

Radical chemistry at a forested continental site: Results from the PROPHET 1997 campaign

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[1] Radical chemistry at a forested site in northern Michigan has been examined using measurements made by a radical amplifier system in the summer of 1997. The radicals show a diurnal variation with the maximum concentration being measured several hours after solar noon. Low but observable concentrations were present at night, but these levels are inconsistent with the previously postulated active nighttime chemistry driven by high concentrations of highly reactive hydrocarbons. A box model, constrained by measured concentrations of CO, O₃, NO, NO₂, isoprene, and peroxyacetylnitrate, was found to simulate both the maximum concentrations and their diurnal variation. Model sensitivity studies indicate that 54% of the radical production comes from sources other than ozone photolysis, and the presence of isoprene has an impact on the radical concentration through impacts on both radical production and loss. *INDEX TERMS*: 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); *KEYWORDS*: radicals, PROPHET, tropospheric chemistry, continental

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1. Introduction

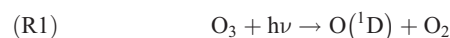
[2] Tropospheric chemistry is predominantly the free radical initiated oxidation of low oxidation number forms of carbon, nitrogen and sulfur, to produce oxidants. The high reactivity of these radicals means that they have short lifetimes and low concentrations, and that catalytic oxidation processes are especially important.

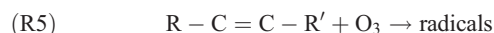
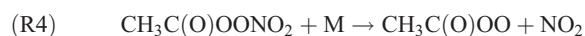
[3] The most common approach to improving understanding of the complex chemistry and meteorology responsible for the chemical state of the atmosphere has been to use a combination of field measurements and computer-based models. In designing tests of the chemistry, radicals are especially important, as their lifetimes are short compared to dynamical processes, which allows the use of simplified dynamic models to probe the chemistry.

[4] It is now possible to measure atmospheric radical concentrations, and a great deal of work has been done to reconcile measurements with our current understanding of the radical chemistry. In the marine environment and free troposphere Penkett *et al.* [1997] and Monks *et al.* [1996] have shown good agreement between conceptual models and observations. In other studies radical measurements have been shown to have good agreement with those generated by computer based chemistry models [e.g., Hofzumahaus *et al.*, 1996; Brune *et al.*, 1998; Reiner *et al.*, 1997; Cantrell *et al.*, 1993; McKeen *et al.*, 1997; Cantrell *et al.*, 1997; Zanis *et al.*, 2000; Burkert *et al.*, 2001].

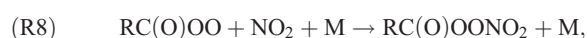
[5] Rural and forested areas still present a challenge to our understanding of atmospheric chemistry in general, and radical chemistry in particular. This is because the simplifying assumptions that can be made in analyzing the chemistry in pristine or urban environments cannot be made. Unlike the free troposphere and marine environments, methane is not the dominant hydrocarbon. Anthropogenic hydrocarbons can be transported into the area and these are supplemented by the natural or biogenic emissions. Also these regions are subject to a range of NO_x conditions. Natural NO_x levels are usually low, especially compared to urban environments, but the transport of higher concentrations from strong urban and industrial source regions often occurs. This challenge is also apparent in the radical chemistry where a large number of radical sources and sinks need to be considered. Radical production can arise from the photolysis of ozone (R1 and R2), photolysis of hydrocarbon oxidation products such as aldehydes (e.g., R3), peroxyacetylnitrate (PAN) decomposition (R4), or alkene ozonolysis (R5).

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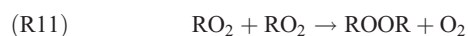
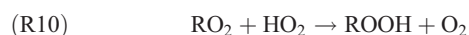
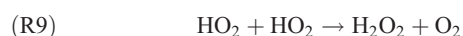




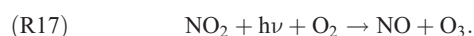
The dominant radical removal reactions are either the reaction of HO with NO₂ to produce nitric acid (R6), organic peroxy radical (denoted by RO₂) reactions with NO to produce nitrates (R7), or peroxyacyl radical reactions with NO₂ to give peroxy nitrates (R8),



or the so-called self-reactions, which largely give rise to peroxides (R9–R11).



Between production and loss the most important radical reactions are those that are catalyzed by the nitrogen oxides, result in the oxidation of hydrocarbons, and produce ozone. Using CO as a surrogate for the hydrocarbons, this chemistry can be summarized by:



Such reactions do not produce or destroy radicals, but they control the relative amounts of the different types of radicals. Since, in any particular environment, different classes of radicals will have different loss rates this control can have an indirect impact on radical concentration. Therefore the successful prediction of radical concentration as a function of time and place is determined the level of understanding of the radical production, propagation and

destruction reactions. The measurement and interpretation of radical concentration measurements in a remote, forested area is a necessary component of obtaining this understanding.

[6] The Program for Research on Oxidants: Photochemistry, Emissions and Transport (PROPHET) aims to characterize regional air pollution episodes in the midwest United States. This region is forested and naturally pristine and clean conditions are often observed. However large urban and industrial sources can greatly perturb the atmospheric environment particularly leading to elevated ozone concentrations. Understanding the details of the chemistry in these environments is necessary to show we can represent the transition region from an urban to a remote area, and also to supply sound information for the protection of these ecosystems from atmospheric induced damage. The focus of the program is a site in northern Michigan where researchers for over 20 institutions undertake measurements, analyze data, and model results [Carroll *et al.*, 2001] with the objective of characterizing relative roles of emissions, transport and chemistry in oxidant production.

[7] This paper examines the radical chemistry at the PROPHET site through the interpretation of a set of radical measurements made in the summer of 1997. These results are interpreted with a simple conceptual model of the controls on the radical chemistry and then in a more quantitative manner using a chemically detailed box model.

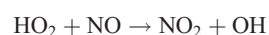
2. Experiment

2.1. Site

[8] The experimental site for PROPHET is located near Pellston, Michigan (45°33'33" N and 84°42'53" W), about 5 km eastward of the University of Michigan Biological Station. The sampling site is situated in the middle of a forested area, with beech and maple being the dominant species. Most of the trace gases are measured in an air sample drawn through a glass manifold from the top of a 31 m high tower, about 15 m above the canopy. The residence time for the air sample in the manifold is less than 2 s. For the very short-lived species, such as the peroxy radical measurements reported here, the instruments are mounted on the tower and the sampling was performed at the top of the tower.

