Reactivity Estimates for Aromatic Compounds

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Abstract

Because the major atmospheric reaction pathways and products for aromatic hydrocarbons are uncertain, they are represented in air quality models using parameterized mechanisms derived by modeling environmental chamber data. Uncertainties in rate constants, experimental conditions and chamber artifacts affect the parameter estimates derived in this manner. The SAPRC-97 mechanism represents aromatic ring fragmentation products by model species MGLY (α-dicarbonyls) and AFG2 (other photoreactive products) with yields derived from aromatics-NO_x experiments conducted in indoor chambers with blacklight or xenon arc light sources. This study explores how experimental and modeling uncertainties affect these chamber-derived aromatics parameters, and in turn the reactivity estimates calculated for the aromatic compounds.

The uncertainty levels (1σ relative to the mean) for the aromatics oxidation parameters range from about 29% for the MGLY yield from 135-trimethylbenzene oxidation to 71% for the MGLY yield from p-xylene. Major causes are uncertainties in rate constants for the aromatics + OH and NO_2 + OH reactions, and the light intensity, chamber radical source parameters and initial aromatic concentrations in the experiments. The chamber radical source parameters are estimated from CO-NO_x and n-butane NO_x experiments, and are sensitive to uncertainties in the rate constants for n-butane or CO + OH, NO_2 + OH, HONO photolysis and the experimental light intensity.

More than 100 parameters of the SAPRC-97 mechanism, including the chamber-derived aromatics parameters, are propagated through incremental reactivity calculations using Monte Carlo analysis with Latin hypercube sampling. The uncertainty levels found for the maximum incremental reactivities (MIRs) of the aromatic compounds range from 27 to 32%, and are about

the same as those for other volatile organic compounds with relatively well-established mechanisms. The uncertainty levels for the maximum ozone incremental reactivities (MOIRs) and equal benefit incremental reactivities (EBIRs) of the aromatics range from 38 to 75% and 30 to 520%, respectively. Uncertainties in relative reactivities for the aromatic compounds range from 13 to 25%, 20 to 63% and 21 to 360% under MIR, MOIR and EBIR conditions. Uncertainties in the relative reactivities of most, but not all of the VOCs studied are smaller than the uncertainties in their absolute incremental reactivities. The exceptions include some slowly reacting compounds under MIR, MOIR and EBIR conditions, and some of the aromatic compounds under EBIR conditions.

From 30% to 70% of the uncertainty in the relative MIRs of the aromatic compounds is contributed by their chamber-derived parameters. Similarly, from 14% to 60% of the uncertainties in the relative MOIRs and from 3% to 56% of the uncertainty in the relative EBIRs of the aromatics is attributed to their chamber-derived parameters. Although the chamber-derived parameters are influential, the rate constant for the reaction CRES (cresol) + NO_3 is the largest contributor to the relatively high uncertainty in the EBIRs of toluene, p-xylene and ethylbenzene.

As long as incremental reactivity estimates for aromatic compounds have to rely on chamber-derived parameters, uncertainty in these estimates could be reduced most by improving the characterization of radical sources, light intensity and initial concentrations in environmental chamber studies, and by reducing uncertainty in the rate constants for NO_2 + OH, aromatics + OH, and CRES + NO_3. Future chamber studies of aromatics chemistry should emphasize low-NO_x conditions to reduce the relatively high uncertainties in MOIR and EBIR estimates.

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1. Introduction

Despite more than two decades of costly control efforts, photochemical air pollution is still a significant environmental problem in many major urban areas of the United States, where ozone concentrations continue to exceed the National Ambient Air Quality Standard (NAAQS) (1,2). One of the difficulties in designing effective and economical control strategies is the fact that ozone is produced from a nonlinear system of chemical reactions involving oxides of nitrogen (NO_x) and volatile organic compounds (VOCs), and local meteorology and ambient conditions also influence its production and distribution.

It is recognized that individual VOC species differ significantly in their effects on ozone formation, due to the differences in their atmospheric reaction rates and in the way in which their reactions affect ozone (3). This relative ozone forming potential of an individual VOC is described as its reactivity. Selectively limiting emissions of highly reactive VOCs is viewed as a cost-effective means to achieve ozone reductions (4). For example, the California Clean Fuels/Low Emissions Vehicles regulation (5) accounts for reactivity differences through a weighting scheme based on maximum incremental reactivities (MIRs). Since VOC reactivities depend on the environment where they are emitted, laboratory results for reactivities cannot be assumed to be the same as their impacts in the atmosphere (6). Modeling provides the most realistic and flexible way to assess many factors that affect ozone formation by VOCs (6). However, the level of confidence in these calculated reactivities depends on the underlying chemical mechanisms.

Uncertainty is inherent in current gas-phase photochemical mechanisms. A critical source of uncertainty is a lack of understanding of the mechanism through which some VOCs are oxidized. One of the most significant areas of uncertainty is the degradation pathways of aromatic hydrocarbons (7).

Aromatic hydrocarbons such as benzene, toluene, xylenes and trimethylbenzenes are of great interest in atmospheric chemistry. They are important constituents of gasoline and reformulated gasolines, vehicle emissions, and ambient air in urban areas (8). For example, aromatic hydrocarbons constitute 30 to 40% of the hydrocarbons emitted in some urban areas (9). Previous research has also shown that xylenes and trimethylbenzenes are highly reactive with respect to ozone formation (6, 8). Moreover, the aromatic hydrocarbons play a significant, and possibly dominant, role in the formation of secondary organic aerosol (8, 10). The reaction of aromatic hydrocarbons with the hydroxyl radical is their major sink in the troposphere. The overall reaction rate constants are well characterized (11) and the initial steps are reasonably well understood. One path (~10%) is H atom abstraction from the C-H bonds of the alkyl-substituent group(s) or (for benzene) the aromatic ring, to form benzyl or alkyl-substituted benzyl radicals (8, 12). Another path (~ 90%) is OH radical addition to form hydroxycyclohexadienyl or alkyl-substituted hydroxycyclohexadienyl radicals (8, 12). However, the subsequent steps are not well understood and the final products are extremely complex because of the wide number of reaction pathways that occur for these molecules (9,11). Product studies under simulated atmospheric conditions for benzene, toluene and xylenes generally account for only 30-50% of the reaction products (8,11).

Because of the gaps in understanding aromatic chemistry, existing chemical mechanisms incorporate parameters estimated from environmental chamber experiments to represent the overall contribution of the unknown intermediates to oxidant formation (13-16). Recent updates to these aromatics oxidation parameters (16) have caused substantial (~ 50%) changes in the reactivity estimates of some aromatic species (17). Previous uncertainty studies (18, 19) have also shown that these chamber-derived aromatics oxidation parameters are the major factors contributing to the estimated 40 to 50% uncertainties in the incremental reactivities of most aromatic compounds. However, a limitation of the previous studies was that the input uncertainties assumed for the parameters representing secondary aromatic chemistry were very subjective.

Although the aromatics oxidation parameters can be estimated from environmental chamber experiments, there are no ideal experiments. Analytical methods for reactants and products have inaccuracies and imprecisions which introduce errors in the amount of initial or injected reactants as well as products (20). There also exist uncertainties in the required knowledge of temperature, light intensity, and spectrum of the photolyzing light and how they vary with time (20). Perhaps the most serious problem is the existence of chamber wall effects (heterogeneous processes involving the walls), which are known to be non-negligible in all current generation chamber experiments and can dominate the results of certain types of experiments (13,21). So, use of environmental chamber experiments to estimate aromatics oxidation parameters requires an auxiliary chamber model to simulate the chemical effects of the chamber itself. However, chamber models have significant uncertainties because the physical and chemical basis for many of these effects is unknown. Furthermore, some chamber effects vary from one experiment to another in a manner that is not always successfully predicted (20). All of these factors can result in uncertainties for estimated parameters, which will in turn affect the chemical mechanisms and calculated reactivities.

1.1 Objectives and Scope of the Study

The considerations discussed above are summarized in Figure 1, which shows the sources of uncertainty in reactivity estimates for aromatic compounds. This study investigates uncertainties in incremental reactivity estimates by considering the uncertainties in the other parameters of the overall mechanism and the uncertainties in the experiments, including chamber artifacts. Identification of the most influential factors should help guide the design of new chamber experiments as well as future mechanism development. The study uses the Statewide Air Pollution Research Center 97 (SAPRC-97) photochemical mechanism (17,22) and the database of environmental chamber experiments (20) from the University of California at Riverside, College of Engineering, Center for Environmental Research and Technology (CE-CERT).

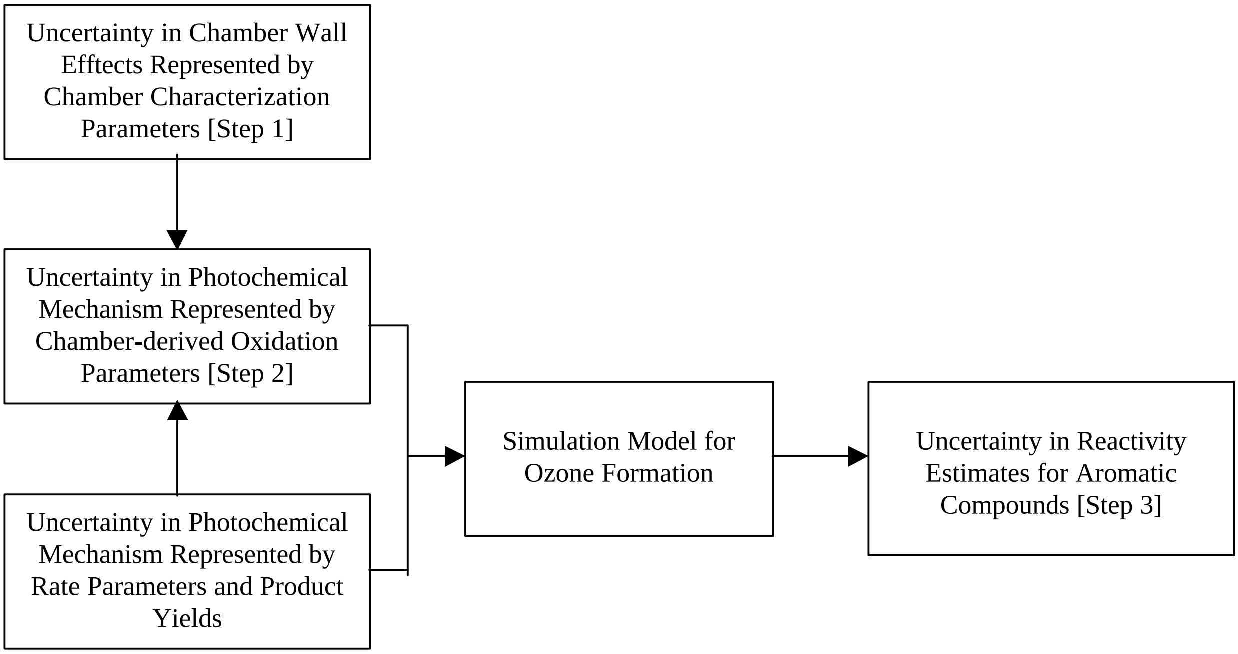


Figure 1. Propagation of Uncertainties in Photochemical Air Quality Model Estimates of Aromatic Compound Reactivities

2. Methods

In order to explore how experimental and modeling uncertainties affect reactivity estimates for aromatic compounds, the optimal estimates and corresponding uncertainties for the chamber characterization parameters and chamber-derived aromatics oxidation parameters must be investigated first. So, this study includes three stages (Figure 1). First, optimal estimates with uncertainties for chamber characterization parameters are calculated by considering the uncertainties in the mechanism and the chamber characterization experiments. Next, optimal estimates for the aromatics oxidation parameters are determined by considering the uncertainties in the mechanism, the experiments and the chamber characterization parameters. Finally, reactivity estimates and the associated uncertainty levels for aromatic compounds and other VOCs are calculated under the constraints of the chamber-derived aromatics oxidation parameters and other mechanism uncertainties.

2.1 Incremental Reactivity Scales

2.1.1 Absolute Incremental Reactivity Scales

The most direct quantitative measure of the degree to which a VOC contributes to ozone formation is its incremental reactivity (IR) (6), which can be calculated as the sensitivity of the predicted ozone concentration to the initial concentrations of each organic compound in a mixture (18):

$$IR_j = \lim_{\Delta[VOC_j]\to 0} \frac{[O_3]_{[VOC_j]+\Delta[VOC_j]} - [O_3]_{[VOC_j]}}{\Delta[VOC_j]} = \frac{\partial[O_3]}{\partial[VOC_j]} \qquad \text{(EQ.1)}$$

Three incremental reactivity scales representing different environmental conditions are used for this study. The maximum incremental reactivity (MIR) scale is used for conditions that maximize the overall incremental reactivity of the base VOC mixture (23):

$$MIR_j = \max\left[\frac{\partial[O_3]_{peak}}{\partial[VOC_j]}\right] \text{ for all } NO_x \text{ levels with constant [VOC]} \qquad \text{(EQ.2)}$$

where $[O_3]_{peak}$ is the peak ozone concentration. MIRs are typically observed at relatively low VOC/NO_x ratios (about 4-6 ppmC/ppm). At lower NO_x levels, the absolute level of ozone production of any individual VOC is expected to be less than under MIR conditions (the level of NO_x, not VOC, becomes the limiting factor) (23). The maximum ozone incremental reactivity scale (MOIR) is used for conditions that yield the maximum possible O_3 concentration with the base VOC mixture. Conditions leading to the MOIR are calculated to occur at higher VOC/ NO_x ratios (about 7-8 ppmC/ppm). The equal benefit incremental reactivity (EBIR) is defined for the conditions where VOC and NO_x reductions are equally effective in reducing ozone (6). “In these scenarios the NO_x inputs are adjusted so that the effect on ozone of a given percentage incremental change in VOC input is the same as the effect of an equal percentage change in NO_x. … The EBIR scenarios represent the lowest NO_x conditions where VOC control is of equal or greater effectiveness for reducing ozone as NO_x control. Thus they represent the lowest NO_x conditions which are of relevance to VOC control, since at lower conditions NO_x control becomes much more effective in reducing ozone.” (6)

2.1.2 Relative Incremental Reactivities

For control strategy purposes, the ratios of incremental reactivities for a given VOC relative to others may be of greater relevance than the incremental reactivities themselves (6). The relative reactivity of a VOC is defined as the ratio of the incremental reactivity of the VOC to the incremental reactivity of the base VOC mixture(6):

$$R\_IR_j = \frac{IR_j}{IR_{base\ \ mixture}} \qquad \text{(EQ.3)}$$

The base VOC mixture used in this study is the mixture of reactive organic gases initially present or emitted in the scenarios, excluding biogenic VOCs and VOCs present aloft. Relative incremental reactivities under MIR, MOIR and EBIR conditons are also investigated in this study.

2.2 SAPRC-97 Mechanism and Chamber-Derived Parameters

The chemical mechanism employed in this study is the SAPRC-97 photochemical mechanism (17) listed in Appendix A-1. The SAPRC mechanisms can explicitly represent a large number of different types of organic compounds but use a condensed representation for many of the reactive organic products (22). The reactions of inorganics, CO, formaldehyde, acetaldehyde, peroxyacetyl nitrate, propionaldehyde, peroxypropional nitrate, glyoxal and its PAN analog, methylglyoxal, and several other product compounds are represented explicitly. The SAPRC-97 mechanism is updated from SAPRC-93 and SAPRC-90 (22). The differences between SAPRC-93 and SAPRC-90 include updates to the formaldehyde absorption cross-sections, the kinetics of PAN formation, the action spectra of the unknown photoreactive aromatic fragmentation products, the mechanisms for the reactions of ozone with alkenes, the reaction of NO with the peroxy radical formed in the reaction of OH radicals with isobutene, the mechanistic parameters for isooctane, and the mechanism for acetone. The major difference between SAPRC-97 and SAPRC-93 is in the mechanism for the aromatic compounds. The updates to the aromatics mechanism are based on new chamber data, especially xenon arc chamber data, used to optimize the mechanism parameters (16). Although the mechanism is being further updated, the aromatic parameterization in the new mechanism is very similar to that used in SAPRC-97. As a result, the conclusions from this study should be applicable to the new version of the mechanism.

2.2.1 Chamber-Derived Aromatics Parameters

The aromatic mechanism in SAPRC-97 uses chamber-derived parameters to represent the chemistry of unknown photoreactive products from aromatic compounds. The model species representing the unknown products are “AFG1”, “AFG2” and “MGLY” (17). “AFG1” represents the glyoxal-like pseudo-species produced from benzene, naphthalene and other aromatics which do not have alkyl groups. “AFG2” represents the methyl glyoxal-like pseudo-species produced from toluene, xylenes, alkyl naphthalenes and other aromatics with alkyl side groups. AFG1 and AFG2 are assumed to undergo reaction with HO and also photolysis, with the same absorption cross sections as acrolein. “MGLY” represents methylglyoxal, the model for its reactions, as well as other uncharacterized products (16, 17) of the aromatics with alkyl side groups. The product yields (represented by parameters called B1U1, B1U2, and B1MG) for these model species, and the overall quantum yield for AFG1 (represented by a parameter called P1U1) are estimated from environmental chamber experiments. For example:

BENZENE + OH. -> #**B1U1** AFG1 + other products

AFG1 + hv -> HO2. + HCOCO-O2. + RCO3., quantum yield = **P1U1**

TOLUENE + OH -> #**B1MG** MGLY + #**B1U2** AFG2 + other products

AFG2 + hv -> HO2. + CO + CCOO2 + RCO3. quantum yield = P1U2

For toluene, ethylbenzene, xylenes and trimethylbenzenes, the value for the AFG2 quantum yield, P1U2, is fixed. However, the estimates for the aromatics oxidation parameters

B1U2 and B1MG depend on the value of the AFG2 quantum yield. Therefore the sensitivities of the estimated aromatics oxidation parameters to the AFG2 quantum yield are also investigated in this study.

2.2.2 Chamber Characterization Parameters

Using chamber experiments to estimate mechanism parameters or to evaluate chemical mechanisms requires consideration of the artifacts in the chamber itself. An auxiliary mechanism or chamber model is used to simulate the chemical effects of the chamber. The auxiliary mechanism used for this study is listed in Appendix A-2. In particular, the chamber-dependent radical sources must be taken into account when estimating aromatics oxidation parameters or evaluating mechanisms using environmental data (24). Two radical source parameters, RSI and HONO-F, are treated as the chamber characterization parameters to be estimated in this study because preliminary sensitivity analysis indicated that they were most influential. RSI represents a NO_2 independent, continuous light-induced release of radicals from the chamber walls (16, 17), which is described by the reaction $hv \rightarrow OH$ with reaction rate $RSI \times K_1$, where K_1 is the NO_2 photolysis rate in the chamber experiment. HONO-F represents the fraction of initial NO_2 converted to HONO prior to irradiation (16, 17). It is called the initial radical source parameter because the initial OH radicals mainly come from HONO photolysis.

2.3 Chamber Experiments

The data base from SAPRC and CE-CERT at UCR contains data for environmental chamber experiments performed in different chambers from 1975 to 1996 (16, 20). In this study, 142 chamber experiments from five different chambers are used. The characteristics of the five chambers are listed in Table 1.

Table 1. SAPRC and CE-CERT Environmental Chambers (16, 17)

ID	Volume (L)	Walls	Lights	Relative Humidity	Character-ization Runs	Aromatics Runs
DTC1 [1]	2x5000	FEP Teflon bags	blacklights	<5%	2	2
DTC2 [2]	2x5000	FEP Teflon bags	blacklights	<5%	6	50
DTC3 [2]	2x5000	FEP Teflon bags	blacklights	<5%	9	4
ITC	6400	FEP Teflon bag	blacklights	50%	4	4
CTC [3]	6000 (single) 2x3500 (dual)	FEP Teflon bags	xenon arc	<5%	21	40

[1] SAPRC DTC

[2] CE-CERT DTC. DTC2 is for the first set of reaction bags and DTC3 is for new bags

[3] CE-CERT CTC

To estimate the values of P1U1, B1U1, B1U2 and B1MG, Carter et al. (16) carried out a series of aromatics-NO_x irradiation experiments during 1994 and 1995, in two dual indoor Teflon chambers, one irradiated by blacklights and the other by xenon arc lights. Multiple experiments were performed for benzene, toluene, ethylbenzene, o-, m- and p-xylenes and the three trimethylbenzene isomers. Older experiments in a blacklight chamber were also used for benzene. Single aromatic compound-NO_x experiments are used to estimate chamber-derived oxidation parameters for each aromatic compound, in order to eliminate confounding from other VOC species. The individual chamber experiments used in this study for the aromatics oxidation parameters are listed in Appendix B-1, along with the major input parameters and their estimated uncertainties and the classifications and grouping for the systematic uncertainties, which are discussed later. The pair of parameters for each compound was estimated by using least squares minimization to match the quantity D($[O_3]$-[NO]), which is defined as the amount of ozone formed plus the NO oxidized ($D([O_3]-[NO])_t = [O_3]_t-([NO]_t-[NO]_0)$), and the aromatics concentrations across the full set of experiments from each chamber. Appendix B-1 also shows examples of the performance of the mechanism for the benzene, toluene- and p-xylene-NO_x experiments, using SAPRC-97 values for the aromatics oxidation parameters.

The chamber-dependent radical sources are estimated from experiments in which the compounds added have insignificant radical sources in their mechanisms. This ensures that reactions causing NO oxidation and ozone formation are initiated almost entirely by radicals formed from the chamber-dependent radical sources. N-butane-NO_x and CO-NO_x experiments are recommended for this purpose (24). The chamber characterization experiments used in this study are listed in Appendix B-2, along with the major input parameters and their estimated uncertainties, and the classification and grouping for systematic uncertainties.

2.4 Stochastic Programming

Determining optimal estimates with uncertainties for chamber characterization parameters and aromatics oxidation parameters is a stochastic parameter estimation problem. In the past, informal “eye-fit” and ordinary least squares techniques (25, 26) have been used to estimate values of chemical parameters from mechanism simulations and chamber data. However, these approaches are not ideal because of nonlinearity in the chemistry, and because uncertainties in the mechanisms and data are ignored. The estimated parameters can vary significantly depending on which experiments are used to obtain them.

Stochastic programming (28, Figure 2) can be used to obtain more stable parameter estimates by considering uncertainties in the experiments and the data. The optimization loop is used to provide optimal estimates of chamber characterization parameters and of aromatics oxidation parameters. The uncertainty analysis loop is used to provide samples of uncertain input parameters to the optimization loop. The procedure terminates when the probability distribution functions of the optimal parameter values are determined. The results are then analyzed using regression analysis to identify the major sources of uncertainty in the parameter estimates and thus provide guidance for designing new experiments.

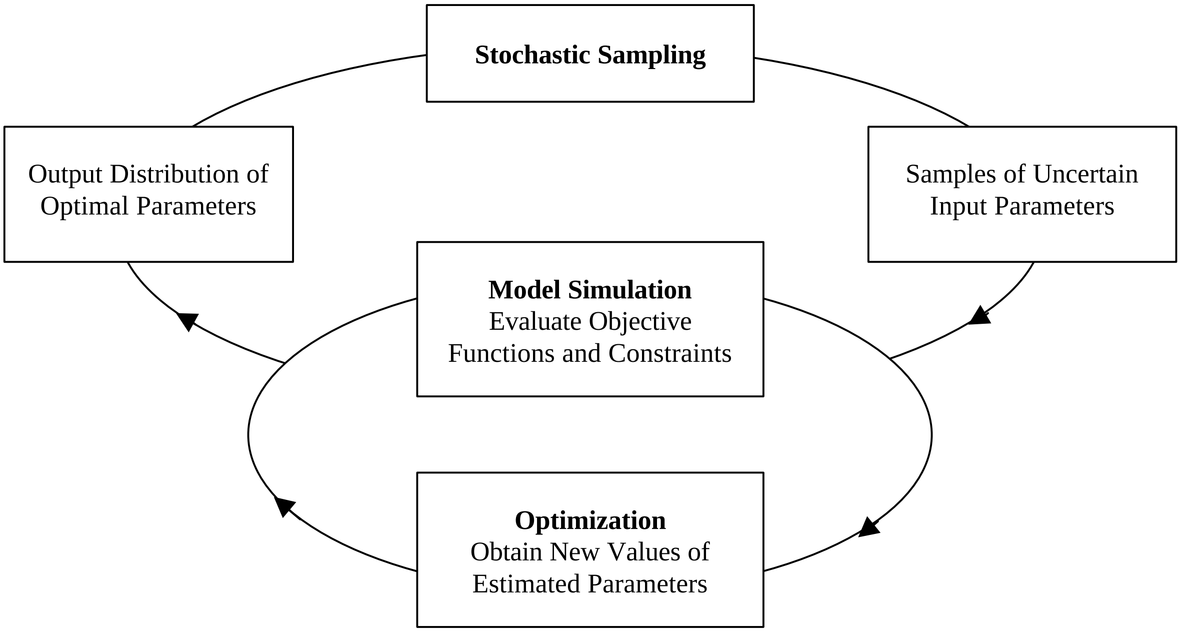


Figure 2. Schematic Diagram of the Study Approach Using Stochastic Programming

2.4.1 Parameter Estimation Problem

In the case with only bound constraints, the stochastic parameter estimation problem can be described mathematically as:

$$f(\underline{\kappa}, \underline{\theta}, \underline{P}; t) = ML(\underline{\kappa}, \underline{\theta}, \underline{P}; t) \qquad \text{(EQ.4)}$$

$$s.t \quad \underline{P_L} \le \underline{P} \le \underline{P_U}$$

where:

f is the objective function for optimization, which is a likelihood function (ML) based on the probability distribution function of errors between experimental measurements and model simulations.

$\underline{P}$ is the vector of parameters to be estimated.

$\underline{P}_L$, $\underline{P}_U$ are the lower and upper bounds for $\underline{P}$.

$\underline{\kappa}$ is the vector of other model parameters and/or experimental conditions with uncertainty, which are treated as random variables with assumed known probability distributions.

$\underline{\theta}$ is the vector of other model parameters and experimental conditions treated as fixed.

t is time.

The maximum likelihood estimate (MLE) under uncertainty is the set of values of $\underline{P}$ satisfying all constraints, for which the likelihood function attains its maximum value (if such a value exists) under uncertainty. For normally distributed parameters with known covariance, MLE reduces to weighted least squares, with the weights given by the elements of the inverse of the covariance matrix (28).

$$\begin{array}{ll} \min & f(\underline{k},\underline{q},\underline{P};t) = \sum_{i=1}^{NC} \underline{X}^{(i)T}\,\underline{W}^{(i)}\,\underline{X}^{(i)} \\ s.t. & \underline{P_L} \le \underline{P} \le \underline{P_U} \end{array} \qquad \text{(EQ.5)}$$

where:

NC is the number of adopted criteria for comparing model and experimental results

$\underline{X}^{(i)}$ is the vector of residuals between model results and measurements for criterion i: $\underline{X}^{(i)} = \underline{C}_s^{(i)}(\underline{\kappa}, \underline{\theta}, \underline{p}; t) - \underline{C}_{exp}^{(i)}(t)$.

$C^{(i)}$ is the value of criterion i for model simulation $\underline{C}_s^{(i)}(\underline{\kappa}, \underline{\theta}, \underline{p}; t)$ and experimental result $\underline{C}_{exp}^{(i)}(t)$.

$\underline{W}^{(i)}$ is the matrix of weight factors for criterion i.

In this study, the primary comparison criterion used is the quantity $D(O_3\text{-}NO)$, which is the difference ($[O_3]$-[NO]) evaluated over the duration of the simulation and experiment. For the aromatics oxidation parameters, the aromatics concentration C(ARO) is used as a second criterion. $D(O_3\text{-}NO)$ has a more direct relationship to the processes that are responsible for ozone formation than does the change in ozone alone (22). In the initial stages of a VOC-NO_x-air irradiation when [NO] exceeds $[O_3]$, these processes are manifested by the consumption of NO. Later, after the bulk of the NO initially present has reacted, these processes are manifested by the formation of ozone (22). The aromatics concentration has a direct relationship with the estimates for the aromatics oxidation parameters. The weight factors are taken as the inverse square of the maximum value of the ith criterion in each experiment, which normalizes the residuals to give equal weight in the optimization to both criteria and to each experiment. These factors are available from the chamber experimental data base (16, 20).

Given the weight factors and comparison criteria, the parameter estimation problem using multiple experiments is:

$$\min \sum_{i=1}^{N}\sum_{t=0}^{tend^i} W_{D(O_3-NO)}{}^{i}\left(D(O3-NO)^{i}{}_{e(t)}-D(O3-NO)^{i}{}_{s(t)}\right)^2+W_{C(ARO)}{}^{i}\left(C(ARO)^{i}{}_{e(t)}-C(ARO)^{i}{}_{s(t)}\right)^2$$

$$s.t \quad \underline{P_L} \le \underline{P} \le \underline{P_U} \qquad \text{(EQ.6)}$$

where:

$W_{D(O3\text{-}NO)}{}^{i}$ is the weight factor for the $D(O_3\text{-}NO)$ data of the ith experiment.

$W_{C(ARO)}{}^{i}$ is the weight factor for the aromatics concentration of the ith experiment.

N is the number of the experiments used.

$D(O_3\text{-}NO)^{i}{}_{e(t)}$ is the experimental result for $D(O_3\text{-}NO)$ for the ith experiment at time t.

$D(O3\text{-}NO)^{i}_{s(t)}$ is the simulation result for $D(O_3\text{-}NO)$ for the ith experiment at time t.

$C(ARO)^{i}_{e(t)}$ is the experimental result for C(ARO) for the ith experiment at time t.

$C(ARO)^{i}_{s(t)}$ is the simulation result for C(ARO) for the ith experiment at time t.

$tend^{i}$ is the experimental and simulation end time for the ith experiment.

2.4.2 Optimization Method

The comparison criterion $D(O_3\text{-}NO)$ and the aromatics concentration have high nonlinearity with respect to the parameters to be estimated, resulting in a highly nonlinear programming (NLP) problem. Successive quadratic programming (SQP) (29, 30) is adopted for this NLP problem because of its fast convergence rate, and because it is a widely used technique for large scale nonlinear optimization for chemical processes (31). The SQP method is also called the projected Lagrangian method. At each iteration the original problem is approximated as a quadratic program where the objective function is quadratic and the constraints are linear. The quadratic programming subproblem is solved for each step to obtain the next trial point. This cycle is repeated until the optimum is reached. The special features of the quadratic subproblem usually give a faster convergence rate than the original problem (32).

2.4.3 Uncertainty Analysis Method

Monte Carlo analysis is used for the uncertainty analysis loop of stochastic programming. The computational requirements of Monte Carlo analysis depend on the number of uncertain input parameters that are treated as random variables. In order to get reasonably accurate results with reasonable computational requirements, first order uncertainty analysis (33) and Latin Hypercube Sampling (LHS) (18, 34) are used. First order sensitivity analysis is used to limit the number of input random variables by identifying the most influential parameters without neglecting significant sources of uncertainty. Given a specified number of uncertain input parameters, LHS further reduces the Monte Carlo computational requirements through selective representative sampling.

2.5 Input Parameter Uncertainties

2.5.1 Identification of the Influential Parameters

The sources of uncertainty considered in this study include the rate parameters and product yields of the SAPRC-97 mechanism and chamber experimental conditions such as reactant and product concentrations, temperature, and lighting. Uncertainty estimates for mechanism parameters are taken primarily from expert panel reviews (35-38). Uncertainty estimates for experimental conditions were estimated for this study by W.P.L. Carter, and are listed in Appendix B. The uncertainty in the experimental conditions is introduced by calibration and/or zero uncertainties, or for NO_2, uncertainties for converter efficiencies for measurement instruments.

Before the stochastic programming runs, first-order uncertainty analyses were performed for simulations of both chamber characterization and aromatics experiments. First-order sensitivity coefficients indicating the response of ozone concentrations to small variations in each of 188 input parameters were calculated using the Direct Decoupled Method (33). The sensitivity coefficients were combined with uncertainty estimates for each of the parameters according to the standard propagation of errors formula. Based on the first-order analysis, the 23 parameters shown in Table 2 account for more than 95% of the uncertainties in the simulated O_3 concentrations for all 142 chamber experiments (Table 1).

For benzene, the first order analysis shows that uncertainties in the initial NO_x concentrations, but not the initial benzene concentrations, are influential to the uncertainty in the simulated ozone concentrations. For the other aromatic compounds, the initial NO_x concentrations have relatively little influence. The possible reason for this is that benzene is so non-reactive that it contributes little to the radical concentrations in the experiments. In contrast, the uncertainties in the initial concentations of the other aromatic compounds will significantly affect the radical levels in the experiments, which in turn affect the level of ozone formation. The first order sensitivity analysis also finds that ozone photolysis is not influential for the simulated ozone concentration in the chamber experiments, although this reaction was identified as an important parameter affecting reactivity estimates under some conditions (18).

Table 2. Influential Parameters Identified by First Order Sensitivity Analysis

Parameter	**Uncertainty Reference**	**Coefficient of Variance ($\sigma_i/\kappa_{i\ \mathrm{nominal}}$)**	**Chamber Char. Parameters**	**Aromatics Parameters**
A1. NO_2 + hv (light intensity)	Appendix B	CTC: 0.16 Others: 0.12	Y [a]	Y
A4. O_3 + NO	NASA 97 (36)	0.10	Y	Y
A5. O_3 + NO_2	NASA 97 (36)	0.14	Y	Y
A17. HONO + hv (action spectra)	NASA97 (36)	0.34 [e]	Y	Y
A18. NO_2 + OH	NASA 94 (35)	0.27	Y	Y
A23. HO_2 + NO	NASA 94 (35)	0.18	Y	Y
A25. HNO_4	NASA 94 (35)	2.40	Y	Y
C13. $CCOO_2$ + NO	NASA 97 (36)	0.34		Y
C14. $CCOO_2$ + NO_2	NASA 94 (35)	0.16		Y
C18. PAN	Bridier 91 (39) Grosjean 94 (40)	0.40		Y
G51. PHEN + NO_3	NASA 97 (36)	0.42		Y
G57. CRES + NO_3	AQIRP 94 (38)	0.75		Y
VOC + OH.	AQIRP 94 (38)		Y [b]	
Aromatics + OH.	AQIRP 94 (38)			Y [c]
initial concentration	Appendix B			Y [d]
RSI	this study			Y
HONO-F	this study			Y

[a] Y indicates the parameter is treated as a random variable in stochastic parameter estimation.

[b] For n-butane-NO_x experiments, the coefficient of variance for NC_4+OH is 0.18.
For CO-NO_x experiments, the coefficient of variance for CO+OH is 0.27.

[c] The coefficients of variance for aromatic compound+OH reactions are:

benzene + OH	0.27	toluene + OH	0.18
o-xylene + OH	0.23	m-xylene + OH	0.23
p-xylene + OH	0.31	ethylbenzene + OH	0.31
trimethylbenzene + OH	0.31		

[d] For benzene, the NO_x initial concentration is treated as a random variable. For other aromatics, the initial concentration of the aromatic compound is treated as a random variable.

[e] The action spectra (product of the cross sections and quantum yields) uncertainty, NASA97 (36)

2.5.2 Treatment of Uncertainties in Monte Carlo Simulations

Table 2 includes three different types of uncertainty. Random uncertainties such as those due to measurement imprecision vary independently from experiment to experiment. Systematic uncertainties are the same or highly correlated for all experiments carried out under the same conditions. An example is uncertainties due to instrument calibration errors in the reactant initial concentrations for the experiments conducted about the same time. The experiments with common systematic uncertainties have been assigned to groups (see Appendix B). Global uncertainties are the same in all simulations. An example is an uncertainty in a rate constant that does not depend on experimental conditions.

Parameters with random uncertainty are sampled independently for each experiment. With systematic uncertainties, the parameter for a given run is calculated as:

$$P^{i,k} = \overline{P}^{i} + \sigma^{i} \delta^{\mathrm{j,k}} \qquad \text{(EQ.7)}$$

where:

$P^{i,k}$ is the parameter value used in the kth Monte Carlo run for the ith experiment.

$\overline{P}^{i}$ is the nominal parameter value for the ith experiment.

σ^i is the uncertainty (standard deviation) of the parameter for the ith experiment.

δ is a measure of the extent to which the varied parameters in all experiments in a given group differ from the nominal values, relative to their uncertainties.

$\delta^{j,k}$ is the value for δ for the kth Monte Carlo run for the jth group of experiments.

For a parameter with both random and systematic uncertainties, the value is calculated as:

$$P^{i,k} = \overline{P}^{i} + \sigma^{i} \delta^{j,k} + \sigma_{\mathrm{r}}^{\mathrm{i}} \qquad \text{(EQ.8)}$$

where:

σ_r^i reflects the effect of the random uncertainty varying for the ith experiment.

For parameters with global uncertainties, the same sample value is used for all experiments for a given Monte Carlo run. We discuss how the samples are produced and applied for the two phases of parameter estimation in the following section.

In the chamber experiments, the uncertainties in the various photolysis rates are not independent. Photolysis rates in model simulations of chamber runs are calculated as the product of the NO_2 photolysis rate, which is measured for the experiment and characterizes the light intensity, and the ratio of the other photolysis rate to that of NO_2:

$$K_i = K_1 \times R_i \qquad \text{(EQ.9)}$$

where:

K_i is the photolysis rate for photolysis reaction i.

K_1 is the NO_2 photolysis rate which is measured for each experiments (see Appendix B)

R_i is the ratio of K_i to $K_{1.}$, which is calculated from the spectral distribution for the experiment and the relevant absorption cross-sections and quantum yields.

So, the variation of K_i should include the variation in the light intensity, which is represented by the variation of the NO_2 photolysis rate for each experiment, the variation in the spectral distribution and the variation in the relevant absorption cross-sections and quantum yields. When the uncertainties in the absorption cross sections and quantum yields are far larger than the uncertainties in the spectral distribution (e.g., for the reaction of HONO photolysis), the variation in the ratio due to the uncertainties in the spectral distribution can be ignored and the photolysis rate i in an experiment for a given run is calculated as:

$$K_i^k = K_1^{k,(j)} \times \frac{\overline{K}_i}{\overline{K}_1} \times f_i^k = \overline{K}_1(1+d^{(j)}s_1)\frac{\overline{K}_i}{\overline{K}_1} f_i^k \qquad \text{(EQ.10)}$$

where:

K_i^k is the value of the rate constant for photolysis reaction i of the kth Monte Carlo run.

$K_1^{k,(j)}$ is the value of the rate constant for NO_2 photolysis in the kth Monte Carlo run for the selected experiment, with the jth type of light source.

$\overline{K}_i$ is the nominal value for the rate constant for the photolysis reaction i.

$\overline{K}_1$ is the nominal value for the rate constant for NO_2 photolysis.

$\delta^{(j)}$ is a random variable with standard normal distribution for the jth type of light source.

σ_1 is the estimated standard deviation for the NO_2 photolysis rate

f_i is the uncertainty factor for the action spectrum of photolysis reaction i. The corresponding standard deviation is $\sigma_i = (f_i - 1.0/f_i)/2.0$.

f_i^k is the value of f_i of the kth Monte Carlo run

The NO_2 photolysis rate and associated uncertainties are given for each experiment in Appendix B. The estimated values for the uncertainty in the ratios due to the uncertainty in the spectral distributions are listed in Appendix B-3.

It is believed that the uncertainties in the reactant initial concentrations mainly come from the systematic uncertainty and that random uncertainties can be ignored. So their treatment follows EQ 7. Further details of the treatment of the uncertainties in the influential parameters identified in Table 2 are shown in Appendix C.

2.5.3 LHS Samples for Stochastic Parameter Estimation

There are several uncertain input variables that are influential for both chamber characterization and aromatics oxidation parameters (Table 2). The relationship between these influential input variables and the chamber characterization parameters must be maintained in estimating the aromatics oxidation parameters. For example, if the RSI value is negatively correlated with the NO_2 photolysis rate, this relationship must be maintained in estimating the aromatics oxidation parameters. To satisfy this requirement, LHS samples are produced including all of the parameters identified as influential for the two stages except RSI and HONO-F. The LHS sample thus includes the NO_2 photoysis rate for the blacklight chambers and the xenon arc chamber as two independent random variables. The reaction rate VOC+OH is included as a dummy variable with a standard normal distribution from which uncertainties for specific reaction rate constants are calculated. A distinct dummy variable with standard normal distribution is used to represent systematic uncertainty in the initial concentrations for each of the five groups of experiments. For aromatics oxidation parameter estimation, the estimated RSI and HONO-F from each run in the sample is added to that run to maintain the correct relationship between the chamber-characterization parameters and the input parameters.

The uncertainties for the reactions $CCOO_2$+NO and $CCOO_2$+NO_2 are treated as correlated with a correlation coefficient of 0.7. The uncertainties in the calculated photolysis rates are correlated with that in the NO_2 photolysis rate as expressed in (EQ.9). The other influential parameters are treated as random variables with independent lognormal distributions. Detailed information on the LHS samples is shown in Appendix C.

2.6 Linear Multivariate Regression Analysis

Linear multivariate regression analysis is applied to the Monte Carlo simulation results to identify the influence of individual uncertain input parameters on the outputs. The general regression model (EQ. 12) is a statistical tool to characterize the relationship between the dependent variable Y and a vector of independent variables, $\underline{X}$.

$$Y = \underline{X} \bullet \underline{b} = b_0 + \sum_{j=1}^{n} b_j \bullet \mathrm{x}_j \qquad \text{(EQ.11)}$$

where:

Y is the dependent variable.

$\underline{X}$ is a vector of independent variables assumed to be independent and normally distributed with the same variance. $\underline{X} = [1, x_1, x_2, \ldots x_n]^T$.

$\underline{\beta}$ is a vector of coefficients, which determine the extent, direction and strength of the association between Y and $\underline{X}$. $\underline{\beta}=[\beta_0, \beta_1, \beta_2, \ldots \beta_n]^T$

This model is usually generated by the least squares method to minimize the errors between the model prediction and the experimental data :

$$\min \quad \underline{e}^T \underline{e} = (\underline{Y} - \underline{\underline{X}}\,\underline{b})^T (\underline{Y} - \underline{\underline{X}}\,\underline{b}) \qquad \text{(EQ.12)}$$

where:

$\underline{\varepsilon}$ is the vector of error between the model prediction and the experimental data, with the independent normal distribution: $\underline{\varepsilon} \sim N(\underline{o}, \sigma\underline{I})$.

$\underline{Y}$ is the vector of the experimental data for the dependent variable.

$\underline{\underline{X}}$ is the matrix of the experimental data for the independent variables.

$\underline{\beta}$ is the vector of the coefficients.

The least squares method gives the optimal coefficients $\underline{\beta}$ as:

$$\underline{b} = (\underline{\underline{X}}^T \underline{\underline{X}})^{-1} \underline{\underline{X}}^T \underline{Y} \qquad \text{(EQ.13)}$$

This result can also be shown in terms of the correlation matrix between the independent variables. This can be derived from the standarized linear regression model (41):

$$Y' = \frac{Y - \overline{Y}}{S_Y} = \sum_{j=1}^{n} b'_j \frac{x_j - \overline{x_j}}{S_{x_j}} = \underline{b}'^T \underline{X}' \qquad \text{(EQ.14)}$$

where:

Y’ is the standardized dependent variable.

$\underline{X}$’ is the vector of the standardized independent variables. $\underline{X}$’ = [x_1’, x_2’, …. X_n’]^T.

$\underline{\beta}$’ is the vector of the standardized regression coefficients. $\underline{\beta}$’ = [β_1’, β_2’, ... β_n’]^T.

S_Y is the standard deviation for the dependent variable Y.

S_{xj} is the standard deviation for predictor variable x_j.

$\overline{Y}$ and $\overline{x}_j$ are mean values for Y and x_j, respectively.

The relationship between the standardized linear regression coefficient β_j’ in the standardized linear regression model (EQ 15) and the general linear regression coefficient β_j for the corresponding general linear regression model (EQ 13) is (42):

$$\frac{b_j'}{b_j} = \frac{S_{x_j}}{S_Y} \qquad \text{(EQ.15)}$$

The advantage of using standardized linear regression coefficients is that they indicate the contribution of the predictors to the total uncertainty of the dependent variable (42):

$$UC_j = \frac{b_j^2 S_{x_j}^2}{S_Y^2} \times 100 = \left(b_j'\right)^2 \times 100 \qquad \text{(EQ.16)}$$

where:

UC$_j$ is the contribution of the jth predictor to the uncertainty in dependent variable Y.

The standardized regression coefficients can be derived from the standardized regression model using the least squares method:

$$\underline{b'} = (\underline{\underline{X'}}^T \underline{\underline{X'}})^{-1} \underline{\underline{X'}}^T \underline{Y'} = \underline{\underline{g}}_{XX}{}^{-1} \underline{g}_{YX} \qquad \text{(EQ.17)}$$

where:

$\underline{\gamma}_{xx}$ is the correlation matrix of the independent variables $\underline{X}$. If the predictors are independent, $\underline{\gamma}_{xx}$ is just an identity matrix

$\underline{\gamma}_{Yx}$ is the vector of coefficients of simple correlation between the dependent variable Y and independent variables $\underline{x}$.

The least squares method can give the correct regression coefficients $\underline{\beta}$ (EQ. 13) and $\underline{\beta}$' (EQ. 17) when the predictors are independent, as assumed in deriving the above equations. If there exists collinearity in the independent variables, $\underline{\underline{X}}^T\underline{\underline{X}}$ and $\underline{\gamma}_{xx}$ are either not full rank, or are ill-conditioned. The result is that the coefficients obtained by the least squares method (EQ. 17) are not stable, meaning that small changes in the data will result in very large changes in the coefficients. Several methods are available to address multicollinearity problems, such as omitting the dependent predictors, or principle component analysis. The first method will lose some information for the regression model, especially when the objective is to estimate the contribution of the predictors to the dependent variable Y. The second method can be hard to interpret. Ridge regression is another choice, which includes all the predictors and addresses the multicollinearity problem by modifying the general least squares regression method (42).

Ridge regression introduces into the general least squares standardized regression model (EQ. 15) a biasing constant (c ≥ 0):

$$\underline{b'} = (\underline{g_{XX}} + c\underline{I})^{-1} \cdot \underline{g_{YX}} \qquad \text{(EQ.18)}$$

A biased estimator may well be the preferred estimator when it has only a small bias and is substantially more precise and stable than an unbiased estimator, since it will have a large probability of being close to the true parameter value (42). Since the SAPRC-97 photochemical mechanism is applied in all three stages of the analysis, there exists serious multicollinearity between the mechanism parameters, the chamber characterization parameters and the chamber-derived oxidation parameters. So ridge regression is applied in this study when the maximum variance inflation factor (VIF) obtained by the unbiased regression is larger than 3.0, which indicates the existence of multicollinearity (42).

3. Stochastic Parameter Estimation Results

In order to explore how experimental and modeling uncertainties affect reactivity estimates for aromatic compounds, stochastic programming (EQ 5) is applied for the chamber characterization parameters and aromatics oxidation parameters. Stochastic programming (Figure 2) provides the distributions of the optimal parameter values, which is the question that an uncertainty analysis must answer. This method can also assess the effects of the input uncertainties on the optimal estimates.

3.1 Parameter Estimation for Chamber Characterization Parameters

Chamber effects are important and can dominate the simulation results of certain types of experiments (17,25). Therefore, optimal estimates with uncertainties for the chamber characterization parameters are first calculated using stochastic programming by considering the uncertainties in the SAPRC-97 mechanism and the chamber characterization experiments. The influential parameters identified in Table 2 for the chamber characterization parameters are treated as random input variables for the Monte Carlo/LHS analysis used in the uncertainty loop.

The chamber characterization parameters in this study are the chamber-dependent radical source parameters RSI and HONO-F. Forty-two n-butane-NO_x or CO-NO_x experiments (Table 1) are used to estimate chamber characterization parameters. Because the chamber wall effects vary from run to run in a manner that is not always successfully predicted (20), some measure of the variability in the best fit chamber characterization parameters must be used as an input for the estimation of the chamber-derived aromatics oxidation parameters. In addition to input uncertainties, the overall uncertainty must reflect how the estimated chamber characterization parameters in a particular experiment vary from the mean of the values from all of the experiments. To account for this run-to-run variability, the method of optimizing parameters separately for each characterization experiment has been adopted. The confidence for the estimation results depends on the confidence in the measured data for that experiment. Then the average and variance for the estimated chamber characterization parameters for the kth Monte Carlo sample are calculated based on the estimated values and weight factors for every experiment:

$$\overline{P}_k = \frac{\sum_{i=1}^{N} W^i P_k^{\,i}}{\sum_{i=1}^{N} W^i} \qquad \text{(EQ.19)}$$

$$s_k = \sqrt{\frac{\sum_{i=1}^{N} W^i (P_k^{\,i} - \overline{P}_k)^2}{\sum_{i=1}^{N} W^i}} \qquad \text{(EQ.20)}$$

where:

$\overline{P}_k$ is the estimated mean value of the parameter P for the kth sample.

P_k^i is the estimated value for the parameter P for the kth sample from the ith experiment.

W^i is the weight factor for the ith experiment.

σ_k is the standard deviation for the estimated values for the parameter P in the kth sample.

The experimental average value and associated variance reported below for the estimated chamber characterization parameters is the average and variance of $\overline{P}_k$ across all of the Monte Carlo samples.

$$\overline{P} = \frac{\sum_{s=1}^{NS} \overline{P}_s}{NS} \qquad \text{(EQ.21)}$$

:

$$s_p = \sqrt{\frac{\sum_{s=1}^{NS} (\overline{P}_s - \overline{P})^2}{NS - 1}} \qquad \text{(EQ.22)}$$

Where:

$\overline{P}$ is the estimated mean value of the parameter P.

σ_p is the standard deviation for the estimated values for the parameter P.

NS is the sample size.

Based on the techniques described in the previous section, the mean and standard deviation of the probability distributions of the chamber characterization parameters for each individual experiment are obtained and listed in Appendix B-2. Table 3 shows the mean and standard deviation from 160 Monte Carlo samples for RSI and HONO-F values averaged over the experiments in each of the five UCR chamber configurations. The table also shows the values of the parameters used previously in SAPRC-97 (16), which were estimated from the same experimental data but without accounting for uncertainty.

