Uncertainty in Reactivity Estimates for N-Butyl Acetate and 2-Butoxy Ethanol

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Lihua Wang and Jana B. Milford
Department of Mechanical Engineering
University of Colorado
Boulder, CO 80309-0427

W.P.L. Carter
Statewide Air Pollution Research Center
University of California
Riverside, CA 92521

Abstract

Incremental reactivity estimates for many high molecular weight hydrocarbons and oxygenated compounds used in consumer products, coatings and solvents are viewed as uncertain because of limited data on their reaction mechanisms and products. This study performs a systematic uncertainty analysis for two solvents of interest for use in consumer products: 2-butoxy ethanol and n-butyl acetate. 2-butoxy ethanol provides an example of a relatively well-studied compound for which product data are available for most reaction pathways and for which incremental reactivity data are available from environmental chamber experiments. In contrast, n-butyl acetate is an example of a compound for which environmental chamber studies have been conducted but for which there are essentially no product data.

As a first step in the study, key mechanistic parameters for 2-butoxy ethanol and n-butyl acetate were estimated from experiments conducted in the University of California at Riverside chambers. The organic nitrate yield for 2-butoxy ethanol in the SAPRC-97 mechanism is estimated to be 0.13 ± 0.02 (mean ± 1σ). For n-butyl acetate, the organic nitrate yield is estimated to be 0.13 ± 0.05 and the probability of the intermediate CH_3-CH_2-CH_2-CH[O.]-O-CO-CH_3 undergoing ester rearrangement to be 0.72 ± 0.22.

Along with uncertainty estimates for other parameters of the SAPRC-97 mechanism, the uncertainties for these chamber-derived parameters were propagated through incremental reactivity calculations using Monte Carlo analysis. The maximum incremental reactivity (MIR), maximum ozone incremental reactivity (MOIR) and equal benefit incremental reactivity (EBIR) are estimated to be 1.12 ± 0.27, 0.59 ± 0.14 and

0.40 ± 0.11 ppm O_3/ppmC respectively for 2-butoxy ethanol and 0.41 ± 0.16, 0.29 ± 0.10 and 0.20 ± 0.08 ppm O_3/ppmC for n-butyl acetate. The corresponding relative reactivities compared to the reactivity of a base mixture are 0.90 ± 0.14, 1.08 ± 0.16 and 1.20 ± 0.19 for 2-butoxy ethanol and 0.34 ± 0.13, 0.53 ± 0.16 and 0.60 ± 0.18 for n-butyl acetate. Uncertainties in the 2-butoxy ethanol reactivity estimates are lower than those estimated previously for many other VOCs. In contrast, the uncertainties in the n-butyl acetate reactivity estimates are at the upper end of the range of uncertainties estimated previously for other VOCs.

The uncertainty estimates for the incremental reactivities take into account the available kinetic data for 2-butoxy ethanol and n-butyl acetate, the product data for 2-butoxy ethanol, and the chamber-derived mechanistic parameter estimates for both compounds. Measurements of the 2-butoxy ethanol + OH rate constant and product yields and chamber-derived estimates of key mechanistic parameters are estimated to have reduced the uncertainty in the relative MIR of 2-butoxy ethanol by 40%, compared to the uncertainty level that was estimated assuming they were not available. The availability of measurements of the n-butyl acetate + OH rate constant is estimated to have reduced the uncertainty in the relative MIR for n-butyl acetate by about 25%.

The relative reactivity estimates for 2-butoxy ethanol are strongly influenced by uncertainty in the rate constants for its reaction with OH and the reaction of higher reactivity ketones (PROD2 in SAPRC) with OH. Rate parameters for n-butyl acetate + OH, O_3 photolysis and NO_2 + OH contribute most to the uncertainty in n-butyl acetate relative reactivity estimates.

From 2 to 3% of the total uncertainty in the relative reactivities of 2-butoxy ethanol is attributable to uncertainty in the chamber-derived yield of organic nitrate from its reaction. About 4 to 7% of the uncertainty in the n-butyl acetate relative reactivities is attributable to the organic nitrate yield in its mechanism. The most influential sources of uncertainty in the 2-butoxy ethanol organic nitrate yield are the parameters that quantify the unknown radical sources in the chamber experiments. The initial concentration of m-xylene and rate constants for PPN formation and decompostion are the largest contributors to the uncertainty in the organic nitrate yield from n-butyl acetate.
Overall, the uncertainty analysis indicates that improved quantification of chamber radical sources and initial conditions would help reduce uncertainty in the n-butyl acetate and 2-butoxy ethanol reaction mechanisms and in turn their incremental reactivity estimates. Reducing uncertainty in chamber experiments would also improve estimates of incremental reactivity for other compounds with chamber-derived parameters in their mechanisms. However, most of the uncertainty in the incremental reactivity estimates for n-butyl acetate and 2-butoxy ethanol is attributable to other parameters of the base SAPRC mechanism and to the rate constants for their primary reactions with OH.
Among the parameters of the base mechanism, improving the representation of higher reactivity ketones and reducing the uncertainty in the ozone action spectra and PAN and PPN rate parameters would have the greatest effect on the relative reactivity estimates.