2.2. Instrumentation

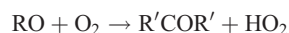
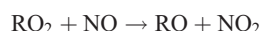
[9] Radicals were measured using a radical detector on the basis of the principle of chemical amplification, similar to that described by *Arias and Hastie* [1996]. The radical detector is a chemical reactor in which radicals oxidize added CO and NO to CO₂ and NO₂. The hydrogen radicals (H, HO, and HO₂) enter into a chain reaction (which respond to R16, R12, R13, respectively):



Since this sequence regenerates the radical, and because there is always excess CO and NO, the radicals cycle through these reactions producing a large number of NO₂ molecules per radical entering the system. The radical concentration can be determined from the NO₂ produced and a knowledge of the number of times a radical cycles through reactions R16, R12, and R13 before being lost to a termination reaction (the chain length). Major termination reactions in this system are reactions R18–R20:



Organic peroxy radicals (RO₂) that are reduced by NO generate an HO₂ radical, through reactions R14 and R15, and are also detected:



Therefore this detector is not specific to a particular type of radical but rather measures the sum of all radicals (RO_x = HO₂ + RO₂ + OH + RO) and the measured quantity is usually called RO_x. However, since the peroxy radicals (RO₂ and HO₂) are the dominant radical species they also dominate the detector response and this instrument is often called a peroxy radical detector. It should be noted here that, in principle, the larger organic peroxy radicals are not measured with the same efficiency as the HO₂ radical. This is because the alkoxy radical reaction with NO has a second channel in addition to (R14) namely the chain termination pathway to produce organic nitrites. As the size of the organic radical increases, so does the branching ratio leading to the nitrate and the smaller the fraction of radicals remaining in the chain mechanism. It should also be noted that experiments have failed to show this dependence on radical size [Ashbourn *et al.*, 1998].

[10] The system employed here used a total CO concentration of 4% and a total NO concentration of 2 ppmv. The reagent cylinders, the mass flow controllers and the data acquisition module were kept in the laboratory, while the NO₂ detector was placed on a platform, about 3 m (2 s) below the sampling inlet. Radical data were collected every minute (with a 20-s dead time and 40-s acquisition time) and are reported as 10-min block averages. The NO₂ concentration was measured using a commercial luminol based detector (LMA-3, Unisearch Associates) that was routinely calibrated against a known concentration of NO₂ in air produced by diluting the output from an NO₂ permeation device. The permeation tube was calibrated against a known mixture of NO₂ obtained by diluting a 6 ppmv standard of NO in N₂ (Scott Specialty gases Certified Standard) with synthetic air and passing the mixture through a chromium trioxide converter which quantitatively converts the NO to NO₂ [Drummond *et al.*,

1989]. Calibration of the radical detector was performed using a radical source on the basis of the photolysis of water vapor in air [Schultz *et al.*, 1995]. This source simultaneously produces radicals and ozone, the later being easily quantified and used as an internal actinometer.

[11] Laboratory work [Mihele and Hastie, 1998; Mihele *et al.*, 1999; Mihele and Hastie, 2000] has shown that the response of the radical detector is sensitive to ambient levels of water vapor. This necessitates that all measurements be corrected for ambient water vapor concentrations, especially as the water vapor in the calibration source is less than 200 ppmv. Since this work was published the results have not been questioned so we now feel that the RO_x data, once corrected for the water vapor interference, can be reported. The RO_x measurements were corrected for water vapor using simultaneously obtained relative humidity measurements along with correction factors in the work of Mihele and Hastie [2000]. The humidity data are reported to be accurate within 0.5% and this correction introduces a small additional error to the measurements so the estimated uncertainty is 30%, although any systematic variation between the wall conditions in the laboratory and field systems cannot be estimated. At high humidities (>80%) there are no laboratory data and an extrapolation was used to estimate the correction. The error in this procedure is unknown and all the data obtained under very high humidity conditions must be regarded as lower limits. These data are not discussed in detail in this paper.

[12] Other measurements used in the discussion below are: ozone, measured by UV absorption [Pippin *et al.*, 2001]; NO measured by chemiluminescence, UV from a 295–385 nm Eppley radiometer, UV-B (280–330 nm) from a Yankee UVB-1 Pyranometer [Thornberry *et al.*, 2001] and isoprene measured by GC/MS [Hurst *et al.*, 2001].

2.3. Model

[13] Modeling was performed using the CREAMS (Chemical Reactions Modeling System), an integrated software package developed by the Meteorological Service of Canada, in the 0-D (box) mode. The photochemistry was the Master Chemical Mechanism (MCM) of Saunders *et al.* [1997]. The base mechanism consists of 486 reactions and 177 chemical species. Clear sky photolysis frequencies are taken from this mechanism and used without modification. Our implementation of the mechanism included the chemistry of carbon monoxide, methane, ethane, formaldehyde, acetaldehyde, PAN, and isoprene along with the known inorganic tropospheric reactions. This limited mechanism is reasonable given the subsequent work of Sumner *et al.* [2001] that showed isoprene to be responsible for 75% of the reactivity toward OH, followed by formaldehyde at 10%, and CO and acetaldehyde at 4% each. This mix accounts for 93% of the known reactivity toward the HO radical. Given the importance of isoprene, its oxidation is treated explicitly in the model. For a single day's data, the model was run for a period of 24 hours starting at midnight. The initial concentrations of methane and ethane were set to 1.7 ppmv and 400 pptv, respectively. Since the objective was to examine whether the model could correctly predict the radical concentration given the available measurements, the model was constrained by resetting the concentrations of CO, O₃, NO, NO₂, isoprene and PAN to the average

