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Appendix 2

## Photochemical Modeling

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## 1. Introduction

This Section describes the air quality simulations performed in support of the analysis of the potential impact on air quality caused by the phase-out of gasoline containing methyl tert-butyl ether and replacement by ethanol-based or non-oxygenated gasoline fuels. A brief description of the air quality model is presented together with the photochemical mechanism chosen. A description of the input files necessary to run each of the scenarios considered is presented, together with a summary of the results. A discussion of model performance is included.

## 2. Flexible Chemical Mechanism Version of the Urban Airshed Model

Photochemical air quality models are a primary tool for understanding the complex interrelationships among pollutants emitted and transported in a given area. Photochemical air quality models are computer models that represent the state-of-the-science understanding of how ozone and other secondary pollutants are formed and their relationship to the primary pollutants emitted by different source categories. They have been used to in assess the effectiveness of air pollution control strategies to achieve the air quality standards. The Flexible Chemical Mechanism Version of the Urban Airshed Model (UAMFCM) is an air quality model that has been used by CARB since 1995.

The UAM-FCM is an adaptation of the Urban Airshed Model (UAM) to provide flexibility in incorporating different Carbon Bond IV or SAPRC-type photochemical mechanisms into the UAM (Kumar et al., 1995). The UAM has been the primary air quality regulatory model for ozone control strategy development. However, it has a hard-coded Carbon Bond IV photochemical mechanism, together with a unique algorithm to solve the set of differential equations representing the chemical transformations that is accurate, robust and fast. The algorithm was designed to take maximum advantage of the Carbon Bond IV features. The treatment of photolytic reactions in the UAM is also unique. All values for the photolytic reaction rates are hard-coded, and depend on the value of the $\mathrm{NO}_{2}$ photolytic reaction rate. The hard-coded approach in the UAM makes it very difficult to study recent and more updated mechanisms, such as those developed by Dr. W.P.L. Carter at the University of Riverside. Any change or update in the Carbon Bond IV mechanism, photolytic rates, or the implementation of a different chemical mechanism requires changes to the UAM code that need to be done by hand. The UAM-FCM, however, can read a text file version of a mechanism and create program subroutines that are readily integrated with the airshed model (Kumar et al., 1995). Below we briefly describe the main aspects of the UAM and the UAM-FCM.

### 2.1 Urban Airshed Model

Morris and Meyers (1990) provide a detailed description of the UAM. Only a brief summary is provided here. The UAM is a gridded 3-dimensional air quality model that can simulate the atmospheric physical and chemical processes that cause air pollution. The basic equation is:

$$
\begin{align*}
\frac{\partial C_{i}}{\partial t}+\frac{\partial\left(u C_{i}\right)}{\partial x}+\frac{\partial\left(v C_{i}\right)}{\partial y}+\frac{\partial\left(w C_{i}\right)}{\partial z}= & \frac{\partial}{\partial x}\left(K_{H} \frac{\partial C_{i}}{\partial x}\right)+\frac{\partial}{\partial y}\left(K_{H} \frac{\partial C_{i}}{\partial y}\right)+\frac{\partial}{\partial z}\left(K_{V} \frac{\partial C_{i}}{\partial z}\right) \\
& +R_{i}+S_{i}+L_{i} \tag{1}
\end{align*}
$$

The first term on the left of Eqn.(1) represents the time-varying concentration of pollutant i, and the last three terms on the left side of Eqn.(1) represent advection. The first three terms on the right side of Eqn.(1) represent turbulent diffusion, $\mathrm{R}_{\mathrm{i}}$ are chemical processes, $\mathrm{S}_{\mathrm{i}}$ are emission processes, and $\mathrm{L}_{\mathrm{i}}$ correspond to pollutant sinks. The other terms in Eqn.(1) are

$$
\begin{array}{ll}
\mathrm{u}, \mathrm{v}, \mathrm{w} & =\text { horizontal and vertical speed wind components } \\
\mathrm{K}_{\mathrm{H}}, \mathrm{~K}_{\mathrm{V}} & =\text { horizontal and vertical turbulent coefficients }
\end{array}
$$

Eqn.(1) is solved for each pollutant and grid cell at each time step in the simulation. As designed, the UAM has hard-coded the Carbon Bond IV (CB4) chemical mechanism. The CB4 version implemented in the UAM was last updated in 1993 by adding radical-radical interactions. As stated before, the hard-coded approach to the atmospheric chemical mechanism used in the UAM prevents the implementation of newer and more up-to-date chemical mechanisms.

### 2.2 UAM-FCM

The UAM-FCM was developed under contract for CARB (Kumar et al., 1995). The UAM-FCM has a software package (the FCM) that reads a text file describing the photochemical mechanism, and creates a set of mechanism-specific programs that are then integrated into the UAM. The FCM allows the user to incorporate reaction specific photolysis rates, by providing a file for each photolytic reaction, with data on cross section and quantum yield for each wavelength of interest. The UAM-FCM has a generalized technique to solve the set of differential equations that is not mechanism specific, but is accurate and robust. The current version of the UAM-FCM can handle up to 220 chemical reactions (including up to 20 photolytic reactions), and up to 140 chemical species.

## 3. SAPRC97

Carter (Carter et al., 1993 and 1997) developed the atmospheric chemical mechanism designated as SAPRC97 (version D), which is readily processed by the UAM-FCM software. To save computing time in solving the set of differential equations that represent the reaction mechanism, only a small number of hydrocarbon species are treated explicitly in this mechanism. In SAPRC, hydrocarbons are grouped together using the lumped-molecule approach. In this approach the reactions of many alkanes, alkenes, and aromatic species that are present in the emissions inventory are represented by lumped reaction mechanisms (Carter, 1990). The computer software calculates the kinetic rates and product yield parameters for the lumped species that best represent the unique hydrocarbon mixture in the emissions inventory (Carter, 1988, 1990). For this study the one-product mechanism is used to represent the reactions of isoprene (Carter, 1996). In addition, explicit reaction mechanisms (as opposed to a lumped representation) for several compounds of interest (such as benzene, 1,3 butadiene, ethanol, and methyl-tertbutyl ether) were added to the original version of the SAPRC97. It was also desired to distinguish between acetaldehyde and formaldehyde formed as by-products of photochemical reactions (secondary), from those emitted directly from sources (primary). The explicit reactions for the additional species were obtained from Dr. Carter's ftp site (ftp://cert.ucr.edu/pub/carter/mech/saprc97.

A complete listing of this photochemical mechanism is provided in Attachment A The list of hydrocarbon species that are treated explicitly is given in Table 1. In addition to the species listed in Table 1, the photochemical mechanism includes a large number of species that are generated by the oxidation of hydrocarbons, as well as a set of chemical reactions that represents the inorganic reactions that take place in air. The mechanism used in our simulations has a total of 99 species and 204 reactions, of which 20 are photolytic. Of the 99 species, 29 are treated as steady state, 4 species are held constant, and hourly average concentrations are generated by the UAM-FCM for the other 66 species.

Table 1
List of Hydrocarbon Species Treated explicitly in SAPRC97

| Name | Symbol |
| :--- | :--- |
| Formaldehyde (secondary) | HCHO |
| Formaldehyde (primary) | FORM |
| Acetaldehyde (secondary) | CCHO |
| Acetaldehyde (primary) | ALD |
| Acetone | ACET |
| Methyl ethyl ketone | MEK |
| Peroxy acetyl nitrate | PAN |
| Peroxy propionyl nitrate | PPN |
| Methane | EH4 |
| Ethene | ISOP |
| Isoprene | C6H6 |
| Benzene | BUTD |
| 1,3-butadiene | PDCB |
| p-dichlorobenzene | PERC |
| Perchloroethylene | DICM |
| Dichloromethylene | ETOH |
| Ethanol | MTBE |
| Methyl tert-butyl ether | GLY |
| Glyoxal | MGLY |
| Methyl Glyoxal | BALD |
| Benzaldehyde | CRES |
| Cresols | PHEN |
| Phenols |  |

## 4. Computer Used

The executable UAM-FCM files were prepared and compiled according to the recommended procedure (Kumar et al., 1995). The emissions inventory corresponding to each year and case under study were used to calculate the reaction rates and product yields of the lumped species. All simulations were run on a Unix workstation. The time to run a 24 -hr episode simulation was about 2 hours and twenty minutes.

## 5. Episode and Domain

The UAM-FCM was applied to a three-day summer ozone episode in the South Coast, the August 26-28, 1987 SCAQS episode. The SCAQS domain has been gridded into 65 X $40 \times 5$ cells. Each horizontal square cell is $5 \times 5 \mathrm{~km}^{2}$, with varying vertical height. The origin of the domain is at $(275,3670)$ in UTM coordinates (Zone 11). The domain is shown in Figure 1. It includes the counties of Los Angeles, Orange, and Kern, and portions of Riverside, San Diego, San Bernardino, and Ventura counties.