Table 3. Chamber Characterization Parameters, ($\overline{P}$) Estimated with Stochastic Programming

Chamber	**Number of Experiments**	**RSI (ppb)**		**HONO-F (%)**	
		SAPRC-97	**This Study** **Mean ± σ (COV)**[c]	**SAPRC-97**	**This Study** **Mean ± σ (COV)**[c]
DTC1	2 [a]	0.057	0.058 ± 0.014 (24%)	0.0	0.012 ± 0.047 (384%)
DTC2	6 [a]	0.170	0.155 ± 0.048 (31%)	0.0	0.269 ± 0.073 (27%)
DTC3	9 [a]	0.060	0.052 ± 0.018 (35%)	0.0	0.644 ± 0.188 (29%)
ITC	4 [a]	0.080	0.066 ± 0.024 (36%)	0.0	3.286 ± 0.264 (8%)
CTC	17 [a] and 4 [b]	0.070	0.055 ± 0.016 (29%)	0.0	0.459 ± 0.207 (45%)

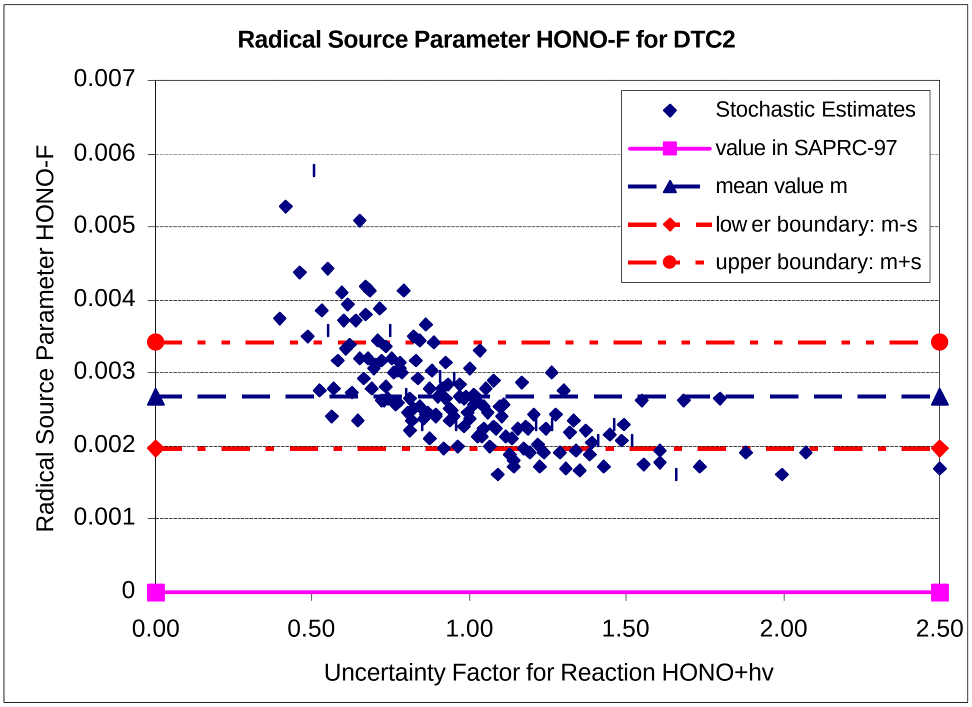
[a] N-butane-NO_x experiments.

[b] CO-NO_x experiments.

[c] Values shown are the mean and standard deviation of 160 Monte Carlo samples for RSI and HONO-F values averaged over the experiments in each chamber. COV=Coefficient of Variation.

The results for RSI are in fairly close agreement with the nominal values used in SAPRC-97. However, the best estimates for HONO-F are not zero as assumed in SAPRC-97. Figure 3 and Table 4 show the stochastic estimation and regression analysis results for the DTC2 chamber as an example. The points shown in Figure 3 are the optimal parameter values obtained with each Monte Carlo/LHS sample. Superimposed on the plots are lines indicating the nominal parameter value from the SAPRC-97 mechanism, and the mean values and mean ± 1σ from the Monte Carlo results. The abscissas in Figure 3 are chosen as the uncertainty factors for the rate parameters of the reactions HONO+hv and NO_2+OH respectively, because they have a strong relationship with the estimated parameters, as shown by the regression results in Table 4. Since the parameters are estimated by matching the experimental O_3 and NO concentrations, the radical concentrations required to match O_3 and NO can be considered fixed. So, when the rate parameter for

HONO+hv is lower, a higher HONO concentration and thus a higher HONO-F value is needed to produce the required initial radical concentrations. Later in the runs, additional radicals are needed to match the O_3 and NO concentrations and they are produced by chamber wall effects represented by RSI. So, with a higher reaction rate for the radical sink reaction NO_2+OH, a larger radical source is required and in turn a higher RSI value is obtained (Figure 3).



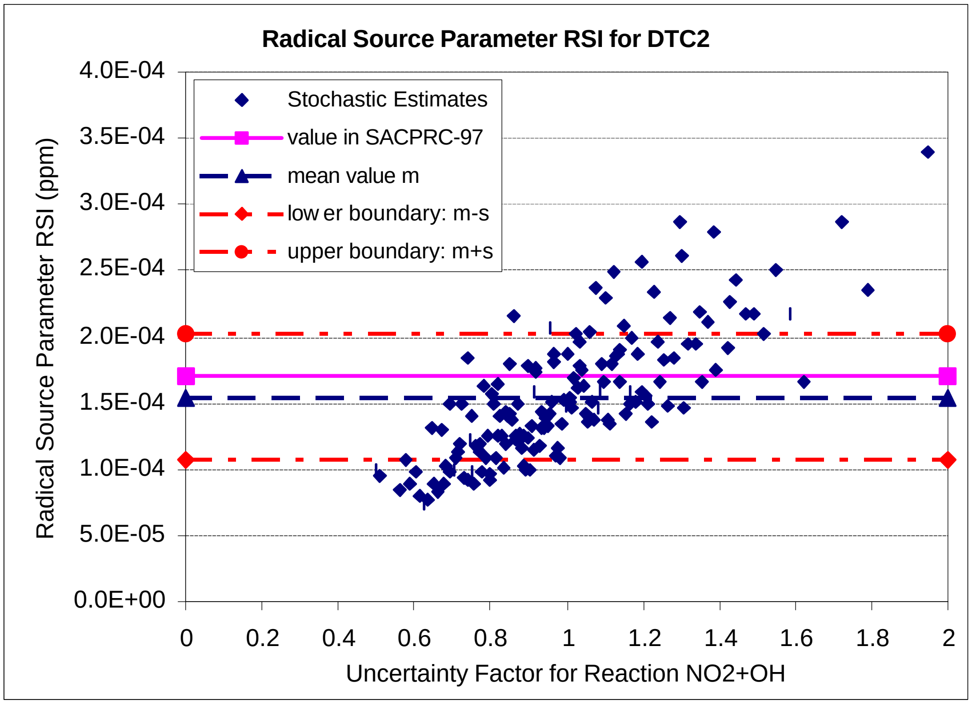


Figure 3. Stochastic Parameter Estimation Results for Chamber Characterization Parameters for DTC2 (160 LHS Samples applied to 6 Chamber Experiments).
(In legend, m represents mean value, s represents standard deviation)

Table 4. Regression Analysis Results for Chamber Characteristic Parameters for DTC2

Parameter	**Input Uncertainty** **($\sigma_i/\kappa_{i\ \text{norminal}}$)**	**HONO-F** [a] Standardized Regression Coefficient [b] (Rank)	**RSI** [a] Standardized Regression Coefficient [b] (Rank)
A1. NO_2 + hv -> (light intensity)	0.12 [c]	-0.42 (2)	-0.37 (3)
A4. O_3 + NO ->	0.10 [d]	0.00	0.07
A5. O_3 + NO_2 ->	0.14 [d]	0.04	0.00
A17. HONO + hv -> (action spectrum)	0.34 [d]	-0.75 (1)	-0.07
A18. NO_2 + OH ->	0.27 [d]	-0.23 (4)	0.78 (1)
A23. HO_2 + NO ->	0.18 [d]	0.00	0.01
A25. HNO_4 ->	2.40 [d]	-0.07	-0.01
159. N-butane + OH. ->	0.18 [d]	-0.32 (3)	-0.47 (2)
Adjusted R^2		**0.89**	**0.97**

[a] The regression model is for normalized predictors.
[b] Standardized regression coefficient $\beta j'$
[c] The uncertainty factor is recommended by Carter, 1998 (25), Appendix B-2
[d] The uncertainty factors are taken from NASA-97 (38), NASA-94 (37), AQIRP-94 (40). Lognormal distributions were assumed.

Stochastic estimation and regression results for the chamber characterization parameters for the other chambers are presented in Appendix D-1. As summarized in Table 3, the uncertainty (1σ relative to the mean) for the chamber characterization parameter RSI is fairly consistent (24 to 36%) for the five different chambers, while the uncertainty (1σ) for the chamber characterization parameter HONO-F varies greatly (from 8% for ITC to 384% for DTC1). Moreover, the absolute value for HONO-F also varies significantly for the five chambers. The variability from experiment to experiment for the estimated RSI values for individual Monte Carlo samples is about 10% for the DTC1 chamber, 10-30% for DTC2, 20-45% for DTC3, 7-20% for the ITC chamber and 33-55% for the CTC chamber. The experimental variability for the estimated HONO-F values is also significant, ranging from 10-118% for the DTC1 chamber, 140-210% for DTC2, 22-85% for DTC3, 130-170% for the ITC chamber, and 70-400% for the CTC chamber. Only the CTC chamber uses both n-butane-NO_x and CO-NO_x experiments to derive the chamber characteristic parameters. Figures D1-6 and D1-7 in Appendix D-1 show that the CO-NO_x experiments give RSI values that average about 30% higher and HONO-F values that average more than 50% lower than those from n-butane-NO_x experiments.

According to the standardized linear regression coefficients, the most influential sources of uncertainty affecting the experimental average values of RSI are the reaction rate constants for NO_2+OH, NO_2+hv, and n-butane+OH or CO+OH. The regression results for RSI are consistent across all five chambers. The most influential parameters for the average HONO-F values in the DTC and CTC chambers are the rate parameters for HONO+hv (action spectra), n-butane+OH, NO_2+OH and NO_2+hv. The decomposition rate for HNO_4 is also influential for HONO-F in the ITC chamber. The parameters found to be influential seem reasonable because the associated reactions are either radical sources or sinks, or are directly related to the chamber characteristic parameters. These factors need to be considered carefully in the design of future chamber characterization runs.

3.2 Parameter Estimation for Aromatics Oxidation Parameters

The optimal estimates and the associated uncertainty levels for the aromatics oxidation parameters are estimated considering the uncertainties in the SAPRC-97 mechanism, the chamber characterization parameters and the experimental conditions. The chamber-derived aromatics oxidation parameters for benzene are B1U1 and P1U1. For the other aromatics, the chamber-derived oxidation parameters are B1U2 and B1MG under the condition of fixed AFG2 quantum yield. One hundred single aromatic compound-NO_x experiments (Table 1) are used in this stage with some specific considerations. First, the relationship between the influential reaction rates and the optimal values of the chamber characterization parameters is maintained as described in the methods section. Second, since the chamber-derived oxidation parameters for aromatic compounds are mechanism parameters, their “true values” should not depend on which chamber and experiment are used to estimate them. To decrease the dependence of the estimated parameters on specific chambers and experiments, several single aromatic compound-NO_x experiments conducted in different chambers are used for each aromatic compound. The objective function for the estimation is to minimize the difference in the simulation results and experimental data over all of the experiments used for a particular aromatic compound, which is exactly the problem described by EQ.6. Finally, the dependence of the estimates for the aromatics oxidation parameters on the value for the AFG2 photolysis quantum yield is studied and discussed in the following section.

Table 5. Aromatics Oxidation Parameters Estimated Using Stochastic Programming

Compound	**Number of Experiments**	**P1 = B1U1/B1U2** [a]		**P2 = P1U1/B1MG** [b]	
		SAPRC97	**This Study Mean ± σ (COV%)**	**SAPRC97**	**This Study Mean ± σ (COV%)**
Benzene	7	1.44	1.446 ± 0.477 (33%)	0.077	0.088 ± 0.034 (40%)
Toluene	10	0.260	0.283 ± 0.097 (34%)	0.964	1.022 ± 0.319 (31%)
Ethylbenzene	8	0.180	0.216 ± 0.096 (44%)	0.199	0.244 ± 0.154 (63%)
p-xylene	11	0.150	0.184 ± 0.083 (45%)	0.168	0.220 ± 0.156 (71%)
m-xylene	22	0.460	0.478 ± 0.156 (33%)	1.599	1.753 ± 0.549 (31%)
o-xylene	12	0.580	0.650 ± 0.195 (30%)	0.806	0.856 ± 0.371 (43%)
123-trimethylbenzene	9	0.660	0.803 ± 0.311 (39%)	1.120	1.080 ± 0.389 (36%)
124-trimethylbenzene	10	0.260	0.303 ± 0.122 (40%)	0.405	0.494 ± 0.242 (49%)
135-trimethylbenzene	11	0.610	0.776 ± 0.311 (40%)	1.164	1.073 ± 0.308 (29%)

[a] The first chamber-derived oxidation parameter P1 is B1U1 for benzene or B1U2 for the other aromatic compounds.

[b] The second chamber-derived oxidation parameter P2 is P1U1 for benzene or B1MG for the other aromatic compounds.

Given the correct LHS samples and 1.0 as the fixed value of the AFG2 quantum yield, stochastic programming gives the distributions for aromatics oxidation parameters, whose mean values and standard deviations are shown in Table 5. The detailed stochastic estimation results are shown in Appendix D-2. The regression analysis results for benzene and toluene are shown in

Tables 6 and 7 as examples. The regression analysis results for other aromatic compounds are shown in Appendix D-2.

Table 6. Regression Analysis for Chamber-Derived Oxidation Parameters for Benzene[a] (Top 7 of 17 Total Random Variables Included for Each Parameter)

Uncertain Input Parameter	**Coefficient of Variance ($\sigma_i/\kappa_{i\ \mathrm{nominal}}$)**	**B1U1 Standardized Regression Coefficient (Rank)**	**P1U1 Standardized Regression Coefficient (Rank)**
NO_2 + hv -> (CTC) (light intensity)	0.16	-0.13 (7)	-0.12 (4)
NO_2 + hv -> for ITC (light intensity)	0.12	0.14 (6)	0.10
NO_2 + OH. ->	0.27	0.28 (3)	0.33 (2)
HNO_4 ->	2.40	0.11	-0.28 (3)
NO_3 + PHEN ->	0.42	-0.05	0.10 (7)
benzene + OH. ->	0.27	-0.33 (1)	-0.55 (1)
HONO-F for CTC	0.46	-0.21 (5)	-0.09
HONO-F for ITC	0.08	0.23 (4)	-0.11 (6)
initial NO_x concentration for ITC (Grp. 1)	0.25–0.28	0.30 (2)	-0.11 (5)
Adjusted R^2		**0.56**	**0.79**

[a] Ridge regression model for normalized predictors.

Table 7. Regression Analysis for Chamber-Derived Oxidation Parameters for Toluene[a] (Top 8 of 23 Total Random Variables Included for Each Parameter)

Uncertain Input Parameter	**Coefficient of Variance** **($\sigma_i/\kappa_{i\ \mathrm{nominal}}$)**	**B1U2** **Standardized Regression Coefficient (Rank)**	**B1MG** **Standardized Regression Coefficient (Rank)**
NO_2 + hv -> for CTC (light intensity)	0.16	0.05	-0.30 (3)
NO_2 + hv -> for DTC (light intensity)	0.12	-0.14 (3)	0.11 (8)
HONO + hv -> (action sprctrum)	0.34	-0.05	-0.20 (6)
NO_2 + OH. ->	0.27	0.52 (1)	0.45 (2)
HNO_4 ->	2.40	-0.12 (5)	-0.03
CCOO2 + NO ->	0.34	-0.11 (6)	-0.06
PAN ->	0.40	-0.10 (7)	-0.02
toluene + OH. ->	0.18	-0.52 (2)	-0.53 (1)
RSI for CTC	0.29	0.09 (8)	-0.29 (4)
HONO-F for CTC	0.45	0.07	-0.27 (5)
initial toluene concentration for DTC1 (Grp. 1)	0.05	-0.12 (4)	0.03
initial toluene concentration for CTC (Grp. 3)	0.06	0.05	-0.11 (9)
initial toluene concentration for CTC (Grp. 4)	0.06	0.04	-0.19 (7)
Adjusted R^2		**0.93**	**0.92**

[a] Ridge regression model for normalized predictors.

The average agreement between values used in SAPRC-97 and the mean values of the aromatics parameters estimated with stochastic programming is about 15%. The uncertainties (1σ relative to the mean) for B1U2 are fairly constant (30 - 45%) for all of the aromatic compounds studied, while the uncertainties for B1MG vary from 29% for 135-trimethylbenzene to 63% for ethylbenzene and 71% for p-xylene. Influential contributors to the uncertainty in B1U1 for benzene are the uncertainties in rate constants for the reactions benzene+OH, NO_2+OH, NO_2 photolysis (or light intensity) for both chambers (CTC and ITC) the uncertainties in the initial concentrations for NO_x for the ITC, and the chamber characterization parameter HONO-F for both chambers. The values of the chamber characterization parameter HONO-F for the two chambers have opposite effects on B1U1 with almost the same contributions. The same parameters, plus the rate constants for the HNO_4 dissociation reaction and PHEN+NO_3 reaction, are also influential contributors to the uncertainty in P1U1 for benzene. The chamber characterization parameter HONO-F and the initial NO_x concentrations for the ITC chamber are also found to be influential for P1U1. However, the chamber characterization parameters for the CTC chamber are not as important for P1U1. The initial NO_x concentrations for the CTC chamber are not influential to the chamber-derived oxidation parameters for benzene.

The influential contributors to the uncertainties in B1U2 for the other aromatic compounds are fairly consistent across compounds, and include uncertainties in the rate constants for the reactions of the aromatics+OH, NO_2+OH, NO_2 photolysis for the DTC chambers, PAN formation and decomposition, and HNO_4 decomposition. The uncertainties in the initial concentrations for the aromatic compounds and in the chamber characterization parameters for the DTC chambers are also influential. The regression results also show that the aromatics oxidation parameters are not sensitive to the chamber characterization parameters for the CTC. Usually, the effects on B1U2 of the chamber characterization parameter RSI for the DTC chambers are more important than those of the HONO-F values for the DTC chambers. One exception is 135-trimethylbenzene, for which B1U2 is more sensitive to HONO-F values in the DTC chambers than to RSI values in the same chambers.

Generally, major contributors to the uncertainty in the aromatics oxidation parameter B1MG are the uncertainties in the rate constants for the reactions of the aromatics+OH, HONO photolysis, NO_2+OH, NO_2 photolysis (or light intensity) for both chambers used (CTC and DTC), and the uncertainties in the initial concentrations and in the chamber characterization parameters (RSI and HONO-F for CTC chambers, and RSI for DTC chambers). The NO_2 photolysis rate in the DTC chambers has positive effects on B1MG, while the NO_2 photolysis rate in the CTC has negative effects on B1MG. The same opposing effects on B1MG are also found in the chamber characterization parameters: RSI and HONO-F for the CTC chamber have negative relationships with B1MG, while RSI for the DTC2 chamber has a positive relationship with B1MG. The effects on B1MG of RSI and HONO-F in the CTC are almost the same. It is also found that B1MG values for ethylbenzene, 124-trimethylbenzene and 135-trimethylbenzene are sensitive to the HNO_4 dissociation rate constant. A special case is that of 135-trimethylbenzene (see Appendix D-2). In this case, the effects of uncertainties in the rate constants for the reaction 135-trimethylbenzene+OH, HONO photolysis and NO_2+OH are negligible, while the uncertainty in the initial aromatics concentrations for the CTC chambers are the most influential factors. Also, uncertainties in the rate constants for PAN decomposition, O_3+NO and uncertainty in the HONO-F value in the DTC chambers are influential.

3.3 Effects of the AFG2 Quantum Yield on Aromatics Oxidation Parameters

The aromatics oxidation parameter values given in Table 5 are calculated using a value of 1.0 for the AFG2 quantum yield, P1U2, as recommended in the SAPRC-97 mechanism. The effects of the value of P1U2 on the estimates for the aromatics oxidation parameters were investigated by simultaneously estimating the three parameters P1U2, B1U2 and B1MG. The effect was further studied by calculating how B1U2 and B1MG values change when the P1U2 value is set to 0.9 instead of 1.0. Results for the three parameter (P1U2, B1U2, and B1MG) estimation problem are given in Table 8. Results for the two parameter estimation problem for B1U2 and B1MG with the AFG2 quantum yield set to 0.9 are given in Table 9.

Table 8. Stochastic Estimates for Three Aromatics Oxidation Parameters

Compound	No. of Experiment	P1 = B1U2 2 Para. Est. 3 Para. Est. Mean (COV)	P2 = B1MG 2 Para. Est.. 3 Para. Est Mean (COV)	P3 = P1U2 SAPRC97 3para. Est. Mean (COV)
Toluene	10	0.283 (34%)	1.022 (31%)	1.0
		0.297 (38%)	1.033 (32%)	0.927 (15%)
Ethylbenzene	8	0.216 (44%)	0.244 (63%)	1.0
		0.292 (47%)	0.305 (59%)	0.579 (27%)
p-xylene	11	0.184 (45%)	0.220 (71%)	1.0
		0.390 (73%)	0.271 (63%)	0.394 (48%)
m-xylene	22	0.478 (33%)	1.753 (31%)	1.0
		0.493 (34%)	1.761 (30%)	0.950 (12%)
o-xylene	12	0.650 (30%)	0.856 (43%)	1.0
		0.666 (31%)	0.872 (44%)	0.961 (10%)
123-tmbenzene	9	0.803 (39%)	1.080 (36%)	1.0
		0.856 (33%)	1.120 (33%)	0.895 (19%)
124-tmbenzene	10	0.303 (40%)	0.494 (49%)	1.0
		0.543 (49%)	0.594 (44%)	0.426 (40%)
135-tmbenzene	11	0.776 (40%)	1.067 (29%)	1.0
		0.860 (31%)	1.087 (29%)	0.837 (25%)

Table 9. Sensitivity of the Optimal Values of Aromatics Oxidation Parameters B1U2 and B1MG to the AFG2 Quantum Yield

Compound	No. of Experiment	P1 = B1U2 P1U2=1.0 [a] P1U2=0.9 [b] Mean (COV)	P2 = B1MG P1U2=1.0[a] P1U2=0.9[b] Mean (COV)	Sensitivity[c] (%Δ/%ΔP1U2)	
				B1U2	B1MG
Toluene	10	0.283 (34%)	1.022 (31%)	-0.39	-0.20
		0.294 (34%)	1.042 (31%)		
Ethylbenzene	8	0.216 (44%)	0.244 (63%)	-0.51	-0.45
		0.227 (44%)	0.255 (62%)		
p-xylene	11	0.184 (45%)	0.220 (71%)	-0.60	-0.23
		0.195 (45%)	0.225 (72%)		
m-xylene	22	0.478 (33%)	1.753 (31%)	-0.50	-0.17
		0.502 (33%)	1.782 (30%)		
o-xylene	12	0.650 (30%)	0.856 (43%)	-0.51	-0.42
		0.683 (30%)	0.892 (43%)		
123-tmbenzene	9	0.803 (39%)	1.080 (36%)	-0.62	-0.33
		0.853 (38%)	1.116 (35%)		
124-tmbenzene	10	0.303 (40%)	0.494 (49%)	-0.53	-0.26
		0.319 (40%)	0.507 (49%)		
135-tmbenzene	11	0.776 (40%)	1.067 (29%)	-0.59	-0.28
		0.822 (39%)	1.103 (29%)		

[a] The parameters (Pi_a) are estimated assuming the value for the AFG2 quantum yield $P1U2_a$ is 1.0.

[b] The parameters (Pi_b) are estimated assuming the value for the AFG2 quantum yield $P1U2_b$ is 0.9.

[c] The sensitivity is calculated as $[(Pi_b - Pi_a)/Pi_a]/[(P1U2_b - P1U2_a)/P1U2_a]$

The results from the three parameter estimation indicate that for toluene, m-xylene and o-xylene, the optimal value for the AFG2 quantum yield is about 0.95 with an uncertainty level of about 12%. For these compounds, the corresponding optimal values for B1U2 and B1MG are within 5% of the values estimated with the AFG2 quantum yield set to 1.0. For 123-trimethylbenzene and 135-trimentylbene, the optimal AFG2 quantum yield is about 0.85, with an uncerainty level of about 20%. The corresponding values for B1U2 and B1MG are within about

10% of the values estimated with the AFG2 quantum yield set to 1.0. Ethylbenzene, p-xylene and 124-trimethylbenzene have optimal values for the AFG2 quantum yield ranging from 0.4 to 0.6 with uncertainty levels of about 30 to 50%. Thus these values are significantly different from the recommended AFG2 quantum yield, and the uncertainties for the aromatics oxidation parameters of these three compounds are higher than those for other aromatic species. We also note that values of B1U2 are more sensitive to the AFG2 quantum yield than are values of B1MG.

The sensitivity analysis results shown in Table 9 indicate that the effects of the AFG2 quantum yield on the optimal B1U2 values are similar for all of the aromatics except toluene: a 1% decrease in the AFG2 quantum yield causes about a 0.55% increase in B1U2. The B1U2 value for toluene is less sensitive to the AFG2 quantum yield. The effects of a 1% decrease in the AFG2 quantum yield on the B1MG values range from a 0.17% increase for m-xylene to a 45% increase for ethylbenzene. These results indicate that most of the aromatics oxidation parameters are sensitive to the value used for the AFG2 quantum yield. However, for toluene, m-xylene and o-xylene, the optimal value of the AFG2 quantum yield is close to 1.0, so the practice of fixing this value while optimizing the B1U2 and B1MG parameters appears to be adequate. In contrast, the cases of ethylbenzene, p-xylene, and 124-trimethylbenzene warrant further study.

4. Incremental Reactivity Estimates

In this section, reactivity estimates of selected aromatic compounds and other VOCs are presented, which account for both experimental and modeling uncertainties. The Monte Carlo/LHS method is applied to estimate uncertainties in MIRs, MOIRs and EBIRs calculated with the SAPRC-97 mechanism. A total of 102 uncertain input parameters are treated as random variables in the reactivity calculations. These 102 parameters include those determined in a previous study to account for more than 98% of the total variance of the output concentrations of O_3, PAN, HCHO, HO, and H_2O_2 under MIR conditions (18). Simulation conditions for the MIR, MOIR and EBIR calculations are shown in Table 10. They represent the average conditions from 39 cities (43). Methods for calculating incremental reactivities and associated uncertainties are the same as those described by Yang et al. (18).

Table 10. Simulation Conditions for MIR, MOIR and EBIR Cases

Latitude	36.22 N	Temperature	296 - 305 K
Declination	16.5	Total HC [a]	15.38 mmol m^{-2} day $^{-1}$
Time	8 am to 6 pm	Total NO_x (for MIR) [a]	4.561 mmol m^{-2} day $^{-1}$
Mixing Height	293 - 1823 m	Total NO_x (for MOIR) [a]	3.028 mmol m^{-2} day $^{-1}$
Photolysis Hgt.	640 m	Total NO_x (for EBIR)	2.059 mmol m^{-2} day $^{-1}$

Initial and Aloft Concentrations (ppm) for Base Mixture [b]

Species	**initial**	**Aloft**	**species**	**initial**	**aloft**
NO_2 (MIR)	4.29×10^{-2}	0.0	HCHO	6.48×10^{-3}	2.25×10^{-3}
NO (MIR)	1.29×10^{-1}	0.0	CCHO [d]	3.90×10^{-3}	3.23×10^{-4}
HONO (MIR)	3.50×10^{-3}	0.0	RCHO [e]	2.30×10^{-3}	0.0
NO_2 (MOIR)	2.85×10^{-2}	0.0	ACET	2.52×10^{-3}	0.0
NO (MOIR)	8.55×10^{-2}	0.0	MEK	8.98×10^{-4}	0.0
HONO (MOIR)	2.33×10^{-3}	0.0	BALD	1.34×10^{-4}	0.0
O_3	0.0	7.04×10^{-2}	ALK1 [f]	5.53×10^{-2}	3.55×10^{-3}
CO	2.03	0.5	ALK2 [f]	1.64×10^{-2}	1.64×10^{-4}
CO_2 [c]	330	330	ARO1 [g]	1.11×10^{-2}	2.22×10^{-4}
H_2O	$1.99\times10^{+4}$	0.0	ARO2 [g]	1.34×10^{-2}	1.11×10^{-4}
methane [c]	1.79	1.79	OLE1 [h]	1.10×10^{-2}	4.67×10^{-4}
isoprene	1.26×10^{-3}	1.09×10^{-4}	OLE2 [h]	8.86×10^{-3}	8.09×10^{-5}
α–pinene	1.0×10^{-4}	0.0	OLE3 [h]	1.03×10^{-2}	0.0
Unknown biogenic	1.0×10^{-4}	0.0			

[a] Initial concentrations plus total emissions. Of the total HC, 60.4% is present as initial concentrations and the rest is emitted during the 10-h simulation. Of the total NO_x, 45.7% is present initially with the rest emitted.

[b] For incremental reactivity calculations, initial concentrations equal to 4.76×10^{-5} ppm are added for each of 30 explicit organic compounds or classes.

[c] Constant concentration species.

[d] Acetaldehyde

[f] Lumped classes of alkanes

[g] Lumped classes of aromatics

[e] Propionaldehyde and higher aldehydes [h] Lumped classes of alkenes

The uncertainty estimates for the input parameters are shown in Table 11. These estimates are updated from those used by Yang et al. (18) and include the chamber-derived estimates for aromatics oxidation parameters described above. For the aromatics oxidation parameters, the Monte Carlo calculations incorporate the correlation between the input uncertainty factors and the stochastic parameter estimation results. For example, the negative correlation between the rate constant of the reaction of toluene+OH and the parameters B1U1 and B1MG (Table 7) is preserved in the Monte Carlo/LHS sampling used to calculate the reactivities. In order to keep the correct correlation of the chamber-derived oxidation parameters for the lumped aromatics species (ARO1 and ARO2) with the chamber-derived oxidation parameters for the explicit aromatic compounds and with the rate constants for the reactions ARO1+OH and ARO2+OH, the chamber-derived oxidation parameters for the lumped aromatics species for each sample are calculated from the chamber-derived oxidation parameters for the explicit aromatic compounds for the corresponding sample. Then the uncertainty factors for the rate constants of ARO1+OH and ARO2+OH for that sample are calculated through the correlation between these parameters and the corresponding chamber-derived oxidation parameters. For example,

$$y = rx + z\sqrt{1-r^2} \quad \text{(EQ. 23)}$$

where:

y is the normalized uncertainty factor with normal distribution for reaction ARO2+OH

x is the standard normalized chamber derived oxidation parameter B1U2 for ARO2

r is the correlation between B1U2 for ARO2 and reaction ARO2+OH

z is a dummy random variable with standard normal distribution.

The preserved correlations between the chamber-derived oxidation parameters and the reaction rate constants are shown in Table 12. The correlation coefficients listed in Table 12 were obtained from unbiased regression analysis, which only included the independent reaction rate constants as predictor variables. These correlation coefficients differ slightly from the ridge regression results given in Tables 6 and 7, but avoid introducing bias into the reactivity calculations. Because we cannot use the same samples as in the previous stages to preserve the correlations for the input parameters, only the strong correlations (larger than 0.3) are preserved. LHS can only accurately reproduce a limited number of pairwise correlations.

Table 11. Uncertainties for SAPRC-97 Input Parameters for Reactivity Calculations

Reaction or Coefficients	**Coefficient of Variance ($\sigma_i/\kappa_{i\ nominal}$)**	**Reaction or Coefficients**	**Coefficient of Variance ($\sigma_i/\kappa_{i\ nominal}$)**
O_3 + NO ->	0.10 $^{(2)a}$	2-methylpentane + OH ->	0.23 $^{(3)}$
$O^1D + H_2O$ ->	0.18 $^{(2)}$	m-cyclopentane + OH ->	0.27 $^{(3)}$
O^1D + M ->	0.18 $^{(2)}$	methanol + OH ->	0.18 $^{(5)}$
NO_2 + OH ->	0.27 $^{(1)}$	ethanol + OH ->	0.18 $^{(5)}$
CO + OH ->	0.27 $^{(2)}$	ethene + OH ->	0.11 $^{(2)}$
HO_2 + NO ->	0.18 $^{(1)}$	propene + OH ->	0.14 $^{(3)}$
$HO_2 + HO_2$ ->	0.27 $^{(2)}$	isopene + OH ->	0.19 $^{(3)}$
$HO_2 + HO_2 + H_2O$ ->	0.27 $^{(1)}$	1,3-butadiene + OH ->	0.19 $^{(3)}$
RO_2 + NO ->	0.42 $^{(2)}$	2-m-1-butene + OH ->	0.18 $^{(3)}$
$RO_2 + HO_2$ ->	0.75 $^{(2)}$	2-m-2-butene + OH ->	0.18 $^{(3)}$
CRES + NO_3 ->	0.75 $^{(3)}$	224-TM-C5 + OH ->	0.18 $^{(3)}$
HCHO + OH ->	0.23 $^{(2)}$	MTBE + OH ->	0.18 $^{(5)}$
CCHO + OH ->	0.18 $^{(2)}$	ETBE + OH ->	0.18 $^{(5)}$
RCHO + OH ->	0.35 $^{(3)}$	ethene + O_3 ->	0.23 $^{(2)}$
CCOO2 + NO ->	0.34 $^{(2)}$	propene + O_3 ->	0.18 $^{(1)}$
CCOO2 + NO_2 ->	0.16 $^{(1)}$	isoprene + O_3 ->	0.35 $^{(3)}$
CCOO2 + HO_2 ->	0.75 $^{(2)}$	1,3-butadiene + O_3 ->	0.42 $^{(3)}$
CCOO2 + RO_2 ->	0.75 $^{(3)}$	2-m-1-butene + O_3 ->	0.35 $^{(3)}$
C2COO2 + NO_2 ->	0.75 $^{(3)}$	2-m-2-butene + O_3 ->	0.42 $^{(3)}$
PPN ->	0.66 $^{(4)}$	Trans-2-butene ->	0.42 $^{(3)}$
PAN ->	0.40 $^{(4)}$	α-pinene + O_3 ->	0.42 (3)
NO_2 + hv -> (action spectra)^b	0.18 $^{(2)}$	ALK2 + OH ->	0.27 $^{(3)}$
NO_3 + hv ->^{b}	0.42 $^{(1)}$	ARO1 + OH ->	0.27 $^{(3)}$
O_3 + hv -> ^{b}	0.27 $^{(2)}$	ARO2 + OH ->	0.27 $^{(3)}$
HCHO + hv ->^{b}	0.34 $^{(2)}$	OLE2 + OH ->	0.18 $^{(3)}$
CCHO + hv ->^{b}	0.34 $^{(3)}$	OLE2 + O_3 ->	0.42 $^{(3)}$
RCHO + hv ->^{b}	0.34 $^{(3)}$	OLE3 + OH ->	0.23 $^{(3)}$
MEK + hv ->^{b}	0.42 $^{(3)}$	OLE3 + O_3 ->	0.42 $^{(3)}$
acetone + hv ->	0.34 (3)	P1U1 ^{c}	0.40 $^{(5)}$
BALD + hv ->	0.42 $^{(3)}$	SC(AFG1,benzene) ^{d}	0.33 $^{(5)}$
benzene + OH ->	0.27 $^{(3)}$	SC(AFG2,toluene) ^{e}	0.34 $^{(5)}$
toluene + OH ->	0.18 $^{(3)}$	SC(MGLY,toluene) ^{f}	0.31 $^{(5)}$

Table 11. (Cont'd) Uncertainties for SAPRC-97 Input Parameters for Reactivity Calculations

Reaction or Coefficients	**Coefficient of Variance ($\sigma_i/\kappa_{i\ nominal}$)**	**Reaction or Coefficients**	**Coefficient of Variance ($\sigma_i/\kappa_{i\ nominal}$)**
ethylbenzene + OH	0.31 (3)	SC(AFG2,ethylbenzene)	0.44 (5)
1,2,3-trimethylbenzene + OH ->	0.31 (3)	SC(MGLY,ethylbenzene)	0.63 (5)
1,2,4-trimethylbenzene + OH ->	0.31 (3)	SC(AFG2,123-TMB)	0.39 (5)
1,3,5-trimethylbenzene + OH ->	0.31 (3)	SC(MGLY,123-TMB)	0.36 (5)
p-xylene + OH ->	0.31 (3)	SC(AFG2,124-TMB)	0.40 (5)
o-xylene + OH ->	0.23 (3)	SC(MGLY,124-TMB)	0.49 (5)
m-xylene + OH ->	0.23 (3)	SC(AFG2,135-TMB)	0.40 (5)
methane + OH ->	0.10 (2)	SC(MGLY,135-TMB)	0.29 (5)
ehtane + OH ->	0.10 (2)	SC(AFG2,p-xylene)	0.45 (5)
propane + OH ->	0.18 (2)	SC(MGLY,p-xylene)	0.71 (5)
trans-2-butene ->	0.18 (3)	SC(AFG2,o-xylene)	0.30 (5)
acetone + OH ->	0.27 (3)	SC(MGLY,o-xylene)	0.43 (5)
α-pinene + OH ->	0.18 (3)	SC(AFG2,m-xylene)	0.33 (5)
BALD + OH ->	0.34 (3)	SC(MGLY,m-xylene)	0.31 (5)
MEK + OH ->	0.27 (3)	SC(AFG1,ARO1) [g]	0.33 (5)
NC_4 + OH ->	0.18(3)	SC(AFG2,ARO1) [g]	0.29 (5)
NC_6 + OH ->	0.18 (3)	SC(MGLY,ARO1) [g]	0.29 (5)
NC_8 + OH ->	0.18 (3)	SC(AFG2,ARO2) [h]	0.23 (5)
$CYCC_6$ + OH ->	0.27 (3)	SC(MGLY,ARO2) [h]	0.20 (5)

[a] The references for the uncertainty estimates are:

1. DeMore et al. 1994 (35)
2. DeMore et al. 1997 (36)
3. Stockwell et al. 1994 (38)
4. Bridier et al. 1991(39), Grosjean et al. 1994 (40)
5. estimated for this study

[b] Only uncertainty in the action spectrum is considered.

[c] quantum yield for photolysis of model species AFG1

[d] product yield for model species AFG1 from reaction benzene+OH

[e] SC(AFG2, aromatics) represents the chamber-derived aromatics oxidation parameter B1U2 (the stoichiometric coefficient for model species AFG2) from reaction aromatics+OH

[f] SC(MGLY, aromatics) represents the chamber-derived aromatics oxidation parameter B1MG (the stoichiometric coefficient for model species MGLY) from reaction aromatics+OH

[g] The sample values of B1U1, B1U2 and B1MG for ARO1 are calculated as the weighted average of the corresponding sample values for benzene, toluene and ethylbenzene, by reactivity-weighted emission mass.

[h] The sample values of B1U2 and B1MG for ARO2 are calculated as the emission mass weighted average of the corresponding sample values for o-xylene, p-xylene, m-xylene, 1,2,3-trimethylbenzene and 1,3,5-trimethylbenzene.

Table 12. Correlated Parameters Used in Reactivity Calculations [a]

Parameter	**Correlated Parameter**	**Correlation**
CCOO2 + NO ->	CCOO2 + NO_2 ->	0.7
P1U1	benzene + OH ->	-0.58
P1U1	NO_2 + OH ->	0.40
SC(AFG1, benzene)	benzene + OH ->	-0.40
SC(AFG1, benzene)	NO_2 + OH ->	0.30
SC(AFG2, toluene)	toluene + OH ->	-0.55
SC(AFG2, toluene)	NO_2 + OH ->	0.68
SC(MGLY, toluene)	toluene + OH ->	-0.57
SC(MGLY, toluene)	NO_2 + OH ->	0.45
SC(AFG2, ethylbenzene)	ethylbenzene + OH ->	-0.73
SC(AFG2, ethylbenzene)	NO_2 + OH ->	0.37
SC(MGLY, ethylbenzene)	ethylbenzene + OH ->	-0.43
SC(MGLY, ethylbenzene)	NO_2 + OH ->	0.36
SC(AFG2, 123-TMB)	123-TMB + OH ->	-0.73
SC(AFG2, 123-TMB)	NO_2 + OH ->	0.35
SC(AFG2, 124-TMB)	124-TMB+OH ->	-0.72
SC(AFG2, 124-TMB)	NO_2 + OH ->	0.36
SC(MGLY, 124-TMB)	124-TMB+OH ->	-0.51
SC(MGLY, 124-TMB)	NO_2 + OH ->	0.38
SC(AFG2, 135-TMB)	135-TMB + OH ->	-0.69
SC(AFG2, 135-TMB)	NO_2 + OH ->	0.38
SC(AFG2, p-xylene)	p-xylene + OH ->	-0.73
SC(AFG2, p-xylene)	NO_2 + OH ->	0.37
SC(MGLY, p-xylene)	p-xylene + OH ->	-0.55
SC(MGLY, p-xylene)	NO_2 + OH ->	0.31
SC(AFG2, o-xylene)	o-xylene + OH ->	-0.70

Table 12. (Cont'd.) Correlated Parameters Used in Reactivity Calculations [a]

Parameter	Correlated Parameter	Correlation
SC(AFG2, o-xylene)	NO_2 + OH ->	0.45
SC(MGLY, o-xylene)	o-xylene + OH ->	-0.50
SC(MGLY, o-xylene)	NO_2 + OH ->	0.44
SC(AFG2, m-xylene)	m-xylene + OH ->	-0.63
SC(AFG2, m-xylene)	NO_2 + OH ->	0.55
SC(MGLY, m-xylene)	m-xylene + OH ->	-0.55
SC(MGLY, m-xylene)	NO_2 + OH ->	0.50
SC(AFG2, ARO1)	ARO1 + OH ->	-0.61
SC(AFG2, ARO2)	ARO2 + OH ->	-0.73

[a] The correlations between the chamber-derived aromatics oxidation parameters and the rate constants for the reactions are obtained from unbiased regression analysis which only includes the independent reaction rate constants as predictors.

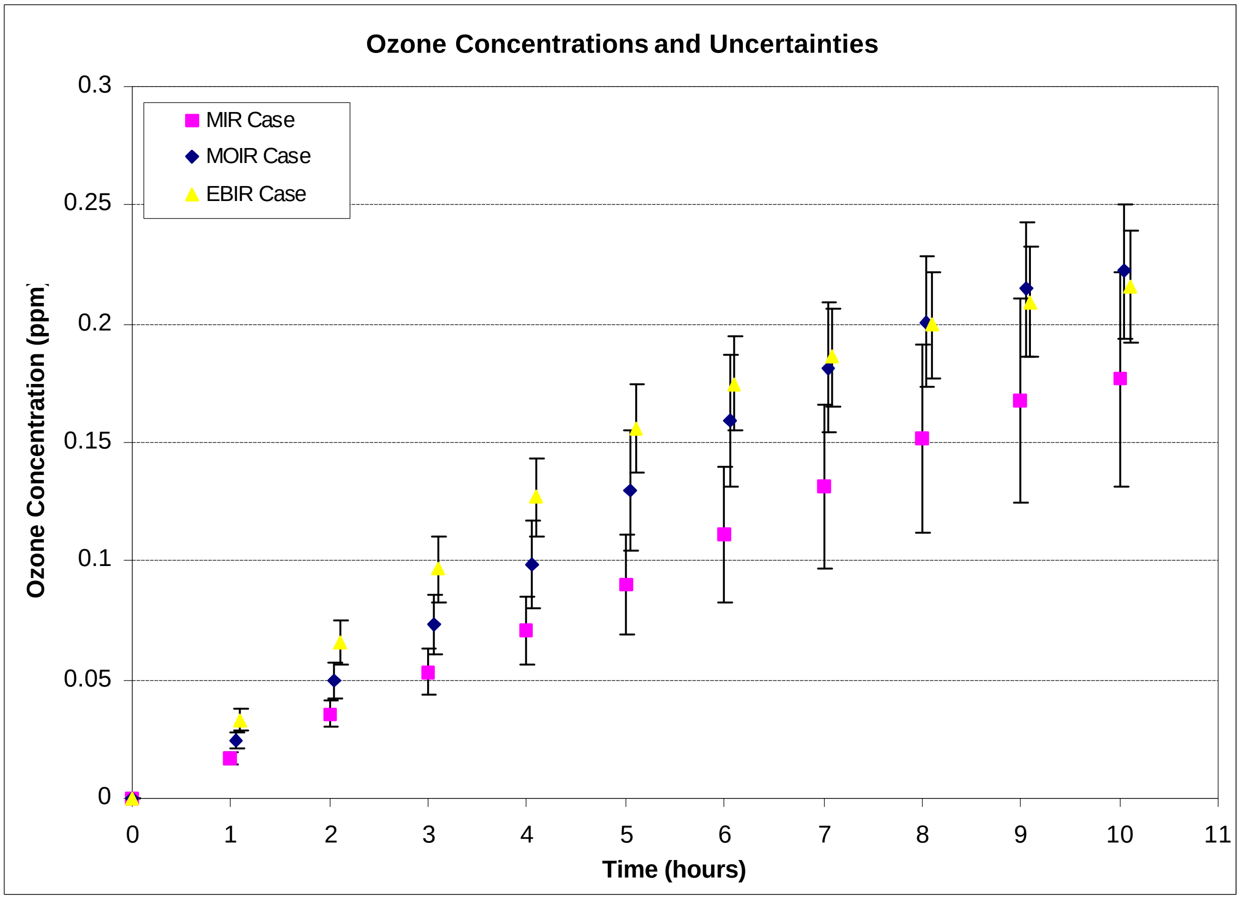


Figure 4. Concentration Profiles of Predicted Ozone Under MIR, MOIR and EBIR Conditions

Figure 4 shows the resulting uncertainties (1σ) in time-varying ozone concentrations predicted for the MIR, MOIR and EBIR conditions. Somewhat higher uncertainty in predicted ozone is seen for the MIR scenario than the MOIR and EBIR scenarios, which end with respective uncertainties of 22%, 12% and 11% compared to the means from the three sets of simulations. Yang et al. (44) also noted a higher uncertainty in ozone for MIR conditions than for MOIR conditions. The regression results for O_3 concentrations in the three cases are listed in Table 13. Ozone exhibits relatively high sensitivity at lower VOC/NO_x ratios (e.g., the MIR case) to the perturbation of the rate constants for O_3, NO_2 and HCHO photolysis, the reactions NO_2

+OH, O^1D+H_2O, O^1D+M, CO+OH, O_3+NO, ARO2+OH and PAN formation, and the chamber-derived aromatics oxidation parameters. At higher VOC/NO_x ratios (e.g., the MOIR and EBIR cases), ozone concentrations become more sensitive to the perturbation of the rate constants for the reactions NO_2 photolysis, NO_2+OH, O_3+NO, NO+HO_2, CO+OH, PAN and PPN formation and decomposition. The chamber-derived aromatics oxidation parameters appear less influential in the MOIR and EBIR cases than in the MIR case. The dominant contributions to the uncertainty in the time averaged O_3 concentrations are associated with the rate constants for the NO_x sink reaction, NO_2+OH, and NO_2 photolysis. Other parameters that strongly influence the uncertainty in ozone concentrations include the rate constants for photolysis of ozone and formaldehyde and the reactions of CO+OH and O_3+NO.

In general, the influential parameters in Table 13 are similar to those found in previous studies (18, 45). However, the reactions for PAN decomposition appear less important for the MIR case than previously seen. Instead, the rate parameters of the reactions involving O^1D and the chamber-derived aromatics oxidation parameter B1MG are relatively influential. The uncertainties in the rate constants of the PAN and PPN formation and decompostion reactions are more influential at reduced NO_x levels.

Table 13. Uncertainty Apportionment of Average Ozone Concentrations [a]

MIR Case (adjusted $R^2 = 0.94$)

Factors	**COV** **($\sigma_i/\kappa_{i\ nominal}$)** [b]	**Standardized Reg. Coef.**	**UC** [c] **(%)**
NO_2 + OH ->	0.27	-0.37	13.9
O_3 + hv ->	0.27	0.37	13.8
NO_2 + hv ->	0.18	0.25	6.29
O^1D + M ->	0.18	-0.24	5.72
O^1D + H_2O ->	0.18	0.22	4.96
HCHO + hv -> $2HO_2$ + CO	0.34	0.22	4.95
CO + OH ->	0.27	0.17	2.87
ARO2 + OH ->	0.27	0.15	2.38
O_3 + NO ->	0.10	-0.14	1.87
CCOO2 + NO ->	0.34	0.12	1.48
SC(MGLY, ARO2)	0.20	0.12	1.45

MOIR case (adjusted $R^2 = 0.94$)

Factors	**COV** **($\sigma_i/\kappa_{i\ nominal}$)** [b]	**Standardized Reg. Coef.**	**UC** [c] **(%)**
NO_2 + hv ->	0.18	0.47	22.1
NO_2 + OH ->	0.27	-0.38	14.5
O_3 + NO ->	0.10	-0.23	5.46
PAN ->	0.40	0.19	3.69
CO + OH ->	0.27	0.19	3.68
CCOO2 + NO ->	0.34	0.18	3.16
NO + HO_2 ->	0.18	0.18	3.14
HCHO + hv -> $2HO_2$ + CO	0.34	0.10	0.98
SC(MGLY, ARO1)	0.29	-0.09	0.85
C2COO2 + NO_2 ->	0.75	-0.08	0.72

Table 13. (Cont'd.) EBIR case (adjusted R^2 = 0.95)

Factors	**COV** $(\sigma_i/\kappa_{i\,\mathrm{nominal}})$ [b]	**Standardized Reg. Coef.**	**UC [c] (%)**
NO_2 + hv ->	0.18	0.52	26.7
NO_2 + OH ->	0.27	-0.35	12.0
O_3 + NO ->	0.10	-0.24	5.93
PAN ->	0.40	0.22	4.64
NO + HO_2 ->	0.18	0.20	3.91
CCOO2 + NO ->	0.34	0.18	3.40
CO + OH ->	0.27	0.16	2.60
RO_2 + HO_2 ->	0.75	-0.11	1.13
C2COO2 + NO_2 ->	0.75	-0.10	0.83
PPN ->	0.66	0.09	0.81

[a] Ridge regression results for normalized predictors

[b] Normalized uncertainty of rate constant and chamber-derived aromatics oxidation parameters.

