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Dependence of ozone production on NO and hydrocarbons in the troposphere

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Abstract. An expression for the production rate of O_3, $P(O_3)$, is derived based on a radical budget equation applicable to low and high NO_x conditions. Differentiation of this equation with respect to NO or hydrocarbons (HC) gives an approximate analytic formula in which the relative sensitivity of $P(O_3)$ to changes in NO or HC depends only on the fraction of radicals which are removed by reactions with NO_x. This formula is tested by comparison with results from a photochemical calculation driven by trace gas observations from the 1995 Southern Oxidants Study (SOS) campaign in Nashville, Tennessee.

Introduction

Early experience with photochemical smog in Los Angeles and other large urban areas led to the conclusion that O_3 production during high O_3 episodes was HC limited and that HC emission reductions were the most effective way of controlling O_3. In recent years there has been a rethinking of the ozone control problem and an increased awareness that NO_x is often the limiting factor, especially in non-urban regions [*Sillman*, 1990, 1993; *NRC*, 1991]. While the optimum strategy for controlling O_3 is still a matter of debate, it is clear is that the occurrence of NO_x limited and hydrocarbon limited conditions at different times and places will have to be taken into account.

The sensitivity of $P(O_3)$ to changes in NO and HC is calculated in this study in two ways. First, from a steady state photochemical model driven by trace gas concentrations observed during the Middle Tennessee Southern Oxidants Study. Second, from a radical budget equation. The latter approach relies on arguments and approximations from *Sillman* (1995), extended here to yield an analytic formula that explicitly gives the sensitivity of $P(O_3)$ to NO and HC. In this approximate formula, whether $P(O_3)$ is NO_x or HC limited is determined solely by the primary pathway for removing free radicals, a result which agrees with qualitative descriptions of O_3 production [e.g., *NRC*, 1991]. As *Sillman* [1995] has noted the radical removal pathway also controls the value of one combination of "indicator species", namely [peroxide]/[HNO_3].

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$P(O_3)$ from Steady State Calculations - Nashville

During the summer of 1995, the SOS conducted a field campaign in the Nashville - Mid Tennessee region directed at understanding the processes responsible for elevated O_3 levels. As part of this program the DOE G-1 aircraft flew 17 flights, mainly in the Nashville metropolitan area. Measurements included O_3, NO, NO_2, PAN, NO_y, CO, hydrocarbons (analyzed at York University, 1995), HCHO, H_2O_2, and organic peroxides. All instruments used for the present study have been described in conjunction with previous field campaigns [*Daum et al.*, 1996; *Lee et al.*, 1996; *Weinstein-Lloyd et al.*, 1996].

For the purpose of illustrating the two approaches of calculating $P(O_3)$ and its derivatives, we rely on data collected during two flights in which the Nashville urban plume was sampled. These flights were conducted in the late morning and early afternoon of 7/15 and 7/18 with most of the data collected in the boundary layer at an altitude of about 500 m. Sampling was also done in the free troposphere, between 1700 and 2800 m on 7/15. Measurements on 7/15 were conducted under stagnation conditions with O_3 concentrations reaching 120 ppb. On 7/18, there was well defined flow with 55 ppb O_3 upwind of the city and about 80 ppb downwind. A wide range of chemical concentrations were encountered on these 2 days; NO_x varied from 0.1 ppb above the boundary layer to 32 ppb in a power plant plume, and isoprene varied from below detection limit (2 ppt) to 3.3 ppb.

Steady state calculations similar to those described in *Kleinman et al.* [1997] were performed using as input the trace gas concentrations that were measured coincident with 13 hydrocarbon samples on 7/15 and 15 samples on 7/18. HCHO was not available on 7/18; the correlation between HCHO and O_3 as determined from the other flights was used instead. Photolysis rate constants were calculated from an Eppley UV radiometer and a radiative transfer program [*Madronich*, 1987] as previously described [*Kleinman et al.*, 1995]. In the calculations, the concentration of O_3, NO, CO, hydrocarbons, HCHO, H_2O_2, and ROOH are constrained to their observed values. A steady state concentration of PAN is assumed. Concentrations of methyl vinyl ketone and methacrolein are estimated to be 250 and 110% of isoprene, respectively, based on an equilibrium mixture governed by OH reactions. The calculations yield the concentrations of fast reacting species including OH, HO_2, RO_2, and NO_2 that are in equilibrium with the measured and estimated

mix of stable compounds. Rate information such as $P(O_3)$ and the fraction of radicals removed by different processes are also calculated.

