Methane photooxidation in the atmosphere: Contrast between two methods of analysis

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Abstract. It is our opinion that over the past 20 years, some atmospheric scientists have used a scientifically incorrect method for finding the contribution of methane to changes in ozone. In any volume element of the atmosphere, the differential equation for ozone D is equal to gross production P minus gross loss L plus transport, which may be written $D = P(\text{methane}) - L(\text{methane}) + P(\text{not methane}) - L(\text{not methane}) + \text{transport}$. If both $P(\text{not methane})$ and $L(\text{not methane})$ are effectively zero, then the full differential equation is equal to the differential equation for the effect of methane, $D(\text{total}) = P(\text{methane}) - L(\text{methane}) + \text{transport}$. An approach was introduced around 1980 that has been widely used since then, with the valid assumption that in the lower troposphere the methane smog reactions are the only source of gross ozone production, $P(\text{methane})$. It concluded that the differential rate equation for total ozone change in such regions gives the net ozone change by the methane process (DE method). However, in the lowest troposphere, there are processes not caused by methane that destroy ozone at all altitudes (notably $O^1D + H_2O = 2OH$), so that L (not methane) is not zero, and thus $D = P(\text{methane}) - L(\text{methane}) - L(\text{not methane}) + \text{transport}$, making the DE method conceptually wrong everywhere. The object of this paper is to solve for how methane changes ozone in the troposphere and stratosphere. *Crutzen* [1973] gave the first treatment of ozone formation in the global troposphere via methane photooxidation. He considered radical attack on methane to produce CH_3 followed by three reaction sequences that go from CH_3 to CO_2, referred to here as the sequence (SEQ) method. The present study substantially extends Crutzen's sequence method: There are five significant branching points as methane is consumed and 34 sequences (different reaction paths) between CH_4 and CO, and more reactions lead to CO_2. A detailed derivation is given here, branching ratios are evaluated, and the results are presented as two complicated, closed, algebraic equations, which are valid from the surface up to the middle stratosphere. The SEQ method contains only ozone changes caused by the presence of methane. This method is implemented with output from the 1997 version of the Lawrence Livermore National Laboratory two-dimensional model. Assuming we carried out the SEQ method correctly, we find the DE method to be a fairly good numerical approximation in some areas and a poor numerical approximation in other areas. Averaged over the troposphere, the net effect of the methane smog process is to destroy OH at a rate 32% as fast as it is formed by the nonmethane process, $O^1D + H_2O = 2OH$. The integral over the global troposphere finds that the net rate of ozone production from methane by the DE is 2.2-fold slower than the SEQ method.
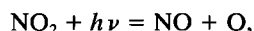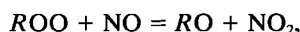
1. Introduction

1.1. Ozone Formation by Photocombustion of Volatile Organic Compounds (VOC)

1.1.1. Urban "smog." First noted in Los Angeles in the mid-1940s, the summer urban haze that irritated eyes, damaged rubber, and spoiled some agricultural plants was named

"smog." Haagen-Smit and coworkers in the early 1950s [*Haagen-Smit*, 1950, 1952; *Haagen-Smit et al.*, 1953; *Haagen-Smit and Fox*, 1954] discovered the overall process to be photochemical oxidation of organic vapors, which, in the presence of nitrogen oxides, produces ozone and complex organic products. *Cadle and Johnston* [1952] and *Johnston* [1956] proposed free radical mechanisms for Haagen-Smit's process. A large literature developed on the subject as summarized by *Starkman* [1970]. Urban and regional air pollution was reviewed and updated by the *National Research Council* [1991]. Ozone formation by organic peroxyl free radicals ROO occurs by way of the simple sequence

$$ROO + NO = RO + NO_2,$$

$$NO_2 + h\nu = NO + O,$$

$$\underline{O + O_2 + M = O_3 + M}$$

Net $\qquad$ $ROO + O_2 + O_3$ $\hfill$ (1)

The process is cyclic in NO_x and consumptive of organic compounds. Almost any gas phase organic specie or "organic volatile compound" (VOC) was found to form smog with NO_x and sunlight, and the organic chemical reactions are extremely complicated. One long-standing conclusion was that methane reacts so slowly with atoms and radicals that it is not important with respect to urban smog.
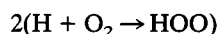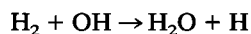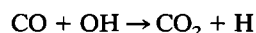
1.1.2. Methane photocombustion according to the sequence method (SEQ method). Although the photooxidation of methane is slow on the timescale of urban air pollution, Crutzen [1973] pointed out that on the timescale of air masses in the global troposphere the methane reactions are a significant source of tropospheric ozone, and this source is comparable to or greater than the transport of ozone to the troposphere from the stratosphere. Crutzen analyzed the problem in terms of the degradation series of structures that occurs as methane is slowly oxidized in the atmosphere:
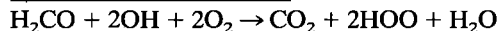
$$CH_4 \rightarrow CH_3 \rightarrow CH_3OO \rightarrow CH_3O$$

$$\rightarrow H_2CO \rightarrow HCO \rightarrow CO \rightarrow CO_2 \qquad (2a)$$
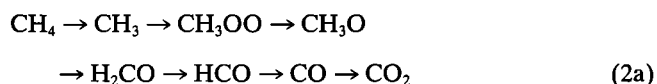
During the photochemical combustion of methane, hydroperoxyl free radicals HOO and CH_3OO radicals are formed as intermediates, which can react with NO to form NO_2 and then ozone (1). There are branch points along this series of structures, and Crutzen [1973] discussed three sequences that produced three, four, or five molecules of ozone for every methane that goes all the way to CO_2. Thus the rate of tropospheric ozone production is a small multiple of the rate of OH + $CH_4 = H_2O + CH_3$. The terms "branch points" and "sequences" are illustrated by (2b), which starts with formaldehyde. The photolysis of formaldehyde gives either H + HCO or H_2 + CO:
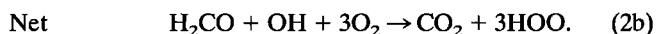
A branch point $\quad H_2CO\ (h\nu) \rightarrow HCO + H$

$\qquad\qquad\qquad H_2\,CO\ (h\nu) \rightarrow CO + H_2$
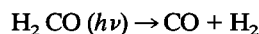
One of two sequences from formaldehyde to carbon dioxide is

A sequence $\quad H_2\,CO\ (h\nu) \rightarrow CO + H_2$

$\qquad\qquad CO + OH \rightarrow CO_2 + H$

$\qquad\qquad H_2 + OH \rightarrow H_2O + H$

$\qquad\qquad \underline{2(H + O_2 \rightarrow HOO)}$

Net $\qquad H_2CO + 2OH + 2O_2 \rightarrow CO_2 + 2HOO + H_2O$

The sequence of reactions starting with formaldehyde $\rightarrow H$ + HCO gives the net reaction

Net $\qquad H_2CO + OH + 3O_2 \rightarrow CO_2 + 3HOO.$ $\hfill$ (2b)

There are four sequences in the reactions between formaldehyde and ozone. Two of these sequences form three ozone molecules and two of these sequences destroy three molecules of ozone.

Quoting Crutzen [1973], Chameides and Walker [1973] discussed the effects of the methane reactions on the troposphere. Johnston and Quitevis [1975] said that if NO_x reactions produce ozone at ground level and destroy ozone in the strato-

sphere, there should be some altitude where these two processes cancel each other to give a region of ozone insensitivity to added NO_x. Following Crutzen's sequential analysis and using chemistry from the 1974 Lawrence Livermore National Laboratory (LLNL) one-dimensional atmospheric model and the Gear routine on the methane reaction sequences, Johnston and Quitevis found this altitude to be about 13 km. Johnston and Podolske [1978] analyzed six sequences from CH_4 to CO_2 and found paths of ozone change per methane destroyed with values from $+4$ to -2. Many of the ideas presented in this paper are discussed by Johnston and Podolske [1978]. This method is called the sequence method or SEQ sequence. Ravinshankara [1988] gives an in-depth review of the chemistry of atmospheric oxidation of methane. In this paper, we take output from the 1997 two-dimensional LLNL model and use it to extend Crutzen's original method, to recognize the significant branch points, to obtain 34 parallel reaction sequences for methane photodegradation to CO, derive branching ratios, and to evaluate the specific contribution of methane, carbon monoxide, and hydrogen reactions to gross ozone production P, gross ozone loss L, and the net change of ozone D.

1.1.3. Methane production of ozone from terms in a differential rate equation (DE method). Around 1980, there appeared a second method of interpreting the effect of methane reactions on ozone [Liu, 1977; Liu et al., 1980; Logan et al., 1981], which is much simpler than the method of following the degradation sequences by the SEQ method. In the lower troposphere the rate of ozone production by photolysis of molecular oxygen is essentially zero. It was argued that any change in ozone must then be caused by air transport or by local photochemical combustion of organic matter or both. Above the boundary layer, methane and carbon monoxide are the dominant volatile organic compounds, and it is assumed that any chemical production of ozone is caused by methane and carbon monoxide HO_x-NO_x "smog" chemistry, here called "the methane process."

1.1.4. Multiple definitions of gross ozone production and loss. In the framework of the DE method, anyone using the terms "gross ozone production" and "gross ozone loss" should define these terms, since the numerical values depends strongly on the definition of "odd oxygen." (1) If a chemical model makes no use of the concept of odd oxygen and no steady state assumptions, the leading positive term $P(O_3)$ in the ozone differential rate equation is the rate of $O + O_2 + M = O_3 + M$, with a typical troposphere value, $P_1 = 3 \times 10^9$ molecules $cm^{-3}\ s^{-1}$; and the leading loss term $L(O_3)$ is $O_3 + h\nu$ (uv-A and vis) $= O_2 + O, L_1 = 3 \times 10^9$. (2) If odd oxygen is defined as $O_x = O_3 + O + O^1D$, odd oxygen is essentially numerically equal to ozone, and the odd oxygen differential equation identically eliminates fast null cycles involving O_3, O, and O^1D. The leading positive term in the ozone differential equation becomes the rate of $NO_2 + h\nu = NO + O, P_2 = 3 \times 10^6$ molecules $cm^{-3}\ s^{-1}$, and the leading negative term is O_3 + NO $= O_2 + NO_2, L_2 = 3 \times 10^6$. (3) The DE method for the methane process is based on an extended definition of odd oxygen, namely,

$$O_x = O_3 + O + O^1D + NO_2, \qquad (3)$$
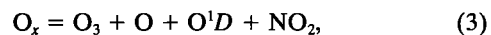
(some authors add other NO_y and/or Cl_y terms, but not including HOO or H). This definition of odd oxygen eliminates a fast null cycle involving NO, NO_2, O, and O_3. It is then (implicitly) assumed that all other ozone chemistry in the lower troposphere is driven by methane photocombustion, and thus
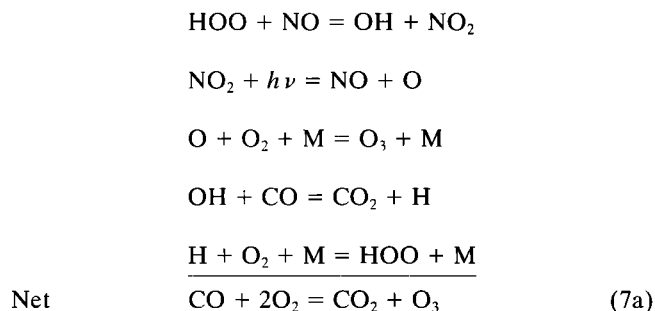
the terms in the differential equation can be interpreted as the contribution of methane reactions to ozone change. The leading positive terms in the extended odd oxygen differential equation are the rates of $CH_3OO + NO$ and $HOO + NO$, which are interpreted as gross ozone production P_{DE}; the leading negative terms, $O^1D + H_2O$, $O_3 + HOO$, and $O_3 + OH$, which are interpreted as gross ozone loss L_{DE}; and the net effect of methane chemistry on ozone is interpreted as $D_{DE} = P_{DE} - L_{DE}$. This interpretation is bewitchingly simple:

$$P_{DE}(O_3) = R(CH_3OO + NO) + R(HOO + NO) \quad (4)$$

$$L_{DE}(O_3) = R(O^1D + H_2O) + R(O_3 + HOO)$$
$$+ R(O_3 + OH) \quad (5)$$

$$D_{DE}(O_3) = P_{DE}(O_3) - L_{DE}(O_3) \quad (6)$$

(6) is identical to "ozone" differential chemical rate equation, where $R(\ \ )$ symbolizes the rate of the enclosed chemical reaction. Additional "minor terms" are noted and discarded in some articles. For the reasons cited above, many authors regard (4), applied in the lower troposphere, as the quantitative measure of gross ozone production by methane photooxidation and regard (5) as the quantitative measure of gross ozone loss due to methane photooxidation [e.g., *Liu et al.*, 1980; *Logan et al.*, 1981; *Levy et al.*, 1985; *Liu et al.*, 1987; *Law and Pyle*, 1993; *Lelieveld and Crutzen*, 1994; *Crutzen*, 1995]. The SEQ method and the DE method agree that $R(CH_3OO + NO)$ is a one-for-one measure of gross ozone production by the methane process in the troposphere. We believe that the interpretation of $R(HOO + NO)$ as a measure of gross ozone production due to methane and CO photooxidation is a conceptual error because the reaction $HOO + NO = OH + NO_2$ occurs in a sequence of reactions that form ozone (7a) and in a null cycle (7b) that does not form ozone. The rate $k[HOO][NO]$ appears with a positive sign in the ozone differential equation, and it indeed produces ozone through sequences such as

$$HOO + NO = OH + NO_2$$

$$NO_2 + h\nu = NO + O$$

$$O + O_2 + M = O_3 + M$$

$$OH + CO = CO_2 + H$$

$$H + O_2 + M = HOO + M$$

| Net | $CO + 2O_2 = CO_2 + O_3$ | (7a) |

but in some cases the reaction $HOO + NO$ is followed, not by $OH + CO$, but by $OH + O_3$ to give a null cycle:

$$HOO + NO \rightarrow NO_2 + OH$$

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

$$O_3 + OH \rightarrow O_2 + HOO$$

| Net | null | (7b) |
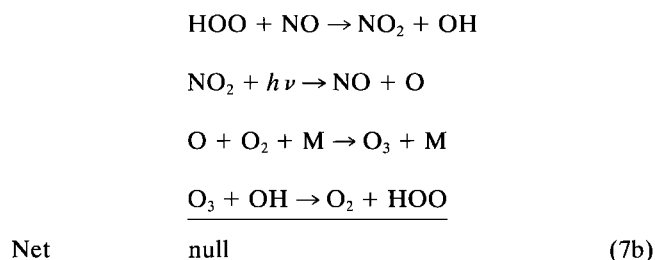
The DE method has eliminated the null cycle involving O_3 and O and the null cycle involving NO, NO_2, and O_3, but it has not

eliminated the null cycle including the reaction $HOO + NO$. Much more seriously, the DE method fails to recognize that a loss reaction not caused by methane is significant at all altitudes (see section 1.1.5).