[c] Uncertainty contribution

For most of the explicit organic compounds and lumped organic compound classes studied, the estimated uncertainties (1σ) in MIRs from the Monte Carlo simulations ranged from 20 to 35% of the mean estimates, while the estimated uncertainties in MOIRs and EBIRs ranged from 20 to 38% and 17 to 38%, respectively. The uncertainties (relative to the mean) for the relative reactivities are about 7 to 36% for the relative MIRs, 6 to 34% for the relative MOIRs and 7 to 30% for the relative EBIRs, for most compounds. These results are listed in Table 14 for nonaromatics and lumped organic compounds and in Table 15 for aromatic compounds. Results

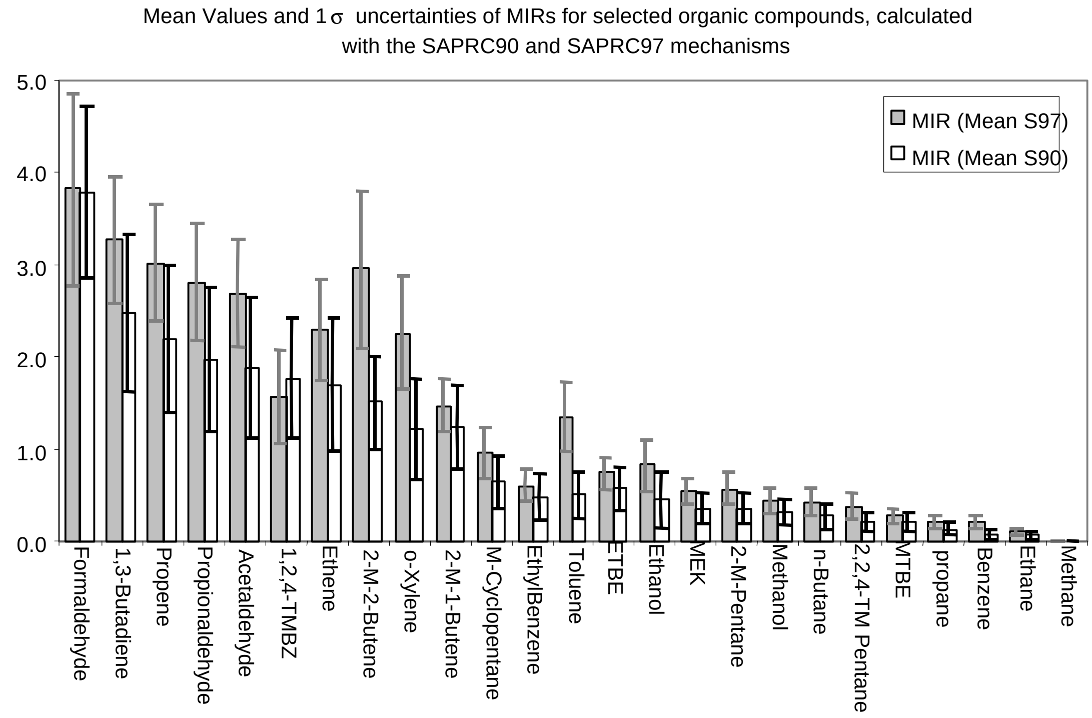


Figure 5. Comparison of MIRs with Yang et al. (44)

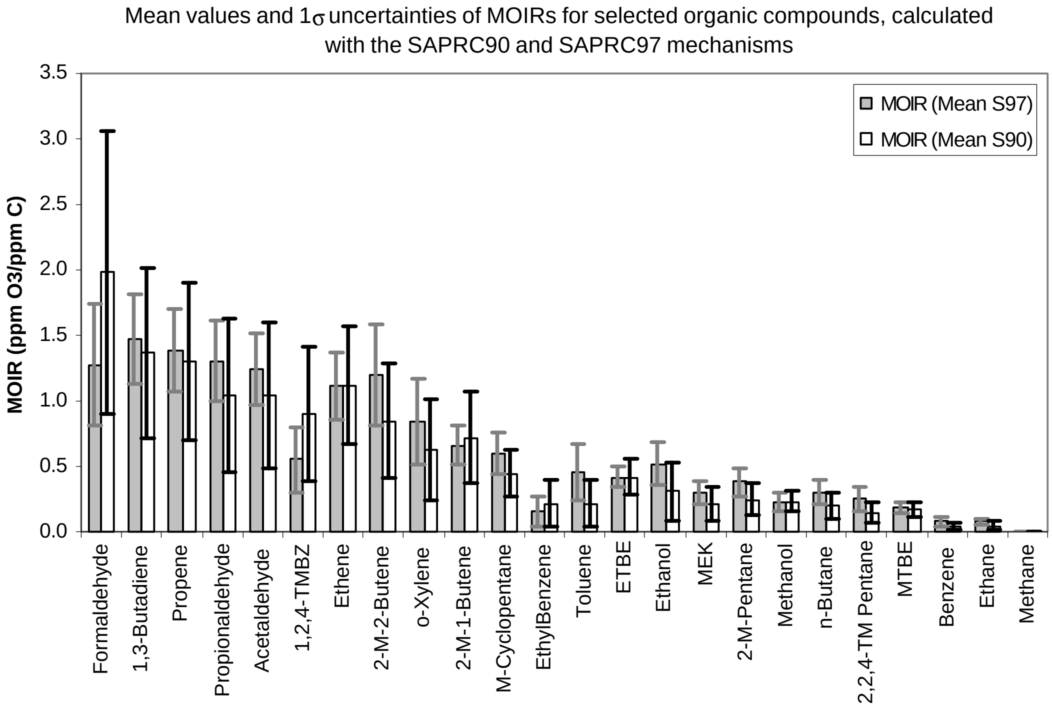


Figure 6. Comparison of MOIRs with Yang et al. (44)

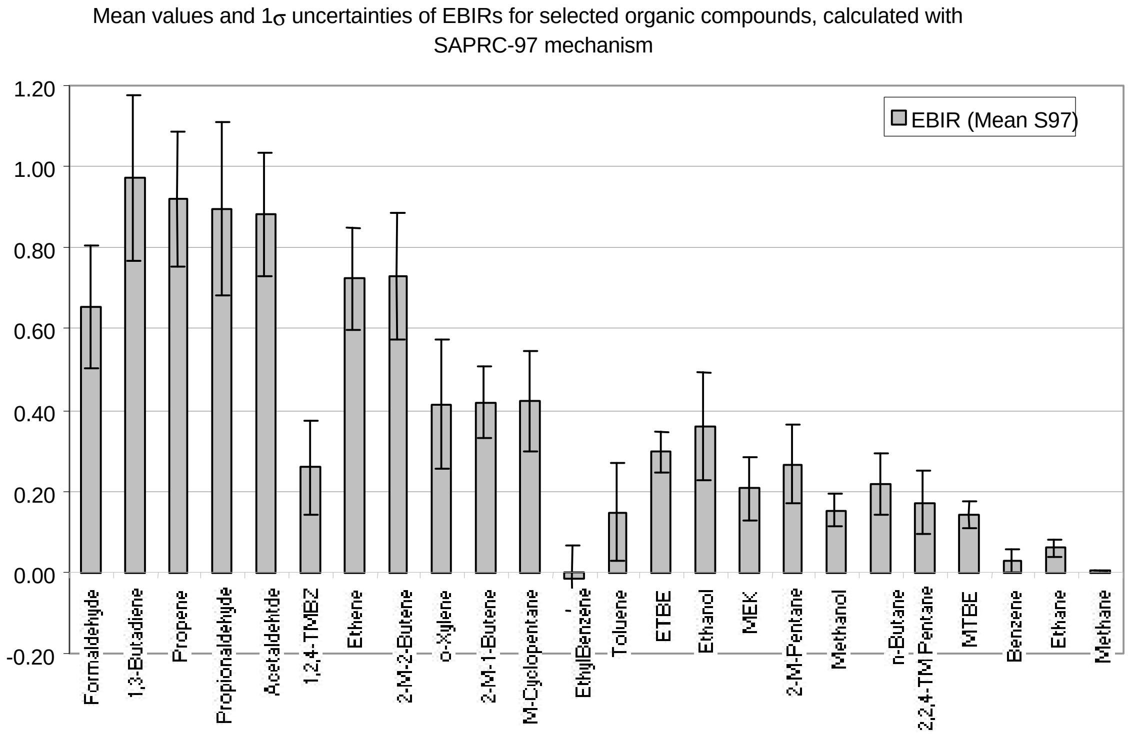
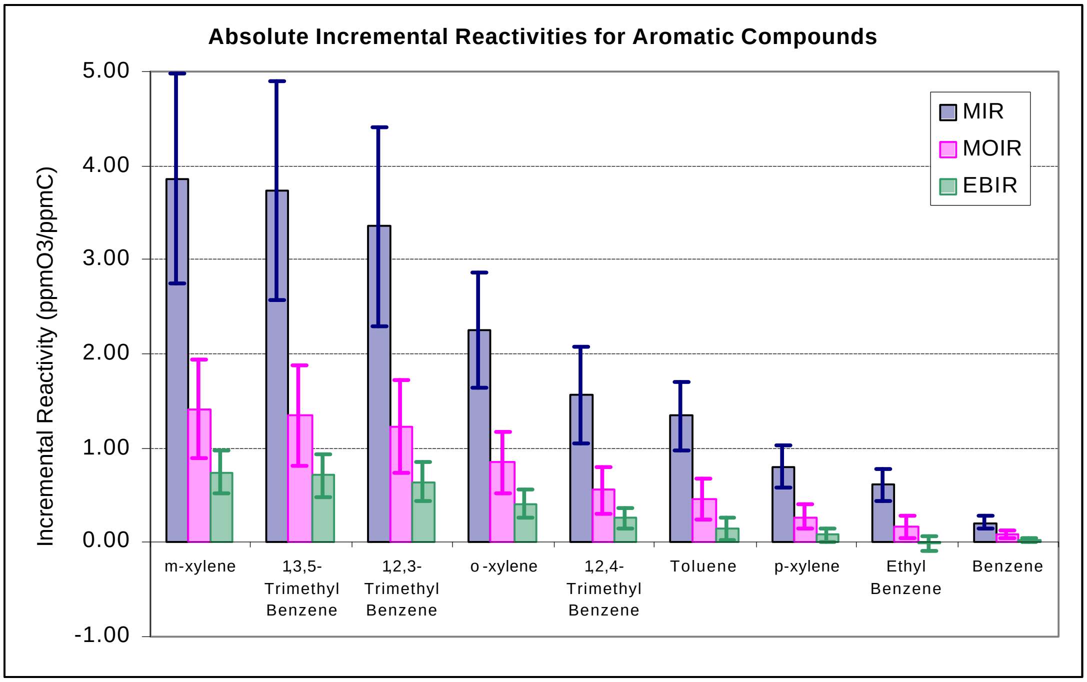

Mean values and 1σ uncertainties of EBIRs for selected organic compounds, calculated with SAPRC-97 mechanism

Figure 7. EBIRs for Selected VOCs Calculated with SAPRC-97 Mechanism

for the subset of compounds studied by Yang et al. (44) using the SAPRC-90 mechanism are also shown in Figure 5 for MIRs and Figure 6 for MOIRs. EBIR results from this study are shown in Figure 7 for the same compounds.

Figures 5 and 6 show that MIR and MOIR estimates calculated with SAPRC-97 are generally higher than those calculated with SAPRC-90, reflecting revisions to the mechanism. One exception is the MIR and MOIR values for 1,2,4-trimethylbenzene, which have been adjusted downward based on recent chamber experiments. Another exception is the MOIR for formaldehyde, which is changed due to changes in the mechanism. Yang et al.’s (44) uncertainty estimates for MIRs ranged from about 30 to 50% of the mean MIR values, and for MOIRs from about 40 to 60%, for most compounds. Uncertainty estimates for most aromatic compounds fell at the upper end of these ranges. This study gives lower uncertainty estimates for both MIRs and MOIRs. The uncertainty level for MIRs ranges from 20 to 35% in most cases, while the uncertainty for MOIRs generally ranges from 20 to 37%.

Figure 8 Absolute Incremental Reactivities for Selected Aromatics Estimated with SAPRC-97



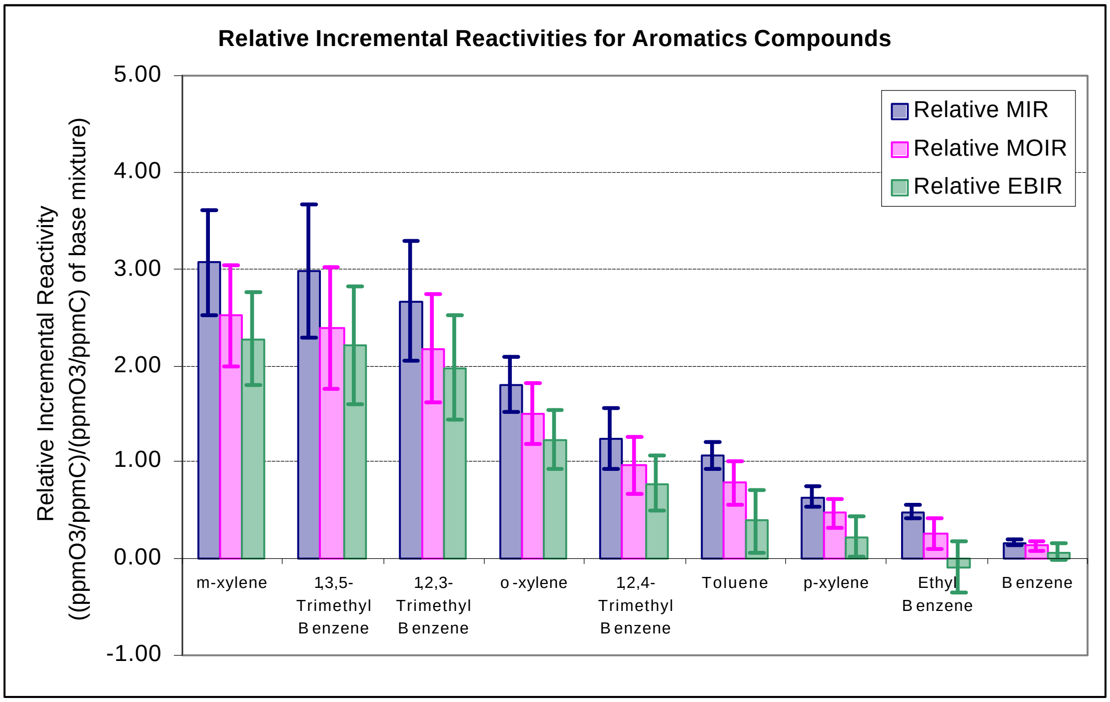


Figure 9 Relative Incremental Reactivities for Selected Aromatics Estimated with SAPRC-97

For aromatics, Figures 8 and 9 show the absolute and relative incremental reactivities calculated with SAPRC-97 for MIR, MOIR and EBIR conditions. The new uncertainty estimates for MIRs of the aromatic compounds are fairly constant, ranging from about 27 to 32%. The uncertainty estimates for their MOIRs range from about 38 to 52%. One exception is the MOIR for ethylbenzene, for which the uncertainty estimate is 75%. The uncertainty estimates for EBIRs of trimethylbenzene and m- and o-xylenes calculated with SAPRC-97 range from about 30 to 45%, while the uncertainty for p-xylene is about 86%. The uncertainty estimates for benzene, toluene and ethylbenzene range from 82% to 520%. The EBIRs for these three compounds are relatively small with a high probability of obtaining negative values due to the formation of organic nitrates.

The relative incremental reactivities show similar levels of uncertainty across the MIR, MOIR and EBIR cases, with generally smaller uncertainties than the absolute incremental reactivities. The uncertainty levels (1σ) for the relative incremental reactivities of the non-aromatic compounds range from 7 to 38% for MIR conditions, 6 to 35% for MOIR conditions, and 7 to 30% for EBIR conditions. For most of the aromatics, the uncertainty in the relative incremental reactivities ranges from 13 to 25% for MIR conditions, 20 to 37% for MOIR conditions and 21 to 37% for EBIR conditions. For MOIR conditions, ethylbenzene is an exception with an uncertainty level of 63%. Relative EBIRs for ethylbenzene, p-xylene, toluene and benzene have exceptionally high uncertainty levels of 360%, 94%, 88% and 130%, respectively.

As mentioned above, uncertainties in relative reactivities for most compounds are smaller than the uncertainties in the corresponding absolute incremental reactivites. However, there are a few exceptions. Relative MIRs for methane, ethane, propane, n-hexane, MTBE and benzaldehyde are more uncertain than their absolute MIRs. Methane and benzaldehyde have relative MOIRs that are more uncertain than their absolute MOIRs. Methane, HCHO, benzaldehyde, MTBE, ARO1, benzene, toluene and p-xylene have greater uncertainty in their relative EBIRs than in their absolute EBIRs.

Table 14. Incremental Reactivites for Selected Nonaromatic and Lumped Organic Compounds [a]

VOC	MIR	MOIR	EBIR	R_MIR [b]	R_ MOIR [b]	R_EBIR [b]
Methane	0.006 (31%)	0.004 (25%)	0.003 (25%)	0.005 (32%)	0.008 (28%)	0.010 (29%)
Ethane	0.108 (36%)	0.081(32%)	0.060 (35%)	0.089 (37%)	0.150 (30%)	0.183 (26%)
Propane	0.202 (35%)	0.148 (31%)	0.106 (33%)	0.166 (38%)	0.272 (30%)	0.324 (25%)
n-butane	0.419 (34%)	0.305 (31%)	0.219 (34%)	0.344 (35%)	0.559 (28%)	0.664 (23%)
n-hexane	0.379 (31%)	0.277 (28%)	0.192 (33%)	0.311 (33%)	0.510 (26%)	0.583 (21%)
2-methyl pentane	0.563 (31%)	0.383 (30%)	0.267 (36%)	0.460 (30%)	0.698 (25%)	0.805 (24%)
Methylcyclopentane	0.952 (28%)	0.603 (26%)	0.422 (29%)	0.775 (24%)	1.099 (20%)	1.287 (18%)
Ethene	2.286 (24%)	1.122 (24%)	0.723 (17%)	1.846 (14%)	2.030 (12%)	2.265 (17%)
propene	3.017 (21%)	1.401 (24%)	0.921 (18%)	2.434 (8%)	2.524 (8%)	2.864 (12%)
Trans-2-butene	3.566 (21%)	1.573 (27%)	1.021 (17%)	2.876 (10%)	2.817 (9%)	3.181 (13%)
1,3-butadiene	3.267 (20%)	1.489 (25%)	0.974 (21%)	2.639 (9%)	2.677 (7%)	3.001 (11%)
2methyl-2butene	2.941 (27%)	1.225 (35%)	0.732 (21%)	2.372 (20%)	2.174 (19%)	2.281 (19%)
2methyl-1butene	1.470 (20%)	0.671 (25%)	0.419 (21%)	1.186 (9%)	1.206 (8%)	1.293 (10%)
α-pinene	0.984 (21%)	0.467 (25%)	0.313 (23%)	0.795 (9%)	0.839 (8%)	0.960 (11%)
Isoprene	2.480 (19%)	1.146 (23%)	0.760 (17%)	2.004 (7%)	2.065 (6%)	2.360 (9%)
Methanol	0.429 (33%)	0.236 (30%)	0.152 (27%)	0.348 (29%)	0.430 (26%)	0.479 (29%)
ethanol	0.819 (34%)	0.520 (32%)	0.360 (37%)	0.664 (30%)	0.943 (27%)	1.089 (28%)
ethyl t-butyl ether	0.732 (24%)	0.424 (21%)	0.296 (17%)	0.596 (19%)	0.775 (14%)	0.927 (17%)
Methyl t-butyl ether	0.267 (29%)	0.189 (23%)	0.141 (22%)	0.219 (30%)	0.349 (24%)	0.445 (23%)
C4 ketones	0.533 (31%)	0.305 (33%)	0.208 (38%)	0.432 (25%)	0.551 (21%)	0.626 (26%)
Acetone	0.284 (31%)	0.148 (33%)	0.097 (36%)	0.229 (24%)	0.266 (26%)	0.295 (28%)
Formaldehyde	3.831 (27%)	1.306 (38%)	0.654 (23%)	3.083 (20%)	2.312 (23%)	2.061 (25%)

Table 14. (Cont'd) Incremental Reactivites for Selected Nonaromatic and Lumped Organic Compounds [a]

VOC	**MIR**	**MOIR**	**EBIR**	**R_MIR** [b]	**R_ MOIR** [b]	**R_EBIR** [b]
Acetaldehyde	2.689 (21%)	1.260 (22%)	0.883 (17%)	2.170 (9%)	2.278 (9%)	2.750 (13%)
C3 aldehydes	2.819 (22%)	1.322 (25%)	0.896 (24%)	2.276 (12%)	2.379 (11%)	2.746 (13%)
Benzaldehyde	-0.111 (81%)	-0.460 (34%)	-0.735 (28%)	-0.106 (105%)	-0.900 (46%)	-2.354 (37%)
ALK1	0.447 (29%)	0.313 (24%)	0.224 (28%)	0.364 (29%)	0.577 (21%)	0.685 (15%)
ALK2	0.398 (29%)	0.266 (28%)	0.175 (37%)	0.325 (27%)	0.488 (25%)	0.525 (25%)
ARO1	1.042 (32%)	0.352 (53%)	0.093(107%)	0.830 (21%)	0.598 (35%)	0.243 (128%)
ARO2	3.134 (25%)	1.158 (35%)	0.600 (26%)	2.509 (13%)	2.043 (16%)	1.841 (17%)
OLE1	2.281 (23%)	1.108 (23%)	0.719 (17%)	1.828 (13%)	2.016 (10%)	2.249 (14%)
OLE2	1.818 (21%)	0.866 (23%)	0.562 (23%)	1.467 (8%)	1.560 (8%)	1.720 (10%)
OLE3	2.313 (22%)	0.987 (29%)	0.593 (21%)	1.864 (11%)	1.759 (8%)	1.824 (9%)
Base Mixture	1.242 (20%)	0.560 (25%)	0.327 (23%)	1.0	1.0	1.0

[a] The unit for absolute incremental reactivity is ppmO_3/ppmC.
The unit for relative incremental reactivity is (ppmO_3/ppmC) /(ppmO_3/ppmC of base mixture)

[b] R_MIR represents relative MIR, R_MOIR represents relative MOIR, and R_EBIR represents relative EBIR.

Table 15. MIR, MOIR and EBIR Estimates for Aromatic Hydrocarbons [a]

Compound	SAPRC-97 mean	SAPRC97 SD/mean (%)	SAPRC-90 Mean [b]	SAPRC90 SD/mean (%)[b]	Relative IR mean	Relative IR SD/mean (%)
MIR						
m-xylene	3.87	28.3	1.44	42.9	3.09	17.5
135-tmbenzene	3.74	30.7	NA	NA [c]	3.00	22.6
123-tmbenzene	3.35	30.8	NA	NA	2.69	23.4
o-xylene	2.27	27.6	1.21	45.0	1.81	16.9
124-tmbenzene	1.56	32.0	1.76	37.0	1.25	24.4
Toluene	1.34	26.7	0.49	52.0	1.07	13.4
p-xylene	0.80	27.0	1.44	42.9	0.64	16.7
Ethylbenzene	0.61	28.6	0.48	52.0	0.48	15.8
Benzene	0.21	30.5	0.07	65.0	0.17	21.3
MOIR						
m-xylene	1.44	37.7	0.74	62.5	2.54	20.6
135-tmbenzene	1.37	40.6	NA	NA	2.41	25.6
123-tmbenzene	1.26	43.7	NA	NA	2.20	26.4
o-xylene	0.87	41.4	0.63	60.0	1.51	22.2
124-tmbenzene	0.54	47.4	0.90	57.0	0.98	30.0
Toluene	0.47	50.0	0.22	83.0	0.80	29.5
p-xylene	0.28	49.3	0.74	62.5	0.47	31.7
Ethylbenzene	0.16	74.5	0.22	85.0	0.27	62.5
Benzene	0.08	51.7	0.04	75.0	0.14	37.4

Table 15. (Cont'd) MIR, MOIR and EBIR Estimates for Aromatic Hydrocarbons [a]

EBIR						
Compound	**SAPRC-97 mean**	**SAPRC97 SD/mean (%)**	**SAPRC-90 Mean [b]**	**SAPRC90 SD/mean (%)[b]**	**Relative IR mean**	**Relative IR SD/mean (%)**
m-xylene	0.75	30.4	NA	NA	2.29	21.1
135-tmbenzene	0.72	31.1	NA	NA	2.23	27.0
123-tmbenzene	0.65	34.7	NA	NA	2.00	27.2
o-xylene	0.41	38.2	NA	NA	1.24	26.8
124-tmbenzene	0.26	44.6	NA	NA	0.78	36.9
Toluene	0.15	82.3	NA	NA	0.40	88.1
p-xylene	0.08	85.4	NA	NA	0.23	93.9
Ethylbenzene	-0.02	519.6	NA	NA	-0.09	360.0
Benzene	0.03	103.2	NA	NA	0.07	129.5

[a] The unit for absolute incremental reactivity is ppmO_3/ppmC.
The unit for relative incremental reactivity is (ppmO_3/ppmC) /(ppmO_3/ppmC of base mixture)

[b] Yang et al., 1996 (44) and Yang (45)

[c] Not available

Table 16. Apportionment of Uncertainty in MIRs [a]

Parameter	**σ/μ [b]**	**Std. Reg. Coef.**	**UC (%) [c]**
Formaldehyde (R^2 = 0.64)			
NO_2 + OH ->	0.27	0.35	12.0
ARO2 + OH ->	0.27	-0.27	7.41
O_3 + hv ->	0.27	-0.21	4.52
HCHO + hv -> $2HO_2$ + CO	0.34	0.21	4.52
HO_2 + NO ->	0.18	0.18	3.39
OLE3 + O_3 ->	0.42	-0.18	3.26
SC(MGLY, ARO2)	0.20	-0.17	2.83
O^1D + M ->	0.18	0.14	1.92
HCHO + OH ->	0.23	-0.13	1.72
O^1D + H_2O ->	0.18	-0.12	1.37
RO_2 + HO_2 ->	0.75	-0.11	1.27
Propene (R^2 = 0.58)			
NO_2 + hv ->	0.18	0.28	8.11
PAN ->	0.40	0.24	5.94
CCOO2 + NO ->	0.34	0.21	4.61
O_3 + hv ->	0.27	-0.21	4.61
HO_2 + NO ->	0.18	0.19	3.62
propene + OH ->	0.14	0.19	3.49
SC(MGLY, ARO2)	0.20	-0.17	2.92
O_3 + NO ->	0.10	-0.17	2.92
O^1D + M ->	0.18	0.13	1.81
O^1D + H_2O ->	0.18	-0.12	1.42
HCHO + hv -> $2HO_2$ + CO	0.34	0.11	1.21
Butane (R^2 = 0.87)			
NC_4 + OH ->	0.18	0.42	17.4
NO_2 + OH ->	0.27	-0.37	13.9
NO_2 + hv ->	0.18	0.33	11.0
PAN ->	0.40	0.22	4.69
CCOO2 + NO ->	0.34	0.21	4.60
O_3 + NO ->	0.10	-0.19	3.63

O_3 + hv ->	0.27	0.16	2.53
ARO2 + OH ->	0.27	0.12	1.42
HCHO + hv -> $2HO_2$ + CO	0.34	0.12	1.39
O^1D + H_2O ->	0.18	0.11	1.28
O^1D + M ->	0.18	-0.11	1.25
MEK (adjusted R^2 = 0.73)			
MEK + OH ->	0.27	0.45	20.5
MEK + hv ->	0.42	0.35	12.1
PAN ->	0.40	0.25	6.32
NO_2 + hv ->	0.18	0.25	6.08
NO_2 + OH ->	0.27	-0.23	5.31
$CCOO_2$ + NO ->	0.34	0.18	3.31
O_3 + NO ->	0.10	-0.15	2.38
C_2COO_2 + NO_2 ->	0.75	-0.13	1.71
HO_2 + NO ->	0.18	0.13	1.65
Benzene (R^2=0.67)			
benzene + OH ->	0.27	0.55	29.8
SC(AFG1, Benzene)	0.33	0.44	19.7
NO_2 + hv ->	0.18	0.32	10.0
P1U1	0.40	0.28	8.02
PAN ->	0.40	0.22	4.93
CCOO2 + NO ->	0.34	0.20	3.96
O_3 + NO ->	0.10	-0.19	3.49
NO_2 + OH ->	0.27	-0.14	2.02
HO_2 + NO ->	0.18	0.13	1.65
Toluene (R^2=0.57)			
NO_2 + hv ->	0.18	0.30	9.22
SC(MGLY, Toluene)	0.31	0.25	6.30
toluene + OH ->	0.18	0.22	5.01
CCOO2 + NO ->	0.34	0.21	4.41
PAN ->	0.40	0.20	3.96
O_3 + NO ->	0.10	-0.18	3.36
SC(MGLY, ARO1)	0.29	0.17	3.02
O_3 + hv ->	0.27	-0.17	2.86

HO_2 + NO ->	0.18	0.17	2.82
O-xylene (R^2=0.63)			
SC(MGLY, O-xylene)	0.43	0.36	12.8
NO_2 + hv ->	0.18	0.26	6.80
CCOO2 + NO ->	0.34	0.20	4.02
PAN ->	0.40	0.18	3.17
O_3 + hv ->	0.27	-0.17	2.92
HO_2 + NO ->	0.18	0.16	2.57
SC(AFG2, O-xylene)	0.28	0.16	2.56
NO_2 + OH ->	0.27	0.15	2.13
O_3 + NO ->	0.10	-0.13	1.69
O^1D + M ->	0.18	0.10	1.06
135TMB (R^2=0.73)			
SC(MGLY,135TMB)	0.29	0.40	16.0
SC(AFG2, 135TMB)	0.45	0.30	9.14
ARO2 + OH ->	0.27	-0.19	3.45
O_3 + hv ->	0.27	-0.18	3.18
HO_2 + NO ->	0.18	0.15	2.13
SC(AFG2, ARO2)	0.23	-0.13	1.62
CCOO2 + NO ->	0.34	0.12	1.51
NO_2 + OH ->	0.27	0.12	1.51
NO_2 + hv ->	0.18	0.11	1.32
O^1D + H_2O ->	0.18	-0.10	1.08
O^1D + M ->	0.18	0.10	1.04
Base Mixture (R^2=0.59)			
NO_2 + hv ->	0.18	0.32	10.2
CCOO2 + NO ->	0.34	0.25	6.33
PAN ->	0.40	0.23	5.47
HO_2 + NO ->	0.18	0.21	4.28
O_3 + NO ->	0.10	-0.19	3.49
O_3 + hv ->	0.27	-0.17	2.83
C2COO2 + NO_2 ->	0.75	-0.13	1.66
O^1D + M ->	0.18	0.11	1.17
OLE3 + OH ->	0.23	0.10	1.01

[a] Ridge regression for normalized predictors
[b] Normalized uncertainty of rate constant and chamber-derived aromatics oxidation parameters
[c] Uncertainty contribution

Table 17. Apportionment of Uncertainty in MOIRs [a]

Parameter	**σ/μ** [b]	**Std. Reg. Coef.**	**UC (%)** [c]
Formaldehyde (R^2=0.90)			
O_3 + hv ->	0.27	-0.56	31.9
O^1D + M ->	0.18	0.36	12.8
O^1D + H_2O ->	0.18	-0.34	11.9
ARO2 + OH ->	0.27	-0.24	5.77
NO_2 + OH ->	0.27	0.22	4.98
SC(MGLY, ARO2)	0.20	-0.21	4.53
OLE3 + O_3 ->	0.42	-0.16	2.42
HO_2 + NO ->	0.18	0.13	1.59
SC(AFG2, ARO2)	0.23	-0.12	1.39
Propene (R^2 = 0.90)			
O_3 + hv ->	0.27	-0.55	30.1
O^1D + M ->	0.18	0.35	12.0
O^1D + H_2O ->	0.18	-0.33	10.8
NO_2 + hv ->	0.18	0.26	6.65
PAN ->	0.40	0.22	4.65
SC(MGLY, ARO2)	0.20	-0.18	3.41
SC(AFG2, ARO2)	0.23	-0.13	1.70
HO_2 + NO ->	0.18	0.12	1.56
ARO1 + OH ->	0.27	-0.11	1.32
CCOO2 + NO ->	0.34	0.11	1.31
CO + OH ->	0.27	-0.11	1.24
Butane (R^2=0.92)			
NC_4 + OH ->	0.18	0.41	17.1
NO_2 + hv ->	0.18	0.41	16.5
PAN ->	0.40	0.34	11.8
NO_2 + OH ->	0.27	-0.28	7.77

CCOO2 + NO ->	0.34	0.26	6.85
O_3 + NO ->	0.10	-0.19	3.43
CO + OH ->	0.27	-0.17	3.04
RO_2 + HO_2 ->	0.75	-0.12	1.53
C2COO2 + NO_2 ->	0.75	-0.12	1.33
MEK (adjusted R^2 = 0.90)			
MEK + OH ->	0.27	0.45	20.4
NO_2 + hv ->	0.18	0.34	11.3
PAN ->	0.40	0.30	8.83
$CCOO_2$ + NO ->	0.34	0.24	5.84
O_3 + hv ->	0.27	-0.23	5.12
MEK + hv ->	0.42	0.19	3.56
O_3 + NO ->	0.10	-0.15	2.34
HO + CO ->	0.27	-0.14	1.95
O^1D + M ->	0.18	0.14	1.86
O^1D + H_2O ->	0.18	-0.14	1.78
Benzene (R^2=0.88)			
O_3 + hv ->	0.27	-0.42	17.5
PAN ->	0.40	0.33	10.8
SC(AFG1, Benzene)	0.33	0.32	9.96
benzene + OH ->	0.27	0.29	8.59
NO_2 + hv ->	0.18	0.29	8.38
O^1D + M ->	0.18	0.25	6.28
O^1D + H_2O ->	0.18	-0.24	5.76
CO + OH ->	0.27	-0.19	3.59
HCHO + hv -> $2HO_2$ + CO	0.34	-0.17	2.93
P1U1	0.40	0.15	2.33
O_3 + NO ->	0.10	-0.13	1.64
CCOO2 + NO ->	0.34	0.13	1.63
SC(MGLY, ARO2)	0.20	-0.11	1.22
Toluene (R^2=0.92)			
O_3 + hv ->	0.27	-0.51	26.2
O^1D + M ->	0.18	0.32	10.5
O^1D + H_2O ->	0.18	-0.30	9.07

HCHO + hv ->$2HO_2$ + CO	0.34	-0.21	4.39
CRES + NO_3 ->	0.75	-0.20	4.04
NO_2 + hv ->	0.18	0.20	3.94
SC(MGLY, Toluene)	0.31	0.18	3.23
Toluene + OH ->	0.18	0.14	2.01
SC(MGLY, ARO2)	0.20	-0.14	1.94
PAN ->	0.40	0.13	1.81
SC(MGLY, ARO1)	0.29	0.12	1.43
O-xylene (R^2=0.89)			
O_3 + hv ->	0.27	-0.49	24.0
O^1D + M ->	0.18	0.31	9.49
O^1D + H_2O ->	0.18	-0.30	9.05
SC(MGLY, O-xylene)	0.43	0.29	8.54
HCHO + hv -> $2HO_2$ + CO	0.34	-0.21	4.27
NO_2 + hv ->	0.18	0.18	3.18
SC(AFG2, O-xylene)	0.30	0.14	2.04
SC(MGLY, ARO2)	0.20	-0.13	1.65
NO_2 + OH ->	0.27	0.13	1.61
CRES + NO_3 ->	0.75	-0.12	1.52
SC(AFG2, ARO2)	0.23	-0.10	1.05
ARO2 + OH ->	0.27	-0.10	1.03
135-TMB (R^2=0.90)			
O_3 + hv ->	0.27	-0.48	22.9
SC(MGLY, 135TMB)	0.29	0.31	9.76
O^1D + H_2O ->	0.18	-0.29	8.64
O^1D + M ->	0.18	0.29	8.56
SC(AFG2, 135TMB)	0.40	0.26	6.50
HCHO + hv -> $2HO_2$ + CO	0.34	-0.21	4.60
ARO2 + OH ->	0.27	-0.17	2.96
SC(MGLY, ARO2)	0.20	-0.13	9.76
Base Mixture (R^2=0.92)			
O_3 + hv ->	0.27	-0.53	27.9
O^1D + M ->	0.18	0.32	10.5
O^1D + H_2O ->	0.18	-0.31	9.78

NO_2 + hv ->	0.18	0.29	8.26
HCHO + hv ->2HO_2 + CO	0.34	-0.19	3.44
PAN ->	0.40	0.18	3.27
CO + OH ->	0.27	-0.13	1.76
CCOO2 + NO ->	0.34	0.12	1.47
CRES + NO_3 ->	0.75	-0.12	1.33
HO_2 + NO ->	0.18	0.11	1.17
RO_2 + HO_2 ->	0.75	-0.11	1.12

[a] Ridge regression for normalized predictors

[b] Normalized uncertainty of rate constant and chamber-derived aromatics oxidation parameters

[c] Uncertainty contribution.

Table 18. Apportionment of Uncertainty in EBIRs [a]

Parameter	σ/μ [b]	**Std Reg. Coef.**	**UC (%)** [c]
Formaldehyde (R^2=0.92)			
O_3 + hv ->	0.27	-0.55	30.3
O^1D + M ->	0.18	0.34	11.4
O^1D + H_2O ->	0.18	-0.33	11.0
ARO2 + OH ->	0.27	-0.24	5.65
NO + HO_2 ->	0.18	0.20	4.19
OLE3 + O_3 ->	0.42	-0.18	3.29
NO_2 + OH ->	0.27	0.18	3.24
SC(MGLY, ARO2)	0.20	-0.18	3.22
NO_2 + hv ->	0.18	0.14	1.85
HCHO + hv ->2HO_2 + CO	0.34	0.13	1.72
CRES + NO_3 ->	0.75	-0.12	1.47
Propene (R^2 = 0.92)			
PAN ->	0.40	0.45	20.0
NO_2 + hv ->	0.18	0.43	18.3
O_3 + hv ->	0.27	-0.35	12.1
CCOO2 + NO ->	0.34	0.28	7.74
O^1D + M ->	0.18	0.21	4.59
O^1D + H_2O ->	0.18	-0.20	3.96
O_3 + NO ->	0.10	-0.17	2.97
PROPENE + OH ->	0.14	0.13	1.70
CO + OH ->	0.27	-0.13	1.65
SC(MGLY, ARO2)	0.20	-0.11	1.31
Butane (R^2=0.91)			
PAN ->	0.40	0.44	19.5
NO_2 + hv ->	0.18	0.41	17.1
NC_4 + OH ->	0.18	0.37	13.8
CCOO2 + NO ->	0.34	0.31	9.64
CO + OH ->	0.27	-0.18	3.20
O_3 + NO ->	0.10	-0.18	3.10
NO_2 + OH ->	0.27	-0.16	2.61

C2COO2 + NO_2 ->	0.75	-0.15	2.23
PPN ->	0.66	0.13	1.61
RO_2 + HO_2 ->	0.75	-0.11	1.25
MEK (adjusted R^2 = 0.90)			
MEK + OH ->	0.27	0.45	17.8
PAN ->	0.40	0.41	16.5
NO_2 + hv ->	0.18	0.36	13.1
$CCOO_2$ + NO ->	0.34	0.31	9.38
C_2COO_2 + NO_2 ->	0.75	-0.18	3.31
O_3 + NO ->	0.10	-0.17	2.85
HO + CO ->	0.27	-0.14	1.88
PPN ->	0.66	0.13	1.68
MEK + hv ->	0.42	0.12	1.37
NO_2 + OH ->	0.27	-0.10	1.01
Benzene (R^2=0.86)			
PAN ->	0.40	0.50	24.7
NO_2 + hv ->	0.18	0.30	8.86
SC(AFG1, Benzene)	0.33	0.23	5.18
O_3 + hv ->	0.27	-0.22	4.87
CO + OH ->	0.27	-0.22	4.86
NO_3 + hv -> NO_2 + O	0.42	0.20	3.97
CCOO2 + NO ->	0.34	0.19	3.50
NO_2 + OH ->	0.27	0.18	3.09
BENZENE + OH ->	0.27	0.16	2.61
O^1D + M ->	0.18	0.13	1.70
O^1D + H_2O ->	0.18	-0.13	1.58
O_3 + NO ->	0.10	-0.12	1.56
P1U1	0.35	0.12	1.53
Toluene (R^2=0.93)			
CRES + NO_3 ->	0.75	-0.45	20.2
O_3 + hv ->	0.27	-0.30	8.78
PAN ->	0.40	0.26	6.66
NO_2 + hv ->	0.18	0.24	5.56
SC(MGLY, Toluene)	0.31	0.21	4.34

$O^1D + M$ ->	0.18	0.20	3.83
$NO_3 + hv$ -> $NO_2 + O$	0.42	0.19	3.49
$O^1D + H_2O$ ->	0.18	-0.17	2.74
CO + OH ->	0.27	-0.16	2.61
SC(MGLY, ARO1)	0.29	0.16	2.57
NO_2 + OH ->	0.27	0.14	1.95
Toluene + OH ->	0.18	0.11	1.25
HCHO + hv ->2HO_2 + CO	0.34	-0.11	1.25
SC(AFG2, Toluene)	0.34	0.11	1.11
O-xylene (R^2=0.91)			
SC(MGLY, O-xylene)	0.43	0.37	14.1
O_3 + hv ->	0.27	-0.31	9.91
NO_2 + hv ->	0.18	0.31	9.65
CRES + NO_3 ->	0.75	-0.28	7.99
PAN ->	0.40	0.24	5.64
$O^1D + M$ ->	0.18	0.19	3.72
$O^1D + H_2O$ ->	0.18	-0.19	3.58
SC(AFG2, O-xylene)	0.30	0.18	3.17
NO_2 + OH ->	0.27	0.17	2.88
CCOO2 + NO ->	0.34	0.15	2.11
$NO_3 + hv$ -> $NO_2 + O$	0.42	0.12	1.48
HCHO + hv ->2HO_2 + CO	0.34	-0.12	1.38
CO + OH ->	0.27	-0.12	1.36
135-TMB (R^2=0.92)			
SC(MGLY, 135TMB)	0.29	0.43	18.9
SC(AFG2, 135TMB)	0.40	0.35	12.6
O_3 + hv ->	0.27	-0.35	12.4
$O^1D + H_2O$ ->	0.18	-0.21	4.52
$O^1D + M$ ->	0.18	0.20	4.09
NO_2 + hv ->	0.18	0.18	3.21
CRES + NO_3 ->	0.75	-0.17	2.91
HCHO + hv ->2HO_2 + CO	0.34	-0.13	1.63
ARO2 + OH ->	0.27	-0.12	1.56
HO_2 + NO ->	0.18	0.12	1.34

Base Mixture (R^2=0.93)			
NO_2 + hv ->	0.18	0.44	19.2
PAN ->	0.40	0.39	14.9
O_3 + hv ->	0.27	-0.30	9.05
CCOO2 + NO ->	0.34	0.26	6.95
CRES + NO_3 ->	0.75	-0.21	4.32
CO + OH ->	0.27	-0.18	3.25
O^1D + M ->	0.18	0.18	3.11
O^1D + H_2O ->	0.18	-0.17	2.82
O_3 + NO ->	0.10	-0.16	2.62
C2COO2 + NO_2 ->	0.75	-0.16	2.56
PPN ->	0.66	0.15	2.29

[a] Ridge regression for normalized predictors. [c] Uncertainty contribution.

[b] Normalized uncertainty of rate constant and chamber-derived aromatics oxidation parameters

Table 19. Apportionment of Uncertainty in Relative MIRs [a]

Parameter	σ/μ [b]	**Std Reg. Coef.**	**UC (%)** [c]
Formaldehyde (R^2=0.90)			
NO_2 + OH ->	0.27	0.44	19.5
ARO2 + OH ->	0.27	-0.40	16.2
HCHO + hv -> $2HO_2$ + CO	0.34	0.30	9.25
SC(MGLY, ARO2)	0.20	-0.28	7.93
NO_2 + hv ->	0.18	-0.22	4.83
OLE3 + O_3 ->	0.42	-0.22	4.78
O_3 + hv ->	0.27	-0.18	3.38
PAN ->	0.40	-0.15	2.15
HCHO + OH ->	0.23	-0.14	2.05
CCOO2 + NO ->	0.34	-0.14	2.00
RCHO + hv ->	0.34	-0.14	1.88
O^1D + M ->	0.18	0.13	1.80
O_3 + NO ->	0.10	0.13	1.65
Propene (R^2 = 0.91)			
SC(MGLY, ARO2)	0.20	-0.49	23.9
HCHO + hv -> $2HO_2$ + CO	0.34	0.36	12.7
PROPENE + OH ->	0.14	0.34	11.7
SC(AFG2, ARO2)	0.23	-0.28	8.00
ARO2 + OH ->	0.27	-0.25	6.08
ARO1 + OH ->	0.27	-0.23	5.11
RCHO + hv ->	0.34	-0.15	2.40
CCHO + hv ->	0.34	0.15	2.18
O_3 + hv ->	0.27	-0.15	2.16
SC(MGLY, ARO1)	0.29	-0.14	1.90
CCHO + OH ->	0.18	0.14	1.84
Butane (R^2=0.89)			
NO_2 + OH ->	0.27	-0.44	19.5
NC_4 + OH ->	0.18	0.38	14.5
O_3 + hv ->	0.27	0.34	11.9
O^1D + M ->	0.18	-0.22	4.70

O^1D + H_2O ->	0.18	0.20	4.14
HCHO + hv -> $2HO_2$ + CO	0.34	0.17	2.81
NO_2 + hv ->	0.18	0.15	2.38
ARO2 + OH ->	0.27	0.12	1.41
PAN ->	0.40	0.11	1.24
MEK (adjusted R^2 = 0.88)			
MEK + OH ->	0.27	0.51	26.9
MEK + hv ->	0.42	0.45	20.6
NO_2 + OH ->	0.27	-0.25	6.50
O_3 + hv ->	0.27	0.17	2.86
HCHO + hv -> $2HO_2$ + CO	0.34	0.13	1.57
NO_2 + hv ->	0.18	0.25	1.41
O^1D + H_2O ->	0.18	0.11	1.30
SC(MGLY, ARO2)	0.20	-0.11	1.25
Benzene (R^2=0.84)			
BENZENE + OH ->	0.27	0.70	48.1
SC(AFG1, BENZENE)	0.33	0.53	27.6
P1U1	0.40	0.27	7.27
NO_2 + OH ->	0.27	-0.25	6.02
NO_2 + hv ->	0.18	0.19	3.46
PAN ->	0.40	0.15	2.29
SC(MGLY, ARO2)	0.20	-0.14	2.04
O_3 + NO ->	0.10	-0.10	1.02
Toluene (R^2=0.78)			
SC(MGLY, TOLUENE)	0.31	0.53	28.6
TOLUENE + OH ->	0.18	0.48	23.4
SC(MGLY, ARO1)	0.26	0.36	12.9
SC(MGLY, ARO2)	0.20	-0.24	5.83
NO_2 + OH ->	0.27	-0.18	3.39
SC(AFG2, TOLUENE)	0.34	0.16	2.58
NO_2 + hv ->	0.18	0.14	2.08
O_3 + hv ->	0.27	-0.14	1.98
ALK2 + OH ->	0.27	-0.11	1.27

ARO1 + OH ->	0.27	-0.11	1.16
SC(AFG2, ARO2)	0.23	-0.10	1.03
O-xylene (R^2=0.87)			
SC(MGLY, O-XYLENE)	0.43	0.67	44.5
SC(AFG2, O-XYLENE)	0.30	0.29	8.44
SC(MGLY, ARO2)	0.20	-0.20	3.98
NO_2 + OH ->	0.27	0.17	2.90
O_3 + hv ->	0.27	-0.14	1.93
ARO2 + OH ->	0.27	-0.14	1.91
HCHO + hv ->2HO_2 + CO	0.34	-0.10	1.09
SC(AFG2, ARO2)	0.23	-0.10	1.04
O^1D + M ->	0.18	0.10	1.00
135-TMB (R^2=0.93)			
SC(MGLY, 135TMB)	0.29	0.51	25.8
SC(AFG2, 135TMB)	0.40	0.43	18.6
ARO2 + OH ->	0.27	-0.25	6.18
SC(MGLY, ARO2)	0.20	-0.16	2.53
NO_2 + OH ->	0.27	0.14	2.07
O_3 + hv ->	0.27	-0.14	2.02
135TMB + OH ->	0.31	0.13	1.81
HCHO + hv -> 2HO_2 + CO	0.34	-0.12	1.54
NO_2 + hv ->	0.18	0.12	1.36
RCHO + hv ->	0.34	-0.10	0.97

[a] Ridge regression for normalized predictors

[b] Normalized uncertainty of rate constant and chamber-derived aromatics oxidation parameters

[c] Uncertainty contribution.

