Sensitivity of ozone production rate to ozone precursors


Atmospheric Sciences Division, Brookhaven National Laboratory, Upton, New York 11973

Judith Weinstein-Lloyd

Chemistry/Physics Department, SUNY/Old Westbury, Old Westbury, New York 11568

Jochen Rudolph

Chemistry Department and Centre for Atmospheric Research, York University, Toronto, Ontario M3J 1P3, Canada

Abstract. The photochemical equations describing O₃ formation in the lower troposphere contain 2 major sink terms for free radicals; combination reactions and reactions with NOx. Knowing the fraction of radicals removed by reactions with NOₓ, termed Lₙ/Q, allows one to predict the sensitivity of O₃ production to NO and VOCs. We derive an analytic formula that gives LN/Q in terms of readily measured O₃ precursors and test this formula using constrained steady state calculations based on field observations gathered in Phoenix, Arizona. The formula quantifies well-known results regarding the effects of dilution, oxidation, and the production of oxidants on the transition from VOC to NOₓ sensitive behavior as an air parcel is advected away from an urban source.

1. Introduction

Ozone is formed in the lower atmosphere by a sequence of chemical reactions requiring sunlight, NOₓ (NO + NO₂), and VOCs. Determining the relation between O₃ and its precursors has been the object of more than 4 decades of research [NARSTO, 2000]. It has been found that O₃ formation depends on NOₓ and VOC emissions in a complicated and non-linear way. Several qualitative generalizations are, however, possible. In an urban plume O₃ becomes more VOC sensitive (i.e., more responsive to a change in VOCs) at high NOₓ to VOC ratios and at high absolute concentrations. As an urban plume is advected away from its source it tends to become more dilute and have a lower NOₓ to VOC ratio. For both reasons a plume will evolve in the direction of being VOC sensitive near its source to being NOₓ sensitive far away [Staffelbach et al., 1997; Duncan and Chameides, 1998; Sillman, 1999].

In this article we consider the sensitivity of the rate of O₃ production, P(O₃), to changes in atmospheric concentrations of NOₓ and VOCs. This problem is a prerequisite to the more complicated problem of determining the response of O₃ to an emissions change. The behavior of P(O₃) is a property of an air mass and can be characterized reasonably well by means of chemical measurements. In contrast, a sensitivity to an emissions change is not a local property [Kleinman, 2000]. It depends on the entire time history of an air mass and therefore cannot be directly observed, although several indirect techniques are available [Cardelino and Chameides, 1995; Sillman, 1995]. In a general sense, we know that the two problems must be related as O₃ concentration is due to O₃ production occurring over the time history of an air mass.

We showed in a previous study [Kleinman et al., 1997] that the sensitivity of P(O₃) to NO and VOCs is given by a simple analytic function of LN/Q, the fraction of free radicals removed by reactions with NOₓ. LN/Q enters our equations from a starting point which is a conservation statement for free radicals (also known as odd-hydrogen and consisting primarily of OH, HO₂, and RO₂s). Production of free radicals occurs principally from photolysis reactions. Radicals are removed by two major categories of reactions; combination reactions between radicals, including HO₂ + HO₂ --> H₂O₂; and reactions between radicals and NOₓ, principally OH + NO₂ --> HNO₃. The conservation statement for free radicals can be written as,

\[ Q = L_R + L_N \]  (1)

where Q is the production rate, Lₐ is the loss rate due to radical-radical reactions, and Lₙ is the loss rate due to all reactions of radicals with NOₓ.

In this study we examine the variable LN/Q. We provide an analytic formula that gives LN/Q in terms of O₃ precursors. This formula can be used to estimate NOₓ and VOC sensitivity based on readily measured concentrations. From the analytic expression for LN/Q it is easy to show how NOₓ and VOC sensitivity depends on the NOₓ to VOC ratio and on absolute concentration.

2. Experiment

During the late spring of 1998, the Atmospheric Chemistry Program of DOE in collaboration with the Arizona Department of Environmental Quality conducted a photochemistry field campaign in the Phoenix metropolitan area. The DOE G-1 aircraft was used to sample the atmosphere upwind, over, and downwind of the metropolitan area. Measurements included, O₃, CO, VOCs, NO, NO₂, NOₓ, HCHO, H₂O₂, organic peroxides, actinic flux, temperature, and dew point. We will use these observations to illustrate and check a series of analytic results that we believe are generally applicable to urban plumes.

