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## Results from the Intergovernmental Panel on Climatic Change Photochemical Model Intercomparison (PhotoComp)

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**Abstract.** Results from the Intergovernmental Panel on Climatic Change (IPCC) tropospheric photochemical model intercomparison (PhotoComp) are presented with a brief discussion of the factors that may contribute to differences in the modeled behaviors of HO<sub>x</sub> cycling and the accompanying O<sub>3</sub> tendencies. PhotoComp was a tightly controlled model experiment in which the IPCC 1994 assessment sought to determine the consistency among models that are used to predict changes in tropospheric ozone, an important greenhouse gas. Calculated tropospheric photodissociation rates displayed significant differences, with a root-mean-square (rms) error of the reported model results ranging from about ±6–9% of the mean (for O<sub>3</sub> and NO<sub>2</sub>) to up to ±15% (H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O). Models using multistream methods in radiative transfer calculations showed distinctly higher rates for photodissociation of NO<sub>2</sub> and CH<sub>2</sub>O compared to models using two-stream methods, and this difference accounted for up to one third of the rms error for these two rates. In general, some small but systematic differences between models were noted for the predicted chemical tendencies in cases that did not include reactions of nonmethane hydrocarbons (NMHC). These differences in modeled O<sub>3</sub> tendencies in some cases could be identified, for example, as being due to differences in photodissociation rates, but in others they could not and must be ascribed to unidentified errors. O<sub>3</sub> tendencies showed rms errors of about ±10% in the moist, surface level cases with NO<sub>x</sub> concentrations equal to a few tens of parts per trillion by volume. Most of these model to model differences can be traced to differences in the destruction of O<sub>3</sub> due to reaction with HO<sub>2</sub>. Differences in HO<sub>2</sub>, in turn, are likely due to (1) inconsistent reaction rates used by the models for the conversion of HO<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> and (2) differences in the model-calculated photolysis of H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O. In the middle tropospheric “polluted” scenario with NO<sub>x</sub> concentrations larger than a few parts per billion by volume, O<sub>3</sub> tendencies showed rms errors of ±10–30%. These model to model differences most likely stem from differences in the calculated rates of O<sub>3</sub> photolysis to O(<sup>1</sup>D), which provides about 80% of the HO<sub>x</sub> source under these conditions. The introduction of hydrocarbons dramatically increased both the rate of NO<sub>x</sub> loss and its model to model differences, which, in turn, are reflected in an increased spread of predicted O<sub>3</sub>. Including NMHC in the simulation approximately doubled the rms error for O<sub>3</sub> concentration.

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## 1. Introduction

Since preindustrial times there has been a steady increase in atmospheric concentrations of radiatively important greenhouse gases such as methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) [Keeling *et al.*, 1982; Kahlil and Rasmussen, 1987]. These increases are expected to be paralleled by increased emissions of nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>) [Dignon and Hameed, 1989]. Photochemical reactions of these gases may generate tropospheric ozone (O<sub>3</sub>) and, indeed, recent evidence suggests that concentrations of tropospheric O<sub>3</sub> have nearly doubled over the last century [Volz and Kley, 1988; Harris *et al.*, 1995]. Such O<sub>3</sub> increases will also tend to enhance the concentration of OH, which drives the removal of many major greenhouse gases. However, the concurrent growth of CH<sub>4</sub> has the opposite effect and will tend to suppress OH [Thompson, 1992]. The net effect on the chemical composition of the troposphere due to the increased emissions during the industrial era is a complex interaction between atmospheric constituents which is dependent on the physical state of the atmosphere (temperature and water vapor), transport and mixing, and chemical interactions.

In order to assess the ultimate chemical and radiative effects that such human-induced perturbations produce on a global scale, it is necessary to accurately model both the transport and the chemical responses of atmospheric gases to these perturbations. In 1994 the Intergovernmental Panel on Climate Change (IPCC) began intercomparisons of both tropospheric transport and photochemical models as a first step toward evaluating coupled global chemical transport models. We report here some of the results from the photochemical portion of that assessment (PhotoComp). For further information on the structure of the intercomparison the reader is referred to Prather *et al.* [1995] and Stordal *et al.* [1995].

PhotoComp was focused on elucidating the variability of results among published models, rather than being an attempt to intercompare, for instance, chemical mechanisms. Therefore, while the chemical mechanisms used in the various models were intentionally not standardized for this

intercomparison, chemistry was limited to relatively simple, well-understood and agreed-upon gas-phase processes such as those described by DeMore *et al.* [1992]. Simulations including only CH<sub>4</sub> and carbon monoxide (CO) oxidation were examined separately from those also including nonmethane hydrocarbon (NMHC) oxidation to isolate differences that various NMHC chemistry parameterizations may introduce. There was no attempt to remove differences in model parameters such as kinetics data (rate constants), radiative transfer formulations, or chemical solvers. The goal of PhotoComp was to evaluate the consistency among models in the simulation of a simply characterized system in order to provide a necessary perspective in interpreting results from the more complicated IPCC model assessments. It should also be stressed that this intercomparison was structured to simulate only one process (i.e., gas-phase photochemistry) from the highly complex and interdependent system of processes present in the atmosphere. Dry deposition and in-cloud wet heterogeneous chemistry, for example, were neglected. In addition to the above stated goals we anticipate that the results presented in this paper should prove useful for modelers who wish to benchmark and evaluate the performance of their photochemical model in comparison with results from the several models presented here.

Input atmospheric and radiative parameters and initial conditions were strictly defined. Radiative calculations were specified as for clear-sky conditions with a solar zenith angle of 23° (July 1, 45°N latitude), a surface albedo of 10%, and an O<sub>3</sub> column equal to that given by the U.S. Standard Atmosphere profile. Six test cases were chosen to represent a range of atmospheric chemical regimes, and specifications for these are listed in Table 1. Conditions for the various cases were based loosely in part on measurements from missions that characterized the "remote" troposphere [e.g., Ridley and Robinson, 1992] and from those that sampled middle tropospheric pollution plumes such as those from biomass burning [e.g., Harriss *et al.*, 1988; Fishman *et al.*, 1996].

Twenty-one participants representing five countries responded with results for the cases with no NMHC chemistry (Marine, Land, Free, and Plume-X), and 16 of these groups

**Table 1.** PhotoComp Specifications and Initial Values

	Marine	Land Land-Bio	Free	Plume-X Plume-HC
Altitude, km	0	0	8	4
T, K	288.15	288.15	236.21	262.17
P, mbar	1,013.25	1,013.25	356.5	616.6
M molecules cm <sup>-3</sup>	2.55 × 10 <sup>19</sup>	2.55 × 10 <sup>19</sup>	1.09 × 10 <sup>19</sup>	1.7 × 10 <sup>19</sup>
H <sub>2</sub> O, % v/v	1.0	1.0	0.05	0.25
H <sub>2</sub> , ppmv	0.5	0.5	0.5	0.5
H <sub>2</sub> O <sub>2</sub> , ppbv	2	2	2	2
O <sub>3</sub> , ppbv	30	30	100	50
NO <sub>x</sub> , pptv <sup>a</sup>	10	200	100	10,000
HNO <sub>3</sub> , pptv	100	100	100	100
CO, ppbv	100	100	100	600
CH <sub>4</sub> , ppbv	1,700	1,700	1,700	1,700
NMHC	none	land, 0 bio, 1 ppbv isoprene	none	X, 0 HC, 115 ppbv <sup>b</sup>

Integrations were performed for 5 days starting July 1, with solar zenith angle 23°.

<sup>a</sup>NO<sub>x</sub> initially equally divided between NO and NO<sub>2</sub>.

<sup>b</sup>Initial values of NMHC for PLUME-HC (in ppbv): C<sub>2</sub>H<sub>6</sub>, 25; C<sub>2</sub>H<sub>4</sub>, 40; C<sub>2</sub>H<sub>2</sub>, 15; C<sub>3</sub>H<sub>8</sub>, 15; C<sub>3</sub>H<sub>6</sub>, 12.5; C<sub>4</sub>H<sub>10</sub>s, 5; toluene, 2; and isoprene, 0.5.

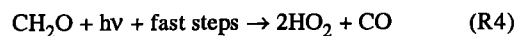
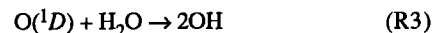
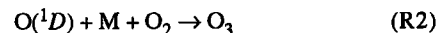
additionally submitted results for the two cases that include NMHC chemistry (Land-Bio and Plume-HC). Table 2 lists these participating groups and contact information. The participants were given initial conditions at noon and were asked to simulate a 5-day period for an isolated chemical system with a diurnal solar cycle. Submitted diagnostics were the predicted noontime values of constituent concentrations, the diurnally averaged values of some radical species (e.g., HO<sub>2</sub> and NO<sub>3</sub>), and photolysis rates. We present here a review of the results from the PhotoComp exercise and discuss the likely sources of variation between the model results. In particular, our analysis emphasizes the cases without NMHC and focuses on the relation between O<sub>3</sub> and HO<sub>x</sub>.