Table 20. Apportionment of Uncertainty in Relative MOIRs [a]

Parameters	σ/μ [b]	**Std. Reg. Coef.**	**UC (%)** [c]
Formaldehyde (R^2=0.91)			
ARO2 + OH ->	0.27	-0.34	11.6
O_3 + hv ->	0.27	-0.33	11.1
NO_2 + OH ->	0.27	0.29	8.43
PAN ->	0.40	-0.29	8.19
CCOO2 + NO ->	0.34	-0.27	7.10
SC(MGLY, ARO2)	0.20	-0.26	6.77
NO_2 + hv ->	0.18	-0.25	6.36
O^1D + M ->	0.18	0.22	4.87
OLE3 + O_3 ->	0.42	-0.20	4.08
O^1D + H_2O ->	0.18	-0.20	4.04
HCHO + hv -> $2HO_2$ + CO	0.34	0.19	3.79
O_3 + NO ->	0.10	0.14	1.86
SC(AFG2, ARO2)	0.23	-0.12	1.47
RCHO + hv ->	0.34	-0.11	1.24
Propene (R^2 = 0.82)			
SC(MGLY, ARO2)	0.20	-0.35	11.9
PROPENE + OH ->	0.14	0.32	10.3
HCHO + hv -> $2HO_2$ + CO	0.34	0.30	9.26
C2COO2 + NO_2 ->	0.75	0.27	7.18
PPN ->	0.66	-0.24	5.66
SC(AFG2, ARO2)	0.23	-0.20	4.16
NO_2 + hv ->	0.18	-0.19	3.63
ARO2 + OH ->	0.27	-0.18	3.20
ARO1 + OH ->	0.27	-0.17	3.01
CRES + NO_3 ->	0.75	0.16	2.69
CO + OH ->	0.27	0.16	2.54
Butane (R^2=0.94)			
NC_4 + OH ->	0.18	0.45	20.2
O_3 + hv ->	0.27	0.38	14.2
NO_2 + OH ->	0.27	-0.33	10.8

$O^1D + M$ ->	0.18	-0.24	5.80
$O^1D + H_2O$ ->	0.18	0.24	5.61
PAN ->	0.40	0.22	4.99
NO_2 + hv ->	0.18	0.19	3.59
CCOO2 + NO ->	0.34	0.18	3.15
HCHO + hv -> $2HO_2$ + CO	0.34	0.17	2.95
ARO2 + OH ->	0.27	0.10	1.09
MEK (adjusted R^2 = 0.91)			
MEK + OH ->	0.27	0.59	35.0
MEK + hv ->	0.42	0.25	6.14
PAN ->	0.40	0.23	5.45
O_3 + hv ->	0.27	0.23	5.36
NO_2 + OH ->	0.27	-0.21	4.39
$CCOO_2$ + NO ->	0.34	0.19	3.74
NO_2 + hv ->	0.18	0.15	2.24
$O^1D + H_2O$ ->	0.18	0.13	1.73
$O^1D + M$ ->	0.18	-0.13	1.58
HCHO + hv -> $2HO_2$ + CO	0.34	0.13	1.58
Benzene (R^2=0.82)			
BENZENE + OH ->	0.27	0.45	20.4
SC(AFG1, BENZENE)	0.33	0.42	17.4
PAN ->	0.40	0.37	14.0
O_3 + hv ->	0.27	-0.24	5.55
NO_2 + hv ->	0.18	0.23	5.12
P1U1	0.40	0.21	4.59
CO + OH ->	0.27	-0.19	3.54
$O^1D + H_2O$ ->	0.18	-0.15	2.27
C2COO2 + NO_2 ->	0.75	0.14	1.92
$O^1D + M$ ->	0.18	0.14	1.88
CCOO2 + NO ->	0.34	0.12	1.55
SC(MGLY, ARO2)	0.20	-0.12	1.45
HCHO + hv -> $2HO_2$ + CO	0.34	-0.12	1.32
O_3 + NO ->	0.10	-0.11	1.29
NO_3 + hv ->	0.42	0.11	1.27

Toluene (R^2=0.93)			
O_3 + hv ->	0.27	-0.42	17.3
SC(MGLY, TOLUENE)	0.31	0.33	10.6
CRES + NO_3 ->	0.75	-0.27	7.14
O^1D + M ->	0.18	0.26	6.91
O^1D + H_2O ->	0.18	-0.25	6.24
TOLUENE + OH ->	0.18	0.24	5.69
SC(MGLY, ARO1)	0.29	0.23	5.44
SC(MGLY, ARO2)	0.20	-0.18	3.41
HCHO + hv -> 2HO_2 + CO	0.34	-0.18	3.40
SC(AFG2, ARO2)	0.23	-0.11	1.26
SC(AFG2, TOLUENE)	0.34	0.11	1.21
O-xylene (R^2=0.92)			
SC(MGLY, OXYLENE)	0.43	0.56	31.9
O_3 + hv ->	0.27	-0.30	8.71
SC(AFG2, OXYLENE)	0.30	0.26	6.84
NO_2 + OH ->	0.27	0.20	4.09
O^1D + M ->	0.18	0.19	3.65
O^1D + H_2O ->	0.18	-0.19	3.47
SC(MGLY, ARO2)	0.20	-0.18	3.15
HCHO + hv -> 2HO_2 + CO	0.34	-0.16	2.71
ARO2 + OH ->	0.27	-0.14	1.87
SC(AFG2, ARO2)	0.23	-0.12	1.36
CRES + NO_3 ->	0.75	-0.10	1.02
135-TMB (R^2=0.93)			
SC(MGLY, 135TMB)	0.29	0.47	22.0
SC(AFG2, 135TMB)	0.40	0.39	15.4
O_3 + hv ->	0.27	-0.24	5.90
ARO2 + OH ->	0.27	-0.22	4.75
PAN ->	0.40	-0.17	2.77
O^1D + H_2O ->	0.18	-0.15	2.40
O^1D + M ->	0.18	0.15	2.16
NO_2 + hv ->	0.18	-0.15	2.13
CCOO2 + NO ->	0.34	-0.14	1.99

SC(MGLY, ARO2)	0.20	-0.14	1.98
HCHO + hv -> 2HO$_2$ + CO	0.34	-0.14	1.90
NO_2 + OH ->	0.27	0.10	1.09
135TMB+ OH ->	0.31	0.10	1.09

[a] Ridge regression for normalized predictors

[b] Normalized uncertainty of rate constant and chamber-derived aromatics oxidation parameters

[c] Uncertainty contribution.

Table 21. Apportionment of Uncertainty in Relative EBIRs [a]

Parameters	**σ/μ [b]**	**Std. Reg. Coef.**	**UC (%) [c]**
Formaldehyde (R^2=0.89)			
PAN ->	0.40	-0.44	19.2
CCOO2 + NO ->	0.34	-0.35	12.0
NO_2 + hv ->	0.18	-0.30	9.00
ARO2 + OH ->	0.27	-0.28	7.81
O_3 + hv ->	0.27	-0.22	4.90
SC(MGLY, ARO2)	0.20	-0.20	4.11
HCHO + hv -> 2HO$_2$ + CO	0.34	0.18	3.22
OLE3 + O_3 ->	0.42	-0.17	2.74
C2COO2 + NO_2 ->	0.75	0.15	2.38
O^1D + M ->	0.18	0.14	2.02
CO + OH ->	0.27	0.14	2.02
O^1D + H_2O ->	0.18	-0.13	1.60
O_3 + NO ->	0.10	0.13	1.60
Propene (R^2 = 0.80)			
C2COO2 + NO_2 ->	0.75	0.30	9.03
CRES + NO_3 ->	0.75	0.28	8.01
PPN ->	0.66	-0.27	7.42
PROPENE + OH ->	0.14	0.26	6.81
SC(MGLY,ARO2)	0.20	-0.25	6.03
NO_2 + hv ->	0.18	-0.22	4.68
CO + OH ->	0.27	0.20	4.06
ARO2 + OH ->	0.27	-0.16	2.43
CCHO + OH ->	0.18	0.14	2.03

SC(AFG2,ARO2)	0.23	-0.14	1.83
HCHO + hv -> $2HO_2$ + CO	0.34	0.13	1.68
PAN ->	0.40	-0.12	1.53
CCOO2 + NO ->	0.34	-0.12	1.39
Butane (R^2=0.93)			
NC_4 + OH ->	0.18	0.54	29.4
PAN ->	0.40	0.30	8.96
NO_2 + OH ->	0.27	-0.28	7.71
O_3 + hv ->	0.27	0.24	5.63
CCOO2 + NO ->	0.34	0.20	3.83
NO_2 + hv ->	0.18	0.17	3.00
O^1D + H_2O ->	0.18	0.15	2.26
O^1D + M ->	0.18	-0.15	2.23
CRES + NO_3 ->	0.75	0.12	1.33
HCHO + hv -> $2HO_2$ + CO	0.34	0.11	1.16
MEK (adjusted R^2 = 0.92)			
MEK + OH ->	0.27	0.62	37.9
PAN ->	0.40	0.30	8.71
$CCOO_2$ + NO ->	0.34	0.23	5.22
MEK + hv ->	0.42	0.19	3.50
NO_2 + OH ->	0.27	-0.17	2.90
NO_2 + hv ->	0.18	0.14	2.06
O_3 + hv ->	0.27	0.13	1.76
CRES + NO_3 ->	0.75	0.12	1.39
C_2COO_2 + NO_2 ->	0.75	-0.11	1.30
PPN ->	0.66	0.10	1.00
Benzene (R^2=0.79)			
PAN ->	0.40	0.49	23.6
NO_2 + hv ->	0.18	0.22	5.01
NO_2 + OH ->	0.27	0.20	4.06
CO + OH ->	0.27	-0.20	3.83
O_3 + hv ->	0.27	-0.19	3.56
NO_3 + hv ->	0.42	0.18	3.24
SC(AFG1, BENZENE)	0.33	0.18	3.19

CCOO2 + NO ->	0.34	0.16	2.58
BENZENE + OH ->	0.27	0.15	2.23
HO_2 + NO ->	0.18	-0.14	1.85
P1U1	0.35	0.13	1.78
C2COO2 + NO_2 ->	0.75	0.12	1.47
O^1D + H_2O ->	0.18	-0.12	1.36
O_3 + NO ->	0.10	-0.10	1.07
O^1D + M ->	0.18	0.10	1.03
Toluene (R^2=0.90)			
CRES + NO_3 ->	0.75	-0.45	20.1
O_3 + hv ->	0.27	-0.26	6.71
SC(MGLY, TOLUENE)	0.31	0.25	6.14
PAN ->	0.40	0.22	4.83
SC(MGLY, ARO1)	0.29	0.18	3.39
NO_3 + hv ->	0.42	0.17	2.94
NO_2 + OH ->	0.27	0.16	2.71
O^1D + M ->	0.18	0.16	2.62
O^1D + H_2O ->	0.18	-0.16	2.54
CO + OH ->	0.27	-0.15	2.22
NO_2 + hv ->	0.18	0.14	1.99
TOLUENE + OH ->	0.18	0.12	1.54
HCHO + hv -> $2HO_2$ + CO	0.34	-0.10	1.05
O-xylene (R^2=0.91)			
SC(MGLY, OXYLENE)	0.43	0.57	32.0
SC(AFG2, OXYLENE)	0.30	0.26	6.84
CRES + NO_3 ->	0.75	-0.24	5.66
NO_2 + OH ->	0.27	0.22	4.68
O_3 + hv ->	0.27	-0.21	4.23
O^1D + H_2O ->	0.18	-0.13	1.79
SC(MGLY, ARO2)	0.20	-0.13	1.73
O^1D + M ->	0.18	0.13	1.71
HCHO + hv -> $2HO_2$ + CO	0.34	-0.12	1.44
ARO2 + OH ->	0.27	-0.12	1.44
C2COO2 + NO_2 ->	0.75	0.12	1.34

SC(AFG2, ARO2)	0.23	-0.10	1.02
135-TMB (R^2=0.92)			
SC(MGLY, 135TMB)	0.29	0.49	23.7
SC(AFG2, 135TMB)	0.40	0.41	16.7
PAN ->	0.40	-0.26	6.85
CCOO2 + NO ->	0.34	-0.19	3.44
ARO2 + OH ->	0.27	-0.18	3.24
NO_2 + hv ->	0.18	-0.15	2.40
O_3 + hv ->	0.27	-0.15	2.33
C2COO2 + NO_2 ->	0.75	0.10	1.07
O^1D + H_2O ->	0.18	-0.10	1.03
SC(MGLY, ARO2)	0.20	-0.10	1.00

[a] Ridge regression for normalized predictors
[b] Normalized uncertainty of rate constant and chamber-derived aromatics oxidation parameters
[c] Uncertainty contribution.

Regression results for incremental reactivities of selected compounds are listed in Tables 16 - 18 and those for relative reactivities in Tables 19 - 21. Regression results for the remaining compounds are presented in Appendix E. The regression results show that MIRs are generally sensitive to the rate parameters for the reactions NO_2 and O_3 photolysis, NO_2+OH, HO_2+NO, O_3+NO, PAN formation and decomposition, and the primary oxidation reaction for the selected compound (e.g., VOC+OH or VOC photolysis). The MIRs for relatively fast reacting compounds such as alkenes and aldehydes are also sensitive to the rate parameters for HCHO photolysis, O^1D chemistry, ARO2+OH, and to the chamber-derived aromatics oxidation parameter B1MG for the lumped aromatic species ARO2. However, the MIRs for relatively slowly reacting compounds such as butane and MEK are not as sensitive to the parameters of the lumped aromatic species ARO2.

The MIR for each aromatic compound is very sensitive to its chamber-derived aromatics oxidation parameters. The MIRs for most of the aromatics belonging to the ARO2 group, such as xylenes and trimethylbenzenes, are also sensitive to the rate parameter for ARO2+OH and the chamber-derived AFG2 or MGLY yields for ARO2.

The aromatics oxidation parameters and the rate constants for reaction with OH for each compound have positive effects on the MIR of that compound. In contrast, the chamber-derived aromatics oxidation parameters for the lumped aromatic species ARO2 and the rate constants for ARO2+OH have negative effects on the MIRs of the explicit aromatic compounds. The negative response is due to the fact that a higher value for the lumped aromatics parameters means higher radical production but simultaneously lower NO_x levels due to PAN formation from AFG2 and MGLY reactions. As a result, the simulation conditions have a higher "effective" VOC/NO_x ratio than the nominal MIR case, and giving lower O_3 reactivities.

The R^2 values for MOIRs and EBIRs are generally higher than those for MIRs, which indicates that the linear model is more appropriate for the higher VOC/NO_x ratio. Rate constants for O_3 and HCHO photolysis, O^1D+H_2O, O^1D+M appear more important for the MOIRs of the selected VOCs than for the MIRs. The MOIRs for relatively fast reacting compounds such as alkenes and aldehydes are also sensitive to the rate parameters for reaction of HO_2+NO and the chamber-derived aromatics oxidation parameters (B1MG and B1U2) for the lumped aromatic species ARO2. The MOIRs for relatively slow reacting compounds such as butane and MEK are also sensitive to the rate parameters for NO_2 photolysis, PAN formation and decomposition, O_3+NO, CO+OH, PPN formation and the primary oxidation reaction for the selected VOC. However, they are not as sensitive to the chamber-derived aromatics oxidation parameters and the reactions for the lumped species ARO2.

The chamber-derived aromatics oxidation parameter B1MG for the lumped aromatic species ARO2 and the rate parameters for ARO2+OH and CRES+NO_3 are more influential for the MOIRs of aromatic compounds than for their MIRs, while the rate parameters for the primary oxidation reactions are less influential in the MOIR case. The MOIR for each aromatic compound is very sensitive to its chamber-derived aromatics oxidation parameters and the rate parameter of NO_2 photolysis. Exceptions include the MOIRs for trimethylbenzene which are not so sensitive to the rate parameter for CRES+NO_3 and NO_2 photolysis. Instead, the MOIRs for trimethylbenzene are sensitive to the chamber-derived oxidaiton paramter B1U2 for each isomer.

The direction of the effects of the chamber-derived aromatics oxidation parameters are the same as those in the MIR case: negative effects of the chamber-derived parameters for the lumped aromatic species on MOIRs for explicit aromatics and positive effects of the chamber-derived parameters for each aromatic species on their corresponding MOIRs. However, for the rate constants that affect the supply of hydroxyl and peroxyl radicals in the simulations (e.g., HCHO photolysis rates), the response of MOIRs is opposite to that of the MIRs. Starting from nominal MOIR conditions, enhanced radical availability leads to lower sensitivity of peak O_3 to added inputs of organic compounds. In contrast, under nominal MIR conditions, the main effect of increased radical availability on MIRs is positive in speeding up the rate of oxidation of the added organic compound or of its reaction intermediates so that more NO to NO_2 conversions occur prior to the end of the simulations (18).

The regression results in the EBIR case are fairly similar to those in the MOIR case except that rate parameters for NO_2 photolysis and CRES + NO_3 are more influential in the EBIR case. In addition, the EBIRs for the aromatic compounds are not as sensitive to the chamber-derived oxidation parameters for the lumped aromatics class ARO2, or to the rate constant for ARO2+OH.

The influential factors for the incremental reactivities of the base mixture are similar to those for the aromatic compounds in each case. These factors generally include the rate parameters for O_3 and NO_2 photolysis, HO_2+NO, O^1D and PAN chemistry for the three cases. At higher VOC/NO_x conditions, such as in the EBIR case, the incremental reactivity for the base mixture is also sensitive to the rate constants for O_3+NO, PPN chemistry, CO+OH and CRES+NO_3. Due to the effects of these factors on the base mixture and each explicit compound, the regression results for relative reactivities (Tables 19-21) show some notable differences from those for the absolute incremental reactivities. In all three cases, relative reactivities of highly reactive compounds such as HCHO and propene exhibit negative sensitivity to the NO_2 photolysis rate, while a positive sensitivity to this parameter is observed in their absolute reactivities. The relative reactivities for slowly reacting compounds such as n-butane and MEK show high, positive sensitivity to the rate parameters for O_3 photolysis and $O^1D + H_2O$ and negative sensitivity to $O^1D + M$. This result indicates that these compounds are more sensitive to the supply of OH than the base mixture, and helps explain how relative reactivities for these compounds can be more uncertain than their absolute reactivities. Uncertainties in the oxidation parameters of the individual aromatic compounds and of the lumped aromatics species are even more influential for their relative reactivities than for their absolute incremental reactivities. Either the rate constants or the product yields of the explicit oxidation reactions are the most influential sources of uncertainty in the relative reactivities of most of the aromatic compounds.

5. Summary and Conclusions

This study has explored how experimental and modeling uncertainties affect reactivity estimates for aromatic compounds. Considering the uncertainties in the mechanism rate parameters and chamber characterization experiments, the optimal estimates for chamber characterization parameters are obtained with uncertainty levels (1σ relative to the mean) ranging from 24 to 36% for RSI and 8 to 45% for HONO-F (except for the DTC1 chamber). The CO-NO_x experiments are found to give somewhat lower RSI and higher HONO-F values than those obtained from the n-butane-NO_x experiments. These chamber characterization parameters are very sensitive to uncertainties in rate constants for n-butane+OH or CO+OH, NO_2+OH and NO_2 photolysis (or light intensity), while the absorption spectra uncertainty for HONO photolysis is also influential for HONO-F. All of these factors need to be considered carefully in the design of future chamber characterization experiments.

The uncertainties for the AFG1 yield from benzene oxidation and the quantum yield for AFG1 photolysis are about 33% and 40%, respectively. The influential contributors to the uncertainties in these parameters are the uncertainties in the rate constants for the reactions of benzene+OH, NO_2+OH, O_3+NO_2, NO_2 photolysis (or light intensity) and in the initial concentrations for NO_x and the chamber characterization parameters. The uncertainties for the chamber-derived parameters for the other aromatics range from 30 to 50% in most cases. Exceptions include the MGLY yields for ethylbenzene and p-xylene oxidation, for which the uncertainties are 63% and 71%, respectively. The average agreement of the mean values with the values used in SAPRC-97 is about 15%. The chamber-derived aromatics oxidation parameters are generally sensitive to uncertainties in the chamber characterization parameters, RSI and HONO-F, in the rate constants for NO_2+OH, aromatics+OH, PAN formation and decomposition and HNO_4 dissociation, and in experimental conditions such as the NO_2 photolysis rate and initial aromatic concentrations.

The uncertainty estimates calculated in this study for the aromatics oxidation parameters are much lower than the subjective estimates used in previous studies (18, 46). These reduced uncertainties and the updated uncertainty estimates for other mechanism parameters also result in reduced estimates of uncertainty in incremental reactivities, compared to previous estimates (18, 46). The uncertainty level for MIRs, MOIRs and EBIRs ranges from about 20 to 35% for most of the VOCs studied. For aromatics, the uncertainty estimates for MIRs are fairly consistent, ranging from about 27 to 32%. The uncertainty estimates for MOIRs and EBIRs range from 38 to 52% and 30% to 45% for most of the aromatics. Exceptions include the MOIR for ethylbenzene, which has an estimated uncertainty of 75%, and the EBIRs for benzene, ethylbenzene, toluene and p-xylene which have greater than 80% uncertainties.

The uncertainties in the relative incremental reactivities are fairly consistent across the three cases for most of the VOCs, ranging from about 10 to 30%. However, the uncertainty in the relative reactivities for ethylbenzene, p-xylene, and toluene differs significantly across the cases. Uncertainties in the relative reactivities of most, but not all compounds are smaller than the uncertainties in their absolute incremental reactivities. The exceptions include some slowly reacting compounds under MIR, MOIR and EBIR conditions, and some of the aromatic compounds under EBIR conditions.

Among the 102 SAPRC-97 parameters treated as random variables in the Monte Carlo simulations, a relatively small set of parameters are broadly influential. These include the rate parameters for NO_2, O_3 and HCHO photolysis, O^1D reactions, PAN formation and decomposition, HO_2 + NO, nitric acid formation, and aromatics oxidation parameters. In particular, uncertainties in AFG2 and MGLY yields from reactions of explicit aromatic compounds are influential for both the absolute and relative reactivities of the respective compounds. Uncertainties in the product yields for the lumped ARO2 class, which are derived from those of the explicit compounds, are influential for the absolute MIRs and MOIRs of rapidly reacting VOCs, and for the relative reactivities of most compounds in all three cases. Estimates of uncertainty in rate parameters for PAN chemistry were lower than those used in previous studies (18, 46), and so were less influential for incremental reactivity estimates. Uncertainty in the NO_2 + OH rate constant appears less influential than in previous studies because the positive correlation of this rate constant with the chamber-derived aromatics oxidation parameters was considered here.

Overall, the uncertainties in the chamber-derived parameters are vey influential for the incremental reactivity estimates of the aromatic compounds. The uncertainties in the chamber-derived parameters of the individual aromatics contribute from 30% to 70%, from 14% to 60% and from 3% to 56% of the uncertainty in their relative MIRs, MOIRs and EBIRs, respectively. Among all of the compounds and cases, the chamber-derived parameters contribute relatively little to the uncertainties in the relative EBIRs for benzene, toluene, p-xylene and ethylbenzene. From 3% (for benzene) to 14% (for p-xylene) of the total uncertainty in the relative EBIRs of these compounds is due to their chamber-derived parameters. For the relative EBIRs of toluene, p-xylene and ethylbenzene a larger source of uncertainty is the rate constant for the reaction CRES + NO_3. Thus this reaction should also be a target for further research.

This study has estimated the effect of uncertainties in chamber experiments and SAPRC-97 parameters on incremental reactivities of aromatic compounds. A fundamental limitation of the analysis is the fact that only the values of the chamber characterization and aromatics oxidation parameters are considered as sources of uncertainty, not their form. In addition, the SAPRC-97 mechanism and its auxiliary chamber model are assumed to accurately adjust for differences between the chamber and the atmospheric conditions for which incremental reactivities are of interest. The only criteria used in the parameter estimation problems are the change in ($[O_3]$-[NO]) and the aromatics concentrations (for the aromatics oxidation parameters). Concentrations of other products such as organic nitrates are not considered, so the parameters estimated here may not accurately represent their chemistry. Finally, input uncertainty estimates used for the chamber experiments and SAPRC-97 rate parameters are subjective, and therefore reflect the biases of the experts who made them.

Given the form of the aromatics oxidation parameters used in the SAPRC-97 mechanism and the approach used to estimate them, this study provides improved estimates of uncertainties in incremental reactivities of aromatic compounds. The subjective estimates of aromatics parameter uncertainties used in previous studies are replaced by propagating experimental and modeling uncertainties through the chamber-derived parameter estimation problem.Correlations between the estimated parameters and the other rate parameters for the mechanism are preserved through all stages of the analysis. Constrained by the experimental data, uncertainty estimates for aromatic compound MIRs are about the same as those for other VOCs with relatively well-established mechanisms. However, MOIRs and EBIRs of aromatic compounds are still estimated to have higher uncertainties than those of most other VOCs. In the absence of significant advances in understanding aromatics oxidation mechanisms, uncertainty in aromatic compound MOIRs and EBIRs could be reduced most by improving the characterization of radical sources, light intensity and initial concentrations in environmental chamber studies, and by reducing uncertainty in the rate constants for NO_2 + OH, aromatics + OH, and CRES + NO_3. Because uncertainties are especially high under MOIR and EBIR conditions, future chamber studies of aromatics chemistry should emphasize low-NO_x conditions.

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References

(1) National Research Council: Rethinking the Ozone Problem in Urban and Regional Air Pollution. National Academic Press, Washington, DC., 1991.

(2) South Coast Air Quality Management District and Southern California Association of Governments: 1994 Air Quality Management Plan - Meeting the Clean Air Challenge.

(3) Carter, W.P.L., Pierce, J.A., Luo, D. and Malkina, I.L.: Environmental Chamber Study of Maximum Incremental Reactivities of Volatile Organic Compounds at Atmospheric Environment. 1995. Internet address: ftp://cert.ucr.edu/pub/carter/pubs.

(4) McBride, S.J., Oravetz, M.A. and Russell, A.G.: Cost-Benefit and Uncertainty Issues in Using Organic Reactivity to Regulate Urban Ozone. *Environmental Science & Technology/News,* 31:238A- 244A, 1997.

(5) California Air Resources Board: Development and Evaluation of Ozone Reactivity Scale for Low-emission Vehicles and Clean Fuel Regulations. State of California Air Resources Board: Sacramento, CA. April, 1992.

(6) Carter, W.P.L.: Development of Ozone Reactivity Scales for Volatile Organic Compounds. *Journal of the Air and Waste Management Association*, 44:881-899, 1994.

(7) Kiotz, B., Barnes, I. and Becker K.H.: New Results on the Atmospheric Photooxidation of Simple Alkylbenzenes. *Chemical Physics*, 231:289-301, 1998.

(8) Kwok, E.S.C., Aschmann S.M., Atkinson, R. and Arey, J.: Products of the Gas-phase Reactions of o-, m- and p-xylene with the OH Radical in the Presence and Absence of NO_x. *J. Chem. Soc. Faraday Trans*., 93(16): 2847-2854, 1997.

(9) Smith D.F., McIver C.D. and Kleindienst T.E.: Primary Product Distribution from the Reaction of Hydroxyl Radicals with Toluene at Ppb NO_x Mixing Ratios. *Journal of Atmospheric Chemistry*, 30(2): 209-228, 1998.

(10) Odum, J.R., Jungkamp, T.P.W., Griffin R.J., Flagan, R.C. and Seinfeld, J.H.: Aromatics, Reformulated Gasoline, and Atmospheric Aerosol Formation. *Environmental Science & Technology,* 31(7):1890 - 1897, 1997.

(11) Andino, J.M., Smith J.N., Flagan R.C., Goddard, W.A. and Seinfeld J.H.: Mechanism of Atmospheric Photooxidation of Aromatics: A Theoretical Study. *Journal of Physical Chemistry,* 100: 10967-10980, 1996.

(12) Forstner H.L., Flagan, R.C. and Seinfeld, J.H.: Secondary Organic Aerosol from Photooxidation of Aromatic Hydrocarbons: Molecular Composition. *Environmental Science & Technology*, 31:1345-1358, 1997.

(13) Killus J.P. and Whitten G.Z.: A Mechanism Describing the Photochemical Oxidation of Toluene in Smog. *Atmospheric Environment,* 16:1973-1988, 1982.

(14) Gery, M.W., Whitten, G.Z., Killus, J.P., and Dodge, M.C.: A Photochemical Mechanism for Urban and Regional Scale Computer Modeling, *Journal of Geophysical Research,* 94:12925-12956, 1989.

(15) Stockwell, W.R., Middleton, P., Chang, J.S. and Tang, X.: The RADM2 Chemical Mechanism for Regional Air Quality Modeling, *Journal of Geophysical Research,* 95:16343-16367, 1990.

(16) Carter,W.P.L. Luo, D., and Malkina, I.L.: 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, Inc., Project M- 9; National Renewable Energy Laboratory, contract ZF-2-12252-07., 1997.

(17) Carter W.P.L.: Development and Application of an Updated Photochemical Mechanism for VOC Reactivity Assessment. Quarterly Report to the California Air Resources Board, Contract N0. 92-329, 1996.

(18) Yang, Y.J., Stockwell, W.R., and Milford, J.B.: Uncertainty in Incremental Reactivities of Volatile Organic Compounds, *Environmental Science & Technology*, 23:1336-1345, 1995.

(19) Bergin,M.S., Russell, A.G., Yang, Y.J., Miford, J.B., Kirchner, F., Stockwell, W.R.: Effects of Uncertainty in SAPRC90 Rate Constants and Product Yields on Reactivity Adjustment Factors for Alternatively Fueled Vehicle Emissions, Report prepared for the National Renewable Energy Laboratory, Contract No.13013-1, Golden,CO,June, 1995.

(20) Carter, W.P.L., Luo, D., Malkina I.L., and Fitz, D.: The University of California, Riverside Environmental Chamber Data Base for Evaluating Oxidant Mechanisms, Indoor Chamber Experiments Through 1993, Volume 1, Cooperative Agreement No.815779, U.S. Environmental Protection Agency, Research Triangle Park, NC., 1996.

(21) Carter, W.P.L., and Lurmann, F.W.: Evaluation of Detailed Gas- Phase Atmospheric Reaction Mechanism Using Environmental Chamber Data, *Atmospheric Environment*, 25A:2771-2806, 1991.

(22) Carter, W.P.L.: A Detailed Mechanism for the Gas-Phase Atmospheric Reactions of Organic Compounds. *Atmospheric Environment*, 24A: 481-518, 1990.

(23) Carter, W.P.L., Luo, D., Malkina, I., and Pierce, J.: Environmental Chamber Studies of Atmospheric Reactivities of Volatile Organic Compounds: Effects of Varying Chamber and Light Source, NREL/TP-425- 7621, 1995.

(24) Carter, W.P.L.: Discussion of Uncertainty in Input Data and Parameters in the Aromatic Optimizations for the SAPRC-97 Mechanism. February 1998.

(25) Whitten, G.Z., Killus, J.P., Johnson, R.G.: Modeling of Auto Exhaust Smog Chamber Data for EKMA Development, EPA-600/3-85- 025, 1985.

(26) Carter, W.P.L.: Documentation of a Gas Phase Photochemical Mechanism for Use in Airshed Modeling, Appendix B to Final Report, California Air Resources Board Contract No. A5-122-32, Statewide Air Pollution Research Center, University of California, Riverside, CA., 1988.

(27) Diweker, U.M.: A Process Analysis Approach to Pollution Prevention. *AIChE Symposium Series*, 90:168-179, 1994.

(28) Bard, Y.: Nonlinear Parameter Estimation, Academic Press, 1974.

(29) Powell, M.J.D.:A Fast Algorithm for Nonlinear Constrained Optimization Calculations. *Dunde Conf. Numerical Anal.*, Dundee, Scotland, 1977.

(30) Han, S.P.: A Globally Convergent Method for Nonlinear Programming. *JOTA*, 22(3), 1977

(31) Biegler, L.T. and Hughes R.R.: Process Optimization: A Comparative Study. *Computers and Chemical Engineering*, 7:645-661, 1983.

(32) Haftka, Raphael T. and Gurdal, Zafer: Elements of Structure Optimization, Kluwer Academic Publishers, 1992.

(33) Dunker, A.M.: The Direct Decoupled Method for Calculating Sensitivity Coefficients in Chemical Kinetics. *Journal of Chemical Physics*, 81: 2385-2393, 1984.

(34) Iman, R.L., and Shortencarier, M.J.: A FORTRAN77 Program and User’s Guide for the Generation of Latin Hypercube and Random Samples for Use with Computer Models, Rep.

SAND83-2365, U.S. Dep. of Energy, Sandia National Laboratory, Albuquerque, N.M, 1984.

(35) DeMore, W.B., Sander, S.P., Golden, D.M., Molina, M.J., Hampson, R.F., Kurylo, M.J., Howard, C.J., Ravishankara, A.R., Kolb, M.J., and Molina M.J.: Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation No. 11, JPL Publ., 94-26, 1994 .

(36) DeMore, W.B., Golden, D.M., Hampson, R.F., Howard, C.J., Ravishankara, A.R., Kolb, M.J., and Molina, M.J.: Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation 12, JPL Publ. 97-4, 1997.

(37) Atkinson, R., Baulch, D.L., Cox, R.A., Hampson, R.F.Jr., Derr, A., Troe, J.: Evaluated Kinetic and Photochemical Data fro Atmospheric Chemistry: Supplement III. IUPAC Subcommittee on Gas Kinetic Data Evalution for Atmospheric Chemistry, *Journal of Phyical and Chemical Reference Data*, 13:1259- 1380, 1989.

(38) Stockwell, W.R., Yang, Y.J. and Milford, J.B.: A Compilation of Estimated Uncertainty Factors for Rate Constants in W.P.L. Carter’s Detailed Mechanism. Prepared for the Automotive Emissions Cooperative Research Program under Coordinating Research Council, Inc. Contract No. AQIRP-19-92, 1994.

(39) Brider, I., Caralp, F., Loirat, H., Lesclaux, R. and Veyret, B.: Kinetic and Theoretical Studies of the Reactions $CH_3C(O)O_2+NO_2+M = CH_3C(O)O_2NO_2+M$ between 248 and 393K and between 30 and 760 Torr. *Journal of Physical Chemistry*, 95: 3594-3600, 1991.

(40) Grosjean, D., Grosjean, E. and Williams II, E.L., *Air & Waste Management Association*, 44:391-396, 1994.

(41) Kleinbaum, D.G., Kupper, L.L., Muller, K.E. and Nizam, A.: Applied Regression Analysis and Other Multivariable Methods. Duxbury Press, 1998.

(42) Neter, J., Kutner, M.H., Nachtsheim, C.J. and Wasserman, W.: Applied Linear Statistical Models, IRWIN, 1996.

(43) Carter, W.P.L.: Updated Maximum Incremental Reactivity Scale for Regulatory Applications, Preliminary Report to the California Air Resources Board, Contract No. 95-308, August 1998.

(44) Yang, Y.J., Stockwell, W.R. and Milford, J.B.: Effect of Chemical Product Yield Uncertainties on Reactivities of VOCs and Emissions from Reformulated Gasolines and Methanol Fuels. *Environmental Science & Technology*, 30:1392-1397, 1996.

(45) Yang, Y.J.: Quantification of Uncertainty in Reactivities of VOC and Emissions From Reformulated Gasoline and Alternative Fuels, Ph.D Thesis, 1995. The University of Connecticut.

Appendix A-1: Listing of the SAPRC-97 Photochemical Mechanism

The chemical mechanism used in this study is given Appendix A-1, which lists the reactions for the SAPRC-97 photochemical mechanism used for parameter estimation and reactivity estimation. The mechanism includes 221 reactions and 97 species. The mechanism is adopted from (17) with added reactions for the lumped species. Those species names used in the mechanism and not defined in (22) are defined on the last page of this appendix.

```
 1 NO2                              -->  1.000 NO     +  1.000 O
 2 O         + O2        + M        -->  1.000 O3     +  1.000 M
 3 O         + NO2                  -->  1.000 NO     +  1.000 O2
 4 O         + NO2                  -->  1.000 NO3    +  1.000 M
 5 O3        + NO                   -->  1.000 NO2    +  1.000 O2
 6 O3        + NO2                  -->  1.000 O2     +  1.000 NO3
 7 NO        + NO3                  -->  2.000 NO2
 8 NO        + NO        + O2       -->  2.000 NO2
 9 NO2       + NO3                  -->  1.000 N2O5
10 N2O5                             -->  1.000 NO2    +  1.000 NO3
11 N2O5      + H2O                  -->  2.000 HNO3
12 NO2       + NO3                  -->  1.000 NO     +  1.000 NO2     +
                                         1.000 O2
13 NO3                              -->  1.000 NO     +  1.000 O2
14 NO3                              -->  1.000 NO2    +  1.000 O
15 O3                               -->  1.000 O      +  1.000 O2
16 O3                               -->  1.000 O1D2   +  1.000 O2
17 O1D2      + H2O                  -->  2.000 HO
18 O1D2      + M                    -->  1.000 O      +  1.000 M
19 HO        + NO                   -->  1.000 HONO
20 HONO                             -->  1.000 HO     +  1.000 NO
21 HO        + NO2                  -->  1.000 HNO3
22 HO        + HNO3                 -->  1.000 H2O    +  1.000 NO3
23 HO        + CO                   -->  1.000 HO2    +  1.000 CO2
24 HO        + O3                   -->  1.000 HO2    +  1.000 O2
25 HO2       + NO                   -->  1.000 HO     +  1.000 NO2
26 HO2       + NO2                  -->  1.000 HNO4
27 HNO4                             -->  1.000 HO2    +  1.000 NO2
28 HNO4      + HO                   -->  1.000 H2O    +  1.000 NO2     +
                                         1.000 O2
29 HO2       + O3                   -->  1.000 HO     +  2.000 O2
30 HO2       + HO2                  -->  1.000 HO2H   +  1.000 O2
31 HO2       + HO2       + M        -->  1.000 HO2H   +  1.000 O2
32 HO2       + HO2       + H2O      -->  1.000 HO2H   +  1.000 O2      +
                                         1.000 H2O
33 HO2       + HO2       + H2O      -->  1.000 HO2H   +  1.000 O2      +
                                         1.000 H2O
34 NO3       + HO2                  -->  1.000 HNO3   +  1.000 O2
35 NO3       + HO2       + M        -->  1.000 HNO3   +  1.000 O2
36 NO3       + HO2       + H2O      -->  1.000 HNO3   +  1.000 O2      +
                                         1.000 H2O
37 NO3       + HO2       + H2O      -->  1.000 HNO3   +  1.000 O2      +
                                         1.000 H2O
38 HO2H                             -->  2.000 HO
39 HO2H      + HO                   -->  1.000 HO2    +  1.000 H2O
40 HO        + HO2                  -->  1.000 H2O    +  1.000 O2
41 RO2       + NO                   -->  1.000 NO
42 RCO3      + NO                   -->  1.000 NO
43 RCO3      + NO2                  -->  1.000 NO2
44 RO2       + HO2                  -->  1.000 HO2
45 RCO3      + HO2                  -->  1.000 HO2
46 RO2       + RO2                  -->
47 RO2       + RCO3                 -->
48 RCO3      + RCO3                 -->
49 RO2R      + NO                   -->  1.000 NO2    +  1.000 HO2
50 RO2R      + HO2                  -->  1.000 OOH
51 RO2R      + RO2                  -->  1.000 RO2    +  0.500 HO2
52 RO2R      + RCO3                 -->  1.000 RCO3   +  0.500 HO2
```

```
53 RO2N      + NO                   -->  1.000 RNO3
54 RO2N      + HO2                  -->  1.000 OOH    +  1.000 MEK     +
                                         1.500 C
55 RO2N      + RO2                  -->  1.000 RO2    +  0.500 HO2     +
                                         1.000 MEK    +  1.500 C
56 RO2N      + RCO3                 -->  1.000 RCO3   +  0.500 HO2     +
                                         1.000 MEK    +  1.500 C
57 R2O2      + NO                   -->  1.000 NO2
58 R2O2      + HO2                  -->
59 R2O2      + RO2                  -->  1.000 RO2
60 R2O2      + RCO3                 -->  1.000 RCO3
61 RO2XN     + NO                   -->  1.000 N
62 RO2XN     + HO2                  -->  1.000 OOH
63 RO2XN     + RO2                  -->  1.000 RO2    +  0.500 HO2
64 RO2XN     + RCO3                 -->  1.000 RCO3   +  1.000 HO2
65 RO2NP     + NO                   -->  1.000 NPHE
66 RO2NP     + HO2                  -->  1.000 OOH    +  6.000 C
67 RO2NP     + RO2                  -->  1.000 RO2    +  0.500 HO2     +
                                         6.000 C
68 RO2NP     + RCO3                 -->  1.000 RCO3   +  1.000 HO2     +
                                         6.000 C
69 OOH                              -->  1.000 HO2    +  1.000 HO
70 HO        + OOH                  -->  1.000 HO
71 HO        + OOH                  -->  1.000 RO2R   +  1.000 RO2
72 HCHO                             -->  2.000 HO2    +  1.000 CO
73 HCHO                             -->  1.000 H2     +  1.000 CO
74 HCHO      + HO                   -->  1.000 HO2    +  1.000 CO      +
                                         1.000 H2O
75 HCHO      + HO2                  -->  1.000 HOCOO
76 HOCOO                            -->  1.000 HO2    +  1.000 HCHO
77 HOCOO     + NO                   -->  1.000 C      +  1.000 NO2     +
                                         1.000 HO2
78 HCHO      + NO3                  -->  1.000 HNO3   +  1.000 HO2     +
                                         1.000 CO
79 CCHO      + HO                   -->  1.000 CCO02  +  1.000 H2O     +
                                         1.000 RCO3
80 CCHO                             -->  1.000 CO     +  1.000 HO2     +
                                         1.000 HCHO   +  1.000 RO2R    +
                                         1.000 RO2
81 CCHO      + NO3                  -->  1.000 HNO3   +  1.000 CCOO2   +
                                         1.000 RCO3
82 RCHO      + HO                   -->  1.000 C2COO2 +  1.000 RCO3
83 RCHO                             -->  1.000 CCHO   +  1.000 RO2R    +
                                         1.000 RO2    +  1.000 CO      +
                                         1.000 HO2
84 NO3       + RCHO                 -->  1.000 HNO3   +  1.000 C2COO2  +
                                         1.000 RCO3
85 ACET      + HO                   -->  1.000 R2O2   +  1.000 HCHO    +
                                         1.000 CCOO2  +  1.000 RCO3    +
                                         1.000 RO2
86 ACET                             -->  1.000 CCOO2  +  1.000 HCHO    +
                                         1.000 RO2R   +  1.000 RCO3    +
                                         1.000 RO2
87 MEK       + HO                   -->  1.000 H2O    +  0.500 CCHO    +
                                         0.500 HCHO   +  0.500 CCOO2   +
                                         0.500 C2COO2 +  1.000 RCO3    +
                                         1.500 R2O2   +  1.500 RO2
88 MEK                              -->  1.000 CCOO2  +  1.000 CCHO    +
                                         1.000 RO2R   +  1.000 RCO3    +
```

```
                                          1.000 RO2
 89 RNO3      + HO                   -->  1.000 NO2    +  0.155 MEK     +
                                          1.050 RCHO   +  0.480 CCHO    +
                                          0.160 HCHO   +  0.110 C       +
                                          1.390 R2O2   +  1.390 RO2
 90 CCOO2     + NO                   -->  1.000 CO2    +  1.000 NO2     +
                                          1.000 HCHO   +  1.000 RO2R    +
                                          1.000 RO2
 91 CCOO2     + NO2                  -->  1.000 PAN
 92 CCOO2     + HO2                  -->  1.000 OOH    +  1.000 CO2     +
                                          1.000 HCHO
 93 CCOO2     + RO2                  -->  1.000 RO2    +  0.500 HO2     +
                                          1.000 CO2    +  1.000 HCHO
 94 CCOO2     + RCO3                 -->  1.000 RCO3   +  1.000 HO2     +
                                          1.000 CO2    +  1.000 HCHO
 95 PAN                              -->  1.000 CCOO2  +  1.000 NO2     +
                                          1.000 RCO3
 96 C2COO2    + NO                   -->  1.000 CCHO   +  1.000 RO2R    +
                                          1.000 CO2    +  1.000 NO2     +
                                          1.000 RO2
 97 C2COO2    + NO2                  -->  1.000 PPN
 98 C2COO2    + HO2                  -->  1.000 OOH    +  1.000 CCHO    +
                                          1.000 CO2
 99 C2COO2    + RO2                  -->  1.000 RO2    +  0.500 HO2     +
                                          1.000 CCHO   +  1.000 CO2
100 C2COO2    + RCO3                 -->  1.000 RCO3   +  1.000 HO2     +
                                          1.000 CCHO   +  1.000 CO2
101 PPN                              -->  1.000 C2COO2 +  1.000 NO2     +
                                          1.000 RCO3
102 GLY                              -->  0.800 HO2    +  0.450 HCHO    +
                                          1.550 CO
103 GLY                              -->  0.130 HCHO   +  1.870 CO
104 GLY       + HO                   -->  0.600 HO2    +  1.200 CO      +
                                          0.400 HCOCOO +  0.400 RCO3
105 GLY       + NO3                  -->  1.000 HNO3   +  0.600 HO2     +
                                          1.200 CO     +  0.400 HCOCOO  +
                                          0.400 RCO3
106 HCOCOO    + NO                   -->  1.000 NO2    +  1.000 CO2     +
                                          1.000 CO     +  1.000 HO2
107 HCOCOO    + NO2                  -->  1.000 GPAN
108 GPAN                             -->  1.000 HCOCOO +  1.000 NO2     +
                                          1.000 RCO3
109 HCOCOO    + HO2                  -->  1.000 OOH    +  1.000 CO2     +
                                          1.000 CO
110 HCOCOO    + RO2                  -->  1.000 RO2    +  0.500 HO2     +
                                          1.000 CO2    +  1.000 CO
111 HCOCOO    + RCO3                 -->  1.000 RCO3   +  1.000 HO2     +
                                          1.000 CO2    +  1.000 CO
112 MGLY                             -->  1.000 HO2    +  1.000 CO      +
                                          1.000 CCOO2  +  1.000 RCO3
113 MGLY                             -->  1.000 HO2    +  1.000 CO      +
                                          1.000 CCOO2  +  1.000 RCO3
114 MGLY      + HO                   -->  1.000 CO     +  1.000 CCOO2   +
                                          1.000 RCO3
115 MGLY      + NO3                  -->  1.000 HNO3   +  1.000 CO      +
                                          1.000 CCOO2  +  1.000 RCO3
116 HO        + PHEN                 -->  0.150 RO2NP  +  0.850 RO2R    +
                                          0.200 GLY    +  4.700 C       +
```

```
                                          1.000 RO2
117 NO3       + PHEN                 -->  1.000 HNO3   +  1.000 BZO
118 HO        + CRES                 -->  0.150 RO2NP  +  0.850 RO2R    +
                                          0.200 MGLY   +  5.500 C       +
                                          1.000 RO2
119 NO3       + CRES                 -->  1.000 HNO3   +  1.000 BZO     +
                                          1.000 C
120 BALD      + HO                   -->  1.000 BZCOO2 +  1.000 RCO3
121 BALD                             -->  7.000 C
122 BALD      + NO3                  -->  1.000 HNO3   +  1.000 BZCOO2
123 BZCOO2    + NO                   -->  1.000 BZO    +  1.000 CO2     +
                                          1.000 NO2    +  1.000 R2O2    +
                                          1.000 RO2
124 BZCOO2    + NO2                  -->  1.000 PBZN
125 BZCOO2    + HO2                  -->  1.000 OOH    +  1.000 CO2     +
                                          1.000 PHEN
126 BZCOO2    + RO2                  -->  1.000 RO2    +  0.500 HO2     +
                                          1.000 CO2    +  1.000 PHEN
127 BZCOO2    + RCO3                 -->  1.000 RCO3   +  1.000 HO2     +
                                          1.000 CO2    +  1.000 PHEN
128 PBZN                             -->  1.000 BZCOO2 +  1.000 NO2     +
                                          1.000 RCO3
129 BZO       + NO2                  -->  1.000 NPHE
130 BZO       + HO2                  -->  1.000 PHEN
131 BZO                              -->  1.000 PHEN
132 NPHE      + NO3                  -->  1.000 HNO3   +  1.000 BZNO2O
133 BZNO2O    + NO2                  -->  2.000 N      +  6.000 C
134 BZNO2O    + HO2                  -->  1.000 NPHE
135 BZNO2O                           -->  1.000 NPHE
136 HO        + AFG1                 -->  1.000 HCOCOO +  1.000 RCO3
137 AFG1                             -->  1.000 HO2    +  1.000 HCOCOO  +
                                          1.000 RCO3
138 HO        + AFG2                 -->  1.000 C2COO2 +  1.000 RCO3
139 AFG2                             -->  1.000 HO2    +  1.000 CO      +
                                          1.000 CCOO2  +  1.000 RCO3
140 CH4       + HO                   -->  1.000 RO2R   +  1.000 HCHO    +
                                          1.000 RO2
141 ETHE      + HO                   -->  0.220 CCHO   +  1.560 HCHO    +
                                          1.000 RO2R   +  1.000 RO2
142 ETHE      + O3                   -->  1.000 HCHO   +  0.700 HCOOH   +
                                          0.120 HO     +  0.120 HO2     +
                                          0.120 CO     +  0.180 H2      +
                                          0.180 CO2
143 ETHE      + NO3                  -->  1.000 NO2    +  2.000 HCHO    +
                                          1.000 R2O2   +  1.000 RO2
144 ETHE      + O                    -->  1.000 HCHO   +  1.000 CO      +
                                          1.000 HO2    +  1.000 RO2R    +
                                          1.000 RO2
145 NC4       + HO                   -->  0.076 RO2N   +  0.924 RO2R    +
                                          0.397 R2O2   +  0.001 HCHO    +
                                          0.571 CCHO   +  0.140 RCHO    +
                                          0.533 MEK    + -0.076 C       +
                                          1.396 RO2
146 NC6       + HO                   -->  0.185 RO2N   +  0.815 RO2R    +
                                          0.738 R2O2   +  0.020 CCHO    +
                                          0.105 RCHO   +  1.134 MEK     +
                                          0.186 C      +  1.738 RO2
147 NC8       + HO                   -->  0.333 RO2N   +  0.667 RO2R    +
                                          0.706 R2O2   +  0.002 RCHO    +
```

```
                                          1.333 MEK    +  0.998 C       +
                                          1.706 RO2
148 PROPEN    + HO                   -->  1.000 RO2R   +  1.000 RO2     +
                                          1.000 HCHO   +  1.000 CCHO
149 PROPEN    + O3                   -->  0.780 HCHO   +  0.400 CCHO    +
                                          0.280 HCOOH  +  0.408 HO      +
                                          0.048 HO2    +  0.228 CO      +
                                          0.072 H2     +  0.162 CO2     +
                                          0.150 CCOOH  +  0.090 CH4     +
                                          0.180 CCOO2  +  0.180 RCO3    +
                                          0.180 RO2R   +  0.180 RO2
150 PROPEN    + NO3                  -->  1.000 R2O2   +  1.000 RO2     +
                                          1.000 HCHO   +  1.000 CCHO    +
                                          1.000 NO2
151 PROPEN    + O                    -->  0.400 HO2    +  0.500 RCHO    +
                                          0.500 MEK    + -0.500 C
152 T2BUTE    + HO                   -->  1.000 RO2R   +  1.000 RO2     +
                                          2.000 CCHO
153 T2BUTE    + O3                   -->  1.000 CCHO   +  0.250 CCOOH   +
                                          0.150 CH4    +  0.150 CO2     +
                                          0.600 HO     +  0.300 CCOO2   +
                                          0.300 RCO3   +  0.300 RO2R    +
                                          0.300 HCHO   +  0.300 CO      +
                                          0.300 RO2
154 T2BUTE    + NO3                  -->  1.000 R2O2   +  1.000 RO2     +
                                          2.000 CCHO   +  1.000 NO2
155 T2BUTE    + O                    -->  0.400 HO2    +  0.500 RCHO    +
                                          0.500 MEK    +  0.500 C
156 CYCC6     + HO                   -->  0.193 RO2N   +  0.807 RO2R    +
                                          0.352 R2O2   +  0.003 HCHO    +
                                          0.333 RCHO   +  0.816 MEK     +
                                          0.003 CO2    +  0.765 C       +
                                          1.352 RO2
157 BENZEN    + HO                   -->  0.236 PHEN   +  0.207 GLY     +
                                          #B1U1 AFG1   +  0.764 RO2R    +
                                          0.236 HO2    +       %C       +
                                          0.764 RO2
158 TOLUEN    + HO                   -->  0.085 BALD   +  0.260 CRES    +
                                          0.118 GLY    +  #B1MG MGLY    +
                                          #B1U2 AFG2   +  0.740 RO2R    +
                                          0.260 HO2    +       %C       +
                                          0.740 RO2
159 C2BENZ    + HO                   -->  0.085 BALD   +  0.260 CRES    +
                                          0.118 GLY    +  #B1MG MGLY    +
                                          #B1U2 AFG2   +  0.740 RO2R    +
                                          0.260 HO2    +        %C      +
                                          0.740 RO2
160 OXYLEN    + HO                   -->  0.040 BALD   +  0.180 CRES    +
                                          0.108 GLY    +  #B1MG MGLY    +
                                          #B1U2 AFG2   +  0.820 RO2R    +
                                          0.180 HO2    +        %C      +
                                          0.820 RO2
161 MXYLEN    + HO                   -->  0.040 BALD   +  0.180 CRES    +
                                          0.108 GLY    +  #B1MG MGLY    +
                                          #B1U2 AFG2   +  0.820 RO2R    +
                                          0.180 HO2    +        %C      +
                                          0.820 RO2
162 PXYLEN    + HO                   -->  0.040 BALD   +  0.180 CRES    +
                                          0.108 GLY    +  #B1MG MGLY    +
```

```
                                          #B1U2 AFG2   +  0.820 RO2R    +
                                          0.180 HO2    +        %C      +
                                          0.820 RO2
163 TMB123    + HO                   -->  0.030 BALD   +  0.180 CRES    +
                                          #B1MG MGLY   +  #B1U2 AFG2    +
                                          0.820 RO2R   +  0.180 HO      +
                                               %C      +  0.820 RO2
164 TMB124    + HO                   -->  0.030 BALD   +  0.180 CRES    +
                                          #B1MG MGLY   +  #B1U2 AFG2    +
                                          0.820 RO2R   +  0.180 HO2     +
                                               %C      +  0.820 RO2
165 TMB135    + HO                   -->  0.030 BALD   +  0.180 CRES    +
                                          #B1MG MGLY   +  #B1U2 AFG2    +
                                          0.820 RO2R   +  0.180 HO2     +
                                               %C      +  0.820 RO2
166 ISOP      + HO                   -->  0.088 RO2N   +  0.912 RO2R    +
                                          0.629 HCHO   +  0.912 ISOPRO  +
                                          0.079 R2O2   +  1.079 RO2     +
                                          0.283 C
167 ISOP      + O3                   -->  0.600 HCHO   +  0.650 ISOPRO  +
                                          0.385 HCOOH  +  0.266 HO      +
                                          0.066 HO2    +  0.066 CO      +
                                          0.099 H2     +  0.099 CO2     +
                                          0.200 R2O2   +  0.200 C2CO02  +
                                          0.200 RO2    +  0.200 RCO3    +
                                          0.150 RCHO   +  0.150 C
168 ISOP      + NO3                  -->  0.800 RCHO   +  0.800 RNO3    +
                                          0.800 RO2R   +  0.200 ISOPRO  +
                                          0.200 R2O2   +  0.200 NO2     +
                                          1.000 RO2    + -2.200 C
169 ISOP      + O                    -->  0.750 ISOPRO +  0.250 C2CO02  +
                                          0.250 RCO3   +  0.500 HCHO    +
                                          0.250 RO2R   +  0.250 RO2     +
                                          0.750 C
170 ISOP      + NO2                  -->  0.800 RCHO   +  0.800 RNO3    +
                                          0.800 RO2R   +  0.200 ISOPRO  +
                                          0.200 R2O2   +  0.200 NO      +
                                          1.000 RO2    + -2.200 C
171 ISOPRO    + HO                   -->  0.293 CO     +  0.252 CCHO    +
                                          0.126 HCHO   +  0.041 GLY     +
                                          0.021 RCHO   +  0.168 MGLY    +
                                          0.314 MEK    +  0.503 RO2R    +
                                          0.210 CCO02  +  0.288 C2CO02  +
                                          0.210 R2O2   +  0.713 RO2     +
                                          0.498 RCO3   + -0.112 C
172 ISOPRO    + O3                   -->  0.020 CCHO   +  0.200 HCHO    +
                                          0.010 GLY    +  0.850 MGLY    +
                                          0.090 MEK    +  0.462 HCOOH   +
                                          0.268 HO     +  0.100 HO2     +
                                          0.155 CO     +  0.119 H2      +
                                          0.165 CO2    +  0.054 CCO02   +
                                          0.114 RCO3   +  0.054 RO2R    +
                                          0.124 RO2    +  0.070 R2O2    +
                                          0.060 HCOCOO + -0.179 C
173 ISOPRO                           -->  0.333 CO     +  0.067 CCHO    +
                                          0.900 HCHO   +  0.033 MEK     +
                                          0.333 HO2    +  0.700 RO2R    +
                                          0.267 CCO02  +  0.700 C2CO02  +
                                          0.700 RO2    +  0.967 RCO3    +
```

```
                                          -0.133 C
174 ISOPRO    + NO3                  -->  0.643 CO     +  0.282 HCHO    +
                                          0.850 RNO3   +  0.357 RCHO    +
                                          0.925 HO2    +  0.075 C2COO2  +
                                          0.075 R2O2   +  0.925 RO2     +
                                          0.075 RCO3   +  0.075 HNO3    +
                                         -2.471 C
175 APIN      + HO                   -->  1.000 RO2R   +  1.000 RCHO    +
                                          1.000 RO2    +  7.000 C
176 APIN      + O3                   -->  0.050 HCHO   +  0.200 CCHO    +
                                          0.500 RCHO   +  0.610 MEK     +
                                          0.075 CO     +  0.050 CCOO2   +
                                          0.050 C2COO2 +  0.100 RCO3    +
                                          0.105 HO2    +  0.160 HO      +
                                          0.135 RO2R   +  0.150 R2O2    +
                                          0.285 RO2    +  5.285 C
177 APIN      + NO3                  -->  1.000 NO2    +  1.000 R2O2    +
                                          1.000 RCHO   +  1.000 RO2     +
                                          7.000 C
178 APIN      + O                    -->  0.400 HO2    +  0.500 RCHO    +
                                          0.500 MEK    +  6.500 C
179 ETHANE    + HO                   -->  1.000 RO2R   +  1.000 CCHO    +
                                          1.000 RO2
180 PROPAN    + HO                   -->  0.039 RO2XN  +  0.961 RO2R    +
                                          0.658 ACET   +  0.303 RCHO    +
                                          0.116 C      +  1.000 RO2
181 MTBE      + HO                   -->  0.020 RO2N   +  0.980 RO2R    +
                                          0.370 R2O2   +  0.390 HCHO    +
                                          0.410 MEK    +  2.870 C       +
                                          1.370 RO2
182 MEOH      + HO                   -->  1.000 HO2    +  1.000 HCHO
183 ETOH      + HO                   -->  0.100 RO2R   +  0.900 HO2     +
                                          0.156 HCHO   +  0.922 CCHO    +
                                          0.100 RO2
184 ETBE      + HO                   -->  0.030 RO2N   +  0.970 RO2R    +
                                          1.160 R2O2   +  1.160 HCHO    +
                                          0.570 MEK    +  2.410 C       +
                                          2.160 RO2
185 C5224T    + HO                   -->  0.110 RO2N   +  0.890 RO2R    +
                                          0.890 RCHO   +  1.110 MEK     +
                                          0.340 C      +  1.000 RO2
186 MECYC5    + HO                   -->  0.153 RO2N   +  0.847 RO2R    +
                                          1.978 R2O2   +  0.283 HCHO    +
                                          0.697 RCHO   +  0.490 MEK     +
                                          0.564 CO     +  0.189 CO2     +
                                          0.153 C      +  2.978 RO2
187 C52ME     + HO                   -->  0.122 RO2N   +  0.005 RO2XN   +
                                          0.873 RO2R   +  0.749 R2O2    +
                                          0.006 HCHO   +  0.023 CCHO    +
                                          0.223 ACET   +  0.545 RCHO    +
                                          0.724 MEK    +  0.137 C       +
                                          1.749 RO2
188 BUT2M1    + HO                   -->  0.900 RO2R   +  0.100 RO2N    +
                                          1.000 RO2    +  0.900 HCHO    +
                                          0.900 MEK
189 BUT2M1    + O3                   -->  1.640 HCHO   +  1.000 MEK     +
                                          0.126 HCOOH  +  0.842 HO      +
                                          0.022 HO2    +  0.022 CO      +
                                          0.032 H2     +  0.032 CO2     +
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                                          0.820 R2O2   +  0.820 CCOO2   +
                                          0.820 RCO3   +  0.820 RO2     +
                                         -2.460 C
190 BUT2M1    + NO3                  -->  1.000 R2O2   +  1.000 RO2     +
                                          1.000 HCHO   +  1.000 MEK     +
                                          1.000 NO2
191 BUT2M1    + O                    -->  0.400 HO2    +  0.500 RCHO    +
                                          0.500 MEK    +  1.500 C
192 BUT2M2    + HO                   -->  0.840 RO2R   +  0.160 RO2N    +
                                          1.000 RO2    +  0.840 CCHO    +
                                          0.840 ACET
193 BUT2M2    + O3                   -->  0.600 CCHO   +  0.400 ACET    +
                                          0.100 CCOOH  +  0.060 CH4     +
                                          0.060 CO2    +  0.840 HO      +
                                          0.720 CCOO2  +  0.720 RCO3    +
                                          0.120 RO2R   +  0.720 HCHO    +
                                          0.120 CO     +  0.720 RO2     +
                                          0.600 R2O2
194 BUT2M2    + NO3                  -->  1.000 R2O2   +  1.000 RO2     +
                                          1.000 CCHO   +  1.000 ACET    +
                                          1.000 NO2
195 BUT2M2    + O                    -->  0.400 HO2    +  0.500 RCHO    +
                                          0.500 MEK    +  1.500 C
196 BUTD13    + HO                   -->  1.000 RO2R   +  1.000 RO2     +
                                          1.000 HCHO   +  1.000 RCHO
197 BUTD13    + O3                   -->  0.780 HCHO   +  1.000 RCHO    +
                                          0.280 HCOOH  +  0.408 HO      +
                                          0.048 HO2    +  0.228 CO      +
                                          0.072 H2     +  0.162 CO2     +
                                          0.150 CCOOH  +  0.090 CH4     +
                                          0.180 CCOO2  +  0.180 RCO3    +
                                          0.180 RO2R   +  0.180 RO2     +
                                         -1.200 C
198 BUTD13    + NO3                  -->  1.000 R2O2   +  1.000 RO2     +
                                          1.000 HCHO   +  1.000 RCHO    +
                                          1.000 NO2
199 BUTD13    + O                    -->  0.400 HO2    +  0.500 RCHO    +
                                          0.500 MEK    +  0.500 C
200 C2CO      + NO2                  -->  1.000 RNO3   + -2.000 C
201 C2CO                             -->  1.000 ACET   +  1.000 HCHO    +
                                          1.000 RO2R   +  1.000 RO2     +
202 ALK1      + HO                   -->  0.877 RO2R   +  0.090 RO2N    +
                                          0.012 HO2    +  0.643 R2O2    +
                                          1.610 RO2    +  0.021 HO      +
                                          0.079 HCHO   +  0.383 CCHO    +
                                          0.200 RCHO   +  0.389 ACET    +
                                          0.267 MEK    +  0.012 CO      +
                                          0.027 GLY    +  0.406 C
203 ALK2      + HO                   -->  0.684 RO2R   +  0.294 RO2N    +
                                          0.921 R2O2   +  1.899 RO2     +
                                          0.002 HCHO   +  0.069 CCHO    +
                                          0.334 RCHO   +  0.040 ACET    +
                                          0.492 MEK    +  0.021 CCOO2   +
                                          0.001 C2COO2  +  0.023 RCO3   +
                                          3.350 C
204 ARO1      + HO                   -->  0.741 RO2R   +  0.259 HO2     +
                                          0.741 RO2    +  0.015 PHEN    +
                                          0.244 CRES   +  0.080 BALD    +
                                          0.124 GLY    +  #B1U1 AFG1    +
```