Characteristics of the Phoenix air basin during the field campaign were a very low humidity, high temperature and solar...
insolation, an emissions mixture dominated by transportation sources, and low biogenic emissions. Twenty two flights were conducted with about half of the flight time used for sampling over high emission region. Clean air was observed in the early morning in the nighttime residual layer and later in the day above the convective boundary layer. A wide range of chemical concentrations were encountered. For example NOx concentration varied from 70 ppt to 39 ppb, O3 from 29 to 92 ppb, and CO from a background of about 120 ppb to 470 ppb. Results are presented in greater detail elsewhere [Fast et al., 2000].

3. Model

We have applied a constrained steady state (CSS) photochemical box model to the Phoenix observations. This model uses as input the trace gas concentrations (excluding NO2) observed from the DOE G-1. The limiting factor in the use of this model is the availability of VOC data which is determined from discrete canister samples. Model predictions include the concentrations of free radicals and NO2 that are in rapid equilibrium with the observed mixture of trace gases. Of particular importance to this study are predictions of the production rate of O3, \( \frac{dP(O_3)}{dP} \); the formation rate of free radicals, \( Q \); and the rate at which radicals are lost by different reaction pathways, \( L_4 \) and \( LR \). The kinetic equations in the model are from the chemical mechanisms of Stockwell et al. [1990] and Paulson and Seinfeld [1992]. PAN is not a calculated variable as it is assumed to be in steady state. The CSS model is the same as previously used and is described in more detail elsewhere [Kleinman et al., 1997; 2000].

CSS calculations have been performed for 123 locations during the Phoenix field campaign. Calculations were repeated with perturbed values of NO or VOCs. A finite difference formula was used to determine the relative sensitivity of \( P(O_3) \) to NO and VOCs. In Figure 1 we compare those results with sensitivities calculated from the following formulas derived by Kleinman et al. [1997]:

\[
\frac{dP(O_3)}{dP(NO)} = \left( 1 - \frac{3}{2} L_4/Q \right) \left( 1 - \frac{1}{2} L_4/Q \right) (2)
\]

It is seen that the variable \( L_4/Q \) provides information on NOx and VOC sensitivity similar to that obtained from the CSS calculations. A low value of \( L_4/Q \) yields NOx sensitive chemistry; a high value VOC sensitive chemistry. The tendency to produce peroxides under NOx sensitive conditions and HNO3 under VOC sensitive conditions was first noted by Silliman [1995] and forms the basis of an Indicator Species method. Similar results have already been presented for Nashville, Tennessee and the New York City metropolitan area [Kleinman et al., 1997; 2000].

4. Theory

The derivation of an analytic formula for \( L_4/Q \) begins with the conservation condition for free radicals expressed in (1). \( L_R \) includes contributions from peroxide formation and biomolecular radical-radical destruction reactions such as OH + HO2. The later reactions are generally less important and will be ignored. As in previous work we express the rate of peroxide formation using an effective rate constant, \( k_{eff} \), defined in terms of the ratio of [HO2] to [RO2] and the individual rate constants for forming H2O2 and ROOH [Kleinman et al., 1997]. RO2 + RO2' reactions are ignored in the analytic equations but not in the CSS model. For each peroxide molecule formed, 2 radicals are lost and

\[
L = 2 k_{eff} ([HO2] + [RO2]) (4)
\]

Combining (1) and (4), we obtain

\[
2 k_{eff} ([HO2] + [RO2]) = Q(1 - L_4/Q) (5)
\]

The primary NOx - radical reaction is

\[
OH + NO2 \rightarrow HNO3 (R1)
\]

and we approximate \( L_R \) as

\[
L_N = k_1 [OH] [NO2] (6)
\]

So far we have dealt with sources and sinks of radicals. Under many conditions each radical that is formed participates in a multi-step chain reaction before that radical is removed [e.g., Silliman et al., 1990; Jeffries and Tonnesen, 1994; Seinfeld and Pandis, 1997; Tonnesen and Dennis, 2000]. The chain contains the following 2 links

\[
\begin{align*}
&\text{dlnP(O3)/dln[NO]} = \left( 1 - \frac{3}{2} L_4/Q \right) \left( 1 - \frac{1}{2} L_4/Q \right) \\
&\text{dlnP(O3)/dln[VOC]} = \left( 1 - \frac{1}{2} L_4/Q \right) (3)
\end{align*}
\]
Figure 3. (a) The dependence of LN/Q on log (α). Solid line is the analytic relation in (12). Data points are determined from Phoenix observations which yield values for α. CSS calculations yield the corresponding values of LN/Q. (b) The dependence of LN/Q on log(NOx).