## 2. Brief Review of HO<sub>x</sub>/O<sub>3</sub> Interactions

The odd-hydrogen radicals (HO<sub>x</sub> = OH + HO<sub>2</sub>) are central to tropospheric chemistry: the major sink for many atmospheric greenhouse gases is reaction with OH, and HO<sub>2</sub> is the essential HO<sub>x</sub> catalyst in the production and loss of tropospheric O<sub>3</sub>. It is thus necessary to understand the chemical cycling of HO<sub>x</sub> and HO<sub>x</sub> reservoirs such as H<sub>2</sub>O<sub>2</sub> in the troposphere. Concentrations of OH and HO<sub>2</sub> may vary by orders of magnitude over the course of a day, because they respond rapidly to changes in incoming solar radiation. HO<sub>x</sub> concentrations are also dependent on abundances of trace gases such as water vapor, O<sub>3</sub>, CO, CH<sub>4</sub>, NO<sub>x</sub>, and NMHC. Aqueous-phase chemistry within clouds is likely to have an additional significant global impact on HO<sub>2</sub> concentrations (this process is neglected in PhotoComp) [e.g., *Lelieveld and Crutzen*, 1990; *Möller and Mauersberger*, 1992]. Although intensive measurement campaigns [e.g., *Perner et al.*, 1987; *Salawitch et al.*, 1994] can test OH and HO<sub>2</sub> calculations under specific circumstances, we are unable to measure the global distribution of OH except as an indirect, integrated quantity [e.g., *Prinn et al.*, 1995]. Therefore we will continue to rely on models to

predict global HO<sub>x</sub> concentrations and the oxidizing capacity of the troposphere.

The primary source of HO<sub>x</sub> in the natural troposphere is from the reaction of metastable atomic oxygen O(<sup>1</sup>D) with water vapor to form the hydroxyl radical (OH) (R3). There are also secondary HO<sub>x</sub> sources from the photolysis of aldehydes ((R4), for example) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (R5), although note that these sources originate from HO<sub>x</sub>.



The abundance of HO<sub>x</sub> further depends on NO<sub>x</sub> concentrations. For NO<sub>x</sub> larger than several parts per billion by volume (ppbv), NO<sub>x</sub> acts primarily as a reducing compound such that the major HO<sub>x</sub> sink is reaction of OH with NO<sub>2</sub> to form the reservoir HNO<sub>3</sub>. For lower NO<sub>x</sub> concentrations the major HO<sub>x</sub> sink is the self-reaction of HO<sub>2</sub> to form the reservoir H<sub>2</sub>O<sub>2</sub> [*Liu et al.*, 1987; *Lin et al.*, 1988; *Sillman et al.*, 1990; *Kleinman*, 1991]. For the remainder of this paper we loosely define the former as a “high- NO<sub>x</sub> regime” (with respect to the HO<sub>x</sub> cycle) and the latter as a “low- NO<sub>x</sub> regime.” The isolated chemical system defined by PhotoComp includes no transport or irreversible losses of H<sub>2</sub>O<sub>2</sub> or HNO<sub>3</sub> (e.g., washout), so that photolysis of the reservoir species may eventually (but not necessarily in 5 days) return the HO<sub>x</sub> and NO<sub>x</sub> back to the system.

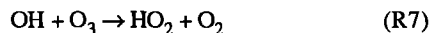
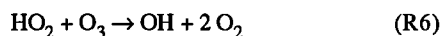
The important reactions responsible for O<sub>3</sub> destruction in the natural troposphere are directly related to HO<sub>x</sub> chemistry,

**Table 2.** PhotoComp Participants

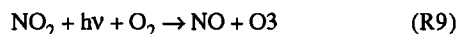
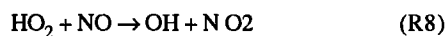
Affiliation	Contact
AER, Inc. (box model code)	Rao Kotamarthi: rao@aer.com
AER, Inc. (2-D code)	Rao Kotamarthi: rao@aer.com
Cambridge University (box model code)	Oliver Wild: oliver@atm.ch.cam.ac.uk
Cambridge University (UGAMP code)	Kathy Law: kathy@atm.ch.cam.ac.uk
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AER, Atmospheric and Environmental Research; UGAMP, Universities Global Atmospheric Modelling Programme; GFDL, Geophysical Fluid Dynamics Laboratory; LLNL, Lawrence Livermore National Laboratory; NASA, National Aeronautics and Space Administration; NYU, New York University; U.C. - Irvine, University of California - Irvine; U.K. Met. Office, United Kingdom Meteorological Office.

as is the photochemical smog reaction that produces  $O_3$ . Noted above, the photolysis of  $O_3$  to  $O(^1D)$  can lead to  $O_3$  loss by the sequence (R1) + (R3), especially within the moist lower troposphere. The direct reactions of  $HO_x$  with  $O_3$  also represent major loss,



while those with  $NO_x$  can catalytically produce  $O_3$ .



Here we examine  $HO_x$  cycling in the PhotoComp simulations without NMHC to determine whether the model to model differences in  $O_3$  tendencies can be traced to (1) photolysis rates, (2) related  $HO_x$  chemical mechanisms, or (3) other hidden differences in formulation or numerical solution.

### 3. Summary of Results

#### 3.1. Photolysis Rates

The mean values and 1 rms error for the four selected photolytic reactions are listed in Table 3 for four altitudes.

Note that

$$\text{rms error} = \sqrt{\sum (C_i - C_{\text{mean}})^2 / N}$$

where  $C_i$  is the individual model results,  $C_{\text{mean}}$  is the mean of model results, and  $N$  is the number of models. These values were calculated from 20 of the models, discarding one obvious

outlier. The rms errors (as a percentage of the mean) are largest for  $CH_2O$  and  $H_2O_2$  photolysis, with values of the order of 10–15%. Errors for these two rates systematically increase with altitude. Root-mean-square errors for  $NO_2$  and  $O_3$  photolysis are generally less than 9%. The errors (as a percentage of the mean) tend to be slightly larger for the diurnally averaged rates, reflecting the magnification of technique-dependent errors with higher zenith angle and longer optical path lengths.

The majority of the models used quantum yields and cross-section data from the Jet Propulsion Laboratory recommendations of *DeMore et al.* [1992]. Five models used data recommended by various earlier references, but any dependence of the differences in photodissociation rates between the models on the choice of photokinetics data used was apparently masked by other larger dependencies.

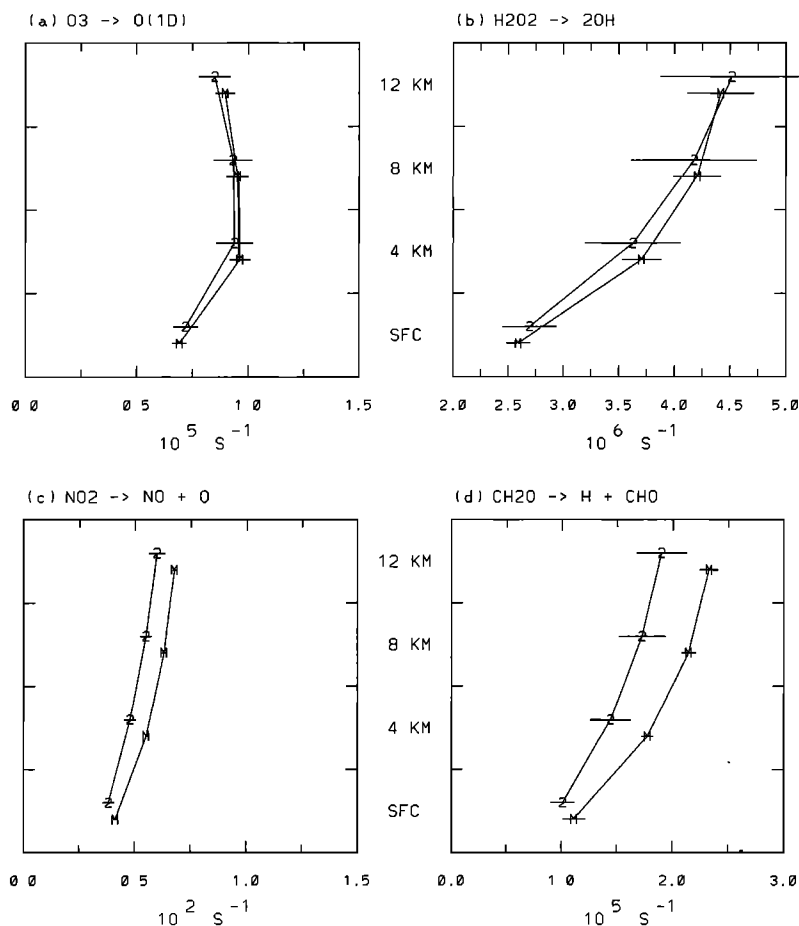
The effect of multiple scattering on photodissociation rates is expected to be significant for molecules whose absorption cross sections are large above about 300 nm [e.g., *Meier et al.*, 1982]. Below this wavelength, absorption accounts for most of the radiative transfer process. For the molecules considered in PhotoComp, multiple scattering is most likely to enhance the photodissociation rates of  $NO_2$  and  $CH_2O$ , which are driven by wavelengths longer than 320 nm, while it should have a lesser effect on those of  $O_3$  (to  $O(^1D)$ ) and  $H_2O_2$ , which emphasize the shorter wavelengths near 310 nm.