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                                          #B1MG MGLY   +  #B1U2 AFG2    +
                                          %C
205 ARO2      + HO                     --> 0.820 RO2R   +  0.180 HO2     +
                                          0.820 RO2    +  0.180 CRES    +
                                          0.036 BALD   +  0.068 GLY     +
                                          #B1MG MGLY   +  #B1U2 AFG2    +
                                                %C
206 OLE1      + HO                     --> 1.000 RO2R   +  1.000 RO2     +
                                          1.560 HCHO   +  0.220 CCHO
207 OLE1      + O3                     --> 1.000 HCHO   +  0.700 HCOOH   +
                                          0.120 HO     +  0.120 HO2     +
                                          0.120 CO     +  0.180 H2      +
                                          0.180 CO2
208 OLE1      + O                      --> 1.000 RO2R   +  1.000 HO2     +
                                          1.000 RO2    +  1.000 HCHO    +
                                          1.000 CO
209 OLE1      + NO3                    --> 1.000 R2O2   +  1.000 RO2     +
                                          2.000 HCHO   +  1.000 NO2
210 OLE2      + HO                     --> 0.858 RO2R   +  0.142 RO2N    +
                                          1.000 RO2    +  0.858 HCHO    +
                                          0.252 CCHO   +  0.606 RCHO    +
                                          1.267 C
211 OLE2      + O3                     --> 0.759 HCHO   +  0.021 CCHO    +
                                          0.635 RCHO   +  0.280 HCOOH   +
                                          0.150 CCOOH  +  0.408 HO      +
                                          0.048 HO2    +  0.228 CO      +
                                          0.162 CO2    +  0.072 H2      +
                                          0.079 CH4    +  0.159 CCOO2   +
                                          0.021 C2COO2 +  0.180 RCO3    +
                                          0.180 RO2R   +  0.180 RO2     +
                                          1.020 C
212 OLE2      + O                      --> 0.400 HO2    +  0.500 RCHO    +
                                          0.500 MEK    +  1.657 C
213 OLE2      + NO3                    --> 1.000 R2O2   +  1.000 RO2     +
                                          1.000 HCHO   +  0.294 CCHO    +
                                          0.706 RCHO   +  1.451 C       +
                                          1.000 NO2
214 OLE3      + HO                     --> 0.861 RO2R   +  0.139 RO2N    +
                                          1.000 RO2    +  0.240 HCHO    +
                                          0.661 CCHO   +  0.506 RCHO    +
                                          0.113 ACET   +  0.086 MEK     +
                                          0.057 BALD   +  0.848 C
215 OLE3      + O3                     --> 0.484 HCHO   +  0.481 CCHO    +
                                          0.309 RCHO   +  0.053 HCOOH   +
                                          0.172 CCOOH  +  0.639 HO      +
                                          0.009 HO2    +  0.236 CO      +
                                          0.014 H2     +  0.117 CO2     +
                                          0.061 CH4    +  0.320 CCOO2   +
                                          0.084 C2COO2 +  0.403 RCO3    +
                                          0.206 RO2R   +  0.403 RO2     +
                                          0.217 R2O2   +  0.020 BZO     +
                                          0.061 MEK    +  0.027 BALD    +
                                          1.129 C
216 OLE3      + O                      --> 0.400 HO2    +  0.500 RCHO    +
                                          0.500 MEK    +  2.205 C
217 OLE3      + NO3                    --> 1.000 R2O2   +  1.000 RO2     +
                                          0.278 HCHO   +  0.767 CCHO    +
                                          0.588 RCHO   +  0.131 ACET    +
                                          0.100 MEK    +  0.066 BALD    +
```

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                                          0.871 C      +  1.000 NO2     +
218 UNKN      + HO                   -->  1.000 RO2R   +  1.000 RO2     +
                                          0.500 HCHO   +  1.000 RCHO    +
                                          6.500 C
219 UNKN      + O3                   -->  0.135 RO2R   +  0.135 HO2     +
                                          0.075 R2O2   +  0.210 RO2     +
                                          0.025 CCOO2  +  0.025 C2COO2  +
                                          0.050 RCO3   +  0.275 HCHO    +
                                          0.175 CCHO   +  0.500 RCHO    +
                                          0.410 MEK    +  0.185 CO      +
                                          5.925 C      +  0.110 HO
220 UNKN      + NO3                  -->  1.000 R2O2   +  1.000 RO2     +
                                          0.500 HCHO   +  1.000 RCHO    +
                                          6.500 C      +  1.000 NO2
221 UNKN      + O                    -->  0.400 HO2    +  0.500 RCHO    +
                                          0.500 MEK    +  6.500 C
```

Explicit organic compound names not defined in (22).

NC4	n-butane	APIN	α-pinene
NC6	n-hexane	PROPAN	Propane
NC8	n-octane	MTBE	Methyl-tert-butyl ether
PROPEN	Propene	MEOH	Methanol
T2BUTE	Trans-2-butene	ETOH	Ethanol
CYCC6	Cyclohexane	ETBE	Ethyl-tert-butyl ether
BENZEN	Benzene	C5224T	2,2,4-trimethylpentane
TOLUEN	Toluene	MECYC5	Methylcyclopentane
C2BENZ	Ethylbenzene	C52ME	2-methylpentane
OXYLEN	o-xylene	BUT2M1	2-methyl-1-butene
MXYLEN	m-xylene	BUT2M2	2-methyl-2-butene
PXYLEN	p-xylene	BUTD13	1,3-butadiene
TMB123	1,2,3-trimethylbenzene		
TMB124	1,2,4-trimethylbenzene		
TMB135	1,3,5-trimethylbenzene		
ISOP	Isoprene		

Appendix A-2: Listing of the Chamber Model

The following list is the chemical mechanism describing the chamber model used in this study. The chamber-dependent radical sources in the model are characterized by the parameters RSI and HONO-F. The mechanism is adopted from (17).

```
O3W)  O3                     -->
N25I) N2O5                   -->  2.000  NOx-WALL
N25S) N2O5          +  H2O     -->  2.000  NOx-WALL
NO2W) NO2                    -->  #yHONO HONO +  (1-#yHONO) NOxWALL
XSHC) HO.                    -->  1.000  HO2.
RSI)  HV            +  #RSI    -->  1.000  HO.
ONO2) HV            +  ENO2    -->  NO2         +  -1.000  NOx-WALL
```

Appendix B-1: Aromatic Runs

The chamber experiments used to estimate the aromatics oxidation parameters are given in the following table, along with the uncertainty information for the initial concentrations, NO_2 photolysis rate and uncertainty group assignments for each experiment. Figures B1-1 - B1-3 show examples of the performance of the mechanism with fitted values for the aromatics oxidation parameters for benzene, toluene and p-xylene-NO_x experiments.

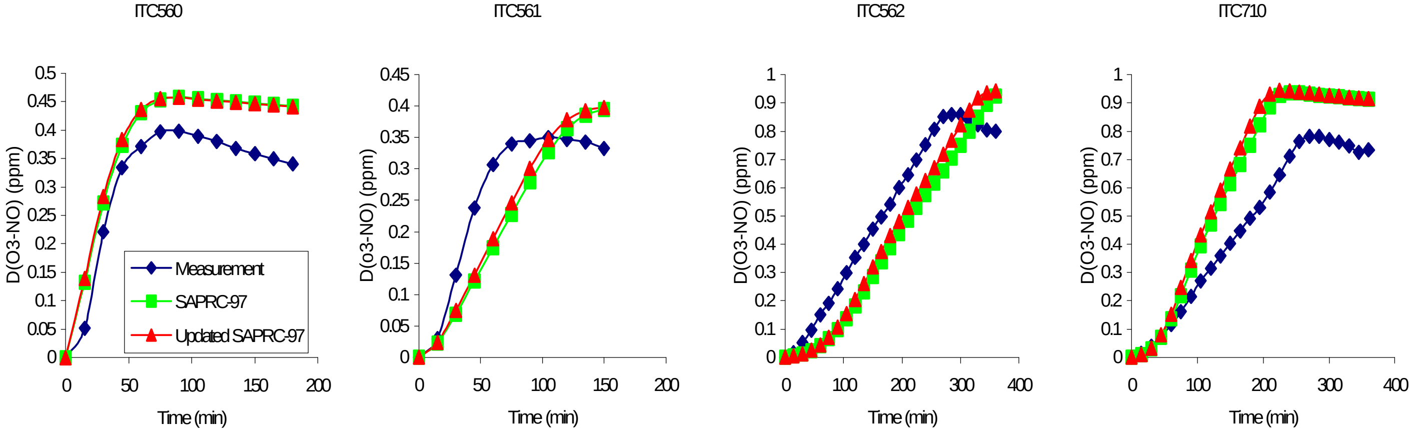
Table B-1 Conditions and Uncertainty Estimates for Aromatics Experiments

		Conditions			**Reactants (ppm) [a]**							**RS-I**
Run	**Date**	**K1 (min^{-1})**		**T**	**Grp**	**NO**		**NO2**		**Aromatic**		**Opt.**
		Value	**Unc'y**	**(K)**		**Init.**	**Unc'y**	**Init.**	**Unc'y**	**Init**	**Unc'y**	**Set**
BENZENE												
SAPRC-97 (B1U1 =1.44 , P1/U = 0.077); This Study (B1U1 = 1.446 +/- 0.477, P1/U = 0.088 +/- 0.034												
ITC560	12/20/82	0.357	0.044	301	1	0.074	0.019	0.034	0.009	57.5	5.7	ITC
ITC561	12/21/82	0.357	0.044	301	1	0.085	0.021	0.029	0.008	6.8	0.7	ITC
ITC562	12/22/82	0.357	0.044	301	1	0.440	0.109	0.129	0.034	7.2	0.7	ITC
ITC710	12/15/83	0.351	0.043	300	2	0.417	0.021	0.117	0.013	14.1	(1.4)	ITC
CTC159A	01/12/96	0.180	0.030	303	3	0.183	0.009	0.082	0.009	33.6	(3.4)	CTC
CTC159B	01/12/96	0.180	0.030	303	3	0.182	0.009	0.080	0.009	16.2	(1.6)	CTC
CTC160A	01/17/96	0.180	0.030	302	3	0.313	0.016	0.185	0.021	18.0	(1.8)	CTC
CTC160B	01/17/96	0.180	0.030	302	20	0.310	0.016	0.184	0.021	33.6	(3.4)	CTC
TOLUENE												
SAPRC-97 (B1U2 = 0.26, B1MG = 0.964)												
This study (B1U2 = 0.283 +/- 0.097, B1MG = 1.022 +/- 0.319)												
DTC042A	05/05/93	0.388	0.047	300	1	0.726	0.036	0.260	0.029	1.07	0.05	DTC1
DTC042B	05/05/93	0.388	0.047	300	1	0.087	0.005	0.011	0.002	0.56	0.03	DTC1
DTC151A	05/12/94	0.252	0.031	298	2	0.279	0.014	0.042	0.005	1.84	0.10	DTC2
DTC155A	05/19/94	0.248	0.030	298	2	0.095	0.005	0.005	0.002	0.64	0.03	DTC2
DTC170A	06/14/94	0.239	0.029	299	2	0.414	0.021	0.079	0.009	2.52	0.14	DTC2
CTC026	10/28/94	0.201	0.033	302	3	0.212	0.011	0.058	0.007	2.01	0.13	CTC
CTC034	11/16/94	0.199	0.033	305	3	0.373	0.019	0.151	0.017	2.21	0.14	CTC
CTC048	12/13/94	0.197	0.032	301	3	0.196	0.010	0.052	0.006	0.95	0.06	CTC
CTC065	01/25/95	0.195	0.032	300	4	0.520	0.026	0.138	0.016	0.97	0.06	CTC
CTC079	02/17/95	0.192	0.032	298	4	0.215	0.011	0.041	0.005	0.50	0.03	CTC
C2-BENZ												
SAPRC-98 (B1U2 = 0.18, B1MG = 0.199)												
This Study (B1U2 = 0.216 +/- 0.096, B1MG = 0.244 +/- 0.154)												
DTC223A	09/29/94	0.224	0.027	299	1	0.213	0.011	0.050	0.006	1.52	0.11	DTC2
DTC223B	09/29/94	0.224	0.027	299	1	0.217	0.011	0.050	0.006	0.76	0.06	DTC2
DTC224A	09/30/94	0.224	0.027	298	1	0.418	0.021	0.113	0.013	1.62	0.12	DTC2
DTC224B	09/30/94	0.224	0.027	298	1	0.439	0.022	0.116	0.013	0.70	0.05	DTC2
CTC057	01/06/95	0.196	0.032	300	2	0.205	0.010	0.066	0.008	2.03	0.15	CTC
CTC092A	03/17/95	0.190	0.031	295	3	0.218	0.011	0.050	0.006	1.03	0.08	CTC
CTC092B	03/17/95	0.190	0.031	295	3	0.215	0.011	0.055	0.006	1.96	0.15	CTC
CTC098B	03/28/95	0.189	0.031	295	3	0.376	0.019	0.118	0.013	1.88	0.14	CTC
M-XYLENE												
SAPRC-97 (B1U2 = 0.46, B1MG = 1.599)												
This Study (B1U2 = 0.478 +/- 0.156, B1MG = 1.753 +/- 0.549)												
DTC073A	07/29/93	0.388	0.047	302	1	0.384	0.019	0.101	0.011	0.113	0.006	DTC2
DTC188A	07/28/94	0.232	0.028	299	2	0.432	0.022	0.121	0.014	0.125	0.014	DTC2
DTC188B	07/28/94	0.232	0.028	299	2	0.445	0.022	0.124	0.014	0.230	0.026	DTC2
DTC189A	07/29/94	0.232	0.028	299	2	0.197	0.010	0.050	0.006	0.251	0.028	DTC2
DTC189B	07/29/94	0.232	0.028	299	2	0.206	0.010	0.053	0.006	0.112	0.013	DTC2
DTC191A	08/03/94	0.232	0.028	298	2	0.422	0.021	0.148	0.017	0.533	0.060	DTC2
DTC191B	08/03/94	0.232	0.028	298	2	0.439	0.022	0.152	0.017	1.103	0.124	DTC2
DTC192A	08/04/94	0.231	0.028	298	2	0.234	0.012	0.063	0.007	0.526	0.059	DTC2
DTC192B	08/04/94	0.231	0.028	298	2	0.132	0.007	0.017	0.003	0.532	0.060	DTC2
DTC193A	08/05/94	0.231	0.028	299	2	0.111	0.006	0.017	0.003	0.288	0.032	DTC2
DTC193B	08/05/94	0.231	0.028	299	2	0.116	0.006	0.015	0.003	0.150	0.017	DTC2
DTC206B	08/30/94	0.228	0.028	299	2	0.235	0.012	0.048	0.006	0.251	0.028	DTC2
DTC294A	11/16/95	0.216	0.026	298	3	0.393	0.020	0.109	0.012	0.126	0.015	DTC3
DTC294B	11/16/95	0.216	0.026	298	3	0.398	0.020	0.110	0.012	0.219	0.026	DTC3
DTC295A	11/17/95	0.216	0.026	297	3	0.251	0.013	0.066	0.008	0.499	0.058	DTC3
DTC295B	11/17/95	0.216	0.026	297	3	0.253	0.013	0.067	0.008	0.222	0.026	DTC3
CTC029	11/08/94	0.200	0.033	300	4	0.219	0.011	0.052	0.006	0.319	0.036	CTC
CTC035	11/17/94	0.199	0.033	301	4	0.211	0.011	0.066	0.008	0.160	0.018	CTC
CTC036	11/18/94	0.199	0.033	302	4	0.362	0.018	0.147	0.017	0.159	0.018	CTC
CTC080	02/21/95	0.192	0.032	298	5	0.403	0.020	0.104	0.012	0.530	0.060	CTC
CTC094A	03/22/95	0.190	0.031	294	5	0.380	0.019	0.110	0.012	0.560	0.063	CTC
CTC094B	03/22/95	0.190	0.031	294	5	0.380	0.019	0.110	0.012	0.573	0.065	CTC
O-XYLENE												
SAPRC-97 (B1U2 = 0.58, B1MG = 0.806)												
This Study (B1U2 = 0.650 +/- 0.195, B1MG = 0.856 +/- 0.371)												
DTC207A	08/31/94	0.228	0.028	299	1	0.228	0.012	0.056	0.007	0.300	0.020	DTC2
DTC207B	08/31/94	0.228	0.028	299	1	0.244	0.012	0.057	0.007	0.664	0.045	DTC2

DTC208A	09/01/94	0.227	0.028	300	1	0.415	0.021	0.106	0.012	0.570	0.038	DTC2
DTC208B	09/01/94	0.227	0.028	300	1	0.444	0.022	0.115	0.013	0.277	0.019	DTC2
DTC209A	09/02/94	0.227	0.028	299	1	0.107	0.006	0.016	0.003	0.257	0.017	DTC2
DTC209B	09/02/94	0.227	0.028	299	1	0.113	0.006	0.014	0.003	0.145	0.010	DTC2
CTC038	11/22/94	0.199	0.033	301	2	0.199	0.010	0.054	0.006	0.304	0.019	CTC
CTC039	11/23/94	0.199	0.033	301	2	0.392	0.020	0.088	0.010	0.159	0.010	CTC
CTC046	12/08/94	0.198	0.033	303	2	0.357	0.018	0.147	0.017	0.300	0.018	CTC
CTC068	01/27/95	0.194	0.032	302	3	0.208	0.011	0.054	0.006	0.637	0.040	CTC
CTC081	02/22/95	0.192	0.032	298	3	0.215	0.011	0.046	0.005	0.536	0.034	CTC
CTC091A	03/16/95	0.191	0.031	295	3	0.225	0.011	0.056	0.007	0.462	0.030	CTC
P-XYLENE												
SAPRC-97 (B1U2 = 0.15, B1MG = 0.168)												
This Study (B1U2 = 0.184 +/- 0.083, B1MG = 0.220 +/- 0.156)												
DTC198A	08/16/94	0.230	0.028	299	1	0.209	0.011	0.055	0.006	0.425	0.021	DTC2
DTC198B	08/16/94	0.230	0.028	299	1	0.218	0.011	0.054	0.006	0.840	0.042	DTC2
DTC199A	08/17/94	0.230	0.028	299	1	0.425	0.021	0.120	0.014	0.834	0.042	DTC2
DTC199B	08/17/94	0.230	0.028	299	1	0.426	0.021	0.124	0.014	0.428	0.021	DTC2
DTC200A	08/18/94	0.229	0.028	299	1	0.104	0.006	0.022	0.003	0.384	0.019	DTC2
DTC200B	08/18/94	0.229	0.028	299	1	0.110	0.006	0.020	0.003	0.195	0.010	DTC2
CTC041	12/01/94	0.198	0.033	300	2	0.223	0.011	0.042	0.005	0.382	0.019	CTC
CTC043	12/05/94	0.198	0.033	301	2	0.200	0.010	0.049	0.006	0.193	0.010	CTC
CTC044	12/06/94	0.198	0.033	301	2	0.380	0.019	0.126	0.014	0.394	0.020	CTC
CTC047	12/12/94	0.197	0.032	301	2	0.223	0.011	0.053	0.006	0.973	0.049	CTC
CTC070	02/01/95	0.194	0.032	301	3	0.397	0.020	0.105	0.012	2.019	0.101	CTC
135-TMB												
SAPRC-97 (B1U2 = 0.61, B1MG = 1.164)												
This Study (B1U2 = 0.776 +/- 0.311, B1MG = 1.073 +/- 0.308)												
DTC194A	08/10/94	0.231	0.028	299	1	0.174	0.009	0.085	0.010	0.169	0.019	DTC2
DTC194B	08/10/94	0.231	0.028	299	1	0.194	0.010	0.087	0.010	0.340	0.038	DTC2
DTC195A	08/11/94	0.231	0.028	300	1	0.320	0.016	0.228	0.026	0.342	0.038	DTC2
DTC195B	08/11/94	0.231	0.028	300	1	0.330	0.017	0.235	0.026	0.167	0.018	DTC2
DTC196A	08/12/94	0.230	0.028	300	1	0.112	0.006	0.022	0.003	0.165	0.018	DTC2
DTC196B	08/12/94	0.230	0.028	300	1	0.117	0.006	0.024	0.003	0.083	0.009	DTC2
DTC206A	08/30/94	0.228	0.028	299	1	0.224	0.011	0.049	0.006	0.138	0.015	DTC2
CTC030	11/09/94	0.200	0.033	300	2	0.415	0.021	0.106	0.012	0.317	0.035	CTC
CTC050	12/15/94	0.197	0.032	303	2	0.220	0.011	0.051	0.006	0.194	0.022	CTC
CTC071	02/02/95	0.194	0.032	300	3	0.413	0.021	0.104	0.012	0.329	0.037	CTC
CTC073	02/07/95	0.193	0.032	297	3	0.221	0.011	0.036	0.005	0.175	0.019	CTC
123-TMB												
SAPRC-97 (B1U2 = 0.66, B1MG = 1.120)												
This Study (B1U2 = 0.803 +/- 0.311, B1MG = 1.080 +/- 0.389)												
DTC211A	09/07/94	0.227	0.028	299	1	0.199	0.010	0.049	0.006	0.131	0.017	DTC2
DTC211B	09/07/94	0.227	0.028	299	1	0.209	0.011	0.050	0.006	0.299	0.038	DTC2
DTC212A	09/08/94	0.227	0.028	299	1	0.400	0.020	0.110	0.013	0.307	0.039	DTC2
DTC212B	09/08/94	0.227	0.028	299	1	0.421	0.021	0.116	0.013	0.163	0.021	DTC2
DTC213A	09/09/94	0.226	0.028	299	1	0.100	0.005	0.011	0.002	0.140	0.018	DTC2
DTC213B	09/09/94	0.226	0.028	299	1	0.104	0.006	0.009	0.002	0.088	0.011	DTC2
CTC054	12/21/94	0.196	0.032	302	2	0.203	0.010	0.027	0.004	0.212	0.027	CTC
CTC075	02/09/95	0.193	0.032	298	3	0.420	0.027	0.100	0.012	0.228	0.029	CTC
CTC076	02/10/95	0.193	0.032	297	3	0.219	0.014	0.039	0.005	0.177	0.023	CTC
124-TMB												
SAPRC-97 (B1U2 = 0.26, B1MG = 0.405)												
This Study (B1U2 = 0.303 +/- 0.122, B1MG = 0.494 +/- 0.242)												
DTC201A	08/19/94	0.229	0.028	299	1	0.198	0.010	0.049	0.006	0.173	0.019	DTC2
DTC201B	08/19/94	0.229	0.028	299	1	0.211	0.011	0.050	0.006	0.301	0.032	DTC2
DTC203A	08/23/94	0.229	0.028	298	1	0.404	0.020	0.107	0.012	0.341	0.037	DTC2
DTC203B	`	0.229	0.028	298	1	0.425	0.021	0.112	0.013	0.175	0.019	DTC2
DTC204A	08/24/94	0.228	0.028	298	1	0.101	0.005	0.019	0.003	0.170	0.018	DTC2
DTC204B	08/24/94	0.228	0.028	298	1	0.109	0.006	0.014	0.003	0.092	0.010	DTC2
CTC056	01/05/95	0.196	0.032	300	2	0.207	0.011	0.047	0.006	0.225	0.024	CTC
CTC091B	03/16/95	0.191	0.031	295	3	0.226	0.011	0.056	0.007	0.463	0.050	CTC
CTC093A	03/21/95	0.190	0.031	294	3	0.354	0.018	0.128	0.014	0.478	0.052	CTC
CTC093B	03/21/95	0.190	0.031	294	3	0.354	0.018	0.137	0.015	1.131	0.122	CTC

[a] Values in parentheses are estimated uncertainties for runs where no calibration uncertainty estimates are available.

BLACK LIGHT



XENON ARC LIGHT

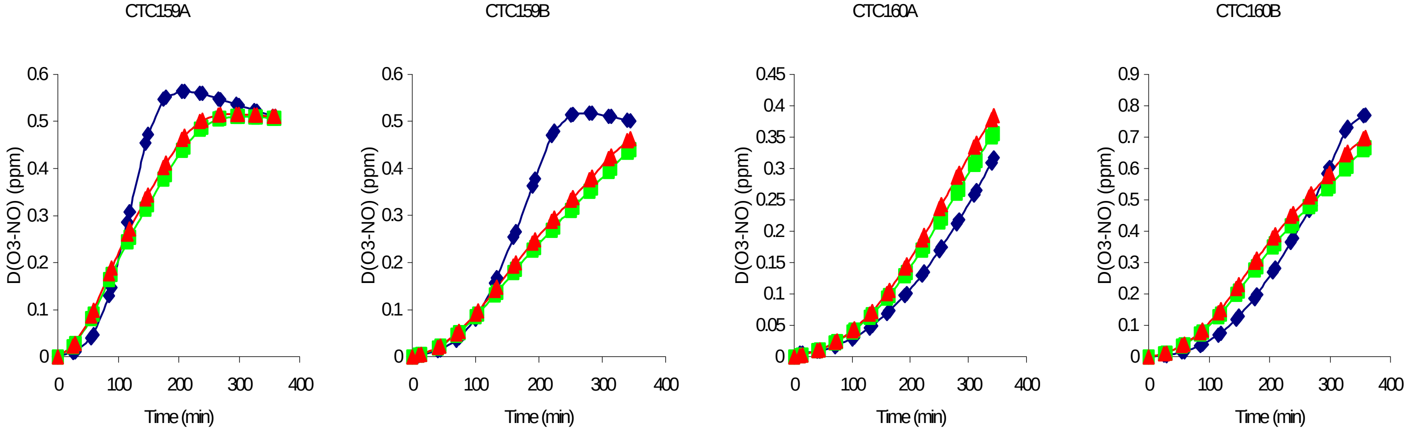
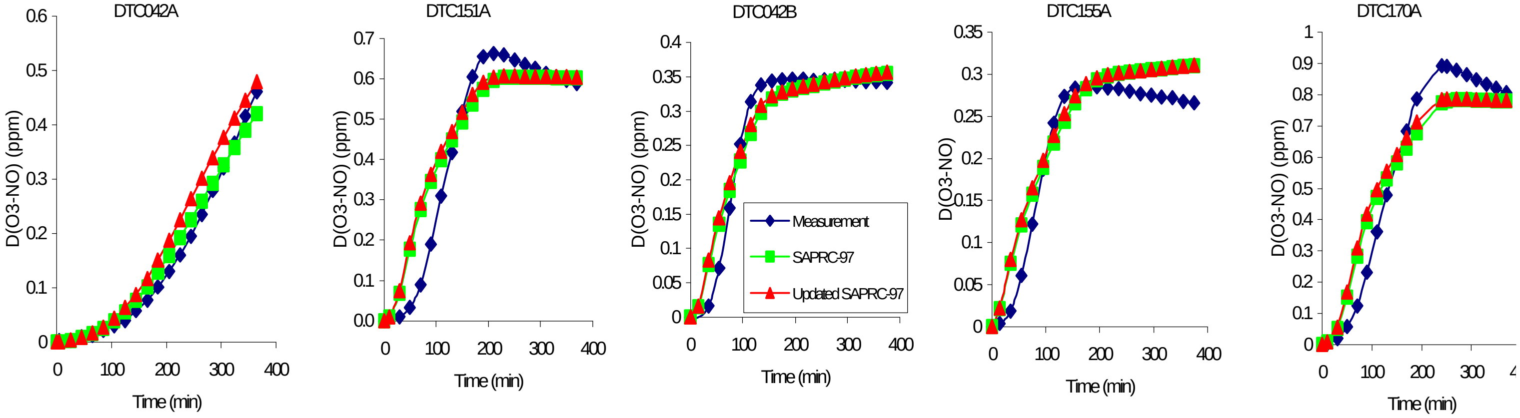


Figure B1-1. Performance of the SAPRC-97 mechanism for benzene-NO$_x$ experiments in blacklight (ITC) and xenon arc light (CTC) chambers. Diamonds = measurements; squares = SAPRC-97 with deterministically estimated parameter values; triangles = SAPRC-97 with mean stochastically estimated parameter values from this study.

Black Light



Xenon Arc Light

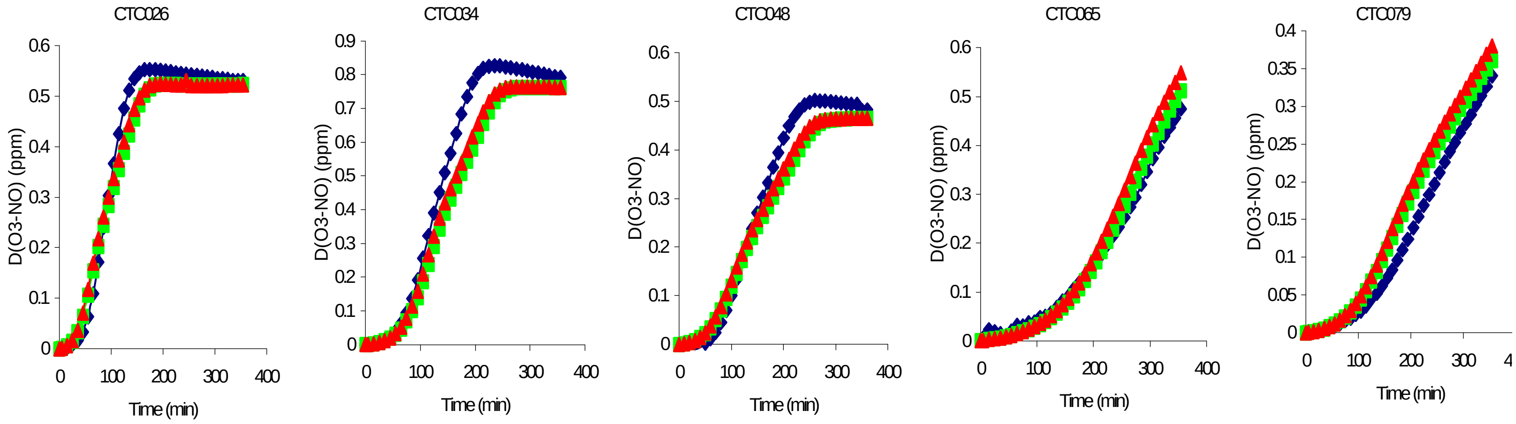
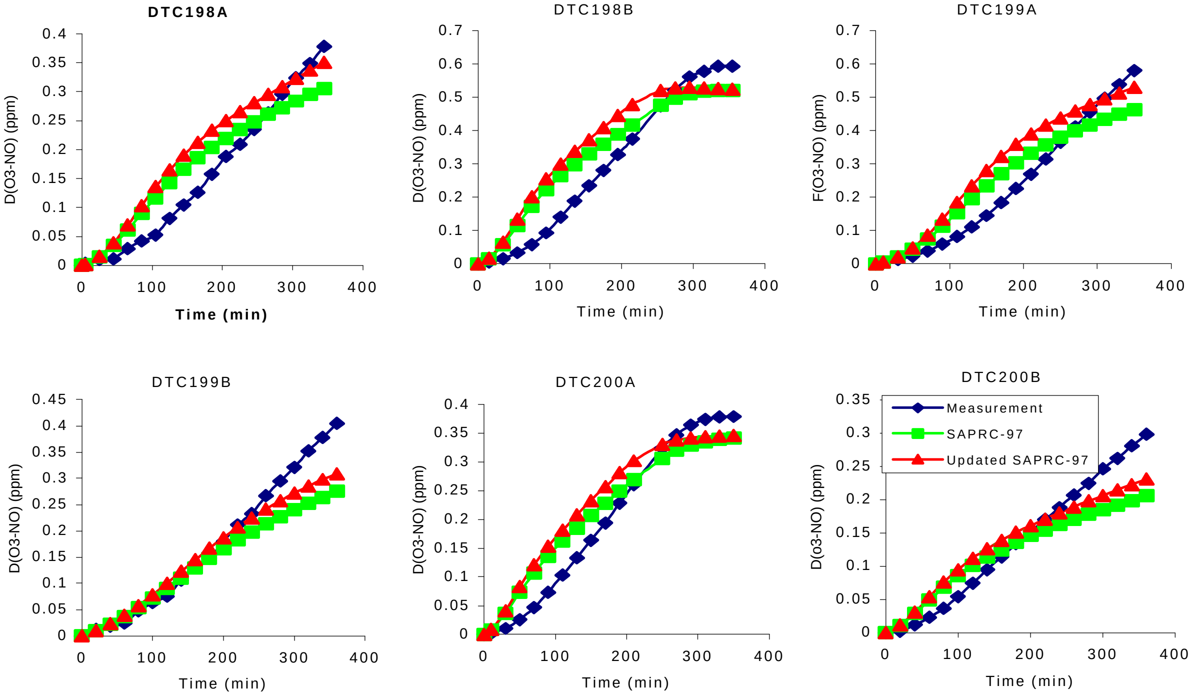


Figure B1-2. Performance of the SAPRC-97 mechanism for toluene-NO_x experiments in blacklight (DTC) and xenon arc light (CTC) chambers. Diamonds = measurements; squares = SAPRC-97 with deterministically estimated parameter values; triangles = SAPRC-97 with mean stochastically estimated parameter values from this study.

BLACK LIGHT



XENON ARC LIGHT

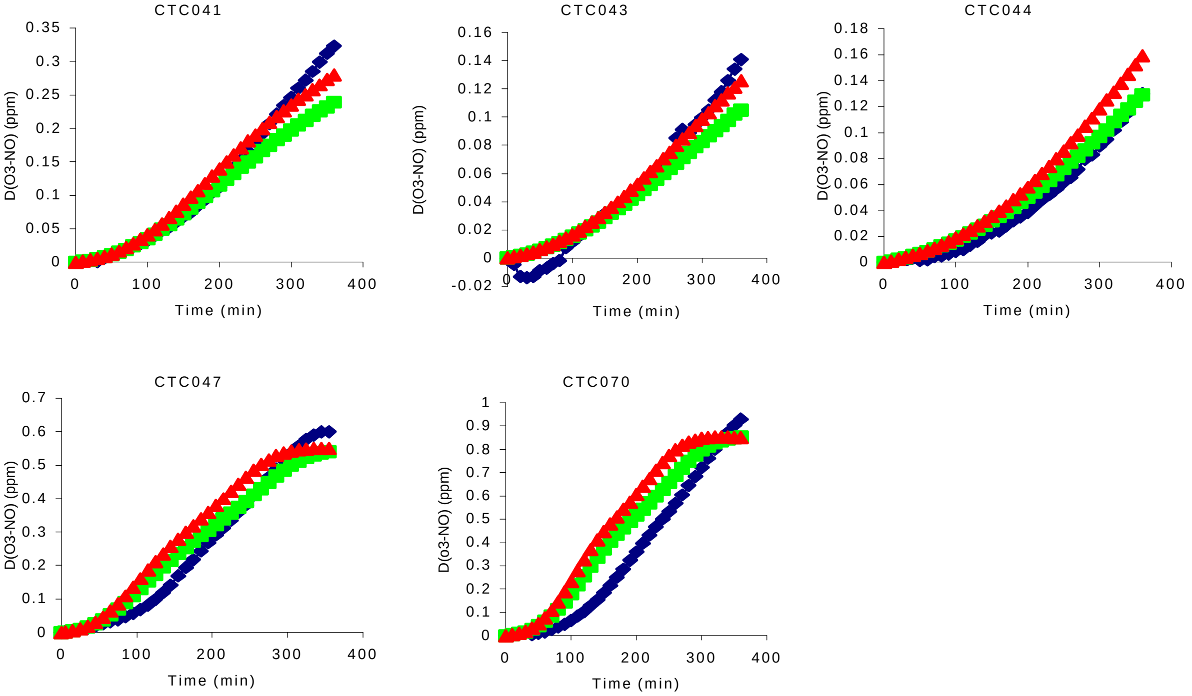


Figure B1-3. Performance of the SAPRC-97 mechanism for p-xylene-NO$_x$ experiments in blacklight (DTC) and xenon arc light (CTC) chambers. Legend as above.

Appendix B-2 Chamber Characterization Experiments

The chamber characterization experiments used for each of the five chambers are given in the following table, along with the uncertainty information for the initial concentrations and NO_2 photolysis rate.

