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INTERPRETATIONS OF STRATOSPHERIC PHOTOCHEMISTRY

Harold S. Johnston and James Podolske

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Interpretations of Stratospheric Photochemistry

By

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Abstract

Trace stratospheric species (parts per billion or less) have negligible effects on ozone (parts per million) unless they interact in catalytic cycles that regenerate the trace species. It is appropriate to regard the components of ozone photochemistry to be catalytic cycles, null cycles, and consumptive sequences, rather than the elementary chemical reactions. A general differential equation for ozone is transformed to an equivalent equation that directly identifies all catalytic cycles and sequences. The novel aspect of this article is the completeness with which this transformation is carried out and used. This method of treating stratospheric photochemistry is particularly useful in planning and in interpreting atmospheric observations. The features of the methane-smog chemistry are clearly brought out. From the mid-values of published measurements of NO_2 and ClO , it appears that NO_2 , ClO , and O_3 are sufficient to destroy ozone as fast as it is formed in the range 23 to 35 km; and NO_x reactions and ClX reactions appear to be roughly equal in importance. There is no need to invoke any new or unknown sink for ozone in this region, if the mid-values of measured NO_2 and ClO are representative of the global average. It is improbable that the high values observed for NO_2 or for ClO are representative of global average values. The magnitude of the contribution of HO_x reactions to ozone photochemistry cannot be found by this method because of lack of observations of HOO in the stratosphere. These conclusions depend on the accuracy of the stratospheric observations and certain rate constants. Additional measurements are needed, especially for HOO , NO_2 , ClO , and HO .

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I. Introduction

Although stratospheric chemistry is indeed complex, there exist some valid simplifying considerations. Ozone is present in the stratosphere with mixing ratios of parts per million. The free radicals, HO_x , NO_x , and Cl_x that attack ozone are present at parts per billion or less. Because of this great disparity in number, a one-way reaction of free radicals with ozone has only a very small effect on ozone, for example

If a trace species reacts in a cyclic manner, such as

it can have a significant direct effect on ozone:

	NO	O_3
Before	10^{-9}	10^{-6}
After one cycle	10^{-9}	0.998×10^{-6}
After two cycles	10^{-9}	0.996×10^{-6}
...		
After 100 cycles	10^{-9}	0.8×10^{-6}

The only way free radicals can have a significant effect on ozone is to participate in processes that are cyclic in radicals and destructive (or productive) of ozone. The essential components of the problem are cyclic, long-chain reactions.

If such cycles are sought by inspection of the mechanism, there will be uncertainty with respect to both completeness and duplication. For years, aeronomers have identified the long-chain processes from characteristic terms in the differential equation for odd oxygen, but recently the numbers of reactions and cycles considered have become large, and no systematic presentation of the subject has been given. This article takes a complex, 80-step O-H-N-C-Cl mechanism, defines odd-oxygen in a simple direct way, and transforms the usual differential rate equation to a form where each and every term is the rate determining step in a catalytic cycle or sequence that forms or destroys ozone. The catalytic cycles are discovered from terms in the differential equation, not by intuition or inspection. The key chemical species in the rate-determining steps of the catalytic cycles and sequences are especially important.

This article is another application of the "method of instantaneous rates" [Johnston and Whitten, 1973; Johnston, 1975]. This method takes atmospheric measurements, and in a simple, separable, one-step calculation derives consequences. In certain cases, firm conclusions (within the accuracy of the atmospheric measurements) can be reached concerning components of the total problem, long before the total problem itself is solved. This method does not displace model calculations, but it is supplementaty to such calculations.

This method is used in this article to interpret the results of a model calculation. Also it is used to interpret the effect of observed values of O_3 , NO_2 , and ClO in the stratosphere. This method is effective in expressing the important variables in the methane- NO_x -smog reactions, which probably form a significant amount of ozone in the lower stratosphere and troposphere.

II. Organizing the Differential Equations

Rates and Rate Constants

Two chemical mechanisms are considered here: A. The 17 photolytic reactions and 63 thermal reactions (excluding k_{34}) of Table 1, involving O-H-N-Cl-CH₄ chemistry. B. The first 11 photolytic reactions and first 34 thermal reactions of Table 1, which is the O-H-N-partial CH₄ mechanism of Chang and co-workers [1974a, 1974b] and that used by Duewer et al. [1977].

The following abbreviated notation is used: A photolytic rate constant is written as j , and the corresponding photolytic rate is written as J , for example

$$\begin{array}{c} j_1 \qquad \qquad \qquad \text{O}_2 + h\nu \rightarrow \text{O} + \text{O} \\ \left(- \frac{d[\text{O}_2]}{dt} \right)_{j_1} = \text{Rate}(j_1) = j_1[\text{O}_2] = J_1 \end{array} \qquad (1)$$

where a square bracket indicates the concentration (molecules cm⁻³) of the enclosed species. A chemical rate constant is written as k , and the corresponding reaction rate is K , for example

After derivations are completed using the condensed J and K notation, some rate expressions are written out in the standard long form.

In the conventional one-dimensional model of stratospheric ozone, each substance S_m in atmospheric vertical band n has a differential equation of the form

$$\frac{d[S_m]_n}{dt} = P_{mn} - L_{mn} \pm T_{m,n-1,n+1} \quad (3)$$

where P represents gross chemical and photochemical production, L represents gross chemical and photochemical loss, and T represents net transport of substance S_m with respect to the adjacent levels $n-1$ and $n+1$. The transport T is calculated from a model of the atmosphere [CIAP Monograph 3, Chapter 4, 1975B], or it is brought about by actual atmospheric motions in the viewpoint of the "method of instantaneous rates" [Johnston and Whitten, 1973]. Each P or L terms typically involves a number of J and K terms.

The concepts of this method are most clearly illustrated in terms of free radicals, which will be treated first. Odd oxygen is the case of primary interest, and it is treated second. The method is also applied to odd hydrogen, odd nitrogen, and odd chlorine.

Free Radicals

"Free radicals" are defined here as any atom or group of atoms with an odd number of electrons. Any atom or group of atoms with an even number of electrons is defined as a "molecule." With this definition, the free radicals in this mechanism are:

The symbol R is used as a general symbol for a free radical.

Since all free radicals have an odd number of electrons and all molecules have an even number of electrons, there are several simple, general relations applying to the reactions of free radicals and molecules.

"Free radical arithmetic" [Johnston, 1970] has some properties in common with the addition of counting numbers:

Addition of Counting Numbers	Free Radical Arithmetic	ΔR
even + even $\rightarrow$ even	$0 + 0 \rightarrow 0$	0
odd + odd $\rightarrow$ even	$1 + 1 \rightarrow 0$	-2
odd + even $\rightarrow$ odd	$1 + 0 \rightarrow 1$	0
even $\rightarrow$ even + even	$0 \rightarrow 0 + 0$	0
even $\rightarrow$ odd + odd	$0 \rightarrow 1 + 1$	+2
odd $\rightarrow$ odd + even	$1 \rightarrow 0 + 1$	0 (5)
even + even $\rightarrow$ even + even	$0 + 0 \rightarrow 0 + 0$	0
even + even $\rightarrow$ odd + odd	$0 + 0 \rightarrow 1 + 1$	+2
odd + odd $\rightarrow$ even + even	$1 + 1 \rightarrow 0 + 0$	-2
odd + odd $\rightarrow$ odd + odd	$1 + 1 \rightarrow 1 + 1$	0
odd + even $\rightarrow$ even + odd	$1 + 0 \rightarrow 0 + 1$	0

In terms of chemical reactions, some examples are

Out of the 80 photochemical and chemical reactions in mechanism A (Table 1, omitting k_{34}), 67 of them involve free radicals. These free radical reactions are entered in Table 2, together with the corresponding free-radical arithmetic and change in radical number, ΔR .

If one glances down the ΔR column of Table 2, one sees that, without exception, the change in free radicals per reaction is either +2, 0, or -2, which follows from the fundamental properties of odd and even numbers and the operation of addition and its inverse. From Table 2, one can write out the differential rate equation for free radicals

$$\begin{aligned}
 \frac{d[R]}{dt} = & 2 J_7 + 2 J_8 + 2 J_{12} + 2 J_{15} + 2 J_{16} + 2 J_{17} + 2 J_{14} \\
 & + 2 K_6 + 2 K_{10} + 2 K_{11} + 2 K_{32} + 2 K_{42} + 2 K_{55} + 2 K_{56} + 2 K_{57} + 2 K_{59} \\
 & - 2 K_8 - 2 K_{18} - 2 K_{19} - 2 K_{20} - 2 K_{24} - 2 K_{27} - 2 K_{31} \\
 & - 2 K_{50} - 2 K_{54} - 2 K_{58}
 \end{aligned} \quad (7)$$

There are 26 terms on the right hand side of this rate equation, all with a coefficient of +2 or -2.

This equation can be used as it stands. However, a potentially troublesome feature about (7) is that some sets of terms involve the small difference between large numbers. For example, there are two terms that involve nitric acid, $2 J_7 - 2 K_{20}$

The net rate of increase or decrease of free radicals due to nitric acid is the small difference between the gross radical production rate, $2 J_7$, and loss rate, $2 K_{20}$. The differential equation for nitric acid is

$$\frac{d[\text{HNO}_3]}{dt} = K_{20} - J_7 - K_{21} \quad (8)$$

The steady-state approximation is that the net difference ϵ in the three terms on the right hand side of (8) is very much less than the largest individual term. If the steady-state condition is a satisfactory approximation, then $2(K_{20} - J_7 - K_{21})$ is zero, and this expression, of zero value, added to $2 J_7 - 2 K_{20}$ in the rate expression (7), replaces this difference between two large numbers by the single term $2 K_{21}$. Especially for the interpretation and discussion of atmospheric chemistry, it is advantageous to simplify the differential equation in this way.

This simplification of the effect of nitric acid on the production and loss of free radicals was based entirely on considerations of the differential equation (7) and the steady-state condition for nitric acid reactions (8). Although it is not necessary to do so, the situation can be described in terms of couplets of reactions. When two radicals are lost by combining to form nitric acid, there are two alternate paths for further reaction:

The chemistry of nitric acid has two components so far as free radicals are concerned, one component is couplet (9) that causes no change in the free radical population and the other component is couplet (10) that reduces free radicals by two. The free-radical chemistry of nitric acid is relatively simple, and this example has been presented in detail clearly to illustrate: (i) the simplification of the differential equation (7) by use of a steady-state approximation, (ii) the consequent replacement of the addition and subtraction of large numbers by a single term representing their difference, and (iii) the interpretation of complex, multi-reaction chemistry in terms of component sequences of reactions.

In this mechanism, it is appropriate to make the steady-state assumption for

If these steady-state approximations are valid, then the 26 term differential equation (7) for free radicals reduces to the following 15 term equation

$$\begin{aligned}
\frac{d[R]}{dt} = & 2 J_{12} + 2 J_{14} + 2 J_{15} + 2 K_6 + 2 K_{10} + 2 K_{11} \\
& + 2 K_{32} + 2 K_{42} + 2 K_{55} + 2 K_{56} \\
& - 2 K_8 - 2 K_{19} - 2 K_{21} - 2 K_{22} - 2 K_{50}
\end{aligned} \tag{12}$$

The 11 terms eliminated from (7) can be identified with reversible null sequences analogous to (9), but more complex in some cases. The 15 terms remaining in (12) correspond to irreversible, single step radical production or loss

or to the rate-determining step in a sequence such as (10). If the steady-state approximations are satisfactory, the problem has been simplified in moving from (7) to (12).

There is a close similarity in the formal mathematical operations of including a species S in the class of free radicals R and of making the steady-state assumption for S and adding the resultant expression to the differential equation for R: The differential equations for R and S are

$$\frac{dR}{dt} = P_R - L_R, \quad \frac{dS}{dt} = P_S - L_S$$

If S is included in the Class of R, the differential equation is

$$\frac{d(R + S)}{dt} = P_R - L_R + P_S - L_S \tag{13A}$$

If the steady-state assumption is made for S, $dS/dt = 0$ and $P_S - L_S = 0$. This expression of value zero is added to the differential equation for free radicals

$$\frac{dR}{dt} = P_R - L_R + 0 = P_A - L_A + P_S - L_S \quad (13B)$$

The right-hand-side of (13A) is the same as that of (13B). For the case of free radicals, the definition of free radicals is unambiguous. The set of free radicals in this mechanism is given by (4), and the substances for which the steady-state approximation was made are listed in (11). For odd oxygen, which is considered in the next section, there is not quite so clear-cut a separation in these two mathematically similar operations: class inclusion and steady-state approximation.

Odd Oxygen

For the full mechanism of Table 1, the differential equation for production and loss of ozone is

$$\begin{aligned} \frac{d[O_3]}{dt} &= k_1[M][O_2][O] \\ &- \left(j_2 + j_3 + k_2[O] + k_{44}[O(^1D)] + k_{45}[O(^1D)] \right) [O_3] \\ &- \left(k_3[NO] + k_{28}[N] + k_{29}[NO_2] \right) [O_3] \\ &- \left(k_{12}[HO] + k_{14}[HOO] + k_{17}[H] \right) [O_3] \\ &- k_{46}[Cl][O_3] \\ &= \left(K_1 - J_2 - J_3 - K_2 - K_{44} - K_{45} \right)^O \\ &- \left(K_3 + K_{28} + K_{29} \right)^N - \left(K_{12} + K_{14} + K_{17} \right)^H - \left(K_{46} \right)^{Cl} \end{aligned} \quad (14)$$

The contributions of the O_x family of reactions, (O , O_2 , O_3), the NO_x family of reactions, (N , NO , NO_2), the HO_x family of reactions, (H , HO , HOO), and the chlorine reactions, (Cl , ClO), are indicated by superscripts on the groups of terms. In a typical model, this is the equation solved by the computer, in parallel with similar equations for other atmospheric species. Over much of the three-dimensional stratosphere, the net difference ($K_1 - J_2 - J_3 - K_2 - K_{44} - K_{45}$) is very small (2 to 5 orders of magnitude) compared to the individual terms K_1 , J_2 , J_3 . For many purposes it is desirable to minimize adding and subtracting the large numbers K_1 and ($J_2 + J_3$), which can be done either by making the steady-state approximation for O and for $O(^1D)$ or by defining "odd oxygen." There is a long-standing tradition in aeronomy of defining odd oxygen in this context.

"Odd oxygen" is defined as the sum of ozone and atomic oxygen

$$O_x = O_3 + O(^3P) + O(^1D)$$

In the troposphere and stratosphere, the concentration of ozone is much larger than the concentration of atomic oxygen, so that odd oxygen is very nearly the same as ozone. The 80 step mechanism includes 42 steps that involve odd oxygen as either reactant or product. These 42 reactions are listed in Table 3. Table 3 is subdivided into odd oxygen reactions associated with odd oxygen species (O_x), with the free radicals based on water (HO_x), with nitrogen free radicals (NO_x), with chlorine-containing free radicals (Cl_x), and with nitrous oxide. The "odd oxygen arithmetic" is the same as the "free radical arithmetic." A substance

not odd oxygen is labeled zero and either O , $O(^1D)$, or O_3 is labeled one. The odd-oxygen arithmetic for each O_x reaction is included in Table 3, and the change in odd oxygen for the reaction, ΔO_x , is also given. The differential equation for odd oxygen can be obtained by inspection of Table 3.

$$\begin{aligned} \frac{d[O_x]}{dt} = & \left(2 J_1 - 2 K_2 - 2 K_{44} - 2 K_{61} \right)^O \\ & + \left(J_4 + J_5 + J_6 + J_{11} + K_7 + K_8 + K_{24} - K_3 - K_4 - K_5 - K_6 \right. \\ & \quad \left. - K_{23} - K_{25} - K_{28} - K_{29} - K_{59} \right)^N \\ & + \left(J_9 + K_{27} - K_{10} - K_{11} - K_{12} - K_{13} - K_{14} - K_{15} - K_{17} - K_{32} - K_{42} \right)^H \\ & + \left(- K_{46} - K_{47} - K_{55} - K_{56} - K_{57} \right)^{Cl} \end{aligned} \quad (15)$$

In the pure oxygen system each elementary reaction, j_1 , k_2 , k_{44} , and k_{61} directly produces or destroys two units of odd oxygen, and all such terms automatically appear in (15) with a coefficient of two.

If one glances down the ΔO_x column of Table 3, one sees that when the free radicals, HO_x , NO_x , and ClX , react with odd oxygen, the change is always by one and only one unit, for example:

odd oxygen loss in a single step

odd oxygen production in a single step

These single-step processes can produce or destroy no more odd oxygen than the original supply of reagent on the left hand side of the equation. Acting by itself, NO can destroy no more ozone than the original amount of NO. Since NO_x , HO_x , ClX are present in the stratosphere many orders of magnitude less than ozone, a single-step, free-radical process does not have an important effect on odd oxygen. A single-step, odd-oxygen-destroying reaction must be followed by another step that either reforms odd oxygen or destroys a second odd oxygen to complete the fundamental requirement: $odd + odd \rightarrow even$.

These general, group-theoretical considerations suggest that if a proper set of steady-state relations are added to the odd-oxygen equation (15), then every term in the differential equation should be multiplied by an even number, 0, ± 2 , and possibly ± 4 . The operation of adding a steady-state relation to the differential equation is explicitly defined here. For a substance A, which is not a member of the odd-oxygen set, the differential rate equation from the mechanism has the form

$$\begin{aligned} \frac{dA}{dt} &= P_A(1) + P_A(2) + \dots + P_A(n) - L_A(1) - L_A(2) - \dots - L_A(m) \\ &= P_A - L_A \end{aligned} \quad (18)$$

The steady-state assumption is that the difference in $P_A - L_A$ is very small compared to the rate of production P_A or loss L_A , and thus

$$P_A - L_A \approx 0 \quad (19)$$

This difference, including all n production terms and all m loss terms (compare 18), of value zero is added to the differential equation (15) to generate a transformed differential equation.

For the mechanism of Table 1, we add to the odd-oxygen equation (15) steady-state relations for the following:

Where the coefficients in (20) is 2 or -1, this coefficient multiplies (19) before it is added to (15). Some authors include one or more of the species in (20) in their definition of odd oxygen, thereby confusing the definition of odd oxygen and the species for which the steady-state assumption is made, compare (13). Clear thinking on this subject is promoted by restricting the definition of odd oxygen to the species O_3 , $\text{O}(^3\text{P})$, and $\text{O}(^1\text{D})$.