The models participating in PhotoComp may be broadly separated into two groups: those using multistream methods of radiative transfer to account for scattering and those using some form of a two-stream method. Specific types of two-stream methods represented by one or more models in PhotoComp include collimated [e.g., *Isaksen et al.*, 1977], isotropic [e.g., *Luther*, 1980], and delta or delta-Eddington [e.g., *Madronich*, 1987]. Of the 20 models represented in Table 3, 16 employed one of the two-stream approximations, and four used multistream approximations.

**Table 3.** Photolysis Rates From PhotoComp Models

	$O_3 + hv \rightarrow$ $O(^1D) + O_2$	$NO_2 + hv \rightarrow$ $NO + O$	$H_2O_2 + hv \rightarrow$ $OH + OH$	$CH_2O + hv \rightarrow$ $H + CHO$
<i>Noon</i>				
Surface	$2.70 (\pm 18) \times 10^{-5}$ ( $\pm 6.7\%$ )	$0.91 (\pm 06) \times 10^{-2}$ ( $\pm 6.1\%$ )	$7.38 (\pm 55) \times 10^{-6}$ ( $\pm 7.4\%$ )	$3.00 (\pm 29) \times 10^{-5}$ ( $\pm 9.7\%$ )
4 km	$3.47 (\pm 22) \times 10^{-5}$ ( $\pm 6.4\%$ )	$1.08 (\pm 08) \times 10^{-2}$ ( $\pm 7.2\%$ )	$9.47 (\pm 93) \times 10^{-6}$ ( $\pm 9.8\%$ )	$4.11 (\pm 52) \times 10^{-5}$ ( $\pm 2.6\%$ )
8 km	$3.38 (\pm 23) \times 10^{-5}$ ( $\pm 6.8\%$ )	$1.16 (\pm 08) \times 10^{-2}$ ( $\pm 7.0\%$ )	$10.20 (\pm 1.23) \times 10^{-6}$ ( $\pm 12.1\%$ )	$4.64 (\pm 61) \times 10^{-5}$ ( $\pm 13.2\%$ )
12 km	$3.08 (\pm 19) \times 10^{-5}$ ( $\pm 6.3\%$ )	$1.18 (\pm 08) \times 10^{-2}$ ( $\pm 6.6\%$ )	$10.38 (\pm 1.42) \times 10^{-6}$ ( $\pm 13.7\%$ )	$4.81 (\pm 61) \times 10^{-5}$ ( $\pm 12.6\%$ )
<i>Diurnal Average</i>				
Surface	$0.71 (\pm 05) \times 10^5$ ( $\pm 7.2\%$ )	$0.39 (\pm 03) \times 10^2$ ( $\pm 7.1\%$ )	$2.67 (\pm 22) \times 10^6$ ( $\pm 8.3\%$ )	$1.04 (\pm 11) \times 10^5$ ( $\pm 10.8\%$ )
4 km	$0.94 (\pm 08) \times 10^5$ ( $\pm 8.0\%$ )	$0.50 (\pm 02) \times 10^2$ ( $\pm 7.8\%$ )	$3.65 (\pm 39) \times 10^6$ ( $\pm 10.6\%$ )	$1.52 (\pm 21) \times 10^5$ ( $\pm 14.0\%$ )
8 km	$0.94 (\pm 08) \times 10^5$ ( $\pm 8.6\%$ )	$0.57 (\pm 02) \times 10^2$ ( $\pm 7.2\%$ )	$4.18 (\pm 50) \times 10^6$ ( $\pm 12.0\%$ )	$1.83 (\pm 26) \times 10^5$ ( $\pm 14.0\%$ )
12 km	$0.86 (\pm 07) \times 10^5$ ( $\pm 8.0\%$ )	$0.61 (\pm 01) \times 10^2$ ( $\pm 7.4\%$ )	$4.49 (\pm 58) \times 10^6$ ( $\pm 13.0\%$ )	$2.00 (\pm 27) \times 10^5$ ( $\pm 13.5\%$ )

Values are mean (per second)  $\pm 1$  rms error (and rms error as percentage of mean).



**Figure 1.** Photodissociation rates calculated by multistream and two-stream radiative transfer models. The mean photodissociation rate (inverse seconds) and  $\pm 1$  rms error (horizontal lines) are calculated for four altitudes (ordinate axis) and are shown for those models using two-stream methods of radiative transfer (indicated by the 2) and those using multistream methods (indicated by the M). Results are shown for (a)  $O_3$  photolysis to  $O(^1D)$ , (b)  $H_2O_2$  photolysis, (c)  $NO_2$  photolysis, and (d)  $CH_2O$  photolysis. Note that the scales vary for each figure.

Figure 1 shows a comparison of diurnally averaged photodissociation means and rms errors for the two-stream and multistream classifications. While there are essentially no differences in the mean rates for  $O_3$  and  $H_2O_2$  (Figures 1a and 1b), the models using multistream code calculate distinctly larger rates for  $NO_2$  and  $CH_2O$  (Figures 1c and 1d). When we remove this bias from the statistics calculations, the rms errors for the diurnally averaged rates are reduced by about one third to between 10% and 11% at all altitudes for  $CH_2O$  and to between 4% and 5% for  $NO_2$  photolysis. There are no corresponding significant changes in the errors for  $O_3$  or  $H_2O_2$ .

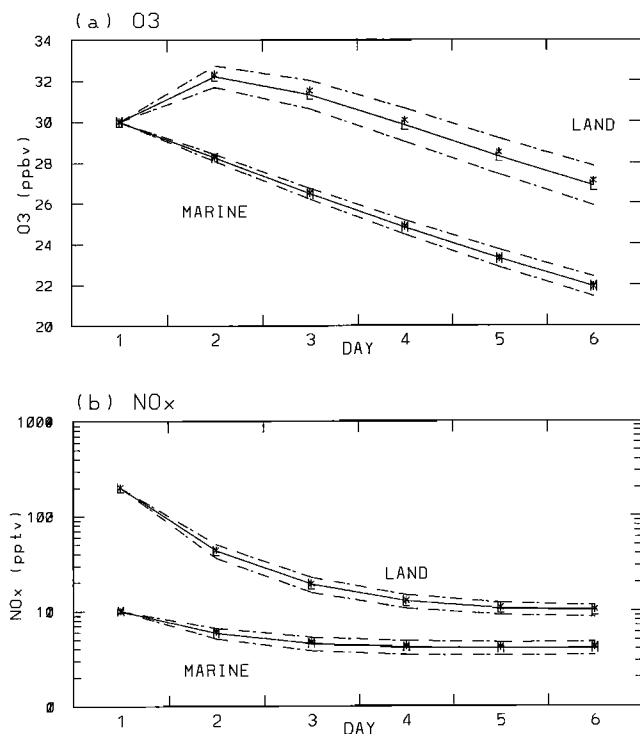
### 3.2. Species Concentration

The 5-day sequence of computed mixing ratios for noontime  $O_3$  and  $NO_x$  are in Figures 2–5 for the six PhotoComp cases. The figures show a basic dependence of the net  $O_3$  tendency on  $NO_x$  concentration. Although the cases span a variety of atmospheric altitudes and conditions, in general, the tendency is negative when  $NO_x$  is less than a few tens of parts per trillion volume (pptv) and positive for higher concentrations.

Conservation of the sum  $NO_x + HNO_4 + HNO_3$  was checked for the surface simulations, and all but two of the models conserved this quantity to better than 99%. The remaining two conserved to better than 95%.