Table B-2 Input Uncertainty Estimates and Parameter Estimation Results for Chamber Characterization Experiments

Run	Date	Conditions				Reactants (ppm) [a]						RS-I	Opt. RS-I			Opt. HONO-F		
		K1 (min^{-1})		T	Grp.	NO		NO2		N-butane/CO		Opt.	(ppb)			(%)		
		Value	Unc'y	(K)		Init.	Unc'y	Init.	Unc'y	Init	Unc'y	Set	Mean	Std. Dev.	σ (%)	mean	Std. Dev.	σ (%)
N-Butane Experiments																		
ITC948	04/23/86	0.351	0.043	301	5	0.175	0.009	0.081	0.009	4.68	(0.47)	ITC	0.064	0.024	37	2.461	0.314	13
ITC939	04/03/86	0.351	0.043	301	5	0.350	0.021	0.183	0.022	4.86	0.24	ITC	0.069	0.026	37	0.786	0.148	19
ITC533	11/10/82	0.363	0.044	303	2	0.079	0.004	0.023	0.003	2.95	0.15	ITC	0.073	0.026	35	3.721	1.020	27
ITC507	05/25/82	0.372	0.045	301	1	0.082	0.005	0.012	0.002	3.75	(0.37)	ITC	0.047	0.021	44	17.33	1.15	7
DTC299B	11/29/95	0.215	0.026	297	19	0.192	(0.019)	0.068	(0.007)	3.43	(0.34)	DTC3	0.042	0.016	38	0.648	0.155	24
DTC299A	11/29/95	0.215	0.026	297	19	0.192	(0.019)	0.070	(0.007)	3.50	(0.35)	DTC3	0.064	0.021	33	0.268	0.165	62
DTC285B	10/26/95	0.218	0.027	298	18	0.196	0.010	0.062	0.007	3.71	0.19	DTC3	0.075	0.023	31	0.211	0.193	91
DTC285A	10/26/95	0.218	0.027	298	18	0.194	0.010	0.063	0.007	3.75	0.19	DTC3	0.089	0.027	30	0.187	0.201	107
DTC253B	08/25/95	0.226	0.028	297	17	0.203	0.010	0.063	0.007	3.70	0.19	DTC3	0.051	0.017	33	0.411	0.178	43
DTC253A	08/25/95	0.226	0.028	297	17	0.203	0.010	0.063	0.007	3.71	0.19	DTC3	0.061	0.020	33	0.386	0.206	53
DTC236A	07/26/95	0.230	0.028	296	16	0.207	0.011	0.056	0.007	3.54	(0.35)	DTC3	0.079	0.022	28	0.298	0.214	72
DTC228B	07/14/95	0.232	0.028	297	16	0.221	0.011	0.061	0.007	1.47	0.07	DTC3	0.039	0.015	39	0.860	0.222	26
DTC228A	07/14/95	0.232	0.028	297	16	0.222	0.011	0.060	0.007	1.47	0.07	DTC3	0.045	0.024	53	0.995	0.272	27
DTC215B	09/14/94	0.226	0.028	299	6	0.455	0.023	0.107	0.012	4.49	0.35	DTC2	0.134	0.038	28	0.7E-5	0.6E-4	900
DTC215A	09/14/94	0.226	0.028	299	6	0.438	0.022	0.102	0.012	4.36	0.34	DTC2	0.111	0.032	29	0.3E-4	0.2E-3	665
DTC171B	06/15/94	0.239	0.029	298	3	0.465	0.023	0.117	0.013	3.95	0.31	DTC2	0.208	0.067	32	0.010	0.059	621
DTC171A	06/15/94	0.239	0.029	298	3	0.468	0.023	0.117	0.013	4.13	0.32	DTC2	0.203	0.074	36	0.365	0.375	103
DTC145B	05/03/94	0.258	0.031	298	2	0.468	0.023	0.190	0.021	4.22	0.33	DTC2	0.151	0.047	31	1.284	8.545	665
DTC145A	05/03/94	0.258	0.031	298	2	0.470	0.024	0.181	0.020	4.27	0.33	DTC2	0.198	0.065	33	1.252	0.293	23
DTC058B	06/07/93	0.388	0.047	301	1	0.191	0.010	0.049	0.006	3.59	0.18	DTC1	0.053	0.013	25	0.013	0.047	371
DTC058A	06/07/93	0.388	0.047	301	1	0.192	0.010	0.049	0.006	3.50	0.17	DTC1	0.066	0.016	25	0.011	0.046	410
CTC135B	06/14/95	0.188	0.031	294	15	0.200	0.010	0.059	0.007	3.32	0.17	CTC	0.070	0.020	29	0.553	0.345	62
CTC135A	06/14/95	0.188	0.031	294	15	0.201	0.010	0.059	0.007	3.36	0.17	CTC	0.062	0.018	30	0.621	0.318	51
CTC120B	05/16/95	0.190	0.031	294	14	0.203	0.010	0.052	0.006	3.50	0.18	CTC	0.045	0.014	31	0.916	0.342	37
CTC120A	05/16/95	0.190	0.031	294	14	0.204	0.010	0.052	0.006	3.51	0.18	CTC	0.039	0.011	29	0.254	0.211	83
CTC114B	05/03/95	0.191	0.031	296	14	0.196	0.010	0.044	0.005	3.59	0.42	CTC	0.062	0.015	24	0.708	0.374	53
CTC114A	05/03/95	0.191	0.031	296	14	0.197	0.010	0.044	0.005	3.62	0.42	CTC	0.061	0.015	24	0.581	0.354	61
CTC099B	03/29/95	0.193	0.032	295	13	0.229	0.012	0.044	0.005	3.44	(0.34)	CTC	0.110	0.023	21	0.173	0.312	181
CTC099A	03/29/95	0.193	0.032	295	13	0.229	0.012	0.044	0.005	3.42	(0.34)	CTC	0.072	0.015	21	0.078	0.164	210
CTC084B	03/03/95	0.195	0.032	299	12	0.205	0.010	0.048	0.006	3.91	0.31	CTC	0.051	0.011	22	0.016	0.148	928
CTC084A	03/03/95	0.195	0.032	299	12	0.203	0.010	0.048	0.006	3.93	0.31	CTC	0.055	0.012	22	0.599	6.236	1041
CTC074	02/08/95	0.196	0.032	297	11	0.210	0.014	0.037	0.005	3.64	0.28	CTC	0.064	0.013	20	0.3E-4	0.2E-3	597
CTC058	01/10/95	0.198	0.033	299	10	0.205	0.010	0.056	0.007	3.55	0.28	CTC	0.107	0.024	22	0.002	0.023	1232
CTC045	12/07/94	0.200	0.033	301	9	0.345	0.017	0.120	0.014	3.61	0.28	CTC	0.029	0.020	70	2.923	0.995	34
CTC042	12/02/94	0.200	0.033	301	9	0.204	0.010	0.052	0.006	3.68	0.29	CTC	0.103	0.029	28	1.299	0.668	51
CTC028	11/03/94	0.202	0.033	304	8	0.215	0.011	0.054	0.006	3.65	0.28	CTC	0.053	0.012	22	0.007	0.081	1114
CTC020	10/20/94	0.203	0.033	304	8	0.185	0.009	0.076	0.009	3.61	0.28	CTC	0.036	0.013	35	0.367	0.165	45
CTC013	10/13/94	0.204	0.034	303	8	0.334	0.021	0.113	0.013	2.98	0.23	CTC	0.035	0.013	38	0.110	0.080	80
CO Experiments																		
CTC090B	03/16/95	0.194	0.032	294	13	0.191	0.010	0.070	0.008	89.1	(8.9)	CTC	0.095	0.042	44	0.125	0.202	162
CTC090A	03/16/95	0.194	0.032	294	13	0.192	0.010	0.070	0.008	89.0	(8.9)	CTC	0.073	0.035	48	0.397	0.315	79
CTC061	01/13/95	0.198	0.033	300	10	0.173	0.009	0.053	0.006	84.7	(8.5)	CTC	0.051	0.025	50	0.307	0.346	113
CTC031	11/10/94	0.202	0.033	300	8	0.206	0.010	0.058	0.007	84.8	(8.5)	CTC	0.096	0.041	42	0.143	0.271	190

Values in parentheses are estimated uncertainties for runs where no calibration uncertainty estimates are available.

Appendix B-3 Ratios of Photolysis Rates Relative to NO_2 for Representative Spectral Distributions

Table B-3 Calculated ratios of photolysis rates relative to NO_2 for all photolysis rate parameters in the SAPRC-97 mechanism for representative spectral distributions.

Phot. Set	k(phot) / k(NO2)					
	CTC (Xenon Arc Lights)			Blacklights		
	Avg Runs 65-141	Avg Runs 200-225	Diff. / Avg.	Carter et al (1995)	Kelly	St.Dev / Avg.
CCHOR	2.24e-4	1.84e-4	-9.7%	2.37e-4	2.51e-4	3.9%
MEGLYOX1	3.07e-4	2.54e-4	-9.4%	4.06e-4	4.27e-4	2.5%
RCHO	8.20e-4	6.81e-4	-9.3%	1.08e-3	1.12e-3	2.1%
KETONE	6.08e-4	5.05e-4	-9.3%	7.98e-4	8.35e-4	2.3%
ACET-93C	3.02e-5	2.52e-5	-9.0%	3.26e-5	3.56e-5	4.4%
HCHONEWR	1.35e-3	1.13e-3	-8.9%	1.74e-3	1.87e-3	3.6%
O3O1D	1.55e-3	1.30e-3	-8.6%	1.33e-3	1.46e-3	4.6%
GLYOXAL1	1.85e-3	1.56e-3	-8.6%	3.11e-3	3.20e-3	1.5%
H2O2	3.54e-4	3.14e-4	-6.0%	7.64e-4	7.67e-4	0.2%
CO2H	3.60e-4	3.23e-4	-5.5%	7.97e-4	7.99e-4	0.1%
HCHONEWM	2.47e-3	2.24e-3	-4.9%	6.43e-3	6.37e-3	-0.5%
ACROLEIN	3.29e-2	3.18e-2	-1.8%	8.22e-2	8.15e-2	-0.4%
BZCHO	6.86e-2	6.71e-2	-1.1%	1.48e-1	1.48e-1	-0.3%
HONO	1.61e-1	1.60e-1	-0.3%	2.80e-1	2.80e-1	0.1%
MEGLYOX2	1.52e-1	1.55e-1	0.8%	1.96e-2	2.05e-2	2.3%
GLYOXAL2	2.42e-1	2.46e-1	0.9%	2.44e-2	2.69e-2	5.0%
O3O3P	5.69e-2	5.91e-2	1.8%	5.32e-3	5.47e-3	1.3%
NO3NO2	2.17e+1	2.26e+1	2.0%	3.38e-1	3.41e-1	0.3%
NO3NO	2.44e+0	2.56e+0	2.4%	1.69e-3	1.68e-3	0.0%

Appendix C Uncertainty Treatment and Sampling Approach

The table gives the details for the uncertainty treatment in this study, including the approach used to incorporate the important correlations between the study phases.

Table C Uncertainty Treatment and Sampling Approach

Important Factors	Aroamtics except Benzene [1]	Benzene	Treatment
A1. NO2 + hv ->	CTC: $K_1^i = \underline{K_1}^i * f_{1c}$	CTC: $K_1^i = \underline{K_1}^i * f_{1c}$	σ_{k1}/K1 is 16% for CTC and 12% for DTC & ITC
	DTC: $K_1^i = \underline{K_1}^i * f_{1d}$	ITC: $K_1^i = \underline{K_1}^i * f_{1d}$	f_{1c}: lognormal distribution with $\mu = 1.0$ and $\sigma = 0.16$
	I: ith experiment	I: ith experiment [1]	f_{1d}: lognormal distribution with $\mu =1.0$ and $\sigma = 0.12$
A4. O3 + NO ->	$K_{A4}^i = \underline{K}_{A4}^i * f_{A4}$	$K_{A4}^i = \underline{K}_{A4}^i * f_{A4}$	f_{A4}: lognormal distribution with $\mu = 1.0$ and $\sigma = 0.096$
A5. O3 + NO2 ->	$K_{A5}^i = \underline{K}_{A5}^i * f_{A5}$	$K_{A5}^i = \underline{K}_{A5}^i * f_{A5}$	f_{A5}: lognormal distribution with $\mu = 1.0$ and $\sigma = 0.140$
A17. HONO + hv ->	$K_{A17}^i = K_1^i * \underline{K}_{A17}^i / \underline{K_1}^i * f_{A17}$		f_{A17}: lognormal distribution with $\mu = 1.0$ and $\sigma = 0.340$
A18. HO + NO2 ->	$K_{A18}^i = \underline{K}_{A18}^i * f_{A18}$	$K_{A18}^i = \underline{K}_{A18}^i * f_{A18}$	f_{A18}: lognormal distribution with $\mu = 1.0$ and $\sigma = 0.265$
A23. HO2 + NO ->	$K_{A23}^i = \underline{K}_{A23}^i * f_{A23}$	$K_{A23}^i = \underline{K}_{A23}^i * f_{A23}$	f_{A23}: lognormal distribution with $\mu = 1.0$ and $\sigma = 0.183$
A25. HNO4 ->	$K_{A25}^i = \underline{K}_{A25}^i * f_{A25}$	$K_{A25}^i = \underline{K}_{A25}^i * f_{A25}$	f_{A25}: lognormal distribution with $\mu = 1.0$ and $\sigma = 2.400$
C13. CCOO2 + NO ->	$K_{C13}^i = \underline{K}_{C13}^i * f_{C13}$		f_{C13}: lognormal distribution with $\mu = 1.0$ and $\sigma = 0.343$
C14. CCOO2 + NO2 ->	$K_{C14}^i = \underline{K}_{C14}^i * f_{C14}$		f_{C14}: lognormal distribution with $\mu = 1.0$ and $\sigma = 0.158$
C18. PAN ->	$K_{C18}^i = \underline{K}_{C18}^i * f_{C18}$		f_{C18}: lognormal distribution with $\mu = 1.0$ and $\sigma = 0.400$
G51. PHEN + NO3 ->		$K_{G51}^i = \underline{K}_{G53}^i * f_{G51}$	f_{G53}: lognormal distribution with $\mu = 1.0$ and $\sigma = 0.420$
G57. CRES + NO3 ->	$K_{G57}^i = \underline{K}_{G57}^i * f_{G57}$		f_{G57}: lognormal distribution with $\mu = 1.0$ and $\sigma = 0.750$
L1. VOC + OH ->	$K_{VOC}^i = \underline{K}_{VOC}^i$*exp($\mu_{normal}+\sigma_{normal}*Z_{VOC}$)	$K_{VOC}^i = \underline{K}_{VOC}^i$*exp($\mu_{normal}+\sigma_{normal}*Z_{VOC}$)	$f_{L1} = \exp(\mu_{normal}+\sigma_{normal} * Z)$ where, Z is a random variable with standard normal distribution. Given the distribution (μ,σ) for the uncertainty factor f for the Reaction rate of a apecified VOC+OH, μ_{normal} and σ_{normal} can be calculated as following: $\mu_{normal} = \ln(1.0/(1.0 + \sigma^2)^{0.5})$ $\sigma_{normal} = (\ln(1.0 + \sigma^2))^{0.5}$
initial concentraion	aromatic compound	NO & NO2	Z_j: standard normal distribution for jth uncertainty group
	$VOC^i = \underline{VOC}^i + \sigma_{VOCi} * Z_j$	$NO^i = \underline{NO}^i + \sigma_{NO} * Z_j$	Totally five independent uncertainty groups are used
	I: ith experiment	$NO2^i = \underline{NO2}^i + \sigma_{NO2} * Z_j$	
	j: jth uncertainty group		
RSI	results from chamber characterization	results from chamber characterization	[2]
HONO-F	results from chamber characterization	results from chamber characterization	[2]

[1] Notation in this table:
I represents the ith experiment
j represents the jth uncertainty group
$\underline{K}$, $\underline{VOC}$, $\underline{NO}$, $\underline{NO2}$ represent the norminal value for the varialbe
K, VOC, NO, NO2 represent the varying value for the varialbe

[2] Methodology for the LHS Samples

a) Use LHS program to produce samples including all the random variables listed above except RSI and HONO-F. For example, the kth sample will include
$f_{1c}^k, f_{1d}^k, f_{A4}^k, f_{A5}^k, f_{A17}^k, f_{A18}^k, f_{A23}^k, f_{A25}^k, f_{C13}^k, f_{C14}^k, f_{C18}^k, f_{G51}^k, f_{G57}^k, Z_{voc}^k, Z_1^k, Z_2^k, Z_3^k, Z_4^k, Z_5^k$

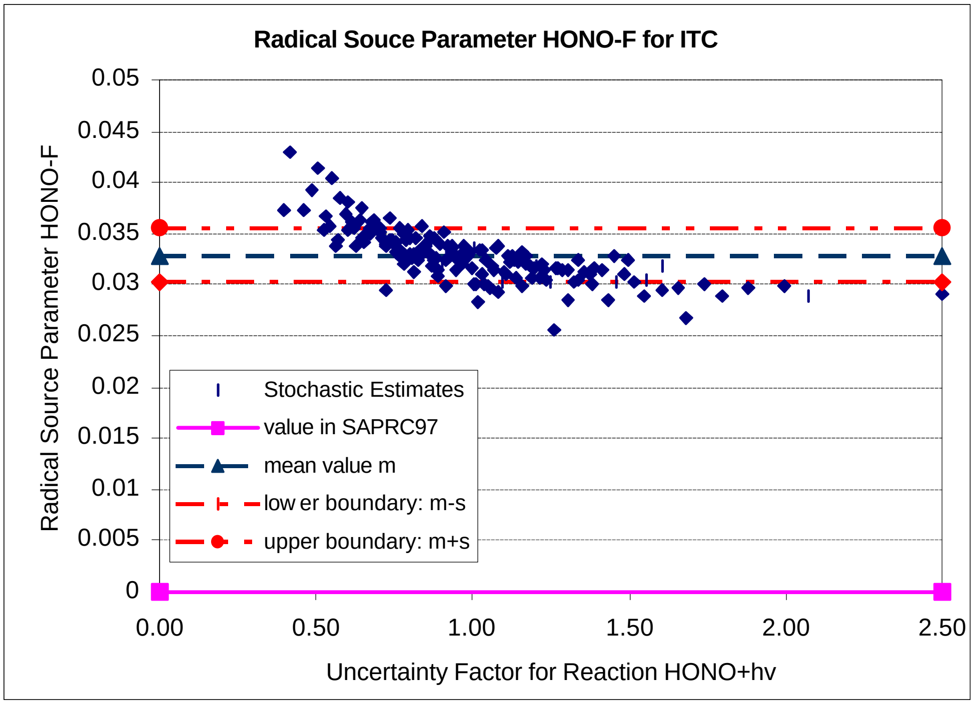
b) From the above LHS samples, select the potential influential factors for chamber-characteization parameter estimation problem. So the kth sample to estimate the chamber-characterization parameters and the corresponding estimated values for RSI and HONO-F will be:
CTC: $f_{1c}^k, f_{A4}^k, f_{A5}^k, f_{A18}^k, f_{A23}^k, f_{A25}^k, Z_{voc}^k$, ----> RSI^k, HONO-F^k
DTC: $f_{1d}^k, f_{A4}^k, f_{A5}^k, f_{A18}^k, f_{A23}^k, f_{A25}^k, Z_{voc}^k$, ----> RSI^k, HONO-F^k
ITC: $f_{1d}^k, f_{A4}^k, f_{A5}^k, f_{A18}^k, f_{A23}^k, f_{A25}^k, Z_{voc}^k$, ----> RSI^k, HONO-F^k
here, Z_{VOC} will be used for the reaction NC4+OH or CO+OH

c) For the aromatics oxidation parameter estimation for all the aromatic compounds except benzene
select the important factors from the whole LHS samples, plus the estimated RSI and HONO-F to from the LHS samples for the parameter estimation problem:
The kth LHS sample for the aromatics oxidation parameter estimation for the aromatics except benzene will be:
$f_{1c}^k, f_{1d}^k, f_{A4}^k, f_{A5}^k, f_{A17}^k, f_{A18}^k, f_{A23}^k, f_{A25}^k, f_{C13}^k, f_{C14}^k, f_{C18}^k, f_{G51}^k, f_{G57}^k, Z_{voc}^k, Z_1^k, Z_2^k, Z_3^k, Z_4^k, Z_5^k, RSI_{CTC}^k$, HONO-$F_{CTC}^k$, RSI_{DTC1}^k, HONO-F_{DTC1}^k, RSI_{DTC2}^k, HONO-F_{DTC2}^k, RSI_{DTC3}^k, HONO-F_{DTC3}^k
From this sample, we can estimate the values for $B1MG^k$, $B1U2^k$

d) For the aromatics oxidation parameter estimation for benzene
select the important factors from the whole LHS samples, plus the estimated RSI and HONO-F to from the LHS samples for the parameter estimation problem:
The kth LHS sample for the aromatics oxidation parameter estimation for benzene will be:
$f_{1c}^k, f_{1d}^k, f_{A4}^k, f_{A5}^k, f_{A18}^k, f_{A23}^k, f_{A25}^k, f_{G51}^k, f_{G57}^k, Z_{voc}^k, Z_1^k, Z_2^k, Z_3^k, RSI_{CTC}^k$, HONO-$F_{CTC}^k$, RSI_{ITC}^k, HONO-F_{ITC}^k
From this sample, we can estimate the values for $B1U1^k$ and $P1U1^k$.

Appendix D-1 Results for Chamber Characterization Parameters

The stochastic results for the chamber characterization parameters (RSI and HONO-F) are shown in Figures D1-1 to D1-7. The regression analysis results for RSI and HONO-F are listed in Tables D1-1 to D1-5.



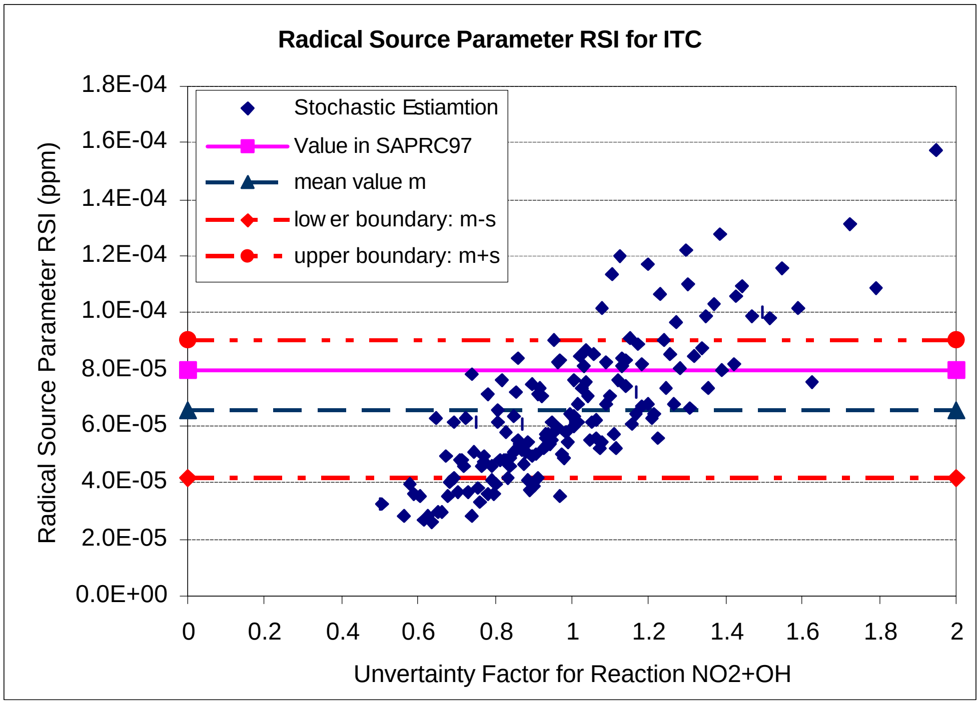
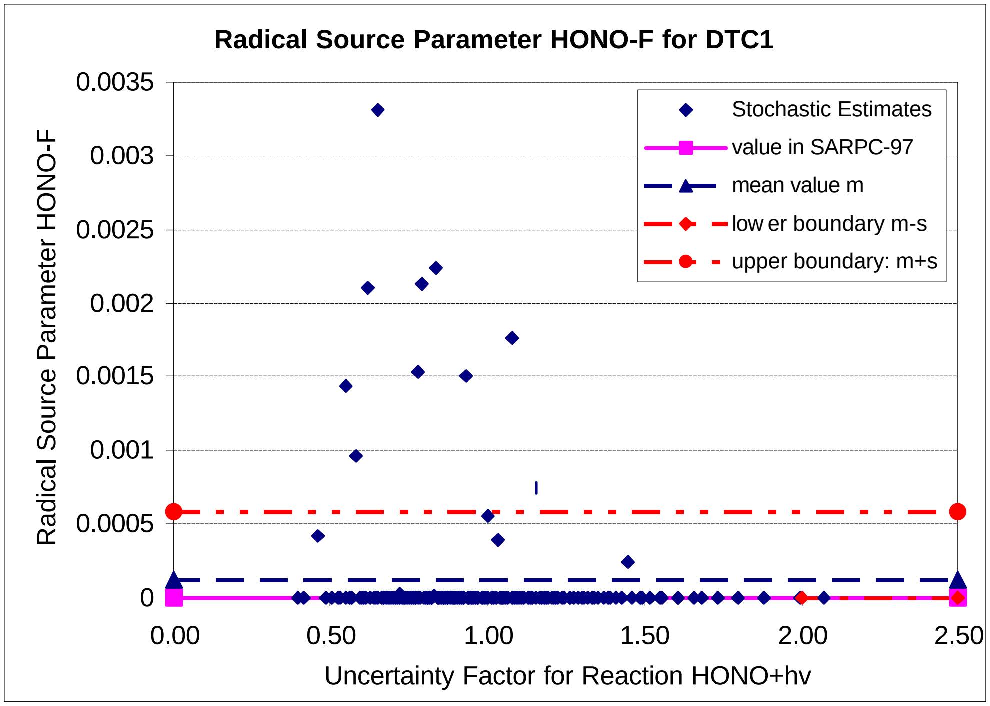


Figure D1-1 Stochastic Parameter Estimation For Chamber Characterization Parameters for ITC (160 LHS Samples Applied to 4 Chamber Experiments)

note: In legend, m represents mean value, s represents standard deviation. The same representation is used for all the figures in Appendix D.



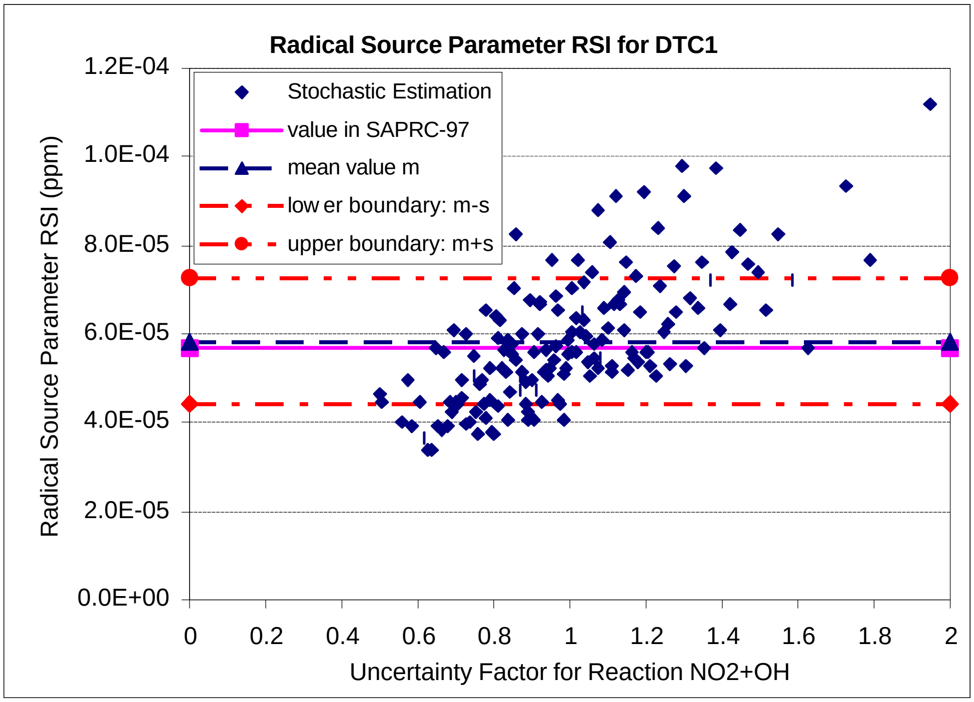


Figure D1-2 Stochastic Parameter Estimation for chamber Characterization Parameters for DTC1 (160 LHS Samples Applied to 2 Chamber Experiments)

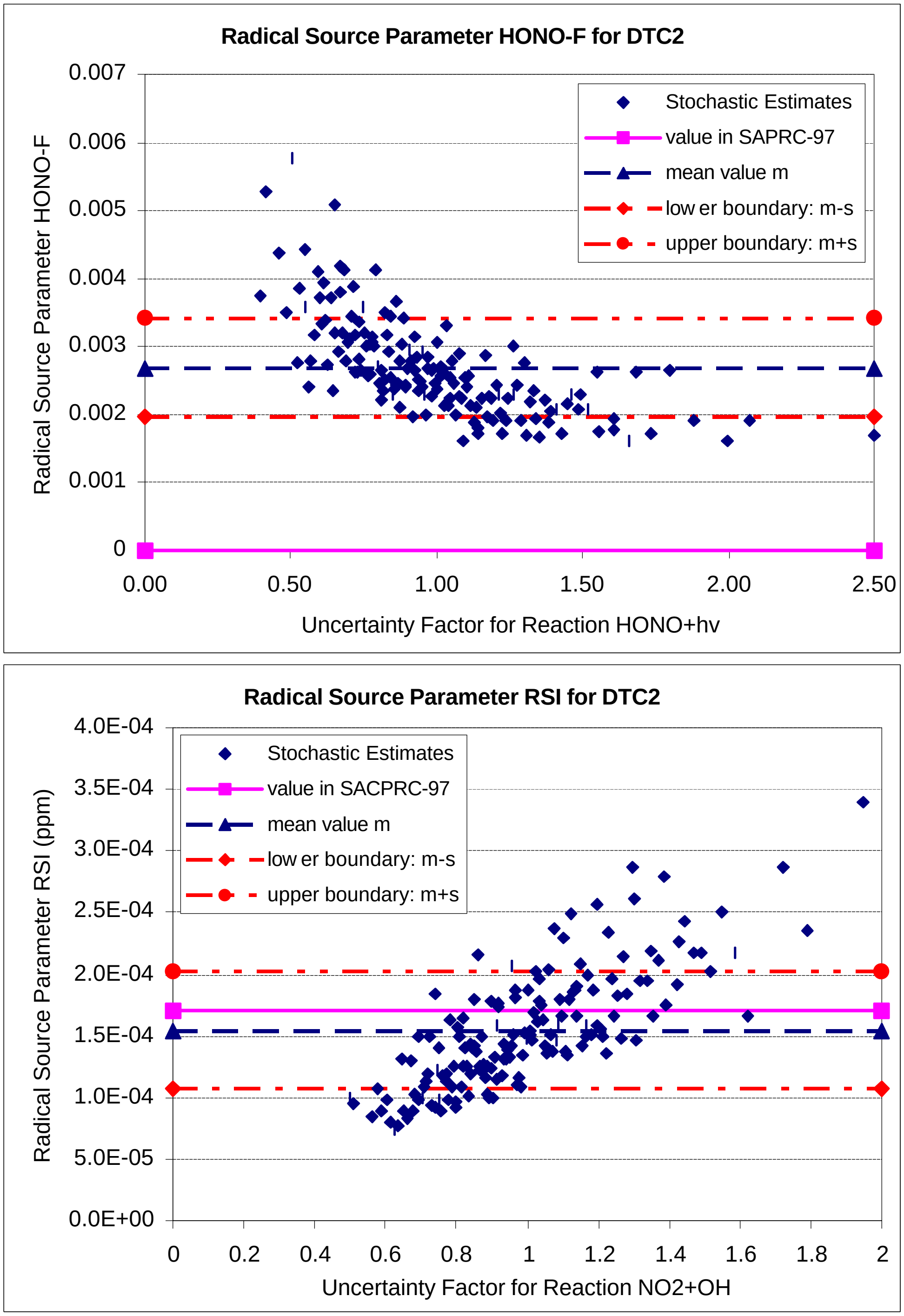
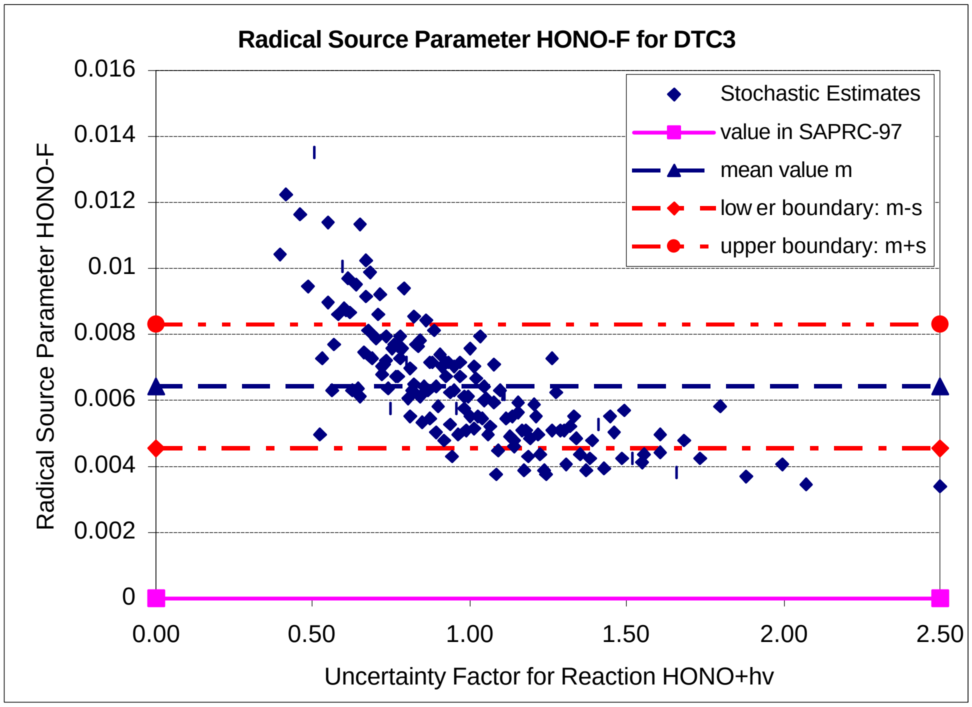


Figure D1-3 Stochastic Parameter Estimation for Chamber Characterization Parameters for DTC2 (160 LHS Samples Applied to 6 Chamber Experiments)



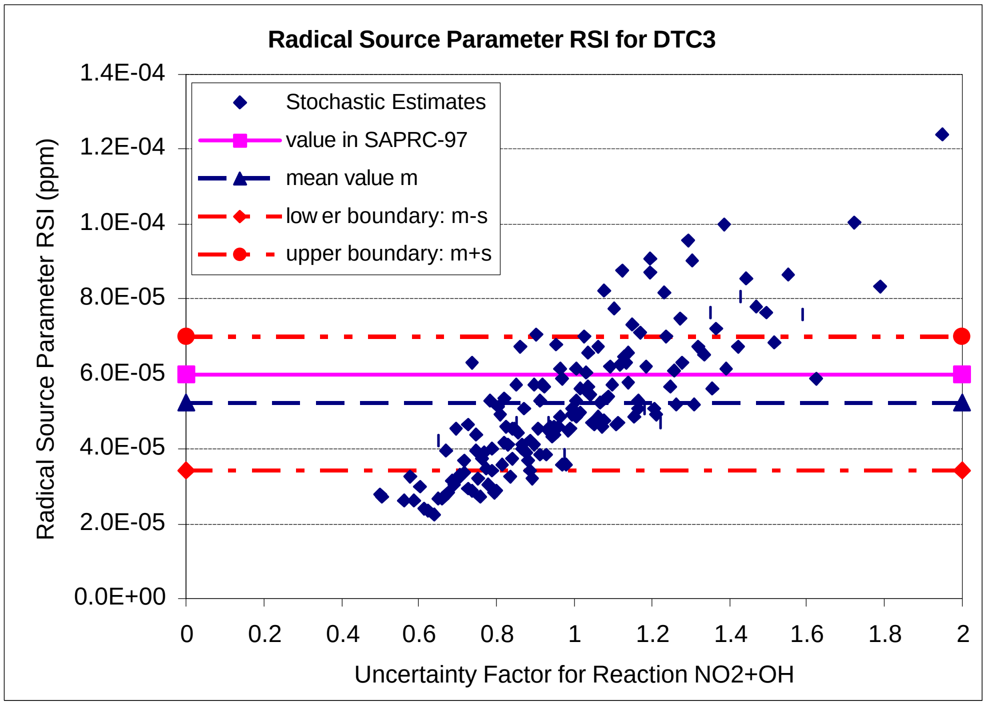
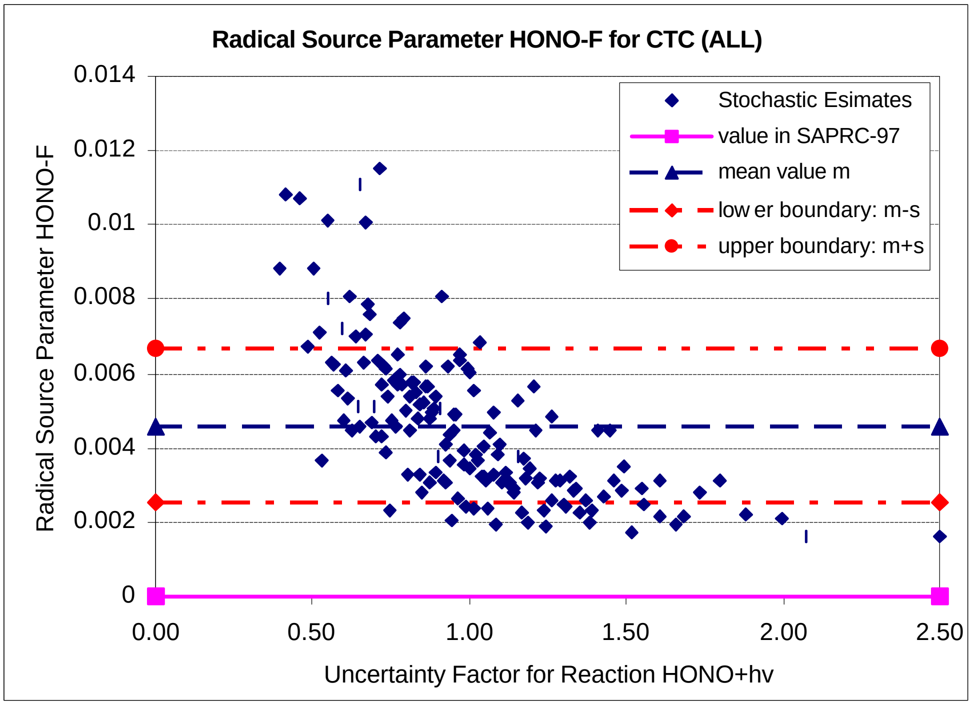


Figure D1-4 Stochastic Parameter Estimation for Chamber characterization Parameters for DTC3 (160 LHS Samples Applied to 9 Chamber Experiments)



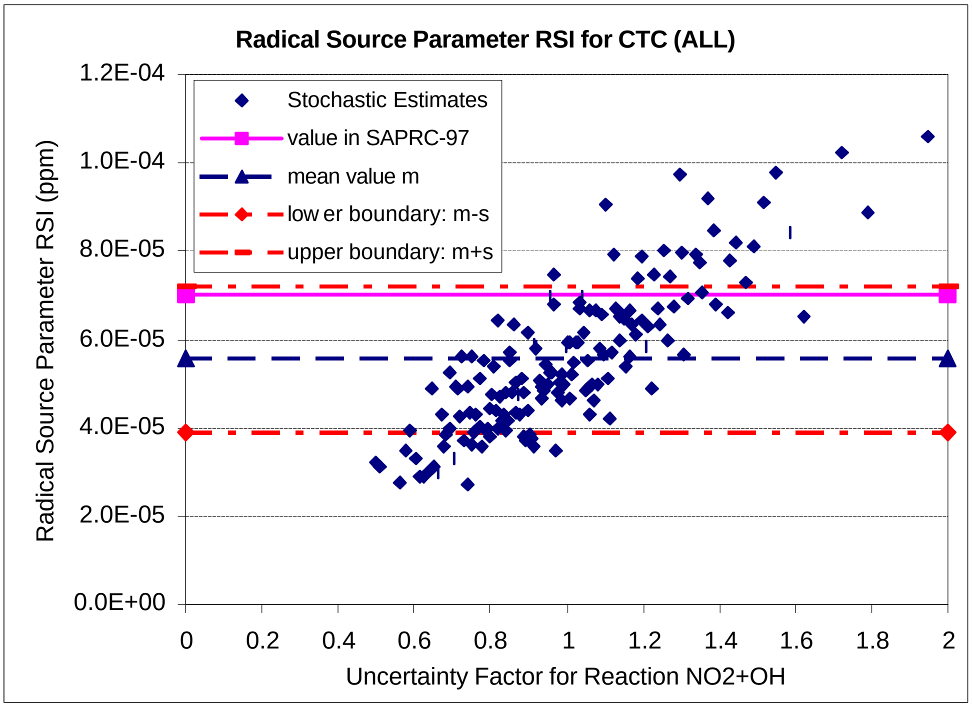
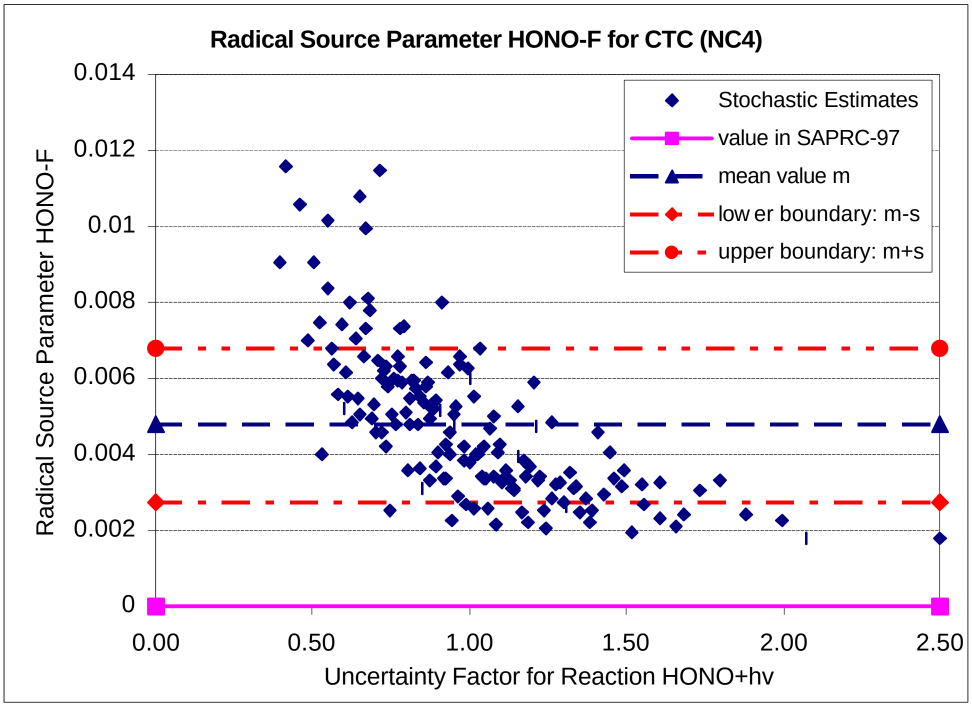


Figure D1-5 Stochastic Parameter Estimation for Chamber Characterization Parameters for CTC (160 LHS Samples Applied to 17 N-butane-NO_x Experiments and 4 CO-NO_x Experiments)



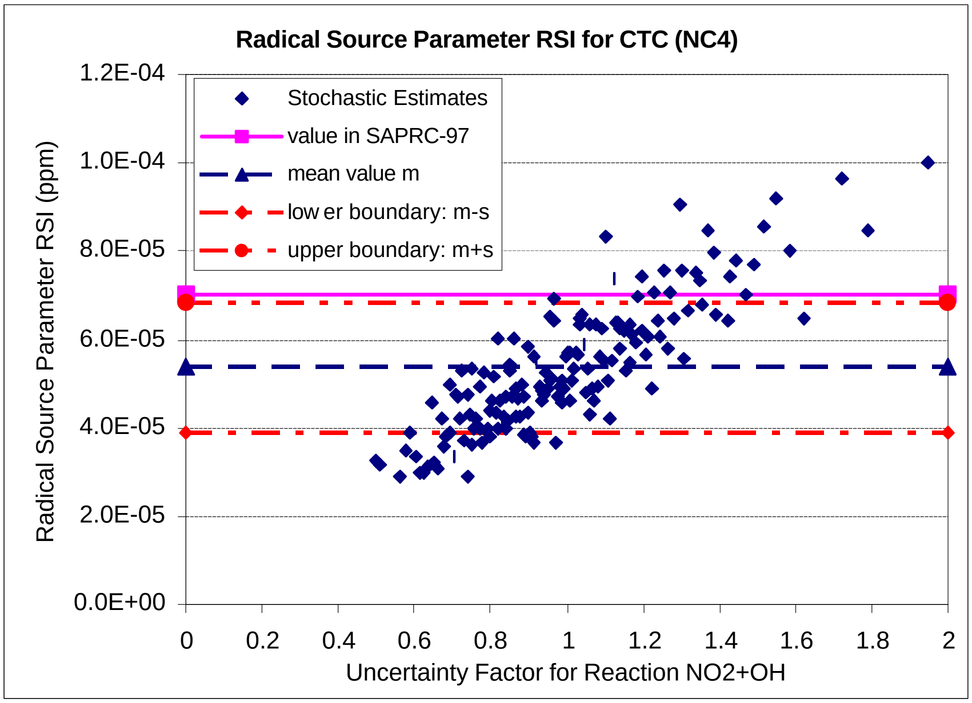
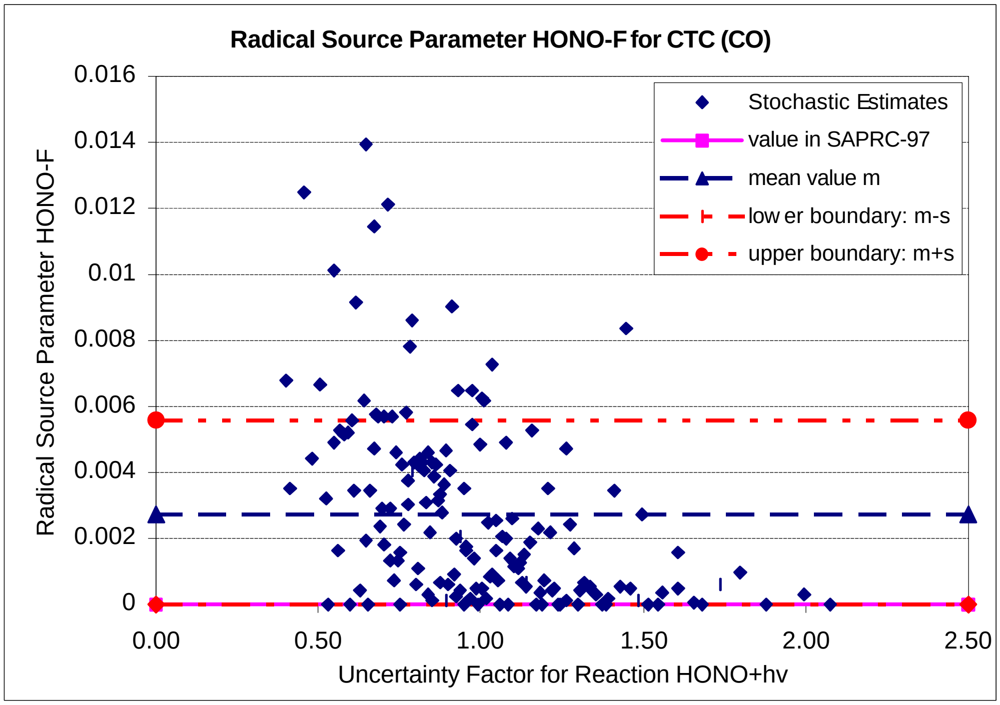


Figure D1-6 Stochastic Parameter Estimation for Chamber-Characterization Parameters for CTC (160 Samples Applied to 17 NC_4-NO_x Experiments)



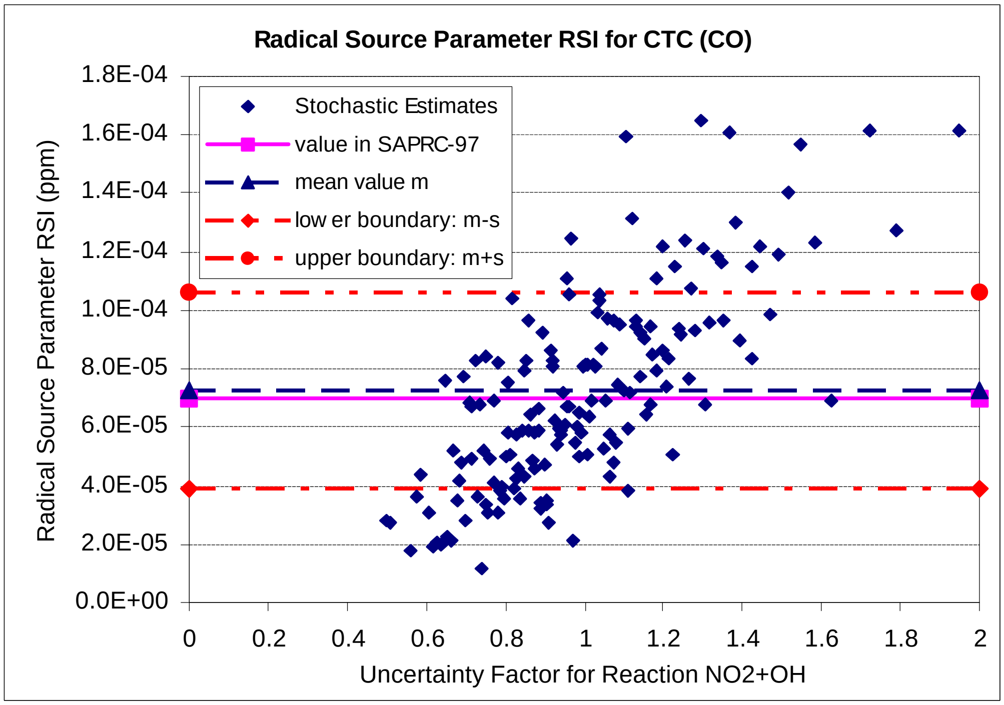


Figure D1-7 Stochastic Parameter Estimation for Chamber Characterization Parameters for CTC (160 LHS Samples Applied to 4 CO-NO_x experiments)

Table D1-1 Regression Analysis for Chamber Characterization Parameters for ITC

Parameter	**Input Uncertainty** **($\sigma_i/\kappa_{i \text{ norminal}}$)**	**HONO-F** [a] Standardized Regression Coefficient [b] (Rank)	**RSI** [a] Standardized Regression Coefficient [b] (Rank)
A1. NO_2 + hv -> (light intensity)	0.12 [c]	-0.27 (3)	-0.26 (3)
A4. O_3 + NO ->	0.10 [d]	-0.20 (4)	0.09 (4)
A5. O_3 + NO_2 ->	0.14 [d]	0.01	-0.01
A17. HONO + hv -> (action spectrum)	0.34 [d]	-0.81 (1)	0.02
A18. NO_2 + OH ->	0.27 [d]	-0.14 (5)	0.79 (1)
A23. HO_2 + NO ->	0.18 [d]	0.04	-0.00
A25. HNO_4 ->	2.40 [d]	0.27 (2)	-0.04
159. N-butane + OH. ->	0.18 [d]	0.11 (6)	-0.51 (2)
Adjusted R^2		**0.87**	**0.96**

[a] The regression model is for normalized predictors.

[b] Standardized regression coefficient $\beta j'$

[c] The uncertainty factor is recommended by Carter, 1998, Appendix B-2

[d] The uncertainty factors are taken from NASA-97, NASA-94, AQIRP-94. Lognormal distributions were assumed.

TableD1-2 Regression Analysis for Chamber Characterization Parameters for DTC1

Parameter	**Input Uncertainty** ($\sigma_i/\kappa_{i\ \mathrm{norminal}}$)	**HONO-F** [a] Standardized Regression Coefficient [b] (Rank)		**RSI** [a] Standardized Regression Coefficient [b] (Rank)	
A1. NO_2 + hv -> (light intensity)	0.12 [c]	-0.14	(4)	-0.51	(3)
A4. O_3 + NO ->	0.10 [d]	0.08		0.07	
A5. O_3 + NO_2 ->	0.14 [d]	0.12	(5)	0.00	
A17. HONO + hv -> (action spectrum)	0.34 [d]	-0.17	(3)	-0.05	
A18. NO_2 + OH ->	0.27 [d]	-0.44	(1)	0.67	(1)
A23. HO_2 + NO ->	0.18 [d]	0.01		0.01	
A25. HNO_4 ->	2.40 [d]	-0.11		-0.02	
159. N-butane + OH. ->	0.18 [d]	0.21	(2)	-0.52	(2)
Adiusted R^2		**0.28**		**0.97**	

[a] The regression model is for normalized predictors.