Figure 1. Modeling Domain

## 6. Basic Input files

The UAM-FCM requires 13 input files that provide information on the initial and boundary conditions of the domain, temperature, wind direction, wind speed, terrain, photolysis rates, reaction rate constants and product yields, and emissions from area and point sources. Mobile sources and biogenic emissions are included in the area source file. The files used in our simulations, (except for the initial and boundary conditions, and area and point source emissions) were prepared by the South Coast Air Quality Management District for the 1994 State Implementation Plan (SCAQMD, 1994). The same diffusion break, region top, metscalars, terrain, temperature and meteorological input files were used in all simulations, since these characterize the meteorological conditions for the episode and terrain. Table 2 provides a description of these files. Other files, such as initial and boundary conditions, point sources and area emissions were created for each specific simulation.

Table 2
List of the Meteorological and Terrain files For SCAQS August 26-28, 1987 Episode

| Input File identification | Description |
| :--- | :--- |
|  |  |
| ms238d11.b, ms239d11.b, ms240d11.b | Metscalar file |
| sim238bl, sim239bl, sim240bl | Control file |
| df238d11.b | Diffusion break file |
| tm238d11.b, tm239d11.b, tm240d11.b | Temperature file |
| rt238d11.b | Region top file |
| tr238d11.b | Terrain file |
| wd238d11.b, wd239d11.b, wd240d11.b | Wind file |

## 7. Region Top and Boundary Conditions

The region top and boundary conditions (together with the point and area sources) are specific to each of the different scenarios considered in this modeling study. The scenarios considered include the years 1997 and 2003 with different types of gasoline. These scenarios are listed in Table 3.

Table 3

## Scenarios Considered for the MTBE Phaseout Study

| Scenario | Description of Motor Vehicle Fuel Used |
| :--- | :--- |
| 1997 | Current MTBE-based Cleaner-Burning Gasoline |
| $2003 /$ mtbe | Year 2003 with MTBE-based Cleaner-Burning Gasoline |
| 2003/et20 | Year 2003 with Ethanol-based fully complying fuel <br> (with oxygen content of 2.0\%) |
| 2003/et35 | Year 2003 with Ethanol-based fully complying fuel <br> (with oxygen content of 3.5\%) |
| 2003/unox | Year 2003 with a non-oxygenated fully complying fuel |
| 2003/et20h | Year 2003 with Ethanol-based fully complying fuel <br> (with oxygen content of 2.0\%). Used headspace factors <br> recommended by Dr. Robert Harley, and the resultant fuel <br> profile was applied to hot soaks and running evaps |
| 2003/et35h | Year 2003 with Ethanol-based fully complying fuel <br> (with oxygen content of 3.5\%). Used headspace factors <br> recommended by Dr. Robert Harley, and the resultant fuel <br> profile was applied to hot soaks and running evaps |

The region top and boundary condition files describe the air quality at the boundaries of the domain under study. These two files specify hourly ambient levels of each of the species in the SAPRC mechanism. For these simulations the region top and boundary conditions were treated as constant for all species throughout the episode. Region top concentrations were essentially the same as those used for the boundary conditions. Table 4 and Table 5 show the pollutant concentrations used for the boundary and region top, respectively.

Table 4
Boundary Baseline Concentration (ppb)

| Species | 1997 | $2003 /$ et20 | $2003 /$ et35 | $2003 / \mathrm{mtbe}$ | $2003 / \mathrm{unox}$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| O3 | 40.0 | 40.0 | 40.0 | 40.0 | 40.0 |
| NO | 0.9095 | 0.8285 | 0.8285 | 0.8285 | 0.8285 |
| NO2 | 1.6832 | 1.4 | 1.4 | 1.4 | 1.4 |
| N2O5 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| HONO | 0.08371 | 0.06913 | 0.06913 | 0.06913 | 0.06913 |
| CO | 200.0 | 200.0 | 200.0 | 200.0 | 200.0 |
| CO2 | 1000.0 | 1000.0 | 1000.0 | 1000.0 | 1000.0 |
| CCHO | 0.5 | 0.53 | 0.53 | 0.53 | 0.53 |
| HCHO | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| RCHO | 0.98 | 0.98 | 0.98 | 0.98 | 0.98 |
| ETHE | 0.829 | 0.7626 | 0.7626 | 0.7626 | 0.7626 |
| CH4 | 1720.0 | 1720.0 | 1720.0 | 1720.0 | 1720.0 |
| ALK1 | 0.49 | 0.49 | 0.49 | 0.49 | 0.49 |
| ALK2 | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 |
| ARO1 | 0.4273 | 0.3962 | 0.3962 | 0.3962 | 0.3962 |
| ARO2 | 0.14507 | 0.13538 | 0.13538 | 0.13538 | 0.13538 |
| OLE1 | 0.7048 | 0.69056 | 0.69056 | 0.69056 | 0.69056 |
| OLE2 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| C6H6 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 |
| NO3 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| HO2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| MTBE | 0.1 | 0.01 | 0.01 | 0.1 | 0.01 |
| ETOH | 0.01 | 0.3 | 0.41 | 0.01 | 0.01 |
| All other <br> species | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |

Table 5 Region Top Concentrations (ppb)

| Species | 1997 | $2003 /$ et20 | $2003 /$ et35 | $2003 / \mathrm{mtbe}$ | $2003 / \mathrm{unox}$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| O3 | 40.0 | 40.0 | 40.0 | 40.0 | 40.0 |
| NO | 0.9095 | 0.8285 | 0.8285 | 0.8285 | 0.8285 |
| NO2 | 1.6832 | 1.4 | 1.4 | 1.4 | 1.4 |
| N2O5 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| HONO | 0.08371 | 0.06913 | 0.06913 | 0.06913 | 0.06913 |
| CO | 200.0 | 200.0 | 200.0 | 200.0 | 200.0 |
| CO2 | 1000.0 | 1000.0 | 1000.0 | 1000.0 | 1000.0 |
| CCHO | 0.5 | 0.53 | 0.53 | 0.53 | 0.53 |
| HCHO | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| RCHO | 0.98 | 0.98 | 0.98 | 0.98 | 0.98 |
| ETHE | 0.829 | 0.7626 | 0.7626 | 0.7626 | 0.7626 |
| CH4 | 1720.0 | 1720.0 | 1720.0 | 1720.0 | 1720.0 |
| ALK1 | 0.49 | 0.49 | 0.49 | 0.49 | 0.49 |
| ALK2 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| ARO1 | 0.4218 | 0.3912 | 0.3912 | 0.3912 | 0.3912 |
| ARO2 | 0.14507 | 0.13538 | 0.13538 | 0.13538 | 0.13538 |
| OLE1 | 0.7048 | 0.69056 | 0.69056 | 0.69056 | 0.69056 |
| OLE2 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| C6H6 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 |
| NO3 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| HO2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| MTBE | 0.1 | 0.01 | 0.01 | 0.1 | 0.01 |
| ETOH | 0.01 | 0.3 | 0.41 | 0.01 | 0.01 |
| All other <br> species | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |

## 8. Initial Conditions

All simulations were started with the same initial conditions given in Table 6. Because of this, only the results of the last simulation day, August 28, are used in the analysis. The results of the last simulation day are insensitive to the initial conditions.

Table 6
Initial Species Concentrations (ppb)

| Species | Concentration |
| :--- | :--- |
| O3 | 70.0 |
| NO | 1.0 |
| NO2 | 2.0 |
| HNO3 | 0.1 |
| HONO | 0.1 |
| CO | 200.0 |
| CO2 | 0.1 |
| H2O2 | 0.1 |
| CCHO | 1.1 |
| HCHO | 5.8 |
| RCHO | 0.98 |
| ETHE | 1.4 |
| CH4 | 1720.0 |
| ALK1 | 0.49 |
| ALK2 | 1.01 |
| ARO1 | 0.7 |
| ARO2 | 0.23 |
| OLE1 | 0.83 |
| OLE2 | 0.23 |
| OLE3 | 0.00 |
| C6H6 | 0.16 |
| All other <br> species | 0.01 |

## 9. Point and Area Sources

Point source emission and area source emission files were prepared for each specific scenario studied. The preparation of each file is discussed elsewhere in this report.

## 10. Sites

Table 7 lists the 20 sites in the South Coast modeling domain used to analyze the results of each different scenario studied. In addition to these sites, the domain peak was also used. Figure 1 shows the site locations in the domain.

Table 7
Sites in the Modeling Domain Used to Study the Impact of Each of the Scenarios Studied.

| Site Name | Id |
| :--- | :--- |
| Anaheim | ANAH |
| Azusa | AZUS |
| Burbank | BURK |
| Los Angeles North Main | CELA |
| Costa Mesa -Mesa Verde Drive | COMV |
| Hawthorne | HAWT |
| La Habra | LABH |
| North Long Beach | LGBH |
| Lynwood | LYNN |
| Pasadena -S. Wilson Avenue | PASA |
| Pico Rivera | PICO |
| Pomona | POMA |
| Reseda | RESE |
| Riverside - Rubidoux | RIVR |
| Riverside -Magnolia | RIVM |
| Santa Clarita -County Fire Station | SCFE |
| San Bernardino -4 ${ }^{\text {th }}$ Street | SNB4 |
| El Toro | TORO |
| Upland | UPLA |
| West Los Angeles -VA Hospital | WSLA |

## 11. Results

As indicated above, only the results of the third day of the episode simulated (August 28) were used in the analysis to avoid dependence on the initial conditions. Table 8 shows the domain peak concentration of the pollutants of interest for each scenario simulated. As shown in Table 8, the domain peak ozone slightly decreases ( $4.0-6.7 \%$ ) from 1997 to 2003 because of reductions in overall emissions. CO shows a more significant decrease (27-35\%). Nitric acid decreases by up to $9.5 \%$. In general the predicted concentrations do not show a large change from 1997 to 2003 for most of the pollutants, except for $\mathrm{NO}, \mathrm{NO} 2, \mathrm{CO}$, ethanol and nitric acid.