With these steady-state relations, the differential equation for ozone is changed from (15) to the following:

$$\begin{aligned}
 \frac{d[O_x]}{dt} = & \left(2 J_1 \right)^O + \left(2K_7 + 2 K_{60} + 2 K_8 + 2 K_{24} \right)^N \\
 & + \left(4 J_{12} + 2 J_{13} + 2 J_{43} - 2 K_{38} \right)^C \\
 & - \left(2 K_2 + 2 K_{44} + 2 K_{61} \right)^O - \left(2 K_4 + 2 J_{10} \right)^N \\
 & - \left(2 K_{14} + 2 K_{15} + 2 K_{17} + 2 K_{18} + 2 K_{19} \right)^H \\
 & - \left(2 K_{47} + 2 K_{50} \right)^{Cl} - \left(2 K_{57} + 2 K_{59} \right)^{NHCl} \\
 & - \left(2 K_5 + 2 K_6 \right)^{N_2O}
 \end{aligned}
 \tag{21}$$

The terms in parentheses respectively refer to ozone production from photolysis of oxygen, ozone production from odd nitrogen reactions, ozone production from the methane- NO_x -smog reactions, ozone destruction by O_x , ozone destruction by NO_x , ozone destruction by HO_x , ozone destruction by ClX , ozone destruction by mixed NHClX reactions, and ozone destruction by nitrous oxide cycles. This differential equation involves no pseudo-production or pseudo-loss of odd oxygen [Johnston and Nelson, 1977]. It properly apportions ozone formation and destruction among the various families of reactants, O_x , NO_x , HO_x , CH_4 , and ClX . It minimizes the problem of small differences between large numbers. No terms are omitted. Every term is multiplied by two.

Although it is not necessary to do so, and it has not been done in deriving (21), each term in (21) can be associated with a catalytic cycle or sequence of consumptive reactions. If a reagent is irreversibly altered in a sequence, for example, $\text{CO} \rightarrow \text{CO}_2$, the process is "consumptive," and the amount of odd oxygen formed or destroyed is limited by the amount of reagent that is consumed. If a reagent changes in one step and is regenerated in another step, the process is "cyclic."

In general, free radicals, HO_x , NO_x , ClX , interact with odd oxygen to change odd oxygen by + or - one unit, Table 3. From the fundamental properties of odd and even numbers, it requires two such processes to convert odd oxygen to even oxygen or even oxygen to odd oxygen. The situation is summarized in Figure 1. If free radical R_1 is converted to free radical R_2 in a process that decreases odd oxygen by one unit ($\Delta = -1$), the cycling of R_2 back to R_1 must involve either an increase ($\Delta = +1$) or a decrease ($\Delta = -1$) of odd oxygen. An increase cancels the decrease of the initial step, and one has a null cycle. A decrease of

odd oxygen in the return loop completes a catalytic cycle ($\Delta = -2$) that destroys ozone. Two steps of $\Delta = +1$ would constitute catalytic formation of odd oxygen. These cycles can be entered at any step. In each cycle there is a rate-determining step, RDS. The rate determining steps in catalytic cycles are given by the terms in (21).

If a reagent destroys one unit of odd oxygen as it changes from R_1 to R_2 and if it forms one unit of odd oxygen as it is reconverted from R_2 to R_1 , the cyclic process has a "null" effect on ozone (of course, null cycles do not appear in the differential equation). In the next section, each term in (21) is examined one-by-one, and the sequences and cycles are identified and written out in full.

Some of the sequences and cycles, and thus the corresponding terms in the differential equation, have effects on odd oxygen that are numerically very small compared to others. However, group theory is not concerned with magnitudes, but rather with symmetries and relationships. One must turn to laboratory data, atmospheric measurements, and model calculations to evaluate the relative importance of terms in (21), and such a study is the content of sections III and IV of this article.

Catalytic Cycles and Consumptive Sequences Derived from the Differential Equations. The first term $2 J_1$ in (21) is the rate determining step in the consumptive sequence that converts oxygen to ozone

This sequence represents the dominant source of atmospheric ozone.

The third term in (21), $2 K_{60}$, represents a true catalytic formation of ozone from nitrogen oxides [Johnston, 1974, 1970]

This reaction is exceedingly slow in the stratosphere but of some importance at sites of high local NO concentrations in the troposphere, such as smoke stacks.

The terms $2 K_7$, $2 K_8$, and $2 K_{24}$ in (21) arise from the photolysis of nitric oxide in the upper stratosphere. K_7 is catalytic in nitric oxide

Processes K_8 and K_{24} represent ozone formation from consumption of NO_x , for example

Although this process is quite important in the atmospheric balance of odd nitrogen, it is negligible compared to (22) in the odd oxygen balance.

The terms $(4 J_{12} + 2 J_{13} + 2 K_{43} - 2 K_{38})$ represent the methane- NO_x -smog reaction, including the effect of branching, between methane,

formaldehyde, and carbon dioxide. Maximum ozone production occurs, namely 4 per CH_4 consumed, if the sequence is

Two ozones are produced per methane consumed if the sequence is either

or

No ozone is produced per methane consumed if the sequence is

The formation of ozone from the methane-smog reaction can be written out from the abbreviated notation

$$\left(\frac{d[\text{O}_3]}{dt} \right)_{\text{smog}} = (4 j_{12} + 2 j_{13} + 2 k_{43}[\text{HO}]) [\text{H}_2\text{CO}] - 2 k_{38}[\text{CH}_3][\text{O}_2] \quad (30)$$

The concentrations of formaldehyde and methyl radicals can be eliminated by means of steady-state relations to give a more readily interpreted expression

$$\left(\frac{d[\text{O}_3]}{dt} \right)_{\text{smog}} = 2 A \left(1 + \frac{j_{12}}{j_{12} + j_{13} + k_{43}[\text{HO}]} - \frac{k_{38}}{k_{35}[\text{M}] + k_{38}} \right) \quad (31)$$

where

$$A = (k_{11}[\text{O}(^1\text{D})] + k_{30}[\text{HO}] + k_{51}[\text{Cl}]) [\text{CH}_4] \quad (32)$$

is the total rate of production of methyl radicals from methane.

The methane-smog reactions are catalytic in NO_x and in HO_x , but represent consumption of methane as a fuel to produce ozone, carbon dioxide, and water as products. The amount of ozone produced is limited by the amount of methane consumed. These catalytic cycles are lengthy and it requires another cycle for each branching path. In view of the probable importance of the methane-smog reactions to global tropospheric ozone [Crutzen, 1972, 1973; Chameides and Walker, 1973; Johnston and Quitevis, 1975; Johnston, 1975; Hidalgo and Crutzen, 1977] these lengthy sequences are written out in full for the case of initiation by hydroxyl radicals. The sequences are somewhat different, when initiated by $\text{O}(^1\text{D})$ or Cl , but the same principles apply.

Maximum ozone production through K_{35} and J_{12}

Intermediate ozone production through k_{38} and j_{12}
 or through k_{38} and k_{43} or through k_{35} and j_{13}

 k_{35}

 j_{13}

There is zero ozone production from methane through path k_{38} and j_{13} if the sequence is:

or

The loss of ozone from O_x reactions in (21) involves three couplets of reactions for which the rate determining steps are K_2 , K_{44} and K_{61} .

The loss of ozone to NO_x reactions in (21) involves two catalytic cycles with rate determining steps K_4 and J_{10} .

The loss of ozone due to HO_x involves catalytic cycles where the rate determining steps are K_{14} , K_{15} , K_{17} , K_{18} , and K_{19} :

The last three cycles are interesting in that the rate determining steps do not involve odd oxygen: $\text{HO} + \text{HOO} \rightarrow \text{H}_2\text{O} + \text{O}_2$ and $\text{HOO} + \text{HOO} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$. However, these reactions measure the amount of $\text{O}({}^1\text{D})$ lost by $\text{O}({}^1\text{D}) + \text{H}_2\text{O} \rightarrow 2 \text{HO}$ that is not reconverted to odd oxygen, for example by $2 \text{HO} \rightarrow \text{H}_2\text{O} + \text{O}$. It can also be shown from the complete differential equation, that even if HOO is produced from methane oxidation, its loss through K_{18} or K_{19} constitutes a net loss of odd oxygen.

This mechanism has one catalytic cycle involving chlorine and chlorine oxide that destroys ozone, and one cycle is catalytic in both chlorine and HO_x

There are two closely related catalytic cycles involving chlorine nitrate and peroxy nitric acid

Finally, there are two cycles (K_5 , K_6) with nitrous oxide as the catalytic intermediate, for example

The net reaction with K_6 is: $2 \text{ O}_3 + \text{N}_2 \rightarrow 2 \text{ O}_2 + 2 \text{ NO}$.

Thus every term in (21) can be identified as the rate determining step in a sequence or cycle that produces two molecules of ozone from three molecules of oxygen or causes the loss of two molecules of ozone.

Incorrect Formulations of Catalytic Cycles. If catalytic cycles are constructed by intuition, some real processes may be counted twice and others may be omitted. The terms in the differential equation come

first, and their interpretation as catalytic cycles is secondary. In some cases one term in the differential equation may represent the rate-determining step in two catalytic cycles with the same net reaction, for example, (46A) and (46B). The listing of catalytic cycles, such as (22) - (52), may overlook such a second, parallel case; but this is of no consequence, since all conclusions are based on the terms in the differential equation.

Catalytic cycles are incorrectly formulated if one does not regenerate all trace species, atoms and free radicals. Two examples from the recent literature will be given of such incorrect formulations of catalytic cycles. On page 100 of Chapter 5 of CIAP Monograph 1 [1975], Johnston wrote out a process for the methane-smog reaction that was cyclic in NO_x but not in hydroxyl radicals; the net reaction was

Since hydroxyl radicals can both destroy ozone and indirectly make more ozone, this expression for the methane-smog reaction is incorrect. However, the calculations that were reported were based on the differential equations, and the calculated quantities were not affected by this wrong interpretation.

Another example of incorrectly formulated catalytic cycles is from Duewer et al. [1977B]. They cited the following catalytic cycle as one that would not be picked up by Johnston and Nelson's [1977] analysis, which is the same analysis as that presented in full in this review:

This sequence of reactions, although cyclic in NO_x , is not a catalytic cycle, but instead it represents ozone destruction by consumption of hydroxyl radicals. Since the concentration of hydroxyl radicals is typically the order of magnitude of 10^6 cm^{-3} and that of ozone is 10^{12} cm^{-3} , such a non-cyclic sequence is unimportant in the ozone balance. The essence of the problem concerns the processes that regenerate HO radicals. The correctly formulated catalytic cycles must be cyclic in all atomic and free-radical species. On the basis of incorrectly formulated catalytic cycles, Duewer et al. [1977A, B] made incorrect portioning of ozone destruction between NO_x and HO_x paths. However, their calculations, as opposed to their interpretations of the calculations, were based on differential equations and stand unaffected by such interpretations. Johnston's [1975] erroneous interpretation and that of Duewer et al. [1977] are parallel in every respect; the clear, rigorous development of this subject is still in progress.

Null Cycles. Many reactions in the mechanism produce or destroy one unit of odd oxygen, but do not appear in the differential equation for odd oxygen (21). Each of these reactions is involved in cycles or sequences that produce or destroy no ozone, that is, the even-numbered coefficient is zero. The reactions involving the change of one unit of

odd oxygen (Table 3) and not appearing in (21) are: $j_2, j_3, j_4, j_5, j_9, j_{11}, k_1, k_3, k_{10}, k_{11}, k_{12}, k_{13}, k_{23}, k_{25}, k_{27}, k_{28}, k_{29}, k_{32}, k_{42},$ and k_{46} . These reactions are involved in sequences or cycles that both form and destroy one unit of odd oxygen, which are called "null cycles" or "do-nothing" cycles. The principal null cycles respectively in the O_x , NO_x , HO_x , and ClX systems are:

Reactions K_{12} and K_{26} can be interpreted as the HO_x catalyzed reaction of nitric oxide and ozone, that is, K_3 . Similarly, reactions K_{46} and K_{48} can be interpreted as the ClX catalyzed reaction of nitric oxide and ozone or K_3 . Thus the three principal null cycles, NO_x , HO_x , and ClX , are structurally the same.

Reaction (26)

is important in atmospheric photochemistry, but to a large extent it is in an indirect way. It converts four ozone-destroying catalytic cycles in the HO_x system, (43), (44), (46), and (47), to null cycles. Also, as will be shown in the discussion of the carbon monoxide smog reactions, K_{26} leads to ozone production from CO combustion whereas K_{14} , $\text{HOO} + \text{O}_3$, leads to ozone destruction.

Two other null cycles are of some special interest.

This null cycle is the orthogonal component to catalytic cycle (42). The recombination of two hydroxyl radicals closes a null cycle, in contrast to the recombination of HO_x by way of $\text{HO} + \text{HOO}$ (47) and $\text{HOO} + \text{HOO}$ (46)

There are many other null cycles, but these are not written out here.

Odd Hydrogen

The free radicals derived from water are defined as "odd hydrogen" or HO_x

The differential equation for odd hydrogen from the mechanism is

$$\begin{aligned}
 \frac{d[HO_x]}{dt} = & J_7 + 2 K_8 + J_{12} + J_{17} + 2 K_{10} + K_{11} + 2 K_{32} \\
 & + K_{37} + K_{38} + K_{39} + 2 K_{42} + K_{49} + K_{52} + K_{59} \\
 & - 2 K_{18} - 2 K_{19} - K_{20} - K_{21} - 2 K_{27} - K_{30} \\
 & - 2 K_{31} - K_{43} - K_{50} - K_{53} - K_{58}
 \end{aligned}
 \tag{61}$$

The steady-state assumptions appropriate for this system are based on the substances and stoichiometries:

The differential equation for odd hydrogen transformed by the steady-state assumptions (62) is

$$\begin{aligned}
 \frac{d[\text{HO}_x]}{dt} = & 2 K_{10} + 2 K_{11} + 2 K_{42} + 2 J_{12} \\
 & - 2 K_{19} - 2 K_{27} - 2 K_{21} - 2 K_{22} - 2 K_{50} - 2 K_{52}
 \end{aligned}
 \tag{63}$$

The terms in (63) can be interpreted as direct production or loss of 2 HO_x radicals, consumptive sequences, and catalytic cycles. Odd hydrogen is directly produced by two elementary reactions

and it is directly destroyed by two elementary reactions

Odd hydrogen is produced by O(¹D) attack on methane where K₁₁ is the rate determining step

Photolysis of formaldehyde to give free radicals also produces 2 units of HO_x

The processes (66 - 68) are consumptive of methane or formaldehyde. It is interesting that K₁₈, HOO + HOO → H₂O₂ + O₂, does not occur directly in the differential equation for odd hydrogen. When K₁₈ is followed by photolysis of H₂O₂, J₈, there is no change in odd hydrogen; but when K₁₈ is followed by K₂₂, two units of odd hydrogen are destroyed

Similarly, nitric acid is an intermediate in HO_x loss

Two catalytic cycles in the chlorine family of reactions destroy HO_x radicals

It is noteworthy that several catalytic cycles, (69), (71), (72), have the same net reaction as reaction (19), $\text{HO} + \text{HOO} \rightarrow \text{H}_2\text{O} + \text{O}_2$.

It is, sometimes, incorrectly stated that carbon monoxide destroys hydroxyl radicals in the atmosphere. It is more nearly proper to say that hydroxyl radicals initiate the carbon monoxide- NO_x -smog reaction, in which hydroxyl radicals are regenerated

This reaction is cyclic in NO_x and HO_x , and it is consumptive with respect to carbon monoxide. This cycle is included as a part of the methane- NO_x -smog reactions (33 - 37). Photochemical combustion of carbon monoxide does not necessarily lead to ozone formation; there is a competing cycle that destroys ozone

Whether the CO photochemical combustion produces or destroys ozone depends on the competition between K_{26} and K_{14} .

These two processes (73 and 74) form or destroy only one ozone molecule, not two or some multiple of two. These cycles irreversibly consume carbon monoxide and the extent of reaction is limited by the supply of carbon monoxide. In any case where consumed reactants contain or accept oxygen atoms, the reagent-limiting process may involve only one unit of odd oxygen (such as, $\text{X} + \text{O}_3 \rightarrow \text{XO} + \text{O}_2$, limited by supply of X).

Odd Nitrogen

Alternate approaches are possible here. Odd nitrogen could be defined as $\text{NO} + \text{NO}_2$, and then the steady-state assumption would be made and tested for N, NO_3 , HNO_3 , HOONO_2 , and ClONO_2 . The method used here is to define odd nitrogen as the sum of all of these species containing one nitrogen atom:

$$\text{NO}_x = \text{N} + \text{NO} + \text{NO}_2 + \text{NO}_3 + \text{HNO}_3 + \text{HOONO}_2 + \text{ClONO}_2 \tag{75}$$

Even nitrogen is N_2 and N_2O , and if the mechanism included N_2O_5 it would be regarded as even nitrogen. With odd nitrogen defined as in (75) and with the steady-state assumption for N_2O , the differential equation from the mechanism of Table 1 is simply

$$\frac{d[\text{NO}_x]}{dt} = 2 K_6 - 2 K_8 - 2 K_{24} \quad (76)$$

These terms are easily interpreted. The first is an elementary reaction

The second term is the rate determining step in a consumptive sequence

The third term is similar

In model calculations, NO_x is destroyed at the earth's surface, but this is achieved by setting boundary values or by defining a lower tropospheric rain-out function.

Odd Chlorine

Odd chlorine is defined as the sum of atomic chlorine, chlorine oxide, hydrogen chloride, and chlorine nitrate

$$\text{ClX} = \text{Cl} + \text{ClO} + \text{HCl} + \text{ClONO}_2 \quad (80)$$

The differential equation from the mechanism is

$$\frac{d[\text{ClX}]}{dt} = 2 J_{14} + 2 J_{15} + 2 K_{55} + 2 K_{56} \quad (81)$$

There is no loss mechanism for ClX except destruction at the ground or rain-out in the lower troposphere. The production terms are photolysis of CFCl_3 and CF_2Cl_2 , and the reaction of $\text{O}(^1\text{D})$ with CFCl_3 and CF_2Cl_2 . This mechanism is incomplete in the ClX system. It does not go beyond the phosgene-like molecules COClF and COF_2 , and it does not include CH_3Cl , CCl_4 , and other organic chlorides. The methods used up to this point could readily be applied to such additional reactions.

III. Interpretation of a Model Calculation

If the equations of an atmospheric model are solved on a large computer, with use of sound numerical techniques, there is no requirement for one to interpret the components of the problem. In this article, we are analyzing a model output in terms of this method for three reasons. First, we want to check the validity of the steady-state relations, which constitute the transformation from a scrambled differential equation, such as (15), to the irreducible, component-revealing equation, such as (21). A second purpose is to identify the numerically large and small terms in the reduced differential equation for odd oxygen, so that we can see which atmospheric species are most important in the real production and loss of ozone. Such information should be used in planning observations of stratospheric species. The third reason is to give one example of how the mountain of computer printout from a model calculation can be resolved into its essential components.

Model

We obtained from Julius Chang a complete copy of his program for a time-dependent, one-dimensional, eddy-diffusion model [Chang, 1974; Chang, Hindmarsh, and Madsen, 1974], set up in terms of chemical reactions k_1 - k_{34} , j_1 - j_{11} of Table 1, which includes O-H-N-C chemistry, but not chlorine chemistry. This model is a sub-set of the one used in the previous section, and thus the solution will be presented with minimum comment.