The simplicity of the DE method arises in part because its users neglect a large number of minor terms in the ozone differential equation as approximated by the extended definition of odd oxygen (equation (3)). When (3) is used as the definition of odd oxygen (as it must be to obtain equations (4) and (5)) with the chemical mechanism of the LLNL model, there are 41 rate terms in the ozone differential equation, not just the five leading terms used by the DE method. It would require a special study to see if these 36 "minor terms" are indeed negligible. (The sequence method as we use it also eliminates some "minor terms," as described in section 2.1.)

If HOO or HOO + H is added to the definition of extended odd oxygen (3), the rate of reaction $HOO + NO = OH + NO_2$ drops out of the extended odd oxygen DE rate equation, and the P and L terms have different algebraic form and numerical values. This extension for odd oxygen eliminates the null cycle that includes the reaction $HOO + NO = OH + NO_2$. The leading production terms are $OH + CO = CO_2 + H$ and $CH_3OO + NO = CH_3O + NO_2$. "Gross ozone production" and "gross ozone loss" are artificial concepts and require explicit definitions.

1.1.5. Failure of the DE method to recognize a large ozone loss process in the lower stratosphere that is not due to methane. The methane reactions do not contribute to the reaction $O^1D + H_2O = 2OH$. This reaction contributes heavily to ozone loss all the way to Earth's surface, activated by transported ozone and any other ozone present. The basic assumption of the DE method is that where there is no nonmethane ozone gross production there is also no nonmethane gross ozone loss. At all altitudes the DE method fails to give the correct algebraic expression of gross ozone loss caused by methane. The DE method gives an almost valid expression for gross ozone production in the lower troposphere from methane, it gives a strong gross loss term throughout the troposphere, and the net production of ozone from methane is always underestimated by the DE method. According to the analysis here, at all altitudes the DE method is scientifically wrong.

1.2. Ultrasimple Illustration of the Principles of the SEQ and DE Methods

1.2.1. Gross ozone production from CO oxidation. Experienced readers may skip this section, where we give an ultrashort set of reactions as an ultrasimple illustration of the nature of the SEQ method. We give here the much simpler derivation of the SEQ method for the case of CO as the only VOC. Table 1 has a highly simplified mechanism of ozone chemistry in the troposphere. The top part of Table 1 gives reactions initiated by $O^1D + H_2O$ in the absence or presence of CO. The middle part gives ozone-related reactions that occur in a troposphere with transported ozone even if there is no VOC, and the bottom part gives reactions that occur in a troposphere with CO as the only VOC. We make a statement with words and then express it in algebra: The rate of chemical ozone production is the rate of formation of HOO by CO, $R(OH + CO)$, multiplied by the fraction $d1$ of this HOO that reacts with NO. From Table 1, we see that $d1 = R(HOO + NO)/[R(HOO + NO) + R(HOO + O3)]$. This ozone production from CO derived by analysis of the sequence of reactions

Table 1. Reactions That Occur in the Absence of Methane, Hydrogen, Carbon Monoxide, or Other Volatile Organic Compounds and in the Additional Reactions That Occur Upon Addition of Carbon Monoxide

	Reaction[a]
Initiation of HO_x	$O_3 + h\nu = O_2 + O^1D + H_2O \rightarrow O + M, O^1D + H_2O \rightarrow 2OH$
Termination of HO_x	$OH + HOO = H_2O + O_2; OH + NO_2 = HNO_3, OH + HNO_3 = H_2O$, etc.

Reactions With O_x, HO_x, NO_x[b]	Additional Reactions With Only CO Added
$O^1D + H_2O \rightarrow 2OH$	no change caused by addition of CO
Cyclic reactions (a) and (b)	cyclic reactions (c) and (d)

	Reaction (a)	Reaction (b)	Reaction (c)	Reaction (d)
	$OH + O3 = HOO + O_2$	$OH + O_3 = HOO + O_2$	$OH + CO = CO_2 + H$	$OH + CO = CO_2 + H$
	$HOO = O_3 = OH + 2O_2$	$HOO + NO = OH + NO_2$	$H + O_2 + M = HOO + M$	$H + O_2 + M = HOO + M$
		$NO2 + h\nu = NO + O$	$HOO + NO = OH + NO_2$	$HOO + O_3 = OH + 2O_2$
		$O + O_2 + M = O_3 + M$	$NO2 + h\nu = NO + O$	
			$O + O_2 + M = O_3 + M$	
Net	$2O_3 = 3O_2$	null	$CO + 2O_2 = CO_2 + O_3$	$CO + O_3 = CO_2 + O_2$
ΔO_3	-2	0	$+1$	-1

[a]These reactions establish $[OH]_{steady\ state}$.
[b]In the absence of CH_4, CO, H_2 or other VOC.

is given here in terms of rate constants and specie concentrations:

$$P_{SEQ}(O_3)_{CO} = k_1[OH][CO]\frac{k_2[HOO][NO]}{k_2[HOO][NO] + k_3[HOO][O3]}$$

(8)

Expression (8) goes to zero in the limit of zero fuel; at this limit, (4) does not go to zero, as it should, but it goes to $R(HOO + NO = OH + NO_2)$, the positive branch of the null cycle (7). Both expressions properly go to zero in the limit of zero nitric oxide.

1.2.2. Gross ozone loss from CO oxidation. The rate of ozone loss from CO is the rate of formation of HOO by CO, $R(OH + CO)$, multiplied by the fraction $d2$ of this HOO that reacts with ozone. From Table 1, we see that $d2 = R(HOO + O_3)/[R(HOO + NO) + R(HOO + O3)]$. This ozone loss from CO derived by analysis of the sequence of reactions is given here in terms of rate constants and specie concentrations:

$$L_{SEQ}(O_3)_{CO} = k_1[OH][CO]\frac{k_3[HOO][O_3]}{k_2[HOO][NO] + k_3[HOO][O3]}$$

(9)

1.2.3. Net ozone change from CO oxidation. With the mechanism of Figure 1, the net change of ozone brought about by the reaction of CO is $D_{SEQ}(O_3)_{CO} = P_{SEQ}(O_3)_{CO} - L_{SEQ}(O_3)_{CO}$. From (8) and (9) this is seen to be

$$D_{SEQ}(O_3)_{CO} = k_1[OH][CO]\frac{k_2[HOO][NO] - k_3[HOO][O_3]}{k_2[HOO][NO] + k_3[HOO][O_3]}$$

(10a)

The net change of ozone caused by CO according to the SEQ method (10a) is not the same as that from the ozone differential equation (6):

$$D_{DE}(O_3)_{CO} = k_2[HOO][NO] - k_3[HOO][O_3]$$

$$- k_4[OH][O_3] - k_5[O^1D][H_2O]$$

(10b)

The portion of ozone destruction by OH and HOO caused by transported ozone and not caused by CO, (Table 1) is included in (10b) but not in (10a). The portion of ozone loss represented by $O^1D + H_2O$ generated from transported ozone and not from CO appears in (10b) but not in (10a). The differential rate equation (DE method, equation (10b)) accounts for all ozone changes, but the SEQ method (equation (10a)) accounts only for the component of ozone change caused by the reaction of carbon monoxide. Regardless of the definition of odd oxygen, the differential rate equation does not resolve this component at any altitude.

1.2.4. Introduction to next sections. One purpose of this article is to use the LLNL model to compare values of $P_{DE}(O_3)$, $L_{DE}(O_3)$, and $D_{DE}(O_3)$ derived by (4) and (5) with values derived by an extended version of Crutzen's more nearly rigorous sequence method to see if this lack of rigor is numerically important. Section 2 gives a detailed derivation of the sequence method (SEQ method) of finding the methane process components of tropospheric and stratospheric ozone change and produces closed algebraic formulas. Section 3 examines the numerical differences between the two methods of estimating the effects of methane photooxidation on tropospheric ozone, according to values taken from the LLNL two-dimensional (2-D) model.

2. Derivation

2.1. Branch Points Along the Methane Reaction Series

To calculate the gross and net rate of ozone change from the methane photocombustion process with the full LLNL chemical mechanism, we start with the rate of conversion of CH_4 to CH_3 and trace the series of carbon-containing structures to CO product. If more than one reaction converts one structure to a later structure, that constitutes a "branching point." We evaluate the "branching probability," which is the normalized relative rate of the two (or more) steps between two successive structures, for all the branching processes that occur between CH_4 and CO. After a long tedious derivation, we present algebraic equations that can be used to carry out this proce-
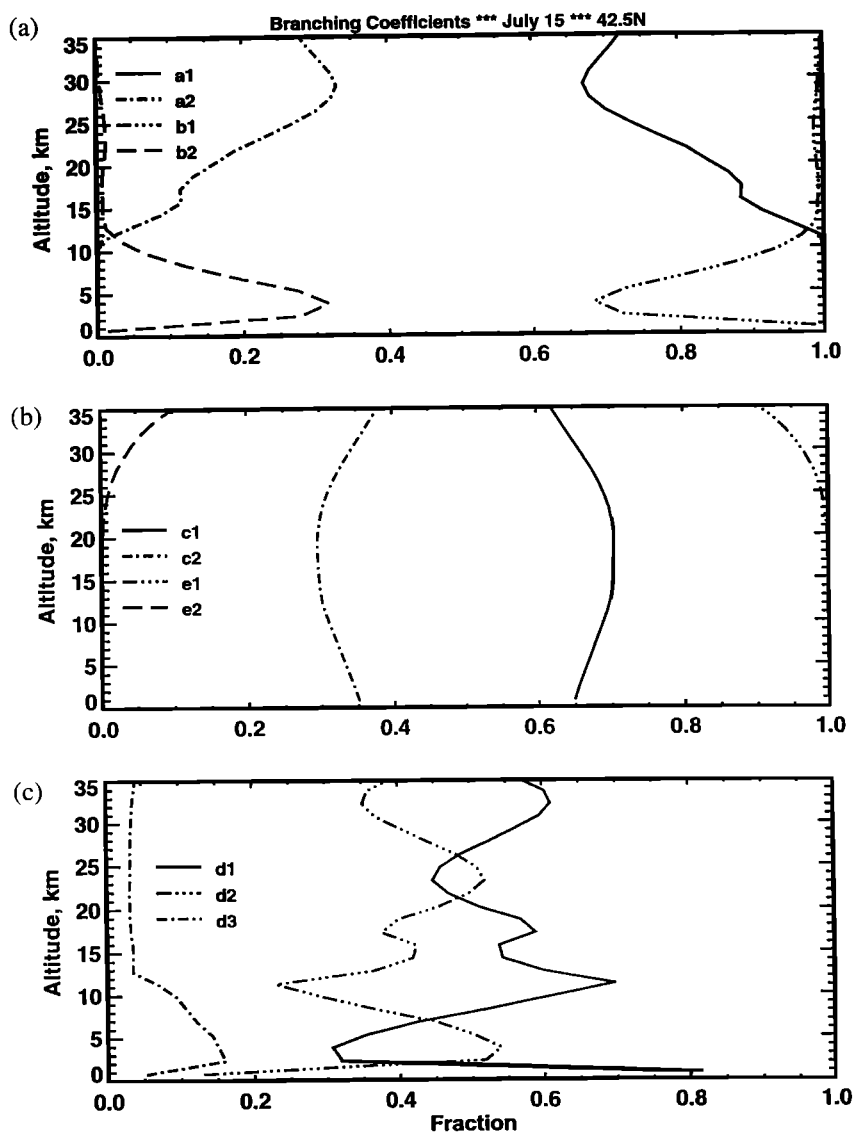
Figure 1. Branching ratios as a function of altitude from 1.5 to 35 km. (a) Probability of initiation: $a1$ (OH + CH_4 or Cl + CH_4); $a2$, initiation by O^1D + CH_4 = OH + CH_3. Probability of CH_3OO branches: $b1$, CH_3OO + NO; $b2$, (CH_3OO + HOO and CH_3OOH + $h\nu$ = CH_3 + OH). (b) Probability of formaldehyde photolysis products: $c1$, CO + H_2; $c2$, H + HCO. Probability of NO_2 branches: $e1$, photolysis; $e2$, reaction with O. (c) Probability of HOO branches: $d1$, HOO + NO; $d2$, sum of five reactions or short sequences that have the net reaction of HOO + O_3; $d3$, sum of three reactions or short sequences that have net reaction HOO + OH. These branching probabilities are based on (15), (16), (18), (20), (21), (23), and (25). LLNL 2-D model of 1997, July, diurnal average, 42.5N, 3 ppb Cl_y.
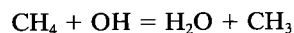
dure. Then we add the contribution of the CO and H_2 reactions, regarding CO and H_2 as independent species that is not solely derived from methane.

