A comparison of chemical mechanisms based on TRAMP-2006 field data

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A B S T R A C T

A comparison of a model using five widely known mechanisms (RACM, CB05, LaRC, SAPRC-99, SAPRC-07, and MCMv3.1) has been conducted based on the TexAQS II Radical and Aerosol Measurement Project (TRAMP-2006) field data in 2006. The concentrations of hydroxyl (OH) and hydroperoxy (HO2) radicals were calculated by a zero-dimensional box model with each mechanism and then compared with the OH and HO2 measurements. The OH and HO2 calculated by the model with different mechanisms show similarities and differences with each other and with the measurements. First, measured OH and HO2 are generally greater than modeled for all mechanisms, with the median modeled-to-measured ratios ranging from about 0.8 (CB05) to about 0.6 (SAPRC-99). These differences indicate that either measurement errors, the effects of unmeasured species or chemistry errors in the model or the mechanisms, with some errors being independent of the mechanism used. Second, the modeled and measured ratios of HO2/OH agree when NO is about 1 ppbv, but the modeled ratio is too high when NO was less and too low when NO is more, as seen in previous studies. Third, mechanism–mechanism HO2/OH differences are less than in cleaner conditions, probably because of the dominance of reactive nitrogen chemistry under polluted conditions.

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1. Introduction

Atmospheric hydroxyl (OH) and hydroperoxy (HO2) radicals (collectively HOx) play a key role in tropospheric chemistry. In urban polluted environments, the atmospheric processes involving OH and HOx radicals can be very complex with the abundant anthropogenic species such as NO and NO2 (collectively NOx) and volatile organic compounds (VOCs) (Sadanaga et al., 2003). These processes in the atmospheric chemistry can be described mathematically by a chemical mechanism, which is essential for air quality modeling. A highly explicit chemical mechanism would be preferred for the modeling because it represents the chemistry of atmosphere as accurately as possible. However, this approach is not practical due to incomplete knowledge of organic reactions and the limited availability of measurements of many higher order VOCs and oxygenated VOCs (OVOCs). Therefore, lumping approaches have been used to develop condensed chemical mechanisms that contain a limited number of reactions and unknown processes. Examples of such condensed mechanisms are Lurmann, Carter and Coyner mechanism (LCC) of Lurmann et al., 1997, Carbon Bond IV (CB4) of Gery et al., 1989, and Regional Atmospheric Chemical Mechanism (RACM) of Stockwell et al., 1997. Therefore two questions arise: (1) are these mechanisms consistent with each other? (2) how do the mechanisms compare to measurements?

Comparisons of some chemical mechanisms have been conducted in previous studies (e.g., Derwent, 1990, 1993; Olson et al., 1997; Kuhn et al., 1998; Jimenez et al., 2003; Luecken et al., 2007). As discussed in these papers, to determine the performance of a mechanism, the model results must be compared with measurements in environmental chambers or in the real atmosphere. However, while the environmental chambers have the advantage of known and controlled VOC mixtures, they have the shortcomings of chamber artifact effects and generally higher initial concentrations of VOCs and NOx than in the real atmosphere. Alternatively, comparing in situ observed HOx radicals with model
simulations has the shortcoming of possible unmeasured important atmospheric constituents, but has the advantage of evaluating chemical mechanisms in the environment of greatest interest – the atmosphere (Stockwell et al., 1997; Dodge, 2000). Unfortunately, \( \text{HO}_x \) was not measured for any of the model comparison studies that were discussed previously. One of the reasons is that until recently, the instruments have not been adequately developed to measure the major constraining atmospheric constituents that are necessary to model \( \text{HO}_x \), particularly a large number of hydrocarbons and photolysis frequencies (Heard and Pilling, 2003). Although several measurements of \( \text{HO}_x \) radicals have been conducted under urban environments in the past decade, the comparisons with modeling results (Table 1) have been limited to one mechanism in the model. In most of these studies, \( \text{HO}_x \) were underestimated, sometimes by a factor of three and even larger (Table 1). Therefore, further comparisons of modeled and observed radicals, especially considering the differences of chemical mechanisms, are necessary to interpret the discrepancies and improve the mechanisms.