The straightforward differential equation for odd oxygen is transformed into the irreducible form (that is, an irreducible degree of small differences between large numbers) by the steady-state relations for substances and stoichiometries:

There remain 15 terms in the differential equation, and each has a straightforward interpretation, which has already been given in terms of the more general mechanism, except that the methane reactions require separate discussion. The interpretation and references to previous equation numbers are as follows:

<u>Terms in Differential Equation</u>	<u>Interpretation</u>	<u>Previous Equation Numbers</u>
$2 J_1$	Production of O_3 from O_2 photolysis	(22) (83)
$+ 2 K_7 + 2 K_8$	Production of ozone from atomic N	(24, 25)
$K_{11} + K_{30}$	Production of O_3 from CH_4 combustion	(see below)
$- 2 K_2$	Destruction of O_3 by O_x reactions	(38)
$- 2 K_4 - 2 J_{10}$	Destruction of O_3 by NO_x reactions	(41, 42)
$- 2(K_{14} + K_{15} + K_{17} + K_{18} + K_{19})$	Destruction of O_3 by HO_x reactions	(43 - 47)
$- 2 K_5 - 2 K_6$	Destruction of ozone by N_2O	(52)

There are no other terms. All terms are appropriately multiplied by two, except for the terms involving the methane-smog production of ozone. In the mechanism itself, the methane reactions are not included in full, but they are abbreviated as

If the conversion of CO to CO₂ is added (73), this simple, abbreviated method gives results only 20 percent lower than that of the full methane mechanism, when numerical values for rate constants are included. Since K_{34} is not a balanced chemical equation and since it violates the basic rule of free-radical addition (it says $\Delta R = 1$), it is not surprising that the methane reactions in this mechanism appear without the factor of two.

Although the group at Livermore [Luther and Gelinas, 1976] have been pioneers in evaluating the effect of scattered and reflected radiation on photochemical rate constants, this particular model involves only the absorption of direct solar radiation. We used Brueckner's and co-workers [1976] values between 178 and 205 nm and Ackerman's [1971] values above 205 nm for solar radiation above the atmosphere.

Chang's program is set up to take any desired model for the vertical eddy-diffusion function, K_z . We used the K_z model proposed by Hunten [1974]. A test was made of Hunten's K_z model. Recently summarized [Sundaraman, 1976] data on the observed vertical distribution of CFC1₃ are given in Figure 2, and the calculated profile based on Hunten's model, as quoted by Ward [1976] is included. Although Hunten's model was said not to fit the first reported profile of CFC1₃, the model fits the full body of data.

We used Hunten's eddy diffusion function in Chang's time-dependent numerical model. This model was integrated for 30 years of model time, and all rates at all altitudes from 0 to 55 kilometers were printed out. From these detailed rates, we checked the validity of the steady-state relations for the species (82), and we evaluated the absolute and relative rates of all ozone production and loss terms in (83).

Checking the Steady-State Relations

After 30 years of model-time integration, the model essentially reaches a steady-state including transport (3) for all species and at all altitudes. In this analysis the steady-state assumption has been made for certain species (82) with respect to chemistry alone. Thus the essence of the steady-state approximations made here is that transport is slow compared to the gross — not net — production or loss terms. From (3) it can be seen that at the true steady-state including transport, $(P-L)/L$ is equal to T/L . The chemical steady-state approximation for a given member of (82) is satisfactory if

$$|(P-L)/L| \ll 1 \quad (85)$$

This test was made for all species in (82). At all altitudes, the absolute value of $(P-L)/L$ was less than 10^{-3} for H, HOO, CH₃, N, NO₂, and NO₃, and thus the steady-state relation is satisfactory for each of these. Special discussion is required for H₂O, HNO₃, and N₂O. The calculated rates of production and loss of HNO₃ and N₂O are given between 5 and 50 km in Table 4.

For nitric acid, the chemical cycling times (9 and 10) in the lower stratosphere and troposphere are sufficiently slow that transport significantly perturbs the steady-state assumption. From Table 4 the degree of this perturbation can be seen to be two percent at 25 km, one percent at 20 km and at 15 km, 4 percent at 10 km, and 19 percent at 5 km. A test of the significance of this minor failure of the steady-state assumption for HNO_3 is to compare the rate of loss of nitric acid with the rate of production of odd oxygen, $L(\text{HNO}_3)/P(\text{O}_x)$, and these ratios are included in Table 4. In general the absolute rate of formation or loss of HNO_3 is very slow compared to odd oxygen production rate, 10^{-6} to 10^{-1} . The worst case is at 25 km where there is a 2 percent failure of the steady-state assumption and where the HNO_3 production rate is 10 percent of that for odd oxygen. This degree of failure of the steady-state relation may be regarded as inconsequential.

The steady-state relation for nitrous oxide, on the other hand, is a total failure. The production of nitrous oxide from singlet oxygen atoms and molecular nitrogen is very slow compared to its destruction by photolysis. Far from (85) being very much less than 1, it varies between 0.8 and 0.999 for the conditions of Table 4. When the steady-state assumption fails for a species, one should remove the steady-state relation, and convert a portion of (83) back to the form it had in (15). However, the production of odd oxygen from nitrous oxide photolysis is a factor 10^3 to 10^5 smaller than the O_x production rate from other species, last line of Table 4. In the odd oxygen equation, but not in the odd nitrogen equation, the nitrous oxide reaction rates may be neglected.

In Chang's model, the water and methane profiles are prescribed and do not change during the calculation. From the prescribed profile, $d[H_2O]/dt$ is zero, which identically satisfies the steady-state condition. However, water is continuously formed from methane oxidation (reactions K_{30} , K_{34} , K_{14} , K_{19} , for example), and from this point of view $d[H_2O]/dt$ is always positive, which contradicts the steady-state assumption. The cycling of water through K_{10} , K_{19} , and intermediate steps is fast compared to the production of water from methane oxidation. From these considerations it appears that the steady-state assumption for water may be satisfactory, but it cannot be confirmed by this model that treats water in an approximate way.

Calculated Rates of Ozone Production and Loss

From Chang's program, all rates in (83) were calculated at all elevations. The contributions of N and N_2O reactions are negligible with respect to odd-oxygen rates (but, of course, not negligible in the odd-nitrogen balance). After dropping these very small terms, (83) is written out in conventional form

$$\begin{aligned}
 \frac{d[O_x]}{dt} = & \left(2 j_1 [O_2] \right) + \left(k_{30} [HO] + k_{11} [O(^1D)] \right) [CH_4] \\
 & - \left(2 k_2 [O] [O_3] \right) \\
 & - \left(2 k_4 [O] [NO_2] + 2 j_{10} [NO_3] \right) \\
 & - \left(2 k_{14} [O_3] [HOO] + 2 k_{15} [O] [HOO] + 2 k_{17} [O_3] [H] \right. \\
 & \quad \left. + 2 k_{18} [HOO]^2 + 2 k_{19} [HO] [HOO] \right)
 \end{aligned} \tag{86}$$

The terms in parentheses are respectively: ozone production from O_x or $P(O_x)$, ozone production from photochemical combustion of methane or $P(CH_4)$, ozone loss due to O_x or $L(O_x)$, ozone loss due to nitrogen oxides or $L(NO_x)$, and five terms of ozone loss due to HO_x reactions or $L(HO_x)$. These rates are presented at 5 km intervals between 0 and 50 km in Table 5, and are plotted from 0 to 55 km in Figures 3 and 4. Odd oxygen production from the photolysis of NO and N_2O are omitted from (86).

The primary production of ozone is the photolysis of molecular oxygen, $2 j_1[O_2]$ in (86), which is given in full as (22). This rate calculated by Chang's model is entered as $P(O_2)$ in Figure 3. The rate changes by 5 orders of magnitude between 14 and 42 kilometers.

The production of ozone from the methane- NO_x -smog reactions is given by $(k_{30}[HO] + k_{11}[O(^1D)])[CH_4]$ in (86), and it terminates on CO. According to the full expression (30-32), Chang's mechanisms underestimates the production of ozone from methane by the factor

$$2 \left\{ 1 + \frac{j_{12}}{j_{12} + j_{13} + k_{43}[HO]} - \frac{k_{38}}{k_{35}[M] + k_{38}} \right\} \quad (87)$$

Although the rate constants in (87) are uncertain, we estimate the expression in parentheses to be about 1.2 in middle and upper stratosphere. This mechanism underestimates ozone formation by this process by a factor of about 2.4. If CO is allowed to go to CO_2 in Chang's mechanism, up to a factor of 2 would be gained.

The calculated rate of ozone production from methane oxidation is included as the curve $P(CH_4)$ in Figure 3. Relative to oxygen photolysis, the rate of ozone production from methane is negligible above 30 km, equal at 17.5 km, and dominant in the troposphere. The rate of ozone

production from the methane-smog reaction is as fast at ground level as the photolysis of oxygen at 27 km. From the methane reactions, the "chemical replacement time" for ozone, defined as

$$\tau = [O_3]/P(CH_4) \quad (88)$$

is between 2 and 3 days at sea level. These model calculations tend to confirm the conclusions of Crutzen [1972, 1973]. The integrated column rate of ozone production from methane is about three percent of the ozone production rate from the photolysis of oxygen.

The destruction of ozone by odd-oxygen species is $2 k_4 [O][O_3]$ in (86), and the couplet of reactions has been given as (38). The rate of this process is labeled $L(O_x)$ in Figure 3.

The terms, $2 k_4 [O][NO_2] + 2 j_{10} [NO_3]$, in (86) give the rate of destruction of ozone by NO_x catalytic cycles (41,42). The loss of ozone due to NO_x reactions is written as $L(NO_x)$ in Figure 3. The curve $L(NO_x)$ corresponds to the case where j_{11} is zero, that is, maximum effect from the NO_3 cycle (42). If j_{10} is set to zero, the $L(NO_x)$ curve very nearly falls on top of the $P(O_2)$ curve below 20 km. In either case the NO_3 reactions are negligible above 25 km.

The five ozone-destroying processes based on HO_x radicals appear in (86) and are given in detail by (43-47). The relative contributions of the five processes are given in Table 5, and the calculated rate of each is plotted in Figure 4. In the troposphere the dominant loss process for ozone is photolysis to give $O(^1D)$, its loss upon reaction with water to form HO_x radicals, and the subsequent recombination of radicals to form water. When two hydroxyl radicals recombine to give

water, ozone is reformed (59); but when $\text{HOO} + \text{HOO}$ and $\text{HO} + \text{HOO}$ are the recombination processes, two ozone molecules have been destroyed (46,47). From 15 to 26 km, the catalytic cycle closed by $\text{K}_{14}(\text{HOO} + \text{O}_3 \rightarrow \text{HO} + \text{O}_2 + \text{O}_2)$ is the dominant HO_x reaction. The cycle completed by $\text{K}_{15}(\text{HOO} + \text{O} \rightarrow \text{HO} + \text{O}_2)$ is the dominant HO_x process above 28 km. The cycle including $\text{K}_{17}(\text{H} + \text{O}_3 \rightarrow \text{HO} + \text{O}_2)$ begins to be important above 40 km, but even by 55 km it accounts for only about 15 percent of the loss of ozone due to the HO_x reactions.

The five terms wherein HO_x radicals destroy ozone, Figure 4, are summed, and the total are plotted as $\text{L}(\text{HO}_x)$ in Figure 3. In the troposphere the destruction of ozone by HO_x radicals is parallel to and about twice the rate of production of ozone by methane. This calculation indicates that transport of ozone from the stratosphere and chemical production of ozone in the troposphere contribute about equally to the tropospheric ozone budget.

The relative importance of various sources and sinks for ozone, according to these calculations, is given in numerical form in Table 5 and graphical form in Figure 3. The destruction of ozone is dominated by HO_x reactions from 0 to 18 km and from 47.5 to 55 km. The NO_2 catalytic cycle (41) dominates ozone destruction from 19 to 40 km. The three families of reactions, O_x , NO_x , and HO_x , are about equally important in destroying ozone between 40 and 45 km.

The chemical ozone production rate and loss rate are not equal in general. Where production exceeds loss, some ozone is transported by air motions to adjacent levels. With this model, production exceeds loss at altitudes 25 to 40 km. Over this "ozone production" range,

the integrated destruction of ozone by NO_x reaction is 71 percent of the integrated rate of ozone formation from oxygen photolysis [compare Johnston, 1975].

The rate of ozone loss L that would destroy all local ozone if it were not replenished by transport or photochemistry in 10 years

$$L = [\text{O}_3]/3.15 \times 10^8 \text{ sec} \quad (89)$$

is drawn in as $\tau(10 \text{ yr})$ in Figure 3. This rate can also be regarded as 10 percent per year or 0.01 percent in 0.001 years. It corresponds to a slow rate in both the troposphere and stratosphere. The reaction rates to the left of the 10 year line in Figure 3 are probably safely regarded as negligible.

This mechanism does not include the chlorine reactions. However, the derivation and application of (83) illustrate the method of instantaneous rates, which will be applied to atmospheric observations, including chlorine reactions in the next section.

IV. Interpretation of Atmospheric Observations

What Needs to be Measured

The differential equation for odd oxygen based on the 80 reactions of Table 1 and the steady-state conditions (20) has been presented as (21). From model calculations of the previous section and from atmospheric observations, one can distinguish between the major and minor terms in (21). Explicitly writing out the major terms and grouping the minor terms, the differential equation for ozone or odd oxygen is:

$$\begin{aligned} \frac{d[O_3]}{dt} \approx \frac{d[O_x]}{dt} = & 2 j_1 [O_2] \\ & + 2 k_{30} [HO] [CH_4] \left(1 + \frac{j_{12}}{j_{12} + j_{13} + k_{43} [HO]} \right) \\ & - 2 k_3 [O] [O_3] - 2 k_4 [O] [NO_2] - 2 k_{47} [O] [ClO] \\ & - 2 \left(k_{14} [HOO] [O_3] + k_{15} [HOO] [O] + k_{18} [HOO]^2 + k_{19} [HOO] [HO] \right) \\ & \pm 2 \times \text{minor terms} \end{aligned} \quad (90)$$

(The minor terms are listed in (21) and they may be included if desired.) This equation is especially useful in interpreting atmospheric observations and in planning measurements in the stratosphere.

According to (90), in any volume element of the troposphere or stratosphere, the instantaneous rate of production of ozone is determined by 3 photolytic rate constants (j_1 , j_{12} , j_{13}), 2 chemical rate constants (k_{30} , k_{43}) and the concentration of 3 species (O_2 , CH_4 , HO). The photochemical constants can be evaluated from laboratory measurements of cross sections and quantum yields and from measured intensities of radiation in the atmosphere — or the radiation intensities may be

calculated from the intensity of solar radiation above the atmosphere, the vertical column of all absorbing and scattering species, and the reflectivity of clouds and surface below. Rate constants as a function of temperature may be measured in the laboratory and transferred to the atmosphere. The concentration of molecular oxygen is well-known in the atmosphere, the methane vertical profile has been measured in a few cases, and spot measurements have been made of hydroxyl radicals. From known laboratory constants and atmospheric measurements, the rate of production of ozone from oxygen photolysis can be calculated with a relatively high degree of confidence. However, the rate of the production of ozone from the methane-smog reactions is uncertain, primarily due to uncertainty about the concentrations of hydroxyl radicals in the atmosphere. So far as we know, there are no published measurements of hydroxyl radical concentrations between 10 to 25 km, the region important for ozone production from methane.

Within the framework of the mechanism of Table 1 and as evaluated by observations and model calculations, the destruction of ozone is dominated by 7 chemical reactions (compare Table 5)

which involve only 5 chemical species in the stratosphere or 6 in the troposphere plus stratosphere

The other 70 or so reactions are important in determining the absolute concentrations of O, O₃, NO₂, ClO, and HOO. If one had accurate values for the 7 rate constants of (91) and if one measured the temperature and the concentrations of the 6 species of (92) in any volume element of the atmosphere, one could evaluate the rate of ozone destruction in that volume element, regardless of radiation density, altitude, air motions, or the concentrations of other species. To be sure, this operation does not answer all questions, since interactions and feedback mechanisms are very important. However, it is possible for well-designed measurements to answer certain questions long before the total problem is solved. Also these considerations point out the importance for wide-spread measurements of stratospheric NO₂, ClO, and HOO and the need for models to be able accurately to estimate the concentrations of these substances.

This section does not review and interpret all observations of stratospheric species; rather it considers a set of recent observations, which are interpreted by this "method of instantaneous rates." Examples will be given of the absolute and relative rates of ozone formation from

oxygen ($2 j_1[O_2]$), from the methane-smog reaction, ozone loss by O_x reactions ($2 k_2[O][O_3]$), ozone loss by NO_x reactions ($2 k_4[O][NO_2]$), and ozone loss by ClX reactions ($2 k_{47}[O][ClO]$). Because of insufficient measurements of tropospheric and stratospheric hydroxyl radical concentrations and because of a lack of published atmospheric measurement of HOO, it is not possible to extend this method to ozone destruction by the free radicals derived from water.

Production of Ozone from Photolysis of Molecular Oxygen

Two sets of solar intensities below 205 nm wavelength were used [Brueckner et al., 1976; Ackerman, 1971]. The intensities of Ackerman [1971] were used above 205 nm. The effect of Rayleigh scattering for radiation below 205 nm was treated in two different ways: for A' and B' [respectively for Ackerman and Brueckner] no correction was made; for B [Brueckner] the radiation below 205 was attenuated by Rayleigh scattering but not further considered. The absorption of solar radiation by the Schumann-Runge bands of oxygen was calculated by the method of Hudson and Mahle [1972]. Multiple order Rayleigh scattering was calculated by the approximate method of Isaksen et al. [1977] at wavelengths above 280 nm. An albedo of 0.3 for the earth's surface was assumed in all cases.

To carry through the calculation of the rate of photolysis of oxygen, one must have the vertical distribution of ozone and of temperature. For 59°N, we used the profiles observed by Evans et al. [1976]. For 44°N we used standard profiles based on 45°N, and for 32°N we used standard profiles for 30°N [Johnston and Whitten, 1973].

The rate of ozone production was calculated for each hour of the day and averaged for 59°N, July 22, which corresponds to the time of and latitude of measurement by Evans et al. [1976]. The results are given in Table 6A for methods A', B', and B. Ackerman's solar intensities give ozone formation rates about 5 percent faster than Brueckner's in the middle and upper stratosphere. The failure to consider loss of Schumann-Runge radiation to Rayleigh scattering, A' and B', gives substantially higher ozone formation rates at 20 km than is found by making this correction, B. The rate of ozone production from photolysis of oxygen at noon, July 22, 59°N based on Evans' ozone profile is given by Figure 5 as $P(O_2)$.

Similar calculations were made for noon conditions at 30°N, fall solar equinox, and these calculations summed over 5 kilometer band widths are entered in Table 6B. At this latitude and at noon, Ackerman's [1971] solar intensities give average ozone formation rates about 6 percent higher than those of Brueckner [1976]. When Schumann-Runge radiation is attenuated by Rayleigh scattering, the vertical column (from 16 to 50 km) rate of ozone formation is reduced by 4 percent, but the local reduction of the calculated ozone formation rate is quite substantial below 25 km. Subsequent calculations in this article use method B.