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1. Introduction

It is widely recognized that individual volatile organic compound (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 (Carter, 1994). The relative change in ozone from a small amount of an individual VOC added to a base mixture of VOCs is described as its incremental reactivity. Substituting low-reactivity VOCs for those with relatively high reactivities is viewed as a potentially cost-effective means to achieve ozone reductions (McBride et al., 1997). Reflecting this idea, the California Clean Fuels/Low Emissions Vehicles regulation (CARB, 1992) accounts for reactivity differences through a weighting scheme based on maximum incremental reactivities (MIRs). The possibility of using reactivity adjustments is being extended to VOCs used in aerosol coatings through the California Low Emissions and Reactivity (CLEAR) regulation (CARB, 1998). The CLEAR program provides a voluntary alternative to mass-based VOC limits for aerosol coatings, and also uses MIRs to quantify VOC reactivities.

Reactivity estimates for many high molecular weight hydrocarbons and oxygenated organic compounds from consumer products, coatings and solvents are viewed as highly uncertain because of gaps in understanding their oxidation mechanisms. Product studies that would allow the mechanisms to be determined are often limited or nonexistent. For these compounds, yields and reaction rates of radicals and stable intermediates are typically estimated based on structural analogy with lighter compounds for which the chemistry has been tested (Carter, 1999a). In addition, incremental reactivities have been measured in environmental chambers for some of these compounds, with mechanistic parameters sometimes adjusted to fit chamber data.

The objective of this study is to estimate uncertainties for two representative VOCs that are used in consumer products, for which a combination of explicit kinetic and product data, structural analogy, and chamber-derived parameter values have been used to estimate incremental reactivities. The compounds selected are the solvents 2-butoxy ethanol (CH_3-CH_2-CH_2-CH_2-O-CH_2-CH_2-OH, a glycol ether) and n-butyl acetate (CH_3-CH_2-CH_2-CH_2-O-CO-CH_3).

2-Butoxy ethanol provides an example of a well-studied compound for which there are product data for most (although not all) of the reaction routes, as well as chamber reactivity data. Most of the pathways of the 2-butoxy ethanol reaction with OH are well characterized. In the SAPRC mechanism, the only parameter that is adjusted based on chamber data is the nitrate yield. Incremental reactivity estimates for this compound may still be uncertain due to uncertainties in its rate constant for reaction with OH, experimental uncertainties in the measured product yields, and uncertainties in the adjusted nitrate yield stemming from uncertainties in both the base mechanism and in the chamber experiments. (The base mechanism is the portion of the SAPRC mechanism that represents the reactions of inorganic species, the common organic products and the intermediate radicals leading to these products.)

N-butyl acetate is an example of a compound for which there are chamber reactivity data but essentially no product data. In this case, the most influential parameters in the estimated mechanism are adjusted to fit the environmental chamber data. Thus incremental reactivity estimates for n-butyl acetate are expected to be influenced by uncertainties in its OH rate constant, in pathway probabilities estimated by structural analogy and in parameters that are adjusted to fit the chamber data.

To estimate uncertainties in incremental reactivities for these compounds, the study proceeds in three steps. First, stochastic programming is used to estimate uncertainties in chamber radical source parameters, which are critical inputs to simulations of chamber incremental reactivity experiments. The uncertainty estimates for radical source parameters account for uncertainties in other experimental conditions including initial reactant concentrations and light intensity, as well as uncertainties in influential rate parameters of the SAPRC-97 mechanism (Carter et al., 1997) used to simulate the experiments. Then, stochastic programming is used to estimate uncertainties in key reaction pathway and organic nitrate yield parameters of n-butyl acetate and 2-butoxy ethanol. These uncertainty estimates account for radical source parameter uncertainties as well as those in SAPRC-97 parameters and other experimental conditions. Chamber experiments conducted by Carter et al. (1998) in the Dividable Teflon Chamber (DTC) at the University of California at Riverside (UCR), College of Engineering, Center for Environmental Research and Technology (CE-CERT) are used to estimate the mechanistic parameters.

