On the Nonlinearity of the Tropospheric Ozone Production

X. LIN, M. TRAINER, and S. C. LIU

Aeronomy Laboratory, Environmental Research Laboratories, National Oceanic and Atmospheric Administration, Boulder, Colorado

The relationship of photochemical ozone production versus photochemical loss of an ozone precursor, that is, either NO\textsubscript{x} or nonmethane hydrocarbons (NMHCs), is studied by using a box model with particular emphasis on the nonlinearity problem of the relationship with respect to the concentration of the precursor. Model calculations indicate that the composition of NMHCs, the ratio of NMHCs to NO\textsubscript{x}, and the background concentrations of natural hydrocarbons, CO, and CH\textsubscript{4} all play important roles in determining the nonlinearity of O\textsubscript{3} production with respect to the loss of NO\textsubscript{x}. In addition, influences on the nonlinearity due to radical loss via reactions of HO\textsubscript{2} with RO\textsubscript{2}, exchanges between PAN and NO\textsubscript{x}, and inclusion of nighttime NO\textsubscript{x} loss processes are also investigated. Mechanisms that contribute to the nonlinearity are discussed. The nonlinear property of O\textsubscript{3} production versus loss of hydrocarbons and CO is different from that of NO\textsubscript{x}. When the sum of CO and all hydrocarbons, including CH\textsubscript{4}, natural NMHCs, and anthropogenic NMHCs, is used as the reference O\textsubscript{3} precursor, the nonlinearity is much less pronounced for ambient conditions usually found in rural air.

INTRODUCTION

In the troposphere the solar UV radiation does not have enough energy to dissociate O\textsubscript{2} directly and produce O\textsubscript{3}. The existence of a high concentration of O\textsubscript{3} in the urban atmosphere prompted Leighton [1961] to suggest that peroxy radicals, such as HO\textsubscript{2} and RO\textsubscript{2} (where R denotes organic radicals), might lead to the oxidation of NO to NO\textsubscript{2}, resulting in the production of O\textsubscript{3} following the photodissociation of NO\textsubscript{2}. The peroxy radicals are produced mostly during the oxidation of hydrocarbons. Photochemical processes involved in O\textsubscript{3} production from oxidation of NMHCs are very complex [Seinfeld, 1986; Finlayson-Pitts and Pitts, 1986]. To facilitate later discussion, a highly simplified scheme is shown,

\[ \text{NMHC} + \text{OH} + \text{O}_2 \rightarrow \text{RO}_2 \]  
\[ \text{RO}_2 + \text{NO} + \text{O}_2 \rightarrow \text{NO}_2 + \text{HO}_2 + \text{CARB} \]  
\[ \text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH} \]  
\[ 2(\text{NO}_2 + \text{hv} + \text{O}_2 \rightarrow \text{NO} + \text{O}_3) \]

Net \[ \text{NMHC} + 4\text{O}_2 + \text{hv} \rightarrow 2\text{O}_3 + \text{CARB} \]  

where CARB stands for carbonyl compounds. Carbonyls undergo further oxidation and produce more O\textsubscript{3}. The scheme shows that both NMHCs and NO\textsubscript{x} (NO + NO\textsubscript{2}) are precursors of O\textsubscript{3}. It also shows that NO\textsubscript{x} and odd hydrogen (OH + HO\textsubscript{2}) are not consumed directly and thus act as catalysts in the production of O\textsubscript{3}. Thus the production of O\textsubscript{3} usually increases with the concentrations of NO\textsubscript{x} and odd hydrogen. In the absence of hydrocarbons, HO\textsubscript{2} can be produced via the reactions

\[ \text{O}_3 + \text{hv}(<315 \text{ nm}) \rightarrow \text{O}(1D) + \text{O}_2 \]  
\[ \text{O}(1D) + \text{H}_2\text{O} \rightarrow 2\text{OH} \]  
\[ \text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H} \]

and

\[ \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \]  

In this scheme, CO replaces the NMHCs as an O\textsubscript{3} precursor. Of course, CH\textsubscript{4} can play the same role.

Because the destruction rates of NO\textsubscript{x} and odd hydrogen depend strongly on the concentrations of NMHCs and NO\textsubscript{x}, the increase of O\textsubscript{3} production is not linearly proportional to the increases in O\textsubscript{3} precursors. In fact, in certain circumstances O\textsubscript{3} production even decreases with increasing concentrations of the precursors. This nonlinear phenomenon is well known for the urban atmosphere and is readily shown by the O\textsubscript{3} isopleths of the Empirical Kinetic Modeling Approach (EKMA), which are used for formulating control strategies [Dodge, 1977a, b; Dimitriades and Dodge, 1983].

There is another way to look at the nonlinear O\textsubscript{3} production problem. Recently, Liu et al. [1987] defined an O\textsubscript{3} production efficiency defined as the number of O\textsubscript{3} molecules produced for each molecule of precursor consumed. They found that the nonlinearity of the efficiency is quite pronounced in the rural and clean background atmosphere and that this nonlinearity may have a significant impact on the budgets of regional and global O\textsubscript{3}.

The composition of NMHCs and the ratios of NMHCs to NO\textsubscript{x} used in the study by Liu et al. [1987] are those observed at Niwot Ridge, Colorado, a rural station. Three important questions are raised by their findings: (1) How sensitive is the nonlinearity with respect to the composition of NMHCs? (2) How does the ratio of NMHCs to NO\textsubscript{x} affect the nonlinearity? (3) How do the background concentrations of natural hydrocarbons, CO, and CH\textsubscript{4}, affect the nonlinearity? These questions will be investigated in this study.

In the following, a box model developed by Liu et al. [1987] with some modifications in the photochemical scheme, as described by Trainer et al. [1987] is used to study ozone production efficiency for various cases that correspond to different hydrocarbon compositions, ratios of NMHCs to NO\textsubscript{x}, and mixtures of NMHCs, CO, CH\textsubscript{4}, and natural hydrocarbons.

To study the dependence of the nonlinearity on the NMHC composition, model calculations with various realistic combinations of NMHCs are needed. However, constraint of computer resources requires models to incorporate only chemistry packages that include a limited number of hydrocarbons.
TABLE 1. Three NHMC Compositions Used in the Present Study

|            | Niwot | ADMP | EKMA |
|------------|-------|------|------|
|            | k_{CH_4} | Percent of Molecules | Percent in Carbon | Percent of Molecules | Percent in Carbon | Percent of Molecules | Percent in Carbon |
| Ethane     | 2.59(-13) | 37.52 | 26.28 | 15.23 | 8.27 |
| Propane    | 1.14(-12) | 21.27 | 22.35 | 33.92 | 36.82 |
| Butane     | 2.54(-12) | 13.23 | 18.53 | 11.43 | 6.21 |
| Ethylene   | 8.36(-12) | 7.71 | 5.40 | 60.94 | 71.25 |
| Propene    | 2.71(-11) | 2.68 | 2.82 | 5.46 | 4.45 |
| Toluene    | 6.00(-12) | 8.38 | 20.53 | 15.23 | 8.27 |
| Formaldehyde | 1.00(-11) | 6.70 | 2.35 | 19.03 | 36.15 |
| Acetaldehyde | 1.60(-11) | 2.51 | 1.76 | 2.99 | 3.42 |
| Reactivity K, cm^3 s^{-1} | 3.75(-12) | 5.33(-12) | 8.93(-12) |

The reactivity of a composition is defined as the reaction rate constant weighted by the percentage of each component in carbon number. Read 2.59(-13) as 2.59 x 10^{-13}.