Ozone Production From Methane

The major term in the production of ozone from the methane NO_x -smog reactions is (87). Ozone is produced at twice the rate of formation of methyl radicals and an additional factor that depends on the branching of formaldehyde photolysis, j_{12} or j_{13} . Isaksen et al. [1977] presented two figures with the photolysis constants j_{12} and j_{13} calculated for

various altitudes, solar angles, and earth albedos. For 60° solar angle and 0.25 albedo, we list their values as a function of altitude in Table 7. Methane has been observed in the stratosphere by several groups, and the results were reviewed by Ackerman et al. [1977]. Table 7 gives Ackerman's average methane values over the altitude range of Anderson's observed hydroxyl radicals. The formaldehyde branching factors were calculated from these data and are listed in Table 7; they vary between 1.15 at 43 km to 1.26 at 30 km. This variation is so slight that one could take an average value of 1.2, and the rate of production of ozone from methane in the middle stratosphere is

$$P_{O_3}(CH_4) = 2.4 k_{30} [HO]_{OBS} [CH_4]_{OBS} \quad (93)$$

It is evident that the methane-smog reaction is a minor source of ozone in the middle and upper stratosphere.

Measured values of hydroxyl radical concentrations are needed in the 10 to 25 km range to establish the rate of ozone and water formation from methane in this region.

Oxygen Atom Concentration

The rate of photolysis of ozone, $j_2 + j_3$, was evaluated for each hour of the day, and the steady-state oxygen atom concentration was found

$$[O]_{ss} = \frac{(j_2 + j_3)[O_3]}{k_1[M][O_2]} \quad (94)$$

Multiple scattering and reflection of radiation was included from 280 to 700 nm. In subsequent figures and tables the 24 hour oxygen-atom concentrations or the appropriate instantaneous concentrations, usually at noon, are presented.

Anderson [1975] measured the concentration of atomic oxygen in situ in the stratosphere on November 25, 32°N, 56° solar angle, Table 8. Using the standard winter distribution of ozone and temperature for 30°N, we calculated the atomic oxygen concentration with a 56° solar angle, Table 8. This calculated profile of atomic oxygen is plotted in Figure 6, together with the concentrations observed by Anderson. There appears to be fairly good agreement between calculated and observed atomic oxygen in Figure 6 and Table 7.

Odd Oxygen Destruction by Ozone

The only important reaction whereby odd oxygen is destroyed by odd-oxygen species is $2 k_3 [O][O_3]$, compare (90). Evans et al.'s [1976] observed ozone and temperature profiles are entered in Table 9. The oxygen-atom concentrations calculated for 59°N, July 22, noon are included in Table 9, and the rates of ozone loss L by this process from 10 to 48 km are included in Figure 5. These rates are based on observed stratospheric ozone and temperature and on a single-step calculation, namely, the calculated concentration of oxygen atoms. In view of the directness of this calculation, these rates of ozone destruction by O_x reactions may be regarded as "observed." This "instantaneous rate" is much closer to observations than the corresponding rate in a model calculation.

The production and loss of ozone due to O_x reactions can be compared in Figure 5 and in Table 9. The ratio $L(\text{due to } O_x)/P$ is 0.31 at 48 km, 0.18 at 40 km, 0.08 at 30 km, 0.30 at 20 km, and it is large below 20 km where the production rate becomes very slow. The integrated loss rate between 20 and 48 km divided by the integrated production rate is 0.16. Over the "ozone production region" of 25 to 35 km the integrated loss rate divided by the corresponding production rate is 0.07.

The last column of Table 8 gives the relaxation time τ of ozone with respect to O_x destruction at noon. The relaxation time τ is the local concentration of ozone, $[O_3]$, divided by the loss rate of ozone due to O_x . This time is that required for total consumption of local ozone if the loss rate L continued at its present value and if ozone was not replaced by either photochemistry or transport. Of course the loss rate does not continue at its present rate and ozone is continuously replaced by transport and photochemistry. The time τ is to be regarded as an instantaneous rate (frequency) expressed in reciprocal units of time. The significance of this time τ is for comparison with other photochemical times and with the time required for transport. In giving such a relaxation time, there is no implicit assumption that there is an absence of air transport over the period. It is simply a matter of comparing the rates of various processes in readily-grasped units of time.

At noon, the ozone relaxation time at 48 km relative to destruction by O_x reactions is 5 hours, at 40 km it is 1.2 days, at 30 km 42 days, and at 20 km 3.7 years. At 14 km, ozone is destroyed by O_x reactions 5 times faster than it is produced by oxygen photolysis (L/P), but the

ozone relaxation time τ at 14 km is 51 years, which demonstrates that the large value of L/P is not significant at this altitude.

Odd Oxygen Destruction by NO_x

The important reaction whereby ozone is destroyed by the oxides of nitrogen is $2 k_4 [\text{O}][\text{NO}_2]$, compare (90). Evans et al. observed nitrogen dioxide from a balloon by sighting on the sun at a 90° angle before sunset. Because of Rayleigh scattering near-ultraviolet (300 to 400 nm) sunset occurs somewhat before visible sunset. At UV sunset nitric oxide is converted to nitrogen dioxide by the reaction, $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$; and nitrogen dioxide no longer is photodissociated, $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$. Near-ultraviolet sunset sets in at low altitudes somewhat sooner than at high altitudes. Evans et al. [1976] and Kerr and Evans [1977] provided elevation-dependent corrections that convert their observed NO_2 profile to either the daytime or the 24 hour average profile. The corrected noon-time NO_2 profile is entered in Table 10A and the 24-hour average profile is in Table 10B. The simultaneously observed ozone concentrations and the calculated oxygen atom concentrations are included in Table 10A and B.

The rate of ozone production P from $2 j_1 [\text{O}_2]$ and ozone loss L from $2 k_4 [\text{O}][\text{NO}_2]$ are given in Table 10A and B. The ratio L/P of ozone destruction by NO_x to production from photolysis of oxygen is given at each altitude of observed NO_2 from 11 to 35 km. At noon, 59°N , July 22, NO_x as reported by Evans destroys ozone at about 50 to 60 percent of the rate of formation between 30 and 35 km, about 60 to 80 percent between 25 and 30 km, and about 100 to 200 percent between 20 and 25 km. In terms of a 24 hour average, at 59°N , July 22, NO_x as reported by Evans

destroys ozone at about 75 to 125 percent the rate of formation between 35 and 30 km, 125 to 200 percent between 30 and 25 km, and much higher percentages at lower elevations. The ratio between column loss, 20 to 35 km, and column production over the same range is 1.14. The loss/production ratio is greater on a 24 hour average basis than for noon-time conditions. This illustrates again the well-known principle that ozone destruction is driven by visible light as well as by ultraviolet radiation, but ozone formation from oxygen occurs only with radiation below 242 nm. The visible radiation that produces oxygen atoms from ozone penetrates the entire atmosphere until shortly before sunset, whereas the ozone-forming radiation below 242 nm is screened out in the lower stratosphere or with a slanting sun. The large ratios L/P in the lowest stratosphere are not interesting since both P and L are very small there, and the local ozone is largely determined by transport and methane-smog chemistry.

The rate of ozone formation at noon, as calculated by methods B and B', is shown in Figure 7, and also shown is the rate of ozone destruction by NO_x as found from Evans' observed NO_2 and ozone.

The last column in Table 10 gives the relaxation time τ of ozone with respect to the observed nitrogen dioxide. The reciprocal $1/\tau$ is the instantaneous destruction frequency of local ozone by local NO_2 . In terms of 24 hour average conditions, the ozone relaxation times with respect to destruction by NO_x are 3 to 7 days between 35 and 31 km, 9 to 32 days from 30 to 26 km, 50 to 207 days from 25 to 21 km, and a matter of years below 20 km.

Nitrogen dioxide was observed by Harries et al. [as reported by Sundararaman, 1976, Figure 10] between 24 and 35 km, 44°N , at noon in

September. The reported concentrations of nitrogen dioxide are given in Table 11A. From Krueger and Minzner's [1976] mid-latitude standard ozone distribution and at the fall equinox at 45, we calculated the oxygen atom concentrations, the rate of ozone production from oxygen photolysis, and the rate of destruction of ozone by NO_x . These quantities are entered in Table 11A. Harries' distribution of NO_2 gives a destruction rate of ozone 140 percent of the ozone photochemical formation rate between 24 and 35 km (Table 11A), and the ozone relaxation time with respect to NO_2 is fairly short 45 to 0.57 days over this altitude range.

Ackerman [1975] observed nitrogen dioxide between 20 and 36 km, and he reported his results as a band between lower and upper limits. Both his lower limit and upper limit are entered in Table 11B. Although the measurements were made from a balloon looking at the sun before sunset, the range of values is taken to include the NO_2 concentration appropriate for noon conditions. The noon-time rate of photochemical production of ozone, the concentration of atomic oxygen, and the upper and lower limits of the rate of ozone destruction by NO_x are in Table 11B. From Ackerman's measurements the ratio of noon-time ozone destruction by NO_x to ozone formation is 0.31 for the lower limit of NO_2 and 0.53 for the upper limit.

The noon-time rate of ozone production $P(\text{O}_2)$ and the noon-time rate of ozone destruction by NO_x , $L(\text{NO}_x)$, are plotted in Figure 8. The large difference above 25 km between Ackerman's observations and Harries' observations is evident from the figure. The observations by Evans et al. are intermediate between those by Harries and by Ackerman.

Odd Oxygen Destruction by ClX

Anderson et al. [1977] have reported three in situ measurements of stratospheric ClO, taken on 28 July 1976, 2 October 1976, and 8 December 1976. All were made at 32°N and close to local noon. The solar angles were respectively 16°, 30°, and 55°. The measured concentrations are entered in Table 12A, B, C and the mixing ratios are plotted in Figure 9. The observed mixing ratios of HCl as reviewed by Sundararaman in his Table 4 [1976] are included in Figure 9.

We used standard ozone distributions for 30°N and for July, September, and January. We used solar angles intended to correspond to the individual cases, but due to our misunderstanding about the exact time of measurements we based our calculations on solar angles 11°, 34°, and 53°. The effect of these differences in solar angle between time of observation and the time basis for the calculation is small. Calculated oxygen atom concentrations, rates of ozone production P by photolysis of oxygen, and rates of ozone loss L by ClX catalysis are included in Table 12A, B, C. The rates of ozone production and loss for each of the three measurements are given in Figure 10.

A notable aspect about the measured ClO concentration is the wide variability from one case to another. At 40 km, the October value is four times the July or December values. At 35 km the concentrations for Oct/July/Dec vary as 4.7/2.3/0.8. At 30 km these ratios are 5.3/3.0/0.37.

The ratio of integrated ozone loss by ClX to integrated ozone production over the ranges of ClO observations is 0.45 for the July values

of ClO, 1.27 for the October values, and 0.25 for the December data.

This spread in values is comparable to that for NO₂ between Ackerman's lower limit, 0.31, to Harries values 1.4. The altitude of maximum value for the ratio L(ClX)/P is 37 to 38 km for all three cases.

The relaxation time for ozone destruction by ClX is quite short in the altitude range 35 to 40 km. With the October distribution of ClO, the ozone relaxation time by ClO is 5 to 10 hours. For the July distribution, the time is about 24 hours. For the December distribution the relaxation time is about 50 hours. With such short relaxation times, the local ozone concentration should be in photochemical steady-state with ClO; the local ozone concentration should reflect the difference between the July and October ClO concentrations, if these differences are real.

V. Discussion

Relative Rate of Ozone Loss by O_x , HO_x , NO_x , and ClX Paths

It is interesting to compare the relative role of O_x , HO_x , NO_x and ClX in the destruction of ozone at various altitudes. The important rates are given in (90). Since measurements of HOO in the stratosphere have not been published, the source of information on the HO_x system comes from model calculations, for example, Table 5. Ozone has been extensively measured and for any measured ozone profile it is easy to evaluate the instantaneous rate of ozone destruction by O_x , $2 k_2 [O][O_3]$, with a single-step calculation. On the basis of Evans' observed ozone profile, such rates are given in Figure 5 and Table 9. The measurements of both NO_2 (Tables 10, 11) and ClO (Table 12) show a wide range of values as follows:

	NO_2	ClO [Anderson]	
Maximum	<u>Harries</u>	October	(95)
Middle	<u>Evans</u>	July	
Minimum	<u>Ackerman</u>	December	

A direct comparison between these diverse systems can be made in terms of the ratio L/P for each. Even though ozone production rates vary from case to case, the ratio of ozone loss L to ozone production P for each case provides a common reference point.

Table 13 gives the ratios of ozone loss to ozone production: For O_x as deduced from Evans' measured ozone, for HO_x as calculated by

Chang's model, for NO_x based on Evans' observed NO_2 , and for ClX based on Anderson's July measurements. The first column in Table 13 gives the ozone relaxation time with respect to ozone formation, that is, it is Evans' local ozone concentration divided by the local ozone production rate (Table 9). These times for July at noon increase from 5 hours at 50 km, to 19 hours at 35 km, and to 76 hours at 30 km; and in all of these cases the ozone concentration is photochemically controlled. The photochemical "ozone replacement" time at 25 km is 535 hours, and in this case the ozone amount is strongly influenced both by local photochemistry and by transport from the "ozone production region" between 25 and 35 km.

According to Table 13, the integrated loss due to O_x reactions between 25 and 35 km is 10 percent the integrated ozone photochemical production over the same range. The corresponding figure is 7 percent for HO_x reactions over the same range, based on calculations with Chang's model. On the basis of Evans' observed NO_2 and O_3 , ozone destruction by NO_x relative to ozone formation is 57 percent. With Anderson's middle value of ClO , the profile measured in July, ClX destroys ozone at 40 percent of its formation rate between 25 and 35 km. In terms of relative rate of ozone destruction and formation between 25 and 35 km, the roles of O_x , HO_x , NO_x (mid values) and ClX (mid values) are as follows:

O_x	0.10	(96)
HO_x	0.07	
NO_x	0.57	
ClX	0.40	

As noted by (95), there is a wide range of measured values of NO_2 and ClO . The last three columns of Table 13 explore the effect of this spread of measured values. At each altitude where ClO and NO_2 are measured, the total rate of ozone destruction, ΣL , is compared to the rate of photochemical ozone production P . This comparison is made for constant values for O_x and HO_x and for the minimum, middle, and maximum values of both NO_2 and ClO . For the column "MIN" the lower limit of Ackerman's NO_2 measurement and Anderson's December ClO measurement were added to the HO_x calculation and the O_x value. The column "MID" used Evans' NO_2 and Anderson's July values of ClO . The column "MAX" added together the ozone-destruction rates from Harries' observed NO_2 and Anderson's October measurements. The ratio of total ozone loss, ΣL , to ozone production at 35, 31, and 28 km is:

	MIN	MID	MAX	
35 km	0.87	1.27	3.2	(97)
31 km	0.68	1.08	2.4	
28 km	0.71	1.11	1.79	

From these values it can be seen that the high values of NO_2 [Harries] and of ClO [Anderson, October] cannot, within the framework of present knowledge concerning the photochemical formation of ozone, represent the global average values of NO_x and ClX . It is possible for high local concentrations to occur, but global ozone cannot be destroyed 2 to 3 times faster than it is made in the ozone production region.

It may be that the observed middle values of NO_2 [Evans'] and ClO [Anderson, July] are not far from global average values. Until more

measurements are made, these middle values appear to be a reasonable estimate of NO_2 and ClO , although there is nothing to exclude the minimum values.

The minimum values destroy ozone at 70 to 90 percent of the local formation rate. In the "ozone production region" one expects somewhat less than 100 percent local destruction of ozone. Even with the minimum observed values of ClO and NO_2 , there appears to be no need to invoke a major unknown sink for ozone in this region of the stratosphere.

Figure 11 presents the middle values of July noon-time ozone destruction by NO_2 (59°N) and ClO (32°), and it includes the rate of ozone destruction by O_x reactions for the same location as the NO_2 observations. For these measured O_3 , NO_2 , and ClO values, it appears that NO_x destroys ozone the fastest of the three families of reactions (O_x , NO_x , ClX) below 32 km, and ClX and NO_x are about equal around 35 kilometers. Because of a lack of measurements of NO_2 above 35 kilometers, this comparison cannot be made at higher altitudes. The destruction of ozone by O_x reactions is much slower than the NO_x and ClX reactions.

"Observed" and Model Rates of Ozone Destruction by NO_x Reactions

Continuing the point of view that Evans' observed NO_2 profile is the best currently available estimate of this quantity, the rate of ozone destruction derived from Evans' measured NO_2 is compared with the rate of ozone destruction calculated with Chang's model (Table 5).

Chang's model uses a fixed solar angle and division by two to represent 24 hour average rates of photochemical reactions, and thus the comparison

needs to be made in terms of 24 hour average rates using Evans' NO_2 profile (Table 10B). Figure 12 presents the 24 hour rate of ozone production and ozone destruction by NO_x , according to Chang's model. It also gives the same quantities for Evans' 24 hour average NO_2 profile. In this case photolysis constants were calculated for every hour of daylight and averaged over 24 hours.

The rate of ozone production at 20 km is equal according to the two methods, but at and above 30 km, our 24 hour average rate of ozone production is about 50 percent higher than that of Chang's model. The difference is probably due to our calculations being based on July conditions and an 18 hour day at 59°N , whereas Chang's model more nearly corresponds to a 12 hour day and mid-latitude conditions. Both methods use Hudson and Mahle's [1972] treatment of the Schumann-Runge region of solar radiation.

Chang's model predicts much slower ozone destruction by NO_x than that based on Evans' measurements. For the rate, $2 k[\text{O}][\text{NO}_2]$ the difference is a factor of 1.4 at 35 km, 2.4 at 30 km, 4 at 25 km, and 8 at 20 km. These differences come from several sources. The NO_2 concentration calculated with Chang's model is about one-third that observed by Evans' at 20 km. Our calculation includes albedo effects and multiple Rayleigh scattering, whereas Chang's model used here includes only direct absorption. Our 24 hour average for July at 59°N included 18 hours of daylight, whereas Chang's model in effect is for 12 hours of daylight. These last two effects cause us to have much larger 24 hour average oxygen atom concentrations than those from Chang's model. These differences between results based on Evans'

observations and Chang's model are cited as a matter of fact with no judgment as to which more nearly represents the real world. Further observations of stratospheric species and further model calculations are needed before one regards the discrepancy of Figure 12 as anything other than a reflection of current uncertainties in this field.

Methane-NO_x-Smog Reactions

It has been known since Haagen-Smit's [1953] work in the early 1950's that the photochemical oxidation of hydrocarbons in the presence of NO_x can produce ozone in urban atmospheres, and the role of NO_x is complex. Small amounts of NO_x produce ozone in the presence of hydrocarbons, but larger amounts inhibit or delay the production of ozone. In studies of urban smog, it was found that the photochemical oxidation of methane was slow compared to air transport through a typical city. Crutzen [1972,1973] and Chameides and Walker [1973] pointed out that the rate of production of ozone from methane and NO_x was significant in the global troposphere. Johnston and Quitevis [1975] reviewed Haagen-Smit's early work, and noted that if NO_x (with methane) produces ozone in the troposphere and destroys ozone in the stratosphere, there must be a cross-over point where added NO_x would be neutral toward ozone. Using the values of CH₄, H₂O, and NO_x derived by Chang from his model and rate constants as they were understood to be then [Hampson and Garvin, 1975], Johnston and Quitevis [1975] and CIAP [1975 A] evaluated the crossover altitude to be 13 km, Figure 13. At 13 km midlatitude, spring equinox an increase of NO_x brings about an equal increase in ozone production from methane and destruction by NO_x, accompanied by the many HO_x reactions that are involved.