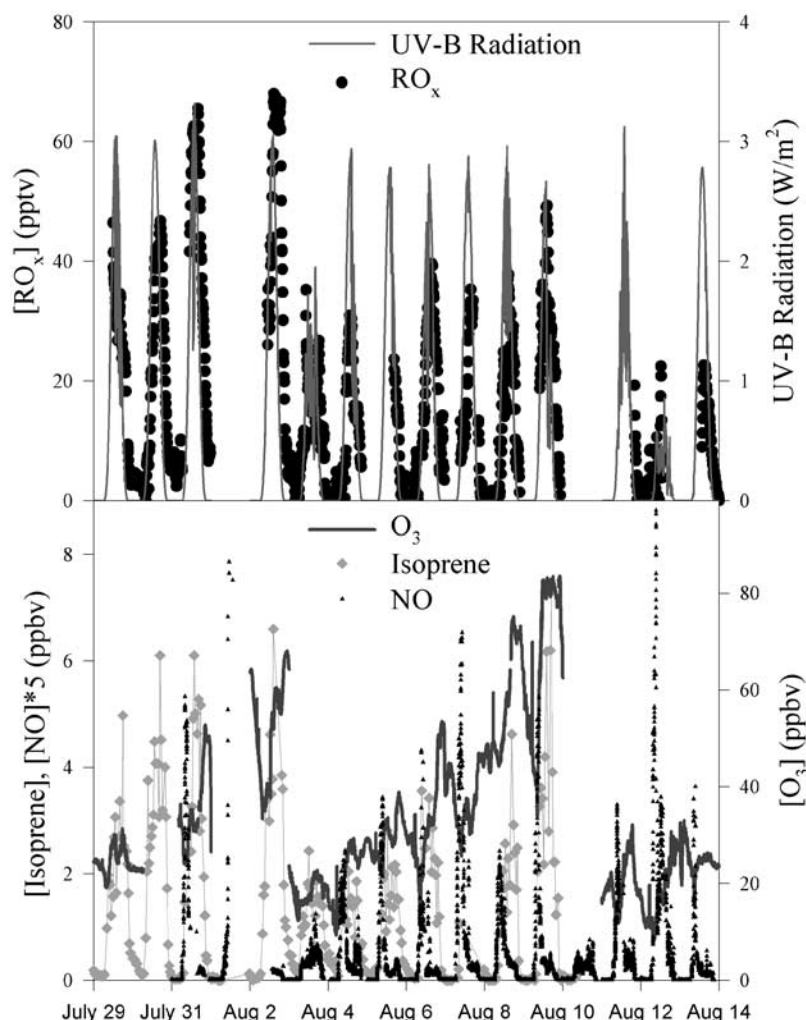


Figure 1. Time series for measurements of RO_x , UV-B radiation (upper panel), O_3 , NO and Isoprene (lower panel) taken during PROPHET 97. See color version of this figure at back of this issue.

measured values every 40 min (the frequency of isoprene measurements).

3. Observations and Discussion

[14] The RO_x radical data for the entire sampling period are shown in Figure 1 (upper panel). Presupposing that photolysis of ozone and aldehydes is a significant source of radicals, the measured radiation that best matches the photolysis of these species, UV-B, is also shown. The measured concentrations of the most likely species to control radical concentrations: ozone; NO; and isoprene are shown in the lower panel. In other work at this site, *Thornberry et al.* [2001] and *Pippin et al.* [2001] have reported a strong influence of air mass origin on nitrogen oxide and ozone concentrations. Air mass trajectories (see <http://www.arl.noaa.gov/ready/hysplit4.html>) have been examined for the measurement period shown in Figure 1. The high ozone and NO_x concentrations are associated with airflow from the more populated areas to the south and southwest of the site whereas the low concentrations occur when air comes from the sparsely populated regions to the north. From 29 to 30 July the airflow is clearly from the north. The increasing

ozone concentrations from 31 July to 2 August are associated with an air mass trajectory change to the southwest. A change in synoptic conditions on 3 August brought clean air from the north for several days, followed by increasingly southerly trajectories until 10 August. This is manifested in the increasing ozone concentrations over this period. The last 4 days are under strong northerly flow and again the ozone concentrations are low.

[15] As expected with any photochemically generated species, the radicals show a strong diurnal variation with a maximum in the afternoon and a minimum concentration at night. The concentrations of the controlling species and the solar radiation show a great deal of day-to-day variation and this is reflected in the variability in the daytime maximum radical concentration that ranged from 20 to 65 pptv. While there are indications that the maximum concentration was related to solar radiation and some of the chemical parameters, or some combination of them, simple relationships are not apparent from visually inspecting the data. A highly significant positive correlation was found between the radical concentration and that of isoprene ($r = 0.8$ on 170 data points), and also with the UVB radiation ($r = 0.7$ on 170 data points). The correlation with UVB radiation would be