Figures 2–5 show the mean of the 21 individual model results for each day and a  $\pm 1$  rms error envelope (dashed lines). The median model value for each day is also shown by an asterisk. Mean and median values were similar in all of the cases without NMHC chemistry (differences of less than 5%; Figures 2 and 3). The two cases with hydrocarbons (Land-Bio and Plume-HC) gave more widely divergent results, in part because of the lack of an agreed-upon standard mechanism and rates, as have been developed for stratospheric chemistry [e.g., DeMore *et al.*, 1992]. For example, the  $O_3$  and  $NO_x$  means and medians diverge by as much as 25% (Figures 4 and 5). Note that results from two of the models participating in the hydrocarbon cases were discarded for this analysis because their reported values of  $NO_x$  were as much as 500 times larger than those from the remaining models.

In the upper troposphere Free case (Figure 3), with moderate-to-low  $NO_x$  values (primarily around 20 to 40 pptv after the first day), there is a slow net destruction of  $O_3$  of only

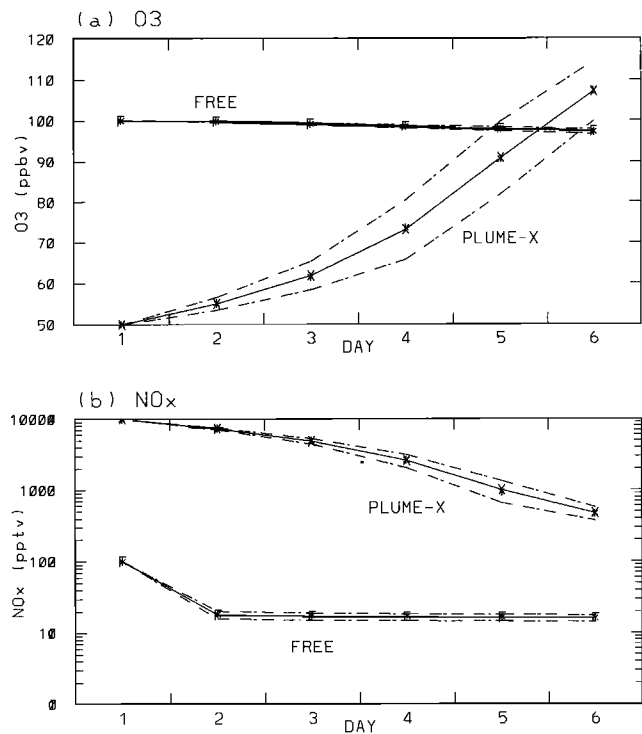


**Figure 2.** Mean and 1 rms error for O<sub>3</sub> and NO<sub>x</sub> from the Marine and Land cases. The mean of the reported noontime values for (a) O<sub>3</sub> in ppbv and (b) NO<sub>x</sub> in pptv is shown by the solid line. Results from the Marine case are indicated with the M, and results from the Land case are shown with the L. Note that the axis for NO<sub>x</sub> mixing ratio is logarithmic. Day 1 (along the abscissa) shows the initial value for the start day, and results are shown for each day of the 5-day run (days 2–6). A  $\pm 1$  rms envelope is shown with dashed lines. Median values for each day are shown with an asterisk.

slightly more than 0.5 ppbv d<sup>-1</sup>. Because of this slower rate of chemistry the rms error around the mean concentrations is less for this particular simulation than for the other simulations with faster rates of oxidant formation: the rms error is less than 1% of the mean for O<sub>3</sub> and less than 15% for NO<sub>x</sub>. The rms error for the O<sub>3</sub> tendency, however, is near 0.1 ppbv d<sup>-1</sup>, which is of the order of 20% of the 0.5 ppbv d<sup>-1</sup> decay rate.

The surface level, low-NO<sub>x</sub> (<10 pptv) Marine results (Figure 2) show a consistent trend of O<sub>3</sub> decreasing by between 1.5 and 2 ppbv d<sup>-1</sup>. In the similar Land case the higher initial concentrations of NO<sub>x</sub> (200 pptv) produce an O<sub>3</sub> increase of about 2 ppbv during the first day. Once NO<sub>x</sub> concentrations fall to less than 20 pptv during the latter several days of the Land case, the ozone decrease parallels that of the Marine case, but with an offset of +5 ppbv. These two cases are identical except for the initial NO<sub>x</sub> and serve as a sensitivity test: the additional 190 pptv of NO<sub>x</sub> produces a net 5 ppbv of O<sub>3</sub>, or a yield of about 26 molecules of O<sub>3</sub> per molecule of NO<sub>x</sub>.

The largest model to model differences in the predicted O<sub>3</sub> concentrations are those for the Plume-X and Plume-HC cases (Figures 3 and 5), with an rms error typically 10–15% of the mean. This is accompanied by a significant scatter in predicted NO<sub>x</sub>, which is of the order of  $\pm 100$  pptv for the Plume-X case. The results from the Plume-X case show higher NO<sub>x</sub> concentrations (>500 pptv) throughout the 5-day period



**Figure 3.** Same as figure 2 for the Free (F) and Plume-X cases (X).

and show O<sub>3</sub> increasing significantly from an early rate of 5 ppbv d<sup>-1</sup> to more than 15 ppbv d<sup>-1</sup> during the last few model days. The introduction of hydrocarbons (Plume-HC) has a significant impact on the NO<sub>x</sub> lifetime and O<sub>3</sub> production. Because of the presence of hydrocarbon oxidation products the subsequent formation of nitrates such as peroxyacetyl nitrate (PAN) as an important reservoir of NO<sub>x</sub> rapidly depletes ambient NO<sub>x</sub>. While NO<sub>x</sub> in the Plume-X case (Figure 3) remains above 1 ppbv for much of the period, it drops to about 50 pptv after only 1 day of integration when NMHC chemistry is considered (Figure 5). As a result the behavior of O<sub>3</sub> is dramatically altered in the Plume-HC case, with an initial increase of 100 ppbv followed by a steady decline in concentration when NO<sub>x</sub> levels are typically 20 pptv. Extrapolating back to day 1, the net O<sub>3</sub> yield for this scenario is about 8 to 10 molecules per molecule of NO<sub>x</sub>, much less than the amount for the unpolluted surface layer.

Although the model to model differences are not excessively large for the low-NO<sub>x</sub> surface Marine and Land cases, it is important to understand why the models differ in these predicted O<sub>3</sub> destruction rates, since most global tropospheric O<sub>3</sub> photochemical destruction occurs in the moist lower troposphere. The mean net O<sub>3</sub> tendency simulated by the models through the last day of integration is about -1.5 ppbv d<sup>-1</sup> for both Marine and Land cases. The model to model rms errors of these loss rates are about 10% of the means, a finding that implies that about one third of the models are predicting O<sub>3</sub> tendencies more than  $\pm 10\%$  from the mean, even though they are all simulating identical conditions. Possible explanations for some of these differences are discussed in the next section.

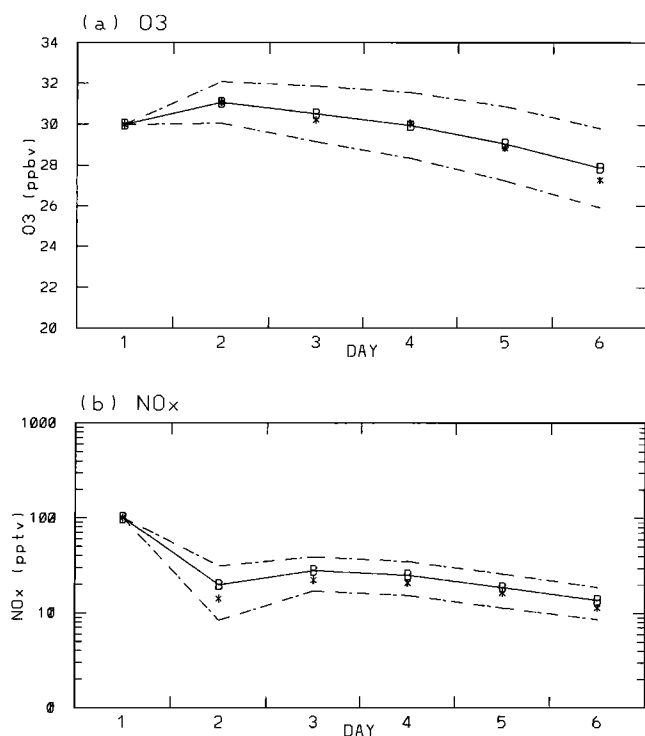


Figure 4. Same as figure 2 for the Land-bio case (B).