[Lloyd et al., 1979; Whitten et al., 1980, Leone and Seinfeld, 1985]. For this study we chose three NMHC compositions: (1) the rural composition observed at Niwot Ridge, Colorado [Liu et al., 1987]; (2) the composition of a representative anthropogenic emission used by a regional acid deposition model [Acid Deposition Modeling Project (ADMP), 1987]; and (3) the so-called "default EKMA" composition [Dodge, 1977a, b]. For simplicity, we will refer to these three NMHC compositions as Niwot, ADMP, and EKMA, respectively, in the text that follows. The components of each composition are listed in Table 1. It should be pointed out that our intention here is not to reproduce the ADMP and EKMA reaction schemes. The purpose is to have a diversified representation of NMHC mixtures in order to study the dependence of the nonlinearity on the NMHC composition. For simplicity, we have made the following adjustments on the ADMP composition. They are as follows: (1) dimethylbutane and xylene are treated as butane and toluene, respectively, and (2) butene is omitted. A comparison between O_3 calculated from our model with the adjusted ADMP composition and that calculated from the regional acid deposition model with the original ADMP composition is made. In these calculations the model starts at 0000 LT, with initial conditions of 30 parts per billion by volume in ppmv of O_3, 1700 ppmv of CH_4, and 300 ppmv of CO. The initial NO_x varies from 0.1 to 1000 ppmv, while the initial anthropogenic NMHCs range from 1 ppbc (ppmv multiplied by carbon number) through 100,000 ppbc. The calculated O_3 values at noon time are presented in Figure 1. It is clear that the two sets of O_3 isopleths show a similar pattern of variations with NO_x and NMHCs. Some differences are expected, as the original ADMP mixture is more reactive. For example, at 10 ppmv of NO_x and 100 ppbc of NMHCs, our model with the adjusted ADMP composition generates 70 ppmv of O_3, whereas the corresponding value from the ADMP model and the original composition is 85 ppmv. The two O_3 values become 195 ppmv and 282 ppmv for NO_x at 100 ppmv and NMHCs at 1000 ppbc, respectively. The nonlinear phenomenon of the O_3 production is closely related to the relative O_3 variation with respect to changes in NO_x and NMHCs that are proportional to the space between isopleths, rather than the absolute value of the isopleth. Therefore differences in absolute O_3 values will not affect significantly the outcome of our study.

In addition to these investigations, effects on the nonlinearity of O_3 production due to combination reactions of HO_2 with RO_2 and the formation of peroxyacetyl nitrate (PAN) are studied. Since nighttime chemistry of NO_x is recognized to be important to the NO_x loss, hence the O_3 production, possible effects of the inclusion of nighttime chemistry on the nonlinearity are also discussed.

Fig. 1. Isopleths of O_3 mixing ratio (in ppbv) at noon, calculated from (a) the adjusted ADMP composition and the box model used in this paper; and (b) the original ADMP composition and the regional acid deposition model (W. Stockwell, private communication, 1988).
NONLINEARITY AND THE HYDROCARBON COMPOSITION

In the troposphere the competition of (2) and (3), with the loss of odd nitrogen, determines how much \( \text{O}_3 \) is formed per \( \text{NO}_x \) consumed. Therefore it is crucial to understand the budgets of odd hydrogen and \( \text{NO}_x \). The major \( \text{NO}_x \) loss during the daytime is

\[
\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}
\]

In the presence of NMHCs, \( \text{NO}_x \) can also be converted into inactive forms, such as PAN, that do not produce \( \text{O}_3 \) directly. PAN is produced via the reaction

\[
\text{CH}_2\text{COO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{PAN} + \text{M}
\]

At room temperature the reverse reaction is efficient enough that PAN and \( \text{NO}_2 \) tend to be in equilibrium. PAN may serve as a temporary storage and a carrier of \( \text{NO}_x \) into the more remote troposphere [Crutzen, 1979; Singh et al., 1985]. In addition, \( \text{NO}_x \) may be lost at nighttime as a result of reactions involving \( \text{NO}_x \) and \( \text{N}_2\text{O}_5 \) [Ehhalt and Drummond, 1982; Platt et al., 1984; Noxon, 1983]. On the other hand, the reaction scheme (1)-(5) implies that in the absence of competing reactions, at least two \( \text{O}_3 \) molecules are formed following each reaction of \( \text{OH} \) with NMHC. Photochemical sinks for odd hydrogen include (10) and recombination reactions of \( \text{HO}_2 \) and \( \text{RO}_2 \) radicals

\[
\begin{align*}
\text{HO}_2 + \text{HO}_2 &\rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
\text{HO}_2 + \text{RO}_2 &\rightarrow \text{ROOH} + \text{O}_2
\end{align*}
\]

followed by the reaction of \( \text{OH} \) with the peroxide. The preceding discussion indicates that interplay of the catalytic cycle and the radical loss reactions determines the production of \( \text{O}_3 \) with respect to the loss of its precursors. Because of the variation of the relative importance of the catalytic cycle versus the termination reactions that result in losses of precursors and odd hydrogen, the production of \( \text{O}_3 \) is not a linear function of the concentrations of its precursors.

Liu et al. [1987] discussed the finding that the total \( \text{O}_3 \) production in a region could be estimated from the total \( \text{NO}_x \) emission flux \( E \) within the region. This can be done by using a formula

\[
S = \frac{EP}{L[\text{NO}_x^2]}
\]

where \( P \) and \( L[\text{NO}_x] \) are the production of \( \text{O}_3 \) and the loss of \( \text{NO}_x \), respectively. It is clear that a large uncertainty would result in the estimated total \( \text{O}_3 \) production if the value of \( P/L[\text{NO}_x] \) varies widely in the region of interest. Both the \( \text{O}_3 \) production and the \( \text{NO}_x \) loss vary with the level of \( \text{NO}_x \) and the composition and abundances of the other \( \text{O}_3 \) precursors, such as hydrocarbons. Liu et al. [1987] found that variations in the \( \text{O}_3 \) production and the \( \text{NO}_x \) loss are often similar and therefore cancel each other. This reduces substantially the uncertainty in the estimated total regional \( \text{O}_3 \) production. However, significant nonlinearity still exists.