Among the year 2003 simulations, the et 35 and et 35 h show the lowest peak ozone concentrations (220.1 and 221.2 ppb respectively), while the Unox case shows slightly higher peak ozone concentration ( 226.6 ppb ). Note also that the CO concentration is higher for the Unox scenario among the year 2003 simulations, and is lowest for the Et35 and Et35h scenarios. The use of oxygenated fuels results in lower CO and hydrocarbon emissions, compared to the non-oxygenated gasoline. Therefore, as shown in Table 9 , it is expected that the simulations using oxygenated gasoline will result in lower predicted ozone and CO concentrations.

Table 8

## Domain Hourly Peak Concentrations

Using Emissions for Each Scenario Considered

|  | Domain Peak (ppb) |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Simulation | O3 | CO | Formaldehyde ${ }^{6}$ | Acetaldehyde ${ }^{6}$ | C6H6 | PAN | PPN | HNO3 |
| 1997 | 235.9 | 3023.6 | 22.7 | 9.2 | 3.4 | 4.4 | 1.4 | 57.7 |
| 2003 |  |  |  |  |  |  |  |  |
| Et20 ${ }^{1}$ | 224.2 | 2189.3 | 22.8 | 8.8 | 2.2 | 4.4 | 1.4 | 52.4 |
| Et35 ${ }^{2}$ | 221.1 | 1968.2 | 22.9 | 8.9 | 2.3 | 4.4 | 1.4 | 52.2 |
| Mtbe ${ }^{3}$ | 222.9 | 2189.1 | 23.1 | 8.7 | 2.2 | 4.2 | 1.4 | 52.3 |
| Unox ${ }^{4}$ | 226.6 | 2262.9 | 22.8 | 8.8 | 2.2 | 4.4 | 1.5 | 52.5 |
| Et20h ${ }^{5}$ | 222.5 | 2189.2 | 22.8 | 8.8 | 1.9 | 4.2 | 1.4 | 52.4 |
| $\mathrm{Et} 35 \mathrm{~h}^{5}$ | 220.1 | 1968.1 | 22.9 | 8.9 | 2.0 | 4.2 | 1.4 | 52.2 |

\(\left.\begin{array}{ll}et 20=ethanol-based fully complying fuel (with oxygen content of 2.0 \% ) <br>
et 35=ethanol-based fully complying fuel (with oxygen content of 3.5 \% ) <br>

mtbe=current MTBE-based cleaner burning gasoline\end{array}\right]\)| unox = non-oxygenated fully complying fuel |
| :--- |
| Harley sensitivity runs (labeled h) differ from et 20 and et 35 in that Harley's headspace calculations |
| derived fuel profile was used for hot soaks and running evaps. |
| formaldehyde and acetaldehyde refer to total concentrations from primary emissions and secondary |
| formation |

Figures 2-6 show hourly ozone, NO, and NO2 for August 26-28, 1987 at Anaheim (ANAH), Burbank (BURK), downtown Los Angeles (CELA), Riverside-Rubidoux (RIVR), and at the domain maximum (GMX). The time plots clearly show that the 1997 and 2003 scenarios have very similar predicted ozone concentrations during the last day of the simulation. There are significant differences in predicted NO2 concentrations between 1997 and 2003, as expected. All 2003 scenarios have the essentially the same predicted NO and NO 2 hourly concentrations.

Figures 7-11 show MTBE, ETOH, and CO time series plots for August 26-28, 1987 at Anaheim, Burbank, downtown Los Angeles, Riverside-Rubidoux, and at the domain peak. The plots are only for the 2003 scenarios (Et20, Et35, Unox, and Mtbe). As expected the 2003/Et35 scenario has highest predicted ethanol concentrations, while the 2003/mtbe is the only scenario with significant MTBE hourly concentrations among all the 2003 scenarios.

Figures 12-16 show time series plots of hourly PAN, PPN, and HNO3 concentrations for August 26-28, 1987 at Anaheim, Burbank, downtown Los Angeles, Riverside-Rubidoux, and at the domain peak. Predicted PAN, PPN, and HNO3 concentrations are all scenarios. Both PAN and PPN show a large peak on the second day of the episode that has significantly decreased by the third day of the episode simulated.

From Figures 2-6, it is clear that although hydrocarbon and NOx emissions decreased from 1997 to 2003, the reduction did not significantly impact the radical flux levels predicted by the photochemical mechanism. This is confirmed by the small impact on the predicted peak ozone concentrations. In addition, the NOx-to-Hydrocarbon ratio may not have significantly changed from 1997 to 2003, which may explain the essentially similar PAN, PPN, and HNO3 predicted concentrations for these years (see figures 12-16).


Figure 2. Time Series for Ozone, NO2, and NO at Anaheim for 1997 and 2003 Scenarios


Figure 3. Time Series for Ozone, NO2, and NO at Burbank for 1997 and 2003 Scenarios


Figure 4. Time Series for Ozone, NO2, and NO at Los Angeles for 1997 and 2003 Scenarios


Figure 5. Time Series for Ozone, NO2, and NO at Riverside for 1997 and 2003 Scenarios


Figure 6. Time Series for Domain Maximum Ozone, NO2, and NO for 1997 and 2003 Scenarios


Figure 7. Time Series for MTBE, ETOH and CO at Anaheim for 2003 Scenarios


Figure 8. Time Series for MTBE, ETOH and CO at Burbank for 2003 Scenarios


Figure 9. Time Series for MTBE, ETOH and CO at Los Angeles for 2003 Scenarios


Figure 10. Time Series for MTBE, ETOH and CO at Riverside for 2003 Scenarios


Figure 11. Time Series for Domain Maximum MTBE, ETOH and CO for 2003 Scenarios


Figure 12. Time Series for PAN, PPN and HNO3 at Anaheim for 1997 and 2003 Scenarios


Figure 13. Time Series for PAN, PPN and HNO3 at Burbank for 1997 and 2003 Scenarios


Figure 14. Time Series for PAN, PPN and HNO3 at Los Angeles for 1997 and 2003 Scenarios


Figure 15. Time Series for PAN, PPN and HNO3 at Riverside for 1997 and 2003 Scenarios


Figure 16. Time Series for PAN, PPN and HNO3 at domain peak for 1997 and 2003 Scenarios

Table 9 shows maximum 24-hour average concentrations in the domain for selected pollutants. As shown, the $24-\mathrm{hr}$ average ozone concentration decreases by less than $4 \%$ from 1997 to 2003 . CO is reduced by up to $28 \%$ for the et 35 and et 35 h scenarios. Similarly, the 24 -hr benzene concentration is reduced by almost $36 \%$ between 1997 and 2003. The $24-$ hr average formaldehyde is reduced by $13 \%$, but the $24-\mathrm{hr}$ average acetaldehyde is unchanged. 24-hr nitric acid concentration is seen to decrease by $12 \%$ from 1997 to 2003, while PPN is essentially unchanged. The impact on 24-hr PAN concentration is also modest, with a decrease of up to $3 \%$ for the 2003/mtbe scenario.

Table 9
Domain 24-hr Average Concentrations For Each Scenario Considered

|  | Domain 24-hr concentration (ppb) |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Simulation | O3 | CO | Formaldehyde ${ }^{6}$ | Acetaldehyde ${ }^{6}$ | C6H6 | PAN | PPN | HNO3 |
| 1997 | 148.0 | 1614 | 11.34 | 6.2 | 1.71 | 2.12 | 0.58 | 36.73 |
| 2003 |  |  |  |  |  |  |  |  |
| Et20 ${ }^{1}$ | 143.5 | 1252 | 9.85 | 6.2 | 1.15 | 2.12 | 0.60 | 32.43 |
| Et35 ${ }^{2}$ | 142.7 | 1149 | 9.88 | 6.2 | 1.18 | 2.11 | 0.57 | 32.30 |
| Mtbe ${ }^{3}$ | 142.9 | 1252 | 9.93 | 6.2 | 1.17 | 2.05 | 0.58 | 32.44 |
| Unox ${ }^{4}$ | 143.9 | 1286 | 9.85 | 6.2 | 1.15 | 2.13 | 0.61 | 32.48 |
| Et20h ${ }^{5}$ | 143.1 | 1252 | 9.76 | 6.2 | 1.10 | 2.06 | 0.60 | 32.36 |
| $\mathrm{Et} 35{ }^{5}$ | 142.4 | 1149 | 9.79 | 6.2 | 1.10 | 2.06 | 0.57 | 32.24 |

1 et20 = ethanol-based fully complying fuel (with oxygen content of 2.0\%)
et35 $=$ ethanol-based fully complying fuel (with oxygen content of 3.5\%)
mtbe $=$ current MTBE-based cleaner burning gasoline
unox = non-oxygenated fully complying fuel
5 Harley sensitivity runs (labeled h) differ from et20 and et35 in that Harley's headspace calculations derived fuel profile was used for hot soaks and running evaps.
6 formaldehyde and acetaldehyde refer to total concentrations from primary emissions and secondary formation

## 12. Sensitivity Simulations

Sensitivity analysis is an evaluation of the model response to variations in one or more of the model inputs. A large increase in hydrocarbon emissions will be expected to change the NOx-tohydrocarbon ratio and significantly impact the radical flux. The sensitivity simulations considered for this study are listed in Table 10. To test the sensitivity of the model to a large increase in emissions, the motor vehicle hydrocarbon and CO emissions were increased by a factor of 3 . However, for the et 35 hCO scenario the hydrocarbon emissions were increased by a factor of 3, and the CO emissions were increased to the same levels as the Unox scenario. The predicted domain peak concentrations from the sensitivity simulations are given in Table 11.