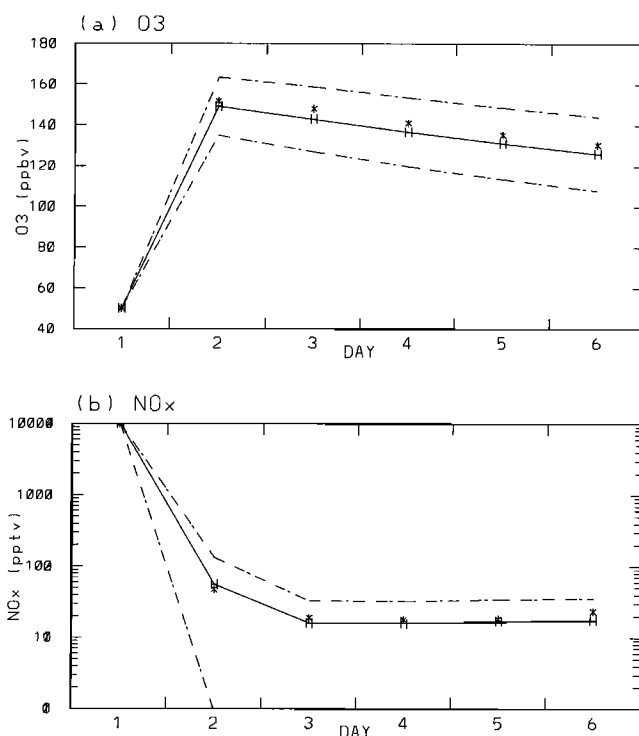


Figure 5. Same as figure 2 for the Plume-HC case (H).

#### 4. Analysis of Model to Model Differences

##### 4.1. Surface Cases

The 5-day sequence of individual model mixing ratios of noontime O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>, and diurnally averaged HO<sub>2</sub> and OH for the surface level Marine case, are shown in Figure 6. The general patterns of behavior presented here are also similar to the Land and (to some extent) the Land-Bio cases. For the purpose of this analysis, three subsets of consistent model behaviors were identified. In general, the subsets were defined as groups of models that displayed similar relative abundances of HO<sub>x</sub> and O<sub>3</sub>. Characteristics of the subsets are described in more detail below. The factors contributing to the different behaviors of these subsets explain much of the total model to model variance shown in Figures 2–5.

The individual model results in Figure 6 are identified by a subset group number. Note that four of the models do not display behavior consistent with any of these three subsets and are denoted with an asterisk. When the results are plotted in this fashion, an apparent relation between the O<sub>3</sub> tendencies and diurnally averaged HO<sub>2</sub> becomes evident (Figures 6a and 6c). That is, subsets with the highest HO<sub>2</sub> concentrations (subsets 1 and 3) show the fastest O<sub>3</sub> destruction rates. A correlation coefficient (*r*) equal to -0.53 (significant to >99%) was calculated between differences from the mean of the individual model O<sub>3</sub> loss rates during each day of the simulation and the accompanying differences in the HO<sub>2</sub> concentration. Alternately, model to model differences from the mean of the photolysis of O<sub>3</sub> (to O(1D)) were not found to have a significant correlation to the differences in the O<sub>3</sub> loss rate.

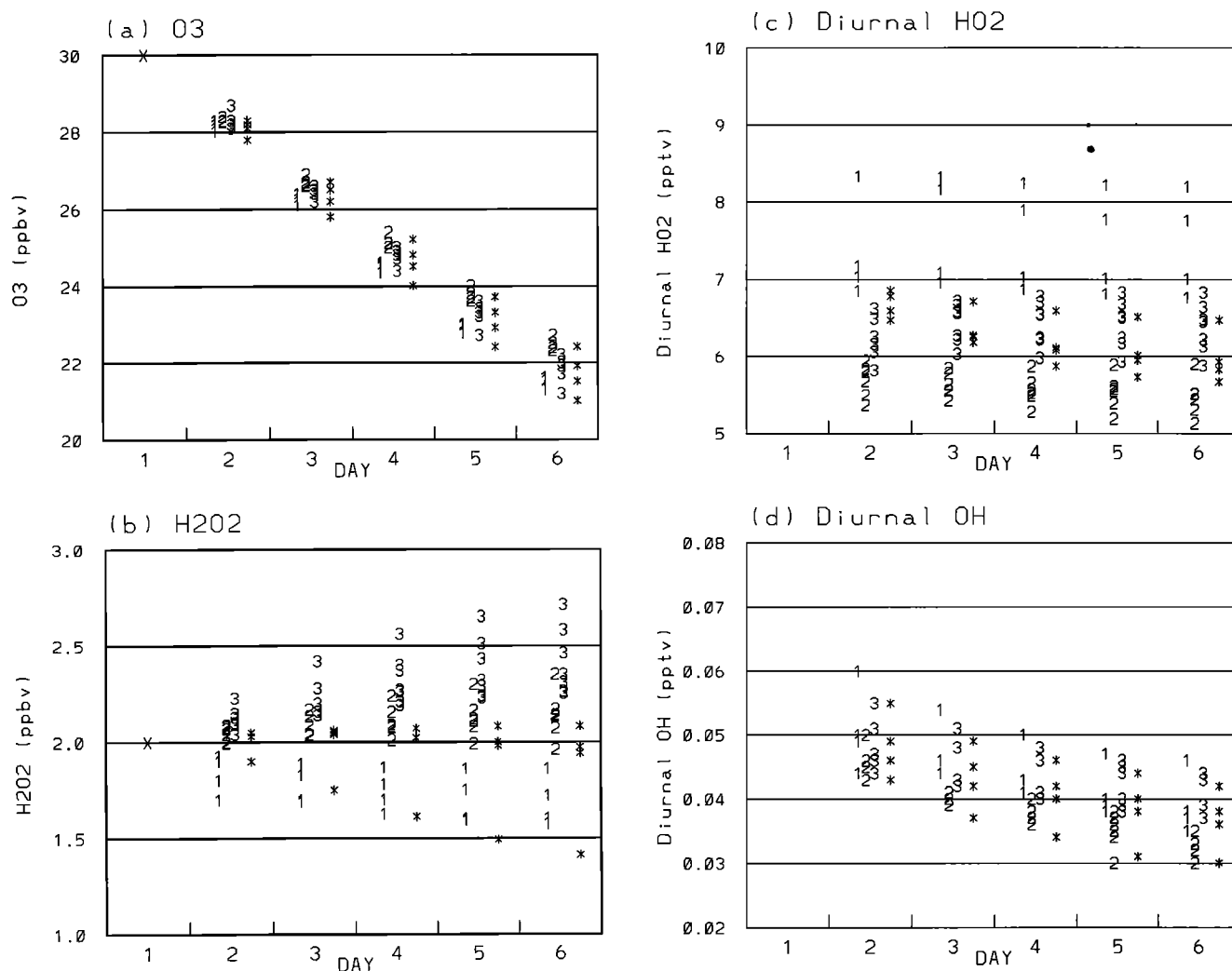
The loss frequency of O<sub>3</sub> due to direct reaction with HO<sub>2</sub>, (R6), is calculated here from the product of the rate constant

[DeMore *et al.*, 1992] and the reported diurnally averaged HO<sub>2</sub> from each model, giving a mean value of  $3.1 \times 10^{-7} \text{ s}^{-1}$  (-0.8 ppbv d<sup>-1</sup>). This corresponds to about one half the total net O<sub>3</sub> loss frequency. The model to model rms error of this single loss,  $0.4 \times 10^{-7} \text{ s}^{-1}$ , constitutes about 80% of the rms error for the total net O<sub>3</sub> loss. We conclude that differences in the predicted loss rates for O<sub>3</sub> in the surface cases can be largely traced to the HO<sub>2</sub> concentrations.

Both subsets 2 and 3 indicate a positive relation between differences in HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> from their respective means, with subset 3 showing larger concentrations of both constituents. In contrast, subset 1 clearly shows the lowest concentrations of H<sub>2</sub>O<sub>2</sub> (Figure 6b) along with the highest concentrations of HO<sub>2</sub>. Evidently, for subset 1 the exchange between HO<sub>x</sub> and H<sub>2</sub>O<sub>2</sub> is shifted in favor of HO<sub>x</sub>. There is no apparent consistency in the differences in the rate of H<sub>2</sub>O<sub>2</sub> photolysis for the models in subset 1; these results span the entire range of reported rates (see Figure 7b). Stockwell [1995] stressed the importance of including the pressure and water vapor dependence of the HO<sub>2</sub>+HO<sub>2</sub> reaction to form H<sub>2</sub>O<sub>2</sub> in atmospheric chemistry models, because omitting them can result in a relative error near the surface as high as 75% [Kircher and Sander, 1984]. The resulting effect is lower H<sub>2</sub>O<sub>2</sub> production and a relatively increased HO<sub>2</sub> concentration. For the conditions in this PhotoComp case, omission of the water vapor dependence reduces the conversion of HO<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> by 35%. It was subsequently verified that the models in subset 1 do not include this H<sub>2</sub>O dependence of the HO<sub>2</sub> self reaction.