In the preceding formula, \( \text{NO}_x \) is chosen as the reference precursor. This choice has two advantages: (1) The loss of \( \text{NO}_x \) on a regional scale is roughly equal to the emission flux, a result of the short photochemical lifetime of \( \text{NO}_x \). (2) \( \text{NO}_x \) is the rate-limiting \( \text{O}_3 \) precursor in relatively clean air [Fishman et al., 1979; Logan et al., 1981]. Later, we will also discuss results from model calculations in which NMHCs are assumed to be the reference \( \text{O}_3 \) precursor.

The quantity \( P/L[\text{NO}_x] \) can be considered to represent the amount of \( \text{O}_3 \) produced for each \( \text{NO}_x \) molecule emitted, because in steady state the \( \text{NO}_x \) loss equals the \( \text{NO}_x \) emissions. We will call the quantity \( \text{O}_3 \) production efficiency.

It is important to note that the definition of absolute \( \text{O}_3 \) production and loss terms is not unique. It depends on how so-called "odd oxygen" is defined [Liu, 1977; Fishman et al., 1979; Levy et al., 1985]. On the other hand, the definition for net production of \( \text{O}_3 \) (i.e., photochemical production minus loss) is unique. Quantities calculated by using net production of \( \text{O}_3 \) are relatively easy to reproduce by other groups. In addition, the net production can be directly compared to the divergence of \( \text{O}_3 \) flux due to transport. In the following, the absolute \( \text{O}_3 \) production will be used only on one occasion, to calculate the \( \text{O}_3 \) production efficiency for the purpose of comparing results from this work with the results of Liu et al. [1987]. In the rest of the study, the net \( \text{O}_3 \) production will be used exclusively.

The nonlinearity of the ozone production efficiency obtained by Liu et al. [1987] (i.e., the Niwot case) is reproduced in profile A of Figure 2, using their definition of ozone production. It has essentially the same values as those of Liu et al. [1987]. Profiles B and C are the corresponding values for the ADMP composition and the EKMA composition, respectively. In these calculations the model is run for 5 days at first. During the 5-day period, \( \text{O}_3 \) is fixed at 40 ppbv, while \( \text{NO}_x \) is fixed at its specified levels (0.1 -- 100 ppbv). The ratio of anthropogenic NMHCs to \( \text{NO}_x \) is taken as 23.4 ppbc/ppbv, the same value used by Liu et al. [1987]. This ratio is about a factor of 5 higher than the ratio in the emissions of anthropogenic NMHCs and \( \text{NO}_x \). The higher ratio is expected for a rural site like Niwot Ridge as a result of the fact that \( \text{NO}_x \) is removed faster photochemically than most NMHCs. The diurnally changing photolysis rates are calculated for conditions at

\[
\begin{align*}
\text{H}_2\text{O} + \text{CH}_4, &\quad \text{fixed at 60% of relative humidity} \\
\text{NO}_x, &\quad \text{fixed at 0.5 ppbv} \\
\text{CO}, &\quad \text{fixed at 0.1 ppbv}
\end{align*}
\]
40°N on July 21 to represent the average summer solar insolation. The overhead ozone column density is fixed at 313 Dobson units and the ground albedo is assumed to be 10%. From 0500 LT on the sixth day, the O₃ mixing ratio is allowed to vary with time. All the results are taken from the sixth day. Since an approximate steady diurnal cycle is obtained from the first 5-day run, we omit the exchanges between PAN and NO₂ in calculating diurnally integrated production and loss for NOₓ and O₃. This will be discussed in more detail later.

Comparison of the three profiles in Figure 2 shows that the nonlinearity of the O₃ production efficiency decreases with the reactivity of anthropogenic NMHCs when the efficiency is defined by using absolute O₃ production. For example, at 0.1 ppbv of NOₓ, the differences in the O₃ production efficiency among the three cases are within 20%. In contrast, at 100 ppbv of NOₓ, the ozone production efficiency for the EKMA case is about 4 times that of the Niwot case. This is reflected in the concentrations of OH and the sum of all peroxy radicals (HO₂ + RO₂), as shown in Figure 3a and Figure 3b, respectively. It is clear that higher reactivity of NMHCs leads to a higher concentration of HO₂ + RO₂, which tends to enhance the O₃ production. The increase in HO₂ + RO₂ reduces the nonlinearity by enhancing O₃ production at high concentrations of NOₓ and NMHCs. The nonlinearity is reduced even further by the decrease of NOₓ loss due to reduced concentrations of OH.

When the net O₃ production is used to calculate the O₃ production efficiency, the results shown in Figure 4 are obtained. For the Niwot and ADMP compositions, the difference in the nonlinearity between Figure 4 and Figure 2 is small in the NOₓ range from 0.4 to 10 ppbv. Below 0.4 ppbv of NOₓ, the O₃ loss significantly suppresses the O₃ production efficiency, because the O₃ loss is almost independent of NOₓ, while O₃ production is roughly proportional to NOₓ [Fishman et al., 1979; Liu et al., 1983]. In fact, the ozone production efficiency becomes negative at NOₓ levels lower than 80 parts per trillion by volume (pptv) as the O₃ loss becomes greater than O₃ production. When the NOₓ level is greater than 10 ppbv, the O₃ production efficiency is also significantly affected by the inclusion of the O₃ loss, especially for the EKMA composition, in which a significant loss of O₃ occurs as a result of its reactions with propene. For the EKMA composition, at 100 ppbv of NOₓ, which corresponds to 585 ppbv of propene, the O₃ production efficiency is a factor of 30 smaller with the O₃ loss included than without the O₃ loss. Because of the large reduction of O₃ production at high NOₓ levels as the O₃ loss is included, the overall nonlinearity is enhanced for all three hydrocarbons compositions. For the EKMA case the ratio of O₃ production efficiency at 1 ppbv NOₓ to that at 100 ppbv NOₓ is greater than 40 in Figure 4, whereas the ratio is only about 1.4 in Figure 2. Contrary to Figure 2, an overall increase of the nonlinearity of the O₃ production efficiency with the reactivity of the hydrocarbon mixture is clearly demonstrated from Figure 4. Some detailed results from model runs are presented in Table 2 for the three NMHC compositions. One can see that at low NOₓ levels (e.g., below 1 ppbv), increase of the NMHC reactivity enhances the O₃ production efficiency.
TABLE 2. Twenty-Four Hour Accumulated NO\textsubscript{x} Loss, Ozone Production, Ozone Loss, Ozone Loss Due to O\textsubscript{3} Plus Ethene, and Ozone Loss Due to O\textsubscript{3} Plus Propene at Various NO\textsubscript{x} Levels for Three NMHC Compositions