For each specie in the LLNL model we rank the rates of its formation and of its loss in decreasing order of rate at 3, 7, 10, 15, 20, 25, and 31 km. We use these data tables to identify significant branching points and to omit a branch that is <1% of the dominant branch or with rate less than 10 molecules cm^{-3} s^{-1}. The methane reaction process is consumptive, not cyclic, with respect to carbon compounds; it is cyclic with respect to free radicals, OH and HOO, and with respect to nitrogen oxides, NO and NO_2. In the series of carbon-containing species (2), there are three branching points: CH_4, CH_3OO, and H_2CO. After these are accounted for, there are
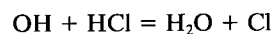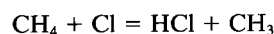
three important paths between HOO and OH, and there is a pair of significant paths between NO_2 and NO.

The process is initiated by three reactions, but the first two are chemically equivalent. The two chemically different initiation processes are
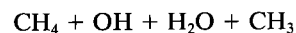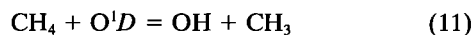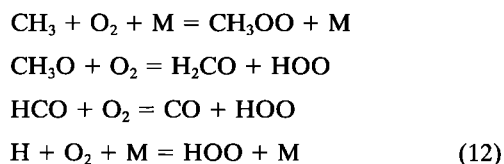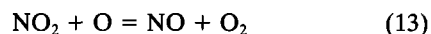
Initial process

$$CH_4 + OH = H_2O + CH_3$$

or

$$CH_4 + Cl = HCl + CH_3$$

$$OH + HCl = H_2O + Cl$$

Net $\qquad CH_4 + OH + H_2O + CH_3$

Initiation process

$$CH_4 + O^1D = OH + CH_3 \tag{11}$$

In the series of structures between CH_4 and CO, some species undergo just one significant reaction

$$CH_3 + O_2 + M = CH_3OO + M$$

$$CH_3O + O_2 = H_2CO + HOO$$

$$HCO + O_2 = CO + HOO$$

$$H + O_2 + M = HOO + M \tag{12}$$

but others undergo two or more significant reactions:

$$CH_3OO + NO = CH_3O + NO_2 \quad \text{versus}$$

$$CH_3OO + HOO = CH_3OOH + O2$$

$$H_2CO + h\nu = H_2 + CO \quad \text{versus}$$

$$H_2CO + h\nu = H + HCO$$

$$HOO + NO = OH + NO_2 \quad \text{versus}$$

$$HOO + O_3 = OH + 2O_2$$

$$OH + HOO = H_2O + O_2$$

$$NO_2 + h\nu = NO + O \quad \text{versus}$$

$$NO_2 + O = NO + O_2 \tag{13}$$
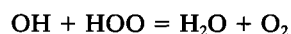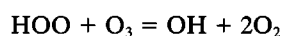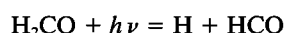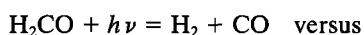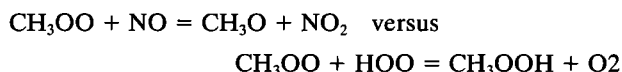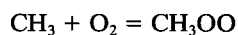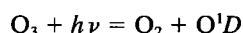
With one pair of chemically different initiation reactions and four branching points (equations (12) and (13)), one of which is threefold, there could be $2^4 \times 3 = 48$ different paths between CH_4 and CO. We carry out an algebraic treatment of the methane photocombustion in terms of these paths, evaluate the probability of each branch at each branching point, find the weighted sum over these multiple paths, and present here the algebraic equations and some of the results. We present 11 modules for reaction sequences between each branching point and the next: A1, A2, B1, B2, C1, C2, D1, D2, D3, E1, E2. We derive 11 branching probabilities between each module: $a1$ to $e2$.

2.2. Modules of Repeated Sequences in Methane Photocombustion

2.2.1. From methane to CH_3OO, A1 and A2, a1 and a2.
We list and sum the chemical reactions between CH_4 and CH_3OO to give the net reaction of that segment of the conversion of CH_4 to CO.

A1 $CH_4 + OH = H_2O + CH_3$, $Cl + CH_4 = HCl + CH_3$,
see (11)

$$CH_3 + O_2 = CH_3OO$$

A1 net CH$_4$ + OH + O$_2$ = H$_2$O + CH$_3$OO $\tag{14a}$

A2 $O^1D + CH_4 = OH + CH_3$ (rds)
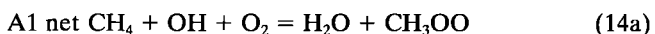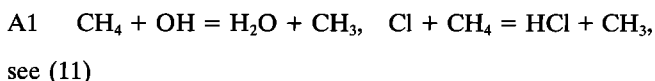
where rds is rate determining step

$$O_3 + h\nu = O_2 + O^1D$$

$$CH_3 + O_2 = CH_3OO$$
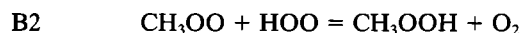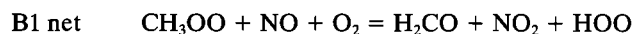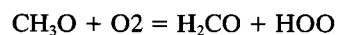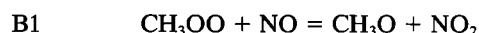
A2 net   CH$_4$ + O$_3$ = CH$_3$OO + OH $\tag{14b}$

The probability $a1$ that the reaction sequence goes according to module A1 is equal to the sum of the two A1 initiation rates divided by the sum of all three initiation rates, where $R(OH + CH4)$ symbolizes the rate of $CH_4 + OH = H_2O + CH_3$, etc.

$$a1 = \frac{R(OH + CH_4) + R(Cl + CH_4)}{R(OH + CH_4) + R(Cl + CH_4) + R(O^1D + CH_4)} \tag{15}$$

The probability $a2$ that the reaction sequence goes according to module A2 could be written $1-a1$, but the full expression is used here and elsewhere.

$$a2 = \frac{R(O^1D + CH_4)}{R(OH + CH_4) + R(Cl + CH_4) + R(O^1D + CH_4)} \tag{16}$$

2.2.2. From CH_3OO to formaldehyde, B1 and B2, b1 and b2.
Over most of the atmosphere, CH_3OO reacts primarily with NO (sequence B1), but CH_3OO reacts at a significant rate with HOO in the lower troposphere (sequence B2).

B1 $CH_3OO + NO = CH_3O + NO_2$

          $CH_3O + O2 = H_2CO + HOO$

B1 net $CH_3OO + NO + O_2 = H_2CO + NO_2 + HOO$

$$\tag{17a}$$

B2 $CH_3OO + HOO = CH_3OOH + O_2$

          $CH_3OOH + h\nu = CH_3O + OH$ (rds)

          $CH_3O + O_2 = H_2CO + HOO$

B2 net $CH_3OO = H_2CO + OH$ $\tag{17b}$

The pair of reactions

$$CH_3OO + HOO = CH_3OOH + O_2$$

$$CH_3OOH + OH = CH3OO + H_2O \quad \text{(rds)}$$

Net   HOO + OH = H$_2$O + O$_2$ $\tag{17c}$
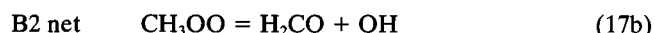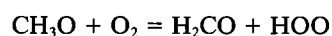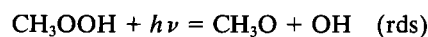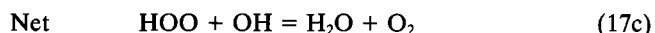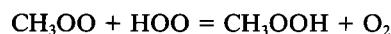
is cyclic in CH_3OO and CH_3OOH, with loss of two HO_x. This reaction has no effect on ozone or the concentrations of CH_3OO and CH_3OOH, but it is an important sink for HO_x in the lowest troposphere.

The branching probabilities, $b1$ and $b2$, are constructed by the relative rates of the branch-point reactions:

$$b1 = \frac{R(CH_3OO + NO)}{R(CH_3OO + NO) + R(CH_3OOH + h\nu)} \tag{18a}$$

$$b2 = \frac{R(CH_3OOH + h\nu)}{R(CH_3OO + NO) + R(CH_3OOH + h\nu)} \tag{18b}$$

We evaluate the rates of all reactions by the LLNL 2-D 1997 model, and from these rates we calculate the branching ratios. Figure 1a shows the relative probabilities of the initiation reactions, $a1$ and $a2$. The fraction of initiation by $O^1D(a2)$ increases almost linearly with altitude from value essentially zero at 12 km to almost 0.4 at 30 km, and it decreases from 30 to 35 km. In the troposphere the attack on CH_4 is essentially

only by OH + CH_4. The fractional contribution of OH and Cl to initiation ($a1$) is a mirror image of $a2$ on Figure 1, and it accounts for at least 60% at all altitudes up to the top of the stratosphere. Figure 1a also shows the branching ratios between the reactions CH_3OO + NO and CH_3OO + HOO followed by photolysis of CH_3OOH. The path $b1$, CH_3OO + NO, dominates at all altitudes, but the other path makes a significant contribution in the troposphere, between 2 and 10 km.

2.2.3. Formaldehyde to CO. Photolysis of formaldehyde leads to two pairs of products, H_2 + CO and HCO + H. As before, we write out the two competing reaction modules, C1 and C2, and the two reaction probabilities, $c1$ and $c2$:

C1	$H_2CO + h\nu = H_2 + CO$
C2	$H_2CO + h\nu = HCO + H$
	$HCO + O_2 = CO + HOO$
	$H + O_2 + M = HOO + M$
C2 net	$H_2CO + 2O_2 = CO + 2HOO$ (19)
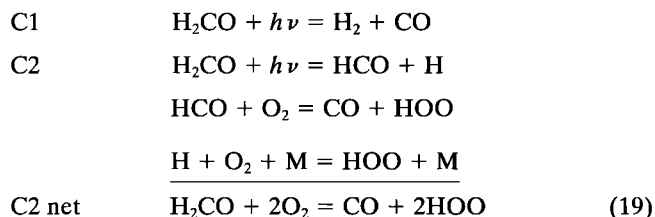
$$c1 =$$
$$\frac{R(H_2CO + h\nu = H_2 + CO)}{R(H_2CO + h\nu = H_2 + CO) + R(H_2CO + h\nu = HCO + H)}$$
(20)

$$c2 =$$
$$\frac{R(H_2CO + h\nu = H + HCO)}{R(H_2CO + h\nu = H_2 + CO) + R(H_2CO + h\nu = HCO + H)}$$
(21)

This reaction path, $c2$, produces two additional units of HO_x, which is an important source of HO_x at some altitudes. Figure 1b gives the branching ratios between the two channels of formaldehyde photolysis. To a first approximation, the products H_2 + CO are formed two thirds of the time, and the products H + HCO are formed one third of the time. Figure 1 shows that $c1$ and $c2$ have only a slight altitude dependence.

2.3. Branching by HOO and NO_2 Reactions

2.3.1. Reactions of HOO. Important reactions of HOO are with NO, O_3, and OH, but there are also four significant reaction sequences that have the same net reaction as that of HOO plus ozone. Reaction of HOO with NO leads to ozone formation (D1), and the direct (D2-1) and four indirect (D2-2, D2-3, D2-4, and D2-5) reactions of HOO with O_3 give ozone loss:

D1	$HOO + NO = OH + NO_2$	(22a)
D2		
D2-1	$HOO + O_3 = OH + 2O_2$	
D2-2	$HOO + O = OH + O_2$	
	$O_3 + h\nu = O_2 + O$	(22b)
Net	$HOO + O_3 = OH + 2O_2$	(22c)
D2-3	$HOO + ClO = HOCl + O_2$	
	$HOCl + h\nu = OH + Cl$	
	$Cl + O_3 = ClO + O_2$	
Net	$HOO + O_3 = OH + 2O_2$	(22d)

D2-4	Same as D2-3 with Cl replaced by Br	
D2-5	$HOO + HOO = H_2O_2 + O_2$	
	$H_2O_2 + h\nu = 2HO$ (rds)	
	$OH + O_3 = HOO + O_2$	
Net	$HOO + O_3 = OH + 2O_2$	(22e)
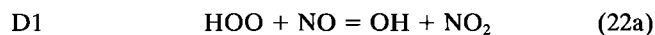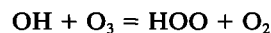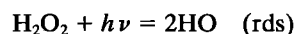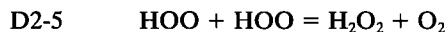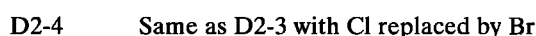
Process D has a third branching point (D3-1) and two reaction pairs (D3-2 and D3-3) with the same net reaction

D3		
D3-1	$HOO + OH = H_2O + O_2$	
D3-2	$HOO + HOO = H_2O_2 + O_2$	
	$H_2O_2 + OH = H_2O + HOO$ (rds)	
Net	$HOO + OH = H_2O + O_2$	
D3-3	$HOO + NO_2 = HOONO_2$	
	$HOONO_2 + OH = H_2O + NO_2 + O_2$ (rds)	
Net	$HOO + OH = H_2O + O_2$	
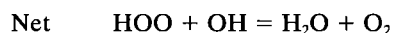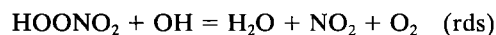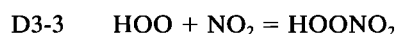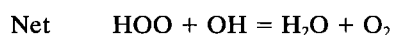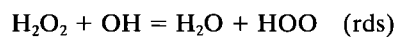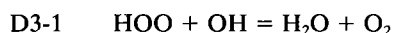
The $d1$, $d2$, and $d3$ branch points require complicated fractions to represent the parallel paths between HOO and OH. By letting X be a symbol for the denominator of a fraction, the equations for these branching ratios are reduced to a reasonable size.

$$X = R(HOO + NO) + R(HOO + O_3) + R(HOO + O)$$
$$+ R(HOO + ClO) + R(HOO + BrO)$$
$$+ R(H_2O_2 + h\nu) + R(HOO + OH) + R(H_2O_2 + OH)$$
$$+ R(HOONO_2 + OH)$$

$$d1 = R(HOO + NO)/X$$ (23a)

$$d2 = [R(HOO + O_3) + R(HOO + O) + R(HOO + ClO)$$
$$+ R(HOO + BrO) + R(H_2O_2 + h\nu)]/X$$ (23b)

$$d3 = [R(HOO + OH) + R(H_2O_2 + OH)$$
$$+ R(HOONO_2 + OH)]/X$$ (23c)

The $d1$–$d2$ branching is especially important, since HOO + NO may lead to ozone production and the other reactions lead to ozone loss by the methane smog process. Fou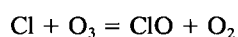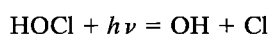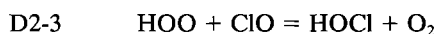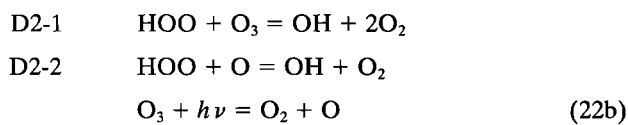r reactions of HOO that are directly or indirectly HOO + O_3 = OH + $2O_2$ compete with HOO + NO as given by $d2$, and these four reactions are important at different altitudes, which explains the complex vertical profiles of $d1$ and $d2$ in Figure 1, and the contribution of $d3$ explains the lack of symmetry of $d1$ and $d2$.