\[
\text{OH} + \text{VOC} \rightarrow \text{HO}_2 \quad (R2)
\]

\[
\text{HO}_2 + \text{NO} \rightarrow \text{OH} \quad (R3)
\]

Note that the full reaction sequence can be more complicated as OH+VOC can produce RO2s, but eventually (in the absence of a radical loss event) an HO2 will be produced to regenerate OH. In the limit that chain propagation is much more important than chain initiation (or equivalently, chain termination) we obtain

\[
(\text{VOC}) = k_j [\text{NO}] [\text{NO}_2] \]

(7)

The term \( k_j[\text{VOC}] \) in (7) is an abbreviation for a summation over all VOCs, including CO and CH4, which can participate in (R2).

From this point on no additional approximations are made. A "constant" γ is defined by

\[
\gamma = \frac{[\text{HO}_2]}{[\text{HO}_2] + [\text{RO}_2]}
\]

(8)

Substituting (8) into (5), we get

\[
2k_{\text{eff}} (\text{HO}_2) \gamma^2 = Q (1 - \text{LN/Q})
\]

(9)

Combining (6) and (7) to eliminate [OH] yields

\[
[\text{HO}_2] = k_j [\text{VOC}] \text{LN} / (k_j [\text{NO}] k_i [\text{NO}_2])
\]

(10)

Substituting (10) into (9) gives a quadratic equation for LN/Q

\[
(1 - \text{LN/Q}) = \frac{2k_{\text{eff}} Q}{\gamma^2} \left[ \frac{k_j [\text{VOC}]}{k_j [\text{NO}] k_i [\text{NO}_2]} \right]^2 (\text{LN/Q})^2
\]

with solution

\[
\text{LN/Q} = \frac{-\alpha/2 + (\alpha^2 + 4\alpha)^{1/2}}{2}
\]

(12)

where

\[
\alpha = \left( \frac{k_j [\text{NO}] k_i [\text{NO}_2]}{k_j [\text{VOC}]} \right)^2 \left( \frac{1}{2Q k_{\text{eff}}} \right)
\]

(13)

Equations (12-13) give LN/Q in terms of concentrations and parameters which can be readily observed or estimated. Q can be determined to reasonable accuracy by measuring O3, H2O, HCHO, and solar intensity. \( k_{\text{eff}} \) and \( \gamma \) depend on the HO2 to RO2 ratio which can be estimated based on specific model calculations or on general experience with similar chemical environments.

5. Comparisons with CSS results

We use the CSS calculations to test the analytic equations for LN/Q. Figure 2 shows a comparison between LN/Q obtained from (12-13) and that obtained from a complete CSS calculation. Two sets of results are shown. In one case (12-13) is evaluated using model predictions for the HO2 to RO2 ratio. In the other case the evaluation is done without this information using a representative value of 2 to 1 for the ratio. The later calculation is done to assess the utility of applying (12-13) using commonly available measurements. Both cases show reasonable agreement.

Equations (12) and (13) show how LN/Q depends on NOx, VOCs, and Q. Perhaps the easiest way to visualize the relation is to note that LN/Q is a monotonic, increasing function of α. Alpha, in turn, is proportional to (NOx2/VOC)2/Q, assuming that both NO and NO2 are proportional to NOx. Thus, LN/Q varies in the same sense as (NOx2/VOC)2/Q; i.e., an increase in NOx yields a higher value of LN/Q (more VOC sensitive) while an increase in VOCs or Q yields a lower value of LN/Q (more NOx sensitive). Because NOx appears to the 4th power in α and VOCs only to the -2 power, LN/Q will be affected more by a change in NOx than by a change in VOCs. Note that, according to (13), it is not the VOC concentration itself that is relevant but the VOC reactivity, \( k_j[\text{VOC}] \).