2. Description of chemical mechanisms

The five mechanisms compared here have been actively in use in research and regulatory applications. The recent revisions of some mechanisms are substantial enough to conduct a new comparison among these mechanisms. General characteristics of these mechanisms are summarized in Table 2. The main features for each mechanism are briefly described below.

RACM (Stockwell et al., 1997) is a revised version of the Regional Acid Deposition Mechanism (RADM2) (Stockwell et al., 1990), which was developed from the first version of RADM (Stockwell, 1986). The main revisions have been performed for organic chemistry such as the oxidation mechanisms for isoprene, \( \alpha \)-pinene, and \( \beta \)-limonene. Most of the organic species are aggregated into the model species based on their similarity in functional groups and reactivity toward \( \text{OH} \). For instance, alkenes other than ethene are represented by three species: terminal alkenes, internal alkenes, and dienes. Some organic species such as formaldehyde and isoprene are treated explicitly.

Carbon Bond Mechanism (CB05) (Yarwood et al., 2005) is updated from the version IV, CB4. In contrast to the previous version, (1) inorganic reactions are extended to simulate remote to polluted urban conditions; (2) two extensions are available to be added to the core mechanism for modeling explicit species and reactive chlorine chemistry. Organic species are lumped according to the carbon bond approach, that is, bond type, e.g., carbon single bond and double bond. Reactions are aggregated based on the similarity of carbon bond structure so that fewer surrogate species are needed in the model. For instance, the single-bonded one-carbon-atom surrogate PAR represents alkanes and most of the alkyl groups. Some organics (e.g., organic nitrates and aromatics) are lumped with the similar manners to RACM.

NASA Langley Research Center mechanism (LaRC, October 2005 version) is updated from the mechanism used in Davis et al. (1993), which adapted the NMHC oxidation mechanism from LCC with modifications to address remote low-\( \text{NO}_x \) conditions (e.g., formation of organic peroxides), includes wet and dry removal rates recommended by Logan et al. (1981). Isoprene chemistry is based on the condensed mechanism from Carter and Atkinson (1996). The lumping technique applied in LaRC is relatively simple. Alkanes, alkenes, aldehydes and aromatics are lumped together respectively. Organic nitrates and peroxides are separated into more groups than those in RACM and CB05.

Statewide Air Pollution Research Center mechanism of Carter (2000) (SAPRC-99) represents a complete update of the SAPRC-90 mechanism of Carter (1990). The mechanism described here is focused on the base mechanism combined with the extended mechanism for lumped VOCs. The main revisions were made to update reaction rates, treat some species explicitly, and condense a few mechanisms. The organic species are lumped based on the similarity of reactivity toward OH, a similar approach to RACM. Using similar but more extensive organic peroxy operators that are used in CB05, a higher condensed mechanism of the peroxy reactions is employed to limit the number of free radical species.

SAPRC-07 (Carter, 2007) is the latest version of SAPRC, which keeps the general structure of SAPRC-99 but adds chlorine chemistry. A different method with 34 steady-state radical operators replaces the 135 steady-state radical operators of SAPRC-99.

### Table 1

<table>
<thead>
<tr>
<th>Campaign</th>
<th>Mechanism</th>
<th>Modeled-to-Observed Ratio (daytime)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{OH} )</td>
<td>( \text{HO}_x )</td>
<td></td>
</tr>
<tr>
<td>LAFRE, summer</td>
<td>LCC</td>
<td>1–1.5</td>
<td>&gt;1</td>
</tr>
<tr>
<td>SOS, summer</td>
<td>ADOM(^a)</td>
<td>0.75</td>
<td>0.64</td>
</tr>
<tr>
<td>PMTACS-NY, summer</td>
<td>RACM(^b)</td>
<td>0.64</td>
<td>0.40</td>
</tr>
<tr>
<td>PUMA, winter</td>
<td>MCMv3.1</td>
<td>0.58</td>
<td>0.56</td>
</tr>
<tr>
<td>PUMA-NY, winter</td>
<td>RACM</td>
<td>0.62</td>
<td>0.10</td>
</tr>
<tr>
<td>MCMA, spring</td>
<td>RACM</td>
<td>0.79</td>
<td>0.57</td>
</tr>
<tr>
<td>TORCH, summer</td>
<td>MCMv3.1</td>
<td>1.24</td>
<td>1.07</td>
</tr>
<tr>
<td>IMPACT-I, winter</td>
<td>RACM</td>
<td>0.86</td>
<td>1.29</td>
</tr>
</tbody>
</table>

\(^a\) Acid Deposition and Oxidants Model mechanism (ADOM) combined with isoprene and \( \pi \)-pinene mechanisms from other literatures.