2.3.2. Branching by way of NO_2 reactions. The NO_2 formed by HOO + NO or CH_3OO + NO may photodissociate into NO + O with production of ozone or react with atomic oxygen NO_2 + O = NO + O_2 with loss of ozone. This branching point needs to be considered when we extend this procedure into the stratosphere

E1	$NO_2 + h\nu = NO + O$	
	$O + O_2 = O_3$	
E1 net	$NO_2 + O_2 = NO + O_3$	(24a)
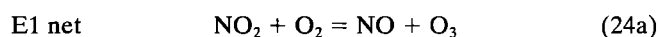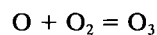
Table 2. Net Chemical Reactions in Going From CH_4 to CO Along 34 Paths

Path i	Modules i	Net Reaction i	ΔO_3	ΔOH
1	A1 + B1 + C1 + D1 + 2E1	$CH_4 + 4O_2 = CO + H_2 + H_2O + 2O_3$	+2	0
2	A1 + B1 + C1 + D1 + 2E2	$CH_4 + 2O_3 = CO + H_2 + H_2O + 2O_2$	−2	0
3	A1 + B1 + C1 + D2 + E1	$CH_4 + O_2 = CO + H_2 + H_2O$	0	0
4	A1 + B1 + C1 + D2 + E2	$CH_4 + 2O_3 = CO + H_2 + H_2O + 2O_2$	−2	0
5	A1 + B1 + C1 + D3 + E1	$CH_4 + 2O_2 + 2OH = CO + H_2 + 2H_2O + O_3$	+1	−2
6	A1 + B1 + C1 + D3 + E2	$CH_4 + 2OH + O_3 = CO + H_2 + 2H_2O + O_2$	−1	−2
7	A1 + B1 + C2 + 3D1 + 4E1	$CH_4 + 8O_2 = CO + H_2O + 4O_3 + 2OH$	+4	+2
8	A1 + B1 + C2 + 3D1 + 4E2	$CH_4 + 4O_3 = CO + H_2O + 4O_2 + 2OH$	−4	+2
9	A1 + B1 + C2 + 3D2 + E1	$CH_4 + 2O_3 = CO + H_2O + O2 + 2OH$	−2	+2
10	A1 + B1 + C2 + 3D2 + E2	$CH_4 + 4O_3 = CO + H_2O + 4O_2 + 2OH$	−4	+2
11	A1 + B1 + C2 + 3D3 + E1	$CH_4 + 2O_2 + 4OH = CO + 4H_2O + O_3$	+1	−4
12	A1 + B1 + C2 + 3D3 + E2	$CH_4 + O_3 + 4OH = CO + 4H_2O + O_2$	−1	−4
13	A1 + B2 + C1	$CH_4 + O_2 = CO + H_2 + H_2O$	0	0
14	A1 + B2 + C2 + 2D1 + 2E1	$CH_4 + 5O_2 = CO + H_2O + 2O_3 + 2OH$	+2	+2
15	A1 + B2 + C2 + 2D1 + 2E2	$CH_4 + 2O_3 = CO + H_2O + O_2 + 2OH$	−2	+2
16	A1 + B2 + C2 + 2D2	$CH_4 + 2O_3 = CO + H_2O + O_2 + 2OH$	−2	+2
17	A1 + B2 + C2 + 2D3	$CH_4 + O_2 + 2OH = CO + 3H_2O$	0	−2
18	A2 + B1 + C1 + D1 + 2E1	$CH_4 + 3O_2 = CO + H_2 + O_3 + 2OH$	+1	+2
19	A2 + B1 + C1 + D1 + 2E2	$CH_4 + 3O_3 = CO + H_2 + 3O_2 + 2OH$	−3	+2
20	A2 + B1 + C1 + D2 + E1	$CH_4 + O_3 = CO + H_2 + 2OH$	−1	+2
21	A2 + B1 + C1 + D2 + E2	$CH_4 + 3O_3 = CO + H_2 + 3O_2 + 2OH$	−3	+2
22	A2 + B1 + C1 + D3 + E1	$CH_4 + O_2 = CO + H_2 + H_2O$	0	0
23	A2 + B1 + C1 + D3 + E2	$CH_4 + 2O_3 = CO + H_2 + H_2O$	−2	0
24	A2 + B1 + C2 + 3D1 + 4E1	$CH_4 + 7O_2 = CO + 3O_3 + 4OH$	+3	+4
25	A2 + B1 + C2 + 3D1 + 4E2	$CH_4 + 5O_3 = CO + 5O_2 + 4OH$	−5	+4
26	A2 + B1 + C2 + 3D2 + E1	$CH_4 + 3O_3 = CO + 2O_2 + 4OH$	−3	+4
27	A2 + B1 + C2 + 3D2 + E2	$CH_4 + 5O_3 = CO + 5O_2 + 4OH$	−5	+4
28	A2 + B1 + C2 + 3D3 + E1	$CH_4 + 2OH + O_2 = CO + 3H_2O$	0	−2
29	A2 + B1 + C2 + 3D3 + E2	$CH_4 + 2O_3 + 2OH = CO + 2O_2 + 3H_2O$	−2	−2
30	A2 + B2 + C1	$CH_4 + O_3 = CO + H_2 + 2OH$	−1	+2
31	A2 + B2 + C2 + 2D1 + 2E1	$CH_4 + 4O_2 = CO + O_3 + 4OH$	+1	+4
32	A2 + B2 + C2 + 2D1 + 2E2	$CH_4 + 3O_3 = CO + 2O_2 + 4OH$	−3	+4
33	A2 + B2 + C2 + 2D2	$CH_4 + 3O_3 = CO + 2O_2 + 4OH$	−3	+4
34	A2 + B2 + C2 + 2D3	$CH_4 + O_3 = CO + 2H_2O$	−1	0

Modules A1 to E2 are defined by (14), (17), (19), (22), and (24), and these equations give the net reaction for each module.

E2 $O_3 + h\nu = O_2 + O$

         $O + NO_2 = NO + O_2$

E2 net $O_3 + NO_2 = NO + 2O_2$ (24b)
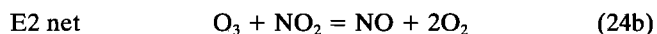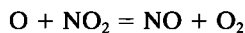
$$e1 = \frac{R(NO_2 + h\nu)}{R(NO_2 + h\nu) + R(NO_2 + O)} \quad (25a)$$

$$e2 = \frac{(NO_2 + O)}{R(NO_2 + h\nu) + R(NO_2 + O)} \quad (25b)$$

These branching ratios are shown by Figure 1b. The fractional contribution of $NO_2 + O$ ($c2$) is small below 24 km, but the rate $NO_2 + O$ exceeds that of $OH + CH_4$ down to 15 km under conditions of Figure 1. Notice that reactions such as $OH + NO_2 + M = HNO_3 + M$ are not included in the denominators of (25), because the rate of these reactions is <1% of that of the reactions $NO_2 + h\nu = NO + O$.

2.4. Combine Modules Between CH_4 and CO

2.4.1. Module {1, 1, 1, 1, 1} as example. We sum the net reactions of modules A1, B1, and C1, to find the coefficients for D1 and E1:

A1 net $CH_4 + OH + O_2 = H_2O + CH_3OO$

B1 net $CH_3OO + NO + O_2 = H_2CO + NO_2 + HOO$

C1 net $H_2CO + h\nu = CO + H_2$

Net {1, 1, 1} $CH_4 + OH + NO + 2O_2$

                 $= CO + H_2 + H_2O + HOO + NO_2$ (26)
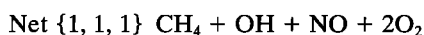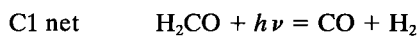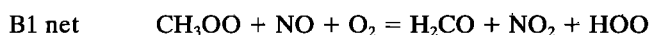
The stoichiometric coefficient of HOO is 1, and thus one unit of D1 is required. One unit of D1 includes one unit of NO and NO_2, and the net reaction of (A1, B1, C1) includes one unit of NO and NO_2. Thus two units of E1 are required, and path (A1, B1, C1, D1, E1) or {1, 1, 1, 1, 1} is obtained, with complete balance of NO_x and HO_x:

Net {1, 1, 1} $CH_4 + OH + NO + 2O_2$

                   $= CO + H_2 + H_2O + HOO + NO_2$

Net D1 $HOO + NO = OH + NO_2$

Net 2 E1 $2(NO_2 + O_2 = NO + O_3)$

Net {1, 1, 1, 1, 1} $CH_4 + 4O_2$

                   $= CO + H_2 + H_2O + 2O_3$ (27)
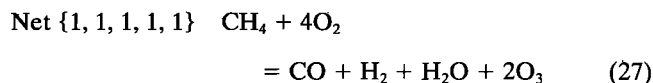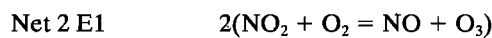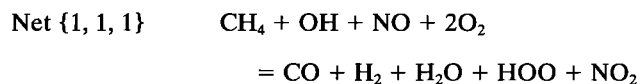
Methane is converted to CO, H_2, and H_2O, and two molecules of ozone are produced by path 1 to give the first row in Table 2. The permutations of D1, D2, D3, E1, and E2 give the first six paths in Table 2.

2.4.2. Module {1, 1, 2, 1, 1} as a qualitatively different example. The path {1, 1, 2} contains a different feature from path {1, 1, 1}: the reaction $H_2CO + h\nu = HCO + H$ increases the net amount of odd hydrogen, and this reaction causes the increase in HO_x in module C2:

A1 net $CH_4 + OH + O_2 = H_2O + CH_3OO$

B1 net $CH_3OO + NO + O_2$

$$= H_2CO + NO_2 + HOO$$

C2 net $H_2CO + 2O_2 = CO + 2HOO$

Net {1, 1, 2} $CH_4 + OH + 4O_2 + NO$

$$= CO + H_2O + 3HOO + NO_2 \quad (28)$$

The coefficient of HOO is 3, so that three units of D1 are required to balance HOO in net {1, 1, 2}. Three units of D1 include three units of NO and NO_2, and the net reaction of (A1, B1, C2) includes one unit of NO and NO2. Thus four units of E1 are required, and path {1, 1, 2, 1, 1} is

Net {1, 1, 2} $CH_4 + OH + 4O_2 + NO$

$$= CO + H_2O + 3HOO + NO_2$$

Net 3D1 $3(HOO + NO = OH + NO_2)$

Net 4E1 $4(NO_2 + O_2 = NO + O_3)$

Net {1, 1, 2, 1, 1} $CH_4 + 8O_2$

$$= CO + H_2O + 4O_3 + 2OH \quad (29)$$

This reaction produces two units of OH. The OH generated by methane photocombustion goes into the pool produced by $O^1D + H_2O$ and is spread out over a large number of reactions. Path {1, 1, 2, 1, 1} is path 7 in Table 2. The other paths in Table 1 are constructed by the method as illustrated above by path {1, 1, 1, 1, 1} and path {1, 1, 2, 1, 1}.