Figure 3a illustrates the monotonic dependence of LN/Q on α. The solid line is the analytic relation given by (12). The data points show the range of values of α observed in Phoenix and the corresponding values of LN/Q calculated from the CSS model. There is a good correspondence between analytic and calculated points. In the Phoenix data set α varies by 13 orders of magnitude. High values occur in samples taken over the downtown high emission rate region, while the lowest values are from the clean free troposphere. As shown in Figure 3b, most of the variability in α (and hence LN/Q) is due to NOx, which appears as a 4th power and furthermore varies by almost 3 orders of magnitude. VOC reactivity and radical production rate affect LN/Q as described by (12-13). However, these variables are less important than NOx because they appear to a lower power in α and also, for the Phoenix data set, their range of values is relatively small. Figure 3b shows that LN/Q is near 1 for values of NOx between the maximum and about 3 ppb. Within this concentration range, P(O3) is very VOC sensitive and remains so, until NOx is lowered past the 3 ppb threshold value. This threshold depends on chemical conditions, specifically the concentration of VOCs and the rate of radical production. Further decreases in NOx are accompanied by a large change in LN/Q and hence a transition between VOC and NOx sensitivity.
6. Discussion and Conclusions

As an air parcel is advected away from its source region, concentrations will change due to oxidation of primary pollutants, dilution and the mixing-in of background air, and the formation of secondary pollutants. We can see how these factors affect L/Q by expressing \( \alpha \) as proportional to NO\(_2\) (NO\(_x\)/VOC)\(^2\)/Q. Oxidation reactions will decrease NO\(_2\) and also decrease (NO\(_x\)/VOC)\(^2\) because NO\(_x\) is more reactive than the average VOC [Duncan and Chameides, 1998]. Dilution, accompanied by the mixing-in of background air, will decrease NO\(_2\) and also (NO\(_x\)/VOC)\(^2\). The later decrease is due to the circumstance that background air tends to have very little NO\(_x\) but can have significant VOC reactivity due to CO and CH\(_4\). Production of O\(_3\) and other photochemical oxidation products such as HCHO will increase Q. All of these factors lead to a decrease in L/Q and therefore contribute to the transition from VOC to NO\(_x\) sensitive behavior as a plume ages.

L/Q is in some ways analogous to photochemical age [e.g., McKeen et al., 1990] in that it is a progress variable that specifies where an air mass is in its chemical and dynamic evolution. Input of fresh emissions into the plume can of course upset the monotonic decrease in L/Q.

The photochemical equations used in typical calculations treat tens to thousands of discrete species. Recently, the photochemical equations have been treated as a dynamical system and the question has been asked as to what number of species is needed to reproduce the behavior of the full set of equations [Field et al., 2001]. Here we are interested in a related question, the number of variables needed to describe steady states. By working with a radical budget equation we are able to write equations for quantities such as P(O\(_3\)) in terms of only 3 variables, NO\(_x\), VOCs, and Q [Kleinman et al., 1997; Daum et al., 2000]. One variable, namely L/Q, is sufficient to quantify the NO\(_x\) and VOC sensitivity of P(O\(_3\)). As we have shown here that variable can be evaluated based on readily measured concentrations.

Acknowledgement. We thank the pilots and flight crew from PNPL for a job well done. We gratefully acknowledge the Atmospheric Chemistry Program within the Office of Biological and Environmental Research of DOE for supporting the Phoenix field and analysis activities and for providing the G-I aircraft. This research was performed under sponsorship of the U.S. Department of Energy under contract DE-AC02-98CH10886.

References


Sillman, S., The relation between ozone, NO\(_x\), and hydrocarbons in urban and polluted rural environments, Atmos. Environ., 33, 1821-1845, 1999.

Sillman, S., The use of NO\(_x\), HCHO, H\(_2\)O\(_2\) and HNO\(_3\) as indicators for ozone-NO\(_x\)-hydrocarbon sensitivity in urban locations, J. Geophys. Res., 100, 14,175-14,188, 1995.


(email: phdaum@bnl.gov; kleinman@bnl.gov; ynlee@bnl.gov; lindan@bnl.gov; srs@bnl.gov.)

J. Weinstein-Lloyd, Chemistry/Physics Department, SUNY/Old Westbury, Old Westbury, NY 11568. (email: jllloyd@bnl.gov.)

J. Rudolph, Chemistry Department and Centre for Atmospheric Research, York University, Toronto, Ontario M3J 1P3, Canada. (email: rudolph@yorku.ca.)

(Received Nov. 7, 2000; revised May 16, 2001; accepted May 17, 2001.)