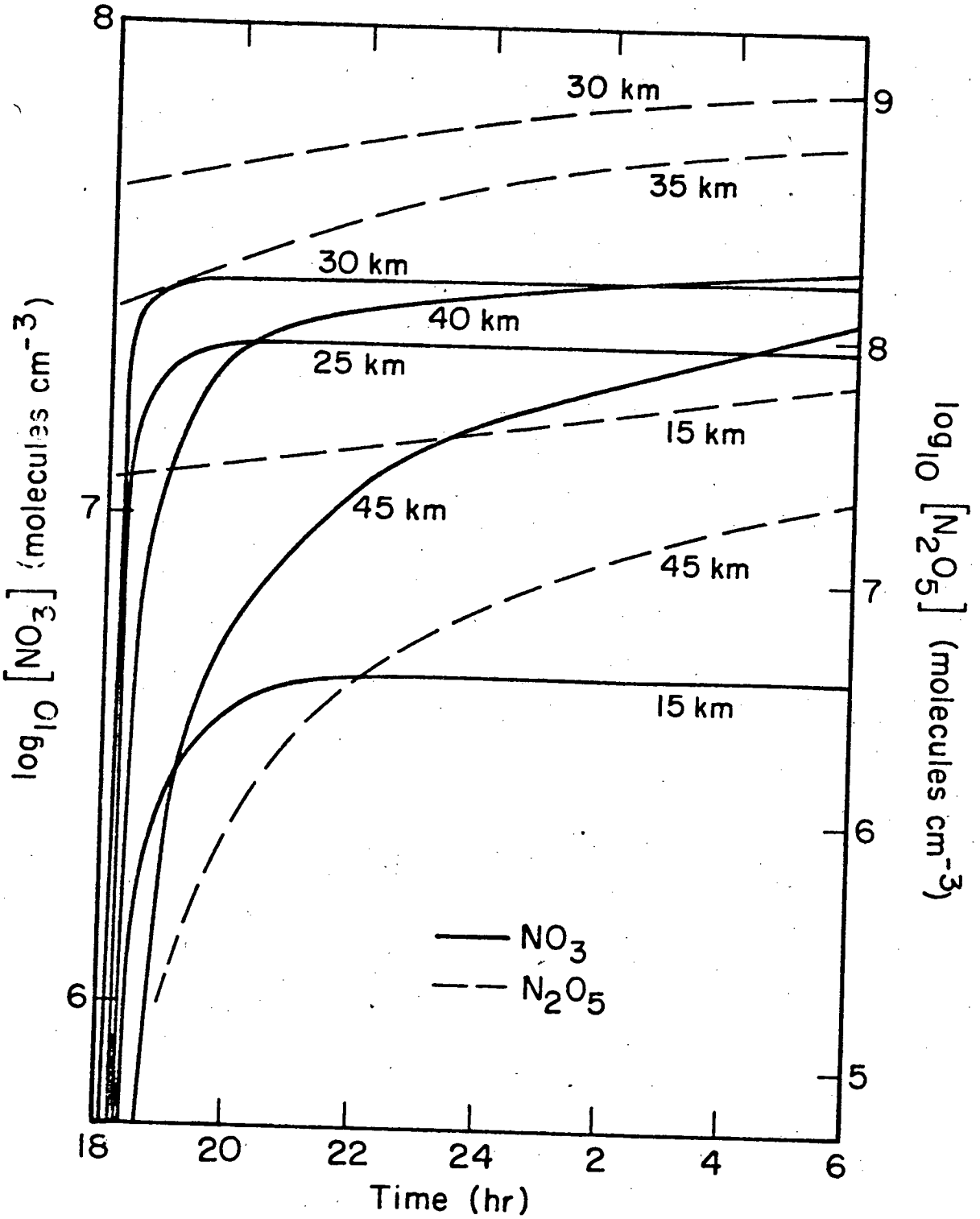
8
7
6
9
8
7
6
5
30 km
35 km
30 km
40 km
25 km
15 km
45 km
45 km
15 km
NO3
N2O5
18
20
22
24
2
4
6
Time (hr)
log10 [NO3] (molecules cm-3)
log10 [N2O5] (molecules cm-3)

XBL 794-9318

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