\(^b\) Supplemented by detailed isoprene oxidation mechanisms from other literatures.

\(^c\) These ratios have been adjusted based on the data corrected by absolute calibration (Ren et al., 2008; Mao et al., 2010).

### Table 2

Characteristics of the chemical mechanisms.

<table>
<thead>
<tr>
<th>Mechanisms</th>
<th>RACM</th>
<th>CB05</th>
<th>LaRC</th>
<th>SAPRC-99</th>
<th>SAPRC-07</th>
</tr>
</thead>
<tbody>
<tr>
<td># of reactions</td>
<td>237</td>
<td>156</td>
<td>279</td>
<td>211</td>
<td>291</td>
</tr>
<tr>
<td>Photolysis</td>
<td>23</td>
<td>23</td>
<td>35</td>
<td>30</td>
<td>34</td>
</tr>
<tr>
<td>Inorganic</td>
<td>35</td>
<td>44</td>
<td>31</td>
<td>45</td>
<td>55</td>
</tr>
<tr>
<td>Organic</td>
<td>179</td>
<td>89</td>
<td>185</td>
<td>136</td>
<td>202(^c)</td>
</tr>
<tr>
<td>Other</td>
<td>–</td>
<td>–</td>
<td>28</td>
<td>–</td>
<td>3</td>
</tr>
<tr>
<td># of species</td>
<td>77</td>
<td>51</td>
<td>109</td>
<td>79</td>
<td>110</td>
</tr>
<tr>
<td>Stable inorganic</td>
<td>17</td>
<td>12</td>
<td>17</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td>Short-lived inorganic</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>4</td>
<td>9</td>
</tr>
</tbody>
</table>

| Stable organic | 32 | 26 | 57 | 42 | 42 | (135)\(^d\) |
| Alkanes | 5 | 3 | 4 | 6 | 6 | (22) |
| Alkenes | 4 | 3 | 2 | 3 | 3 | (17) |
| Biogens | 3 | 2 | 1 | 2 | 2 | (3) |
| Aromatics | 3 | 3 | 3 | 3 | 4 | (18) |
| Carbonyls | 9 | 5 | 10 | 13\(^e\) | 13 | (16) |
| Organic nitrates | 3 | 3 | 11 | 5 | 5 | 217 |
| Organic peroxydes | 3 | 2 | 19 | 2 | 2 | 800 |
| Organic acids | 2 | 3 | 2 | 5 | 5 | 76(3) |
| Other | – | 2 | 6 | 3 | 2 | 56 |
| Short-lived organic | 24 | 9 | 28 | 16 | 42\(^f\) | (982) |

\(^d\) With extended mechanism for lumped VOCs.

\(^e\) 72 of these are reactions of steady-state peroxy radical operators.

\(^f\) Including four steady-state inorganic operators, such as \( \text{SO}_2 \).

\(^c\) Numbers of primary emitted VOCs are shown within parentheses.

\(^e\) Including BALD (aromatic aldehydes).

\(^f\) Including 29 steady-state organic operators, such as \( \text{HCHO} \).

\(^g\) Number of the organic peroxy radicals.
(5 of these are inorganic operators) is used to represent 72 radical reactions. An important revision is that the mechanisms for many types of VOCs are added or improved, resulting in over 20% increase of reactivity estimates. Only lumped VOCs reactions are used here to extend the base mechanism too.

Master Chemical Mechanism (MCM) is the only near-explicit chemical mechanism compared in this study. The latest version, MCMv3.1 (available at the MCM website: http://mcm.leeds.ac.uk/MCM) has been updated by Bloss et al. (2005) based on recent improved understanding of aromatic photo-oxidation. The chemistry is developed using the protocol described by Jenkin et al. (1997) and has three previous versions: MCMv1 (Derwent et al., 1998), MCMv2 (Jenkin et al., 2000), and MCMv3 (Jenkin et al., 2003; Saunders et al., 2003), in which the aromatic chemistry is developed based on previous work and updated by new data from recent research. In addition to experimental data, many reactions are estimated from structure-reactivity relationships (SAR) method.