2.4.3. Rules of compound probability. If there are two independent events, x and y, with probabilities Π_x and Π_y, the probability of x and y is the product: $\Pi_{x \text{ and } y} = \Pi_x \times \Pi_y$; the probability of x or y is the sum $\Pi_x + \Pi_y$. We have evaluated the probability of each initiation of the methane reaction sequence, $a1$ and $a2$, and the branching probability at each branch point, $b1$, $b2$, $c1$, $c2$, $d1$, $d2$, $d3$, $e1$, and $e2$. The probability of a given path i, Π_i, for a specified initiation "ai and branch bi and branch ci and branch di and branch ei" is the product $\Pi_i = ai\ bi\ ci\ di\ ei$. The rate of that path is the rate of initiation times the probability of the path, R(initiation) $\times \Pi_i$. The rate of change of ozone due to path i, R_i, is R(initiation) $\times P_i \times (\Delta O_3)_i$, where the stoichiometric factors ΔO_3 can be found by inspection of the net reactions and is given for each path in Table 2. The net rate of change of ozone as a result of the methane going from CH_4 to CO is the sum (operation "or") of R_i over every path i. To this sum we add the contribution by CO and by H_2

$$D_{SEQ}(O_3)_{CO} + D_{SEQ}(O_3)_{H2}$$

$$= \{R(CO + OH) + R(H_2 + OH)\}$$

$$\cdot (d1\ e1 - d1\ e2 - d2) \quad (30a)$$

to give the net ozone change caused by CO, H_2, and methane plus its photocombustion products:

$$D_{SEQ}(O_3)_{CH4} = \sum_i R(CH_4 \text{ initiation})_i \times \Pi_i \times (\Delta O_3)_i$$

$$+ \sum_i R(CO \text{ and } H_2 \text{ initiation})_i \times \Pi_i \times (\Delta O_3)_i \quad (30b)$$

with all permutations of i. The sum of all positive terms in this expression is defined as the gross rate of ozone production by the methane process:

$$P_{SEQ}(O_3) = [R(CH_4 + OH) + R(CH_4 + Cl)]$$

$$\cdot (2(a1\ b1\ c1\ d1\ e1\ ) + (a1\ b1\ c1\ d3\ e1)$$

$$+ 4(a1\ b1\ c2\ d1\ eq)) + (a1\ b1\ c2\ d3\ e1)$$

$$+ 2(a1\ b2\ c2\ d1\ e1)\}$$

$$+ [R(CH_4 + O^1D)] \cdot \{a2\ b1\ c1\ d1\ e1)$$

$$+ e(a2\ b1\ c2\ d1\ e1) + (a2\ b2\ c2\ d1\ e1)\}$$

$$+ [R(OH + CO) + R(OH + H_2)]\cdot\{d1\ e1\}$$

$$(31)$$

The sum of all negative terms in (30) is defined as the gross ozone loss rate by the methane reactions:

$$L_{SEQ}(O_3) = [R(CH_4 + OH) + R(CH_4 + Cl)]$$

$$\cdot \{(2(a1\ b1\ c1\ d1\ e2)) + 2(a1\ b1\ c1\ d2\ e2)$$

$$+ (a1\ b1\ c1\ d3\ e2) + 4(a1\ b1\ c2\ d1\ e2)$$

$$+ 2(a1\ b1\ c2\ d2\ e1)) + 4(a1\ b1\ c2\ d2\ e2)$$

$$+ (a1\ b1\ c2\ d3\ e2) + 2(a1\ b2\ c2\ d1\ e2)$$

$$+ 2(a1\ b2\ c2\ d2)\}$$

$$+ [R(CH_4 + O^1D)] \cdot \{3(a2\ b1\ c1\ d1\ e2)$$

$$+ (a2\ b1\ c1\ d2\ e1) + 3(a2\ b1\ c1\ d2\ e2)$$

$$+ 2(a2\ b1\ c1\ d3\ e2) + 5(a2\ b1\ c2\ d1\ e2)$$

$$+ 3(a2\ b1\ c2\ d2\ e1) + 5(a2\ b1\ c2\ d2\ e2)$$

$$+ 2(a2\ b1\ c2\ d3\ e2) + (a2\ b2\ c1)$$

$$+ e(a2\ b2\ c2\ d1\ e2) + 3(a2\ b2\ c2\ d2)$$

$$+ (a2\ b2\ c2\ d3)\}$$

$$+ [R(OH + CO) + R(OH + H_2)]$$

$$\cdot \{(d1\ e2) + d2\} \quad (32)$$

The net rate of ozone change is the difference between gross production and gross loss:

$$D_{SEQ}(O_3) = P_{SEQ}(O_3) - L_{SEQ}(O_3) \quad (33)$$

To evaluate the SEQ rates of ozone production, loss, and net change as caused by the methane process, we need to evaluate from the final model output the 11 branching ratios and the five initiation rates:

Branching ratios: $a1$, $a2$, $b1$, $b2$, $c1$, $c2$, $d1$, $d2$, $d3$, $e1$, $e2$

Initiation: $R(CH_4 + OH)$, $R(CH_4 + Cl)$, $R(CH_4 + O^1D)$, $R(OH + CO)$, $R(OH + H_2)$ in each model cell. In spite of the complexity of the derivation, the implementation of the SEQ method involves only substituting model output data into two closed algebraic equations, (31) and (32), followed by one operation of subtraction (33).

2.5. OH Formation and Loss From Methane Reactions

When initiation is by $CH_4 + O^1D$, two molecules of OH are eventually produced per methane consumed, and two molecules of OH are eventually produced per methane consumed when formaldehyde photolysis products are HCO + H. Two molecules of HO_x are lost when the reaction $CH_3OOH + OH = CH_3OO + H_2O$ occurs (reaction (17c)) and for each occurrence of module D3. For each module in Table 2, the coefficient of gross OH change by methane photocombustion is given by terms in the ΔOH column. The production and loss equations of OH are

$$P_{SEQ}(OH) = [R(CH_4 + OH) + R(CH_4 + Cl)]$$

$$\cdot \{2(a1\ b1\ c2\ d1\ e1) + 2(a1\ b1\ c2\ d1\ e2)$$

$$+ 2(a1\ b1\ c2\ d2\ e1) + 2(a1\ b1\ c2\ d2\ e2)$$

$$+ 2(a1\ b2\ c2\ d1\ e1) + 2(a1\ b2\ c2\ d1\ e2)$$

$$+ 2(a1\ b2\ c2\ d2)\}$$

$$+ [R(CH_4 + O^1D)] \cdot \{2(a2\ b1\ c1\ d1\ e1)$$

$$+ 2(a2\ b1\ c1\ d1\ e2) + 2(a2\ b1\ c1\ d2\ e1)$$

$$+ 2(a2\ b1\ c1\ d2\ e2) + 4(a2\ b1\ c2\ d1\ e1)$$

$$+ 4(a2\ b1\ c2\ d1\ e2) + 4(a2\ b1\ c2\ d2\ e1)$$

$$+ 4(a2\ b1\ c2\ d2\ e2) + 2(a2\ b2\ c1)$$

$$+ 4(a2\ b2\ c2\ d1\ e1) + 4(a2\ b2\ c2\ d1\ e2)$$

$$+ 4(a2\ b2\ c2\ d2)\}$$ (34)

$$L_{SEQ}(OH) = [R(CH_4 + OH) + R(CH_4 + Cl)]$$

$$\cdot \{2(a1\ b1\ c1\ d3\ e1) + 2(a1\ b1\ c1\ d3\ e2)$$

$$+ 4(a1\ b1\ c2\ d3\ e1) + 4(a1\ b1\ c2\ d3\ e2)$$

$$+ 2(a1\ b2\ c2\ d3)\} + [R(CH_4 + O^1D)]$$

$$\cdot \{2(a2\ b1\ c2\ d3\ e1) + 2(a2\ b1\ c2\ d3\ e2)\}$$

$$+ [R(OH + CO) + R(OH + H_2)] \cdot 2(d3)$$ (35)

3. Results

3.1. LLNL 1997 Two-Dimensional Model

The new LLNL 2-D chemical-radiative-transport (CRT) model or LOTUS (Livermore operator-split two-dimensional zonal-average U system), determines the atmospheric distributions of chemically active atmospheric trace constituents in the troposphere and stratosphere. The individual components (i.e., chemistry, advection, diffusion) from the previous LLNL 2-D CRT have been improved and modularized and are solved in an operator split manner. LOTUS can be integrated in either a diurnal or diurnal average manner. The model domain extends from pole to pole and from the surface to 84 km. The horizontal resolution is 5° in latitude and the vertical coordinate corresponds to the logarithm of pressure, with a resolution of 1.5 km. Below is a brief description of the photochemical component of LOTUS; for a description of the dynamical and radiative processes see *Kinnison et al.* [1994].

The photochemistry represents the tropospheric and stratospheric interactions of actinic solar flux and the species families O_x, NO_y, ClO_y, HO_y, BrO_y, and CH_4 and its oxidation products. The chemical mechanism incorporates 46 transported species. There are 118 thermal and 38 photolytic reactions. Source gases present in the model include NO_x, N_2O, CH_4, CO_2, CO, the chlorine containing compounds CFC-11, -12, -113, HCFC-22, CCl_4, CH_3CCl_3, CH_3Cl, and the bromine containing compounds CH_3Br, CF_2ClBr, and CF_3Br. The thermal reaction rate constants are taken from the NASA panel recommendations provided by *DeMore et al.* [1997]. Absorption cross section information is assembled from a variety of sources, including DeMore et al. Hydrolysis of $ClONO_2$, N_2O_5, and $BrONO_2$ on the surface of stratospheric sulfate aerosol are included as the probable dominant heterogeneous process. In addition, the reactions of $ClONO_2$, HOCl, and HOBr with HCl on sulfate aerosol are included. Representation of the rate constants for the above heterogeneous reactions follows the work of *Hanson and Ravishankara* [1994]. In the photochemical operator, the continuity equation is solved for each individual specie (i.e., no lumping of species into chemical families or steady state approximations are made) using a variable time step, variable order, implicit technique for solving stiff numerical systems with strict error control. This solution technique (SMVGEARII) has recently been developed by *Jacobson* [1995].

All model results from this study are consistent with integrating the continuity equation in a diurnal manner, therefore eliminating any errors incurred by integrating in a diurnal average mode using diurnal average coefficients. The model is run to steady state conditions to be compared with the current atmosphere.

3.2. Calculated Local Changes of Ozone by Methane Process, SEQ and DE Methods

3.2.1. Data taken from model to illustrate the SEQ and DE methods. From output of a model run, we extract from each volume element 13 chemical reaction rates, and five photolysis rates to evaluate the 11 branching probabilities and the five initiation rates given in section 2.4 by the method of instantaneous rates [*Solomon et al.*, 1980]. We substitute these values into equations (30)–(33) and (34) and thus find net ozone change by the methane system $D_{SEQ}(O_3)$, gross ozone production by methane $P_{SEQ}(O_3)$, and gross ozone loss by methane $L_{SEQ}(O_3)$ from 1.5 to 35 km altitude, 67.5°N to 67.5°S latitude, July, diurnal average. For the DE method we extract five reaction rates and evaluate $D_{DE}(O_3)$, $P_{DE}(O_3)$, and $L_{DE}(O_3)$ from (4), (5), and (6). We present a portion of these data as Tables 3–6 and Figures 2–6 to illustrate the principles of this article.

3.2.2. Branching ratios. In the methane reaction process, there are four significant two-way branching points and one three-way branching point, including two competing initiation steps (equations (15), (16), (18), (20), (21), (23), and (25)). Figure 1 shows vertical profiles of these branching probabilities between 1.5 and 35 km for July, 42.5°N, diurnal average. There is an implicit assumption behind our evaluation of branching ratios, illustrated by the following discussion that is applicable to regions where the reaction $O + NO_2$ is unimportant. We assume that a specie produced by the methane reactions has the same probabilities of subsequent reactions as the general pool of this same specie. With this assumption the rate of ozone production by the reaction of OH with CO is the rate of the reaction $CO + OH = CO_2 + H$, which is always followed by $H + O_2 = HOO$, multiplied by the fraction with which bulk

HOO reacts with NO, relative to other significant bulk reactions of HOO. This verbal analysis leads directly to the desired fraction, $d1$, given by (23). Thus $k[\text{CO}][\text{OH}]\ d1$ is the component of $R(\text{CO} + \text{OH})$ that forms ozone, $k[\text{CO}][\text{OH}]\ d2$ is the component of $R(\text{CO} + \text{OH})$ that destroys ozone, and $k[\text{CO}][\text{OH}]\ d3$ is neutral with respect to ozone.

3.2.3. Vertical profiles.

In Figures 2–4 we present vertical profiles for July, 42.5°N, diurnal average, 1.5 to 35 km. Figure 2 presents the vertical profiles of three rates based on the sequence method: gross ozone production, $P_{\text{SEQ}}(\text{O}_3)$; gross ozone loss, $L_{\text{SEQ}}(\text{O}_3)$; and net ozone change, $D_{\text{SEQ}}(\text{O}_3)$. The net rate of ozone change $D_{\text{SEQ}}(\text{O}_3)$ is positive at all altitudes except between 2 and 7 km, where the negative net ozone change is not shown on this logarithmic plot. A local maximum rate of ozone production from the methane process is 6×10^4 molecules $\text{cm}^{-3}\ \text{s}^{-1}$ at 8 km altitude, which gives a local ozone chemical replacement time $\{[\text{O}_3]/D_{\text{SEQ}}(\text{O}_3)\}$ of about six months. Figure 2 does not show a strong spur of calculated net ozone production in the boundary region 0 to 1.5 km. Figure 2 includes the vertical profile of the ozone production rate from photolysis of molecular oxygen. Below 14 km, gross ozone production from the methane process is more rapid than that from oxygen photolysis at this latitude and season.

Figure 3 shows vertical profiles of gross ozone production at 42.5°N by the SEQ method (31) and the DE method (4), $R(\text{HOO} + \text{NO}) + R(\text{CH}_3\text{OO} + \text{NO})$. The two methods agree numerically within $\pm 40\%$ between 2.25 and 11.25 km altitude, but the DE method gives larger rates of gross ozone production at altitudes above 6 km, exceeding a factor of 3 above 12 km.

Figure 4 shows vertical profiles of gross ozone loss by the SEQ method (32) and the DE method (5), $R(\text{O}^1D + \text{H}_2\text{O}) + R(\text{O}_3 + \text{HOO}) + R(\text{O}_3 + \text{OH})$. For 42.5°N the DE method gives larger rates of gross ozone loss at all altitudes, by about 20% at 2.25 km and exceeding a factor of 2 above 9 km.

Figure 3. Comparison of vertical profiles of gross ozone production from methane as found by the SEQ method and the DE method over a wide range of altitude.