| NMHC Composition | Niwot | ADMP | EKMA |
|------------------|-------|------|------|
| NO\textsubscript{x} = 0.1 ppbv |
| NO\textsubscript{x} loss | 2.92(9) | 2.87(9) | 2.66(9) |
| O\textsubscript{3} production | 1.86(11) | 1.89(11) | 1.96(11) |
| O\textsubscript{3} loss | 1.21(11) | 1.21(11) | 1.24(11) |
| O\textsubscript{3} loss due to O\textsubscript{3} + ethylene | 1.97(8) | 2.18(8) | 0 |
| O\textsubscript{3} loss due to O\textsubscript{3} + propene | 4.76(8) | 7.24(8) | 4.07(9) |
| NO\textsubscript{x} = 1 ppbv |
| NO\textsubscript{x} loss | 6.15(10) | 5.72(10) | 4.32(10) |
| O\textsubscript{3} production | 1.48(12) | 1.59(12) | 1.79(12) |
| O\textsubscript{3} loss | 2.54(11) | 2.71(11) | 3.58(11) |
| O\textsubscript{3} loss due to O\textsubscript{3} + ethylene | 3.66(9) | 4.20(9) | 0 |
| O\textsubscript{3} loss due to O\textsubscript{3} + propene | 8.84(9) | 1.40(10) | 8.26(10) |
| NO\textsubscript{x} = 10 ppbv |
| NO\textsubscript{x} loss | 7.36(11) | 6.89(11) | 4.87(11) |
| O\textsubscript{3} production | 8.03(12) | 9.67(12) | 1.33(13) |
| O\textsubscript{3} loss | 1.31(12) | 1.87(12) | 5.39(12) |
| O\textsubscript{3} loss due to O\textsubscript{3} + ethylene | 1.24(11) | 1.61(11) | 0 |
| O\textsubscript{3} loss due to O\textsubscript{3} + propene | 3.00(11) | 5.32(11) | 3.43(12) |
| NO\textsubscript{x} = 100 ppbv |
| NO\textsubscript{x} loss | 5.04(12) | 4.93(12) | 3.83(12) |
| O\textsubscript{3} production | 4.28(13) | 5.72(13) | 1.19(14) |
| O\textsubscript{3} loss | 2.10(13) | 3.45(13) | 1.16(14) |
| O\textsubscript{3} loss due to O\textsubscript{3} + ethylene | 4.51(12) | 5.93(12) | 0 |
| O\textsubscript{3} loss due to O\textsubscript{3} + propene | 1.08(13) | 1.96(13) | 9.47(13) |

Production and loss are given in units of cm\textsuperscript{-3} s\textsuperscript{-1}; NMHC is scaled to NO\textsubscript{x} by 23.4. Read 2.93(9) as 2.93 \times 10\textsuperscript{9}.

Fig. 5. O\textsubscript{3} production efficiency calculated from the ADMP composition for various NMHCs/NO\textsubscript{x} (ppbv/ppbv) levels: curve A, 0.3; curve B, 1; curve C, 4; curve D, 23.4; curve E, 50; curve F, 100; curve G, 300.

When levels of atmospheric NMHCs are low, the O\textsubscript{3} production efficiency depends on levels of CO, CH\textsubscript{4} and natural hydrocarbons. Consequently, the nonlinearity will depend on the levels of those species. Figure 6 shows results from four model runs for the ADMP composition. Curve A shows a baseline run with standard ADMP composition (i.e., curve D in Figure 5); curve B, a run with isoprene removed; curve C, a run with isoprene and CH\textsubscript{4} removed; and curve D, run with isoprene, CH\textsubscript{4} and CO removed. As expected, the O\textsubscript{3} production efficiency decreases when isoprene, CH\textsubscript{4}, and CO are

through both increased O\textsubscript{3} production and decreased NO\textsubscript{x} loss. On the other hand, at higher NO\textsubscript{x} levels increase of the reactivity reduces the O\textsubscript{3} production efficiency because of increased O\textsubscript{3} loss, mostly due to the O\textsubscript{3} reaction with alkenes.

The dependence of the nonlinearity on the ratio of NMHCs to NO\textsubscript{x} is studied by varying the ratio over a wide range in the model calculations. O\textsubscript{3} production efficiencies for seven cases, corresponding to ratios of 0.3, 1, 4, 23.4, 50, 100, and 300, respectively, are plotted in Figure 5 for the ADMP composition. This range of the ratio more than covers the values found in rural and urban atmospheres, according to a survey by Stockwell et al. [1988]. The degree of nonlinearity remains large for all cases. It is seen that below 10 ppbv of NO\textsubscript{x}, the O\textsubscript{3} production efficiency increases with the ratio of NMHCs to NO\textsubscript{x}. The increase of the efficiency is due to the combined effect of smaller OH concentration and greater HO\textsubscript{2} + RO\textsubscript{2} concentration. However, when NO\textsubscript{x} is above 10 ppbv, a tendency for the efficiency to decrease with the ratio becomes apparent. This is because the higher ratio leads to greater O\textsubscript{3} loss through its reaction with alkenes and, consequently, sup-

Fig. 6. O\textsubscript{3} production efficiency calculated from (curve A) the baseline run, (curve B) run with isoprene removed, (curve C) run with isoprene and CH\textsubscript{4} removed, and (curve D) run with isoprene, CH\textsubscript{4}, and CO removed, respectively.
removed. It is interesting to note that the \( \text{O}_3 \) production efficiency is essentially linear when isoprene, CO, and \( \text{CH}_4 \) are absent and NMHCs are linearly scaled to \( \text{NO}_x \). The change of \( \text{O}_3 \) production efficiency in the four model runs can be understood by examining the concentrations of \( \text{OH} \) and \( \text{HO}_2 + \text{RO}_2 \), as plotted in Figure 7. A noticeable feature in Figure 7a is the major role that CO plays in suppressing the abundance of \( \text{OH} \) at \( \text{NO}_x \) levels below 1 ppbv. The change in \( \text{OH} \) leads to a change in the \( \text{NO}_2 \) sink through the reaction of \( \text{NO}_2 \) with \( \text{OH} \), and consequently, a change in the \( \text{O}_3 \) production efficiency. However, as we can see from Figure 6, the variation of the \( \text{O}_3 \) production efficiency does not show an abrupt shift from curve C to curve D at low \( \text{NO}_x \) levels. This is because a more efficient supply of \( \text{RO}_2 \) from NMHCs than \( \text{HO}_2 \) from CO elevates the total amount of \( \text{HO}_2 + \text{RO}_2 \) and thus partly compensates for the relatively large change in \( \text{NO}_2 \) loss between curve C and curve D. Results from other model runs show that this also applies to Niwot and EKMA cases.