Several common characteristics of these mechanisms can be found: (1) The inorganic mechanisms are very similar. (2) Four organic species (methane, ethene, isoprene, and formic acid) are treated explicitly. (3) Except MCM, most of the mechanisms use lumping approaches to reduce the great number of organic reactions and/or to restrict their sizes so that emissions inventories can be used. At the same time, the chemical mechanisms have some significant differences. These differences occur in the following characteristics: (1) the lumping approaches for organic species, intermediates and products; (2) assumptions for unknown or poorly studied reactions, such as aromatics chemistry; (3) condensing processes for certain organic reactions; (4) pressure and temperature dependence of rate constants, especially for organic chemistry; (5) poorly understood photolysis parameters; (6) treatment of deposition processes or heterogeneous reactions. To focus the comparison on the mechanism itself other than the differences due to the rates or heterogeneous reactions, the last three features can be eliminated by applying the same rates for all reactions including photolysis as well as the same set of dry depositions for the modeling.

3. Method

The measurements of HOx were performed in Houston, Texas during TRAMP-2006 campaign from August to September 2006. The simulations of HOx were conducted in a zero-dimensional box model using each mechanism described above constrained by the same model input data measured simultaneously. This work differs from previous comparisons of mechanisms in several ways: (1) it includes the latest versions of mechanisms (SAPRC-07 and MCMv3.1) and a mechanism that has never been compared before (LaRC); (2) it is based on real atmosphere conditions; (3) it focuses on comparisons of OH and HO2; (4) it is compared to the simultaneous in situ observations; and (5) it is studied for varied conditions over a month-long duration.

3.1. Site description

The latest report of Environmental Protection Agency (EPA) (EPA, 2008) shows Houston, the fourth largest metropolitan area in the United States, was still one of the areas with the highest ground-level O3 concentrations in 2006. TRAMP was aimed at understanding air pollution in the Houston area. Further information is available at http://www.tceq.state.tx.us/nvq/exraqc.html. Measurements used in this modeling comparison were made at the top of the Moody Tower on the campus of University of Houston, 60 m above the ground. The Moody Tower site (29° 43’ 3.50’’ N, 95° 20’ 28.50’’ W) was located at the south of the downtown area of Houston. A few kilometers to the east of this site is the Port of Houston (Ship Channel), one of the busiest sea ports in United States. However the measurement site is sufficiently far away from most individual surface emission sources and thus represents urban boundary layer conditions (Lefer and Rappengluck, 2010).

3.2. Measurements

The instruments used to measure HOx, GTHOS (the Penn State Ground Based Tropospheric Hydrogen Oxides Sensor), is described in detail in Falloon et al. (2004) and Mao et al. (2010). Only a brief description is presented here. Air is pulled through a pin hole into a low-pressure chamber in which OH is detected by laser-induced fluorescence (LIF). OH is both excited and detected with the $A^2\Sigma$ ($'v=0$) $\rightarrow X^2\Pi$ ($'v=0$) transition near 308 nm. HO2 is first reacted with reagent NO to form OH and is then detected with LIF. OH and HO2 are detected simultaneously into two low-pressure detection cells.

GTHOS is calibrated by producing known amounts of OH and HO2 by photolyzing water vapor in high-purity air. The detection limits for OH and HO2 are about 0.01 parts per trillion by volume (pptv) and 0.1 pptv, respectively, with a 2σ confidence level and 1-min integration time. Absolute uncertainty at the 2σ confidence level was estimated to be ±32% (Falloon et al., 2004).

Meteorological parameters, photolysis rates, gas-phase species were also measured simultaneously. Individual measurements were described in Lefer and Rappengluck (2010), Lefer et al. (in this issue), Leuchner and Rappengluck (2010), Luke et al. (2010) and Stutz et al. (2010). A brief summary of the measurements of model constraints is listed in Table 3. The good agreement between measured and calculated OH reactivity during TRAMP campaign (Mao et al., 2010) indicates that important OH reactors were all measured and included in the models.