Duewer et al. [1977 A] pointed out, among other things, that if certain rate constants were varied within Garvin and Hampson's stated uncertainty limits, the crossover point of Figure 13 could move up in altitude. Haagen-Smit's [1953] mechanism for urban smog, Crutzen's [1972, 1973] analysis of the global tropospheric methane smog reactions, Johnston and Quitevis' [1975] examination of the crossover between ozone production and ozone destruction by NO_x near the tropopause, and Duewer et al.'s [1977] analysis of the uncertainty of this crossover point with respect to uncertainty of rate constants are all normal steps in the evolution of our understanding of this subject.

Recently some rate constants have been measured that are substantially different from the values that were reported in 1974-75, and tabulated by CIAP for use by modelers, in particular:

<u>Reaction</u>	<u>CIAP (298 K)</u>	<u>Recent</u>	<u>Reference</u>
$\text{HO} + \text{HOO} \rightarrow \text{H}_2\text{O} + \text{O}_2$	2×10^{-11} to 2×10^{-10}	5.1×10^{-11}	<u>Burrows et al.</u> [1977]
$\text{O} + \text{HOO} \rightarrow \text{HO} + \text{O}_2$	1.5×10^{-11} (estimate, no data)	3.5×10^{-11}	<u>Burrows et al.</u> [1977]
$\text{HOO} + \text{NO} \rightarrow \text{HO} + \text{NO}_2$	$(0.6 \text{ to } 6) \times 10^{-13}$	8.1×10^{-12}	<u>Howard and</u> <u>Evenson</u> [1977]

Also, the rate constants for hydroxyl radicals with nitrogen dioxide to form nitric acid have changed somewhat. When these newly measured rate constants are incorporated in Chang's model, the rate of ozone production from the methane-smog reaction is that plotted in Figure 12. In this case the crossover altitude between production and destruction of ozone

by NO_x is at 17.5 km, Figure 12, which is significantly higher than that found by Johnston and Quitevis by the same method in 1974, Figure 13.

The crossover altitude between ozone production from methane as calculated from Chang's model and ozone destruction as deduced from Evans' observed NO_2 and O_3 is 15 km (Figure 12), but since Chang's calculation refers to 45°N and Evans' observations were 59°N , this comparison can be interpreted only as a call for a study of this effect as a function of latitude and season.

VI. Conclusions

As shown by our examination of the general differential equation for ozone, the measurement of the concentrations of key chemical species in the atmosphere is sufficient to evaluate the rates of ozone production and loss. In this article we applied this method to published observed atmospheric measurements of O_3 , O , NO_2 , ClO , HO , and CH_4 . Except for ozone, these measurements remain disappointingly few and show a wide spread in values.

Monograph 1, page 5-35 of the Climatic Impact Assessment Program [CIAP, 1975 A] states: "The present stratosphere will not be understood chemically until the calculated, instantaneous global rate of ozone formation ... is balanced by calculated, instantaneous global rates of destruction, based on observed concentrations of key trace species and established values of photochemical and gas kinetic rate constants. To understand the perturbed stratosphere, at least this much must be known about the present stratosphere." Although a few very informative profiles of NO_2 and ClO have been observed, to date, January 1978, there are not enough stratospheric observations of NO_2 , ClO , HO , and HOO to provide the test posed in Chapter 5, CIAP, as the minimum that needs to be obtained.

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References

- Ackerman, M., Ultraviolet solar radiation related to mesospheric processes, in Mesospheric Models and Related Experiments, edited by Fiocco, pp. 149-159, D. Reidel Publishing, 1971.
- Ackerman, M., J. C. Fontanella, D. Frimout, A. Girard, N. Louisnard, and C. Muller, Simultaneous measurements of NO and NO₂ in the stratosphere, Planet. Space Sci., 23, 651-660, 1975.
- Ackerman, M., D. Frimout, A. Girard, M. Gottignies, and C. Muller, Stratospheric HCl from infrared spectra, Geophys. Res. Lett., 3, 81-83, 1976.
- Ackerman, M. D. Rimout, and C. Muller, Stratospheric methane measurements and predictions, Aeronomica Acta, 180, 1-24, 1977.
- Anderson, J. G., The absolute concentration of O(³P) in the earth's stratosphere, Geophys. Res. Lett., 2, 231-234, 1975.
- Anderson, J. G., J. J. Margitan, and D. H. Stedman, Atomic chlorine and the chlorine monoxide radical in the stratosphere: Three in situ observations, Science, 198, 501-503, 1977.
- Brueckner, G. E., J.-D. F. Bartoe, O. K. Moe, and M. E. Van Hoosier, Absolute solar ultraviolet intensities and their variations with solar activity. I. The wavelength region 1750-2100 Å, Astrophysical Journal, 209, 935-944, 1976.
- Burrows, J. P., G. W. Harris, and B. A. Thrush, Rates of reaction of HOO with HO and O studied by laser magnetic resonance, Nature, 267, 233-234, 1977.
- Chameides, W., and J. C. G. Walker, A photochemical theory of tropospheric ozone, J. Geophys. Res., 78, 8751-8769, 1973.

- Chang, J. S., Simulations, Perturbations, and Interpretations, Proc. Third Conf. on CIAP, DOT-TSC-OST-74-15, pp. 330-341, Department of Transportation, Cambridge, Mass., 1974 A.
- Chang, J. S., A. C. Hindmarsh, and N. K. Madsen, Simulation of chemical kinetics transport in the stratosphere, in Stiff Differential Systems, edited by R. A. Willoughby, pp. 51-65, Plenum, New York, 1974 B.
- Climatic Impact Assessment Program, Monograph 1, The Natural Stratosphere of 1974, Chapter 5, DOT-TST-75-51, National Technical Information Service, Springfield, Virginia, 1350 pp., 1975 A.
- Climatic Impact Assessment Program, Monograph 3, The Stratosphere Perturbed by Propulsion Effluents, Chapter 4, DOT-TST-75-63, National Technical Information Service, Springfield, Virginia, 765 pp., 1975 B.
- Committee on Extension to the Standard Atmosphere, U.S. Standard Atmosphere, 1976, U.S. Government Printing Office, Washington, D.C., 1976.
- Committee on Extension to the Standard Atmosphere, U.S. Standard Atmosphere, 1976, U.S. Government Printing Office, Washington, D.C., 1976.
- Crutzen, P. J., Gas phase nitrogen and methane chemistry in the atmosphere, Report No. AP10, Institute of Meteorology, University of Stockholm, Sweden, 1972 A.
- Crutzen, P. J., Minor constituents in the stratosphere and troposphere, Pure and Applied Geophys., 106-108, 1385-1399, 1973.
- Duewer, W. H., D. J. Wuebbles, H. W. Ellsaesser, and J. S. Chang, NO_x catalytic ozone destruction: Sensitivity to rate coefficients, J. Geophys. Res., 82, 935-942, 1977 A.
- Reply. J. Geophys. Res., 82, 2599-2605, 1977 B.

- Evans, W. F. J., J. B. Kerr, D. I. Wardle, J. C. McConnell, B. A. Ridby, and H. I. Schiff, Intercomparison of NO, NO₂, and HNO₃ measurements with photochemical theory, Atmosphere, 14, 189-198, 1976.
- Farmer, C. B., O. F. Raper, and R. H. Norton, Spectroscopic detection and vertical distribution of HCl in the troposphere and stratosphere, Geophys. Res. Lett., 3, 13-16, 1976.
- Haagen-Smit, A. J., C. E. Bradley, and M. M. Fox, Ozone formation in photochemical oxidation of organic substances, Ind. Eng. Chem., 45, 2086-2089, 1953.
- Hampson, R. F., and D. Garvin, Chemical kinetic and photochemical data for modeling atmospheric chemistry, Technical Note 866, National Bureau of Standards, Washington, D.C., 1975.
- Harries, J. E., D. G. Moss, N. R. W. Swann, G. F. Neill, and P. Gildwarg, Simultaneous measurements of H₂O, NO₂, and HNO₃ in the daytime stratosphere from 15 to 35 km, Quoted by N. Sundararaman, 1976 (see below).
- Hidalgo, H., and P. J. Crutzen, The tropospheric and stratospheric composition perturbed by NO_x emissions of high-altitude aircraft, J. Geophys. Res., 82, 5833-5866, 1977.
- Howard, C. J., and J. K. Evenson, Kinetics of the reaction of HO₂ with NO, Geophys. Res. Lett., 10, 437-440, 1977.
- Hudson, R. D., and S. H. Mahle, Photodissociation rates of molecular oxygen in the mesosphere and lower thermosphere, J. Geophys. Res., 77, 2902-2914, 1972.
- Hunten, D. M., Estimates of stratospheric pollution by an analytic method, Proc. Nat. Acad. Sci. U.S.A., 72, 4711-4715, 1975.

- Isaksen, I. S. A., K. Midtbö, J. Dunne, and P. J. Crutzen, A simplified method to include molecular scattering and reflection in calculations of photon fluxes and photodissociation rates, Report No. 20, Institute for Geophysics, University of Oslo, pp. 1-21, 1976.
- Johnston, H. S., Reactions in the atmosphere, Project Clean Air, Task Force 7, Section 3, 25 pp., University of California Press, 1970.
- Johnston, H. S., and G. Whitten, Instantaneous photochemical rates in the global stratosphere, Pure Appl. Geophys., 106-108, 1468-1489, 1973.
- Johnston, H. S., Catalytic reduction of stratospheric ozone by nitrogen oxides, in Advances in Environmental Science and Technology, Vol. 4, edited by James N. Pitts, Jr., and Robert L. Metcalf, pp. 264-380, John Wiley and Sons, Inc., 1974.
- Johnston, H. S., and E. Quitevis, The oxides of nitrogen with respect to urban smog, supersonic transports, and global methane, in Radiation Research, Proceedings of the Fifth International Conference on Radiation Research, edited by O. F. Nygaard, H. I. Adler, and W. K. Sinclair, pp. 1299-1313, Academic Press, New York, 1975.
- Johnston, H. S., Global ozone balance in the natural stratosphere, Rev. Geophys. Space Phys., 13, 637-649, 1975.
- Johnston, H. S., and H. Nelson, Comment on 'NO_x catalytic destruction: Sensitivity to rate coefficients,' J. Geophys. Res., 82, 2593-2598, 1977.
- Kerr, J. B., and W. F. J. Evans, The effect of NO₂ changes at twilight on tangent ray NO₂ measurements, Geophys. Res. Lett., 4, 577-579, 1977.

- Krueger, A. J., and R. A. Minzner, A midlatitude ozone model for the 1976 U.S. standard atmosphere, J. Geophys. Res., 81, 4477-4481, 1976.
- Lazrus, A. L., B. W. Gandrud, R. N. Woodard, and W. A. Sedlacek, Stratospheric halogen measurements, Geophys. Res. Lett., 2, 439-441, 1975.
- Lin, C. L., W. B. DeMore, $O(^1D)$ production in ozone photolysis near 3100 Å, J. Photochem., 2, 161-164, 1974.
- Luther, F. M., and R. J. Gelinas, Effect of multiple scattering and surface albedo on atmospheric photodissociation rates, J. Geophys. Res., 81, 1125-1132, 1976.
- Raper, O. F., C. B. Farmer, and R. A. Toth, The vertical distribution of HCl in the 20-40 km region of the stratosphere, paper presented at the International Conference on the Stratosphere and Related Problems, Logan, Utah, September 15-17, 1976.
- Sundararaman, N., Summary of Upper Atmospheric Data, FAA-EQ-77-2, U.S. Department of Transportation, Federal Aviation Administration, Office of Environmental Quality, Washington, D.C., 52 pp., October 1976.
- Ward, R. B., Science Update, Freon Products Laboratory, DuPont Company, Wilmington, Del., No. 2, p. 3, 1976.
- Williams, W. J., J. J. Kusters, A. Goldman, and D. G. Murcray, Measurement of the stratospheric mixing ratio of HCl using infrared absorption technique, Geophys. Res. Lett., 3, 383-385, 1976.

Appendix

Calculation of Global Average Photolysis Constants

In order to simplify the calculation of instantaneous global average photolysis rate constants, or j -values, we devised a method of choosing ten "representative" solar zenith angles at which to calculate local j -values and then average the j -values (not the intensities) to get a global average. The angles were arrived at by dividing the disk of solar radiation incident on the earth's atmosphere into ten rings of equal area, projecting the rings onto the earth's surface to get the range of solar zenith angles each ring corresponds to, and then taking the median solar zenith angle of the range to "represent" that ring. By assuming j -values on the dark side of the earth are zero, instantaneous global-average j -values can be calculated.

The calculations took into account solar radiation from 178 to 750 nm. Region I is the wavelength region 178-205 nm, the Schumann-Runge region of oxygen. Here O_2 absorption and photodissociation are treated using the method of Hudson and Mahle [1972], and the wavelength bins were chosen to correspond to bands (e) to (s) of their method. Region II consists of 1 nm bins from 205-280 nm, Region III is 1 nm bins from 280-400 nm, and Region IV is 5 nm bins from 400-750 nm. Solar radiation intensities used in Region I were from Brueckner [1976], while those for II, III and IV are from Ackerman [1971]. Solar intensities in Region I and II were calculated assuming a pure absorption by O_2 and O_3 , including loss due to Rayleigh scattering, while in Region III and IV they were calculated using a simplified model [Isaksen et al., 1977] for including

five orders of Rayleigh scattering and surface reflection. In all calculations a reflection coefficient of 0.3 was used. Air density and temperature profile data used are those from the U.S. Standard Atmosphere of 1962(5) for mid-latitudes, while ozone profile data are those of Krueger and Minzner [1976]. The photolysis constants in Table 1 were obtained in this way.

Additional calculations, as described in this report, were made for specific times and latitudes.

Along with calculating j-values, we also calculated steady-state concentrations of $O(^1D)$ and $O(^3P)$. These were calculated according to the formula

$$[O(^1D)] = \frac{j_3[O_3]}{k_{33}[N_2] + k_{33}[O_2]}$$

$$[O(^3P)] = \frac{(j_2 + j_3)[O_3]}{k_1[M][O_2]}$$

Quantum yield data for $O_3 \rightarrow O_2 + O(^1D)$ were those of Lin and Demore [1974].

Figure Captions

Figure 1. Graphical summary of wherein null and catalytic cycles are the components of stratospheric photochemistry of ozone. The transformed differential equation (21) identifies the rate-determining steps in all catalytic cycles. The catalytic cycles discussed in this article are interpretations of the terms in the differential equation (21), which remains the controlling statement.

Figure 2. Test of Hunten's eddy diffusion function against vertical distribution of CFCl_3 as reported by Sundararaman [1976].

Figure 3. Calculated production and loss of ozone, according to Chang's mechanism and numerical method and according to Hunten's eddy diffusion function. $P(\text{O}_2)$ is production of ozone from photolysis of oxygen (22), $P(\text{CH}_4)$ is production of ozone from methane- NO_x -smog reaction according to term including CH_4 in (86). $L(\text{O}_x)$ is loss of ozone due to reactions of odd oxygen species (38, 39, 40). $L(\text{NO}_x)$ is loss of ozone from (41, 42). $L(\text{HO}_x)$ is loss of ozone from the sum of five processes (43, 44, 45, 46, 47). τ (10 years) is limit of rates where local ozone is destroyed by all processes at a rate of 10 percent per year; the region to the left of this line is regarded as negligibly slow for most purposes.

Figure 4. Calculated ozone destruction by five processes involving HO_x free radicals: $\text{HOO} + \text{O}_3$, (43); $\text{HOO} + \text{O}$, (44); $\text{H} + \text{O}_3$, (45); $\text{HOO} + \text{HOO}$, (46); and $\text{HO} + \text{HOO}$, (47).

Figure 5. Calculated rate of production of ozone from the photolysis of oxygen $\text{P}(\text{O}_2)$ based on observed ozone distribution for 59°N , July, and based on observed solar radiation above the atmosphere: Ackerman [1971], Brueckner et al. [1976]. Destruction of ozone by odd oxygen species (38, 39, 40) based on observed ozone profile by Evans et al. [1976].

Figure 6. Observed atomic oxygen [Anderson, 1975] and calculated atomic oxygen based on standard ozone profile, November 25, 32°N , 56° solar angle.

Figure 7. Rate of ozone destruction $\text{L}(\text{NO}_x)$ by observed NO_2 [Evans et al., 1976] and calculated atomic oxygen compared with rate of ozone production $\text{P}(\text{O}_2)$ under same conditions. July 22, noon, solar angle, 38.4° , latitude 59°N .

Figure 8. Similar to Figure 7. Ozone loss from NO_x based on observed NO_2 [A. Harries et al. as quoted by Sundararaman, 1976; B. Ackerman et al., 1974]. Solar angle 44° .

Figure 9. Observed stratospheric ClO and HCl. ClO as reported by Anderson et al. [1977]. HCl as summarized by Sundararaman [1976]: A. Farmer et al. [1976]; B. Williams et al. [1976]; C. Ackerman et al. [1976]; D. Lazrus et al. [1975]; E. Raper et al. [1976]. Total equivalent chlorine in chlorofluoromethanes and other organic chlorides in troposphere indicated by arrows.

Figure 10. Production of ozone from O_2 photolysis, $P(O_2)$, as calculated from solar radiation and standard ozone profiles. Destruction of ozone by ClX, $L(ClX)$, as calculated from observed ClO [Anderson et al., 1977] and calculated atomic oxygen. Production of ozone from methane-smog reaction $P(CH_4)$ as calculated from observed methane and hydroxyl radicals (Table 7).

Figure 11. Comparison of ozone loss rates, based on observed ozone, Evans' observed NO_2 , Anderson's mid-value observed ClO, and on calculated atomic oxygen. Noon. O_x and NO_x , $60^\circ N$; ClX, $32^\circ N$.

Figure 12. Comparison of production of ozone and loss of ozone from NO_x . A, based on observations of Evans et al. B. Calculated from Chang's model. Twenty-four hour averages. Production of ozone from methane-smog reaction according to Chang's model.

Figure 13. Ozone formation from methane-NO_x-smog reactions and ozone destruction by reaction K₄ as calculated by Johnston and Quitevis [1975]. The cross-over altitude was 13 km.

COMPLEXITY

Hundreds of Reactions, Scores of Free Radicals
Valid, Partial Simplification

Effect of radical is minute, unless cycled.
If cycled, each cycle is either catalytic or null. Rate-Determining steps in catalytic cycles are uniquely important.