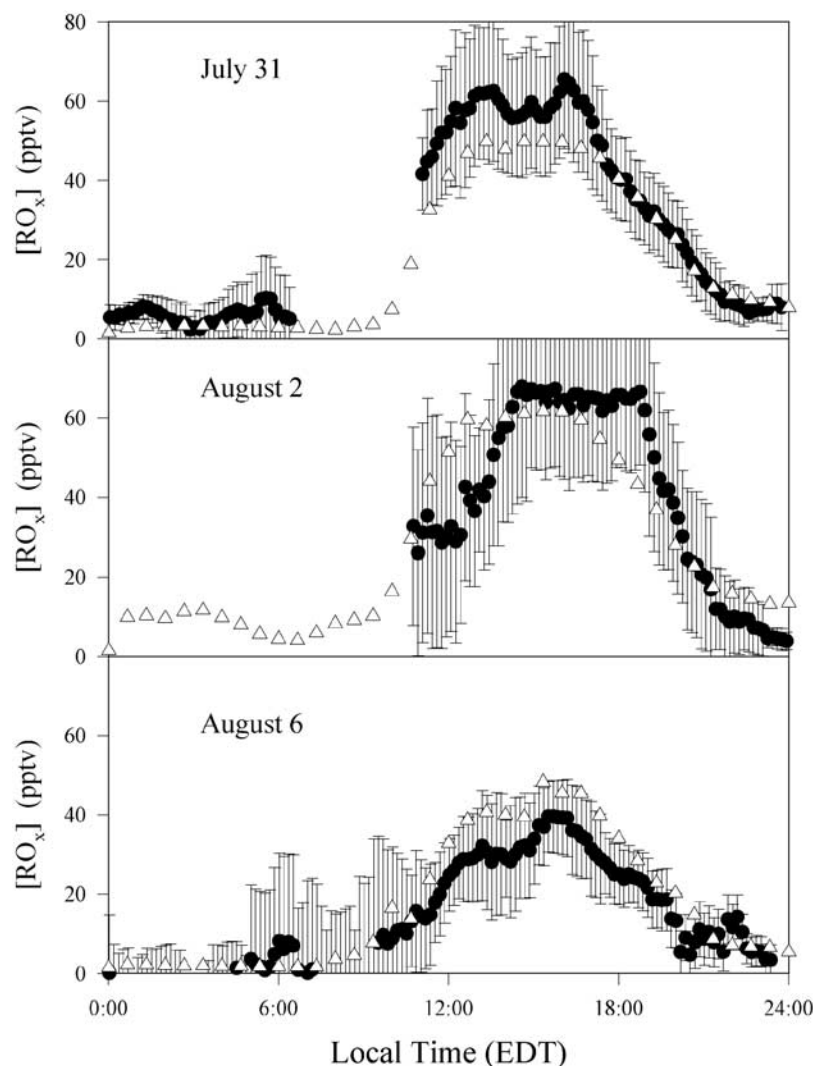


Figure 2. Measured RO_x (solid circles) and RO_x predicted by a 0-D Model (open triangles) for 31 July and 2 and 6 August.

expected, but the dependence of isoprene concentration on solar radiation at this site [Westberg *et al.*, 2001] may well be driving much of the radical-isoprene correlation. Despite the apparent coincidence in the maxima of radical and ozone concentrations in Figure 1 and the overall correlation coefficient, r , of 0.3, the trends in subsets of the data led to the conclusion that there was no general correlation between their concentrations across the data set. The correlation between the radical concentration and the product of the UVB radiation and the ozone concentration, as suggested by Penkett *et al.* [1997] slightly improved upon the correlation observed with the UVB alone. Simple analysis of correlations supports the importance of UVB and perhaps isoprene but more detailed analysis is required to learn the nature of the factors controlling the radical concentration.

[16] Figure 2 shows data for three specific days for which there is the most complete data coverage and that will be the focus of much of the discussion below. This figure more clearly shows that the maximum radical concentration was recorded in the midafternoon (3–4 pm EDT), well after the solar noon (1:40 pm EDT). This midafternoon maximum is similar to that observed in a number of photochemically

produced species reported for this site: namely ozone [Thornberry *et al.*, 2001], isoprene nitrates [Ostling *et al.*, 2001], and formaldehyde [Sumner *et al.*, 2001]. These species have much longer lifetimes than the radicals, so their diurnal variations are at least partly driven by transport [Sumner *et al.*, 2001]. The correlation of NO_x and ozone concentrations with air mass origin further points toward the importance of transport [Thornberry *et al.*, 2001]. In contrast, the short lifetime of the radicals means that transport of the radicals themselves is not an important process although the transport of the controlling precursors may be important. Consideration of the transport of precursors needs a detailed meteorological analysis, however, a study of the radical chemistry can be conducted in the context of the simultaneously measured precursors, independent of their origin. This is the approach taken below.

[17] Penkett *et al.* [1997] developed a useful expression for the steady state concentration of radicals, in terms the dominant photolysis rate and measurable species concentrations. This derivation assumed: that ozone photolysis is the only radical source; that the water concentration was constant; and that methane was the dominant reactive

hydrocarbon and that its concentration was constant. It was then used to show that radical concentrations would be expected to correlate with $J_{O_3} * [O_3]$ (where J_{O_3} is the photolysis rate coefficient for ozone and $[O_3]$ is the ozone concentration) under high NO_x conditions or the square root of $J_{O_3} * [O_3]$ for low NO_x conditions. This analysis has been successfully used to explain the variability of radical concentrations in both clean marine [Penkett *et al.*, 1997; Carpenter *et al.*, 1997] and free tropospheric [Zanis *et al.*, 1999, 2000] air masses.

[18] In a continental area, such as the PROPHET site, the assumptions of Penkett *et al.* [1997] are no longer valid. There are other radical sources, such the photolysis of carbonyl compounds, ozone reactions with alkenes, especially isoprene, and PAN decomposition. Unlike the marine and free troposphere environments, forested sites have diurnally varying NO_x and hydrocarbon concentrations. In appendix 1 we generalize the derivation of the Penkett *et al.* [1997] expression for the expected RO_x concentration to give equation (1). It introduces the production of radicals from other sources (reactions R3–R5) as a parameter, γ , that is the fractional radical production arising from sources other than ozone photolysis. Radicals can be lost by reaction with NO_x in addition to self-reactions among the peroxy radicals, so the parameter $\beta = L_{NO_2}/L_{SR}$ the ratio of radical loss by reaction with NO_2 to self-reaction is introduced. It uses the same parameters as Penkett *et al.* [1997]: $\alpha = [HO_2]/[RO_x]$, the ratio of HO_2 to RO_2 radicals; and f the fraction of the $O(^1D)$ atoms from reaction R1 that react with water.

$$[RO_x] \approx \sqrt{\frac{2fJ_{O_3}[O_3](1+\gamma)}{2k_{16}\alpha(1+\beta)}} = \sqrt{\frac{fJ_{O_3}[O_3]}{k_{16}}} \sqrt{\frac{1}{\alpha}} \sqrt{\frac{1}{1+\beta}} \sqrt{1+\gamma} \quad (1)$$

This equation reduces to the low NO_x expression of Penkett *et al.* [1997] if one makes the assumptions that ozone is the only radical source ($\gamma = 0$), there are very low NO_x concentrations so that $\beta \ll 1$ ($L_{SR} \gg L_{NO_2}$), that the water concentration is constant ($f = \text{constant}$) and the hydrocarbon concentration is constant (which, with $\beta \ll 1$, gives $\alpha \approx \text{constant}$).

[19] This form of equation (1) can be used to qualitatively examine the observed diurnal and day-to-day variability of the RO_x concentration. The most obvious factor controlling the radical concentration is the rate of ozone photolysis, $J_{O_3} * [O_3]$. This can be seen in the diurnal variation, and in the daily maxima where, for days when the ozone or the UV irradiance is low, the radical concentrations are low. For example on 3 and 12 August the UV irradiance and the ozone concentrations are both low, and the RO_x concentration is low. On the other hand, on 2 August the UV irradiance and ozone concentrations are high resulting very high radical concentrations. However, in this environment, factors other than the radical production from ozone must be significant, as evidenced by 9 August where high UV irradiance and the highest ozone concentrations do not yield the highest radical concentrations. An examination of the other factors in equation (1) is necessary to rationalize these observations.