3.3. The zero-dimensional box model

Five photochemical mechanisms (RACM, CB05, LaRC, SAPRC-99, SAPRC-07, and MCMv3.1) were applied in a zero-dimensional box model to calculate the concentrations of HOx radicals. In order to assure that the differences of gas-phase chemical mechanisms are meaningful, several factors were standardized. Rate coefficients of reactions for all mechanisms were updated by the most recent data evaluation by Jet Propulsion Laboratory (JPL) (Sander et al., 2006) if applicable. Additional to gas-phase reactions, dry deposition rates were assigned for PAN and its analogues (0.2 cm s$^{-1}$) from Derwent (1996), for organic nitrates (1.1 cm s$^{-1}$), H2O2 (1.1 cm s$^{-1}$), CH3OOH and its analogues (0.55 cm s$^{-1}$), HCHO (0.33 cm s$^{-1}$) from Brasseur et al. (1998), for other organic aldehydes (0.11 cm s$^{-1}$, assumed about 1/3 of HCHO’s rate, based on Zhang et al., 2002). These rates were applied over the depth of the mixing layer (assumed 300 m at night and 1300 m for daytime, similar to Emmerson et al. (2007)). Moreover, a full set of photolysis rates were constrained in each model. The photolysis frequencies of clear sky condition were converted from the Madronich Tropospheric Ultraviolet and Visible (TUV) model (http://www.acd.ucar.edu/TUV) or calculated based on the solar zenith angle (SZA) equations in Jenkin et al. (1997) and then scaled by measurement of J$\text{NO}_2$.

Concentrations of OVOCs (except HCHO) were only available for acetaldehyde, acetone/propanal mixture, and methyl vinyl ketone (MVK)/methylacrolein (MACR) mixture for about 20 days. A constant ratio of MVK/MACR (1.5 by volume ratio) was assumed based on
Stroud et al. (2001). Median diurnal variations were used to fill the data gaps so that the modeling can be conducted for the whole campaign period. In addition, OVOCs measured by DNPH (2,4-dinitrophenylhydrazine) method at a nearby monitoring site (29° 44′ 01″ N, 95° 15′ 27″ W, 9525 Clinton Dr., 12 km east of downtown Houston) of Texas Commission on Environmental Quality (TCEQ) was used to supplement and estimate the OVOC concentrations during this campaign:

(1) A good correlation between propanal and HCHO ($R = 0.85$) was found at this site based on the measurements from August to September 2006 with a linear fit of $\frac{[\text{propanal}]}{[\text{HCHO}]} = 0.034 \times [\text{HCHO}] + 0.14$. This correlation is used to estimate the concentration of propanal based on the HCHO observed at Moody Tower.

(2) The concentration of acetone was estimated based on the concentration of the acetone/propanal mixture subtracted by the propenal concentration estimated in (1).

(3) Averaged concentrations of three carbonyl species measured at this site in August and September 2006 (0.19 ppbv of butyraldehyde, 0.32 ppbv of crotonaldehyde, and 0.13 ppbv of benzaldehyde) were assumed for these higher aldehydes.

The data of meteorological parameters, inorganic model constraints (NO, NO$_2$, O$_3$, and CO, SO$_2$), and photolysis rates were averaged to 10 min to be constrained in the model. Constant mixing ratios were assumed for CH$_4$ (1.896 ppmv) and H$_2$ (500 pptv).