Examination of subsets 2 and 3 reveals that differences in OH from the mean (Figure 6d) generally display a positive relation to differences from the mean for both H<sub>2</sub>O<sub>2</sub> and HO<sub>2</sub>. As was discussed earlier, the photolysis of O<sub>3</sub> is the primary source of HO<sub>x</sub>, and photolysis of H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O is an important pathway in the regeneration of HO<sub>x</sub> from HO<sub>x</sub>





**Figure 6.** Individual model results for the Marine case. Each model is identified with a subset number 1, 2, or 3. Models that don't fit into any subset are shown with an asterisk. Noontime values for each day of the simulation (along the abscissa) are shown for (a) O<sub>3</sub> in ppbv and (b) H<sub>2</sub>O<sub>2</sub> in ppbv. Diurnally averaged values for the previous 24 hours are shown for (c) HO<sub>2</sub> in pptv and (d) OH in pptv.

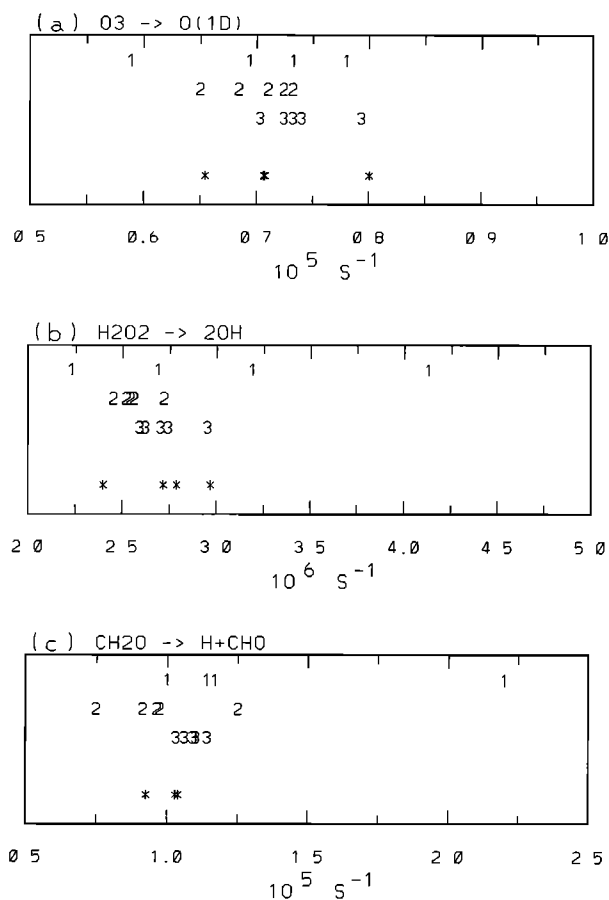
reservoir species. A cursory examination of diurnally averaged photolysis rates used by the models in subsets 2 and 3 (Figure 7) suggests that with one or two exceptions there is a tendency for subset 2 models to calculate slightly slower rates than subset 3 for the photodissociations of H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O in the boundary layer. The diurnally averaged production of HO<sub>x</sub> from each of these pathways was estimated for the last day of model integration by using the appropriate model reported concentrations and diurnally averaged photolysis rates. These are shown in Table 4, along with calculated correlations between the photolysis rates that drive the production pathways and HO<sub>2</sub> concentrations. As expected, the dominant production of HO<sub>x</sub> is the pathway initiated by the photolysis of O<sub>3</sub>. However, the largest rms errors are calculated for the sources from H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O photolysis, and the model to model differences in HO<sub>2</sub> are most closely correlated with differences in the photolysis rate of these constituents.

The behaviors of these subsets imply that for the surface, low-NO<sub>x</sub> PhotoComp regimes, differences between the models in HO<sub>x</sub> are the dominant factors leading to the varying O<sub>3</sub> loss rates. Differences in HO<sub>2</sub> are likely due to (1) inconsistencies

in the conversion rate of HO<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> and (2) variations in HO<sub>x</sub> sources from reservoir species, such as differences in the H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O photolysis rates. Note that as discussed previously, H<sub>2</sub>O<sub>2</sub> photolysis rates, while showing rms errors of the order of 8% of the mean near the surface, did not show a systematic dependence on the choice of multistream versus two-stream radiative code or on the choice of photokinetics data used by the models. However, the choice of multistream versus two-stream radiative code contributed about one third of the rms error associated with the rate for CH<sub>2</sub>O photodissociation. Additional contributions to differences between the models could be due to a combination of factors such as choice of time steps, which range from 1 s to several hours for the models represented here, or numerical solvers used, although the recent work of *Stolarski et al.* [1995] suggests that this makes little difference.

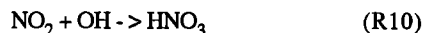
#### 4.2. Plume-X Case

Results from the Plume-X simulation (Figure 8) show clear changes in HO<sub>x</sub> chemistry as NO<sub>x</sub> concentrations decrease from an initial value of 10 ppbv to less than 1 ppbv after



**Figure 7.** Diurnally averaged photolysis rates at the surface. Rates are shown in inverse seconds for the diurnally averaged surface level photolysis rate for (a) O<sub>3</sub> (to O(<sup>1</sup>D)), (b) H<sub>2</sub>O<sub>2</sub>, and (c) CH<sub>2</sub>O. Each model is identified with a subset number 1, 2, or 3 or with an asterisk, as in Figure 6.

5 days (Figure 8b). Concentrations of NO<sub>x</sub> greater than 2 ppbv throughout the first part of the simulation suppress HO<sub>x</sub> radicals (Figure 8c) due to rapid formation of nitric acid (HNO<sub>3</sub>).



The growth rate of HNO<sub>3</sub> (not shown) is initially 2.5 to 3 ppbv d<sup>-1</sup> but slows to <1 ppbv d<sup>-1</sup> toward the end of the

simulation as NO<sub>x</sub> concentrations decrease. The transition from a “high-NO<sub>x</sub>” to a “low-NO<sub>x</sub>” regime is also reflected in the behavior of H<sub>2</sub>O<sub>2</sub> (not shown). The initial net tendency of H<sub>2</sub>O<sub>2</sub> is to decrease while total HO<sub>x</sub> is suppressed, but as NO<sub>x</sub> concentrations fall and HO<sub>x</sub> increases, H<sub>2</sub>O<sub>2</sub> reverses trend and begins to increase as its production rate becomes larger than its photolytic destruction.