Table 10 Sensitivity Scenarios

| Scenario | Description |
| :--- | :--- |
| Sens/1997 | Increased motor vehicle CO and ROG by factor of 3 |
| Sens/2003/Et35h | Increased motor vehicle CO and ROG by factor of 3 for the <br> Et35h fuel |
| Sens/2003/Et35hCO | Increased motor vehicle ROG by factor of 3 for the Et35h <br> fuel, but CO levels same as for 2003/unox scenario |

Table 11
Domain Hourly Peak Concentrations
Using Emissions for Each Scenario Considered

| Sensitivity <br> Simulation | Domain Peak (ppb) |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | O3 | CO | Formaldehyde ${ }^{2}$ | Acetaldehyde ${ }^{2}$ | C6H6 | PAN | PPN | HNO3 |
| Sens/1997 ${ }^{1}$ | 422.1 | 7447.6 | 37.3 | 19.2 | 9.1 | 18.0 | 5.5 | 70.0 |
| Sens/2003 |  |  |  |  |  |  |  |  |
| Et $35 h^{1}$ | 318.2 | 4347.7 | 25.4 | 14.6 | 4.7 | 11.7 | 3.5 | 54.1 |
| Unox ${ }^{1}$ | 340.8 | 5193.1 | 25.7 | 14.0 | 5.4 | 12.1 | 3.7 | 54.4 |
| Et35hCO ${ }^{1}$ | 325.5 | 5292.6 | 25.4 | 14.6 | 4.7 | 11.6 | 3.4 | 54.3 |

1. Sensitivity simulations have Motor Vehicle ROG*3 and CO*3 (except for Et 35 hCO which has same CO emissions as Unox)
2. formaldehyde and acetaldehyde refer to total concentrations from primary emissions and secondary formation

Comparing Table 9 and Table 11, it is clear that predicted species concentrations increased significantly when the motor vehicle hydrocarbon and CO emissions were increased by a factor of 3 . As expected, the 1997 scenario shows a larger increase in peak concentrations than the 2003 scenarios. This effect is due to the larger motor vehicle emissions in 1997. For example, peak ozone increases by a factor of 1.79 in 1997, whereas it only increases by a factor of 1.44 in 2003/et 35 h . Acetaldehyde increases by a factor of almost 2 in 1997 compared to 1.64 in 2003/et 35 h.

The Sens/2003/Et35hCO was created by increasing the motor vehicle hydrocarbon emissions by a factor of 3, but keeping the CO emissions at the Sens/2003/Unox levels. This is equivalent to an increase in CO and hydrocarbon emissions in theSens/2003/Et35h (this is because the oxygenated fuels produce less CO emissions than non-oxygenated fuels). From Table 11, the predicted CO peak concentration in the 2003/Unox and 2003/Et35hCO are similar, as expected. However, the increase in CO emissions causes the predicted ozone to be slightly higher in the Et 35 hCO scenario compared to the Et 35 h simulation. The Et 25 hCO simulation shows that the difference in CO emissions between the Et 35 h and the Unox scenarios account for about $1 / 3$ of the peak ozone increase.

## 13. Model Performance

A performance evaluation is the process of establishing that the air quality model is adequately reproducing the chemical and physical processes that generate smog. One aspect of model performance includes the sensitivity simulations described in the previous section. In this section we test the model's
ability to reproduce measured air quality data. For this purpose, an area and point emission inventory was prepared for a 1987 baseline simulation. Differences and ratios of observed and simulated peak concentrations were calculated for each day of the August 26-28, 1987 episode in the SCAQS domain.

Several statistical measures were used (ARB, 1992), including the Mean Absolute Gross Error (MAGE)

$$
M A G E=\sum \frac{\left|C_{s}-C_{o}\right|}{N}
$$

Where N is the number of observations, $\mathrm{C}_{\mathrm{s}}$ is the simulated concentration and $\mathrm{C}_{\mathrm{o}}$ is the observed concentration; Mean Absolute Normalized Gross Error (MANGE)

$$
M A N G E=\frac{1}{N} \sum \frac{\left|C_{s}-C_{o}\right|}{C_{o}}
$$

Mean Bias (MBIAS):

$$
M B I A S=\sum \frac{C_{s}-C_{o}}{N} ;
$$

Normalized Mean Bias (NBIAS):

$$
\text { NBIAS }=\frac{1}{N} \sum \frac{C_{s}-C_{o}}{C_{o}}
$$

and the Unpaired Peak Estimation Accuracy (UPEA)

$$
U P E A=\frac{C_{s}^{\max }-C_{o}^{\max }}{C_{o}^{\max }}
$$

Where $\mathrm{C}_{\mathrm{s}}{ }^{\text {max }}$ is the maximum estimated 1-hr concentration at any site in the domain, and $\mathrm{C}_{\mathrm{o}}{ }^{\text {max }}$ is the maximum observed 1-hr concentration at any site in the domain.

The average statistics for all sites in the domain are given in Table 12 August 28, 1987. The UAM-FCM SAPRC97 tends to overpredict peak ozone only $4 \%$. Peak NO2 is within 10 percent of observed domain peak, but the model significantly under predicts peak CO and NO.

Table 12
UAM-FCM with SAPRC97
Model Performance Evaluation (SCAQS Domain)

|  | O3 | CO | NO | NO2 |
| :--- | :--- | :--- | :--- | :--- |
| Peak Ratio | 1.04 | 0.79 | 0.44 | 1.07 |
| MBIAS (pphm) | 2.8 | -14.2 | -4.9 | -1.4 |
| MAGE (pphm) | 3.8 | 77.1 | 5.1 | 3.1 |
| NBIAS | 0.32 | 0.07 | 0.71 | -0.14 |
| MANGE | 0.38 | 0.48 | 0.76 | 0.60 |
| UPEA | 0.29 | -0.08 | 0.09 | 0.37 |

Although the UAM has been widely applied to a number of episodes (see for example, Morris and Meyers, 1990), the UAM-FCM, on the other hand, has limited application since its development in 1995. Therefore it was considered appropriate to examine the model performance of the UAM-FCM when using a different chemical mechanism, such as the Carbon-Bond IV(CB-IV).

The CB-IV chemical mechanism uses the lumped structure approach to represent the atmospheric oxidation of hydrocarbons in ambient air (Gery et al., 1989). Carbon-bond surrogates are used to represent the chemistry of the three most common type of carbon bonds (single: PAR, double: OLE, and the CHOgroup: ALD2), and two molecular surrogates represent the chemistry of aromatic compounds (monoalkylbenzenes: TOL -based on toluene, di-and trialkylbenzenes: XYL -based on m-xylene). Ethene, isoprene, ethanol, methanol, formaldehyde, methylglioxal, glioxal, PAN are treated explicitly.

Carbon-Bond IV (version 6.21) was implemented into the UAM-FCM. We prepared area and point source emissions files, together with initial and boundary conditions for the August 26-28,1987 episode using speciation appropriate for the CB-IV mechanism. Table 13 summarizes the performance of the UAM-FCM with CBIV. Compared to the performance of the SAPRC97 mechanism in Tables 13, CBIV tends to under predict peak ozone concentration $11 \%$ on the last day of the episode. However, both SAPRC97 and CB-IV have similar average performance for CO, NO and NO2. Overall, the UAM-FCM has similar model performance with either SAPRC97 or CB-IV. Figures 17 to 21 show a comparison of ozone, NO and NO2, as predicted by SAPRC97 and CB-IV, for Anaheim, Burbank, Downtown Los Angeles, Riverside and for the maximum concentration in the domain.