[b] Standardized regression coefficient βj'

[c] The uncertainty factor is recommended by Carter, 1998, Appendix B-2

[d] The uncertainty factors are taken from NASA-97, NASA-94, AQIRP-94. Lognormal distributions were assumed.

Table D1-3 Regression Analysis for Chamber Characterization Parameters for DTC2

Parameter	**Input Uncertainty** ($\sigma_i/\kappa_{i\ \mathrm{norminal}}$)	**HONO-F** [a] Standardized Regression Coefficient [b] (Rank)		**RSI** [a] Standardized Regression Coefficient [b] (Rank)	
A1. NO_2 + hv -> (light intensity)	0.12 [c]	-0.42	(2)	-0.37	(3)
A4. O_3 + NO ->	0.10 [d]	0.00		0.07	
A5. O_3 + NO_2 ->	0.14 [d]	0.04		0.00	
A17. HONO + hv -> (action spectrum)	0.34 [d]	-0.75	(1)	-0.07	
A18. NO_2 + OH ->	0.27 [d]	-0.23	(4)	0.78	(1)
A23. HO_2 + NO ->	0.18 [d]	0.00		0.01	
A25. HNO_4 ->	2.40 [d]	-0.07		-0.01	
159. N-butane + OH. ->	0.18 [d]	-0.32	(3)	-0.47	(2)
Adjusted R^2		**0.89**		**0.97**	

[a] The regression model is for normalized predictors.

[b] Standardized regression coefficient βj'

[c] The uncertainty factor is recommended by Carter, 1998, Appendix B-2

[d] The uncertainty factors are taken from NASA-97, NASA-94, AQIRP-94. Lognormal distributions were assumed.

Table D1-4 Regression Analysis for Chamber Characterization Parameters for DTC3

Parameter	**Input Uncertainty** ($\sigma_i/\kappa_{i\ norminal}$)	**HONO-F** [a] Standardized Regression Coefficient [b] (Rank)		**RSI** [a] Standardized Regression Coefficient [b] (Rank)	
A1. NO_2 + hv -> (light intensity)	0.12 [c]	-0.33	(3)	-0.33	(3)
A4. O_3 + NO ->	0.10 [d]	-0.04		0.08	
A5. O_3 + NO_2 ->	0.14 [d]	0.03		-0.02	
A17. HONO + hv -> (action spectrum)	0.34 [d]	-0.80	(1)	-0.02	
A18. NO_2 + OH ->	0.27 [d]	-0.41	(2)	0.81	(1)
A23. HO_2 + NO ->	0.18 [d]	-0.00		0.01	
A25. HNO_4 ->	2.40 [d]	-0.09		0.00	
159. N-butane + OH. ->	0.18 [d]	-0.12	(4)	-0.39	(2)
Adjusted R^2		**0.92**		**0.92**	

[a] The regression model is for normalized predictors.

[b] Standardized regression coefficient βj'

[c] The uncertainty factor is recommended by Carter, 1998, Appendix B-2

[d] The uncertainty factors are taken from NASA-97, NASA-94, AQIRP-94. Lognormal distributions were assumed.

Table D1-5 Regression Analysis for Chamber Characterization Parameters for CTC

(17 NC_4-NO_x Experiments and 4 CO-NO_x Experiments)

Parameter	**Input Uncertainty** ($\sigma_i/\kappa_{i\ \mathrm{norminal}}$)	**HONO-F** [a] Standardized Regression Coefficient [b] (Rank)		**RSI** [a] Standardized Regression Coefficient [b] (Rank)	
A1. NO_2 + hv -> (light intensity)	0.12 [c]	-0.37	(3)	-0.05	
A4. O_3 + NO ->	0.10 [d]	-0.02		0.05	
A5. O_3 + NO_2 ->	0.14 [d]	0.02		0.00	
A17. HONO + hv -> (action spectrum)	0.34 [d]	-0.74	(1)	-0.07	
A18. NO_2 + OH ->	0.27 [d]	-0.49	(2)	0.83	(1)
A23. HO_2 + NO ->	0.18 [d]	-0.03		0.01	
A25. HNO_4 ->	2.40 [d]	-0.08		-0.02	
159. N-butane + OH. ->	0.18 [d]	-0.08		-0.53	(2)
Adjusted R^2		**0.94**		**0.97**	

[a] The regression model is for normalized predictors.

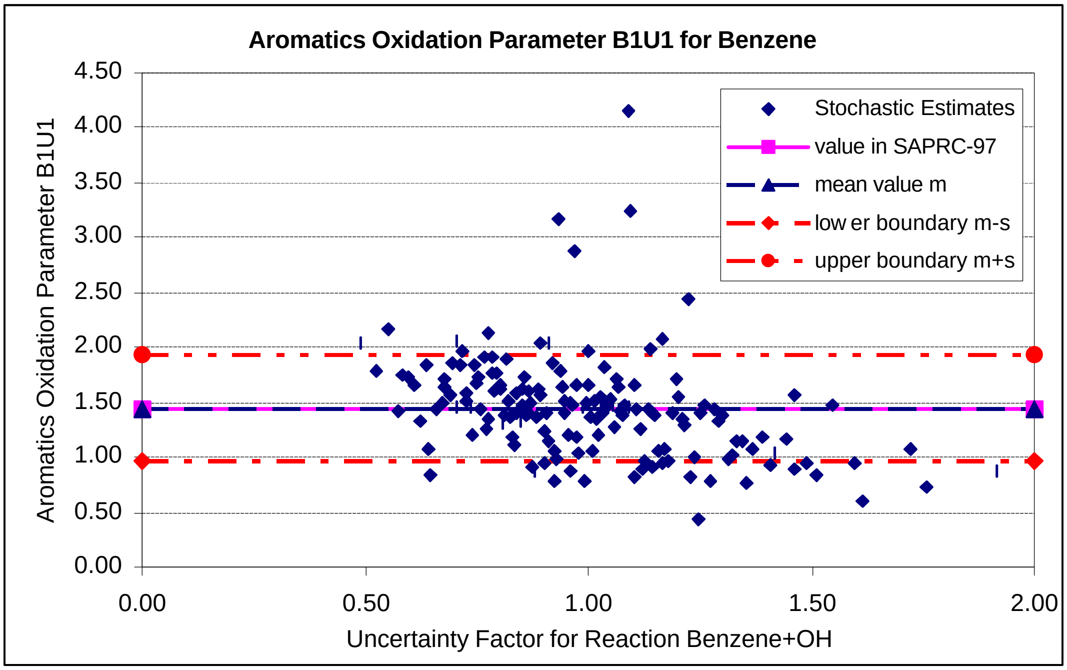
[b] Standardized regression coefficient $\beta j'$

[c] The uncertainty factor is recommended by Carter, 1998, Appendix B-2

[d] The uncertainty factors are taken from NASA-97, NASA-94, AQIRP-94. Lognormal distributions were assumed.

Appendix D-2 Results for Aromatics Oxidation Parameters

The stochastic estimation results for the aromatics oxidation parameters are shown in Figures D2-1 to D2-9. The corresponding regression analysis results are shown in Tables D2-1 to D2-9.



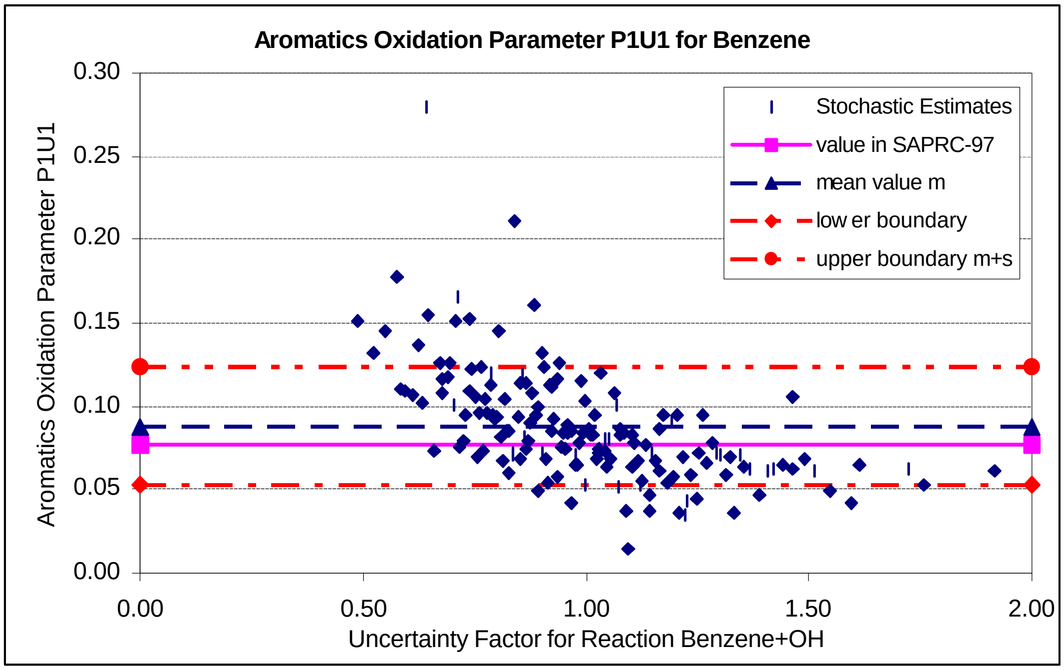
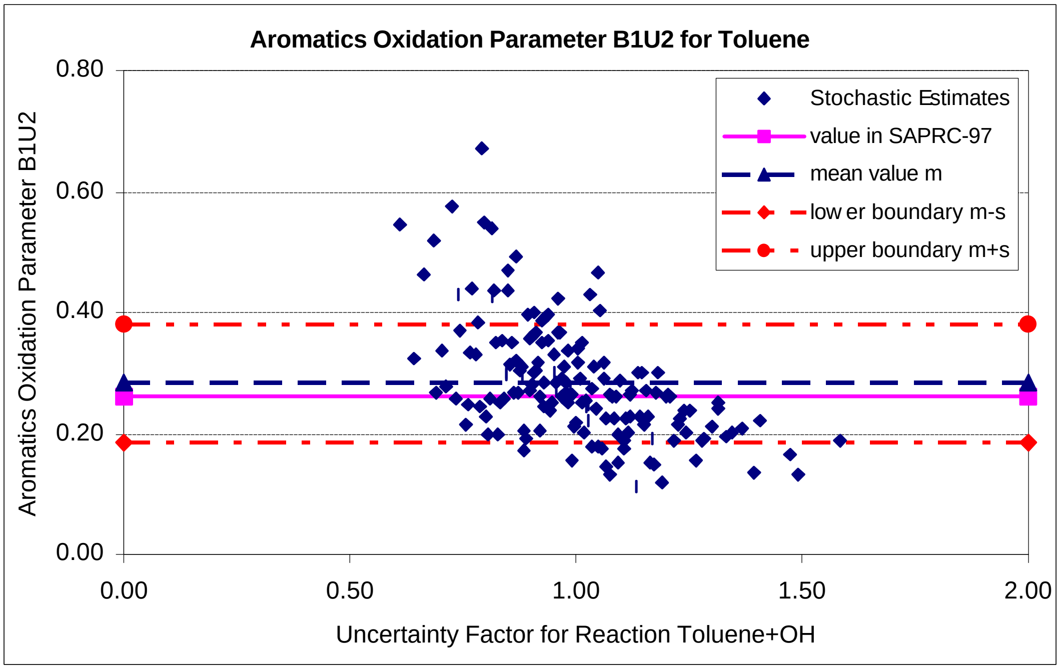


Figure D2-1 Stochastic Parameter Estimation for Aromatics Oxidation Parameters for Benzene (160 LHS Samples Applied to 7 Benzene-NO$_x$ Experiments)



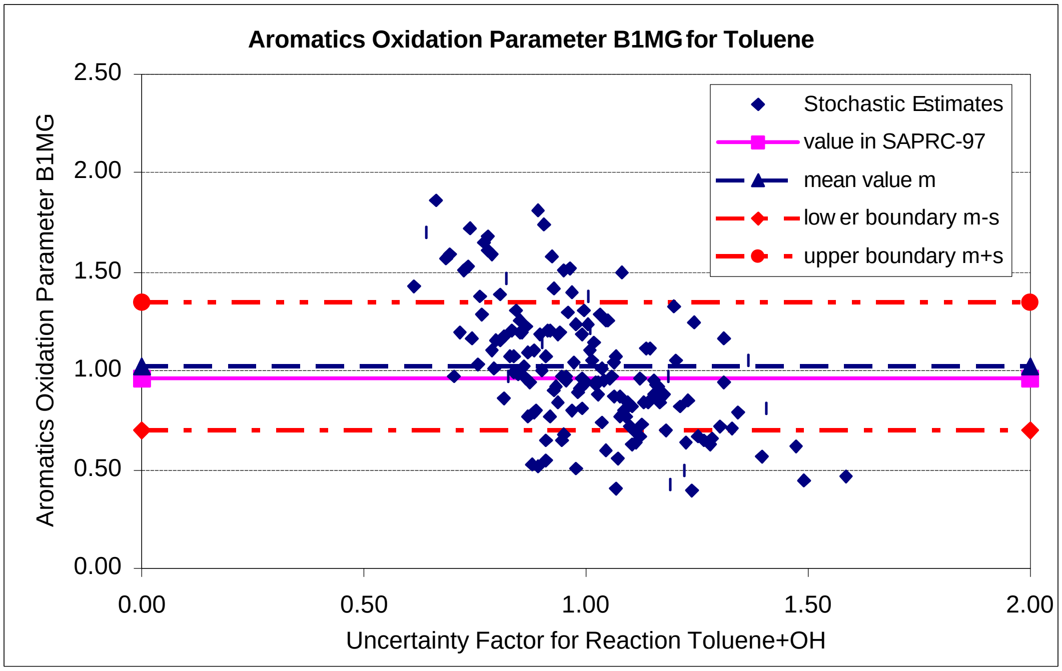
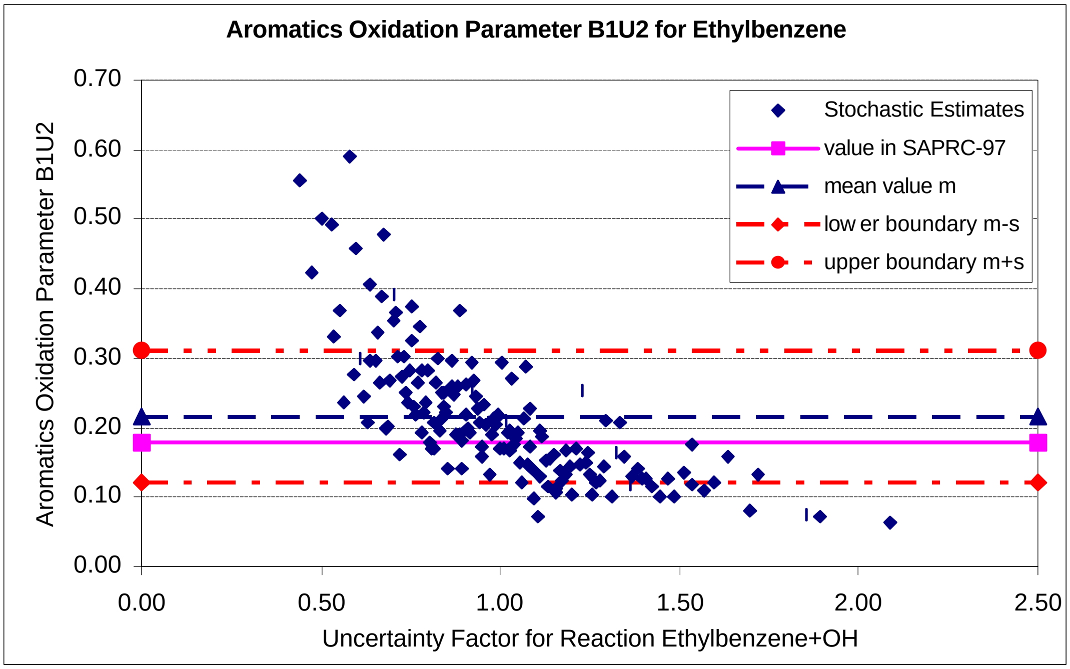


Figure D2-2 Stochastic Parameter Estimation for Aromatics Oxidation Parameters for Toluene (160 LHS Samples Applied to 10 Toluene-NO_x Experiments)



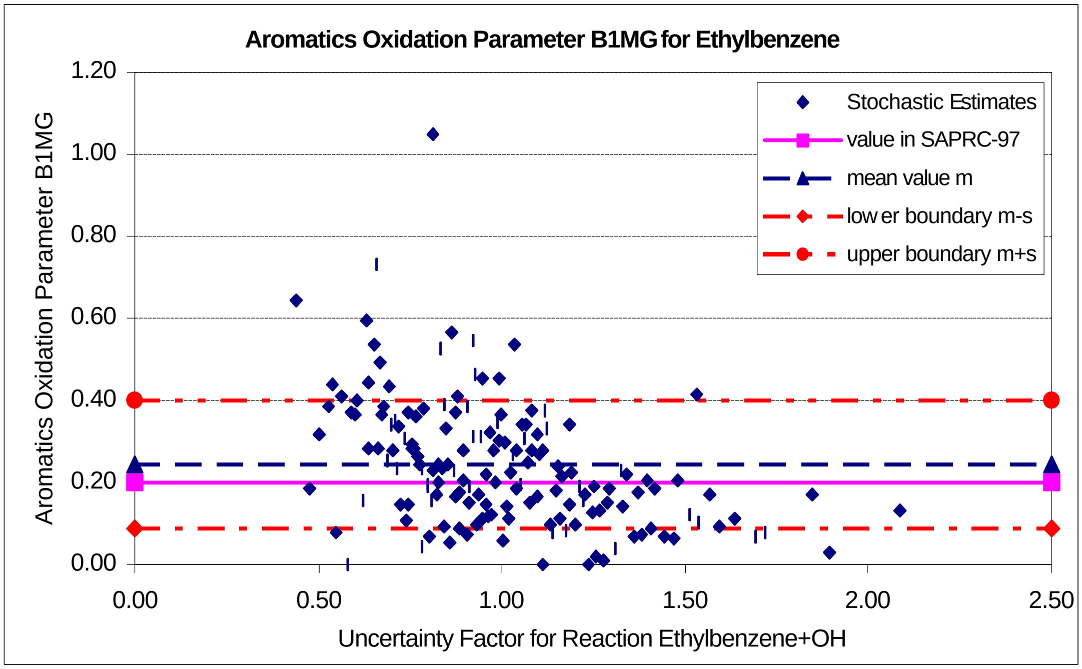
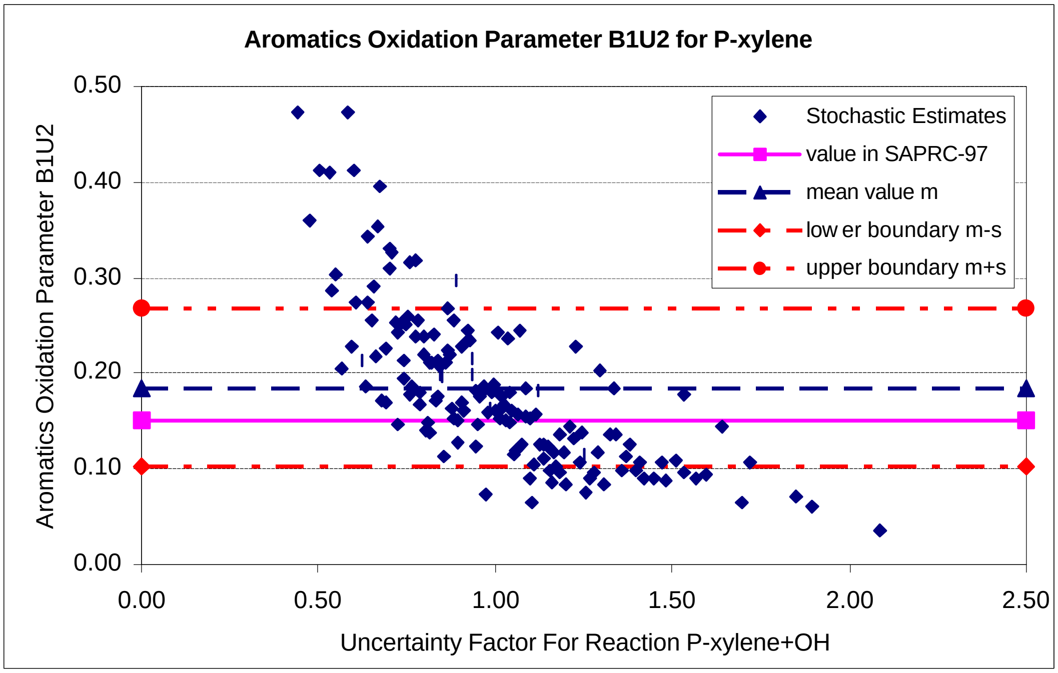


Figure D2-3 Stochastic Parameter Estimation for Aromatics Oxidation Parameters for Ethylbenzene (160 LHS Samples Applied to 8 Ethylbenzene-NO_x Experiments)



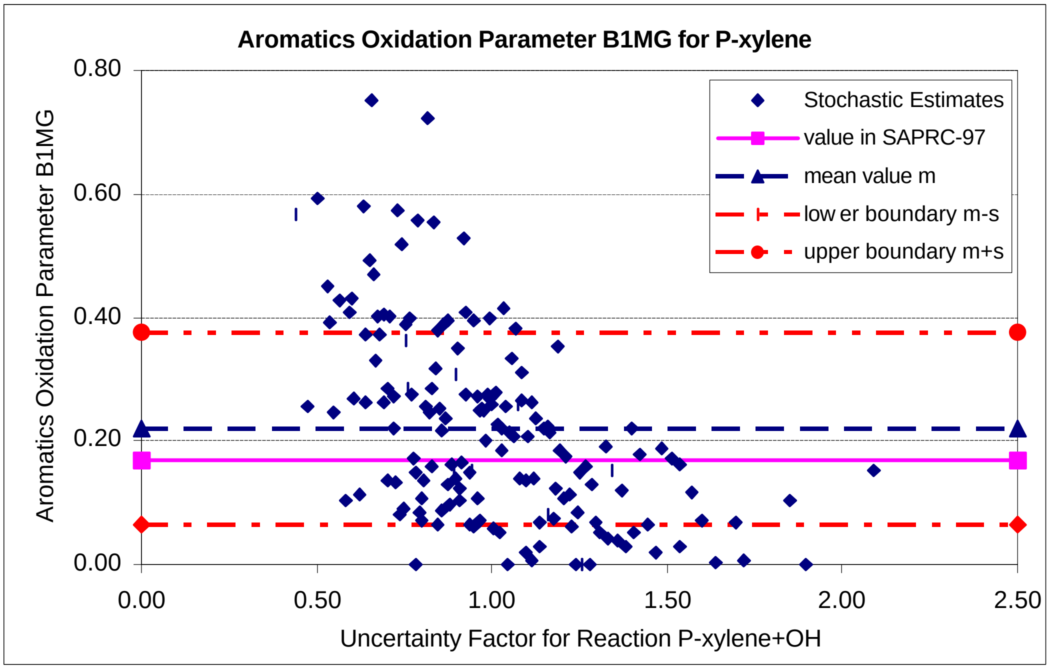
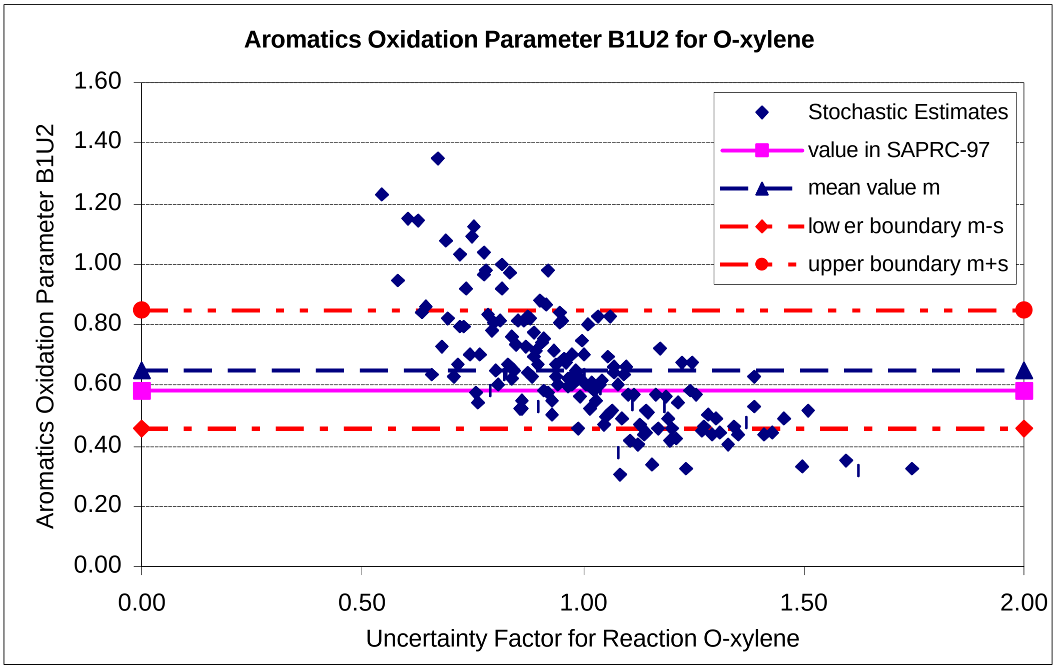


Figure D2-4 Stochastic Parameter Estimation for Aromatics Oxidation Parameters for P-xylene (160 LHS Samples Applied to 11 P-xylene-NO_x Experiments)



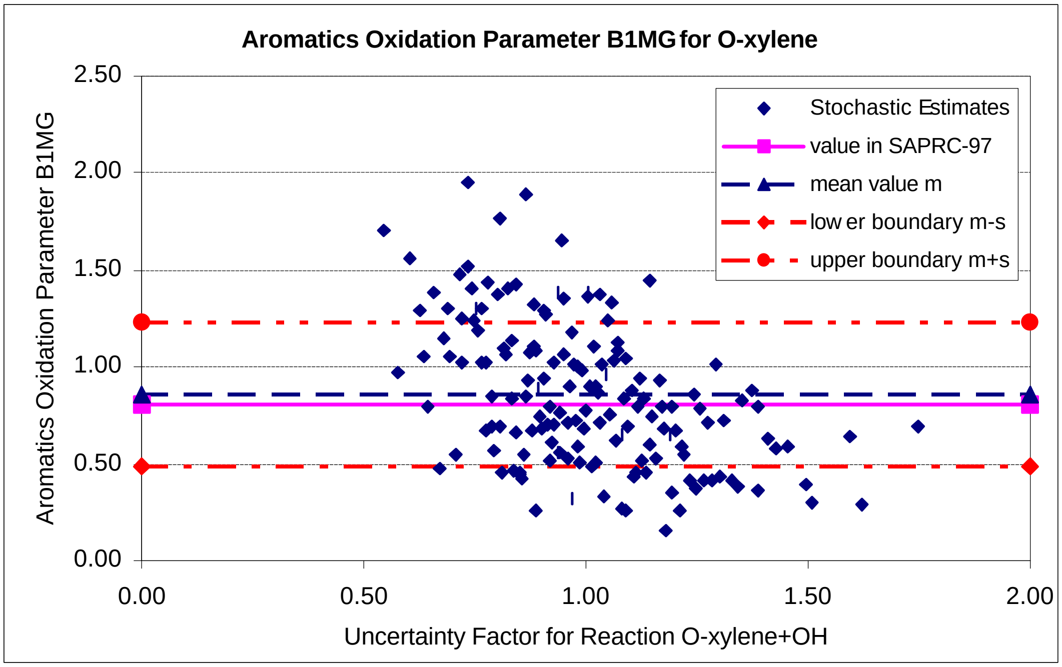


Figure D2-5 Stochastic Parameter Estimation for Aromatics Oxidation Parameters for O-xylene (160 LHS Samples applied to 12 O-xylene-NO_x Experiments)

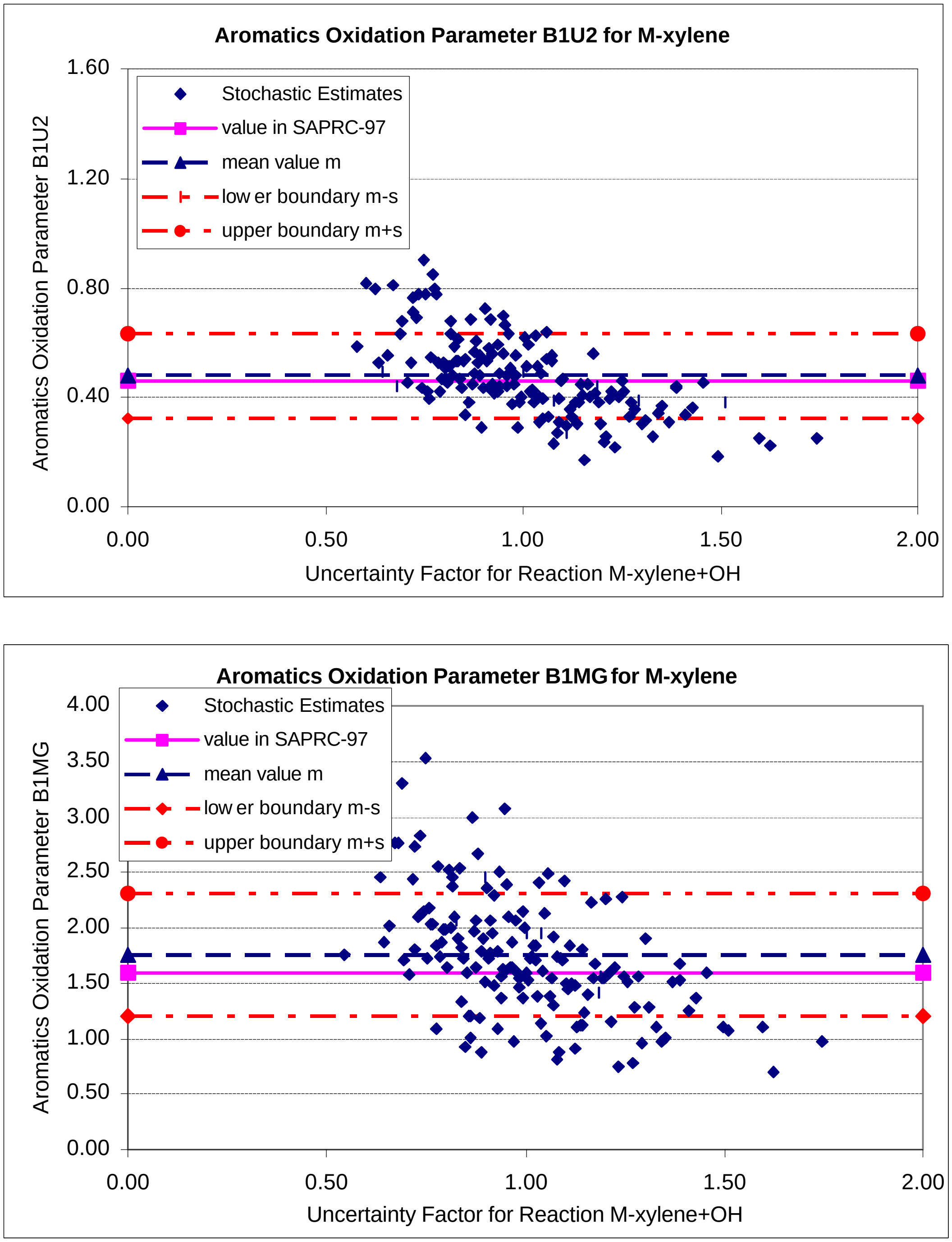
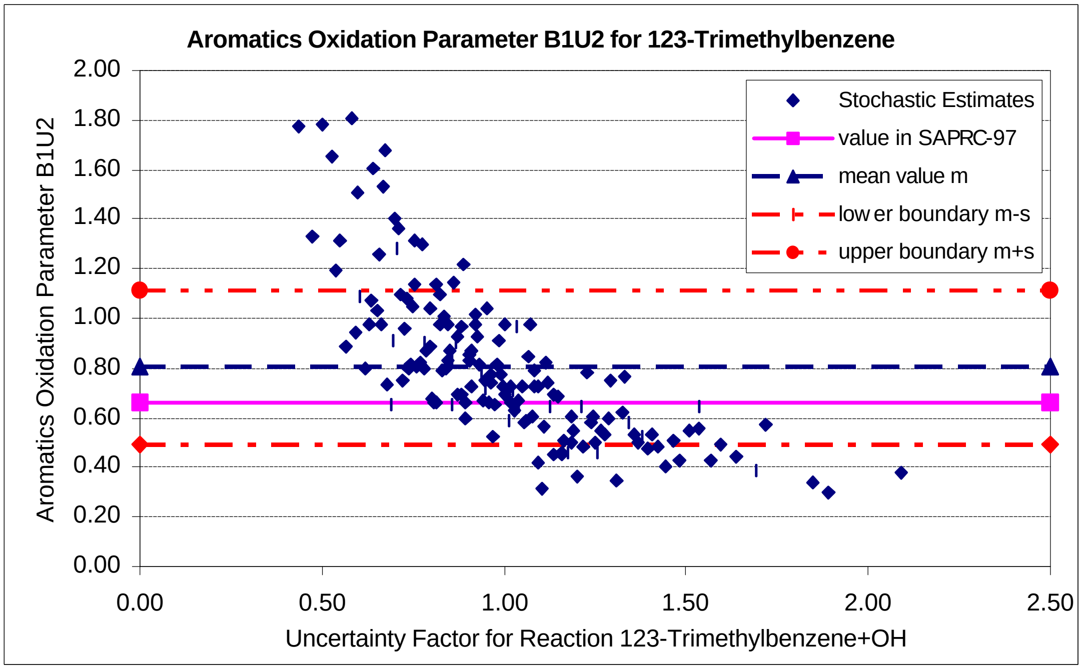


Figure D2-6 Stochastic Parameter Estimation for Aromatics Oxidation Parameters for M-xylene (160 LHS Samples Applied to 22 M-xylene-NO_x Experiments)



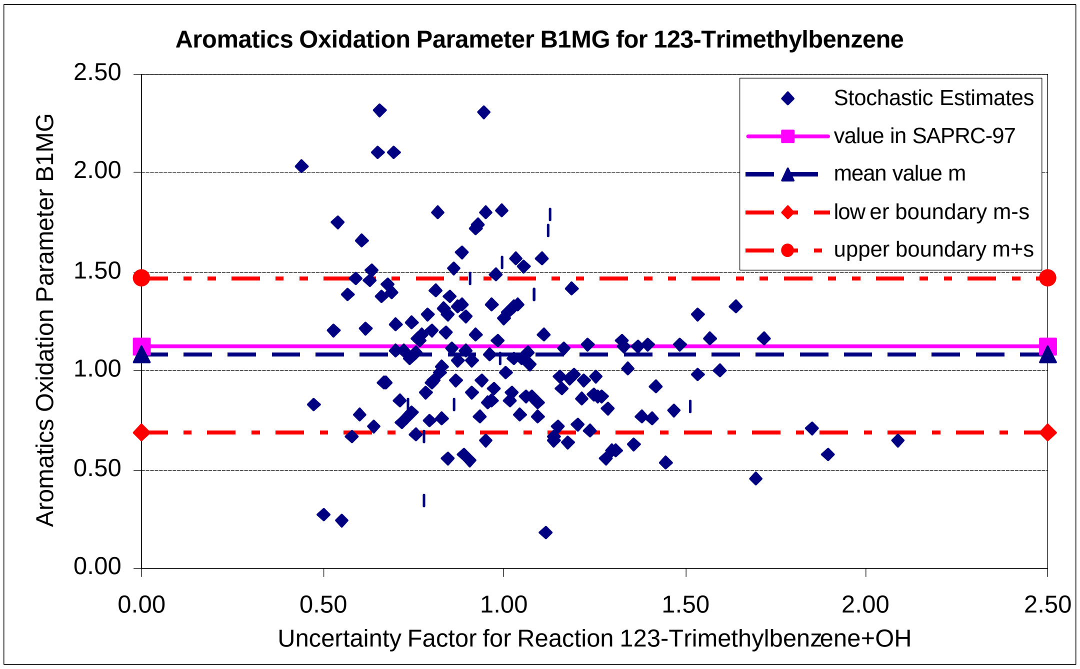
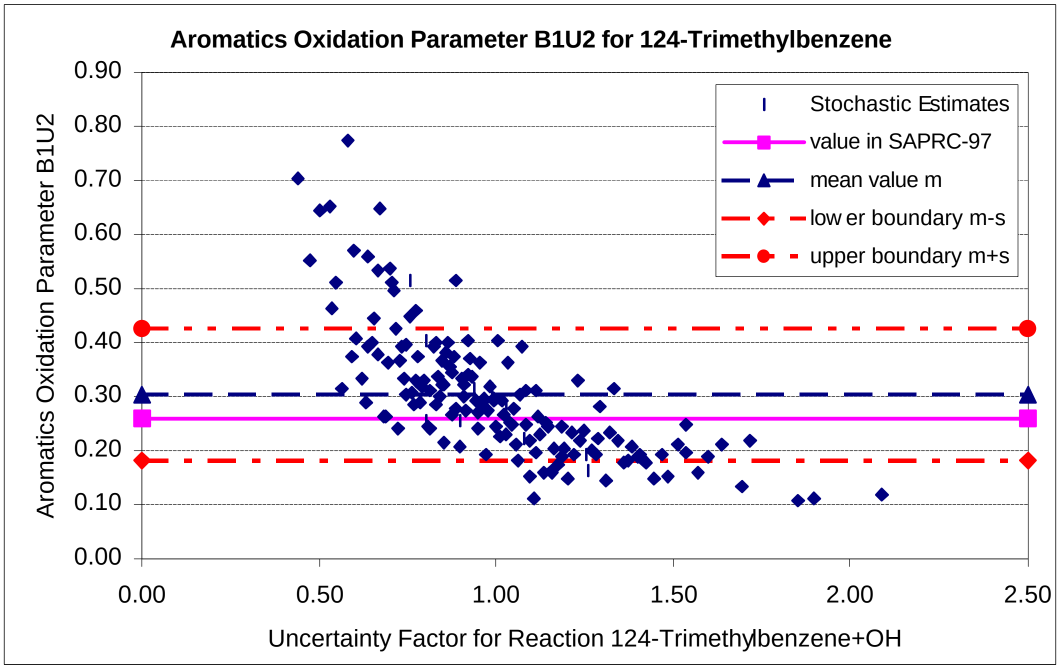


Figure D2-7 Stochastic Parameter Estimation for Aromatics Oxidation Parameters for 123-Trimethylbenzene (160 LHS Samples Applied to 9 123-Trimethylbenzene-NO_x Experiments)



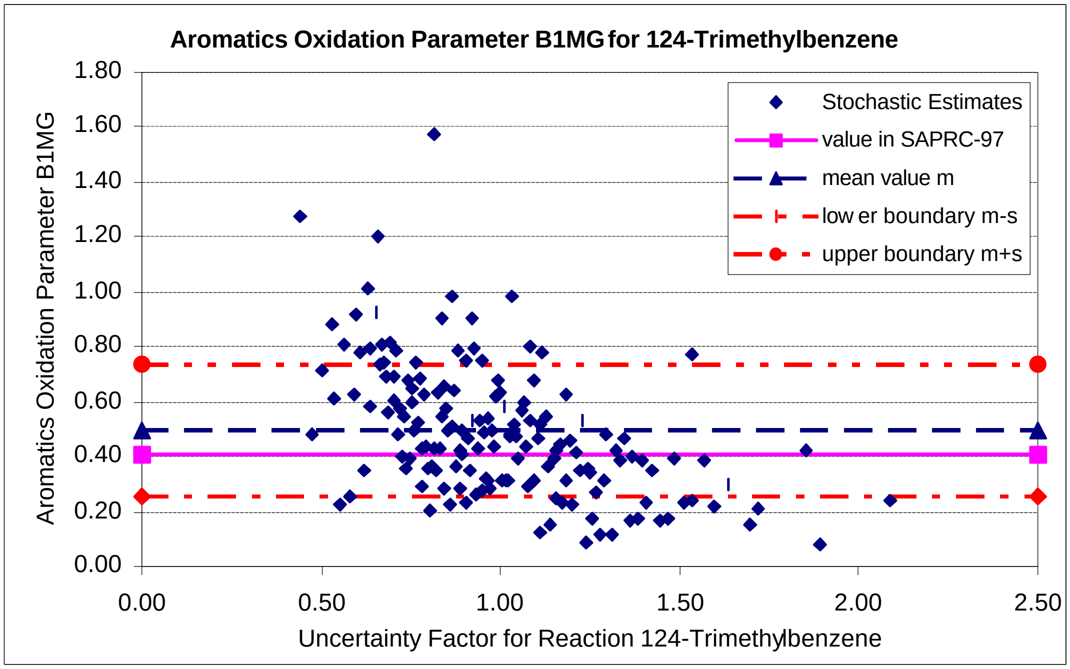
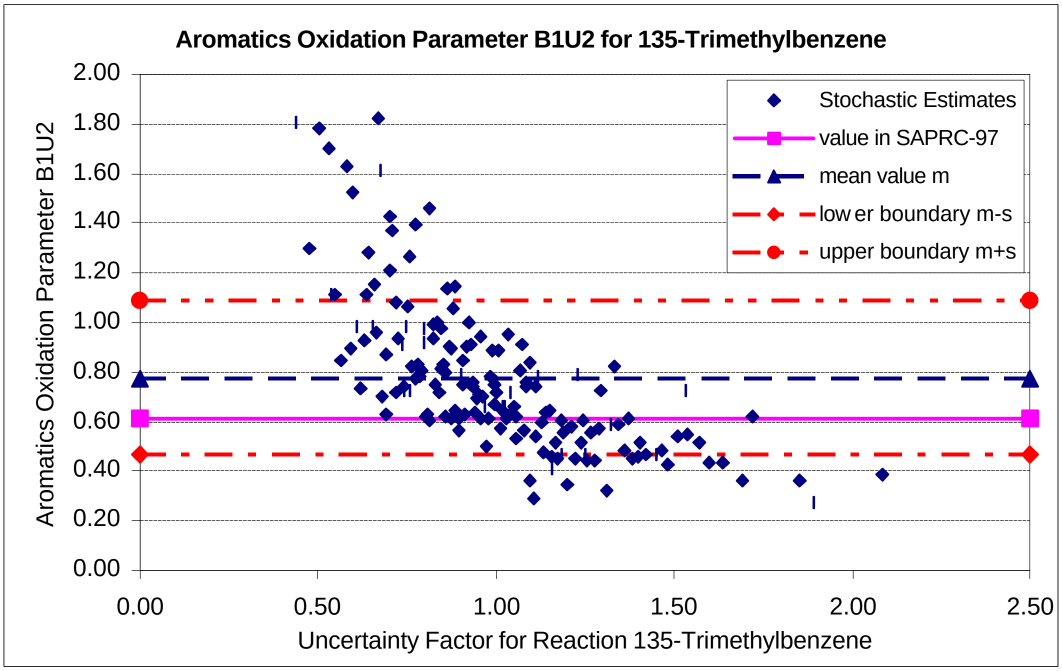


Figure D2-8 Stochastic Parameter Estimation for Aromatics Oxidation Parameters for 124-Trimethylbenzene (160 LHS Samples Applied to 10 124-Trimethylbenzne-NO_x Experiments)



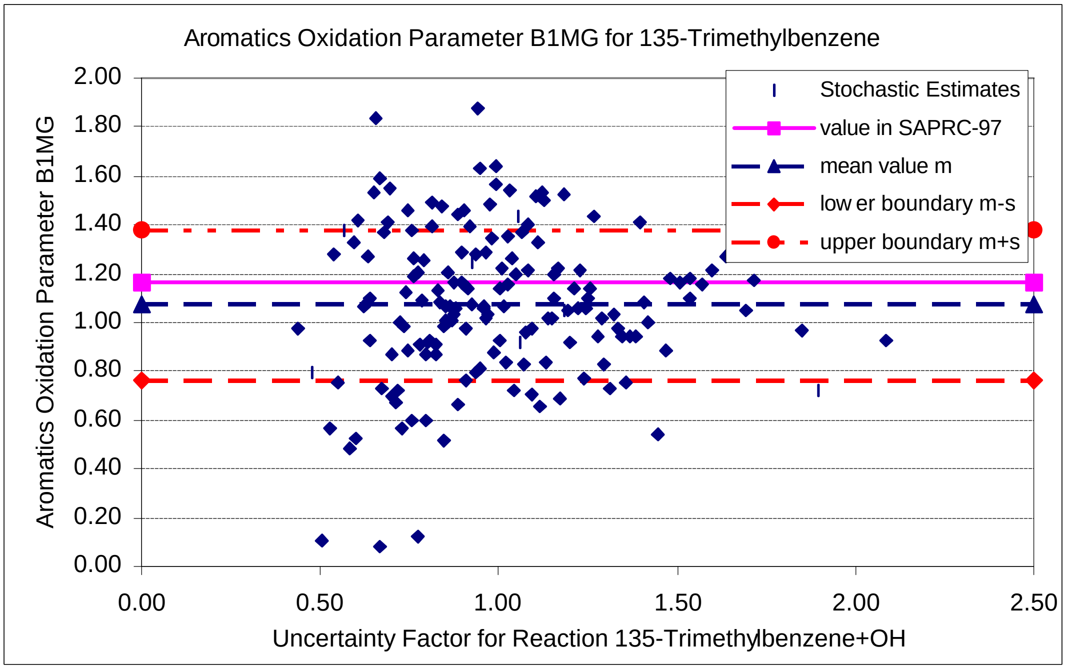


Figure D2-9 Stochastic Parameter Estimation for Aromatics Oxidation Parameters for 135-Trimethylbenzene (160 LHS Samples Applied to 11 135-Trimethylbenzene-NO_x Experiments)

Table D2-1 Regression Analysis for Aromatics Oxidation Parameters for Benzene [a]

Uncertain Input Parameter	**Coefficient of Variance ($\sigma_i/\kappa_{i\ nominal}$)**	**B1U1 Standardized Regression Coefficient (Rank)**	**P1U1 Standardized Regression Coefficient (Rank)**
NO_2 + hv -> (CTC) (light intensity)	0.16	-0.13 (7)	-0.12 (4)
NO_2 + hv -> for ITC (light intensity)	0.12	0.14 (6)	0.10 (8)
NO_2 + OH. ->	0.27	0.28 (3)	0.33 (2)
HNO_4 ->	2.40	0.11 (9)	-0.28 (3)
NO_3 + PHEN ->	0.42	-0.05	0.10 (7)
benzene + OH. ->	0.27	-0.33 (1)	-0.55 (1)
RSI for CTC	0.29	-0.12 (8)	-0.06
HONO-F for CTC	0.46	-0.21 (5)	-0.09
RSI for ITC	0.36	0.00	0.05
HONO-F for ITC	0.08	0.23 (4)	-0.11 (6)
initial NO_x concentration for ITC (Grp. 1)	0.27	0.30 (2)	-0.11 (5)
Adjusted R^2		**0.56**	**0.79**

[a] The ridge regression model is for normalized predictors.

Table 2 Regression Analysis for Aromatics Oxidation Parameters for Toluene [a]

Uncertain Input Parameter	**Coefficient of Variance ($\sigma_i/\kappa_{i\ nominal}$)**	**B1U2 Standardized Regression Coefficient (Rank)**	**B1MG Standardized Regression Coefficient (Rank)**
NO_2 + hv -> for CTC (light intensity)	0.16	0.05	-0.30 (3)
NO_2 + hv -> for DTC (light intensity)	0.12	-0.14 (3)	0.11 (8)
HONO + hv -> (action sprctrum)	0.34	-0.05	-0.20 (6)
NO_2 + OH. ->	0.27	0.52 (1)	0.45 (2)
HNO_4 ->	2.40	-0.12 (5)	-0.03
CCOO2 + NO ->	0.34	-0.11 (6)	-0.06
PAN ->	0.40	-0.10 (7)	-0.02
toluene + OH. ->	0.18	-0.52 (2)	-0.53 (1)
RSI for DTC1	0.24	0.08	0.03
RSI for CTC	0.29	0.09	-0.29 (4)
HONO-F for CTC	0.45	0.07	-0.27 (5)
initial toluene concentration for DTC1 (Grp. 1)	0.05	-0.12 (4)	0.03
initial toluene concentration for CTC (Grp. 3)	0.06	0.05	-0.11 (9)
initial toluene concentration for CTC (Grp. 4)	0.06	0.04	-0.19 (7)
Adjusted R^2		**0.93**	**0.92**

[a] The ridge regression model is for normalized predictors.

Table D2-3 Regression Analysis for Aromatics Oxidation Parameters for Ethylbenzene [a]

Uncertain Input Parameter	**Coefficient of Variance ($\sigma_i/\kappa_{i\,nominal}$)**	**B1U2 Standardized Regression Coefficient (Rank)**		**B1MG Standardized Regression Coefficient (Rank)**	
NO_2 + hv -> for CTC (light intensity)	0.16	0.01		-0.30	(4)
NO_2 + hv -> for DTC (light intensity)	0.12	-0.16	(5)	0.12	
HONO + hv -> (action spectrum)	0.34	-0.05		-0.14	
NO_2 + OH. ->	0.27	0.45	(2)	0.23	(8)
HNO_4 ->	2.40	-0.09	(6)	-0.17	(9)
CCOO2 + NO ->	0.34	-0.08	(8)	-0.05	
PAN ->	0.40	-0.06		0.00	
ethylbenzene + OH. ->	0.31	-0.71	(1)	-0.41	(1)
RSI for DTC2	0.31	-0.25	(3)	0.31	(2)
HONO-F for DTC2	0.29	-0.08	(7)	0.03	
RSI for CTC	0.29	0.06		-0.28	(5)
HONO-F for CTC	0.45	-0.04		-0.31	(3)
initial ethylbenzene concentration for DTC2 (Grp. 1)	0.07	-0.19	(4)	0.24	(7)
initial ethylbenzene concentration for CTC (Grp. 3)	0.08	0.06		-0.28	(6)
Adjusted R^2		**0.92**		**0.86**	

[a] The ridge regression model is for normalized predictors.