### Table 3. Twenty-Four Hour Accumulated Ozone Production, Ozone Loss, \( \text{NO}_x \) Loss, and 24-Hour Averaged Ozone Production Efficiency and Concentrations of \( \text{OH} \), \( \text{HO}_2 \), and \( \text{RO}_2 + \text{HO}_2 \) at 12:00 for Various \( \text{NO}_x \) Levels and for ADMP NMHC Composition

| \( \text{NO}_x \) (ppbv) | Baseline Run | Same, But Excluding Reactions of \( \text{RO}_2 + \text{HO}_2 \) | Same, but Including Reactions Between PAN and \( \text{NO}_x \) |
|-------------------------|--------------|------------------------------------------------------|------------------------------------------------------|
| \( \text{NO}_x = 0.1 \text{ ppbv} \) |
| \( \text{O}_3 \) production | 1.89(11)    | 2.40(11)     | 2.29(11)     |
| \( \text{O}_3 \) loss | 1.21(11)    | 1.32(11)     | 1.61(11)     |
| \( \text{O}_3 \) net production | 6.79(10)    | 1.08(11)     | 6.78(10)     |
| \( \text{NO}_2 \) loss | 2.87(9)     | 2.88(9)      | 2.86(9)      |
| \( \text{O}_3 \) production efficiency | 23.7        | 37.5         | 23.7         |
| \( \text{OH} \) | 4.63(6)     | 4.42(6)      | 4.63(6)      |
| \( \text{HO}_2 \) | 6.13(8)     | 7.20(8)      | 6.13(8)      |
| \( \text{RO}_2 + \text{HO}_2 \) | 1.37(9)    | 1.93(9)      | 1.37(9)      |
| \( \text{NO}_x = 1 \text{ ppbv} \) |
| \( \text{O}_3 \) production | 1.59(12)    | 1.71(12)     | 2.14(12)     |
| \( \text{O}_3 \) loss | 2.71(11)    | 2.94(11)     | 8.36(11)     |
| \( \text{O}_3 \) net production | 1.32(12)    | 1.42(12)     | 1.30(12)     |
| \( \text{NO}_2 \) loss | 5.72(10)    | 5.93(10)     | 5.72(10)     |
| \( \text{O}_3 \) production efficiency | 23.1        | 23.9         | 22.8         |
| \( \text{OH} \) | 8.06(6)     | 8.24(6)      | 8.06(6)      |
| \( \text{HO}_2 \) | 8.96(8)     | 9.85(8)      | 8.93(8)      |
| \( \text{RO}_2 + \text{HO}_2 \) | 1.55(9)    | 1.74(9)      | 1.54(9)      |
| \( \text{NO}_x = 10 \text{ ppbv} \) |
| \( \text{O}_3 \) production | 9.67(12)    | 1.01(13)     | 2.02(13)     |
| \( \text{O}_3 \) loss | 1.87(12)    | 2.00(12)     | 1.28(13)     |
| \( \text{O}_3 \) net production | 7.83(12)    | 5.07(12)     | 7.41(12)     |
| \( \text{NO}_2 \) loss | 6.89(11)    | 7.12(11)     | 6.91(11)     |
| \( \text{O}_3 \) production efficiency | 11.4        | 11.4         | 10.7         |
| \( \text{OH} \) | 8.22(6)     | 8.46(6)      | 8.24(6)      |
| \( \text{HO}_2 \) | 1.34(9)     | 1.44(9)      | 1.33(9)      |
| \( \text{RO}_2 + \text{HO}_2 \) | 2.45(9)    | 2.62(9)      | 2.41(9)      |
| \( \text{NO}_x = 100 \text{ ppbv} \) |
| \( \text{O}_3 \) production | 5.72(13)    | 5.87(13)     | 1.84(14)     |
| \( \text{O}_3 \) loss | 3.45(13)    | 3.63(13)     | 1.66(14)     |
| \( \text{O}_3 \) net production | 2.27(13)    | 2.25(13)     | 1.86(13)     |
| \( \text{NO}_2 \) loss | 4.93(12)    | 5.09(12)     | 4.94(12)     |
| \( \text{O}_3 \) production efficiency | 4.60        | 4.42         | 3.76         |
| \( \text{OH} \) | 5.25(6)     | 5.36(6)      | 5.26(6)      |
| \( \text{HO}_2 \) | 3.01(9)     | 3.16(9)      | 2.79(9)      |
| \( \text{RO}_2 + \text{HO}_2 \) | 5.16(9)    | 5.43(9)      | 4.76(9)      |

Production and loss are given in units of cm\(^{-3}\) s\(^{-1}\); production efficiency is given in units of molecules of ozone produced per \( \text{NO}_2 \) molecule consumed; concentration is given in units of cm\(^{-3}\); NMHC is scaled to \( \text{NO}_x \) by 23.4. Read 1.89(11) as 1.89 \times 10\(^{11}\).

As stated earlier, in our calculations conversions between PAN and \( \text{NO}_2 \) are omitted because the diurnally integrated conversion rates are nearly equal and cancel each other in most cases. It is important to check the accuracy of this assumption. In Table 3 a comparison of the baseline run and a run with the conversion terms included for the ADMP hydrocarbon composition is presented. It is clear that inclusion of the exchanges does not significantly affect the net \( \text{O}_3 \) production. Even at a high level, such as \( \text{NO}_x = 100 \text{ ppbv} \), the effect is limited to 20%. When the exchanges between PAN and \( \text{NO}_2 \) are included, the increase in \( \text{O}_3 \) production is almost canceled by the increase in the \( \text{O}_3 \) loss, which indicates that a
quasi-chemical steady state in the conversion is reached after the initial 5-day run. In fact, for low NO\textsubscript{x} (e.g., less than 1 ppbv) a run with less than 5 days is enough to reach such a quasi-steady state. If we regard the part of NO\textsubscript{x} transformed into the form of PAN as a loss of NO\textsubscript{x}, the nonlinearity of the O\textsubscript{3} production efficiency will be enhanced, because the PAN formation becomes comparable to and greater than the NO\textsubscript{x} loss through the OH and NO\textsubscript{2} reaction as the NO\textsubscript{x} level increases. For example, in the case of ADMP composition, the daily gain of PAN is only 7% of the diurnally integrated rate of the OH and NO\textsubscript{2} reaction at 0.1 ppbv of NO\textsubscript{x}, whereas the former is 2 times the latter at 100 ppbv of NO\textsubscript{x}. However, PAN acts as a temporary reservoir for NO\textsubscript{x}, and the part of NO\textsubscript{x} that is in the form of PAN will eventually be converted back to NO\textsubscript{x}. Therefore we have chosen to exclude the PAN formation from the NO\textsubscript{x} loss.

In calculations we have made so far, the concentrations of NO\textsubscript{x} and NMHCs are held constant. These conditions are appropriate for a steady state situation in which the losses of NO\textsubscript{x} and NMHCs are replenished by emissions or transport. Another way to investigate the problem is to view it as an initial value problem; that is, values of NO\textsubscript{x} and NMHCs are calculated in the continuity equations from their initial values. This approach was taken in creating the isolopes in Figure 1 and is the approach traditionally adopted by the EKMA control strategy. Figure 8 illustrates the O\textsubscript{3} production efficiencies plotted against initial NO\textsubscript{x} for the Niwot, the ADMP, and the EKMA compositions. Here initial NHMCs are scaled to the initial NO\textsubscript{x} with a factor of 23.4, as before. In these calculations, NO\textsubscript{x} and NMHCs are computed by assuming no emission sources and therefore decrease with time. The profiles in Figure 8 should be compared to those of Figure 4. The degree of nonlinearity of Figure 8 is substantially smaller than that in Figure 4. This is expected because the O\textsubscript{3} production efficiency is a value integrated over a day and thus represents an averaged quantity. Since photochemical lifetimes of reactive hydrocarbons and NO\textsubscript{x} are short compared to a day, the O\textsubscript{3} production efficiency for certain initial NO\textsubscript{x} and NMHC levels represents a value averaged over a wide range of NO\textsubscript{x} and NMHC concentrations. For example, in the case of the ADMP composition, an initial 100 ppbv of NO\textsubscript{x} at 0500 LT will result in 42 ppbv of NO\textsubscript{2}, 39 ppbv of HNO\textsubscript{3}, and 19 ppbv of PAN at noon. In addition, there is another factor involved in reducing the nonlinearity of O\textsubscript{3} production efficiency, that is, the changing NMHCs to NO\textsubscript{x} ratio. Our model calculations indicated that the ratio generally increases with time in the initial value mode. Therefore the value of O\textsubscript{3} production efficiency is also averaged over a range of NMHCs to NO\textsubscript{x} ratios. These two averaging procedures suppress the nonlinearity of O\textsubscript{3} production efficiency. 