Effects of changing NO or hydrocarbons are determined by taking the difference between a base case calculation and one in which the concentration of NO or HC is incremented by 10% and then held fixed. The HC increment is applied to CH_4 and CO as well as anthropogenic and biogenic hydrocarbons. In the short time period (5 minutes) that is allowed for the system to respond to the incremented NO or HC, a new equilibrium is reached by the fast reacting species, OH, HO_2, RO_2, and NO_2 (as verified by examining the time dependence of these species), but the slower reacting species do not have a chance to respond. The base case and incremented calculations are used to determine relative sensitivities, $d\ln P(O_3)/d\ln[NO]$ and $d\ln P(O_3)/d\ln[HC]$. A value of 1 for these quantities means that an n% change in the concentration of NO or HC yields an n% change in $P(O_3)$. These relative sensitivities are a measure of the effect of a hypothetical instantaneous change in [NO] or [HC]. They are useful in understanding the process of O_3 formation and its dependence on precursors but should not be confused with descriptors of emission changes, i.e., $d[O_3]/dE_{NO}$ or $d[O_3]/dE_{HC}$, which provide the change in O_3 concentration due to an emissions change at some upwind point.

The calculations indicate that $P(O_3)$ is close to zero at low NO_x and increases to a maximum value of about 30 (14) ppb h^{-1} as NO_x increases to about 14 (4) ppb on 7/15 (7/18). A further increase in NO_x causes $P(O_3)$ to decrease, a result which is attributed to the effects of NO_x as an inhibitor of free radical chemistry at high NO_x concentration [see e.g., *NRC*, 1991].

The dependence of $d\ln P(O_3)/d\ln[NO]$ and $d\ln P(O_3)/d\ln[HC]$ on NO_x is shown in Figure 1a. As NO_x levels increase there is a tendency for an increased sensitivity to HC and a decreased sensitivity to NO, culminating in a negative sensitivity to NO at the highest NO_x levels. Ozone production is said to be NO_x limited at low $[NO_x]$ where $d\ln P(O_3)/d\ln[NO] > d\ln P(O_3)/d\ln[HC]$. At high $[NO_x]$, $d\ln P(O_3)/d\ln[HC] > d\ln P(O_3)/d\ln[NO]$, and O_3 production is HC limited. Similar curves depict the response of O_3 concentration to changes in NO and HC emission rates [see e.g., *Cardelino and Chameides*, 1995].

In Figure 1b we plot the relative sensitivities that are shown in Figure 1a as a function of the fraction of radicals which are lost by reactions of the type Radical+NO_x → products. This fraction, denoted as L_N/Q, is calculated for each sample as the ratio of the loss rate from R+NO_x reactions, L_N, to the total radical production rate, Q. Because PAN is assumed to be in steady state, it does not contribute to Q as a radical source or to L_N as a radical sink. A comparison of Figures 1a and 1b indicates that there is significantly less scatter when the independent variable is L_N/Q. This result is shown below to follow from analytic expressions in which the relative sensitivities of $P(O_3)$ depend on L_N/Q but not on NO or NO_x alone.

$P(O_3)$ from Radical Budget

The only significant chemical source of ozone in the troposphere is from the reaction of peroxy radicals with NO, producing NO_2.