[20] The impact of the factor f is small. This factor relates to the concentration of gas phase water. Although there can be large variations in the relative humidity, much of this is driven by temperature variations, so the actual variation in concentration is small. The term $\sqrt{1+\gamma}$ reflects the impact of radical sources other than ozone photolysis. These are thought to be primarily photolysis of carbonyl compounds, ozone reaction with isoprene, and PAN decomposition. The model results (see below) suggest that these sources can increase the radical source strength by up to 54% of that from ozone photolysis, while Tan *et al.* [2001] indicate an even higher level. Thus the term, $\sqrt{1+\gamma}$, could increase the radical concentration by a factor of 1.3 over that in the absence of additional sources. This would be sufficient to explain the magnitude of day-to-day variations not already explained by the variability in the UV irradiance and ozone concentration, although there are insufficient measurements to confirm this. The impact of the diurnal variability of γ on radical concentrations can be more readily examined. Formaldehyde has been measured at this site and found to have a strong diurnal variation [Sumner *et al.*, 2001] with a maximum concentration in the afternoon. Thus the photolysis of formaldehyde and, by analogy, larger aldehydes would be an increasingly important radical source in the afternoon. The emissions of biogenic hydrocarbons, of which isoprene is a known contributor [Hurst *et al.*, 2001; Barket *et al.*, 2001; Westberg *et al.*, 2001], are driven largely by temperature and so their concentrations rise through the afternoon. The radical source from ozone reactions with these compounds will also rise, although the modeling below and Tan *et al.* [2001] indicate this is a minor source in this environment. The higher afternoon temperatures will cause increased production of radicals from the decomposition of PAN and other peroxyacyl nitrates. Thus three identified additional radical sources are expected to be larger contributors in the afternoon, so the value of γ in equation (1) and the predicted radical concentrations would be expected to rise in the afternoon consistent with the observations.

[21] In this environment the ratio of radical loss by self-reaction and reaction with NO_x (β) is complicated by the strong diurnal variation in NO_x [Thornberry *et al.*, 2001]. Morning concentrations reach 2 ppbv but drop to below 600 pptv in the afternoon. Since the daytime maxima in radical concentration occur in the afternoon, it is the changes in β at the low NO_x concentrations in the afternoon that may impact the RO_x concentration. At this time the self-reaction of the peroxy radicals is the dominant radical loss mechanism and so β is less than unity and the variation of $1/\sqrt{1+\beta}$ in equation (1) and its impact on RO_x concentrations is small.

[22] The dependence of α on conditions is the most difficult to determine. Explicitly it is the fraction of RO_x radicals that exist as HO_2 . Since the peroxy radicals have far higher concentrations than HO or other organic radicals, this can be regarded as the ratio of HO_x radicals to the total radical load. If the CO concentration is considered roughly constant, higher hydrocarbon concentrations will decrease α , as the HO attack on hydrocarbons will produce more organic RO_2 radicals relative to the HO_x production from the attack on CO. Low NO concentrations would also decrease α because the conversion of organic peroxy

radicals to HO_x radicals begins with the reduction of the radical, which is most efficiently done by NO. Higher isoprene and lower NO concentrations occur in the afternoon so both these effects will tend to increase the predicted RO_x concentrations. There is a small impact owing to changes in water concentration where an increase will decrease α as it increases the HO₂ loss through the increased rate of the termolecular channel of reaction R9. However, quantifying all these impacts in the context of the concepts of equation (1) is not possible with the data set available from this study. Application of the model below gives some indication of the importance of α in determining the RO_x concentration.

[23] Examination of the three parameters α , β , and γ in equation (1) suggests that there should be an increase in radical concentrations in the afternoon. This is consistent with the observations, suggesting a fair understanding of the chemistry at this site, but a quantitative comparison requires the application of the chemical model below.

[24] Measurable radical concentrations persisted into the early evening with the minimum radical concentrations recorded after midnight, similar to that reported at more southerly rural site [Cantrell *et al.*, 1992]. After sunset, the photochemical production of radicals ceases, thus the radicals observed either remain from the daytime, or are produced by non-photochemical radical sources. It appears that both processes are active in this environment. The initial decrease in concentration after sunset has an observed half-life of 1–2 hours. This comparatively slow decay is similar to that observed and explained elsewhere. It is likely due to the preponderance of organic peroxy radicals over hydroperoxy radicals [Monks *et al.*, 1996]. The initial hydroxyl radical attack on a hydrocarbon produces an organic peroxy radical. Normally this radical reacts with NO (R14) but in the evening this site has extremely low NO concentrations [Thornberry *et al.*, 2001] because of the low solar irradiance and the absence of a source. Therefore immediately after sunset the radicals are primarily lost by reactions (R9) and (R10) involving the HO₂ radicals, as the rate coefficients for these reactions are much higher than that for pairs of organic peroxy radicals. The HO₂ radicals will therefore be severely depleted in which case the only loss process for the remaining organic peroxy radicals are the self-reactions (of the type, R11) which have much smaller rate coefficients. At mixing ratios of a few pptv, the half-life for these processes are in the order of a few hours, giving a slow evening radical decay as observed.

[25] On many nights, even after this decay would have been expected to lower the radical concentrations to below measurable levels, there were still observable radical concentrations. The humidity on most of those nights was below 80% so that the correction for the relative humidity was still within the range of the laboratory experiments. The correction is larger than in the daytime, leading to the increased errors in the nighttime data in Figure 2, but the observed concentrations are clearly non-zero. Peroxy radical concentrations often exceeded 5 pptv. These observations are consistent with the subsequent observations of high nighttime OH ($1.1 \times 10^6 \text{ cm}^{-3}$) and HO₂ (1–4 pptv) concentrations at this site, by Faloona *et al.* [2001], and the concurrent observed loss of isoprene in the dark [Hurst *et al.*, 2001].