**Effects of Uncertainty in Photochemistry**

There are significant gaps and uncertainties in our understanding and treatment of the photochemistry. It is not practical to quantify all of the uncertainty factors of the nonlinearity of O\textsubscript{3} production efficiency. In the following, however, we will examine the effects on the nonlinearity due to two major uncertainties in the photochemistry, namely, combination reactions of RO\textsubscript{2} with HO\textsubscript{2} and the nighttime sink of NO\textsubscript{x}.

In our model runs the combination reactions of RO\textsubscript{2} with HO\textsubscript{2} are included. These reactions have significant impact on abundances of HO\textsubscript{2} and RO\textsubscript{2} radicals and hence the O\textsubscript{3} production efficiency. However, reaction rates and products formed in these reactions are still quite uncertain at the present time. In the model, we adopt a value of $7.7 \times 10^{-14} \times \exp(1300/T) \text{ cm}^3 \text{s}^{-1}$ for the HO\textsubscript{2} reaction with CH\textsubscript{3}O\textsubscript{2}, as recommended by the Jet Propulsion Laboratory [DeMore et \textit{al.}, 1985], and a value of $3 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$ for reactions of HO\textsubscript{2} with all other higher RO\textsubscript{2}, as recommended by \textit{Atkinson} and \textit{Lloyd} [1984]. As for the products of the reactions, we take CH\textsubscript{3}OOH as the surrogate. To examine the effect of these combination reactions on the nonlinearity of O\textsubscript{3} production, we ran the model without the combination reactions of HO\textsubscript{2} and RO\textsubscript{2}. Model results corresponding to the ADMP composition case are presented in Table 3. One can see that exclusion of HO\textsubscript{2} reactions with RO\textsubscript{2} increases peroxy radical concentrations, especially at low NO\textsubscript{x} levels. At these levels the combination reactions compete with reactions of peroxy radicals and NO in converting the radicals [\textit{Carter \textit{et \textit{al.}}, 1979}].

As for the O\textsubscript{3} production efficiency, the value is increased at NO\textsubscript{x} levels below 1 ppbv when the combination reactions are removed. For example, the efficiency is increased by 58% at NO\textsubscript{x} = 0.1 ppbv. On the other hand, when NO\textsubscript{x} is above 10 ppbv, the efficiency is only slightly changed. This pattern is also valid for the Niwot and EKMA cases. In summary, the role played by the combination reactions of HO\textsubscript{2} with RO\textsubscript{2} in a photochemical system is to reduce the overall nonlinearity of O\textsubscript{3} production efficiency, mainly through suppressing the efficiency at NO\textsubscript{x} levels below 1 ppbv.

Another uncertainty in the chemistry that may significantly affect the O\textsubscript{3} production efficiency is the nighttime chemistry of NO\textsubscript{x}. During the night, NO\textsubscript{2} is converted to NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} through reactions

\[ \text{NO}_2 + O_3 \rightarrow \text{NO}_3 + O_2 \]  
\[ \text{NO}_2 + \text{NO}_3 + M \rightarrow \text{N}_2\text{O}_5 + M \]  

This process is followed immediately by the thermal decomposition of N\textsubscript{2}O\textsubscript{5}:

\[ \text{N}_2\text{O}_5 + M \rightarrow \text{NO}_2 + \text{NO}_3 + M \]
TABLE 4. Twenty-Four Hour Averaged Ozone Production Efficiency Calculated With and Without NO₂ plus O₃, With and Without Nighttime NO₃ Loss for Three NMHC Compositions at Various NOₓ Levels

| NOₓ, ppbv | Niwot NMHC Composition | ADMP NMHC Composition | EKMA NMHC Composition |
|-----------|------------------------|-----------------------|-----------------------|
| 0.1       | 12.73                  | 13.52                 | 14.93                 |
| 1         | 11.50                  | 12.70                 | 15.72                 |
| 10        | 2.29                   | 2.49                  | 2.57                  |
| 100       | 0.09                   | 0.05                  | -0.13                 |
| **With Night NO₃ Loss** |                       |                       |                       |
| 0.1       | 22.21                  | 23.66                 | 26.99                 |
| 1         | 20.08                  | 23.12                 | 33.46                 |
| 10        | 9.12                   | 11.41                 | 16.22                 |
| 100       | 4.33                   | 4.60                  | 0.75                  |

Efficiency calculated in units of molecules of ozone produced per NOₓ molecule consumed; NMHC is scaled to NOₓ by 23.4.

Figure 9 shows the O₃ production efficiency calculated under this assumption for three NMHC compositions. Remarkable reductions of the efficiency are apparent. The overall nonlinearity of the efficiency generally increases compared to Figure 4. A numerical comparison between Figure 9 and Figure 4 of the O₃ production efficiency at various NOₓ levels is presented in Table 4. The negative efficiency at NOₓ = 100 ppbv for the EKMA case, when the nighttime NO₃ loss is included, indicates that O₃ loss exceeds O₃ production as result of the inclusion of (12) as O₃ loss. If we choose the ratio of O₃ production efficiency at NOₓ = 1 ppbv to that at NOₓ = 10 ppbv as a measure of the overall nonlinearity of the O₃ production efficiency, the overall nonlinearity is raised from 2.20 to 5.02, from 2.03 to 5.10, and from 2.06 to 6.12, for the three NMHC compositions, respectively. It should be noted that the effect would double if N₂O₅, instead of NO₃, is assumed to be removed totally.