$$HO_2 + NO \rightarrow NO_2 + OH \qquad (R1)$$

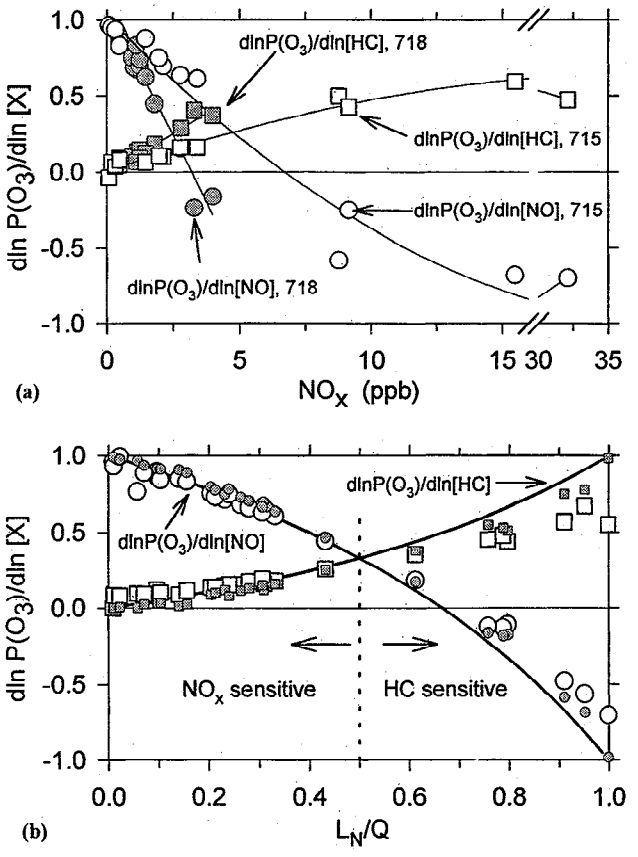

Figure 1. The relative sensitivity of O_3 production rate to [NO] and [HC], $d\ln P(O_3)/d\ln[NO]$ and $d\ln P(O_3)/d\ln[HC]$, as a function of (a) NO_x and (b) the fraction of radicals removed by reactions with NO or NO_2, L_N/Q. $P(O_3)$ is defined by (1) and does not include destruction processes. Symbols on panel (a) are results from steady state model calculations as identified in figure. Thin lines are a quadratic fit to data points illustrating that different fits are obtained for 7/15 and 7/18. Open symbols in panel (b) are the same sensitivities as shown in panel (a), but plotted as a function of the calculated process variable, L_N/Q. Analytic formula without organic nitrate (16-17) is shown by solid line. Shaded symbols are from (14-15) and differ from solid line by the organic nitrate term.

$$RO_2 + NO \rightarrow (1-\delta)\, NO_2 + \delta \text{ organic nitrate} + (1-\delta)\, RO \qquad (R2)$$

Ozone is produced with nearly a 100% yield from the subsequent photolysis of NO_2 and reaction of O atom with O_2. The O_3 production rate can therefore be expressed as

$$P(O_3) = k_t([HO_2]+[RO_2])[NO] \qquad (1)$$

where k_t is a weighted average rate constant for (R1) and (R2) which can be defined to take into account nitrate formation in (R2), i.e.,

$$k_t = k_1([HO_2]/([HO_2+RO_2]) + (1-\delta)\, k_2\, [RO_2]/([HO_2+RO_2]) \qquad (2)$$

Equation (1) forms the basis for many observational based studies on ozone production [see e.g., *Ridley et al.*, 1992; *Kleinman et al.*, 1995]. We will use this equation along with a radical budget equation for peroxy radical concentration in order to determine $P(O_3)$ and its sensitivity to changes in NO and HC. Our starting point is a statement that the production rate for radicals (odd hydrogen = OH + HO_2 + RO_2), Q, must equal the sum of radical sinks:

$$Q = 2k_3[HO_2]^2 + 2k_4[HO_2][RO_2] + L_R + L_N \quad (3)$$

k_3 and k_4 are rate constants for the reactions,

$$2\,HO_2 \rightarrow H_2O_2 + O_2 \quad (R3)$$

$$HO_2 + RO_2 \rightarrow ROOH + O_2 \quad (R4)$$

The first 2 terms in (3) therefore represent loss of radicals due to production of H_2O_2 and organic peroxides. L_R represents all other radical - radical reactions including $OH+HO_2$ and RO_2 + $R'O_2$. L_N includes all radical loss reactions between free radicals and NO or NO_2 including $OH+NO_2 \rightarrow HNO_3$ and RO_2+NO $\rightarrow$ organic nitrate. Equation (3) can be re-arranged to give the total peroxy radical concentration:

$$[HO_2] + [RO_2] = (Q - L_R - L_N)^{1/2}/(2k_{eff})^{1/2} \quad (4)$$

where k_{eff} is an effective rate constant for peroxide formation,

$$k_{eff} = k_3(1-\alpha)^2 + k_4(1-\alpha)\,\alpha \quad (5)$$

$$\alpha = [RO_2]/([HO_2] + [RO_2])$$

Substituting (4) into (1) gives

$$P(O_3) = k_t/(2k_{eff})^{1/2}(Q-L_R-L_N)^{1/2}[NO] \quad (6)$$

In previous studies we have evaluated O_3 production rates using (6) under low NO_x conditions where the term L_N can be ignored [*Kleinman et al.*, 1995, 1997]. In this study we include this term as we are interested in a wide range of conditions extending from low to high NO_x. As in the low NO_x case we will ignore the term L_R as being small compared with peroxide formation.

Relative sensitivities (i.e., dlnP/dln[NO] = ([NO]/P)dP/d[NO]) are obtained by differentiating (6) with respect to [NO] or [HC]:

$$\frac{d\ln P(O_3)}{d\ln[NO]} = 1 - \frac{1/2\,[NO]\,dL_N/d[NO]}{Q - L_N} \quad (7)$$

$$\frac{d\ln P(O_3)}{d\ln[HC]} = \frac{-1/2\,[HC]\,dL_N/d[HC]}{Q - L_N} \quad (8)$$

The dependence of Q on [NO] and [HC] is zero because the radical precursors (mainly O_3 and HCHO) are constrained to their observed values and therefore don't change with a change in NO or HC. The dependence of k_t and k_{eff} on NO and HC is generally small and has been ignored.

The key to using (7) and (8) is to find a good approximation for $dL_N/d[NO]$ and $dL_N/d[HC]$. First, we note that, as in the steady state calculation, PAN is assumed to be in equilibrium, and is neither a source or sink for radicals. Thus, radical loss is due mainly to production of HNO_3 and organic nitrate ($RONO_2$):

$$L_N \approx P(HNO_3) + P(RONO_2) = k_5[OH][NO_2] + \delta' P(O_3) \quad (9)$$

where k_5 is the rate constant for $OH+NO_2 \rightarrow HNO_3$ and production of $RONO_2$ has been written in terms of an average nitrate yield, δ', using (R2). According to *Sillman* [1990], the rate of O_3 production can be approximated by the rate at which OH reacts with hydrocarbons (including CO):

$$P(O_3) = k_6[OH][HC] \quad (10)$$

where k_6 is an effective rate constant for OH+hydrocarbon $\rightarrow$ HO_2 or RO_2. Although (10) does not apply to clean situations where HO_x cycling is inefficient, in those cases L_N/Q is near zero and a poor approximation to this term can be tolerated. Substituting (10) into (9) and assuming that NO is proportional to NO_2 (i.e., $[NO]=[NO_2]/\gamma$) and then differentiating, yields,

$$L_N = (\gamma k_5/k_6)([NO]/[HC])P(O_3) + \delta' P(O_3) \quad (11)$$

$$[NO]dL_N/d[NO] = L_N(1+d\ln P(O_3)/d\ln[NO]) - \delta' P(O_3) \quad (12)$$

$$[HC]dL_N/d[HC] = L_N(d\ln P(O_3)/d\ln[HC] - 1) + \delta' P(O_3) \quad (13)$$

Substituting (12-13) into (7-8) yields,

$$\frac{d\ln P(O_3)}{d\ln[NO]} = \frac{1 - 3/2\,L_N/Q + 1/2\,\delta' P(O_3)/Q}{1 - 1/2\,L_N/Q} \quad (14)$$

$$\frac{d\ln P(O_3)}{d\ln[HC]} = \frac{1/2\,L_N/Q - 1/2\,\delta' P(O_3)/Q}{1 - 1/2\,L_N/Q} \quad (15)$$