3.2.4. Latitude and altitude variations.

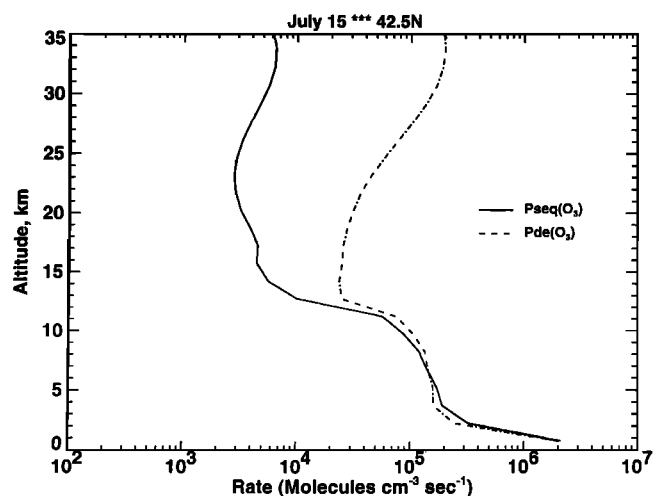Latitude and altitude features of the relation of DE method results and SEQ method results are given by Figure 5. The gross production ratio, $P_{\text{DE}}(\text{O}_3)/P_{\text{SEQ}}(\text{O}_3)$, given by Figure 5a, is <1 at low altitudes and >1 in the upper troposphere and lower stratosphere, and $P_{\text{DE}}(\text{O}_3)$ is equal to $P_{\text{SEQ}}(\text{O}_3)$ at the crossover points, where the ratio is 1.0. The gross loss ratio $L_{\text{DE}}(\text{O}_3)/L_{\text{SEQ}}(\text{O}_3)$, given by Figure 5b, and without exception, the gross ozone loss found by the DE method is larger than that found by the SEQ method, with factors varying from 1.2 to 1.6 below 6 km and from 1.1 to 4 below 10 km.

In Figure 6 we compare the net rate of ozone change D as calculated by the SEQ method with that calculated from the DE method (equations (4), (5), and (6)) on a linear plot as a function of altitude. These vertical profiles vary strongly with latitude. At each latitude the shapes are similar, even for the highly structured profiles at 67.5°N. In all cases the sequence method gives larger net ozone change or smaller net ozone loss.

More details are found in Tables 3–6, altitude is given in

Figure 2. Calculated vertical profiles by the sequence (SEQ) method of (1) gross ozone production from methane reactions, $P_{\text{SEQ}}(\text{O}_3)$; (2) gross ozone loss, $L_{\text{SEQ}}(\text{O}_3)$; and (3) net ozone change, $D_{\text{SEQ}}(\text{O}_3)$, over a wide range of altitudes for model conditions of Figure 1. Where the net rate is negative, it is not shown on the logarithmic plot. These profiles are found by use of equations (30)–(33). For comparison, the rate of ozone production by photolysis of molecular oxygen is included.
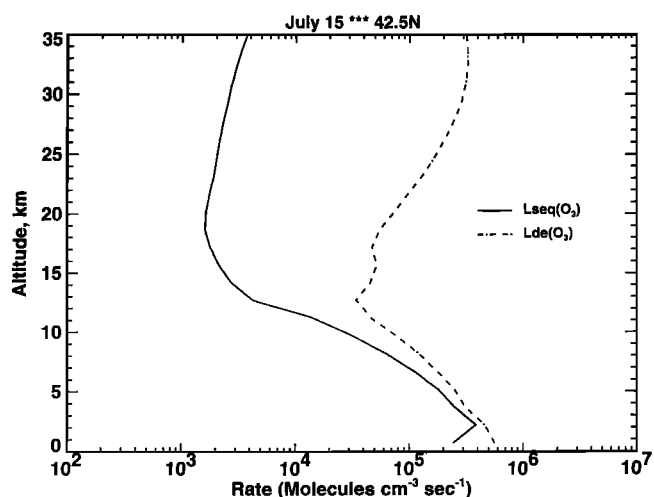
Figure 4. Comparison of vertical profiles of gross ozone loss as found by two methods over a wide range of altitude.
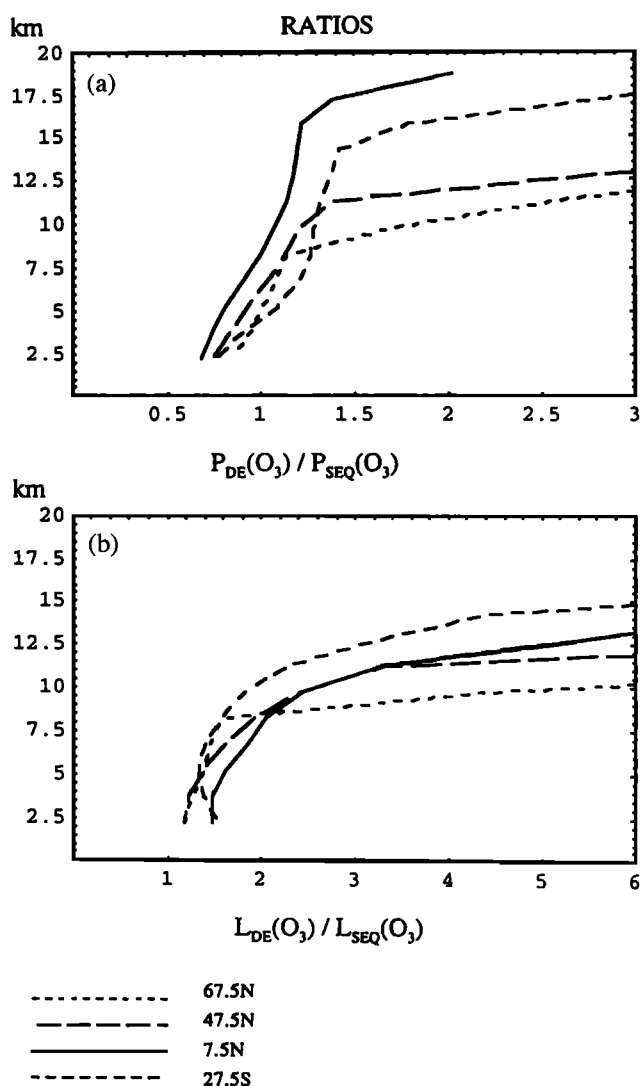
Figure 5. (a) Ratio of gross ozone production by two methods, $P_{DE}(O_3)/P_{SEQ}(O_3)$, as a function of latitude and altitude in the troposphere and lower stratosphere. (b) Ratio of gross ozone loss by two methods, $L_{DE}(O_3)/L_{SEQ}(O_3)$, as a function of latitude and altitude.

terms of each vertical bin center, from 2.25 to 18.75 km, and seven latitudes are given from 47.5°S (winter) to 67.5°N (summer) during July. Tables 3–6 include results for all but the lowest vertical grid element and list diurnal average values of gross ozone production, gross ozone loss, and net ozone change.

The gross ozone production by the SEQ method, $P_{SEQ}(O_3)$, is given in Table 3. The gross ozone loss by the SEQ method, $L_{SEQ}(O_3)$, is also given in Table 3. The ratio of gross ozone production by the DE method relative to the SEQ method, $P_{DE}(O_3)/P_{SEQ}(O_3)$, is given in Table 4. Excepting the winter southern hemisphere, the two methods of calculating gross ozone production agree within ±30% below 9 km. The DE method gives larger gross ozone production in the lower stratosphere, up to factor of 2.1 at 10 km and up to a factor of 7 at 16 km. The ratio of gross ozone loss by the DE method relative to the SEQ method, $L_{DE}(O_3)/L_{SEQ}(O_3)$ is given by Table 4. Without exception, the DE method gives larger gross ozone loss than that given by the SEQ method, by factors up to 7 in the troposphere. In the lower stratosphere the DE method

gives much greater gross ozone production and much greater gross ozone loss than the SEQ method.

The net ozone change by the SEQ method, $D_{SEQ}(O_3)$, is given in Table 5, and the net ozone change by the DE method, $D_{DE}(O_3)$, is also given in Table 5. The two methods differ with respect to distributions of positive and negative net ozone change over latitudes and altitudes. In the northern summer hemisphere, 88% of $D_{SEQ}(O_3)$ values are positive, and 42% of the $D_{DE}(O_3)$ values are positive. In the southern winter hemisphere, 33% of the $D_{SEQ}(O_3)$ are positive and 19% of the $D_{DE}(O_3)$ are positive.

Table 6 shows the percentage difference (PD) of net ozone change between the SEQ method and DE method:

$$PD = \frac{[D_{SEQ}(O_3) - D_{DE}(O_3)] \times 100}{|D_{SEQ}(O_3)|} \quad (36)$$

In all cases, the sequence method gives larger values of net ozone production than the DE method. The percentage differences in Table 6 show complex variation as a function of latitude and altitude. The best agreement between the two methods occurs at 7.5°S and 7.5°N, 11 to 18 km, where they differ by only 0 to 26%. Out of the 84 entries in Table 6, 46 show disagreement greater than 100%. Out of the 42 entries at altitudes below 10 km in Table 6, 24 show disagreement greater than 100%. The extremely large percentage difference at 7.5°N and 3.75 km altitude is not significant, since it is caused by the value of $D_{SEQ}(O_3)$ being almost zero at that point (compare Figure 6). In the troposphere the DE method calculates comparable gross ozone production, larger gross ozone loss, and less net ozone production than the SEQ method (Tables 4 and 6 and Figures 5 and 6).

3.3. Calculated Changes of OH by Methane Photooxidation, SEQ Method

Hydroxyl radicals are consumed in initiating the carbon monoxide "smog" process (CO + OH = CO$_2$ + H), but hydroxyl radicals are regenerated at the end of the sequence by the $d1$ branch (HOO + NO = OH + NO$_2$) and $d2$ branch (HOO + O$_3$ = OH + 2O$_2$) (compare Table 1). The HOO generated by the CO smog reactions lead to HO$_x$ destruction by way of the $d3$ branch. The reaction (O^{1}D + H$_2$O → 2OH) has the free radical arithmetic, "even plus even gives odd plus odd," 0 + 0 = 1 + 1; the breaking of an even number can give two odd numbers [Johnston and Podolske, 1978]. The $d1$ and $d2$ branches of the CO reaction sequence have HO$_x$ free radical arithmetic of the form, 0 + 1 = 1 + 0, there is no change. The $d3$ branch, however, has the form 1 + 1 = 0 + 0, and there is then reduction of HO$_x$.

The situation with respect to HO$_x$ in the full methane process is more complex. One unit of OH is consumed in initiating the methane process by reaction A1 (14), and for 19 out of the 34 paths in Table 2, two or four units of OH are produced, and for seven cases in Table 2, there is loss of two or four units of OH. The increase of odd hydrogen arises from three reactions in the methane process that have free radical (odd electron) arithmetic of the form, even + even = odd + odd, or 0 + 0 = 1 + 1:

$$O^1D + CH_4 = OH + CH_3,$$

$$H_2CO + h\nu = HCO + H$$

$$CH_3OOH + h\nu = CH_3O + OH$$
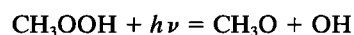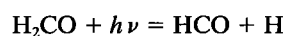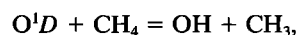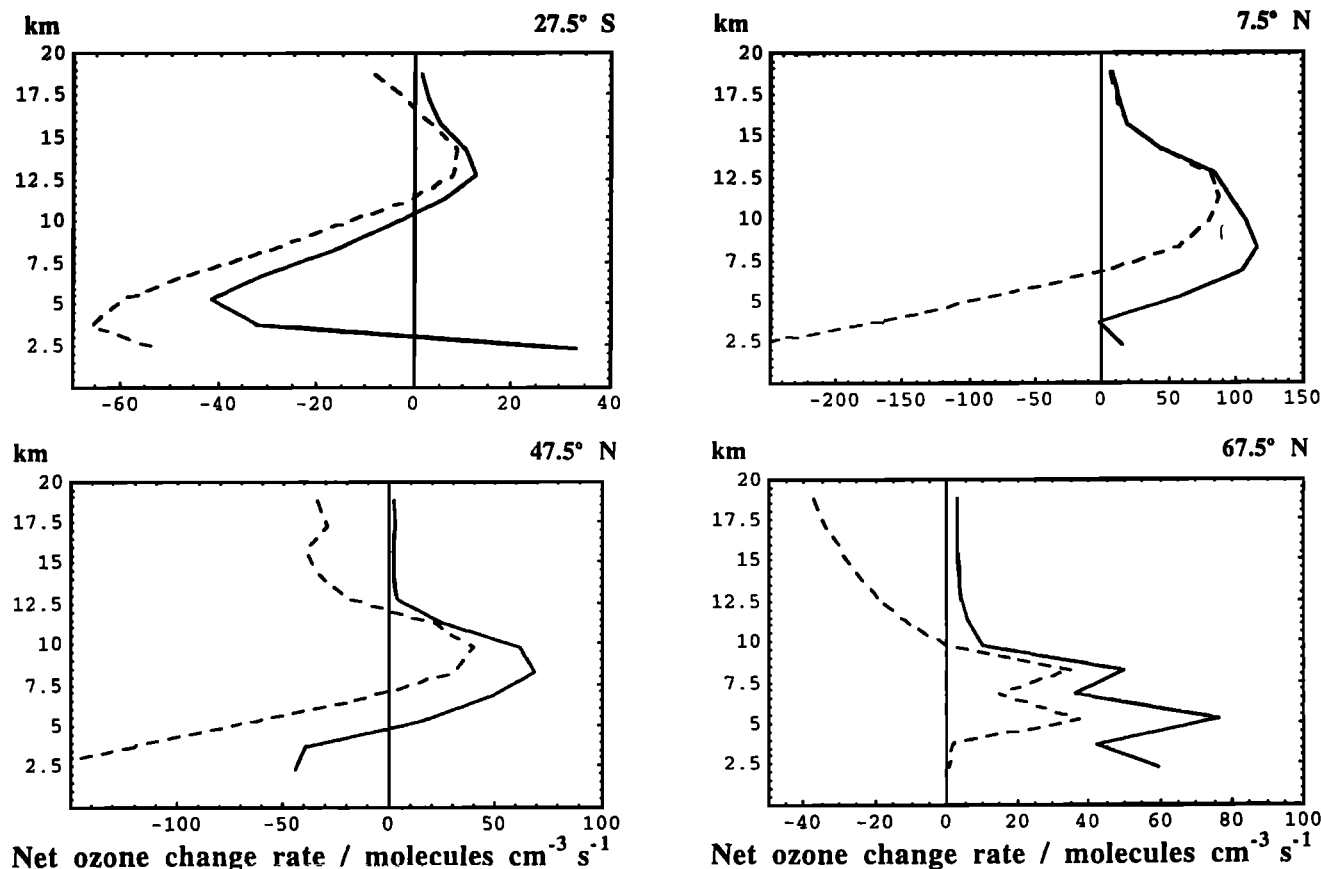
Figure 6. Comparison of vertical profiles of net ozone change by methane process, $D(O_3)$, as calculated by the sequence method (solid lines) and the method using terms in the differential equation (dashed lines) at four latitudes.