Table 13
UAM-FCM with CB4
Model Performance Evaluation
(SCAQS Domain)

|  | O3 | CO | NO | NO2 |
| :--- | :--- | :--- | :--- | :--- |
| Peak Ratio | 0.89 | 0.77 | 0.58 | 1.00 |
| MBIAS (pphm) | -0.10 | -25.1 | -3.8 | -1.3 |
| MAGE (pphm) | 2.70 | 77.1 | 4.5 | 2.8 |
| NBIAS | 0.05 | 0.00 | -0.49 | -0.12 |
| MANGE | 0.24 | 0.46 | 0.67 | 0.56 |
| UPEA | 0.04 | -0.02 | 0.83 | 0.30 |



Figure 17. Comparison of Predicted Ozone, NO and NO2 by SAPRC97 and CB-IV against ambient data at Anaheim (SCAQS 1987)


Figure 18. Comparison of Predicted Ozone, NO and NO2 by SAPRC97 and CB-IV against ambient data at Burbank (SCAQS 1987)


Figure 19. Comparison of Predicted Ozone, NO and NO2 by SAPRC97 and CB-IV against ambient data at Los Angeles (SCAQS 1987)


Figure 20. Comparison of Predicted Ozone, NO and NO2 by SAPRC97 and CB-IV against ambient data at Riverside (SCAQS 1987)


Figure 21. Comparison of Predicted Ozone, NO and NO2 by SAPRC97 and CB-IV against ambient data at the Domain maximum (SCAQS 1987)

## 14. Exposure

Domain Population Exposure to pollutant $\mathrm{k}\left(\mathrm{P}_{\mathrm{k}}\right)$ was defined as a 24-hr average

$$
P_{k}=\sum_{i j} \sum_{t=0}^{t=23} C_{i j}^{k}(t) * p_{i j} * \frac{1}{24}
$$

Where $\mathrm{C}_{\mathrm{ij}}{ }^{\mathrm{k}}(\mathrm{t})$ is the simulated hourly concentration of pollutant k at cell $(\mathrm{i}, \mathrm{j})$ of the domain and starting time t , and $\mathrm{p}_{\mathrm{ij}}$ is the population in cell (i,j). Population data was obtained from the Department of Finance (1993) and extrapolated from the 1990 baseline year to 1997 and 2003 using factors provided by the Department of Finance. The population data was further gridded for each year of interest. The population exposure was calculated using the results of the last simulated day of the episode. Table 14 shows 24 -hr average population exposure for ozone and carbon monoxide (CO).

Table 14
Domain 24-hr average Population Exposure To Ozone and CO on August 28, 1987 (ppm*person/1000)

| Scenario | Ozone <br> Exposure | Carbon Monoxide <br> Exposure |
| :--- | :---: | :---: |
| 1997 | $1,061.2$ | $15,662.8$ |
| 2003/Mtbe | $1,250.8$ | $14,198.7$ |
| 2003/Et20 | $1,257.9$ | $14,201.8$ |
| 2003/Et20h | $1,251.7$ | $14,200.8$ |
| 2003/Et35 | $1,249.2$ | $13,204.2$ |
| 2003/Et35h | 1245.0 | $13,203.2$ |
| 2003/Unox | $1,263.1$ | $14,533.4$ |

2003 ozone exposure increases up to $18.5 \%$ for the oxygenated fuels over the base year, and $19 \%$ for the Unox scenario. CO exposure decreases almost $9 \%$ for the oxygenated fuels, and $7 \%$ for the Unox scenario . The increase in ozone exposure is probably due to increased population. From Table 9a, the 24hr ozone concentration is expected to decrease by about $4 \%$ from 1997 to 2003. However, the total population in the domain is estimated to increase from 16,926,408 in 1997 to 18,703,580 (i.e., about a $10 \%$ increase) in 2003. The decrease in CO is consistent with the expected decrease in CO emissions from 1997 to 2003 , tempered by an increase in population.

## 15. Model Use

It is important to bear in mind that the model results for this study are being used in a relative, rather than absolute sense. That is, the model was used to estimate the change from 1997 MTBE gasoline to ethanol-containing and non-oxygenated gasolines in 2003, rather than predict absolute values in 2003. The estimated changes were then used to adjust the base base year measurements to future values. The modeling community is in general agreement that models are best used in a relative sense.

## 16. References

Air Resources Board, "Technical Guidance Document: Photochemical Modeling." Air Resources Board. April 1992.

Carter, W. P. L., D. Luo, and I. L. Malkina (1997), "Environmental Chamber Studies for Development of an Updated Photochemical Mechanism for VOC Reactivity Assessment," final report to California Air Resources Board Contract 92-345, Coordinating Research Council Project M-9, and National Renewable Energy Laboratory Contract ZF-2-12252-07. November 26.

Carter, William P.L., "Condensed Atmospheric Photooxidation Mechanisms for Isoprene." Atmos. Environ. Vol. 30, 4275-4290 (1996).

Carter, W. P. L, D. Luo, I. L. Malkina, and J. A. Pierce (1993): "An Experimental and Modeling Study of the Photochemical Ozone Reactivity of Acetone," Final Report to Chemical Manufacturers Association Contract No. KET-ACE-CRC-Carter, W. P. L. (1995): "Computer Modeling of Environmental Chamber Studies of Maximum Incremental Reactivities of Volatile Organic Compounds," Atmos. Environ., 29, 2513-2527.

Carter, William, P.L. "A Detailed Mechanism for the Gas-Phase Atmospheric Reactions of Organic Compounds". Atmos. Environ., 24A, 481-518 (1990)

Carter, William, P.L, "Appendix C Documentation for the SAPRC Atmospheric Photochemical Mechanism Preparation and Emissions Processing Programs for Implementation in Airshed Models". Prepared for the Air Resources Board. Contract No. A5-122-32. October, 1988.

Department of Finance, "Population Projections by Race Ethnicity for California and it Counties 19902040" Report 93-P-1. Official Population Projections. Department of Finance. Demographic Research Unit. April 1993.

Whitten, Gary Z., Henry Hogo, and James P. Killus, " The Carbon-Bond Mechanism: A Condensed Kinetic Mechanism for Photochemical Smog." Environ. Sci. Technol. Vol. 14, 690-700 (1980).

Gery, Michael, Gary Z. Whitten, James P. Killus, and Marcia C. Dodge, "A Photochemical Kinetics Mechanism for Urban and Regional Scale Computer Modeling." J. Geophys. Res. Vol. 94, 12,925-12,956 (1990).

Kumar, Naresh, Lurmann, Frederick W., and Carter, William P.L., "Development of the Flexible Chemical Mechanism Version of the Urban Airshed Model. Final Report STI-94470-1508-FR. Prepared for California Air Resources Board, Sacramento, CA. August, 1995.

Kumar, Naresh, Lurmann, Frederick W., and Carter, William P.L., Assessment of Effects of Chemical Uncertainty on Airshed Model Results. Report to the California Air Resources Board. Contract No. 93716. Statewide Air Pollution Research Center. Riverside, California. June 13, 1996.

Morris, Ralph E., Myers, Thomas, C. "Users's Guide for the Urban Airshed Model. Volume I: Users Manual for UAM (CB-IV)". Systems Applications, Inc.. EPA-450/4-90-007A. June 1990. Airshed

South Coast Air Quality Management District, "Final. 1994 Air Quality Management Plan". September 1994.

Attachment A. SAPRC97 Photochemical Reaction Mechanism

This Attachment includes a listing of the SAPRC97 mechanism. A separate listing is provided for the isoprene reaction mechanism and for other species treated explicitly. The SAPRC mechanism used in the study described in this report included all the reactions listed in this Attachment. Interpretation of reactions rates constants can be found in Kumar et a. (1996).

## A. 1 SAPRC97




C4) $9.7 \mathrm{E}-15,-1.242$
C4A) 2.4E+12, 13.91
C4B) SAMEK B1
C9) $2.8 \mathrm{E}-12, \quad 5.00$
C10) 5.55E-12, -0.618
C11A) $\mathrm{PF}=\mathrm{CCHOR}$
C12) 1.4E-12, 3.696
C25) 8.5E-12 -0.50
C26) $\mathrm{PF}=\mathrm{RCHO}$
C27) $1.4 \mathrm{E}-12,3.696$
C38) 4.81E-13 0.4572 .0
C39) $\mathrm{PF}=$ ACET-93C
C44) 2.92E-13-0.823 2.0
C57) $\mathrm{PF}=\mathrm{KETONE}$