[26] Current understanding of radical chemistry is unable to explain the high OH concentrations reported at this site by Faloona *et al.* [2001]. Recent modeling studies have attempted to model these nighttime radical levels [Faloona *et al.*, 2001; Sillman *et al.*, 2002]. While it is now generally accepted that the reactions of ozone with alkenes will produce OH radicals at night [e.g., Paulson *et al.*, 1998], to generate the observed OH radical concentrations in this environment both modeling groups need to invoke a major OH source over and above those normally considered. The oxidation of larger terpenes, such as a terpinene by ozone has been suggested as a possible source. While this can be used to explain the OH concentrations it is unsatisfactory, as it would also produce five times the observed levels of HO₂ radicals [Faloona *et al.*, 2001]. This problem is even more extreme for the RO₂ radicals where predicted concentrations of over 65 pptv are predicted [Sillman *et al.*, 2002]. This is more than an order of magnitude higher than the nighttime values reported here and actually exceeds the daytime levels. While the RO_x measurements indicate a lower limit of as much as 5 pptv and, as described above, the radical detector should be less sensitive to the larger organic peroxy radicals, it seems extremely unlikely that it would be completely unable to measure the prodigious radical concentrations suggested by this mechanism. We must therefore agree with Faloona *et al.* [2001] and Sillman *et al.* [2002] that there is a substantial shortfall in our understanding of nighttime radical chemistry in pristine, low NO_x, environments.

4. Estimating Radical Concentrations Using Ozone Production and the Pseudo Steady State Approximation

[27] The use of equation (1) above has been shown to be valuable in rationalizing the variations in the observations of radical concentration. However, the lack of precise ozone photolysis rates and a full understanding of the chemistry affecting α and β precludes the determination of absolute radical concentrations. Two methods exist for estimating the radical concentration, the local ozone production and the Pseudo Steady State Approximation (PSSA).

[28] The ozone production rate can be determined from the rate of NO₂ photolysis. Assuming NO₂ is in steady state, and noting that the production of NO₂ by the reaction of NO with ozone will conserve ozone, the rate of ozone production is given by

$$\frac{d[\text{O}_3]}{dt} = J_{\text{NO}_2}[\text{NO}_2] = k_{14}[\text{RO}_2 + \text{HO}_2][\text{NO}] \approx k_{14}[\text{RO}_x][\text{NO}].$$

This calculation can be used to estimate radical concentrations for a data set where ozone concentration changes are only due to chemistry and the NO changes are small. Since the measurements are made at a site that is continually receiving air from upwind, it is essential that cases be selected where there is confidence that the upwind air masses and those at the site are identical. This was done by selecting an afternoon period where there was no apparent change in air mass. In these cases the increase in ozone concentration can be attributed to photochemical production and the production rate simply determined by $\Delta[\text{O}_3]/\Delta t$.

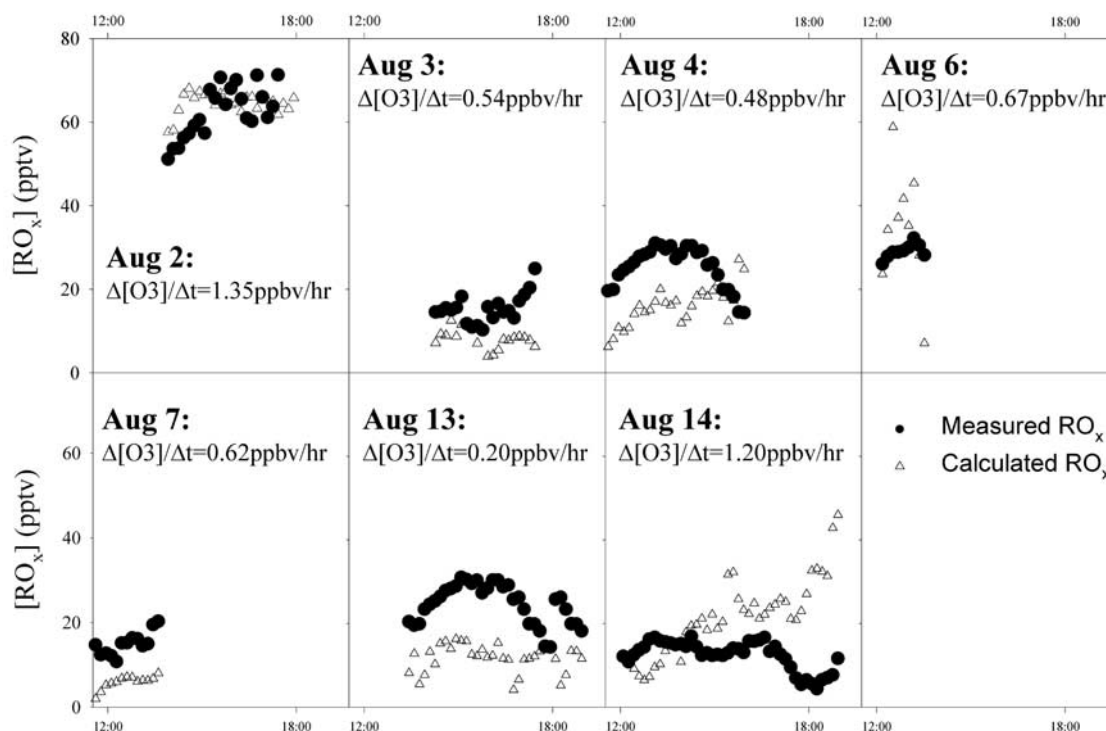


Figure 3. Comparison between measured RO_x (solid circles) and RO_x estimated using the local ozone production (open hexagons).

These results could be compared directly to the product $k_{14}[\text{RO}_x][\text{NO}]$, or a RO_x concentration could be inferred. Thornberry [2001] has shown that, in this environment, the number of ozone molecules produced for each NO_x molecule oxidized ranges from 25 to 40. This means that the loss in NO_x by reaction is less than 5% of the increase in ozone, and since the analysis takes place in the afternoon, the partitioning of NO_x between NO and NO_2 changes very slowly. Hence it is reasonable to assume the NO concentration in the air mass where the ozone is being produced is constant at the concentration measured at the site. Thus a RO_x concentration that is representative of this air mass can be calculated. Consistency between this calculation and the measured RO_x at the site would support a regionally uniform radical concentration and give additional confidence to the RO_x data. RO_x concentrations were calculated by this method for several days. For each of these, an afternoon ozone production rate was determined and the RO_x concentration determined for each NO measurement point during this period. A comparison of these results with the measured concentrations is shown in Figure 3. The averaged RO_x are in relatively good agreement with the measured concentrations at the site, indicating that the radical concentrations have similar concentrations over the region contributing to the local ozone production.