There is a catalytic cycle that destroys two units of HO_x, where CH_3OO and CH_3OOH are the catalytic pair (compare (17c)):

$$CH_3OO + HOO = CH_3OOH + O_2 \quad 1 + 1 = 0 + 0$$

$$CH_3OOH + OH = CH_3OO + H_2O \quad 0 + 1 = 1 + 0$$

$$\text{Net} \quad HOO + OH = H_2O + O_2 \quad 1 + 1 = 0 + 0 \tag{37}$$
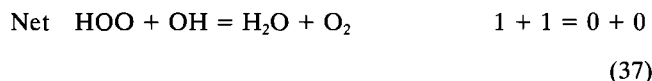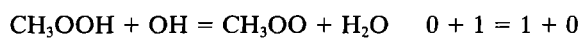
There is a competing sequence that is neutral with respect to odd hydrogen:

$$CH_3OO + HOO = CH_3OOH + O_2 \quad 1 + 1 = 0 + 0$$

$$CH_3OOH + h\nu = CH_3O + OH \quad 0 + 0 = 1 + 1$$

$$\text{Net } CH_3OO + HOO = CH_3O + OH + O_2 \quad 1 + 1 = 1 + 1 + 0 \tag{38}$$
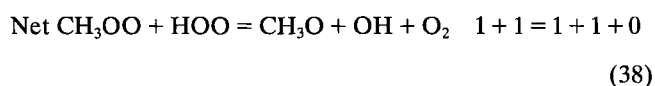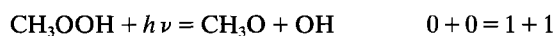
so that reaction $CH_3OOH + OH$ is the rate-determining step in (37). In (37) and (38), the reactions are followed by the odd electron arithmetic. The catalytic cycle (37) does not affect ozone and is not included in Table 2. In the paths in Table 2 the reaction $O^1D + CH_4$ represents loss of one unit of ozone and is counted as such.

Figure 7 presents vertical profiles from 1.5 to 35 km altitude of $D(OH)$, $P(OH)$, and $L(OH)$ as found by the SEQ method,

and for comparison, the profile of twice the rate of $O^1D + H_2O = 2OH$ is included. Above 12 km altitude, there is net production of OH from the methane-smog process including the contribution of CO and H_2, but below 12 km altitude, there is net OH loss, Figure 7. The ratio of $D_{SEQ}(OH)/2R(O^1D + H_2O)$ is shown by Figure 8. In general, the singlet oxygen and water reaction produces OH faster than the methane process, but at about 12 km altitude the methane process produces OH at almost half the rate of the reaction $O^1D + H_2O = 2OH$. Above 12 km, gross OH loss rate from methane reactions is slow, but between 12 and 15 km altitude, the gross OH loss rate increases by a factor of 100. The rapid loss of OH at low altitudes is caused by the catalytic cycle (37).

3.4. Calculated Integrated Ozone Rates in the Global Troposphere

3.4.1. Comparison with Crutzen. Using the three-dimensional MOGUNTA model, *Crutzen* [1995] calculated the integrated global rates of transport of ozone from the stratosphere to the troposphere, the gross and net chemical rates of ozone production by the DE method (equations (4), (5), (6)), and the rates of reaction $O^1D + H_2O = 2OH$ and HOO and $OH + O_3$, given in Table 7. Except for the rate of transport of ozone from the stratosphere, we calculate these quantities from the LLNL two-dimensional model used in this study (Table 7). Using the DE mechanism, the LLNL model agrees with the DE mechanism results of the MOGUNTA model

Table 3. Gross Ozone Production $P_{SEQ}(O_3)$, and Gross Ozone Loss, $L_{SEQ}(O_3)$, Calculated by Sequence Method, as Function of Altitude and Latitude

Altitude, km	Latitude						
	47.5°S	27.5°S	7.5°S	7.5°N	27.5°N	47.5°N	67.5°N
	Gross Ozone Production, $P_{SEQ}(O_3)$, molecules $cm^{-3} s^{-1}$						
18.75	225.	2,426.	5,423.	7,662.	5,047.	3,897.	4,378.
17.25	267.	3,406.	8,957.	11,837.	6,436.	4,456.	4,304.
15.75	331.	5,830.	14,958.	19,468.	12,617.	4,208.	4,584.
14.25	449.	12,693.	26,996.	44,022.	36,415.	5,354.	5,374.
12.75	804.	17,088.	43,787.	88,338.	72,583.	9,021.	6,973.
11.25	2451.	14,636.	45,699.	105,196.	93,449.	30,571.	9,783.
9.75	471.	12,147.	45,720.	133,677.	125,834.	90,284.	16,698.
8.25	433.	10,962.	46,781.	170,103.	153,282.	125,763.	97,080.
6.75	778.	11,160.	47,218.	201,972.	178,578.	149,375.	103,580.
5.25	2,571.	18,034.	56,299.	221,525.	202,684.	179,830.	179,862.
3.75	10,237.	46,071.	84,266.	221,238.	244,380.	183,735.	161,681.
2.25	37,125.	133,798.	202,993.	368,129.	450,277.	288,480.	211,263.
	Gross Ozone Loss by SEQ Method, $L_{SEQ}(O_3)$, molecules $cm^{-3} s^{-1}$						
18.75	1,041.	1,202.	732.	812.	1,166.	1,765.	1,374.
17.25	1,178.	991.	410.	509.	1,260.	2,004.	1,467.
15.75	1,372.	846.	686.	624.	1,030.	2,505.	1,647.
14.25.	1,693.	2,192.	1,635.	1,519.	1,908.	3,310.	2,049.
12.75	2,416.	4,800.	4,375.	4,286.	5,668.	4,898.	2,732.
11.25	3,695.	8,868.	10,415.	10,038.	13,908.	6,506.	3,971.
9.75	5,347.	17,024.	26,822.	26,448.	37,881.	28,926.	6,428.
8.25	6,249.	27,452.	51,905.	55,007.	79,042.	57,122.	46,819.
6.75	7,296.	42,300.	88,271.	97,927.	137,651.	100,902.	67,023.
5.25	9,020.	59,685.	131,337.	162,605.	219,646.	165,471.	103,525.
3.75	9,932.	78,099.	174,883.	223,200.	312,387.	222,439.	119,133.
2.25	10,009.	100,591.	243,414.	353,008.	512,363.	332,807.	151,635.

Diurnal average, July, winter in southern hemisphere (SH), summer in northern hemisphere (NH), LLNL 2-D model (1997).

within 3% for the gross ozone production, within 9% for gross ozone loss terms, and the two models agree within 11% for the calculated HO_x rates. Thus it happens that the LLNL two-dimensional model agrees rather well with these quantities calculated with Crutzen's three-dimensional model. We calculated the integrals for P, L, and D by the sequence method (Table 7), some values of which are

Transport from stratosphere [*Crutzen*, 1995]

$$1.0 \times 10^{13} \text{ mol yr}^{-1} \qquad (39)$$

Net chemical source [*Crutzen*, 1995]

$$D_{DE}(O_3) = 1.6 \times 10^{13} \text{ mol yr}^{-1} \qquad (40)$$

Net chemical source (this paper)

$$D_{DE}(O_3) = 2.44 \times 10^{13} \text{ mol yr}^{-1}$$

Net chemical source (this paper)

$$D_{SEQ}(O_3) = 5.42 \times 10^{13} \text{ mol yr}^{-1} \qquad (41)$$

The net chemical source of tropospheric ozone by the SEQ method is a factor of 2.2 greater than that found from the same LLNL model using the DE method. Our use of (41) of extended *Crutzen* [1973] SEQ method finds about 3.4 times as much net ozone production from the methane smog system as *Crutzen* [1995] finds with the DE method (43). Both methods agree with Crutzen's original conclusion that the net chemical production of ozone in the troposphere from the methane-smog process exceeds the gross rate of ozone transport into the troposphere from the stratosphere.

Table 4. Ratios of Gross Rate of Ozone Production as Given by DE Method Divided by Gross Rate of Ozone Production as Given by SEQ Method and Same Information for Gross Ozone Loss

Altitude, km	Latitude						
	47.5°S	27.5°S	7.5°S	7.5°N	27.5°N	47.5°N	67.5°N
	$P_{DE}(O_3)/P_{SEQ}(O_3)$						
18.75	11.23	4.01	2.26	2.02	4.63	7.47	8.82
17.25	9.12	2.86	1.40	1.38	3.51	6.06	7.75
15.75	7.36	1.79	1.23	1.22	1.65	6.20	6.40
14.25	5.57	1.42	1.22	1.20	1.29	4.62	4.97
12.75	3.48	1.37	1.21	1.17	1.27	2.80	3.69
11.25	1.63	1.32	1.18	1.14	1.23	1.39	2.57
9.75	2.11	1.28	1.10	1.07	1.14	1.21	1.70
8.25	1.99	1.26	1.05	1.00	1.04	1.13	1.14
6.75	1.74	1.20	0.99	0.90	0.93	1.03	1.08
5.25	1.40	1.09	0.93	0.81	0.85	0.93	1.01
3.75	1.10	0.90	0.83	0.74	0.79	0.84	0.94
2.25	0.96	0.77	0.74	0.68	0.74	0.75	0.85
	Ratio $L_{DE}(O_3)/L_{SEQ}(O_3)$						
18.75	28.35	14.87	13.16	12.82	26.23	35.88	55.05
17.25	22.17	12.12	10.32	10.35	20.10	28.05	46.07
15.75	16.85	8.16	6.19	7.89	10.34	25.96	35.93
14.25	11.52	4.39	5.25	7.27	7.52	17.48	25.29
12.75	5.93	3.21	3.93	5.39	5.86	9.00	16.49
11.25	1.86	2.28	2.66	3.28	3.77	3.33	9.32
9.75	1.14	1.82	2.08	2.44	2.65	2.41	4.42
8.25	1.12	1.58	1.82	2.05	2.04	1.93	1.60
6.75	1.15	1.41	1.67	1.85	1.71	1.62	1.45
5.25	1.20	1.33	1.54	1.62	1.47	1.39	1.40
3.75	1.34	1.38	1.50	1.47	1.35	1.23	1.26
2.25	1.60	1.54	1.59	1.48	1.36	1.17	1.18

Table 5. Net Ozone Change (D) Caused by Methane Reactions calculated by Two Methods as Function of Altitude and Latitude

Altitude, km	Latitude						
	47.5°S	27.5°S	7.5°S	7.5°N	27.5°N	47.5°N	67.5°N
Net Change of Ozone by Sequence Method, $D_{SEQ}(O_3)$, molecules $cm^{-1} s^{-1}$							
18.75	−8.17e2	1.22e3	4.69e3	6.85e3	3.88e3	2.13e3	3.00e3
17.25	−9.12e2	2.42e3	8.55e3	1.13e4	5.18e3	2.45e3	2.84e3
15.75	−1.04e3	4.98e3	1.43e4	1.88e4	1.16e4	1.70e3	2.94e3
14.25	−1.24e3	1.05e4	2.54e4	4.25e4	3.45e4	2.04e3	3.33e3
12.75	−1.61e3	1.23e4	3.94e4	8.41e4	6.69e4	4.12e3	4.24e3
11.25	−1.24e3	5.77e3	3.53e4	9.52e4	7.95e4	2.41e4	5.81e3
9.75	−4.88e3	−4.88e3	1.89e4	1.07e5	8.80e4	6.14e4	1.03e4
8.25	−5.82e3	−1.65e4	−5.12e3	1.15e5	7.42e4	6.86e4	5.03e4
6.75	−6.52e3	−3.11e4	−4.11e4	1.04e5	4.09e4	4.85e4	3.66e4
5.25	−6.45e3	−4.17e4	−7.50e4	5.89e4	−1.70e4	1.44e4	7.63e4
3.75	3.05e2	−3.20e4	−9.06e4	−1.96e3	−6.80e4	−3.87e4	4.25e4
2.25	2.71e4	3.32e4	−4.04e4	1.51e4	−6.21e4	−4.43e4	5.96e4
Net Change of Ozone by DE Method, $D_{DE}(O_3)$, molecules $cm^{-3} s^{-1}$							
18.75	−2.70e4	−8.16e3	2.64e3	5.10e3	−7.21e3	−3.42e4	−3.71e4
17.25	−2.37e4	−2.27e3	8.33e3	1.11e4	−2.71e3	−2.92e4	−3.43e4
15.75	−2.07e4	3.51e3	1.41e4	1.89e4	1.02e4	−3.89e4	−2.98e4
14.25	−1.70e4	8.41e3	2.44e4	4.17e4	3.26e4	−3.31e4	−2.51e4
12.75	−1.15e4	7.91e3	3.56e4	8.03e4	5.93e4	−1.88e4	−1.93e4
11.25	−2.89e3	−9.22e2	2.60e4	8.72e4	6.22e4	2.07e4	−1.18e4
9.75	−5.07e3	−1.56e4	−5.56e3	7.87e4	4.27e4	3.94e4	−1.21e2
8.25	−6.13e3	−2.95e4	−4.52e4	5.72e4	−1.16e3	3.10e4	3.52e4
6.75	−7.06e3	−4.64e4	−1.00e5	1.72e1	−6.87e4	−9.06e3	1.46e4
5.25	−7.19e3	−5.96e4	−1.50e5	−8.45e4	−1.49e5	−6.31e4	3.73e4
3.75	−2.04e3	−6.6e4	−1.92e5	−1.65e5	−2.29e5	−1.20e5	1.67e3
2.25	1.96e4	−5.22e4	−2.38e5	−2.70e5	−3.65e5	−1.71e5	4.58e2

Diurnal average, July, winter in SH, summer in NH, 1997 version of LLNL 2-D model. Read −8.17e2 as -8.17×10^2.