C95) 2.191E-11, 1.408
C13) SAMEK B2
C14) SAMEK B4
C15) SAMEK B6
C16) SAMEK B9
C17) SAMEK B10
C18) FALLOFF
4.90E-03 23.9720 .0
$4.00 \mathrm{E}+1627.0790 .0$
$0.30 \quad 1.00$
!
C28) SAMEK B2
C29) 8.4E-12 0.00 .0
C30) SAMEK B6
C31) SAMEK B9
C32) SAMEK B10
C33) 1.6E+17, 27.966
TBON) $2.4 \mathrm{E}-11$
TBOD) $7.5 \mathrm{E}+14,16.2$
C58A) $\mathrm{PF}=$ GLYOXAL1
C58B) $\mathrm{PF}=\mathrm{GLYOXAL} 2$
C59) $\quad 1.14 \mathrm{E}-11$
C60) SAMEK C12
C62) SAMEK B2
C63) SAMEK B4
C64) SAMEK C18
C65) SAMEK B6
C66) SAMEK B9
C67) SAMEK B10
C68A) PF=MEGLYOX1
C68B) $\mathrm{PF}=\mathrm{MEGLYOX} 2$
C69) $\quad 1.72 \mathrm{E}-11$
C70) SAMEK C12
G46) 2.63E-11
G51) $\quad 3.6 \mathrm{E}-12$
$; \mathrm{HCHO}+\mathrm{HO} 2=\mathrm{HOCOO}$
$; \mathrm{HOCOO}=\mathrm{HO} 2+\mathrm{HCHO}$
$; \mathrm{HOCOO}+\mathrm{NO}=\mathrm{XC}+\mathrm{NO} 2+\mathrm{HO} 2$
$; \mathrm{HCHO}+\mathrm{NO} 3=\mathrm{HNO} 3+\mathrm{HO} 2+\mathrm{CO}$
$; \mathrm{CCHO}+\mathrm{HO}=\mathrm{CCO}-\mathrm{O} 2+\mathrm{H} 2 \mathrm{O}+\mathrm{RCO} 3$
$; \mathrm{CCHO}+\mathrm{HV}=\mathrm{CO}+\mathrm{HO} 2+\mathrm{HCHO}+\mathrm{RO} 2-\mathrm{R}+\mathrm{RO} 2$
$; \mathrm{CCHO}+\mathrm{NO} 3=\mathrm{HNO} 3+\mathrm{CCO}-\mathrm{O} 2+\mathrm{RCO} 3$
$; \mathrm{RCHO}+\mathrm{HO}=\mathrm{C} 2 \mathrm{CO}-\mathrm{O} 2+\mathrm{RCO} 3$
$; \mathrm{RCHO}+\mathrm{HV}=\mathrm{CCHO}+\mathrm{RO} 2-\mathrm{R}+\mathrm{RO} 2+\mathrm{CO}+\mathrm{HO} 2$
$; \mathrm{NO} 3+\mathrm{RCHO}=\mathrm{HNO} 3+\mathrm{C} 2 \mathrm{CO}-\mathrm{O} 2+\mathrm{RCO} 3$
$; \mathrm{ACET}+\mathrm{HO}=\mathrm{R} 2 \mathrm{O} 2+\mathrm{HCHO}+\mathrm{CCO}-\mathrm{O} 2+\mathrm{RCO} 3+\mathrm{RO} 2$
; $\mathrm{ACET}+\mathrm{HV}=\mathrm{CCO}-\mathrm{O} 2+\mathrm{HCHO}+\mathrm{RO} 2-\mathrm{R}+\mathrm{RCO} 3+\mathrm{RO} 2$
$; \mathrm{MEK}+\mathrm{HO}=\mathrm{H} 2 \mathrm{O}+\# .5$ " $\mathrm{CCHO}+\mathrm{HCHO}+\mathrm{CCO}-\mathrm{O} 2+\&$
$\mathrm{C} 2 \mathrm{CO}-\mathrm{O} 2$ " $+\mathrm{RCO} 3+$ \#1.5 "R2O2 + RO2 "
$; \mathrm{MEK}+\mathrm{HV}+\# 0.1=\mathrm{CCO}-\mathrm{O} 2+\mathrm{CCHO}+\mathrm{RO} 2-\mathrm{R}+\mathrm{RCO} 3 \&$ $+\mathrm{RO} 2$
$; \mathrm{RNO} 3+\mathrm{HO}=\mathrm{NO} 2+\# .155 \mathrm{MEK}+\# 1.05 \mathrm{RCHO}+\&$
\#. $48 \mathrm{CCHO}+$ \#. $16 \mathrm{HCHO}+$ \#. $11 \mathrm{XC}+$ \#1.39 "R2O2 + RO2 "
$; \mathrm{CCO}-\mathrm{O} 2+\mathrm{NO}=\mathrm{CO} 2+\mathrm{NO} 2+\mathrm{HCHO}+\mathrm{RO} 2-\mathrm{R}+\mathrm{RO} 2$
$; \mathrm{CCO}-\mathrm{O} 2+\mathrm{NO} 2=\mathrm{PAN}$
$; \mathrm{CCO}-\mathrm{O} 2+\mathrm{HO} 2=\mathrm{XOOH}+\mathrm{CO} 2+\mathrm{HCHO}$
$; \mathrm{CCO}-\mathrm{O} 2+\mathrm{RO} 2=\mathrm{RO} 2+\# .5 \mathrm{HO} 2+\mathrm{CO} 2+\mathrm{HCHO}$
$; \mathrm{CCO}-\mathrm{O} 2+\mathrm{RCO} 3=\mathrm{RCO} 3+\mathrm{HO} 2+\mathrm{CO} 2+\mathrm{HCHO}$
$; \mathrm{PAN}=\mathrm{CCO}-\mathrm{O} 2+\mathrm{NO} 2+\mathrm{RCO} 3$

```
\(; \mathrm{C} 2 \mathrm{CO}-\mathrm{O} 2+\mathrm{NO}=\mathrm{CCHO}+\mathrm{RO} 2-\mathrm{R}+\mathrm{CO} 2+\mathrm{NO} 2+\mathrm{RO} 2\)
\(; \mathrm{C} 2 \mathrm{CO}-\mathrm{O} 2+\mathrm{NO} 2=\mathrm{PPN}\)
; \(\mathrm{C} 2 \mathrm{CO}-\mathrm{O} 2+\mathrm{HO} 2=\mathrm{XOOH}+\mathrm{CCHO}+\mathrm{CO} 2\)
; \(22 \mathrm{CO}-\mathrm{O} 2+\mathrm{RO} 2=\mathrm{RO} 2+\) \#. \(5 \mathrm{HO} 2+\mathrm{CCHO}+\mathrm{CO} 2\)
\(; \mathrm{C} 2 \mathrm{CO}-\mathrm{O} 2+\mathrm{RCO} 3=\mathrm{RCO} 3+\mathrm{HO} 2+\mathrm{CCHO}+\mathrm{CO} 2\)
\(; \mathrm{PPN}=\mathrm{C} 2 \mathrm{CO}-\mathrm{O} 2+\mathrm{NO} 2+\mathrm{RCO} 3\)
; \(\mathrm{C} 2(\mathrm{C})-\mathrm{O}+\mathrm{NO} 2=\mathrm{RNO} 3+\) \#-2 XC
; \(\mathrm{C} 2(\mathrm{C})-\mathrm{O}=\mathrm{ACET}+\mathrm{HCHO}+\mathrm{RO} 2-\mathrm{R}+\mathrm{RO} 2\)
\(; \mathrm{GLY}+\mathrm{HV}=\# .8 \mathrm{HO} 2+\# .45 \mathrm{HCHO}+\# 1.55 \mathrm{CO}\)
;GLY + HV + \#0.029 = \#.13 HCHO + \#1.87 CO
\(; \mathrm{GLY}+\mathrm{HO}=\# .6 \mathrm{HO} 2+\# 1.2 \mathrm{CO}+\# .4\) "HCOCO-O2 + \&
RCO3 "
;GLY + NO3 = HNO3 + \#. \(6 \mathrm{HO} 2+\# 1.2 \mathrm{CO}+\&\)
\#. 4 "HCOCO-O2 + RCO3 "
\(; \mathrm{HCOCO}-\mathrm{O} 2+\mathrm{NO}=\mathrm{NO} 2+\mathrm{CO} 2+\mathrm{CO}+\mathrm{HO} 2\)
\(; \mathrm{HCOCO}-\mathrm{O} 2+\mathrm{NO} 2=\mathrm{GPAN}\)
\(; \mathrm{GPAN}=\mathrm{HCOCO}-\mathrm{O} 2+\mathrm{NO} 2+\mathrm{RCO} 3\)
\(; \mathrm{HCOCO}-\mathrm{O} 2+\mathrm{HO} 2=\mathrm{XOOH}+\mathrm{CO} 2+\mathrm{CO}\)
\(; \mathrm{HCOCO}-\mathrm{O} 2+\mathrm{RO} 2=\mathrm{RO} 2+\# .5 \mathrm{HO} 2+\mathrm{CO} 2+\mathrm{CO}\)
\(; \mathrm{HCOCO}-\mathrm{O} 2+\mathrm{RCO} 3=\mathrm{RCO} 3+\mathrm{HO} 2+\mathrm{CO} 2+\mathrm{CO}\)
\(; \mathrm{MGLY}+\mathrm{HV}=\mathrm{HO} 2+\mathrm{CO}+\mathrm{CCO}-\mathrm{O} 2+\mathrm{RCO} 3\)
;MGLY + HV + \#. \(107=\mathrm{HO} 2+\mathrm{CO}+\mathrm{CCO}-\mathrm{O} 2+\mathrm{RCO} 3\)
;MGLY \(+\mathrm{HO}=\mathrm{CO}+\mathrm{CCO}-\mathrm{O} 2+\mathrm{RCO} 3\)
\(; \mathrm{MGLY}+\mathrm{NO} 3=\mathrm{HNO} 3+\mathrm{CO}+\mathrm{CCO}-\mathrm{O} 2+\mathrm{RCO} 3\)
;HO + PHEN = \#. \(15 \mathrm{RO} 2-\mathrm{NP}+\) \#. \(85 \mathrm{RO} 2-\mathrm{R}+\) \#. \(2 \mathrm{GLY}+\&\)
\#4.7 XC + RO2
;NO3 + PHEN = HNO3 + BZ-O
```