[29] Application of the Pseudo Steady State Approximation (PSSA) [Cantrell *et al.*, 1993; Parrish *et al.*, 1986] gave estimated concentrations that had little correlation with those measured, ranging from 0.2 to 5 times the measured mixing ratio. As in the work of Carpenter *et al.* [1998], the PSSA results have too much variation to test current understanding of the nitrogen or radical chemistry using

this data set. A more detailed analysis using a larger data set has drawn similar conclusions [Thornberry, 2001].

5. Modeling

[30] The chemistry occurring at this site involves a number of chemical reactions of similar rates, so that a simplified analytical treatment is not possible. While the application of equation (1) leads to a qualitative understanding of the controls on radical concentration, a quantitative test for consistency between the radical concentrations and other measured parameters requires a fully detailed model to be run for conditions under which the measurements were made. As the lifetimes of radical are much shorter than the timescales associated with the transport of air masses to the measurement site, a model that concentrates on the chemistry of the radicals need not incorporate any detailed meteorology. Thus the box (0-D) model described above should be appropriate to probe the measured radical levels provided no attempt is made to consider the origin and fate of the radical precursors. The model has been severely constrained by using the measured observations of the non-radical parameters, where available. The objective was to use the best understanding of the chemistry, and the available measurements to predict the radical concentration and its diurnal variation for comparison with the RO_x measurements. This differs from the modeling of Sillman *et al.* [2002], where a one-dimensional Lagrangian transport and photochemistry model was used interpret a number of observations where transport to this site was important, and is more similar to the modeling performed by Tan *et al.* [2001] to examine the OH and HO_2 chemistry.

[31] Modeling studies were performed for the three days shown in Figure 2. This included two clear sky days, 31 July and 2 August, and one partly cloudy day, 6 August. The calculated total radical concentrations from the model are compared with the measured RO_x concentrations in Figure 2. The model reproduces the absolute values of the total radical concentrations within the experimental errors, for all periods of the day. The model accurately duplicates the diurnal variation of the radicals, including the late evening decay of radicals. The chemical mechanism in the model contains detailed self-reactions of the organic peroxy radicals, and the agreement with the measurements affirms the importance of these reactions in controlling radical concentrations in the early evening.

[32] The model maintains RO_x concentrations throughout the night in agreement with the measurements. The model runs began at midnight and, for computational stability, were initiated with 2 pptv of radicals. Under most conditions these radicals persisted for several hours. In addition there is a small radical production that maintains a concentration of 2–3 pptv throughout the night. The radical production does not need to be large to maintain these concentrations as the organic peroxy radicals have a very long lifetime. Since it contains limited hydrocarbon chemistry, the model has limited ability to produce radicals at night. The major radical source is the reaction of isoprene with ozone, but even this is small because the isoprene concentrations at this site are generally very low at night [Hurst *et al.*, 2001]. The nitrate radical chemistry is included but the nitrogen oxide concentrations are so small that nitrate chemistry is unimportant. The model has no terpene inputs as in the works of Faloona *et al.* [2001] and Sillman *et al.* [2002], but does not need to invoke them to match the observed total radical concentrations.

[33] Faloona *et al.* [2001] and Sillman *et al.* [2002] addressed the problem of nighttime measured HO radical concentrations being much higher than that predicted by their models by including the reaction of a reactive terpene. Addition of the highly reactive terpene to the model described here has a similar impact on the nighttime radical chemistry, as reported by Sillman *et al.* [2002]. The increases in HO and HO_2 radical concentrations are as predicted by both of the other studies however there is a much greater impact on the peroxy radical concentrations reaching over 60 pptv. Relating these predictions to the radical detector measurements, it is difficult to imagine that the instrument could have its sensitivity suppressed by over an order of magnitude under these conditions. Thus while it appears necessary to modify models to account for the HO concentrations measured by other groups, the postulate of a high concentration of a highly reactive terpene would generate organic radical concentrations that are inconsistent with the measurements reported here.

[34] The model was used to attempt to quantify some of the terms in equation (1). The model contains all the radical sources described above: ozone and aldehyde photolysis; PAN thermal decomposition; and isoprene ozonolysis; along with ROOH photolysis (including H_2O_2 and organic peroxides). Therefore it was possible to examine the relative importance of these sources and obtain an estimate of γ . Ozone photolysis was the major radical source. Two methods were used to determine the contribution of each of the

additional sources. First, each source was switched off independently and the resulting midafternoon radical concentration compared with the base case. Second, the radical production rates, over the same period, were extracted from the model. Radical sources other than ozone photolysis were found to be small, and so these two methods yielded similar results despite the expected non-linearity of the chemistry. PAN decomposition is the dominant nighttime radical source and while it reached half of the ozone photolysis source in the early morning of 31 July, over the course of the three days modeled it accounted for about 15% of the total radical production. The photolysis of aldehydes was also responsible for about 15% of the radical production, while isoprene ozonolysis contributed less than 5% and the photolysis of peroxides less than 0.5%. Therefore these additional radical sources are about 35% of the total during the day, so $\gamma = 0.35/0.65 = 0.54$.

[35] The ratio $\beta = L_{\text{NO}_2}/L_{\text{SR}}$, the ratio of radical loss by reaction with NO_2 to self-reaction is close to unity once the morning pulse in NO_x has passed. Since equation (1) includes the term $1/\sqrt{1 + \beta}$, the impact of this term on the radical concentration is small.

[36] As indicated above the variation and impact of α is the most difficult to generalize. Over the range of conditions encountered in this modeling study, the term $1/\sqrt{\alpha}$ varies from 1 to 1.5 so it can have a major impact on the calculated radical concentration as well as predictions of its variability. It is the importance of this parameter, and the difficulty in determining its value from measurements and simple arguments, that limits the use of equation (1) in this environment.