In many cases, as explicitly illustrated below, formation of organic nitrate can be ignored. A particularly simple expression results which gives the sensitivity of $P(O_3)$ with respect to NO and HC in terms of a single independent variable, L_N/Q:

$$\frac{d\ln P(O_3)}{d\ln[NO]} = \frac{1 - 3/2\,L_N/Q}{1 - 1/2\,L_N/Q} \quad (16)$$

$$\frac{d\ln P(O_3)}{d\ln[HC]} = \frac{1/2\,L_N/Q}{1 - 1/2\,L_N/Q} \quad (17)$$

The mechanistic significance of L_N/Q is that it distinguishes low NO_x states in which radicals are removed by forming peroxides from high NO_x states in which radicals are removed by reactions with NO_x [*Sillman*, 1990; *Kleinman*; 1991, 1994]. As discussed by *Sillman* [1995], the correspondence between low and high NO_x states and the production of peroxides or HNO_3 as the primary photochemical end product serves as the basis for using the ratio [peroxide]/[HNO_3] as an indicator for whether O_3 production is NO_x or HC limited. Note, however, the different time scales. L_N/Q gives sensitivities at the present moment, while the indicator ratio reflects the past history of an air mass.

In Figure 1b we compare $d\ln P(O_3)/d\ln[NO]$ and $d\ln P(O_3)/d\ln[HC]$ from (16-17) with the corresponding quantities determined from steady state simulations of the Nashville data set. On a qualitative level we see that the analytic formulas capture the significant features in the Nashville calculations. Equations (16-17) show a curve - crossing at exactly L_N/Q = 1/2, which separates NO from HC limited conditions. This result, which was previously found by *Sillman* [1995], is seen to be a good approximation to the Nashville data points. At the curve crossing, NO and HC reductions are equally effective in reducing $P(O_3)$. However, the relative sensitivities have a value of 1/3 indicating that neither reduction is particularly effective. At L_N/Q = 2/3, there is a zero crossing of $d\ln P(O_3)/d\ln[NO]$, close to what the Nashville data shows. Figure 1b also shows the sensitivities from (14-15) with the organic nitrate term calculated from the steady state box model. The difference between the shaded symbols and solid curve in Figure 1b represents the effect of organic nitrate which is seen to be small, in spite of the presence of more than 3 ppb of isoprene (with δ' = 0.15) in several samples. A comparison between the open and shaded symbols indicates that including organic nitrate generally improves the agreement between theoretical and calculated

sensitivities. *Sillman* [1995] has discussed the effects of PAN on the NO-HC transition point. He arrives at the criteria $P(HNO_3) = 2\ P(\text{Peroxide})$, where "P" is production rate. This reduces to $L_N/Q = 1/2$ if $P(PAN) = 0$ and gives $L_N/Q > 1/2$ if $P(PAN) > 0$. This result also follows from (11)-(15) if P(PAN) replaces $\delta' P(O_3)$.

Conclusion

A radical budget equation for O_3 production rate yields realistic sensitivities to changes in NO and HC under both low and high NO_x conditions as judged by a comparison with steady state model results from the SOS field campaign in Nashville, TN. The most important factor in determining the sensitivity of $P(O_3)$ to NO and HC is the fraction of radicals that are removed by reactions of the type Radical + $NO_x \rightarrow$ products, a result that agrees with the use of the "indicator species" ratio, $[\text{peroxide}]/[HNO_3]$, to diagnose NO_x and HC limited conditions [*Sillman*, 1995]. A crossover from NO to HC sensitive conditions occurs when 1/2 of radicals are removed by R+NO_x. NO is counter- productive to O_3 production when more than 2/3 of radicals are removed by reactions with NO_x. Although the present study is concerned with the dependence of $P(O_3)$ on NO and HC, not the dependence of $[O_3]$ on emissions, it is likely that the two problems are linked as $[O_3]$ is due to O_3 production over the past history of an air parcel. It therefore seems worthwhile to investigate whether the insensitivity of $P(O_3)$ to changes in NO and HC over a wide range of L_N/Q, contributes significantly to the problem of controlling peak O_3 concentrations.

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