### 4. Results

#### 4.1. Model: measurement comparisons

#### 4.1.1. OH

OH was measured from 11 August to 27 September 2006. Average daytime (06:00–18:00 CST) and nighttime (18:00–06:00 CST) mixing ratios were $0.33 \pm 0.23$ pptv ($7.9 \times 10^{5}$ cm$^{-3}$) and $0.087 \pm 0.066$ pptv ($2.1 \times 10^{5}$ cm$^{-3}$), respectively. For most days, the measured OH is generally greater than the modeled OH for all mechanisms, especially during the afternoon (e.g., on 2 Sep, Fig. 1), although there are several days the behavior of daytime OH is well captured by some models, e.g., $[\text{OH}]_{\text{mod}} = [\text{OH}]_{\text{obs}} \times 0.98$ ($R^2 = 0.82$) is found by the LaRC model on 26 Sep (Fig. 1). The diurnal cycles of the simulations for each mechanism (Fig. 2a) behave similarly. For daytime, RACM, CB05 and LaRC models have very similar diurnal cycles with higher calculated OH. SAPRC-99 and SAPRC-07 models behave similarly with lower OH. SAPRC-07 model produces about 20% more daytime OH than SAPRC-99 model. The model result of MCMv3.1 falls in the middle and is similar to RACM, CB05 and LaRC in the morning and to SAPRC-99 in the afternoon. The largest discrepancy between model and measurement occurs starting about noon and lasts the whole afternoon (11:30–17:30 CST). For all mechanisms, modeled OH is significantly less than measured OH with the average modeled-to-observed ratios of 0.69 (CB05 and RACM), 0.67 (LaRC), 0.65 (SAPRC-07), 0.59 (MCMv3.1), and 0.53 (SAPRC-99). Modeled OH only correlated with the measurement at morning rush hour ($R^2 = 0.48–0.62$ when linear fits were constrained to the origin of the coordinates) and during late afternoon ($R^2 = 0.54–0.66$). The slopes of the
linear regression vary from 0.81 (SAPRC-99) to 1.34 (RACM) for morning rush hour but drop to the range of 0.51 (SAPRC-99) to 0.69 (CB05) in late afternoon. Nighttime OH simulations show poor correlation with observations ($R^2$'s are <0.19) and very low average modeled-to-observed ratios of 0.26 (SAPRC-07), 0.22 (RACM), 0.18 (CB05), 0.15 (SAPRC-99), 0.11 (MCMv3.1), and 0.06 (LaRC). This result is similar to that of other field studies that used GTHOS for OH measurements. Statistically, significant difference was observed between measured and modeled OH by all mechanisms through $t$-test at 1$\sigma$ confidence level even considering the model uncertainties (Table 4) and measurement uncertainties.

4.1.2. HO2

HO2 was measured from 13 August to 27 September 2006. Average daytime and nighttime concentrations were 22 ± 18 pptv and 11 ± 7.8 pptv, respectively. The HO2 calculations by each mechanism also show similar daily variation (e.g., on 29 Aug and 2 Sep, Fig. 1) but with generally lower HO2 values. For all mechanisms, the modeled HO2 was less than the measured HO2, especially during the afternoon. The median diurnal cycle of HO2 (Fig. 2b) shows the diurnal peak of 48 pptv at 13:30 CST, 1 h later than the OH peak time. This behavior is consistent with previous measurements during MCMA (Shirley et al., 2006). The modeled HO2 (Fig. 2b) also shows similar behavior but with lower predicted concentrations for all mechanisms. Better than the correlations of OH, the correlation of observed and predicted HO2 was good for daytime ($R^2 > 0.69$). Good agreement was found in the morning for the models with most mechanisms, except for SAPRC-99 (slope = 0.67), but especially for CB05 (slope = 0.86). The underestimates were also significant during the afternoon with lower model-to-measured ratios of 0.71 (SAPRC-07), 0.68 (CB05), 0.62 (MCMv3.1), 0.61 (LaRC), 0.60 (RACM), and 0.54 (SAPRC-99). The models with the mechanisms that produce lower OH tend to produce lower HO2 except that the HO2 production of SAPRC-07 model is greatly enhanced although its OH production remains relatively low. At night, the model with most mechanisms produces only 60–70% of the measured HO2, although LaRC model is only 20% of the measured value. Similar to the comparison between measured and modeled OH, the $t$-test at 1$\sigma$ confidence level indicates that the difference between measured and modeled HO2 by all mechanisms are statistically significant.

4.1.3. HO2/OH ratio

The ratio of HO2 to OH has been examined in previous studies (e.g., Stevens et al., 1997; Ren et al., 2003a; Emmerson et al., 2005; Shirley et al., 2006) and used as an indicator of the cycling of OH and HO2. During the TRAMP-2006 Campaign, the typical ratio was 30–80 with median value of 66. This ratio was observed to decrease with increasing NO concentration (Fig. 3) as expected due to the OH production from the reaction of NO with HO2. However, all models with different mechanisms calculate a much steeper slope of HO2/OH ratio vs. NO than is measured (Fig. 3). This difference is consistent with other field studies, including SOS (Martinez et al., 2003), PMTACS-NY2001 (Ren et al., 2003b), and PUMA (Emmerson et al., 2005). Good agreement between the modeled and measured ratios occurs when NO was about 1 ppbv. The difference among mechanisms is not obvious because modeled OH and HO2 are both less than measured OH and HO2. One exception is SAPRC-07 model, which yields a higher ratio because modeled HO2 is greater than the measured HO2 and the modeled OH is less than the measured OH.