As mentioned earlier, an interesting question is the degree of nonlinearity of O₃ production efficiency when NMHCs, instead of NOₓ, are used as the reference precursor. To investigate the problem, we present three profiles in Figure 10 for the Niwot, ADMP, and EKMA compositions, respectively. They are O₃ production efficiencies calculated by using the sum of photochemical losses of CO, CH₄, and NMHCs, rather than the loss of NOₓ. The nighttime loss of NOₓ is included in these calculations. We continue to use NOₓ as the coordinate in Figure 10. It is obvious that the same nonlinearity will remain if NOₓ is replaced by NMHCs as the horizontal coordinate, since they are scaled by a constant ratio. The new O₃ production efficiency is essentially linear in the range of NOₓ value between 0.3 and 15 ppbv that is commonly found in rural air [Fehsenfeld et al., 1988]. One can see that the efficiency varies between 0.5 and 2 in this NOₓ range. Particularly for the two more realistic atmospheric NMHC compositions on a regional scale (Niwot and ADMP), the efficiency is confined to between 1 and 2. In other words, one to two O₃ molecules are produced for every molecule of CO or hydrocarbons that is oxidized. It appears that we may avoid the nonlinear problem in estimating regional O₃ budget by using CO and hydrocarbons as the reference precursor. However, while the nonlinearity problem is alleviated in this situation, one can no longer assume that loss rates of CO and hydro-
carbons are the same as their emission fluxes within the region where NOx is between 0.3 and 15 ppbv. Because of their long photochemical lifetimes, substantial amounts of CO, CH4, and other hydrocarbons emitted within the region will be transported and oxidized outside the region where the NOx level is substantially below 0.3 ppbv and the nonlinearity is much greater.

Although the major objective of this study is to investigate the chemistry aspect of the nonlinearity of the O3 production efficiency, it is clear that transport processes also play an important role. For example, transport processes tend to dilute secondary hydrocarbons and O3 to values significantly lower than those calculated by our model. The net effect is to reduce the nonlinearity. By using a box model the effect of transport has been neglected in this study. A transport process that has a direct impact on the nighttime sink of NOx is the formation of a shallow nocturnal inversion layer near the surface. In such a situation the exchange between the surface layer and the air aloft is inefficient. As a result, there usually is not enough O3 in the surface layer to react with NO and NO2 to form NOx, especially at high NOx levels. Therefore the high degree of nonlinearity shown in Figure 9 should be regarded as an upper limit. In this context we note that transport processes do not always reduce the degree of nonlinearity. For instance, transport of PAN, formaldehyde, and other similar secondary compounds from urban centers to rural areas will increase the nonlinearity by shifting ozone production from the former area to the latter. Obviously, a realistic study of the nonlinearity can best be accomplished by using a three-dimensional model with realistic transport parameterizations and emission sources.

**Implications for Ozone Budget and Distribution**

The existence of various degrees of nonlinearity relative to NOx and NMHCs has several important implications for the budget and distribution of ozone and therefore its control strategy. An obvious implication can be readily seen from Figure 4 or 9. It shows that for a constant area-integrated NOx emission flux, a concentrated emission source produces significantly less total ozone than a diffused emission source, except for NOx levels less than 0.3 ppbv. This means that atmospheric transport processes play an important role in increasing the ozone production efficiency because the transport processes tend to diffuse concentrated sources [Liu et al., 1987]. To evaluate accurately the budget and distribution of ozone, models with realistic transport processes are needed. This usually implies sophisticated three-dimensional models. On the other hand, if one's objective is to estimate an integrated regional ozone budget to within a factor of 3, a relatively simple approach can be adopted [Liu et al., 1987]. For example, to estimate the total ozone production in the eastern United States, our results show that knowledge of the average concentrations of NOx, CO, and hydrocarbons and the emission rate of NOx is probably enough. These parameters can then be used in the formula $S = EP[\{NOx\}]$, given earlier, to estimate the total ozone production. This is possible because the degree of nonlinearity in rural air is small enough to allow the ozone efficiency to be represented by an average value.

An interesting phenomenon of ozone distribution in the eastern United States is that rural ozone levels observed in the summer are either comparable to or frequently even higher than values of urban areas. This is surprising, because the levels of ozone precursors in urban atmosphere are usually an order of magnitude or more greater than those of rural air. For instance, NOx mixing ratios in rural air in industrialized countries usually lie in the range between 0.2 and 20 ppbv [Fehsenfeld et al., 1988], while the values of urban areas range from tens to hundreds of ppbv [e.g., U.S. Environmental Protection Agency (EPA), 1983]. We believe that the nonlinearity shown in this study is a major factor that contributes to this phenomenon. This can be demonstrated by the following example.

For simplicity, we assume that the NOx level is 5 ppbv in rural air and 50 ppbv over an urban area. In addition, we assume that the ratio of NMHCs to NOx is 23.4 for the former and 2 for the latter. Adopting the ADMP hydrocarbon composition, from the profiles in Figures 4 and 5 the ozone production efficiency can be seen to be 14 in the rural air and 2 in the urban air. This compensates, to a large degree, for the factor of 10 disparity in the NOx concentrations of the two areas.

It is clear that the nonlinearity will have important impacts on the control strategy for urban as well as rural oxidants. The factors that affect the degree of nonlinearity have to be considered in formulating an effective control strategy.

**Conclusions**

In this paper we have shown the dependence of the nonlinearity of the O3 production efficiency, defined as net O3 production divided by NOx loss, on various parameters. These include the NMHCs composition, the ratio of NMHCs to NOx, and the background abundance of natural hydrocarbons, CO and CH4. Generally, the overall nonlinearity increases with both the reactivity of the hydrocarbon mixture and the ratio of NMHCs to NOx. The increase of the nonlinearity is due (1) to enhancement of O3 production through increased RO2 and HO2, (2) to reduction of NOx loss through decreased OH at lower NOx levels; and (3) to increase in O3 destruction, that is attributed mainly to reactions of O3 with alkenes, at higher NOx levels. The background natural hydrocarbons, CO and CH4 play a very important role in generating the nonlinearity. When CO, CH4, and natural hydrocarbons are absent and NMHCs are scaled to NOx, the O3 production efficiency varies almost linearly with NOx in most situations.

In addition to these findings, our model study also reveals the effects of combination reactions of peroxy radicals (HO2 and RO2) on the nonlinearity of O3 production efficiency in the photochemical system. The radical combination reactions generally reduce the nonlinearity by substantially suppressing O3 production efficiency at low NOx levels.

When nighttime NOx loss is included in the model calculation, O3 production efficiency drops substantially for all levels of NOx. The drop is due to increased loss of both NOx and O3. The overall nonlinearity of the O3 production efficiency is increased by a factor more than 2 because of a relatively greater effect at higher NOx.

The nonlinear property also exists if this O3 production efficiency is defined as net O3 production, divided by total loss of CO, CH4, and NMHCs. In this case the O3 production efficiency becomes almost linear in a NOx range from 0.3 to 15 ppbv that is usually found in rural air [Fehsenfeld et al., 1988]. However, the smaller nonlinearity of the new O3 production efficiency in this NOx range will not reduce the complexity in estimating regional O3 budget, because the losses of CO, CH4, and some NMHCs can not be approximated by
their regional emission fluxes as a result of their long photochemical lifetimes.

The nonlinearity has several important implications for the budget and distribution of ozone. It shows that for a constant area-integrated NOx emission flux, a concentrated emission source produces significantly less total ozone than a diffused source, except at very low NOx levels. This may be the major factor that contributes to the observed phenomenon in the eastern United States that rural ozone levels are comparable to values in urban areas. The nonlinearity also implies that atmospheric transport processes tend to increase the ozone production by diffusing concentrated NOx sources.