Fig. 1

Atmospheric CFC₁₃ Volume Mixing Ratios

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Observed Atomic Oxygen (Anderson, 1975) and Calculated Atomic Oxygen Based on Standard Ozone Profile (November 25, 32°N, 56° Solar Angle).

Fig. 6

Production and Loss of Ozone Based on Observed NO_2 and O_3 (Evan's *et al.*, 1976), 59°N , July 22, Noon, Solar Angle 38.4° .

Fig. 7

Production and Loss of Ozone Based on Observed NO_2
(A. Harries *et al.*, 1976; B. Ackerman *et al.*, 1974)
Solar Angle 44°

Fig. 8

Fig. 9

Production and Loss of Ozone Based on Observed ClO
(Anderson *et al.*, 1977) 32°N, Noon.

Fig. 10

Comparison of Ozone Loss Rates, Based on Observed Ozone, Nitrogen Dioxide, and Chlorine Oxide, and on Calculated Atomic Oxygen. Noon; O_x and NO_x , $60^\circ N$; Cl_x , $32^\circ N$.

Fig. 11

Comparison of Production of Ozone and Loss of Ozone from NO_x ; A. Based on Observations of Evans *et al.*, B. Calculated from Chang's Model.

Fig. 12

Fig. 13

Table 1. Photochemical and chemical mechanism.

Photolytic reaction		Global average value sec ⁻¹ at km			
		15	25	35	45
A.	j ₁ O ₂ + hν → O + O	2.92(-15)	3.79(-12)	9.40(-11)	4.32(-10)
	j ₂ O ₃ + hν → O ₂ + O	4.12(-4)	4.57(-4)	4.95(-4)	5.09(-4)
	j ₃ O ₃ + hν → O ₂ + O(¹ D)	1.54(-5)	7.32(-5)	5.04(-4)	2.96(-3)
	j ₄ NO ₂ + hν → NO + O	8.27(-3)	9.21(-3)	9.62(-3)	9.83(-3)
	j ₅ N ₂ O + hν → N ₂ + O(¹ D)	2.44(-12)	3.80(-9)	7.00(-8)	2.06(-7)
	j ₆ NO + hν → N + O	7.3 (-37)	7.45(-17)	1.27(-8)	3.43(-7)
	j ₇ HNO ₃ + hν → HO + NO ₂	4.25(-7)	1.78(-6)	1.59(-5)	4.36(-5)
	j ₈ H ₂ O ₂ + hν → HO + HO	2.23(-5)	2.98(-5)	4.52(-5)	8.03(-5)
	j ₉ HOO + hν → HO + O				
	j ₁₀ NO ₃ + hν → NO + O ₂				
	j ₁₁ NO ₃ + hν → NO ₂ + O				
B.	j ₁₂ H ₂ CO + hν → H + HCO				
	j ₁₃ H ₂ CO + hν → H ₂ + CO				
	j ₁₄ CF ₂ Cl ₂ + hν → CF ₂ Cl + Cl	5.81(-12)	1.16(-8)	2.45(-7)	8.00(-7)
	j ₁₅ CFC1 ₃ + hν → CFC1 ₂ + Cl	1.34(-10)	1.89(-7)	3.31(-6)	8.66(-6)
	j ₁₆ ClONO ₂ + hν → ClO + NO ₂				
	j ₁₇ HOONO ₂ + hν → HOO + NO ₂				

continued

Table 1. (continued)

		Rate Constants	
Thermal Reactions		A (cm ³ molecule ⁻¹ sec ⁻¹)	E/R (°K)
A.	k ₁ O + O ₂ + M → O ₃ + M	1.07(-34) ^a	-510.
	k ₂ O + O ₃ → O ₂ + O ₂	1.9 (-11)	2300.
	k ₃ O ₃ + NO → NO ₂ + O ₂	2.1 (-12)	1450.
	k ₄ O + NO ₂ → NO + O ₂	9.1 (-12)	-
	k ₅ N ₂ O + O(¹ D) → N ₂ + O ₂	5.5 (-11)	-
	k ₆ N ₂ O + O(¹ D) → NO + NO	5.5 (-11)	-
	k ₇ N + O ₂ → NO + O	5.5 (-12)	3220.
	k ₈ N + NO → N ₂ + O	8.2 (-11)	410.
	k ₉ N + NO ₂ → NO + NO	2.0 (-11)	800.
	k ₁₀ O(¹ D) + H ₂ O → 2 HO	2.3 (-10)	-
	k ₁₁ O(¹ D) + CH ₄ → HO + CH ₃	1.3 (-10)	-
	k ₁₂ O ₃ + HO → O ₂ + HOO	1.5 (-12)	1000.
	k ₁₃ O + HO → H + O ₂	1.0 (-10)	250.
	k ₁₄ O ₃ + HOO → HO + O ₂ + O ₂	1.0 (-13)	1525.
	k ₁₅ O + HOO → HO + O ₂	1.0 (-10)	250.
	k ₁₆ H + O ₂ + M → HO ₂ + M	2.1 (-32) ^a	-290.
	k ₁₇ H + O ₃ → HO + O ₂	1.2 (-10)	560.
	k ₁₈ HOO + HOO → H ₂ O ₂ + O ₂	5.0 (-12)	500.
	k ₁₉ HO + HOO → H ₂ O + O ₂	5.1 (-11)	-
	k ₂₀ HO + NO ₂ + M → HNO ₃ + M	-4.0 (-12) x [M]/[1.12(18) + M]	
	k ₂₁ HO + HNO ₃ → H ₂ O + NO ₃	8.0 (-14)	-
	k ₂₂ HO + H ₂ O ₂ → H ₂ O + HOO	1.0 (-11)	750.
	k ₂₃ N ₂ + O(¹ D) + M → N ₂ O + M	3.5 (-37) ^a	-
	k ₂₄ N + NO ₂ → N ₂ O + O	-2.0 (-11)	800.

continued

Table 1. (continued)

Thermal Reactions		Rate Constants	
		A ($\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$)	E/R ($^{\circ}\text{K}$)
A. (continued)			
k_{25}	$\text{NO} + \text{O} + \text{M} \rightarrow \text{NO}_2 + \text{M}$	$1.55(-33)^a$	-584.
k_{26}	$\text{HOO} + \text{NO} \rightarrow \text{HO} + \text{NO}_2$	$8.0 (-12)$	-
k_{27}	$\text{HO} + \text{HO} \rightarrow \text{H}_2\text{O} + \text{O}$	$1.0 (-11)$	550.
k_{28}	$\text{N} + \text{O}_3 \rightarrow \text{NO} + \text{O}_2$	$5.0 (-12)$	650.
k_{29}	$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$	$1.2 (-13)$	2450.
k_{30}	$\text{HO} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$	$2.35(-12)$	1710.
k_{31}	$\text{HO} + \text{HO} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$	$1.25(-32)^a$	-900.
k_{32}	$\text{H}_2\text{O}_2 + \text{O} \rightarrow \text{HO} + \text{HOO}$	$2.75(-12)$	2125.
k_{33}	$\text{O}(^1\text{D}) + \text{M} \rightarrow \text{O} + \text{M}$	$2.0 (-11)$	-107.
$(k_{34}$	$\text{CH}_3 + \dots \rightarrow 2 \text{HOO} + \text{CO})$		
B.			
k_{35}	$\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{OO} + \text{M}$	$2.6 (-31)^a$	-
k_{36}	$\text{CH}_3\text{OO} + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2$	$3.3 (-12)$	500.
k_{37}	$\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{H}_2\text{CO} + \text{HOO}$	$1.6 (-13)$	3300.
k_{38}	$\text{CH}_3 + \text{O}_2 \rightarrow \text{H}_2\text{CO} + \text{HO}$	$3.0 (-16)$	-
k_{39}	$\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HOO}$	$6.0 (-12)$	-
k_{40}	$\text{HO} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$	$1.4 (-13)$	-
k_{41}	$\text{HO} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$	$3.6 (-11)$	2590.
k_{42}	$\text{O}(^1\text{D}) + \text{H}_2 \rightarrow \text{HO} + \text{H}$	$9.9 (-11)$	-
k_{43}	$\text{HO} + \text{H}_2\text{CO} \rightarrow \text{H}_2\text{O} + \text{HCO}$	$1.4 (-11)$	-
k_{44}	$\text{O}_3 + \text{O}(^1\text{D}) \rightarrow \text{O}_2 + \text{O}_2$	$1.2 (-10)$	-
k_{45}	$\text{O}_3 + \text{O}(^1\text{D}) \rightarrow \text{O}_2 + \text{O} + \text{O}$	$1.2 (-10)$	-

continued

Table 1. (continued)

Thermal Reactions		Rate Constants	
		A ($\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$)	E/R ($^{\circ}\text{K}$)
B. (continued)			
k_{46}	$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	2.7 (-11)	257.
k_{47}	$\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$	7.7 (-11)	130.
k_{48}	$\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$	2.2 (-11)	-
k_{49}	$\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$	3.5 (-11)	2290.
k_{50}	$\text{Cl} + \text{HOO} \rightarrow \text{HCl} + \text{O}_2$	3.0 (-11)	-
k_{51}	$\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$	7.3 (-12)	1260.
k_{52}	$\text{Cl} + \text{H}_2\text{O}_2 \rightarrow \text{HCl} + \text{HOO}$	1.7 (-12)	384.
k_{53}	$\text{HO} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$	3.0 (-12)	425.
k_{54}	$\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M}$	5.1 (-33) ^a	-1033.
k_{55}	$\text{CF}_2\text{Cl}_2 + \text{O}(^1\text{D}) \rightarrow \text{ClO} + \text{CF}_2\text{Cl}$	2.0 (-10)	-
k_{56}	$\text{CFCI}_3 + \text{O}(^1\text{D}) \rightarrow \text{ClO} + \text{CFCI}_2$	2.3 (-10)	-
k_{57}	$\text{ClONO}_2 + \text{O} \rightarrow \text{O}_2 + \text{ClO} + \text{NO}$	4.5 (-12)	840.
k_{58}	$\text{HOO} + \text{NO}_2 + \text{M} \rightarrow \text{HOONO}_2 + \text{M}$	1.0 (-32) ^a	-
k_{59}	$\text{HOONO}_2 + \text{O} \rightarrow \text{HO} + \text{NO}_2 + \text{O}_2$		
k_{60}	$2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2$	3.3 (-39) ^a	-530.
k_{61}	$\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$	4.8 (-33) ^a	-
k_{62}	$\text{CF}_2\text{Cl} + \text{O}_2 \rightarrow \text{COF}_2 + \text{ClO}$		
k_{63}	$\text{CFCI}_2 + \text{O}_2 \rightarrow \text{COFCl} + \text{ClO}$		
k_{64}	$\text{NO} + \text{NO}_3 \rightarrow 2 \text{NO}_2$	1.9×10^{-11}	-

^a
 $\text{cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$

Table 2. Reactions involving free radicals and the change in free radicals for each step.

	Reaction	Radical Arithmetic	ΔR
k_3	$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	$1 + 0 \rightarrow 1 + 0$	0
k_4	$\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$	$1 + 0 \rightarrow 1 + 0$	0
k_6	$\text{N}_2\text{O} + \text{O}(^1\text{D}) \rightarrow \text{NO} + \text{NO}$	$0 + 0 \rightarrow 1 + 1$	+2
k_7	$\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$	$1 + 0 \rightarrow 1 + 0$	0
k_8	$\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$	$1 + 1 \rightarrow 0 + 0$	-2
k_9	$\text{N} + \text{NO}_2 \rightarrow \text{NO} + \text{NO}$	$1 + 1 \rightarrow 1 + 1$	0
k_{10}	$\text{H}_2\text{O} + \text{O}(^1\text{D}) \rightarrow \text{HO} + \text{HO}$	$0 + 0 \rightarrow 1 + 1$	+2
k_{11}	$\text{CH}_4 + \text{O}(^1\text{D}) \rightarrow \text{CH}_3 + \text{HO}$	$0 + 0 \rightarrow 1 + 1$	+2
k_{12}	$\text{O}_3 + \text{HO} \rightarrow \text{O}_2 + \text{HOO}$	$0 + 1 \rightarrow 0 + 1$	0
k_{13}	$\text{O} + \text{HO} \rightarrow \text{H} + \text{O}_2$	$0 + 1 \rightarrow 1 + 0$	0
k_{14}	$\text{O}_3 + \text{HOO} \rightarrow \text{HO} + \text{O}_2 + \text{O}_2$	$0 + 1 \rightarrow 1 + 0 + 0$	0
k_{15}	$\text{O} + \text{HOO} \rightarrow \text{HO} + \text{O}_2$	$0 + 1 \rightarrow 1 + 0$	0
k_{16}	$\text{H} + \text{O}_2 \xrightarrow{\text{M}} \text{HOO}$	$1 + 0 \rightarrow 1$	0
k_{17}	$\text{H} + \text{O}_3 \rightarrow \text{HO} + \text{O}_2$	$1 + 0 \rightarrow 1 + 0$	0
k_{18}	$\text{HOO} + \text{HOO} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$1 + 1 \rightarrow 0 + 0$	-2
k_{19}	$\text{HO} + \text{HOO} \rightarrow \text{H}_2\text{O} + \text{O}_2$	$1 + 1 \rightarrow 0 + 0$	-2
k_{20}	$\text{HO} + \text{NO}_2 \rightarrow \text{HNO}_3$	$1 + 1 \rightarrow 0$	-2
k_{21}	$\text{HO} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_3$	$1 + 0 \rightarrow 0 + 1$	0
k_{22}	$\text{HO} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HOO}$	$1 + 0 \rightarrow 0 + 1$	0
k_{24}	$\text{N} + \text{NO}_2 \rightarrow \text{N}_2\text{O} + \text{O}$	$1 + 1 \rightarrow 0 + 0$	-2
k_{25}	$\text{NO} + \text{O} \xrightarrow{\text{M}} \text{NO}_2$	$1 + 0 \rightarrow 1$	0
k_{26}	$\text{HOO} + \text{NO} \rightarrow \text{HO} + \text{NO}_2$	$1 + 1 \rightarrow 1 + 1$	0
k_{27}	$\text{HO} + \text{HO} \rightarrow \text{H}_2\text{O} + \text{O}$	$1 + 1 \rightarrow 0 + 0$	-2
k_{28}	$\text{N} + \text{O}_3 \rightarrow \text{NO} + \text{O}_2$	$1 + 0 \rightarrow 1 + 0$	0

Continued

Table 2 (continued)

	Reaction	Radical Arithmetic	ΔR
k_{29}	$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$	$1 + 0 \rightarrow 1 + 0$	0
k_{30}	$\text{HO} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$	$1 + 0 \rightarrow 0 + 1$	0
k_{31}	$\text{HO} + \text{HO} \xrightarrow{\text{M}} \text{H}_2\text{O}_2$	$1 + 1 \rightarrow 0$	-2
k_{32}	$\text{H}_2\text{O}_2 + \text{O} \rightarrow \text{HO} + \text{HOO}$	$0 + 0 \rightarrow 1 + 1$	+2
k_{35}	$\text{CH}_3 + \text{O}_2 \xrightarrow{\text{M}} \text{CH}_3\text{OO}$	$1 + 0 \rightarrow 1$	0
k_{36}	$\text{CH}_3\text{OO} + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2$	$1 + 1 \rightarrow 1 + 1$	0
k_{37}	$\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{H}_2\text{CO} + \text{HOO}$	$1 + 0 \rightarrow 0 + 1$	0
k_{38}	$\text{CH}_3 + \text{O}_2 \rightarrow \text{H}_2\text{CO} + \text{HO}$	$1 + 0 \rightarrow 0 + 1$	0
k_{39}	$\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HOO}$	$1 + 0 \rightarrow 0 + 1$	0
k_{40}	$\text{HO} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$	$1 + 0 \rightarrow 0 + 1$	0
k_{41}	$\text{HO} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$	$1 + 0 \rightarrow 0 + 1$	0
k_{42}	$\text{H}_2 + \text{O}(^1\text{D}) \rightarrow \text{HO} + \text{H}$	$0 + 0 \rightarrow 1 + 1$	+2
k_{43}	$\text{HO} + \text{H}_2\text{CO} \rightarrow \text{H}_2\text{O} + \text{HCO}$	$1 + 0 \rightarrow 0 + 1$	0
k_{46}	$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	$1 + 0 \rightarrow 1 + 0$	0
k_{47}	$\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$	$1 + 0 \rightarrow 1 + 0$	0
k_{48}	$\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$	$1 + 1 \rightarrow 1 + 1$	0
k_{49}	$\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$	$1 + 0 \rightarrow 0 + 1$	0
k_{50}	$\text{Cl} + \text{HOO} \rightarrow \text{HCl} + \text{O}_2$	$1 + 1 \rightarrow 0 + 0$	-2
k_{51}	$\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$	$1 + 0 \rightarrow 0 + 1$	0
k_{52}	$\text{Cl} + \text{H}_2\text{O}_2 \rightarrow \text{HCl} + \text{HOO}$	$1 + 0 \rightarrow 0 + 1$	0
k_{53}	$\text{HO} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$	$1 + 0 \rightarrow 0 + 1$	0
k_{54}	$\text{ClO} + \text{NO}_2 \xrightarrow{\text{M}} \text{ClONO}_2$	$1 + 1 \rightarrow 0$	-2
k_{55}	$\text{CF}_2\text{Cl}_2 + \text{O}(^1\text{D}) \rightarrow \text{CF}_2\text{Cl} + \text{ClO}$	$0 + 0 \rightarrow 1 + 1$	+2
k_{56}	$\text{CFC}_2\text{Cl}_3 + \text{O}(^1\text{D}) \rightarrow \text{CFC}_2\text{Cl}_2 + \text{OCl}$	$0 + 0 \rightarrow 1 + 1$	+2
k_{57}	$\text{ClONO}_2 + \text{O} \rightarrow \text{O}_2 + \text{ClO} + \text{NO}$	$0 + 0 \rightarrow 0 + 1 + 1$	+2

Continued

Table 2 (continued)

	Reaction	Radical Arithmetic	ΔR
k_{58}	$\text{HOO} + \text{NO}_2 \xrightarrow{\text{M}} \text{HOONO}_2$	$1 + 1 \rightarrow 0$	-2
k_{59}	$\text{HOONO}_2 + \text{O} \rightarrow \text{HO} + \text{NO}_2 + \text{O}_2$	$0 + 0 \rightarrow 1 + 1 + 0$	+2
k_{60}	$2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$	$1 + 1 + 0 \rightarrow 1 + 1$	0
k_{62}	$\text{CF}_2\text{Cl} + \text{O}_2 \rightarrow \text{COF}_2 + \text{ClO}$	$1 + 0 \rightarrow 0 + 1$	0
k_{63}	$\text{CFCl}_2 + \text{O}_2 \rightarrow \text{COFCl} + \text{ClO}$	$1 + 0 \rightarrow 0 + 1$	0
k_{64}	$\text{NO} + \text{NO}_3 \rightarrow \text{NO}_2 + \text{NO}_2$	$1 + 1 \rightarrow 1 + 1$	0
j_4	$\text{NO}_2 \rightarrow \text{NO} + \text{O}$	$1 \rightarrow 1 + 0$	0
j_6	$\text{NO} \rightarrow \text{N} + \text{O}$	$1 \rightarrow 1 + 0$	0
j_7	$\text{HNO}_3 \rightarrow \text{HO} + \text{NO}_2$	$0 \rightarrow 1 + 1$	+2
j_8	$\text{H}_2\text{O}_2 \rightarrow 2\text{HO}$	$0 \rightarrow 1 + 1$	+2
j_9	$\text{HOO} \rightarrow \text{HO} + \text{O}$	$1 \rightarrow 1 + 0$	0
j_{10}	$\text{NO}_3 \rightarrow \text{NO} + \text{O}_2$	$1 \rightarrow 1 + 0$	0
j_{11}	$\text{NO}_3 \rightarrow \text{NO}_2 + \text{O}$	$1 \rightarrow 1 + 0$	0
j_{12}	$\text{H}_2\text{CO} \rightarrow \text{H} + \text{HCO}$	$0 \rightarrow 1 + 1$	+2
j_{14}	$\text{CF}_2\text{Cl}_2 \rightarrow \text{CF}_2\text{Cl} + \text{Cl}$	$0 \rightarrow 1 + 1$	+2
j_{15}	$\text{CFCl}_3 \rightarrow \text{CFCl}_2 + \text{Cl}$	$0 \rightarrow 1 + 1$	+2
j_{16}	$\text{ClONO}_2 \rightarrow \text{ClO} + \text{NO}_2$	$0 \rightarrow 1 + 1$	+2
j_{17}	$\text{HOONO}_2 \rightarrow \text{HOO} + \text{NO}_2$	$0 \rightarrow 1 + 1$	+2

Table 3. Reactions involving odd oxygen and the change in odd oxygen for each step.