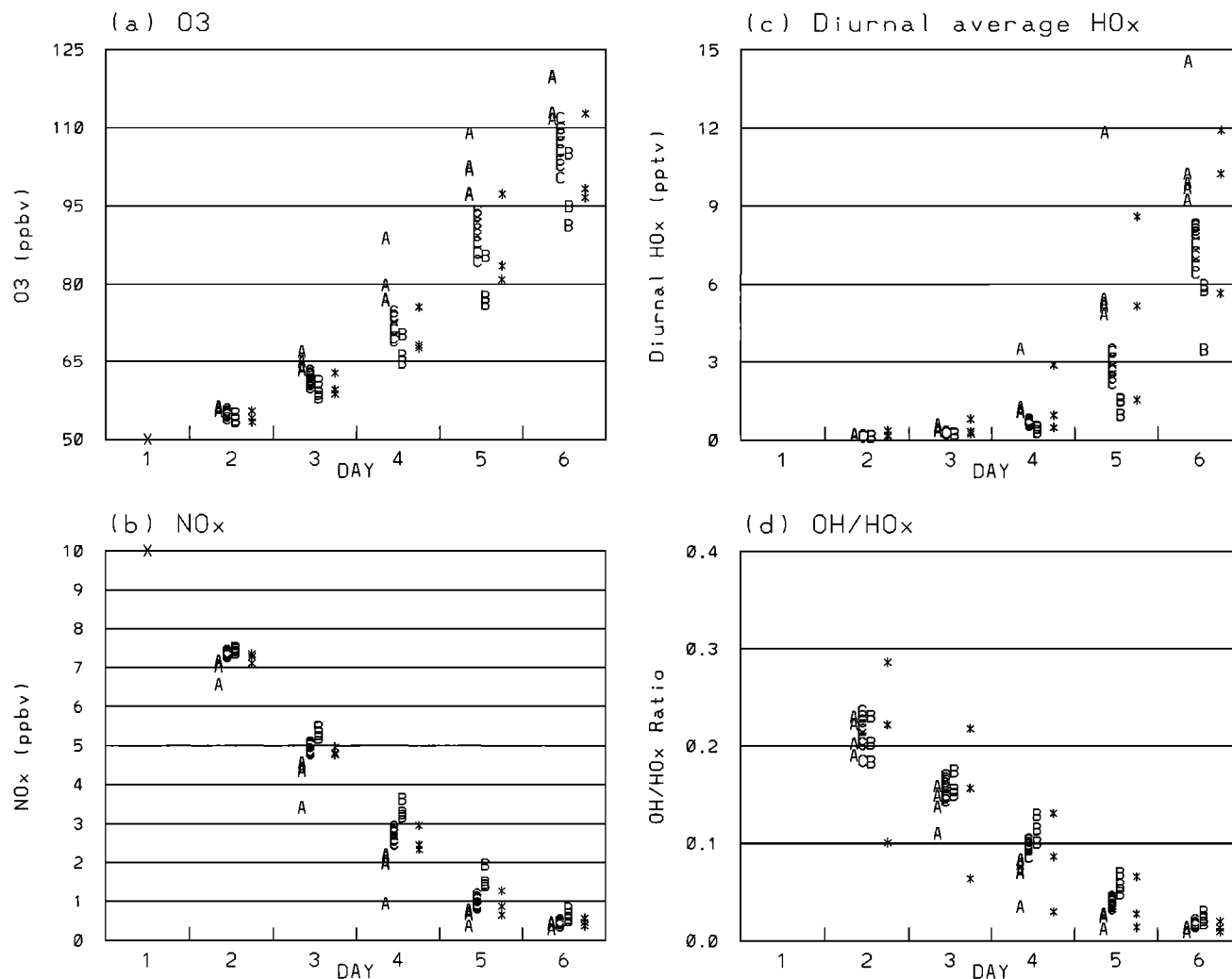
A secondary effect of the “high-NO<sub>x</sub>” regime is an increased OH:HO<sub>x</sub> ratio (Figure 8d), because the OH:HO<sub>2</sub> balance is strongly controlled by the conversion of HO<sub>2</sub> to OH by NO (R8). After NO<sub>x</sub> concentrations fall below 2 ppbv at the end of the simulation, HO<sub>x</sub> radicals increase dramatically, and the OH:HO<sub>x</sub> ratio also begins to decrease.

O<sub>3</sub> concentrations increase consistently throughout the simulation (Figure 8a), but the increase is more rapid after the NO<sub>x</sub> levels fall and HO<sub>x</sub> recovers. There has been much discussion in the literature concerning O<sub>3</sub> production efficiency as a function of NO<sub>x</sub> concentration [e.g., Liu et al., 1987; Lin et al., 1988; Sillman et al., 1990; Fehsenfeld and Liu, 1993]. For these simple, no-NMHC conditions, this efficiency is directly related to the OH:HO<sub>x</sub> ratio and the HO<sub>x</sub> radical concentration. Under high-NO<sub>x</sub> conditions, HO<sub>x</sub> radicals are suppressed, and OH:HO<sub>x</sub> ratios increase. This effect causes the rate of NO<sub>x</sub> removal (via conversion to HNO<sub>3</sub>, (R7)) to be large in relation to the initial step in the O<sub>3</sub> production process (conversion of NO to NO<sub>2</sub>, (R8)). The result is a lower O<sub>3</sub> production efficiency, defined as the ratio of O<sub>3</sub> formation to NO<sub>x</sub> removal.

The model to model rms error in O<sub>3</sub> production is initially quite large in this case, up to 30% of the daily average production rate. By the fifth day, however, the models are in better agreement, and the mean rate of production is 16.3 ppbv d<sup>-1</sup>, with an rms error of only about 2 ppbv d<sup>-1</sup>, or 11%. To understand the Plume-X case, we have regrouped the 21 models into three subsets denoted A, B, and C. Again, the subsets were primarily defined with respect to similar relative abundances of O<sub>3</sub>, HO<sub>x</sub>, and NO<sub>x</sub>. Three models did not obviously fall into any of the subsets and are denoted with an asterisk in Figure 8. The subsets in Figure 8 show a positive relation between concentrations of HO<sub>x</sub> and the O<sub>3</sub> production rate; i.e., subset A shows highest values for O<sub>3</sub> and diurnally averaged HO<sub>x</sub> (Figures 8a and 8c), while subset B shows the lowest values, and subset C results lie between. Additionally, there is an apparent negative relation between model to model differences in HO<sub>x</sub> and NO<sub>x</sub> and between differences in HO<sub>x</sub> and the OH:HO<sub>x</sub> ratio (subset A shows lowest values for NO<sub>x</sub> and

**Table 4.** Diurnally Averaged HO<sub>x</sub> Production Rates for Marine Case Subsets 2 and 3: Last Day of Integration

HO <sub>x</sub> Production Pathway	Diurnal Mean Production of HO <sub>x</sub> , molecules cm <sup>-3</sup> s <sup>-1</sup>	Root Mean Square Error, molecules cm <sup>-3</sup> s <sup>-1</sup>	Correlation (r) of Photolysis Rate to Diurnal HO <sub>2</sub> Mixing Ratio
O <sub>3</sub> + hv → O( <sup>1</sup> D)	5.9 × 10 <sup>5</sup>	± 0.22 × 10 <sup>5</sup>	-0.11 (not significant)
O( <sup>1</sup> D) + H <sub>2</sub> O → 2OH			
CH <sub>2</sub> O + hv + fast steps → 2HO <sub>2</sub> + CO	1.1 × 10 <sup>5</sup>	± 0.30 × 10 <sup>5</sup>	+0.68 (significant to 99% confidence)
H <sub>2</sub> O <sub>2</sub> + hv → 2OH + O <sub>2</sub>	3.0 × 10 <sup>5</sup>	± 0.34 × 10 <sup>5</sup>	+0.54 (significant to 99% confidence)



**Figure 8.** Individual model results for the Plume-X case. Each model is identified with a subset letter A, B, or C. Models that don't fit into any subset are shown with an asterisk. Noontime values for each day of the simulation (along the abscissa) are shown for (a) O<sub>3</sub> in ppbv and (b) NO<sub>x</sub> in ppbv. Diurnally averaged values for the previous 24 hours are shown for (c) HO<sub>x</sub> in pptv and (d) OH:HO<sub>x</sub> ratio.

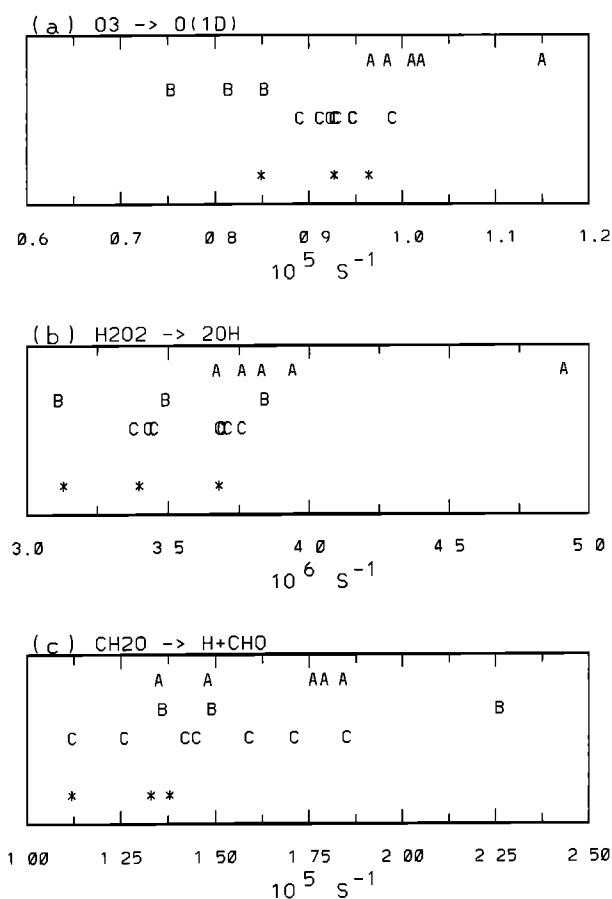
OH:HO<sub>x</sub>, subset B shows the highest, and subset C lies between). These patterns of deviation are fully consistent with the general mean behavior of the NO<sub>x</sub> and HO<sub>x</sub> systems described above. This finding suggests that the factors that drive the model to model differences are related to the same parameterizations that control the mean photochemical behavior of HO<sub>x</sub> in the high- and low-NO<sub>x</sub> systems.