Table D2-4 Regression Analysis for Aromatics Oxidation Parameters for P-xylene [a]

Uncertain Input Parameter	**Coefficient of Variance ($\sigma_i/\kappa_{i\ nominal}$)**	**B1U2 Standardized Regression Coefficient (Rank)**		**B1MG Standardized Regression Coefficient (Rank)**	
NO_2 + hv -> for CTC (light intensity)	0.16	0.01		-0.29	(4)
NO_2 + hv -> for DTC (light intensity)	0.12	-0.17	(4)	0.11	(10)
HONO + hv -> (action spectrum)	0.34	-0.03		-0.20	(7)
NO_2 + OH. ->	0.27	0.46	(2)	0.26	(5)
HNO_4 ->	2.40	-0.14	(5)	0.06	
CCOO2 + NO ->	0.34	-0.08		-0.02	
PAN ->	0.40	-0.06		0.01	
P-xylene + OH. ->	0.31	-0.71	(1)	-0.51	(1)
RSI for DTC2	0.31	-0.28	(3)	0.25	(6)
RSI for CTC	0.29	0.07		-0.38	(2)
HONO-F for CTC	0.45	0.03		-0.31	(3)
initial pxylene concentration for DTC2 (Grp. 1)	0.05	-0.11	(6)	0.12	(9)
initial pxylene concentration for CTC (Grp. 2)	0.05	-0.02		-0.18	(8)
initial pxylene concentration for CTC (Grp. 3)	0.05	0.03		-0.02	
Adjusted R^2		**0.92**		**0.87**	

[a] The ridge regression model is for normalized predictors.

Table D2-5 Regression Analysis for Aromatics Oxidation Parameters for O-xylene [a]

Uncertain Input Parameter	**Coefficient of Variance ($\sigma_i/\kappa_{i\ nominal}$)**	**B1U2 Standardized Regression Coefficient (Rank)**		**B1MG Standardized Regression Coefficient (Rank)**	
NO_2 + hv -> for CTC (light intensity)	0.16	0.01		-0.27	(6)
NO_2 + hv -> for DTC (light intensity)	0.12	-0.17	(4)	0.13	(10)
HONO + hv -> (action spectrum)	0.34	-0.07		-0.21	(7)
NO_2 + OH. ->	0.27	0.47	(2)	0.37	(2)
HNO_4 ->	2.40	-0.18	(3)	0.11	
CCOO2 + NO ->	0.34	-0.14	(7)	0.03	
PAN ->	0.40	-0.13	(8)	0.06	
O-xylene + OH. ->	0.23	-0.67	(1)	-0.45	(1)
RSI for DTC2	0.31	-0.15	(6)	0.18	(8)
RSI for CTC	0.29	0.05		-0.29	(4)
HONO-F for CTC	0.45	0.02		-0.34	(3)
initial oxylene concentration for DTC2 (Grp. 1)	0.07	-0.16	(5)	0.15	(9)
initial oxylene concentration for CTC (Grp. 2)	0.06	0.03		-0.28	(5)
initial oxylene concentration for CTC (Grp. 3)	0.06	0.02		-0.05	
Adjusted R^2		**0.93**		**0.92**	

[a] The ridge regression model is for normalized predictors.

Table D2-6 Regression Analysis for Aromatics Oxidation Parameters for M-xylene [a]

Uncertain Input Parameter	**Coefficient of Variance ($\sigma_i/\kappa_{i\ nominal}$)**	**B1U2 Standardized Regression Coefficient (Rank)**		**B1MG Standardized Regression Coefficient (Rank)**	
NO_2 + hv -> for CTC (light intensity)	0.16	0.02		-0.19	(6)
NO_2 + hv -> for DTC (light intensity)	0.12	-0.16	(4)	0.12	(8)
HONO + hv -> (action spectrum)	0.34	-0.09		-0.12	(9)
NO_2 + OH. ->	0.27	0.48	(2)	0.38	(2)
HNO_4 ->	2.40	-0.09	(8)	-0.04	
CCOO2 + NO ->	0.34	-0.12	(5)	-0.03	
PAN ->	0.40	-0.12	(6)	0.02	
M-xylene + OH. ->	0.23	-0.59	(1)	-0.49	(1)
RSI for DTC2	0.31	-0.06		0.14	(7)
RSI for CTC	0.29	0.06		-0.19	(5)
HONO-F for CTC	0.45	0.04		-0.22	(4)
initial mxylene concentration for DTC2 (Grp. 2)	0.11	-0.09		-0.02	
initial mxylene concentration for DTC3 (Grp. 3)	0.12	-0.22	(3)	0.09	
initial mxylene concentration for CTC (Grp. 4)	0.11	0.09	(7)	-0.36	(3)
initial mxylene concentration for CTC (Grp. 5)	0.11	0.05		-0.11	(10)
Adjusted R^2		**0.93**		**0.90**	

[a] The ridge regression model is for normalized predictors.

Table D2-7 Regression Analysis for Aromatics Oxidation Parameters for 123-TMB [a]

Uncertain Input Parameter	**Coefficient of Variance ($\sigma_i/\kappa_{i\ nominal}$)**	**B1U2 Standardized Regression Coefficient (Rank)**		**B1MG Standardized Regression Coefficient (Rank)**	
NO_2 + hv -> for CTC (light intensity)	0.16	-0.01		-0.26	(2)
NO_2 + hv -> for DTC (light intensity)	0.12	-0.15	(4)	0.20	(6)
HONO + hv -> (action spectrum)	0.34	-0.07		-0.10	(9)
NO_2 + OH. ->	0.27	0.36	(2)	0.16	(8)
HNO_4 ->	2.40	-0.13	(6)	0.04	
CCOO2 + NO ->	0.34	-0.14	(5)	-0.01	
PAN ->	0.40	-0.11	(8)	0.08	
123-trimethylbenzene + OH. ->	0.31	-0.71	(1)	-0.22	(3)
RSI for DTC2	0.31	-0.11	(7)	0.17	(7)
RSI for CTC	0.29	0.04		-0.22	(4)
HONO-F for CTC	0.45	-0.01		-0.21	(5)
initial 123-TMB concentration for DTC2 (Grp. 1)	0.13	-0.18	(3)	0.09	
initial 123-TMB concentration for CTC (Grp. 2)	0.13	0.01		-0.10	(10)
initial 123-TMB concentration for CTC (Grp. 3)	0.13	0.06		-0.65	(1)
Adjusted R^2		**0.90**		**0.86**	

[a] The ridge regression model is for normalized predictors.

Table D2-8 Regression Analysis for Aromatics Oxidation Parameters for 124-TMB [a]

Uncertain Input Parameter	**Coefficient of Variance ($\sigma_i/\kappa_{i\ nominal}$)**	**B1U2 Standardized Regression Coefficient (Rank)**	**B1MG Standardized Regression Coefficient (Rank)**
NO_2 + hv -> for CTC (light intensity)	0.16	0.02	-0.28 (2)
NO_2 + hv -> for DTC (light intensity)	0.12	-0.16 (5)	0.09
HONO + hv -> (action spectrum)	0.34	-0.05	-0.11 (11)
NO_2 + OH. ->	0.27	0.42 (2)	0.27 (3)
HNO_4 ->	2.40	-0.10 (6)	-0.26 (4)
CCOO2 + NO ->	0.34	-0.10 (7)	-0.05
PAN ->	0.40	-0.09 (8)	0.01
124-trimethylbenzene + OH. ->	0.31	-0.70 (1)	-0.48 (1)
RSI for DTC2	0.31	-0.21 (4)	0.21 (8)
RSI for CTC	0.29	0.06	-0.19 (10)
HONO-F for CTC	0.45	0.03	-0.25 (5)
initial 124-TMB concentration for DTC2 (Grp. 1)	0.11	-0.25 (3)	0.22 (7)
initial 124-TMB concentration for CTC (Grp. 2)	0.11	0.02	-0.19 (9)
initial 124-TMB concentration for CTC (Grp. 3)	0.11	0.05	-0.23 (6)
Adjusted R^2		**0.92**	**0.87**

[a] The ridge regression model is for normalized predictors.

Table D2-9 Regression Analysis for Aromatics Oxidation Parameters for 135-TMB [a]

Uncertain Input Parameter	**Coefficient of Variance ($\sigma_i/\kappa_{i\ nominal}$)**	**B1U2 Standardized Regression Coefficient (Rank)**	**B1MG Standardized Regression Coefficient (Rank)**
NO_2 + hv -> for CTC (light intensity)	0.16	-0.02	-0.20 (5)
NO_2 + hv -> for DTC (light intensity)	0.12	-0.14 (5)	0.28 (2)
O3 + NO ->	0.10	0.08	-0.17 (10)
HONO + hv -> (action spectrum)	0.34	-0.06	-0.04
NO_2 + OH. ->	0.27	0.33 (2)	0.03
HNO_4 ->	2.40	-0.22 (3)	0.17 (9)
CCOO2 + NO ->	0.34	-0.14 (4)	0.03
PAN ->	0.40	-0.09 (7)	0.18 (7)
135-trimethylbenzene + OH. ->	0.31	-0.68 (1)	0.07
RSI for DTC2	0.31	-0.05	0.17 (8)
HONO-F for DTC2	0.27	-0.09 (8)	0.16 (11)
RSI for CTC	0.29	0.05	-0.23 (4)
HONO-F for CTC	0.45	-0.02	-0.19 (6)
initial 135-TMB concentration for DTC2 (Grp. 1)	0.11	-0.13 (6)	-0.02
initial 135-TMB concentration for CTC (Grp. 2)	0.11	0.01	-0.28 (3)
initial 135-TMB concentration for CTC (Grp. 3)	0.11	0.04	-0.43 (1)
Adjusted R^2		**0.87**	**0.69**

[a] The ridge regression model is for normalized predictors.

Appendix E Regression Analysis for Incremental Reactivities

The regresssion analysis results for all of the aromatic compounds are listed in the following tables for the MIR, MOIR and EBIR cases.

Table E-1 Apportionment of Uncertainty in MIRs [a]

Reactions or Chamber-derived parameter	σ/μ [b]	standardized reg. coeff.	UC (%) [c]
Benzene (R^2=0.67)			
benzene + OH ->	0.27	0.55	29.8
SC(AFG1, Benzene)	0.33	0.44	19.7
NO_2 + hv ->	0.18	0.32	10.0
P1U1	0.40	0.28	8.02
PAN ->	0.40	0.22	4.93
CCOO2 + NO ->	0.34	0.20	3.96
O_3 + NO ->	0.10	-0.19	3.49
NO_2 + OH ->	0.27	-0.14	2.02
HO_2 + NO ->	0.18	0.13	1.65
Toluene (R^2=0.57)			
NO_2 + hv ->	0.18	0.30	9.22
SC(MGLY, Toluene)	0.31	0.25	6.30
toluene + OH ->	0.18	0.22	5.01
CCOO2 + NO ->	0.34	0.21	4.41
PAN ->	0.40	0.20	3.96
O_3 + NO ->	0.10	-0.18	3.36
SC(MGLY, ARO1)	0.29	0.17	3.02
O_3 + hv ->	0.27	-0.17	2.86
HO_2 + NO ->	0.18	0.17	2.82
Ethylbenzne (R^2=0.54)			
SC(MGLY, Ethylbenzne)	0.63	0.35	12.0
NO_2 + hv ->	0.18	0.28	7.83
ethylbenzene + OH ->	0.31	0.23	5.35
PAN ->	0.40	0.20	3.87
CCOO2 + NO ->	0.34	0.17	3.00
O_3 + NO ->	0.10	-0.16	2.70
HO_2 + NO ->	0.18	0.16	2.70
O_3 + hv ->	0.27	-0.16	2.55
SC(AFG2, Ethylbenzene)	0.44	0.13	1.57

O^1D + M ->	0.18	0.12	1.33
O-xylene (R^2=0.63)			
SC(MGLY, O-xylene)	0.43	0.36	12.8
NO_2 + hv ->	0.18	0.26	6.80
CCOO2 + NO ->	0.34	0.20	4.02
PAN ->	0.40	0.18	3.17
O_3 + hv ->	0.27	-0.17	2.92
HO_2 + NO ->	0.18	0.16	2.57
SC(AFG2, O-xylene)	0.28	0.16	2.56
NO_2 + OH ->	0.27	0.15	2.13
O_3 + NO ->	0.10	-0.13	1.69
O^1D + M ->	0.18	0.10	1.06
P-xylene (R^2=0.58)			
SC(MGLY, P-xylene)	0.71	0.32	10.1
NO_2 + hv ->	0.18	0.23	5.45
PAN ->	0.40	0.18	3.24
CCOO2 + NO ->	0.34	0.18	3.17
O_3 + hv ->	0.27	-0.17	3.03
HO_2 + NO ->	0.18	0.17	2.95
NO_2 + OH ->	0.27	0.15	2.20
O_3 + NO ->	0.10	-0.13	1.77
SC(AFG2, P-xylene)	0.45	0.12	1.49
SC(MGLY, ARO2)	0.20	-0.10	1.02
M-xylene (R^2=0.65)			
SC(MGLY, M-xylene)	0.31	0.39	15.2
NO_2 + OH ->	0.27	0.20	4.08
O_3 + hv ->	0.27	-0.20	4.05
NO_2 + hv ->	0.18	0.20	3.82
HO_2 + NO ->	0.18	0.17	2.92
CCOO2 + NO ->	0.34	0.15	2.14
PAN ->	0.40	0.14	2.09
O^1D + M ->	0.18	0.12	1.44
O_3 + NO ->	0.10	-0.12	1.42
ARO2 + OH ->	0.27	-0.12	1.39

$O^1D + H_2O$ ->	0.18	-0.10	1.01
123TMB (R^2=0.68)			
SC(MGLY,123TMB)	0.36	0.47	22.4
SC(AFG2, 123TMB)	0.39	0.40	16.2
O_3 + hv ->	0.27	-0.18	3.36
HO_2 + NO ->	0.18	0.15	2.31
NO_2 + hv ->	0.18	0.14	1.99
123TMB + OH ->	0.31	0.14	1.88
SC(MGLY, ARO2)	0.20	-0.13	1.69
ARO2 + OH ->	0.27	-0.12	1.56
NO_2 + OH ->	0.27	0.12	1.47
CCOO2 + NO ->	0.34	0.12	1.37
PAN ->	0.40	0.11	1.31
O_3 + NO ->	0.10	-0.10	1.05
O^1D + M ->	0.18	0.10	1.01
124TMB (R^2=0.72)			
SC(MGLY,124TMB)	0.49	0.47	21.9
NO_2 + OH ->	0.27	0.24	5.98
NO_2 + hv ->	0.18	0.18	3.08
SC(AFG2, 124TMB)	0.40	0.16	2.45
O_3 + hv ->	0.27	-0.15	2.20
PAN ->	0.40	0.14	1.86
HO_2 + NO ->	0.18	0.13	1.61
CCOO2 + NO ->	0.34	0.12	1.56
SC(MGLY, ARO2)	0.20	-0.11	1.23
O_3 + NO ->	0.10	-0.10	1.03
O^1D + M ->	0.18	0.10	0.98
135TMB (R^2=0.73)			
SC(MGLY,135TMB)	0.29	0.40	16.0
SC(AFG2, 135TMB)	0.45	0.30	9.14
ARO2 + OH ->	0.27	-0.19	3.45
O_3 + hv ->	0.27	-0.18	3.18
HO_2 + NO ->	0.18	0.15	2.13
SC(AFG2, ARO2)	0.23	-0.13	1.62

CCOO2 + NO ->	0.34	0.12	1.51
NO_2 + OH ->	0.27	0.12	1.51
NO_2 + hv ->	0.18	0.11	1.32
O^1D + H_2O ->	0.18	-0.10	1.08
O^1D + M ->	0.18	0.10	1.04
Base Mixture (R^2=0.59)			
NO_2 + hv ->	0.18	0.32	10.2
CCOO2 + NO ->	0.34	0.25	6.33
PAN ->	0.40	0.23	5.47
HO_2 + NO ->	0.18	0.21	4.28
O_3 + NO ->	0.10	-0.19	3.49
O_3 + hv ->	0.27	-0.17	2.83
C2COO2 + NO_2 ->	0.75	-0.13	1.66
O^1D + M ->	0.18	0.11	1.17
OLE3 + OH ->	0.23	0.10	1.01

[a] Ridge regression for normalized predictors

[b] Normalized uncertainty of rate constant and chamber-derived aromatics oxidation parameters

[c] Uncertainty contribution.

Table E-2 Apportionment of Uncertainty in MOIRs [a]

Reactions or Chamber-derived parameter	σ/μ [b]	standardized reg. coeff.	UC (%) [c]
Benzene (R^2=88)			
O_3 + hv ->	0.27	-0.42	17.5
PAN ->	0.40	0.33	10.8
SC(AFG1, Benzene)	0.33	0.32	9.96
benzene + OH ->	0.27	0.29	8.59
NO_2 + hv ->	0.18	0.29	8.38
O^1D + M ->	0.18	0.25	6.28
O^1D + H_2O ->	0.18	-0.24	5.76
CO + OH ->	0.27	-0.19	3.59
HCHO + hv -> $2HO_2$ + CO	0.34	-0.17	2.93
P1U1	0.40	0.15	2.33
O_3 + NO ->	0.10	-0.13	1.64
CCOO2 + NO ->	0.34	0.13	1.63
SC(MGLY, ARO2)	0.20	-0.11	1.22
Toluene (R^2=0.92)			
O_3 + hv ->	0.27	-0.51	26.2
O^1D + M ->	0.18	0.32	10.5
O^1D + H_2O ->	0.18	-0.30	9.07
HCHO + hv ->$2HO_2$ + CO	0.34	-0.21	4.39
CRES + NO_3 ->	0.75	-0.20	4.04
NO_2 + hv ->	0.18	0.20	3.94
SC(MGLY, Toluene)	0.31	0.18	3.23
Toluene + OH ->	0.18	0.14	2.01
SC(MGLY, ARO2)	0.20	-0.14	1.94
PAN ->	0.40	0.13	1.81
SC(MGLY, ARO1)	0.29	0.12	1.43
Ethylbenzne (R^2=0.90)			
O_3 + hv ->	0.27	-0.49	24.3
O^1D + M ->	0.18	0.32	10.3
CRES + NO_3 ->	0.75	-0.30	8.91
O^1D + H_2O ->	0.18	-0.29	8.13

SC(MGLY, Ethylbenzne)	0.63	0.24	5.98
HCHO + hv ->$2HO_2$ + CO	0.34	-0.21	4.59
CO + OH ->	0.27	-0.15	2.11
NO_2 + OH ->	0.27	0.14	1.83
NO_2 + hv ->	0.18	0.13	1.69
SC(MGLY, ARO2)	0.20	-0.12	1.51
SC(AFG2, Ethylbenzene)	0.44	0.11	1.28
ARO2 + OH ->	0.27	-0.11	1.14
O-xylene (R^2=0.89)			
O_3 + hv ->	0.27	-0.49	24.0
O^1D + M ->	0.18	0.31	9.49
O^1D + H_2O ->	0.18	-0.30	9.05
SC(MGLY, O-xylene)	0.43	0.29	8.54
HCHO + hv -> $2HO_2$ + CO	0.34	-0.21	4.27
NO_2 + hv ->	0.18	0.18	3.18
SC(AFG2, O-xylene)	0.30	0.14	2.04
SC(MGLY, ARO2)	0.20	-0.13	1.65
NO_2 + OH ->	0.27	0.13	1.61
CRES + NO_3 ->	0.75	-0.12	1.52
SC(AFG2, ARO2)	0.23	-0.10	1.05
ARO2 + OH ->	0.27	-0.10	1.03
P-xylene (R^2=0.89)			
O_3 + hv ->	0.27	-0.48	22.7
O^1D + M ->	0.18	0.31	9.73
O^1D + H_2O ->	0.18	-0.28	7.85
SC(MGLY, P-xylene)	0.71	0.27	7.39
CRES + NO_3 ->	0.75	-0.21	4.29
HCHO + hv -> $2HO_2$ + CO	0.34	-0.20	3.94
NO_2 + OH ->	0.27	0.16	2.62
SC(MGLY, ARO2)	0.20	-0.14	2.04
NO_2 + hv ->	0.18	0.14	1.98
ARO2 + OH ->	0.27	-0.12	1.33
M-xylene (R^2=0.91)			
O_3 + hv ->	0.27	-0.51	25.7

O^1D + M ->	0.18	0.32	9.96
O^1D + H_2O ->	0.18	-0.31	9.59
SC(MGLY, M-xylene)	0.29	0.29	8.67
HCHO + hv -> $2HO_2$ + CO	0.34	-0.22	4.98
NO_2 + OH ->	0.27	0.15	2.31
NO_2 + hv ->	0.18	0.15	2.13
ARO2 + OH ->	0.27	-0.14	1.85
HO_2 + NO ->	0.18	0.11	1.11
123-TMB (R^2=0.89)			
O_3 + hv ->	0.27	-0.47	22.1
SC(MGLY, 123TMB)	0.36	0.37	14.0
O^1D + M ->	0.18	0.29	8.57
SC(AFG2, 123TMB)	0.39	0.28	7.99
O^1D + H_2O ->	0.18	-0.27	7.43
HCHO + hv -> $2HO_2$ + CO	0.34	-0.19	3.70
SC(MGLY, ARO2)	0.20	-0.15	2.26
ARO2 + OH ->	0.27	-0.14	1.99
SC(AFG2, ARO2)	0.23	-0.12	1.35
NO_2 + hv ->	0.18	0.11	1.20
NO_2 + OH ->	0.27	0.10	1.00
124-TMB (R^2=0.89)			
O_3 + hv ->	0.27	-0.43	18.2
SC(MGLY, 124TMB)	0.49	0.38	14.6
O^1D + M ->	0.18	0.27	7.29
O^1D + H_2O ->	0.18	-0.26	6.88
HCHO + hv -> $2HO_2$ + CO	0.34	-0.19	3.48
NO_2 + OH ->	0.27	0.18	3.08
SC(MGLY, ARO2)	0.20	-0.15	2.12
SC(AFG2, 124TMB)	0.40	0.14	1.92
CRES + NO_3 ->	0.75	-0.13	1.65
NO_2 + hv ->	0.18	0.12	1.34
ARO2 + OH ->	0.27	-0.11	1.30
135-TMB (R^2=0.90)			
O_3 + hv ->	0.27	-0.48	22.9

SC(MGLY, 135TMB)	0.29	0.31	9.76
$O^1D + H_2O$ ->	0.18	-0.29	8.64
O^1D + M ->	0.18	0.29	8.56
SC(AFG2, 135TMB)	0.40	0.26	6.50
HCHO + hv -> $2HO_2$ + CO	0.34	-0.21	4.60
ARO2 + OH ->	0.27	-0.17	2.96
SC(MGLY, ARO2)	0.20	-0.13	9.76
Base Mixture (R^2=0.92)			
O_3 + hv ->	0.27	-0.53	27.9
O^1D + M ->	0.18	0.32	10.5
$O^1D + H_2O$ ->	0.18	-0.31	9.78
NO_2 + hv ->	0.18	0.29	8.26
HCHO + hv ->$2HO_2$ + CO	0.34	-0.19	3.44
PAN ->	0.40	0.18	3.27
CO + OH ->	0.27	-0.13	1.76
CCOO2 + NO ->	0.34	0.12	1.47
CRES + NO_3 ->	0.75	-0.12	1.33
HO_2 + NO ->	0.18	0.11	1.17
$RO_2 + HO_2$ ->	0.75	-0.11	1.12

[a] Ridge regression for normalized predictors

[b] Normalized uncertainty of rate constant and chamber-derived aromatics oxidation parameters

[c] Uncertainty contribution.

Table E-3 Apportionment of Uncertainty in EBIRs [a]

Reactions or Chamber-derived parameter	σ/μ [b]	standardized reg. coeff.	UC (%) [c]
Benzene (R^2=86)			
PAN ->	0.40	0.50	24.7
NO_2 + hv ->	0.18	0.30	8.86
SC(AFG1, Benzene)	0.33	0.23	5.18
O_3 + hv ->	0.27	-0.22	4.87
CO + OH ->	0.27	-0.22	4.86
NO_3 + hv -> NO_2 + O	0.42	0.20	3.97
CCOO2 + NO ->	0.34	0.19	3.50
NO_2 + OH ->	0.27	0.18	3.09
BENZENE + OH ->	0.27	0.16	2.61
O^1D + M ->	0.18	0.13	1.70
O^1D + H_2O ->	0.18	-0.13	1.58
O_3 + NO ->	0.10	-0.12	1.56
P1U1	0.35	0.12	1.53
Toluene (R^2=0.93)			
CRES + NO_3 ->	0.75	-0.45	20.2
O_3 + hv ->	0.27	-0.30	8.78
PAN ->	0.40	0.26	6.66
NO_2 + hv ->	0.18	0.24	5.56
SC(MGLY, Toluene)	0.31	0.21	4.34
O^1D + M ->	0.18	0.20	3.83
NO_3 + hv -> NO_2 + O	0.42	0.19	3.49
O^1D + H_2O ->	0.18	-0.17	2.74
CO + OH ->	0.27	-0.16	2.61
SC(MGLY, ARO1)	0.29	0.16	2.57
NO_2 + OH ->	0.27	0.14	1.95
Toluene + OH ->	0.18	0.11	1.25
HCHO + hv ->$2HO_2$ + CO	0.34	-0.11	1.25
SC(AFG2, Toluene)	0.34	0.11	1.11
Ethylbenzene(R^2=0.94)			

CRES + NO_3 ->	0.75	-0.58	33.2
SC(MGLY, Ethylbenzene)	0.63	0.24	6.22
NO_2 + OH ->	0.27	0.23	5.50
O_3 + hv ->	0.27	-0.22	4.95
NO_3 + hv -> NO_2 + O	0.42	0.22	4.93
CO + OH ->	0.27	-0.18	3.37
O^1D + M ->	0.18	0.16	2.68
SC(AFG2, Ethylbenzene)	0.44	0.13	1.74
O^1D + H_2O ->	0.18	-0.13	1.64
O-xylene (R^2=0.91)			
SC(MGLY, O-xylene)	0.43	0.37	14.1
O_3 + hv ->	0.27	-0.31	9.91
NO_2 + hv ->	0.18	0.31	9.65
CRES + NO_3 ->	0.75	-0.28	7.99
PAN ->	0.40	0.24	5.64
O^1D + M ->	0.18	0.19	3.72
O^1D + H_2O ->	0.18	-0.19	3.58
SC(AFG2, O-xylene)	0.30	0.18	3.17
NO_2 + OH ->	0.27	0.17	2.88
CCOO2 + NO ->	0.34	0.15	2.11
NO_3 + hv -> NO_2 + O	0.42	0.12	1.48
HCHO + hv ->2HO_2 + CO	0.34	-0.12	1.38
CO + OH ->	0.27	-0.12	1.36
M-xylene(R^2=0.92)			
SC(MGLY, M-xylene)	0.31	0.41	17.0
O_3 + hv ->	0.27	-0.35	11.9
NO_2 + hv ->	0.18	0.28	7.98
O^1D + M ->	0.18	0.20	4.13
CRES + NO_3 ->	0.75	-0.20	4.13
O^1D + H_2O ->	0.18	-0.20	3.99
PAN ->	0.40	0.18	3.29
NO_2 + OH ->	0.27	0.17	2.98
HCHO + hv ->2HO_2 + CO	0.34	-0.13	1.70
O_3 + NO ->	0.10	-0.11	1.16

HO_2 + NO ->	0.18	0.10	1.03
P-xylene(R^2=0.92)			
CRES + NO_3 ->	0.75	-0.50	24.9
SC(MGLY, P-xylene)	0.71	0.30	8.95
O_3 + hv ->	0.27	-0.26	6.59
NO_2 + OH ->	0.27	0.23	5.41
NO_2 + hv ->	0.18	0.19	3.64
NO_3 + hv -> NO_2 + O	0.42	0.18	3.20
O^1D + M ->	0.18	0.18	3.09
CO + OH ->	0.27	-0.17	2.75
O^1D + H_2O ->	0.18	-0.15	2.13
PAN ->	0.40	0.13	1.73
SC(AFG2, P-xylene)	0.45	0.12	1.55
123-TMB (R^2=0.92)			
SC(MGLY, 123TMB)	0.36	0.50	24.9
SC(AFG2, 123TMB)	0.39	0.38	14.6
O_3 + hv ->	0.27	-0.33	10.9
NO_2 + hv ->	0.18	0.23	5.32
O^1D + M ->	0.18	0.20	4.12
CRES + NO_3 ->	0.75	-0.18	3.31
O^1D + H_2O ->	0.18	-0.18	3.14
PAN ->	0.40	0.12	1.40
123-TMB + OH ->	0.31	0.11	1.22
HCHO + hv ->2HO_2 + CO	0.34	-0.11	1.15
NO_2 + OH ->	0.27	0.10	1.06
NO_3 + hv -> NO_2 + O	0.42	0.10	1.05
HO_2 + NO ->	0.18	0.10	1.03
SC(MGLY, ARO2)	0.20	-0.10	1.00
124-TMB (R^2=0.92)			
SC(MGLY, 124TMB)	0.49	0.46	21.4
CRES + NO_3 ->	0.75	-0.30	9.00
O_3 + hv ->	0.27	-0.27	7.44
NO_2 + OH ->	0.27	0.23	5.28
NO_2 + hv ->	0.18	0.21	4.62

SC(AFG2, 124TMB)	0.40	0.17	3.00
O^1D + M ->	0.18	0.17	2.79
O^1D + H_2O ->	0.18	-0.16	2.66
CO + OH ->	0.27	-0.11	1.19
PAN ->	0.40	0.11	1.12
135-TMB (R^2=0.92)			
SC(MGLY, 135TMB)	0.29	0.43	18.9
SC(AFG2, 135TMB)	0.40	0.35	12.6
O_3 + hv ->	0.27	-0.35	12.4
O^1D + H_2O ->	0.18	-0.21	4.52
O^1D + M ->	0.18	0.20	4.09
NO_2 + hv ->	0.18	0.18	3.21
CRES + NO_3 ->	0.75	-0.17	2.91
HCHO + hv ->2HO_2 + CO	0.34	-0.13	1.63
ARO2 + OH ->	0.27	-0.12	1.56
HO_2 + NO ->	0.18	0.12	1.34
Base Mixture (R^2=0.93)			
NO_2 + hv ->	0.18	0.44	19.2
PAN ->	0.40	0.39	14.9
O_3 + hv ->	0.27	-0.30	9.05
CCOO2 + NO ->	0.34	0.26	6.95
CRES + NO_3 ->	0.75	-0.21	4.32
CO + OH ->	0.27	-0.18	3.25
O^1D + M ->	0.18	0.18	3.11
O^1D + H_2O ->	0.18	-0.17	2.82
O_3 + NO ->	0.10	-0.16	2.62
C2COO2 + NO_2 ->	0.75	-0.16	2.56
PPN ->	0.66	0.15	2.29

[a] Ridge regression for normalized predictors

[b] Normalized uncertainty of rate constant and chamber-derived aromatics oxidation parameters

[c] Uncertainty contribution.

Table E-4 Regression Analysis for Relative MIRs

Reactions or Chamber-derived parameter	σ/μ [b]	standardized reg. coeff.	UC (%) [c]
Benzene (R^2=0.84)			
BENZENE + OH ->	0.27	0.70	48.1
SC(AFG1, BENZENE)	0.33	0.53	27.6
P1U1	0.40	0.27	7.27
NO_2 + OH ->	0.27	-0.25	6.02
NO_2 + hv ->	0.18	0.19	3.46
PAN ->	0.40	0.15	2.29
SC(MGLY, ARO2)	0.20	-0.14	2.04
O_3 + NO ->	0.10	-0.10	1.02
Toluene (R^2=0.78)			
SC(MGLY, TOLUENE)	0.31	0.53	28.6
TOLUENE + OH ->	0.18	0.48	23.4
SC(MGLY, ARO1)	0.26	0.36	12.9
SC(MGLY, ARO2)	0.20	-0.24	5.83
NO_2 + OH ->	0.27	-0.18	3.39
SC(AFG2, TOLUENE)	0.34	0.16	2.58
NO_2 + hv ->	0.18	0.14	2.08
O_3 + hv ->	0.27	-0.14	1.98
ALK2 + OH ->	0.27	-0.11	1.27
ARO1 + OH ->	0.27	-0.11	1.16
SC(AFG2, ARO2)	0.23	-0.10	1.03
Ethylbenzene(R^2=0.66)			
SC(MGLY, ETHYLBENZENE)	0.63	0.64	41.3
Ethylbenzene + OH ->	0.31	0.45	20.4
SC(AFG2, ETHYLBENZENE)	0.44	0.25	6.29
SC(MGLY, ARO2)	0.20	-0.20	4.06
O_3 + hv ->	0.27	-0.18	3.11
O^1D + M ->	0.14	0.14	1.92
SC(AFG2, ARO2)	0.23	-0.10	1.06
HCHO + hv ->$2HO_2$ + CO	0.34	-0.10	0.98
ALK2 + OH ->	0.27	-0.10	0.97

NO_2 + hv ->	0.18	0.10	0.95
O-xylene (R^2=0.87)			
SC(MGLY, O-XYLENE)	0.43	0.67	44.5
SC(AFG2, O-XYLENE)	0.30	0.29	8.44
SC(MGLY, ARO2)	0.20	-0.20	3.98
NO_2 + OH ->	0.27	0.17	2.90
O_3 + hv ->	0.27	-0.14	1.93
ARO2 + OH ->	0.27	-0.14	1.91
HCHO + hv ->2HO_2 + CO	0.34	-0.10	1.09
SC(AFG2, ARO2)	0.23	-0.10	1.04
O^1D + M ->	0.18	0.10	1.00
M-xylene(R^2=0.93)			
SC(MGLY, MXYLENE)	0.31	0.62	38.6
NO_2 + OH ->	0.27	0.27	7.46
ARO2 + OH ->	0.27	-0.21	4.42
O_3 + hv ->	0.27	-0.19	3.51
HCHO + hv -> 2HO_2 + CO	0.34	-0.14	2.04
O^1D + M ->	0.18	0.12	1.52
O^1D + H_2O ->	0.18	-0.11	1.23
RCHO + hv ->	0.34	-0.10	1.02
P-xylene(R^2=0.76)			
SC(MGLY, PXYLENE)	0.71	0.60	35.8
SC(MGLY, ARO2)	0.20	-0.21	4.46
SC(AFG2, PXYLENE)	0.45	0.20	3.93
NO_2 + OH ->	0.27	0.18	3.23
O_3 + hv ->	0.27	-0.13	1.79
ARO2 + OH ->	0.27	-0.13	1.72
HCHO + hv -> 2HO_2 + CO	0.34	-0.12	1.33
ARO1 + OH ->	0.27	-0.11	1.20
O^1D + M ->	0.18	0.09	0.87
123-TMB (R^2=0.92)			
SC(MGLY, 123TMB)	0.36	0.63	40.1
SC(AFG2, 123TMB)	0.39	0.50	24.9
SC(MGLY, ARO2)	0.20	-0.21	4.30

ARO2 + OH ->	0.27	-0.19	3.60
123TMB + OH ->	0.31	0.17	2.98
NO_2 + OH ->	0.27	0.15	2.34
O_3 + hv ->	0.27	-0.14	2.03
HCHO + hv -> $2HO_2$ + CO	0.34	-0.11	1.29
SC(AFG2, ARO2)	0.23	-0.10	1.05
O^1D + M	0.18	0.10	1.01
124-TMB (R^2=0.90)			
SC(MGLY, 124TMB)	0.49	0.61	37.4
NO_2 + OH ->	0.27	0.27	7.36
SC(AFG2, 124TMB)	0.40	0.21	4.25
SC(MGLY, ARO2)	0.20	-0.18	3.36
ARO2 + OH ->	0.27	-0.13	1.76
O_3 + hv ->	0.27	-0.12	1.40
HCHO + hv -> $2HO_2$ + CO	0.34	-0.11	1.14
O^1D + M ->	0.18	0.09	0.90
135-TMB (R^2=0.93)			
SC(MGLY, 135TMB)	0.29	0.51	25.8
SC(AFG2, 135TMB)	0.40	0.43	18.6
ARO2 + OH ->	0.27	-0.25	6.18
SC(MGLY, ARO2)	0.20	-0.16	2.53
NO_2 + OH ->	0.27	0.14	2.07
O_3 + hv ->	0.27	-0.14	2.02
135TMB + OH ->	0.31	0.13	1.81
HCHO + hv -> $2HO_2$ + CO	0.34	-0.12	1.54
NO_2 + hv ->	0.18	0.12	1.36
RCHO + hv ->	0.34	-0.10	0.97

[a] Ridge regression for normalized predictors
[b] Normalized uncertainty of rate constant and chamber-derived aromatics oxidation parameters
[c] Uncertainty contribution.

Table E-5 Regression Analysis for Relative MOIRs [a]

Reactions or Chamber-derived parameter	σ/μ [b]	standardized reg. coeff.	UC (%) [c]
Benzene (R^2=0.82)			
BENZENE + OH ->	0.27	0.45	20.4
SC(AFG1, BENZENE)	0.33	0.42	17.4
PAN ->	0.40	0.37	14.0
O_3 + hv ->	0.27	-0.24	5.55
NO_2 + hv ->	0.18	0.23	5.12
P1U1	0.40	0.21	4.59
CO + OH ->	0.27	-0.19	3.54
O^1D + H_2O ->	0.18	-0.15	2.27
C2COO2 + NO_2 ->	0.75	0.14	1.92
O^1D + M ->	0.18	0.14	1.88
CCOO2 + NO ->	0.34	0.12	1.55
SC(MGLY, ARO2)	0.20	-0.12	1.45
HCHO + hv -> $2HO_2$ + CO	0.34	-0.12	1.32
O_3 + NO ->	0.10	-0.11	1.29
NO_3 + hv ->	0.42	0.11	1.27
Toluene (R^2=0.93)			
O_3 + hv ->	0.27	-0.42	17.3
SC(MGLY, TOLUENE)	0.31	0.33	10.6
CRES + NO_3 ->	0.75	-0.27	7.14
O^1D + M ->	0.18	0.26	6.91
O^1D + H_2O ->	0.18	-0.25	6.24
TOLUENE + OH ->	0.18	0.24	5.69
SC(MGLY, ARO1)	0.29	0.23	5.44
SC(MGLY, ARO2)	0.20	-0.18	3.41
HCHO + hv -> $2HO_2$ + CO	0.34	-0.18	3.40
SC(AFG2, ARO2)	0.23	-0.11	1.26
SC(AFG2, TOLUENE)	0.34	0.11	1.21
Ethylbenzene(R^2=0.90)			
O_3 + hv ->	0.27	-0.42	17.3
CRES + NO_3 ->	0.75	-0.37	13.5
SC(MGLY, ETHYLBENZENE)	0.63	0.31	9.39
O^1D + M ->	0.18	0.27	7.40
O^1D + H_2O ->	0.18	-0.25	6.39
HCHO + hv -> $2HO_2$ + CO	0.34	-0.19	3.50
NO_2 + OH ->	0.27	0.18	3.40
SC(AFG2, ETHYLBENZENE)	0.44	0.16	2.46
CO + OH ->	0.27	-0.14	2.05
SC(MGLY, ARO2)	0.20	-0.13	1.77
NO_3 + hv ->	0.42	0.11	1.76
ARO2 + OH ->	0.27	-0.11	1.13
Ethylbenzene + OH ->	0.31	0.10	1.09

O-xylene (R^2=0.92)			
SC(MGLY, OXYLENE)	0.43	0.56	31.9
O_3 + hv ->	0.27	-0.30	8.71
SC(AFG2, OXYLENE)	0.30	0.26	6.84
NO_2 + OH ->	0.27	0.20	4.09
O^1D + M ->	0.18	0.19	3.65
O^1D + H_2O ->	0.18	-0.19	3.47
SC(MGLY, ARO2)	0.20	-0.18	3.15
HCHO + hv -> $2HO_2$ + CO	0.34	-0.16	2.71
ARO2 + OH ->	0.27	-0.14	1.87
SC(AFG2, ARO2)	0.23	-0.12	1.36
CRES + NO_3 ->	0.75	-0.10	1.02
M-xylene(R^2=0.94)			
SC(MGLY, MXYLENE)	0.31	0.56	31.8
O_3 + hv ->	0.27	-0.28	7.72
NO_2 + OH ->	0.27	0.24	5.71
ARO2 + OH ->	0.27	-0.19	3.57
O^1D + M ->	0.18	0.18	3.28
HCHO + hv -> $2HO_2$ + CO	0.34	-0.17	2.96
O^1D + H_2O ->	0.18	-0.17	2.96
CCOO2 + NO ->	0.34	-0.12	1.49
PAN ->	0.40	-0.12	1.35
SC(AFG2, ARO2)	0.23	-0.10	1.10
SC(AFG2, M-XYLENE)	0.33	0.10	1.09
P-xylene(R^2=0.89)			
SC(MGLY, PXYLENE)	0.71	0.43	18.7
O_3 + hv ->	0.27	-0.33	10.7
CRES + NO_3 ->	0.75	-0.25	6.34
NO_2 + OH ->	0.27	0.22	5.02
O^1D + M ->	0.18	0.21	4.56
O^1D + H_2O ->	0.18	-0.20	3.89
SC(MGLY, ARO2)	0.20	-0.17	2.94
HCHO + hv -> $2HO_2$ + CO	0.34	-0.17	2.87
SC(AFG2, PXYLENE)	0.45	0.17	2.84
ARO2 + OH ->	0.27	-0.13	1.79
123-TMB (R^2=0.93)			
SC(MGLY, 123TMB)	0.36	0.58	33.8
SC(AFG2, 123TMB)	0.39	0.46	21.6
O_3 + hv ->	0.27	-0.23	5.50
SC(MGLY, ARO2)	0.20	-0.18	3.23
ARO2 + OH ->	0.27	-0.18	3.11
O^1D + M ->	0.18	0.16	2.63
HCHO + hv -> $2HO_2$ + CO	0.34	-0.13	1.74
PAN ->	0.40	-0.13	1.73
O^1D + H_2O ->	0.18	-0.13	1.70
NO_2 + OH ->	0.27	0.12	1.55
CCOO2 + NO ->	0.34	-0.12	1.44

SC(AFG2, ARO2)	0.23	-0.12	1.33
124-TMB (R^2=0.91)			
SC(MGLY, 124TMB)	0.49	0.55	30.6
NO_2 + OH ->	0.27	0.25	6.32
O_3 + hv ->	0.27	-0.23	5.31
SC(AFG2, 124TMB)	0.40	0.20	3.91
SC(MGLY, ARO2)	0.20	-0.16	2.71
O^1D + M ->	0.18	0.16	2.47
O^1D + H_2O ->	0.18	-0.14	1.95
HCHO + hv -> 2HO_2 + CO	0.34	-0.13	1.76
ARO2 + OH ->	0.27	-0.12	1.56
CRES + NO_3 ->	0.75	-0.11	1.21
135-TMB (R^2=0.93)			
SC(MGLY, 135TMB)	0.29	0.47	22.0
SC(AFG2, 135TMB)	0.40	0.39	15.4
O_3 + hv ->	0.27	-0.24	5.90
ARO2 + OH ->	0.27	-0.22	4.75
PAN ->	0.40	-0.17	2.77
O^1D + H_2O ->	0.18	-0.15	2.40
O^1D + M ->	0.18	0.15	2.16
NO_2 + hv ->	0.18	-0.15	2.13
CCOO2 + NO ->	0.34	-0.14	1.99
SC(MGLY, ARO2)	0.20	-0.14	1.98
HCHO + hv -> 2HO_2 + CO	0.34	-0.14	1.90
NO_2 + OH ->	0.27	0.10	1.09
135TMB+ OH ->	0.31	0.10	1.09

[a] Ridge regression for normalized predictors

[b] Normalized uncertainty of rate constant and chamber-derived aromatics oxidation parameters

[c] Uncertainty contribution.

Table E-6 Regression Analysis for Relative EBIRs

Reactions or Chamber-derived parameter	σ/μ [b]	standardized reg. coeff.	UC (%) [c]
Benzene (R^2=0.79)			
PAN ->	0.40	0.49	23.6
NO_2 + hv ->	0.18	0.22	5.01
NO_2 + OH ->	0.27	0.20	4.06
CO + OH ->	0.27	-0.20	3.83
O_3 + hv ->	0.27	-0.19	3.56
NO_3 + hv ->	0.42	0.18	3.24
SC(AFG1, BENZENE)	0.33	0.18	3.19
CCOO2 + NO ->	0.34	0.16	2.58
BENZENE + OH ->	0.27	0.15	2.23
HO_2 + NO ->	0.18	-0.14	1.85
P1U1	0.35	0.13	1.78
C2COO2 + NO_2 ->	0.75	0.12	1.47
O^1D + H_2O ->	0.18	-0.12	1.36
O_3 + NO ->	0.10	-0.10	1.07
O^1D + M ->	0.18	0.10	1.03
Toluene (R^2=0.90)			
CRES + NO_3 ->	0.75	-0.45	20.1
O_3 + hv ->	0.27	-0.26	6.71
SC(MGLY, TOLUENE)	0.31	0.25	6.14
PAN ->	0.40	0.22	4.83
SC(MGLY, ARO1)	0.29	0.18	3.39
NO_3 + hv ->	0.42	0.17	2.94
NO_2 + OH ->	0.27	0.16	2.71
O^1D + M ->	0.18	0.16	2.62
O^1D + H_2O ->	0.18	-0.16	2.54
CO + OH ->	0.27	-0.15	2.22
NO_2 + hv ->	0.18	0.14	1.99
TOLUENE + OH ->	0.18	0.12	1.54
HCHO + hv -> $2HO_2$ + CO	0.34	-0.10	1.05
Ethylbenzene(R^2=0.90)			
CRES + NO_3 ->	0.75	-0.54	28.7
NO_2 + OH ->	0.27	0.24	5.91
O_3 + hv ->	0.27	-0.24	5.63
SC(MGLY, ETHYLBENZENE)	0.63	0.20	4.01
NO_3 + hv ->	0.42	0.20	3.89
CO + OH ->	0.27	-0.20	3.81
O^1D + M ->	0.18	0.15	2.35
O^1D + H_2O ->	0.18	-0.15	2.24
PAN ->	0.40	0.13	1.73
SC(AFG2, ETHYLBENZENE)	0.44	0.13	1.65
NO_2 + hv ->	0.18	0.11	1.19

O-xylene (R^2=0.91)			
SC(MGLY, OXYLENE)	0.43	0.57	32.0
SC(AFG2, OXYLENE)	0.30	0.26	6.84
CRES + NO_3 ->	0.75	-0.24	5.66
NO_2 + OH ->	0.27	0.22	4.68
O_3 + hv ->	0.27	-0.21	4.23
O^1D + H_2O ->	0.18	-0.13	1.79
SC(MGLY, ARO2)	0.20	-0.13	1.73
O^1D + M ->	0.18	0.13	1.71
HCHO + hv -> $2HO_2$ + CO	0.34	-0.12	1.44
ARO2 + OH ->	0.27	-0.12	1.44
C2COO2 + NO_2 ->	0.75	0.12	1.34
SC(AFG2, ARO2)	0.23	-0.10	1.02
M-xylene(R^2=0.93)			
SC(MGLY, MXYLENE)	0.31	0.62	38.1
NO_2 + OH ->	0.27	0.20	3.85
ARO2 + OH ->	0.27	-0.18	3.08
O_3 + hv ->	0.27	-0.17	2.93
PAN ->	0.40	-0.15	2.19
C2COO2 + NO_2 ->	0.75	0.14	1.97
CCOO2 + NO ->	0.34	-0.13	1.82
PPN ->	0.66	-0.12	1.49
HCHO + hv -> $2HO_2$ + CO	0.34	-0.12	1.45
O^1D + M ->	0.18	0.11	1.30
O^1D + H_2O ->	0.18	-0.10	1.05
P-xylene(R^2=0.90)			
CRES + NO_3 ->	0.75	-0.50	25.2
SC(MGLY, PXYLENE)	0.71	0.33	11.2
NO_2 + OH ->	0.27	0.25	6.18
O_3 + hv ->	0.27	-0.21	4.32
NO_3 + hv ->	0.42	0.16	2.51
CO + OH ->	0.27	-0.16	2.49
SC(AFG2, PXYLENE)	0.45	0.15	2.28
O^1D + M ->	0.18	0.13	1.82
O^1D + H_2O ->	0.18	-0.13	1.62
HCHO + hv -> $2HO_2$ + CO	0.34	-0.10	1.03
NO_2 + hv ->	0.18	0.10	0.98
ARO2 + OH ->	0.27	-0.10	0.90
123-TMB (R^2=0.93)			
SC(MGLY, 123TMB)	0.36	0.62	38.3
SC(AFG2, 123TMB)	0.39	0.49	23.5
PAN ->	0.40	-0.19	2.76
ARO2 + OH ->	0.27	-0.15	2.31
CCOO2 + NO ->	0.34	-0.15	2.29
O_3 + hv ->	0.27	-0.15	2.19
SC(MGLY, ARO2)	0.20	-0.14	2.06
123-TMB + OH ->	0.31	0.13	1.67

C2COO2 + NO_2 ->	0.75	0.13	1.60
O^1D + M ->	0.18	0.11	1.28
124-TMB (R^2=0.92)			
SC(MGLY, 124TMB)	0.49	0.55	29.8
NO_2 + OH ->	0.27	0.26	6.72
CRES + NO_3 ->	0.75	-0.25	6.37
SC(AFG2, 124TMB)	0.40	0.20	3.82
O_3 + hv ->	0.27	-0.16	2.71
SC(MGLY, ARO2)	0.20	-0.13	1.60
O^1D + M ->	0.18	0.11	1.27
ARO2 + OH ->	0.27	-0.11	1.12
PAN ->	0.40	-0.10	1.05
O^1D + H_2O ->	-0.14	-0.10	1.01
135-TMB (R^2=0.92)			
SC(MGLY, 135TMB)	0.29	0.49	23.7
SC(AFG2, 135TMB)	0.40	0.41	16.7
PAN ->	0.40	-0.26	6.85
CCOO2 + NO ->	0.34	-0.19	3.44
ARO2 + OH ->	0.27	-0.18	3.24
NO_2 + hv ->	0.18	-0.15	2.40
O_3 + hv ->	0.27	-0.15	2.33
C2COO2 + NO_2 ->	0.75	0.10	1.07
O^1D + H_2O ->	0.18	-0.10	1.03
SC(MGLY, ARO2)	0.20	-0.10	1.00

[a] Ridge regression for normalized predictors

[b] Normalized uncertainty of rate constant and chamber-derived aromatics oxidation parameters

[c] Uncertainty contribution.