By using a box model the present study is limited to examining the nonlinearity arising from photochemical processes. Moreover, many of the model calculations made were not realistic, because transport processes were omitted. It would be very valuable if this problem could be studied with a three-dimensional model that includes realistic parameterizations for transport processes.

Acknowledgments. We thank W. Stockwell for helpful discussions and for providing Figure 1b. This research has been funded as part of the National Acid Precipitation Program by the National Oceanic and Atmospheric Administration.

REFERENCES

Acid Deposition Modeling Project, Development and implementation of chemical mechanisms for the regional acid deposition model (RADM), Report to U.S. Environmental Protection Agency, Research Triangle Park, N. C., 1987.

Atkinson, R., and A. C. Lloyd, Evaluation of kinetic and mechanistic data for modeling of photochemical smog, J. Phys. Chem. Ref. Data, 13, 315-444, 1984.

Carter, W. P. L., A. C. Lloyd, J. L. Sprung, and J. N. Pitts, Jr., Progress in the validation of a detailed mechanism for the photodissociation of propane and n-butane in photochemical smog, Int. J. Chem. Kinet., 11, 45-111, 1979.

Crutzen, P. J., The role of NO and NO2 in the chemistry of the stratosphere and troposphere, Annu. Rev. Earth Planet Sci., 7, 443-472, 1979.

DeMore, W. B., D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, J. J. Margitan, M. J. Molina, and A. R. Ravishankara, Chemical kinetics and photochemical data for use in stratospheric modeling, Evaluation 7, JPL Publ., 85-37, 217 pp., 1985.

Dimitriades, B., and M. Dodge (Ed.), Proceedings of the Empirical Kinetic Modeling Approach (EKMA) Validation Workshop, EPA Rep. EPA-600/9-83-014, U.S. Environ. Prot. Agency, Research Triangle Park, N. C., 1983.

Dodge, M. C., Combined use of modeling techniques and smog chamber data to derive ozone precursor relationship, Proceedings of the International Conference on Photochemical Oxidant Pollution and Its Control, vol. II, edited by B. Dimitriades, EPA-600/3-77/001b, pp. 881-889, U.S. Environ. Prot. Agency, Research Triangle Park, N. C., 1977a.

Dodge, M. C., Effect of selected parameters on predictions of a photochemical model, EPA-600/3-77/049, U.S. Environ. Prot. Agency, Research Triangle Park, N. C., June, 1977b.

Ehnhalt, D. H., and T. W. Drummond, The tropospheric cycle of NOx in Chemistry of the Unpolluted and Polluted Troposphere, edited by H. W. Georgii and W. Jaeschke, D. Reidel, Hingham, Mass., 1982.

Fehsenfeld, F. C., D. D. Parrish, and D. W. Fahey, The measurement of NOx in the nonurban troposphere, in Tropospheric Ozone, edited by I. S. A. Isaksen, D. Reidel, Hingham, Mass., 1988.

Finlayson-Pitts, B. J., and J. N. Pitts, Jr., Atmospheric Chemistry: Fundamentals and Experimental Techniques, John Wiley, New York, 1986.

Fishman, J. S., Solomon, and P. J. Crutzen, Observational and theoretical evidence in support of a significant in-situ photochemical source of tropospheric ozone, Tellus, 31, 432-446, 1979.

Leighton, P. A., Photochemistry of Air Pollution, Academic, San Diego, Calif., 1961.

Leone, J. A., and J. H. Seinfeld, Comparative analysis of chemical reaction mechanisms for photochemical smog, Atmos. Environ., 19, 437-464, 1985.

Levy, H. B., II, J. D. Mahlman, W. J. Moxum, and S. C. Liu, Tropospheric ozone: The role of transport, J. Geophys. Res., 90, 3753-3771, 1985.

Liu, S. C., Possible effects on tropospheric O3 and OH due to NO emissions, Geophys. Res. Lett., 4, 325-328, 1977.

Liu, S. C., M. McFarland, D. Kley, O. Zafiriou, and B. Huerbert, Tropospheric NOx and O3 budgets in the equatorial Pacific, J. Geophys. Res., 88, 1360-1368, 1983.

Liu, S. C., M. Trainer, F. C. Fehsenfeld, D. D. Parrish, E. J. Williams, D. W. Fahey, G. Hübner, and P. C. Murphy, Ozone production in the rural troposphere and the implications for regional and global ozone distributions, J. Geophys. Res., 92, 4191-4207, 1987.

Lloyd, A. C., F. W. Lurmann, D. A. Godden, J. F. Hutchins, A. Q. Eschenroeder, and R. A. Nordisieck, Development of the ELSTAR photochemical air quality simulation model and its evaluation relative to the LARPP data base, NTIS PB-80-108-19, Natl. Tech. Inf. Serv., Springfield, Va., 1979.

Logan, J. A., M. J. Prather, S. C. Wofsy, and M. B. McIntoy, Tropospheric chemistry: A global perspective, J. Geophys. Res., 86, 7210-7254, 1981.

Novon, J. F., NOx and NO2 in the mid-Pacific troposphere, J. Geophys. Res., 88, 11,017-11,021, 1983.

Platt, U. F., A. M. Winer, H. W. Biermann, R. Atkinson, and J. H. Pitts, Jr., Measurement of nitrate radical concentrations in continental air, Environ. Sci. Technol., 18, 365-369, 1984.

Senfeld, J. H., Atmospheric Chemistry and Physics of Air Pollution, John Wiley, New York, 1986.

Singh, H. B., et al., Relationship between peroxyacetyl nitrate (PAN) and nitrogen oxides in the clean troposphere, Nature, 318, 347-349, 1985.

Stockwell, W. R., J. D. Milford, G. J. McRae, P. Middleton, and J. S. Chang, Nonlinear coupling in NOx-SO2-reactive organic system, Atmos. Environ., in press, 1988.

Trainor, M. E., Y. Hsie, S. A. McKen, R. Talamraju, D. D. Parrish, F. C. Fehsenfeld, and S. C. Liu, Impact of natural hydrocarbons on hydroxyl and peroxy radicals at a remote site, J. Geophys. Res., 92, 7254, 1981.

Whitten, G. Z., H. Hogo, and J. P. Killus, The carbon bond mechanism: A condensed kinetic mechanism for photochemical smog, Environ. Sci. Technol., 4, 690-700, 1980.

U.S. Environmental Protection Agency, National air quality and emissions trends report, 1981, EPA 450/4-83-011, Research Triangle Park, N. C., 1983.

X. Lin, S. C. Liu, and M. Trainer, Aeronomy Laboratory, Environmental Research Laboratory, R/E/AL4, National Oceanic and Atmospheric Administration, 325 Broadway, Boulder, CO 80303.

(Received May 16, 1988; revised September 23, 1988; accepted September 27, 1988.)