Figure 9 shows model calculated diurnal averages of photolysis rates for O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and CH<sub>2</sub>O at 4 km (the height of the Plume-X simulation). While there is no distinction between subsets for H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O photolysis (Figures 9b and 9c), there is a strong relation between the selected subsets and differences in the O<sub>3</sub> photolysis rates from the mean at this altitude. For instance, subset A, which shows highest values of HO<sub>x</sub>, also clearly shows highest values for O<sub>3</sub> photolysis (Figure 9a). O<sub>3</sub> photolysis (followed by reaction of O(<sup>1</sup>D) with water vapor) accounts for about 80% of the HO<sub>x</sub> source under these conditions and is expected to have a major impact on HO<sub>x</sub> concentrations [see also Thompson and Stewart, 1991].

Table 5 lists the contribution to the total HO<sub>x</sub> source from the photolysis of O<sub>3</sub>, CH<sub>2</sub>O, and H<sub>2</sub>O<sub>2</sub>. In this analysis the largest positive correlation between HO<sub>2</sub> and photolysis rates was calculated for O<sub>3</sub> photolysis. This calculation suggests that model to model differences in the HO<sub>x</sub> sources that drive the differences in HO<sub>x</sub> also subsequently have effects on the differences in NO<sub>x</sub> and in the O<sub>3</sub> production rate for the Plume-X case.

#### 4.3. Hydrocarbon Cases

There is no widely accepted standard for hydrocarbon oxidation schemes, as there is for inorganic chemistry and CO and CH<sub>4</sub> oxidation [DeMore *et al.*, 1992]. Most of the models here use NMHC oxidation schemes that are derived from one of three common sources, although many include model-specific modifications to these schemes: (1) the lumped molecule approach such as RADM-II [Stockwell *et al.*, 1990], (2) the lumped molecule with surrogate species approach [e.g., Lurmann *et al.*, 1986], and (3) the lumped structure approach



**Figure 9.** Diurnally averaged photolysis rates at 4 km. Rates are shown in inverse seconds for the diurnally averaged 4 km photolysis rate for (a)  $\text{O}_3$  (to  $\text{O}(^1D)$ ), (b)  $\text{H}_2\text{O}_2$ , and (c)  $\text{CH}_2\text{O}$ . Each model is identified with a subset number A, B, or C or with an asterisk, as in Figure 7.

such as Carbon-Bond IV [Gery *et al.*, 1989]. We find no obvious consistency of results as a function of these groups, however.

While the general trends of trace species are consistent within the group of 14 models that include results from the NMHC cases (e.g., large  $\text{O}_3$  production at beginning of Plume-HC simulation, followed by a gradual decay), the scatter among the model results is quite large. Studies such as the one by

Hough [1988] present a highly structured comparison of various mechanisms that focus on the specific hydrocarbon chemistry scheme used, removing as many other sources of variation as possible. As was discussed previously, such a comparison of photochemical oxidant mechanisms was not the intent of PhotoComp or in the scope of this report. Rather, we present the results for the Plume-HC and Land-Bio cases here (Figures 4 and 5) to illustrate the marked increased scatter of results produced by this group of models when NMHC chemistry is introduced.

The cases including hydrocarbons can be compared with the corresponding cases without NMHC chemistry, i.e., Land-Bio to the Land case and Plume-HC to the Plume-X case. In both instances the rms error for the predicted  $\text{O}_3$  concentration on day 5 of the simulation is approximately doubled with the addition of NMHCs. The rms error for  $\text{NO}_x$  also increases dramatically, from 15% to nearly 40% in the Land/LandBio cases. The treatment of NMHC introduces a production of PAN and other nitrates into the system. Various treatments of these species are likely to contribute to the scatter of  $\text{NO}_x$  seen in Figures 4 and 5.

### 5. Summary

While PhotoComp was constructed with the specific goal to examine consistency among models for simple gas-phase photochemistry, the results reproduced some of the fundamental characteristics of tropospheric chemical processes previously described in the literature, such as the dependence of  $\text{O}_3$  production on  $\text{NO}_x$  concentration and the nonlinear behavior of  $\text{O}_3$  production efficiency per  $\text{NO}_x$  molecule as a function of  $\text{NO}_x$  concentration (e.g., 26 molecules of  $\text{O}_3$  per additional molecule of  $\text{NO}_x$  in the clean surface layer and 8–10 molecules of  $\text{O}_3$  per molecule of  $\text{NO}_x$  in the highly concentrated mid-troposphere plume).

Small but systematic differences were found between models in the simulation of the moist, lower tropospheric cases (e.g., Marine). These differences are important, because most of the global photochemical destruction of  $\text{O}_3$  occurs in the remote lower troposphere under conditions similar to the Marine case. The 10% rms error for the net  $\text{O}_3$  tendency in this case is primarily due to model to model differences in the rate of reaction of  $\text{O}_3$  with  $\text{HO}_2$ . The differences in  $\text{HO}_2$ , in turn, can be traced to (1) inconsistent conversion rates for  $\text{HO}_2$  to  $\text{H}_2\text{O}_2$  due to some models leaving out the water vapor dependence for the self-reaction of  $\text{HO}_2$  and (2) differences in the rates of

**Table 5.** Diurnally Averaged  $\text{HO}_x$  Production Rates for Plume-X Case; All Models: Last Day of Integration

$\text{HO}_x$ Production Pathway	Diurnal Mean Production of $\text{HO}_x$ , molecules $\text{cm}^{-3} \text{ s}^{-1}$	Root Mean Square Error, molecules $\text{cm}^{-3} \text{ s}^{-1}$	Correlation (r) of Photolysis Rate to Diurnal $\text{HO}_2$ Mixing Ratio
$\text{O}_3 + \text{hv} \rightarrow \text{O}(^1D)$	$5.67 \times 10^5$	$\pm 0.90 \times 10^5$	+0.69 (significant to 99% confidence)
$\text{O}(^1D) + \text{H}_2\text{O} \rightarrow 2\text{OH}$			+0.13 (not significant)
$\text{CH}_2\text{O} + \text{hv} + \text{fast steps} \rightarrow 2\text{HO}_2 + \text{CO}$	$0.84 \times 10^5$	$\pm 0.16 \times 10^5$	+0.49 (significant to 99% confidence)
$\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2\text{OH} + \text{O}_2$	$0.80 \times 10^5$	$\pm 0.37 \times 10^5$	

photodissociation reactions that are secondary sources of HO<sub>x</sub>. While the choice of radiative transfer method had a significant impact on the rates of species that are photolytically destroyed in the longer wavelengths (NO<sub>2</sub> and CH<sub>2</sub>O), this had little or no effect on the photolysis rates calculated for those species driven by the relatively shorter wavelengths (O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>).

In the middle tropospheric case (Plume-X) with high initial concentrations of NO<sub>x</sub> a significant correlation was found between differences of HO<sub>x</sub> from the mean and differences of the photolytic source term initiated by photolysis of O<sub>3</sub>. These differences in turn affect the model-calculated decay of NO<sub>x</sub> and the associated O<sub>3</sub> production rate, which had rms errors between 10% and 30%. Models predicted O<sub>3</sub> concentrations for the high-altitude Free case that were in closer agreement because of the slow chemistry under the prescribed conditions, but the rms error for O<sub>3</sub> tendency was about 20% of the decay rate. The introduction of hydrocarbons to the system further exacerbates the model to model differences, since NO<sub>x</sub> then decays in less than a day to both HNO<sub>3</sub> and PAN, and the scatter between model results for both NO<sub>x</sub> and O<sub>3</sub> increases. In both of the cases that consider hydrocarbons the rms error for O<sub>3</sub> concentration approximately doubled when NMHCs were included.

One of the most significant factors contributing to differences between these models is, not surprisingly, the radiative calculations for photolysis rates, which display typical rms errors of 5–15% of the mean. While it would be useful to pinpoint photodissociation rates in future intercomparisons such as this one in order to understand differences in chemistry, this error between models is still within the general range of accuracy for photokinetics data such as those of DeMore *et al.* [1992]. A useful next step might include a closer examination of model-generated diurnal cycles of photodissociation rates and a comparison of these with data.

The results from this intercomparison indicate that even for the simulation of extremely simple situations, there can be discrepancies in resulting constituent concentration and tendencies among model simulations that can be significant in some cases. Such model calculations are becoming increasingly important in assessments of future atmospheric composition and climate.

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