4.2. HOx budget

To identify the mechanism differences in simulating the production and loss processes, the average contributions of major reactions for initiation, propagation, and termination of OH and HO2 radicals are calculated for three time periods: morning rush hour (06:00–09:00 CST), daytime (09:00–18:00 CST), and nighttime (18:00–06:00 CST) (Fig. 4).

![Fig. 1. Model-measurement comparison for OH (2 and 26 September) and HO2 (29 August and 2 September). The OH mixing ratio of 0.6 pptv is equivalent to an OH concentration of about $1.4 \times 10^7$ cm$^{-3}$.

Fig. 1. Model-measurement comparison for OH (2 and 26 September) and HO2 (29 August and 2 September). The OH mixing ratio of 0.6 pptv is equivalent to an OH concentration of about $1.4 \times 10^7$ cm$^{-3}$.
The differences between the OH and HO₂ that was measured and that was modeled with the different mechanisms were examined by two tests. The first test examined differences among the model runs with the different mechanisms as a function of some environmental parameters. The second test examined the
possibility that an unknown HO$_x$ source was responsible for the measured HO$_x$ being greater than the modeled HO$_x$. Differences in the model calculations of HO$_x$ should be due to the treatment of organic chemistry. Examining the sensitivity of the model differences to environmental conditions should provide information for understanding why the different chemical mechanisms perform differently. However, the mechanism sensitivity was not easily found for any one single model constraint because some important constraints, such as NO$_x$, tend to correlate to others, such as VOCs.

One approach is to examine the model sensitivity to clean air versus polluted air. Daily maximum concentration of PAN and ozones

\[
\begin{align*}
\text{O}(1D)+\text{H}_2\text{O} & \quad 56, 56, 56, 56, 56 \\
\text{O}+\text{alkenes} & \quad 2, 2, 2, 2, 2 \\
\text{HONO}+hv & \quad 1, 1, 1, 1, 1 \\
\text{Other sources} & \quad 0, 0, 0, 0, 0 \\
\text{Total:} & \quad 107, 107, 107, 107, 107 \\
\text{RO}_2+\text{NO} & \quad 701, 401, 718, 636, 835 \\
\text{O VOC}+hv & \quad 73, 37, 65, 69 \\
\text{O}+\text{alkenes} & \quad 6, 8, 1, 0, 4 \\
\text{Other} & \quad 17, 20, 26, 10, 2 \\
\text{Total:} & \quad 812,502,782,711,910 \\
\text{OH} & \quad 37, 3, 1, 4, 8 \\
\text{HO} & \quad 53, 1, 1, 1, 1 \\
\text{Other sources} & \quad 5, 0, 0, 1, 1 \\
\text{Total:} & \quad 7, 3, 1, 4, 8 \\
\end{align*}
\]
that the concentrations of NO
13, 20, 25, 26 Sep. Daily averages of ancillary measurements show
Aug, and 17, 21, 22 Sep; 'polluted' on 20, 21, 29–31 Aug, and 1, 4, 6,
available. Conditions were classified as follows: 'clean' on 27, 28
the 16 days for which model-measurement comparisons were
relative clean or polluted conditions. The comparison was done for
RO2 determine the loss rate of OH and HO2. Thus, the amounts of
each 1 h bin, units in ppbv h
and its diurnal variation (lines connected markers representing the median value for
each 1 h bin, units in ppbv h
and HO2 through the reaction \( \text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M} \), which
is represented the same in all the mechanisms. Thus, the details of
the organic chemistry are likely to be less important. In clean
conditions, however, the reactions of HO2 with RO2, and RO2 with
RO2 and their reaction rate coefficients with HO2 and each other are
important in determining the OH and HO2 amounts.