[37] Isoprene is the dominant reactive hydrocarbon in rural and forested areas and its presence has a major impact on ozone production. The sensitivity of the radical chemistry to the presence of isoprene was examined by comparing model predictions from runs with and without isoprene. Changes in the isoprene concentration had an impact on the concentrations of almost all species generated in the model, driven by a two-fold increase in OH concentration when the isoprene was removed. This is consistent with the estimate that 75% of the OH radicals at this site react with isoprene [Sumner *et al.*, 2001]. The consequences of this OH increase ripple through all of the chemistry. The major radical loss mechanism is the reaction of OH with NO_2 to produce nitric acid, so an OH increase actually reduces the total radical concentration, along with generating a two-fold increase in nitric acid concentration. The decreased hydrocarbon oxidation also reduces the production of the reactive oxidation products, for example formaldehyde decreases by a factor of three. This in turn lowers the radical production and coupled with the increased loss rate, lowers the radical concentration by 30%. These effects act in the same direction leading to a decrease in the calculated ozone concentration, affirming the importance of isoprene in the production of ozone in rural and forested environments.

6. Conclusions

[38] The radical detector has been shown to generate a valuable data set for testing understanding of radical chemistry at a forested site. The data have indicated that some of the assumptions used in modeling studies to simulate HO

radical concentrations at night are not realistic. The modeling study here shows that our current understanding of the radical chemistry at a forested site is able to explain both the total radical concentration, and its variations. The conceptual model, while useful, is limited in its ability to explain the impacts of changes that influence the balance between radical loss mechanisms. The use of the observed ozone production to predict radical concentrations has some utility but the PSSA assumption was found to be a very poor predictor of radical concentrations.

Appendix A

[39] Following Penkett *et al.* [1997] we assume that the radicals are in steady state:

$$\frac{d[RO_x]}{dt} = P_{RO_x} - L_{SR} - L_{NO_2} = 0,$$

where P_{RO_x} is the rate of radical production, and L_{SR} and L_{NO_2} are the loss rates of radicals due to self-reaction and reaction with NO_2 respectively.

[40] Assuming that the photolysis of ozone is the major radical source and allowing the additional radical sources to contribute an additional fraction γ to the production this becomes

$$\frac{d[RO_x]}{dt} = 2fJ_{O_3}[O_3](1 + \gamma) - L_{SR} - L_{NO_2} = 0,$$

where F is the fraction of $O(^1D)$ that react with water and J_{O_3} is the ozone photodissociation coefficient. The loss by self-reaction is due to reactions R16 and R17 and observing that $k_{16} \approx k_{17}$, and setting $\alpha = [HO_2]/[RO_x]$, the self reaction loss becomes

$$\begin{aligned} L_{SR} &= 2k_9[HO_2][HO_2] + 2k_{10}[HO_2][RO_x] \\ &\approx 2k_9[HO_2]([HO_2] + [RO_x]) = 2k_9[HO_2][RO_x] \\ &= 2k_9\alpha[RO_x]^2. \end{aligned}$$

Introducing $\beta = L_{NO_2}/L_{SR}$, a parameter that describes the dominant loss mechanism, the steady state for RO_x radicals becomes

$$\frac{d[RO_x]}{dt} = 2fJ_{O_3}[O_3](1 + \gamma) - 2k_9\alpha(1 + \beta)[RO_x]^2 = 0.$$

This yields an expression for the RO_x concentration:

$$[RO_x] \approx \sqrt{\frac{2fJ_{O_3}[O_3](1 + \gamma)}{2k_9\alpha(1 + \beta)}} = \sqrt{\frac{fJ_{O_3}[O_3]}{k_9}} \sqrt{\frac{1}{\alpha}} \sqrt{\frac{1}{1 + \beta}} \sqrt{1 + \gamma}.$$

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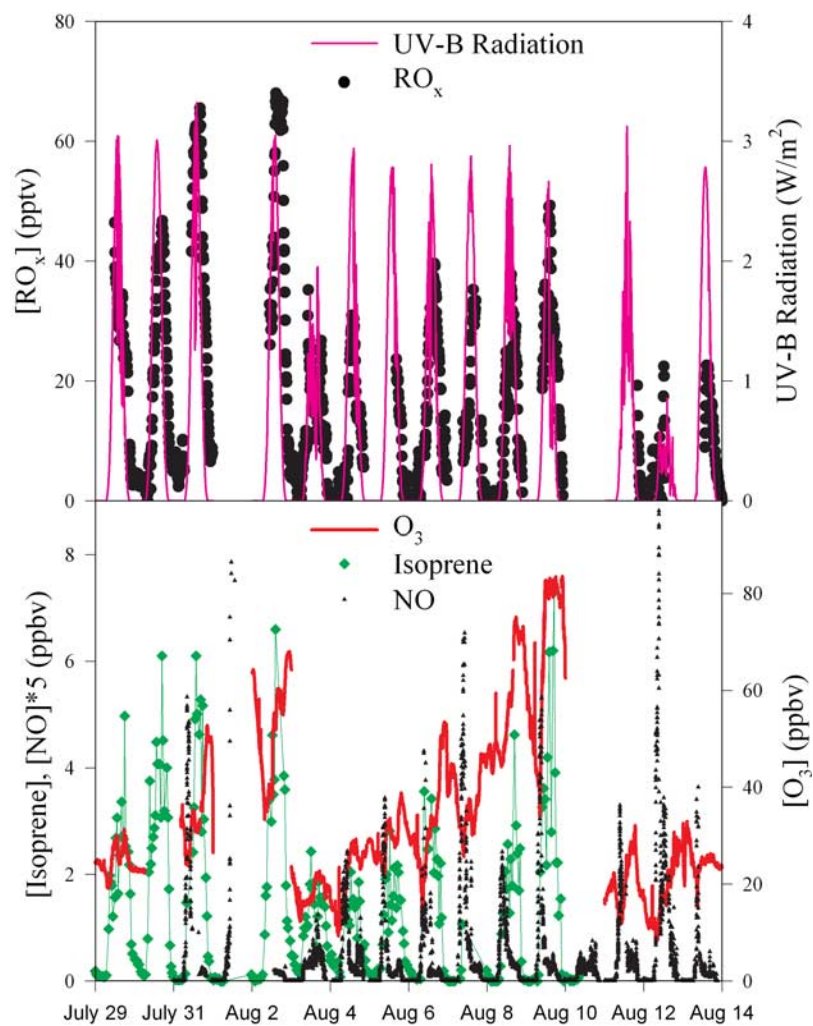


Figure 1. Time series for measurements of RO_x , UV-B radiation (upper panel), O_3 , NO and Isoprene (lower panel) taken during PROPHET 97.