4. Discussion

4.1. Calculated Integrated OH Rates in the Global Troposphere

As found by the SEQ method and LLNL model, the gross production and gross loss of OH (35) are integrated from 1.5 km to the tropopause from 70S to 70N in model day July 15:

$$P_{SEQ}(OH) = 1.76 \times 10^{13} \text{ mol yr}^{-1}$$

$$L_{SEQ}(OH) = 3.92 \times 10^{13} \text{ mol yr}^{-1}$$

$$D_{SEQ}(OH) = -2.16 \times 10^{13} \text{ mol yr}^{-1} \qquad (42)$$

Table 6. Percentage Difference Between the Net Rage of Change of Ozone as Given by SEQ Method and DE Method: $100 \, [D_{SEQ}(O_3) - (D_{DE}(O_3)]/|(D_{SEQ}(O_3)|$

Altitude, km	Latitude						
	47.5°S	27.5°S	7.5°S	7.5°N	27.5°N	47.5°N	67.5°N
18.75	3206.	767.	44.	26.	286.	1704.	1334.
17.25	2499.	194.	3.	2.	152.	1292.	1308.
15.75	1886.	30.	1.	−0.	12.	2387.	1116.
14.25	1266.	20.	4.	2.	5.	1720.	855.
12.75	615.	36.	10.	4.	11.	556.	555.
11.25	132.	116.	26.	8.	22.	14.	304.
9.75	4.	219.	129.	27.	51.	36.	101.
8.25	5.	79.	783.	50.	102.	55.	30.
6.75	8.	49.	144.	100.	268.	119.	60.
5.25	11.	43.	100.	243.	778.	540.	51.
3.75	769.	106.	112.	8301.	237.	210.	96.
2.25	28.	257.	488.	1887.	488.	287.	99.

where mole is 6.02×10^{23} molecules. For comparison, the integrated rate of OH production by the reaction of singlet atomic oxygen with water is

$$2R(O^1D + H_2O) = 6.8 \times 10^{13} \text{ mol yr}^{-1} \qquad (43)$$

Averaged over the troposphere, the net effect of the natural methane smog process is to destroy OH 32% as fast as it is formed by $O^1D + H_2O = 2OH$.

4.2. Comparison of SEQ and DE Methods

In section 1.1.5, we argue that of the five reactions that occur in the DE method (equations (4) and (5)), four of them occur even in the absence of methane and its reaction products, (HOO + NO), (O_3 + HOO), (O_3 + OH), and (O^1D + H_2O), and one of them destroys ozone at all altitudes, which contradicts the basic assumption that the DE method should give correct net ozone change in the lowest stratosphere. Crutzen's [1973] sequence method as extended here has the ability to separate these components in any air parcel from Earth's surface to the middle stratosphere if one knows the local value of 13 chemical rates and five photolysis rates (equations (31) and (32)). Ideally, the knowledge of rates would come from simultaneous measurements of species concentrations and a table of rate coefficients, but in this paper it is from the LLNL 2-D model.

In the troposphere, the DE method, relative to the SEQ method, gives larger gross ozone production in many regions and less gross ozone production in a few regions, and thus the two methods are numerically the same at the crossing points. Below 6 km at all latitudes and between 7.5°S to 7.5°N at all
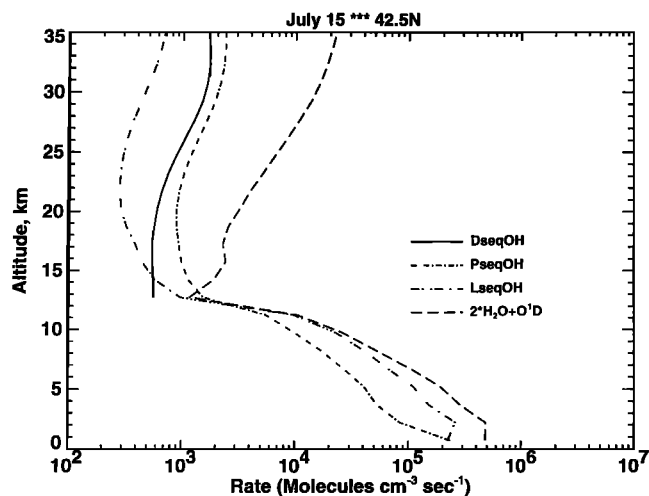
Figure 7. The calculated methane components of gross OH production, $P_{SEQ}(OH)$, gross OH loss, $L_{SEQ}(OH)$, and net OH change, $D_{SEQ}(OH)$, as a function of altitude for model conditions as in Figure 1. Also plotted are the rate of OH production from the reaction of singlet atomic oxygen with water.

tropospheric altitudes, the DE method and the SEQ method give the same gross ozone production within ±40% (Table 4 and Figure 5a). In the upper troposphere the DE method gives up to twice as much gross ozone production as the SEQ method.

Over the troposphere and stratosphere at all latitudes and altitudes the DE method finds larger gross ozone loss than that found by the SEQ method by factors between 1.1 to 7.9 in the troposphere and by factors up to 55 at 19 km altitude (Figure 5b and Table 4).

The net rate of ozone change $D(O_3)$ caused by the methane process is the important quantity, and the comparison between the two methods for this quantity is complicated (Table 6 and Figure 6). In the troposphere the net ozone production by the SEQ method is larger than that by the DE method for all cases.
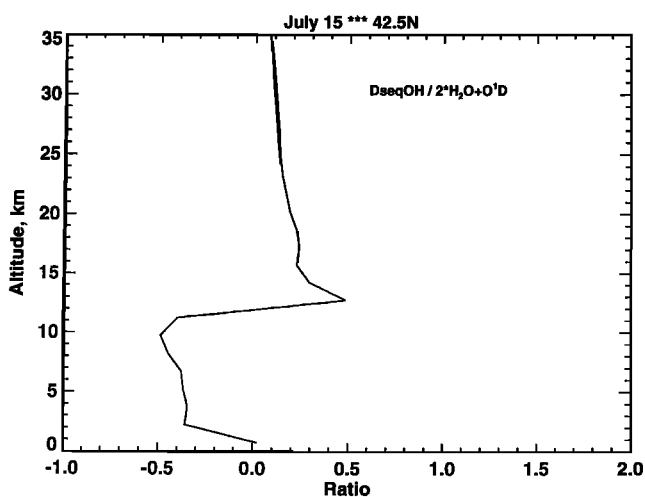
Figure 8. The ratio of net OH production from methane reactions to the rate of OH production from the reaction of singlet atomic oxygen with water. This ratio has a sharp peak, equal to 0.5, at the tropopause.

This analysis, again, confirms [*Crutzen*, 1973] that there is substantial net chemical production of ozone in the troposphere by the methane process. Over the global troposphere we find that the net ozone production by the SEQ method is 5.4 times the rate of ozone transported from the stratosphere to the troposphere and 2.2 times our value using the DE method (Table 7).

In the stratosphere the DE method gives much larger gross ozone production and much larger gross ozone loss than the SEQ method, but the SEQ method gives larger net ozone production. However, the contribution of methane to ozone production in the stratosphere is much less than that of oxygen photolysis, and it is probably of only academic interest. This paper calls attention, again, to a strong methane-induced catalytic cycle in the lower troposphere that destroys odd hydrogen, where the catalyst is the pair, CH_3OO/CH_3OOH (36).

4.1.1. Applications to volatile organic compounds (VOC) other than methane. If (1) the rate of radical attack on RH (where RH is any organic compound containing at least one atom of hydrogen, H, and R is the rest of the molecule) is known, (2) the identity of the primary and secondary products of RH is known, and (3) the rate coefficients for RH attack and for all important secondary reactions are known, then the SEQ method can be used to solve for the specific contribution of RH to ozone change, regardless of how many other species are in the atmosphere.

4.1.2. Simplicity. The DE method is much simpler than the SEQ method. The complexity of the SEQ method is in its derivation. Once derived for a model, entering the SEQ method into the model is a simple job of program writing, and then using the method is a simple calculation for a modern computer. For educational purposes the idea of the SEQ method can be simply stated as follows: The net production of ozone from volatile organic compounds is roughly equal to the number of VOC that react multiplied by the number of carbon atoms in the VOC times a factor, usually between -2 and $+2$; the factor is complex to discuss, varies over the atmosphere, but it is readily evaluated by a computer.

4.1.3. Subsonic aircraft. There is current interest in the environmental effects of subsonic aircraft in the troposphere and in the lowest stratosphere. Subsonic passenger aircraft typically cruise between altitudes of 11 to 13 km, which is in the troposphere at some latitudes and in the lowermost stratosphere at other latitudes. With minor exception the SEQ method gives much larger net ozone production from methane

Table 7. Comparison of Global Tropospheric Ozone Production and Loss Terms in This Paper (LLNL 2-D Model) According to the Second Method (P_{DE}, L_{DE}, D_{DE}) With the Same Terms Found by Crutzen (3-D Model), and the Values Found Using Our Extension of Crutzen's First Method (P_{SEQ}, L_{SEQ}, D_{SEQ})

	Crutzen, DE Terms	LLNL, DE Terms	LLNL, Sequence
P, gross production	8.2	8.45	9.34
L, gross loss	6.6	6.01	3.92
D, net change	1.6	2.44	5.42
Rate, O^1D + H_2O	3.8	3.4	
Rate, HOO and OH + O_3	2.8	2.6	
From stratosphere	1.0		

The numbers are multiples of 10^{13} mol yr^{-1}.

than the DE method in the stratosphere. Table 6 includes the difference between net ozone change as found by the SEQ and DE methods at 11.25 and at 12.75 km at each of seven latitudes. The range of variation between the two methods, $D_{SEQ}(O_3) - D_{DE}(O_3)$, is from +4% to +615% over the subsonic flight corridors.

One matter of interest is how NO_x from subsonic aircraft affects ozone changes in the methane process. Atmospheric models can estimate the overall effect of how assumed increases in such aircraft changes ozone, and NO_x is known to affect tropospheric and lowest stratospheric ozone in many ways: The NO_2 and NO and the NO_3 and NO catalytic cycles destroy ozone (a small effect at these altitudes); NO inhibits ozone destruction by HO_x, ClO_x, and BrO_x catalytic cycles by reactions of the form $AO_x + NO = A + NO_2$; NO_2 reversibly binds ozone-active OH, ClO, and BrO into ozone-inactive nitrates; and NO_x plays multiple nonlinear roles in the methane smog process. For subsonic aircraft environmental impact, it is desirable to have a reliable method of separating the NO_x-ozone effect of the methane process from the other roles of atmospheric NO_x.

5. Conclusions

5.1. DE Method Concepts

By failing to recognize a significant gross loss of ozone by a nonmethane process at all altitudes the DE method is logically wrong at all altitudes.

5.2. Comparison of Net Ozone Change Found by SEQ and DE Methods

5.2.1. The lowermost stratosphere.
In the technically defined "lowermost stratosphere," that is, the stratosphere at pressure altitudes lower than the tropical tropopause, the SEQ method finds net ozone production everywhere to be greater than that found by the DE method; the difference is small at tropical latitudes, but the difference at higher latitudes is as high as a factor 24.

5.2.2. The global troposphere.
According to the LLNL 2-D model integrated over the troposphere, the global net ozone production by methane photooxidation as found by the SEQ method is 2.2-fold larger than that found by the DE method.

5.3. Applications

5.3.1. To volatile organic compounds (VOC) other than methane.
If enough product distributions and rate coefficients are known, the SEQ method can be used to solve for the specific contribution of any VOC to ozone change.

5.3.2. To subsonic aircraft.
At the cruise altitude of subsonic passenger aircraft, 11 to 13 km, the latitudinal variation net ozone production between the two methods is from +4% to +615%, which indicates that the DE method is unsuitable for testing the effect of subsonic aircraft on atmospheric methane. The SEQ method can do this job.

5.4. Production and Loss of OH and HO_x

The SEQ method separately identifies the amount of OH produced and lost in the methane-smog process. Averaged over the troposphere, the net effect of the methane smog process is to decrease the rate of OH production by 32%.

5.5. Summarizing Statement

Chemistry in the troposphere is three-dimensional, and no two-dimensional model can adequately represent the troposphere. We do not regard these results to be firm on an absolute basis, but we do regard them to be a realistic demonstration that the conceptually flawed DE method of interpreting the methane-smog process in the troposphere, although agreeing fairly well numerically with the SEQ method in some regions, disagrees seriously in other regions and disagrees seriously with the net ozone change integrated over the global troposphere. Thus we conclude that the DE method is not a reliable numerical approximation for the effect of methane on ozone. We propose that our extension of Crutzen's sequence method is, or could be developed into, a reliable tool for identifying the component of ozone change caused by the methane and other organic chemical processes.

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