| G52) | 4.2E-11 | $\begin{aligned} & ; \mathrm{HO}+\mathrm{CRES}=\# .15 \mathrm{RO} 2-\mathrm{NP}+\# .85 \mathrm{RO} 2-\mathrm{R}+\# .2 \mathrm{MGLY}+\& \\ & \# 5.5 \mathrm{XC}+\mathrm{RO} 2 \end{aligned}$ |
| :---: | :---: | :---: |
| G57) | 2.1E-11 | ;NO3 + CRES $=\mathrm{HNO} 3+\mathrm{BZ}-\mathrm{O}+\mathrm{XC}$ |
| G30) | $1.29 \mathrm{E}-11$ | $; \mathrm{BALD}+\mathrm{HO}=\mathrm{BZ}-\mathrm{CO}-\mathrm{O} 2+\mathrm{RCO} 3$ |
| G31) | $\mathrm{PF}=\mathrm{BZCHO}$ | ;BALD + HV + \#. $05=$ \#7 XC |
| G32) 1.4 | $1.4 \mathrm{E}-12,3.747$ | ; BALD + NO3 = HNO3 + BZ-CO-O2 |
| G33) | SAMEK B2 | $; \mathrm{BZ}-\mathrm{CO}-\mathrm{O} 2+\mathrm{NO}=\mathrm{BZ}-\mathrm{O}+\mathrm{CO} 2+\mathrm{NO} 2+\mathrm{R} 2 \mathrm{O} 2+\mathrm{RO} 2$ |
| G34) 8.4 | 8.4E-12 0.00 .0 | $; \mathrm{BZ}-\mathrm{CO}-\mathrm{O} 2+\mathrm{NO} 2=\mathrm{PBZN}$ |
| G36) | SAMEK B6 | ;BZ-CO-O2 + HO2 = XOOH + $\mathrm{CO} 2+\mathrm{PHEN}$ |
| G37) | SAMEK B9 | $; \mathrm{BZ}-\mathrm{CO}-\mathrm{O} 2+\mathrm{RO} 2=\mathrm{RO} 2+\# .5 \mathrm{HO} 2+\mathrm{CO} 2+\mathrm{PHEN}$ |
| G38) | SAMEK B10 | $; \mathrm{BZ}-\mathrm{CO}-\mathrm{O} 2+\mathrm{RCO} 3=\mathrm{RCO} 3+\mathrm{HO} 2+\mathrm{CO} 2+\mathrm{PHEN}$ |
| G35) 1. | $1.6 \mathrm{E}+15,25.90$ | $; \mathrm{PBZN}=\mathrm{BZ}-\mathrm{CO}-\mathrm{O} 2+\mathrm{NO} 2+\mathrm{RCO} 3$ |
| G43) 1.3 | $1.3 \mathrm{E}-11,-0.596$ | $; \mathrm{BZ}-\mathrm{O}+\mathrm{NO} 2=\mathrm{NPHE}$ |
| G44) | SAMEK B5 | ; BZ-O + HO2 = PHEN |
| G45) | $1.0 \mathrm{E}-3$ | ; $\mathrm{BZ}-\mathrm{O}=\mathrm{PHEN}$ |
| G58) | $3.6 \mathrm{E}-12$ | $; \mathrm{NPHE}+\mathrm{NO} 3=\mathrm{HNO} 3+\mathrm{BZ}(\mathrm{NO} 2)-\mathrm{O}$ |
| G59) | SAMEK G43 | ;BZ(NO2)-O + NO2 = \#2 XN + \#6 XC ! DINITROPHENOL |
| G60) | SAMEK B5 | $; \mathrm{BZ}(\mathrm{NO} 2)-\mathrm{O}+\mathrm{HO} 2=\mathrm{NPHE}$ |
| G61) | SAMEK G45 | ;BZ(NO2)-O = NPHE |
| G7) | $1.14 \mathrm{E}-11$ | $; \mathrm{HO}+\mathrm{AFG1}=\mathrm{HCOCO}-\mathrm{O} 2+\mathrm{RCO} 3$ |
| G8) | $\mathrm{PF}=$ ACROLEIN | ; $\mathrm{AFG} 1+\mathrm{HV}+\# 0.077=\mathrm{HO} 2+\mathrm{HCOCO}-\mathrm{O} 2+\mathrm{RCO} 3$ |
| U2OH) | ) $1.72 \mathrm{E}-11$ | $; \mathrm{HO}+\mathrm{AFG} 2=\mathrm{C} 2 \mathrm{CO}-\mathrm{O} 2+\mathrm{RCO} 3$ |
| U2HV) | ) $\mathrm{PF}=$ ACROLEIN | $; \mathrm{AFG} 2+\mathrm{HV}=\mathrm{HO} 2+\mathrm{CO}+\mathrm{CCO}-\mathrm{O} 2+\mathrm{RCO} 3$ |
| RCH4) | ) $6.255 \mathrm{E}-132.5482 .0$ | ; $\mathrm{CH} 4+\mathrm{HO}=\mathrm{HCHO}+\mathrm{RO} 2-\mathrm{R}+\mathrm{RO} 2$ |
| RZ1) | 1.0 | $\begin{aligned} & ;(\mathrm{HCHO} 2)=\text { \#. } 7 \mathrm{HCOOH}+\# .12 \text { "HO }+\mathrm{HO} 2+\mathrm{CO} "+\& \\ & \# .18 \text { "H2 + CO2" } \end{aligned}$ |
| RZ2) | 1.0 | $\begin{aligned} & ;(\mathrm{CCHO} 2)=\# .25 \mathrm{CCOOH}+\# .15 \text { "CH4 + CO2" + \#. } 6 \mathrm{HO}+\& \\ & \text { \#. } 3 \text { "CCO-O2 + RCO3 " + \#. } 3 \text { "RO2-R + HCHO + CO + \& } \\ & \text { RO2 " } \end{aligned}$ |
| RZ3) | 1.0 | $\begin{aligned} & ;(\mathrm{RCHO} 2)=\# .25 \mathrm{CCOOH}+\# .15 \mathrm{CO} 2+\# .6 \mathrm{HO}+\& \\ & \text { \#. } 3 \text { "C2CO-O2 + RCO3 " + \#. } 3 \text { "RO2-R + CCHO + CO + \& } \\ & \mathrm{RO} 2 \text { " + \#. } 55 \mathrm{XC} \end{aligned}$ |
| RZ4) | 1.0 | $;(\mathrm{C}(\mathrm{C}) \mathrm{CO} 2)=\mathrm{HO}+\mathrm{R} 2 \mathrm{O} 2+\mathrm{HCHO}+\mathrm{CCO}-\mathrm{O} 2+\mathrm{RCO} 3+\mathrm{RO} 2$ |
| RZ5) | 1.0 | $;(\mathrm{C}(\mathrm{R}) \mathrm{CO} 2)=\mathrm{HO}+\mathrm{CCO}-\mathrm{O} 2+\mathrm{CCHO}+\mathrm{R} 2 \mathrm{O} 2+\mathrm{RCO} 3+\mathrm{RO} 2$ |
| RZ6) | 1.0 | $\begin{aligned} & ;(\mathrm{CYCCO} 2)=\# .3 \mathrm{HO}+\mathrm{C} 2 \mathrm{CO}-\mathrm{O} 2+\mathrm{R} 2 \mathrm{O} 2+\mathrm{RCO} 3+\& \\ & \mathrm{RO} 2 "+\# .3 \mathrm{RCHO}+\# 4.2 \mathrm{XC} \end{aligned}$ |
| RZ7) | 1.0 | $;(\mathrm{BZCHO} 2)=$ \#. 5 "BZ-O + R2O2 + CO + HO " |
| ETOH) | ) $1.960 \mathrm{E}-12-0.870$ | $; \mathrm{ETHE}+\mathrm{HO}=\mathrm{RO} 2-\mathrm{R}+\mathrm{RO} 2+\# 1.56 \mathrm{HCHO}+\# .22 \mathrm{CCHO}$ |
| ETO3) | ) $9.140 \mathrm{E}-155.127$ | $; \mathrm{ETHE}+\mathrm{O} 3=\mathrm{HCHO}+(\mathrm{HCHO} 2)$ |
| ETN3) | ) $5.430 \mathrm{E}-126.043$ | $; \mathrm{ETHE}+\mathrm{NO} 3=\mathrm{R} 2 \mathrm{O} 2+\mathrm{RO} 2+$ \#2 HCHO +NO 2 |
| ETOA) | ) $1.040 \mathrm{E}-111.574$ | $; \mathrm{ETHE}+\mathrm{O}=\mathrm{RO} 2-\mathrm{R}+\mathrm{HO} 2+\mathrm{RO} 2+\mathrm{HCHO}+\mathrm{CO}$ |
| A1OH) |  | ALK1 $=$ \#A1OHRR RO2-R + \#A1OHNR RO2-N $+\&$ HXN RO2-XN + \#A1OHNP RO2-NP + \#A1OHRH HO2 + \& R2 R2O2 + \#A1OHRS RO2 + \#A1OHA1 HCHO + \& HA2 CCHO + \#A1OHA3 RCHO + \#A1OHK3 ACET + \& K4 MEK + \#A1OHCO CO + \#A1OHC2 CO2 + \& HPH PHEN + \#A1OHCR CRES + \#A1OHBZ BALD + \& GL GLY + \#A1OHMG MGLY + \#A1OHU1 AFG1 + \& U2 AFG2 + \#A1OHTB C2(C)-O + \#A1OHQ1 CCO-O2 + \& Q2 C2CO-O2 + \#A1OHQS RCO3 + \#A1OHXC XC |
| ! |  |  |
| A2OH) |  |  |



```
!
O2O3)
O2OA
O2N3)
O3OH)
!
O3O3)
O3OA)
O3N3)
;OLE3 + NO3 = #O3N3N2 NO2 + #O3N3N3 HNO3 + &
#O3N3RH HO2 + #O3N3RR RO2-R + #O3N3RN RO2-N + &
#O3N3R2 R2O2 + #O3N3RS RO2 + #O3N3A1 HCHO + &
#O3N3A2 CCHO + #O3N3A3 RCHO + #O3N3K3 ACET + &
#O3N3K4 MEK + #O3N3BZ BALD + #O3N3XC XC
```