	Reaction	Odd Oxygen Arithmetic	ΔO_x
(a) Pure O_x reactions			
k_1	$O + O_2 \xrightarrow{M} O_3$	$1 + 0 \rightarrow 1$	0
k_2	$O + O_3 \rightarrow O_2 + O_2$	$1 + 1 \rightarrow 0 + 0$	-2
k_{33}	$O(^1D) \xrightarrow{M} O$	$1 \rightarrow 1$	0
k_{44}	$O_3 + O(^1D) \rightarrow O_2 + O_2$	$1 + 1 \rightarrow 0 + 0$	-2
k_{45}	$O_3 + O(^1D) \rightarrow O_2 + O + O$	$1 + 1 \rightarrow 0 + 1 + 1$	0
k_{61}	$O + O \xrightarrow{M} O_2$	$1 + 1 \rightarrow 0$	-2
j_1	$O_2 \rightarrow O + O$	$0 \rightarrow 1 + 1$	+2
j_2	$O_3 \rightarrow O_2 + O$	$1 \rightarrow 0 + 1$	0
j_3	$O_3 \rightarrow O_2 + O(^1D)$	$1 \rightarrow 0 + 1$	0
(b) O_x reactions involving HO_x			
k_{10}	$H_2O + O(^1D) \rightarrow 2HO$	$0 + 1 \rightarrow 0 + 0$	-1
k_{11}	$CH_4 + O(^1D) \rightarrow CH_3 + HO$	$0 + 1 \rightarrow 0 + 0$	-1
k_{12}	$O_3 + HO \rightarrow HOO + O_2$	$1 + 0 \rightarrow 0 + 0$	-1
k_{13}	$O + HO \rightarrow H + O_2$	$1 + 0 \rightarrow 0 + 0$	-1
k_{14}	$O_3 + HOO \rightarrow HO + O_2 + O_2$	$1 + 0 \rightarrow 0 + 0 + 0$	-1
k_{15}	$O + HOO \rightarrow HO + O_2$	$1 + 0 \rightarrow 0 + 0$	-1
k_{17}	$O_3 + H \rightarrow HO + O_2$	$1 + 0 \rightarrow 0 + 0$	-1
k_{27}	$HO + HO \rightarrow H_2O + O$	$0 + 0 \rightarrow 0 + 1$	+1
k_{32}	$H_2O_2 + O \rightarrow HO + HOO$	$0 + 1 \rightarrow 0 + 0$	-1
k_{42}	$H_2 + O(^1D) \rightarrow HO + H$	$0 + 1 \rightarrow 0 + 0$	-1
j_9	$HOO \rightarrow HO + O$	$0 \rightarrow 0 + 1$	+1

continued

Table 3 (continued)

	Reaction	Odd Oxygen Arithmetic	ΔO_x
(c) O_x reactions involving NO_x			
k_3	$O_3 + NO \rightarrow NO_2 + O_2$	$1 + 0 \rightarrow 0 + 0$	-1
k_4	$O + NO_2 \rightarrow NO + O_2$	$1 + 0 \rightarrow 0 + 0$	-1
k_6	$N_2O + O(^1D) \rightarrow 2NO$	$0 + 1 \rightarrow 0 + 0$	-1
k_7	$N + O_2 \rightarrow NO + O$	$0 + 0 \rightarrow 0 + 1$	+1
k_8	$N + NO \rightarrow N_2 + O$	$0 + 0 \rightarrow 0 + 1$	+1
k_{24}	$N + NO_2 \rightarrow N_2O + O$	$0 + 0 \rightarrow 0 + 1$	+1
k_{25}	$NO + O \xrightarrow{M} NO_2$	$0 + 1 \rightarrow 0$	-1
k_{28}	$N + O_3 \rightarrow NO + O_2$	$0 + 1 \rightarrow 0 + 0$	-1
k_{29}	$NO_2 + O_3 \rightarrow NO_3 + O_2$	$0 + 1 \rightarrow 0 + 0$	-1
k_{57}	$ClONO_2 + O \rightarrow O_2 + ClO + NO$	$0 + 1 \rightarrow 0 + 0 + 0$	-1
k_{59}	$HOONO_2 + O \rightarrow HO + NO_2 + O_2$	$0 + 1 \rightarrow 0 + 0 + 0$	-1
j_4	$NO_2 \rightarrow NO + O$	$0 \rightarrow 0 + 1$	+1
j_6	$NO \rightarrow N + O$	$0 \rightarrow 0 + 1$	+1
j_{11}	$NO_3 \rightarrow NO_2 + O$	$0 \rightarrow 0 + 1$	+1
(c') Additional O_x reactions involving N_2O			
k_5	$N_2O + O(^1D) \rightarrow N_2 + O_2$	$0 + 1 \rightarrow 0 + 0$	-1
k_{23}	$N_2 + O(^1D) \xrightarrow{M} N_2O$	$0 + 1 \rightarrow 0$	-1
j_5	$N_2O \rightarrow N_2 + O(^1D)$	$0 \rightarrow 0 + 1$	+1
(d) O_x reactions involving ClX			
k_{46}	$Cl + O_3 \rightarrow ClO + O_2$	$0 + 1 \rightarrow 0 + 0$	-1
k_{47}	$ClO + O \rightarrow Cl + O_2$	$0 + 1 \rightarrow 0 + 0$	-1
k_{55}	$CF_2Cl_2 + O(^1D) \rightarrow ClO + CF_2Cl$	$0 + 1 \rightarrow 0 + 0$	-1
k_{56}	$CFC1_3 + O(^1D) \rightarrow ClO + CFC1_2$	$0 + 1 \rightarrow 0 + 0$	-1

Table 4. Test of the steady-state approximation for nitric acid and nitrous oxide (rates in units of molecules $\text{cm}^{-3} \text{sec}^{-1}$).

Altitude, km	5	10	15	20	25	30	35	40	45	50
$P(\text{HNO}_3)/10^2$	2.7	1.4	13.4	32.0	49.6	79.4	54.7	14.6	0.9	0.03
$(P-L)/L(\text{HNO}_3)$	0.19	0.04	0.01	0.01	0.02	2(-3)	-7(-3)	-8(-3)	-5(-2)	-6(-2)
$P(\text{O}_3)/10^5$	1.38	0.31	0.11	0.27	3.75	19.7	51.1	77.0	74.6	51.2
$L(\text{HNO}_3)/P(\text{O}_3)$	2(-3)	4(-3)	0.12	0.12	0.10	4(-3)	1(-3)	2(-4)	1(-5)	7(-7)
$P(\text{N}_2\text{O})$	0.2	0.1	0.2	0.4	0.5	0.5	0.4	0.3	0.1	-
$L(\text{N}_2\text{O})$	1.1	1.2	5.6	38	224	558	482	187	56	19
$(P-L)/L(\text{N}_2\text{O})$	0.82	0.92	0.96	0.99	1.00	1.00	1.00	1.00	1.00	1.00
$L(\text{N}_2\text{O})/P(\text{O}_3)$	8(-6)	4(-5)	5(-4)	1(-3)	6(-4)	3(-4)	9(-5)	2(-5)	8(-6)	4(-6)

Table 5. Chemical production and loss for various species (molecules $\text{cm}^{-3} \text{sec}^{-1}$).^a

Altitude, km	0	5	10	15	20	25	30	35	40	45	50
$P(\text{O}_3)/10^5$	9.17	1.38	0.31	0.11	0.27	3.75	19.7	51.1	77.0	74.6	51.2
$\text{O}_2 + h\nu$ %	-	-	-	2.2	91.9	99.5	99.9	100	100	100	100
CH_4 , smog %	100	100	100	97.8	8.1	0.5	0.1	-	-	-	-
$L(\text{O}_3)/10^5$	16.2	3.50	0.72	0.25	0.66	3.78	19.2	51.0	77.0	75.0	51.3
O_x %	-	-	-	0.5	7.8	12.8	11.8	14.4	25.9	40.0	32.7
HO_x %	99.6	99.9	99.8	90.3	34.7	13.6	6.5	6.6	12.8	38.0	61.6
NO_x %	0.4	0.1	0.2	9.2	57.4	73.6	81.7	79.0	61.3	22.0	5.7
$L(\text{HO}_x)/10^5$	16.1	3.5	0.72	0.23	0.23	0.51	1.25	3.39	9.88	28.5	31.6
$\text{HOO} + \text{O}_3$ %	9.9	19.8	15.9	51.2	77.8	59.1	24.2	5.1	0.7	0.1	-
$\text{HOO} + \text{O}$ %	-	-	0.1	1.0	7.7	29.5	65.5	87.7	90.2	86.9	86.1
$\text{H} + \text{O}_3$ %	-	-	-	-	-	-	0.2	1.2	6.6	12.3	13.6
2HOO %	68.4	55.4	32.7	7.3	2.2	1.7	0.9	0.3	-	-	-
$\text{HO} + \text{HOO}$ %	21.7	24.8	51.4	40.9	12.2	9.8	9.2	5.7	2.5	0.7	0.3

^aCalculated from Chang's [1974] mechanism, Hunten's K_z function, and rate constants as understood to be in 1977.

Table 6.A. The rate of ozone production P derived from observed ozone (Evans et al., 1976), 59°N, July 22, 24 hour average. Schumann-Runge region calculated by method of Hudson and Mahle (1972). Multiple order Rayleigh scattering and attenuation above S-R region by method of Isaksen et al. (1976). B, solar intensities by Brueckner et al. (1976). A, solar intensities by Ackerman (1971). B, S-R region attenuated by Rayleigh scattering; B', A', S-R region not attenuated by Rayleigh scattering.

	2 j[O ₂]				2 j[O ₂]		
	P(B)	P(B')	P(A')		P(B)	P(B')	P(A')
48	8.15(6)	8.27(6)	8.68(6)	28	1.63(6)	1.92(6)	2.06(6)
47	9.27(6)	9.42(6)	9.86(6)	27	1.14(6)	1.38(6)	1.48(6)
46	9.71(6)	9.88(6)	1.03(7)	26	7.68(5)	9.55(5)	1.03(6)
45	1.01(7)	1.03(7)	1.07(7)	25	5.00(5)	6.43(5)	6.91(5)
44	1.04(7)	1.06(7)	1.11(7)	24	3.16(5)	4.22(5)	4.53(5)
43	1.06(7)	1.09(7)	1.14(7)	23	1.87(5)	2.62(5)	2.81(5)
42	1.07(7)	1.10(7)	1.15(7)	22	1.02(5)	1.50(5)	1.60(5)
41	1.07(7)	1.10(7)	1.15(7)	21	5.09(4)	7.96(4)	8.51(4)
40	1.05(7)	1.09(7)	1.14(7)	20	2.40(4)	4.03(4)	4.29(4)
39	1.02(7)	1.06(7)	1.11(7)	19	1.06(4)	1.92(4)	2.03(4)
38	9.69(6)	1.01(7)	1.06(7)	18	4.28(3)	8.52(3)	8.99(3)
37	9.04(6)	9.50(6)	9.97(6)	17	1.61(3)	3.55(3)	3.72(3)
36	8.23(6)	8.70(6)	9.16(6)	16	5.51(2)	1.37(3)	1.41(3)
35	7.34(6)	7.82(6)	8.25(6)	15	1.48(2)	4.14(2)	4.14(2)
34	6.37(6)	6.85(6)	7.24(6)	14	3.88(1)	1.28(2)	1.28(2)
33	5.42(6)	5.89(6)	6.25(6)	13	8.20	3.25(1)	3.25(1)
32	4.52(6)	4.97(6)	5.28(6)	12	1.35	6.62	6.62
31	3.67(6)	4.09(6)	4.36(6)	11	0.17	1.10	1.10
30	2.91(6)	3.30(6)	3.52(6)	10	0.02	0.15	0.15
29	2.23(6)	2.57(6)	2.76(6)				

Table 6.B. Rate of formation of ozone from photolysis of oxygen, as affected by different solar intensities and methods of correcting for Rayleigh scattering in the Schumann-Runge region.

KM	$P(O_3)$ molecules $cm^{-2} sec^{-1}/10^{12}$			Ratios	
	A'	B'	B	A'/B'	B/B'
46-50	7.25	6.81	6.76	1.06	0.99
41-45	10.34	9.83	9.71	1.05	0.99
36-40	11.16	10.58	10.31	1.06	0.97
31-35	8.37	7.85	7.42	1.07	0.95
26-30	3.85	3.57	3.18	1.08	0.91
21-25	0.98	0.90	0.71	1.08	0.79
16-20	0.10	0.11	0.06	1.06	0.61
TOTAL	42.1	39.7	38.2	1.06	0.96

Solar angle 33.9° noon, October 2, $30^\circ N$. Multiple Rayleigh scattering and reflection above 205 nm. A' and B', no correction of Schumann-Runge region for Rayleigh scattering. B, Schumann-Runge radiation attenuated by Rayleigh scattering.

A'. Ackerman, 1971.

B' and B. Brueckner, 1977.

Table 7. Rate of production of ozone from methane-NO_x-smog reaction based on observed methane (Ackerman, 1977) and observed hydroxyl radicals (Anderson, 1975).

KM	$\frac{[\text{CH}_4]}{10^{10}}$	$\frac{[\text{HO}]}{10^7}$	T,K	$\frac{k_{30}}{10^{-15}}$	$\frac{k_{43}}{10^{-11}}$	$\frac{j_{12}^b}{10^{-4}}$	$\frac{j_{13}^b}{10^{-4}}$	Factor ^c	$\frac{P(\text{O}_3)}{10^3}$	$\frac{\tau(\text{CH}_4)^d}{10^7 \text{ sec}}$
44	0.66		261							
43	(0.88) ^a	2.8	259	3.36	1.14	0.85	1.50	1.15	1.88	1.12
42	1.18		256							
41			254							
40	1.91		252							
39	(2.27)	2.15	249	2.54	1.10	0.80	1.50	1.17	2.87	1.90
38	2.69		247							
37	(3.37)	2.2	245	2.26	1.08	0.75	1.47	1.16	3.89	2.08
36	4.23		242							
35	(5.44)	0.95	240	1.94	1.06	0.70	1.45	1.22	2.34	5.57
34	7.00		237							
33	(9.20)	1.3	235	1.65	1.04	0.67	1.40	1.20	4.67	4.73
32	12.1	1.05	233	1.55	1.03	0.65	1.39	1.21	4.66	6.24
30	21.5	0.42	229	1.35	1.01	0.62	1.35	1.26	2.92	1.77

^a Methane values in parentheses are geometrical average of the observed value one km above and one km below.

^b Photolysis constants are for 60° solar angle, 0.25 albedo (Isaksen et al., 1977).

^c $1 + j_{12}/(j_{12} + j_{13} + k_{43}[\text{HO}])$, factor in (90).

^d $\tau = [\text{CH}_4]/k_{30}[\text{HO}][\text{CH}_4]$.

Table 8. Atomic oxygen observed (32°N, 56° solar angle, November 25, Anderson, 1975) and calculated from standard ozone (30°N, 54° solar angle, December 8).

KM	$\frac{[O_3]}{10^{12}}$	[O] calc	[O] obs	$\frac{[O]_{obs}}{[O]_{calc}}$
39	0.67	1.36(9)	1.0(9)	0.74
38	0.79	1.04(9)	7.5(8)	0.72
37	0.95	8.11(8)	4.4(8)	0.54
36	1.14	6.31(8)	4.6(8)	0.73
35	1.33	4.81(8)	3.4(8)	0.71
34	1.54	3.66(8)	3.9(8)	1.07
33	1.77	2.77(8)	3.7(8)	1.34
32	2.04	2.11(8)	2.4(8)	1.14
31	2.33	1.62(8)	2.8(8)	1.73
30	2.66	1.25(8)	2.3(8)	1.84
29	3.03	9.55(7)	1.2(8)	1.26
28	3.44	7.33(7)	1.1(8)	1.50
27	3.88	5.60(7)	8.1(7)	1.45
26	4.31	4.23(7)	6.0(7)	1.42
Σ 26 to 39 km		5.73(14)	4.87(14)	0.85
molecules $\text{cm}^{-2} \text{sec}^{-1}$				

Table 9. The rate of ozone destruction (L) from observed ozone and from calculated atomic oxygen (Evans et al., 1976). 38° solar angle, noon, 59°N, July 22.