Including an additional \( \text{HO}_2 \) source should improve the agreement
between the modeled and measured \( \text{HO}_2 \), and provide an
estimate of the magnitude of possible missing sources. Because the
model-measurement differences varied both day by day and during
the day, the \( \text{HO}_2 \) for one typical day, 2 September, was chosen for
analysis, as shown in Fig. 1. The model was run with fifteen different
values of an additional \( \text{OH} \) source using each mechanism. Model
runs with different values of an additional \( \text{OH} \) source for all
mechanisms provide an idea of the magnitude of the improvement
in the model/measurement comparison for the time periods when
the measured \( \text{HO}_2 \) exceeded the modeled \( \text{HO}_2 \) (Fig. 6). An additional
\( \text{OH} \) source of \( 1–2 \times 10^7 \text{ cm}^{-3} \text{ s}^{-1} \) brings modeled and measured
\( \text{HO}_2 \) into better agreement. A \( \text{HO}_2 \) source of this size is equal to or
greater than the known \( \text{HO}_2 \) sources (please see Fig. 4). In addition,
different values of additional source are required for \( \text{OH} \) and \( \text{HO}_2 \).
Thus, a missing \( \text{HO}_2 \) source does not resolve the model-measurement
discrepancy.

5. Conclusions

Prior to this study, it was not known how \( \text{OH} \) and \( \text{HO}_2 \) calculated
by a model using different mechanisms would compare to \( \text{OH} \) and
\( \text{HO}_2 \) measurements in a polluted urban environment, a situation for
which the chemical mechanisms were developed. The result that
the modeled \( \text{OH} \) and \( \text{HO}_2 \) are generally less than the measured \( \text{OH} \)
and \( \text{HO}_2 \) despite the mechanism used in the model is statistically
significant. The possible reasons for this result include the
following: errors in the measured precursor species or the \( \text{HO}_2 \)
measurements themselves; the existence of unmeasured atmos-
pheric constituents that influence \( \text{HO}_2 \); or errors in the model or in

Fig. 5. Calculated ozone instantaneous production (small markers, units in ppbv h
and its diurnal variation (lines connected markers representing the median value for
each 1 h bin, units in ppbv h

Fig. 6. The mean modeled-to-observed ratio of \( \text{OH} \) (black) and \( \text{HO}_2 \) (grey) by the
models with RACM (up triangles), CB05 (down triangles), LaRC (circles), SAPRC-99
(squares), SAPRC-07 (left triangles), and MCMV3.1 (diamonds) as a function of addi-
tional \( \text{HO}_2 \) source (in the form of \( \text{OH} \) source) on Sep 2, 2006.
the chemistry that is common to all mechanisms. At present, it is not possible for us to distinguish among these possibilities. These discrepancies between measured and modeled HO2 are evident in the diurnal profiles, but cannot be resolved by the addition of an unknown HO2 source to the model.

The discrepancy between the measured and modeled behavior of the HO2/NO ratio as a function of NO is independent of the different mechanisms. The observation of this effect by several different research groups using different measurement techniques suggests it is not an artifact of a measurement technique but is instead unknown chemistry. Because the HO2 behavior at high NO has direct implications for the calculated ozone production rates, this issue needs to be resolved.

At the same time, the model runs with different mechanisms produce a range of HO2 values, some of which agree better with the measurements than the others, indicating that the differences are systematic and not random due to noise in the measurements of chemical species used to constrain the models. Thus, the differences between HO2 produced by the models with different mechanisms are likely the result of differences in the mechanisms themselves. It is not possible to state that any mechanism is better than another, but only that one agrees better with the measured HO2 than another during the conditions of the TRAMP-2006 study. The OH from the different model mechanisms follows the approximate order of CB05 ≥ RACM ≥ LaRC ≥ SAPRC-07 > MCMv3.1 ≥ SAPRC-99 and the HO2 follows the order SAPRC-07 ≥ CB05 > RACM ~ MCMv3.1 ≥ LaRC > SAPRC-99.

This comparison of OH and HO2 calculated by a model with several different mechanisms and measured directly applies only to the Houston site in summer 2006 and cannot a priori be applied to other environments. However, fairly complete data sets exist from numerous previous studies and even more field studies are being conducted or planned. By applying this same approach to all of these other studies, it may be possible to find patterns that will lead to a resolution of the HO2 discrepancies among the model with different mechanisms and the measurements.

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References