## A. 2 Reactions of Isoprene

| REACTIONS | ENE (Condensed - 1) |
| :---: | :---: |
| ISOH) 2.54E-11-0.81 | $; \mathrm{ISOP}+\mathrm{HO}=\# .088 \mathrm{RO} 2 \mathrm{~N}+$ \#. $912 \mathrm{RO} 2 \mathrm{R}+\&$ |
|  |  |
|  | \#1.079 RO2 |
| ! | \#1.079 RO2 + \#. 283 XC |
| ISO3) 7.86E-15 3.80 | $\begin{aligned} & ; \mathrm{ISOP}+\mathrm{O} 3=\# .4 \mathrm{HCHO}+\# .6 \mathrm{ISPD}+\# .55 \mathrm{BHCHO} 2+\& \\ & \# .2 \mathrm{CC} 3 \mathrm{O} 2+\# .2 \mathrm{CC} 3 \mathrm{HO} 2 \end{aligned}$ |
| ! | \#. $2 \mathrm{CC} 3 \mathrm{O} 2+$ \#. $2 \mathrm{CC} 3 \mathrm{HO} 2+$ \#. 05 XC |
| ISOA) 3.60E-11 |  |
|  | $\mathrm{RCO} 3+\# 2 \mathrm{HCHO}+\mathrm{RO} 2 \mathrm{R}+\mathrm{RO} 2 "$ |
| !ISOA) 3.60E-11 |  |
| ! | $\mathrm{RCO} 3+\# 2 \mathrm{HCHO}+\mathrm{RO} 2 \mathrm{R}+\mathrm{RO} 2 "$ |
| ISN3) 3.03E-12 0.89 |  |
|  | \#. 2 "ISPD + R2O2 + NO2" + RO2 |
| ! | \#. 2 "ISPD + R2O2 + NO2" + RO2 + \#-2.2 XC |
| ISN2) 1.50E-19 |  |
|  | \#.2 "ISPD + R2O2 + NO" + RO2 |
| ! | \#. 2 "ISPD + R2O2 + NO" + RO2 + \#-2.2 XC |
| $!$ ! |  |
| IPOH) 3.36E-11 |  |
|  |  |
|  |  |
|  | \#. 21 R 2 O 2 + \#. $713 \mathrm{RO} 2+$ \#. 498 RCO 3 |
| ! | \#. 21 R 2 O 2 + \#. $713 \mathrm{RO} 2+$ \#. $498 \mathrm{RCO} 3+$ \#-. 112 XC |
| IPO3) 7.11E-18 | $\begin{aligned} & ; \text { ISPD + O3 = \#. } 02 \mathrm{CCHO}+\# .04 \mathrm{HCHO}+\# .01 \mathrm{GLY}+\& \\ & \text { \#. } 84 \mathrm{MGLY}+\# .09 \mathrm{MEK}+\text { \#. } 66 \mathrm{BHCHO} 2+\& \end{aligned}$ |
|  | \#. $09 \mathrm{HCOCHO} 2+$ + $18 \mathrm{HOCCHO} 2+$ \#. $06 \mathrm{C} 2 \mathrm{O} 2 \mathrm{CHO}+\&$ |
|  | \#. $01 \mathrm{COHC2O} 2$ |
| ! | \#. 01 COHC2O2 + \#-. 39 XC |
| IPHV) $\mathrm{PF}=$ ACROLEIN |  |
|  |  |
|  |  |
|  | \#. 967 RCO3 |
| ! | \#. $967 \mathrm{RCO} 3+\#$-. 133 XC |
| IPN3) 1.0E-15 | ;ISPD + NO3 = \#. $643 \mathrm{CO}+$ \#. $282 \mathrm{HCHO}+$ \#. $85 \mathrm{RNO} 3+\&$ |
|  | \#. $357 \mathrm{RCHO}+$ \#. $925 \mathrm{HO} 2+$ \#. $075 \mathrm{C} 3 \mathrm{O} 3+\&$ |
|  | \#. 075 R 2 O 2 + \#. $925 \mathrm{RO} 2+$ \#. $075 \mathrm{RCO} 3+$ \#. 075 HNO 3 |
| ! | \#. 075 R 2 O 2 + \#. $925 \mathrm{RO} 2+$ \#. $075 \mathrm{RCO} 3+$ \#. $075 \mathrm{HNO} 3+\&$ |
| ! | \#-2.471 XC |
| ISZ1) 1.0 | $; \mathrm{CC3O} 2=\mathrm{HO}+\mathrm{R} 2 \mathrm{O} 2+\mathrm{HCHO}+\mathrm{C} 3 \mathrm{O} 3+\mathrm{RO} 2+\&$ |
|  | RCO3 |
| ISZ2) 1.0 | ; $\mathrm{CC} 3 \mathrm{HO} 2=$ \#. $75 \mathrm{RCHO}+$ \#. 25 ISPD |
| (ISZ2) 1.0 | ; CC 3 HO 2 = \#. $75 \mathrm{RCHO}+$ \#. $25 \mathrm{ISPD}+$ \#. 5 XC |
| MAZ1) 1.0 | $; \mathrm{C} 2 \mathrm{O} 2 \mathrm{CHO}=\mathrm{HO}+\mathrm{R} 2 \mathrm{O} 2+\mathrm{HCHO}+\mathrm{HC} 2 \mathrm{O} 4+\mathrm{RO} 2+\&$ |
|  | RCO 3 |
| M1Z1) 1.0 |  |
|  | \#.3 "RO2R + HCHO + CO + RO2" |
| ! | \#. 3 "RO2R + HCHO + CO + RO2" + \#. 8 XC |
| M2Z1) 1.0 | ; $\mathrm{HCOCHO} 2=$ \#. 12 " $\mathrm{HO} 2+$ \#2 $\mathrm{CO}+\mathrm{HO} "+\&$ |
|  | \#. 51 HCHO |
| !M2Z1) 1.0 |  |
| ! | \#.51 "CO2 + HCHO" |
| M2Z2) 1.0 | $; \mathrm{COHC} 2 \mathrm{O} 2=\mathrm{HO}+\mathrm{MGLY}+\mathrm{HO} 2+\mathrm{R} 2 \mathrm{O} 2+\mathrm{RO} 2$ |
| END OF FIL |  |

## A. 3 Explicit Reaction Mechanisms for Selected Hydrocarbons

```
OH001) 2.500E-12 0.397 0.000 ;C6H6 + HO = #.236 PHEN + #.207 GLY & 
                                    + #1.44 AFG1 + #.764 RO2-R + #. 236 HO2 &
                                    + #1.29 XC + #.764 RO2
!
OH033) 1.480E-11-0.890 0.000 ; BUTD + HO = RO2-R + RO2 + HCHO + RCHO
!
O3033) 1.340E-14 4.537 0.000
!
N3033) 1.000E-13 0.000 0.000
    + NO2
!
OA033) 2.100E-11 0.000 0.000 ;BUTD + O = #.4 HO2 + #.5 RCHO + #.5 MEK &
        + #.5 XC
!
OH018) 3.840E-13 0.000 0.000 ;PDCB + HO = #.236 PHEN + #.207 GLY & 
    + #1.44 AFG1 + #.764 RO2-R + #.236 HO2 &
+ #1.29 XC + #.764 RO2
OH152) 9.640E-12 2.403 0.000
!
OH086) 6.14E-18 1.987 2.000
!
AS1) 6.14E-25 ; AS = AS
CR1) 6.14E-25 ; CRVI = CRVI
C1) PF=HCHONEWR ;FORM + HV = #2 HO2 + CO
C2) PF=HCHONEWM ;FORM + HV = H2 + CO
C3) 1.125E-12 -1.288 2.0 ;FORM + HO = HO2 + CO + H2O
C4) 9.7E-15, -1.242
C9) 2.8E-12, 5.00
!
C10) 5.55E-12, -0.618
C11A) PF=CCHOR
C12) 1.4E-12, 3.696
!
OH091) 5.560E-13-1.057 2.000 ;ETOH + HO = #.1 RO2-R + #.9 HO2 &
+ #.156 HCHO + #.922 CCHO + #. 1 RO2
!
OH108) 6.129E-13 -0.914 2.000 ;MTBE + HO = #.02 RO2-N + #.98 RO2-R &
+ #.37 R2O2 + #.39 HCHO + #.41 MEK + #2.87 XC &
+ #1.37 RO2
! END OF FILE
```