KM	Concentrations		T	Rates		Ratio L/P	τ [O ₃]/L
	$\frac{[O_3]}{10^{12}}$	[O]		$2 j[O_2]$ P	$2 k[O][O_3]$ L		
48	0.081	6.28(9)	276	1.48(7)	4.66(6)	0.31	0.20 day
46	0.129	4.57(9)	275	1.86(7)	5.22(6)	0.28	0.29
44	0.196	3.46(9)	272	2.10(7)	5.48(6)	0.26	0.41
42	0.300	2.42(9)	268	2.32(7)	5.17(6)	0.22	0.67
40	0.463	1.59(9)	262	2.43(7)	4.31(6)	0.18	1.2
38	0.717	1.02(9)	256	2.40(7)	3.48(6)	0.15	2.4
36	1.12	6.51(8)	250	2.19(7)	2.80(6)	0.13	4.6
34	1.69	4.02(8)	244	1.84(7)	2.08(6)	0.11	9.4
32	2.21	2.20(8)	238	1.42(7)	1.17(6)	0.082	22
30	2.74	1.23(8)	236	1.00(7)	7.50(5)	0.075	42
28	3.72	7.77(7)	232	6.19(6)	5.44(5)	0.088	79
26	4.35	4.31(7)	230	3.23(6)	3.23(5)	0.10	156
24	4.16	2.00(7)	227	1.47(6)	1.26(5)	0.086	382
22	5.34	1.29(7)	225	5.24(5)	9.52(4)	0.18	1.8 yrs
20	4.90	6.15(6)	225	1.37(5)	4.16(4)	0.30	3.7
18	4.19	2.77(6)	225	2.71(4)	1.66(4)	0.61	8.0
16	2.32	8.15(5)	225	3.87(3)	2.62(3)	0.68	28
14	2.37	4.46(5)	225	2.99(2)	1.46(3)	4.9	51
12	2.62	2.63(5)	225	1.15(1)	9.52(2)	-	87
10	0.58	3.10(4)	225	0.17	2.48(1)	-	742
Σ molecules cm ⁻² sec ⁻¹ 20 to 48 km				4.04(13)	6.32(12)	0.16	

Table 10.A. The rate of ozone destruction L derived from observed ozone and nitrogen dioxide and from calculated atomic oxygen concentration (noon, 59°N, July 22, solar angle 38.40). The calculated rate of ozone production P from O_2 photolysis.

KM	Concentrations			Rates (noon)		Ratio L/P	τ [O ₃]/L
	$\frac{[O_3]}{10^{12}}$	$\frac{[NO_2]}{10^9}$	[O]	$2 j[O_2]$ P	$2 k[O][NO_2]$ L		
35	1.37	1.06	5.10(8)	2.04(7)	9.80(6)	0.48	1.6 days
34	1.69	1.32	4.02(8)	1.84(7)	9.70(6)	.53	2.0
33	1.93	1.68	2.95(8)	1.64(7)	9.00(6)	.55	2.5
32	2.21	2.00	2.20(8)	1.42(7)	8.00(6)	.56	3.2
31	2.45	2.27	1.64(8)	1.21(7)	6.78(6)	.56	4.2
30	2.74	2.64	1.23(8)	1.00(7)	5.91(6)	.59	5.4
29	3.19	2.82	9.76(7)	8.07(6)	5.02(6)	.62	7.4
28	3.72	3.10	7.77(7)	6.19(6)	4.39(6)	.71	9.8
27	4.02	3.35	5.76(7)	4.57(6)	3.51(6)	.77	13
26	4.35	3.38	4.31(7)	3.23(6)	2.67(6)	.83	19
25	4.26	3.29	2.92(7)	2.21(6)	1.76(6)	.80	28
24	4.16	3.52	2.00(7)	1.47(6)	1.28(6)	.87	38
23	4.71	3.55	1.60(7)	9.17(5)	1.04(6)	1.13	52
22	5.34	3.53	1.29(7)	5.24(5)	8.30(5)	1.58	74
21	5.11	3.25	8.87(6)	2.77(5)	5.24(5)	1.89	113
20	4.90	3.31	6.15(6)	1.37(5)	3.71(5)	2.71	153
19	4.53	3.00	4.12(6)	6.36(4)	2.25(5)	3.54	233
18	4.19	2.56	2.77(6)	2.71(4)	1.29(5)	4.76	376
17	3.12	1.85	1.50(6)	1.07(4)	5.03(4)	4.72	2.0 year
16	2.32	1.58	8.18(5)	3.87(3)	2.36(4)	6.1	3.1
15	2.35	1.53	6.04(5)	1.08(3)	1.68(4)	16	4.4
14	2.37	1.43	4.46(5)	2.99(2)	1.17(4)	39	6.4
13	2.49	1.53	3.43(5)	6.65(1)	9.30(3)	140	8.5
12	2.62	1.36	2.63(5)	1.15(1)	6.5(3)	565	13
11	1.23	1.19	8.95(4)	1.58	1.93(3)	1220	20
Σ 20 to 35 km				1.19(13)	7.06(12)	0.59	

Table 10.B. The rate of ozone destruction (L) derived from observed ozone and nitrogen dioxide, and from calculated 24 hour average atomic oxygen concentrations. The calculated rate of ozone production (P) from O_2 photolysis (24 hour average). 59°N, July 22 (Evans et al., 1976).

KM	Concentrations ^a			Rates ^b (24 hr ave.)		Ratio L/P	τ^c [O ₃]/L
	[O ₃] 10 ¹²	[NO ₂] 10 ⁹	[O]	2 j[O ₂] P	2 k[O][NO ₂] L		
35	1.37	1.19	2.64(8)	7.34(6)	5.70(6)	0.78	3 days
34	1.69	1.49	2.11(8)	6.37(6)	5.73(6)	0.90	3
33	1.93	1.90	1.57(8)	5.42(6)	5.43(6)	1.00	4
32	2.21	2.27	1.19(8)	4.52(6)	4.91(6)	1.09	5
31	2.45	2.57	9.01(7)	3.67(6)	4.21(6)	1.15	7
30	2.74	2.91	6.89(7)	2.91(6)	3.66(6)	1.26	9
29	3.19	3.12	5.53(7)	2.23(6)	3.14(6)	1.41	12
28	3.72	3.35	4.46(7)	1.63(6)	2.72(6)	1.67	16
27	4.02	3.48	3.34(7)	1.14(6)	2.11(6)	1.85	22
26	4.35	3.38	2.52(7)	7.68(5)	1.55(6)	2.02	32
25	4.26	2.90	1.72(7)	5.00(5)	9.80(5)	1.96	50
24	4.16	3.27	1.18(7)	3.16(5)	7.03(5)	2.22	68
23	4.71	3.24	9.48(6)	1.87(5)	5.59(5)	3.0	98
22	5.34	3.24	7.64(6)	1.02(5)	4.50(5)	4.4	137
21	5.11	2.97	5.28(6)	5.09(4)	2.86(5)	5.6	207
20	4.90	3.02	3.66(6)	2.40(4)	2.01(5)	8.4	0.8 year
19	4.53	2.71	2.45(6)	1.06(4)	1.21	11	1.2
18	4.19	2.41	1.65(6)	4.28(3)	7.23(4)	17	1.8
17	3.12	1.79	8.92(5)	1.61(3)	3.11(4)	19	3.2
16	2.32	1.41	4.84(5)	5.51(2)	1.24(4)	23	5.9
15	2.35	1.28	3.57(5)	1.48(2)	8.30(3)	56	9.0
14	2.37	1.15	2.63(5)	Small	5.51(3)	-	14
13	2.49	1.33	2.01(5)	-	4.85(3)	-	16
12	2.62	1.54	1.54(5)	-	4.32(3)	-	19
Σ 20 to 35 km				3.72(12)	4.23(12)	1.14	

^aMolecules cm⁻³, 2.64(8) = 2.64 × 10⁸.

^bMolecules cm⁻³ sec⁻¹.

^cFormally, this is the time required for the local ozone to be destroyed by the current loss rate due to NO_x. It is a readily grasped statement of the local, instantaneous rate of reaction.

Table 11.A. The rate of ozone destruction (L) derived from observed nitrogen dioxide (Harries et al., 1976), standard ozone, and calculated atomic oxygen.

The calculated rate of O_3 production (P) from O_2 photolysis. $44^\circ N$,
September, noon.

KM	Concentrations			Rates (noon)		Ratio L/P	τ [O_3]/L days
	$\frac{[O_3]}{10^{12}}$	$\frac{[NO_2]}{10^9}$	[O]	$2 j[O_2]$ P	$2 k[O][NO_2]$ L		
35	1.32	3.19	4.64(8)	1.54(7)	2.69(7)	1.75	0.57
34	1.50	3.93	3.52(8)	1.42(7)	2.52(7)	1.78	0.69
33	1.70	4.30	2.67(8)	1.29(7)	2.09(7)	1.62	0.94
32	1.91	4.28	2.04(8)	1.14(7)	1.59(7)	1.39	1.39
31	2.14	4.65	1.56(8)	9.95(6)	1.32(7)	1.33	1.87
30	2.38	4.78	1.19(8)	8.45(6)	1.03(7)	1.22	2.7
29	2.71	4.39	9.25(7)	6.95(6)	7.39(6)	1.06	4.2
28	3.04	4.10	7.10(7)	5.51(6)	5.30(6)	0.96	6.6
27	3.37	3.67	5.38(7)	4.19(6)	3.59(6)	0.86	10.9
26	3.66	3.45	4.01(7)	3.05(6)	2.52(6)	0.82	16.8
25	3.91	3.06	2.95(7)	2.11(6)	1.64(6)	0.78	28
24	4.04	2.72	2.10(7)	1.39(6)	1.04(6)	0.75	45
Σ 24 to 35 km				9.55(12)	1.34(13)	1.40	

Table 11B. The rate of ozone destruction L derived from observed nitrogen dioxide (Ackerman, 1974) and from calculated atomic oxygen concentration. 44°N , May.

KM	Concentrations				Rates (noon)			Ratios	
	$\frac{[\text{O}_3]}{10^{12}}$	$[\text{NO}_2]/10^9$		$[\text{O}]$	$2 j[\text{O}_2]$	$2 k[\text{O}][\text{NO}_2] = L$		L/P	
		Lower	Upper	Noon	P	Lower	Upper	Lower	Upper
36	1.14	0.40	0.80	6.10(8)	1.64(7)	4.44(6)	8.88(6)	0.27	0.52
35	1.32	0.47	0.90	4.64(8)	1.54(7)	3.97(6)	7.60(6)	0.26	0.49
34	1.50	0.50	1.02	3.52(8)	1.42(7)	3.20(6)	6.53(6)	0.23	0.46
33	1.70	0.70	1.25	2.67(8)	1.29(7)	3.40(6)	6.07(6)	0.26	0.47
32	1.91	0.90	1.60	2.04(8)	1.14(7)	3.34(6)	5.94(6)	0.29	0.52
31	2.14	1.1	2.0	1.56(8)	9.95(6)	3.12(6)	5.68(6)	0.31	0.57
30	2.38	1.4	2.2	1.19(8)	8.45(6)	3.03(6)	4.76(6)	0.36	0.56
29	2.71	1.5	2.5	9.25(7)	6.95(6)	2.53(6)	4.21(6)	0.36	0.61
28	3.04	1.6	2.5	7.10(7)	5.51 (6)	2.07(6)	3.23(6)	0.38	0.59
27	3.37	1.62	2.5	5.38(7)	4.19(6)	1.59(6)	2.45(6)	0.38	0.58
26	3.66	1.6	2.5	4.01(7)	3.05(6)	1.17(6)	1.82(6)	0.38	0.60
25	3.91	1.55	2.5	2.95(7)	2.11(6)	8.32(5)	1.34(6)	0.39	0.64
24	4.04	1.5	2.4	2.10(7)	1.39(6)	5.73(5)	9.17(5)	0.41	0.66
23	4.10	1.4	2.2	1.47(7)	8.65(5)	3.69(5)	5.89(5)	0.43	0.68
22	4.09	1.2	2.0	1.01(7)	5.08(5)	2.21(5)	3.68(5)	0.43	0.72
21	4.00	1.1	1.8	6.90(6)	2.79(5)	1.38(5)	2.26(5)	0.50	0.81
20	3.83	1.0	1.6	4.62(6)	1.41(5)	8.41(4)	1.35(5)	0.60	0.95
Σ 20 to 36 km, molecules $\text{cm}^{-2} \text{sec}^{-1}$					1.14(13)	3.47(12)	6.07(12)	0.31	0.53

Table 12. The rate of ozone destruction (L) driven from observed ClO
(Anderson et al., 1977), and from calculated atomic oxygen
based on standard ozone. 32°N, noon.

Concentrations				Rates (noon)		Ratio L/P	τ [O ₃]/L days
KM	$\frac{[O_3]}{10^{12}}$	$\frac{[ClO]}{10^8}$	[O]	$2 j[O_2]$ P	$2 k[O][ClO]$ L		
A.	July 28, 1976. Solar angle 14°						
40	0.611	0.36	2.20(9)	2.47(7)	6.92(6)	0.28	1.02
39	0.769	0.43	1.77(9)	2.48(7)	6.65(6)	0.27	1.34
38	0.958	1.10	1.41(9)	2.44(7)	1.36(7)	0.56	0.82
37	1.17	1.90	1.10(9)	2.37(7)	1.83(7)	0.77	0.74
36	1.41	2.47	8.51(8)	2.26(7)	1.84(7)	0.81	0.89
35	1.65	2.30	6.40(8)	2.14(7)	1.29(7)	0.60	1.48
34	1.90	2.10	4.81(8)	1.99(7)	8.83(6)	0.44	2.59
33	2.17	3.45	3.59(8)	1.83(7)	1.08(7)	0.59	2.3
32	2.48	2.87	2.70(8)	1.66(7)	6.77(6)	0.41	4.2
31	2.85	3.08	2.06(8)	1.47(7)	5.55(6)	0.38	6.0
30	3.25	3.00	1.57(8)	1.27(7)	4.12(6)	0.32	9.1
29	3.69	2.48	1.19(8)	1.07(7)	2.58(6)	0.24	17
28	4.07	2.65	8.87(7)	8.79(6)	2.05(6)	0.23	23
27	4.25	2.27	6.27(7)	7.03(6)	1.24(6)	0.18	40
26	4.36	2.37	4.39(7)	5.48(6)	9.09(5)	0.17	56
25	4.52	1.57	3.10(7)	4.17(6)	4.25(5)	0.10	123
24	4.56	2.00	2.14(7)	3.06(6)	3.74(5)	0.12	141
23	4.26	0.84	1.37(7)	2.19(6)	1.01(5)	0.05	490
Σ 23 to 40, molecule cm ⁻² sec ⁻¹				2.65(13)	1.21(13)	0.45	

continued

Table 12. (continued)

KM	Concentrations			Rates (noon)		Ratio L/P	τ [O ₃]/L days
	[O ₃]	[ClO]	[O]	2 j[O ₂]	2 k[O][ClO]		
	10 ⁻¹²	10 ⁻⁸		P	L		
B. October 2, 1976. Solar angle 34°							
41	0.461	1.0	2.69(9)	2.11(7)	2.35(7)	1.11	0.23
40	0.579	1.3	2.19(9)	2.13(7)	2.49(7)	1.17	0.27
39	0.714	1.9	1.69(9)	2.13(7)	2.81(7)	1.32	0.29
38	0.872	3.4	1.30(9)	2.09(7)	3.86(7)	1.85	0.26
37	1.06	4.0	1.00(9)	2.03(7)	3.50(7)	1.72	0.31
36	1.27	3.75	7.62(8)	1.94(7)	2.50(7)	1.29	0.59
35	1.50	4.7	5.84(8)	1.81(7)	2.40(7)	1.33	0.72
34	1.81	5.3	4.61(8)	1.67(7)	2.14(7)	1.28	0.98
33	2.14	6.0	3.59(8)	1.50(7)	1.88(7)	1.26	1.32
32	2.47	6.4	2.78(8)	1.31(7)	1.56(7)	1.19	1.84
31	2.80	5.7	2.13(8)	1.13(7)	1.06(7)	0.94	3.0
30	3.12	5.3	1.61(8)	9.47(6)	7.46(6)	0.79	4.8
29	3.46	4.6	1.21(8)	7.76(6)	4.86(6)	0.63	8.2
28	3.76	5.3	8.92(7)	6.19(6)	4.13(6)	0.67	10
Σ 28 to 41, molecules cm ⁻² sec ⁻¹				2.22(13)	2.82(13)	1.27	

continued

Table 12. (continued)

KM	Concentrations			Rates (noon)		Ratio L/P	τ [O ₃]/L days
	$\frac{[O_3]}{10^{12}}$	$\frac{[ClO]}{10^8}$	[O]	$2 j_1 \frac{[O_2]}{P}$	$2 k [O][ClO]$ L		
C. December 8, 1976. Solar angle 54°.							
40	0.576	0.30	1.81(9)	1.63(7)	4.75(6)	0.29	1.4
39	0.674	0.40	1.36(9)	1.58(7)	4.75(6)	0.30	1.6
38	0.791	0.60	1.04(9)	1.52(7)	5.45(6)	0.36	1.7
37	0.952	0.74	8.11(8)	1.44(7)	5.25(6)	0.36	2.1
36	1.14	0.80	6.32(8)	1.34(7)	4.42(6)	0.33	3.0
35	1.33	0.80	4.81(8)	1.22(7)	3.36(6)	0.28	4.6
34	1.54	0.75	3.66(8)	1.10(7)	2.40(6)	0.22	7.4
33	1.77	0.65	2.77(8)	9.62(6)	1.57(6)	0.16	13
32	2.04	0.56	2.11(8)	8.21(6)	1.03(6)	0.13	23
31	2.33	0.47	1.62(8)	6.80(6)	6.65(5)	0.10	40
30	2.66	0.37	1.25(8)	5.42(6)	4.04(5)	0.075	76
29	3.03	0.34	9.55(7)	4.15(6)	2.84(5)	0.068	124
28	3.44	0.27	7.33(7)	3.03(6)	1.73(5)	0.057	230
27	3.88	0.29	5.60(7)	2.09(6)	1.42(5)	0.068	316
26	4.31	0.20	4.23(7)	1.36(6)	7.39(4)	0.054	675
25	4.73	0.17	3.15(7)	8.21(5)	4.68(4)	0.057	1170
Σ 25 to 40				1.40(13)	3.48(12)	0.25	

Table 13. Comparison of relative rates of production and loss of ozone.

Noon, July, north mid-latitudes.

KM	$[O_3]/P$ T HR	$(L/P)_{mid}$				$\Sigma L/P$		
		O_x Evans	HO_x Calc	NO_x Evans	ClX Anderson	Min	Mid	Max
40	5.3	0.18	0.04		0.28			
39		0.16			0.27			
38	8.3	0.15			0.56			
37		0.13			0.77			
36	14	0.13			0.81			
35	19	0.12	0.07	0.48	0.60	0.87	1.27	3.2
34	26	0.11	0.06	0.53	0.44	0.77	1.14	3.2
33	33	0.09	0.06	0.55	0.59	0.68	1.29	3.0
32	43	0.08	0.06	0.56	0.41	0.68	1.10	2.7
31	56	0.08	0.06	0.56	0.38	0.68	1.08	2.4
30	76	0.08	0.07	0.59	0.32	0.63	1.07	2.1
29	110	0.08	0.07	0.62	0.24	0.70	1.01	1.84
28	226	0.09	0.08	0.71	0.23	0.71	1.11	1.79
27	244	0.09	0.09	0.77	0.18	0.73	1.13	
26	374	0.10	0.11	0.83	0.17	0.75	1.21	
25	535	0.09	0.14	0.80	0.10	0.80	1.13	
24	786	0.09	0.18	0.87	0.12		1.27	
23	1427	0.12	0.24	1.13	0.05		1.54	
22		0.18	0.34	1.58				
21		0.22	0.52	1.89				
20		0.29	0.86	2.71				
$\Sigma L/\Sigma P$ 25 to 35 km		0.10	0.07	0.57	0.40		1.14	

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