The estimates of uncertainty in the chamber-derived parameters, together with estimates of uncertainty in other SAPRC-97 parameters, are then propagated through incremental reactivity calculations using Monte Carlo analysis with Latin hypercube sampling. In addition to this case, which accounts for the chamber experiments and available product and kinetic data for 2-butoxy ethanol and n-butyl acetate, two other cases were considered. Uncertainties in incremental reactivities were also estimated assuming that no direct measurements or chamber-derived estimates of product yields were available, and assuming that neither measurements of the 2-butoxy ethanol or n-butyl acetate + OH rate constants nor direct measurements or chamber-derived estimates of product yields were available. The additional cases allow us to assess the effect of the measurements and chamber studies in reducing uncertainty in incremental reactivities.

The methods used in this study are similar to those applied by Wang et al. (1999) for aromatic compounds. The one major difference is that in the previous study optimal parameter estimates were derived from single aromatics-NO_x experiments, whereas incremental reactivity experiments are used in the current study. In incremental reactivity experiments, two experiments are conducted side-by-side, one in which a base mixture of organic compounds is irradiated with NO_x and one in which the test compound of interest is added to the base mixture of organics.

2. Methods

2.1 SAPRC-97 Mechanism and Chamber-derived Parameters

The chemical mechanism employed in this study is the SAPRC-97 mechanism (Carter et al., 1997). The mechanism explicitly represents a large number of different organic compounds but uses a condensed representation for many of their products. The reactions of inorganics, CO, formaldehyde, acetaldehyde (CCHO), propionaldehyde (RCHO), peroxyacetyl nitrate (PAN), peroxypropional nitrate (PPN), glyoxal (GLY), methylglyoxal (MGLY), and several other product compounds are represented explicitly. The SAPRC-97 mechanism is updated from SAPRC-93, which in turn is an update from SAPRC-90 (Carter, 1990). Differences between SAPRC-93 and SAPRC-90 include updates to the HCHO absorption cross-sections, the kinetics of PAN formation, the action spectra of the unknown aromatic oxidation products and the reactions of O_3 with alkenes. The major difference between SAPRC-97 and SAPRC-93 is in the aromatic compound oxidation parameters, which were updated using new environmental chamber data. The SAPRC mechanism has just been extensively revised (Carter, 1999a). However, SAPRC-97 was used in this study for consistency with past work on uncertainties in chamber-derived parameters for aromatic compounds (Wang et al., 1999). Comparisons between SAPRC-97 and an interim updated version, SAPRC-98, are given below for parameters and incremental reactivities of 2-butoxy ethanol and n-butyl acetate. SAPRC-98 was the latest version available when the calculations were performed for this report, and is very similar to the version finalized as SAPRC-99 (Carter, 1999a).

2.1.1 2-Butoxy Ethanol Mechanism

2-Butoxy ethanol (CH_3-CH_2-CH_2-CH_2-O-CH_2-CH_2-OH) is assumed to react in the atmosphere primarily with OH radicals. The SAPRC mechanism for this compound uses an OH reaction rate constant of 2.57×10^{-11} cm^3 $molecules^{-1}$ s^{-1}. This is the average of values given in three studies: 2.31×10^{-11} (Dagaut et al., 1988), 2.45×10^{-11} (Stemmler et al., 1996) and 2.94×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Aschmann and Atkinson, 1998). The comparatively low value of Hartmann et al. (1986) is not included in the average. An uncertainty of 25% is assigned for this rate constant, based on these studies and its uncertainty category (Carter, 1998).

The mechanism for the subsequent reactions is generated using an automated procedure, incorporating estimates of branching ratios for attack of OH radicals at different positions, and branching ratios for competing reactions of the radicals that are formed (Carter, 1999a). The major reactions derived for 2-butoxy ethanol are summarized in Table 1 and are also shown in Figure 1, along with estimates of the relative contributions of each of these reactions. (Minor reaction pathways, and reactions of alkyl radicals with O_2 forming the corresponding peroxy radical, are not shown.) In terms of model species used in the SAPRC-98 mechanism, the overall process is represented as:

$$\text{OH + BUO-ETOH} \rightarrow \text{0.887 RO2-R. + 0.113 RO2-N. + 0.136 R2O2. +}$$
$$\text{0.55 HCHO + 0.015 CCHO + 0.32 RCHO +}$$

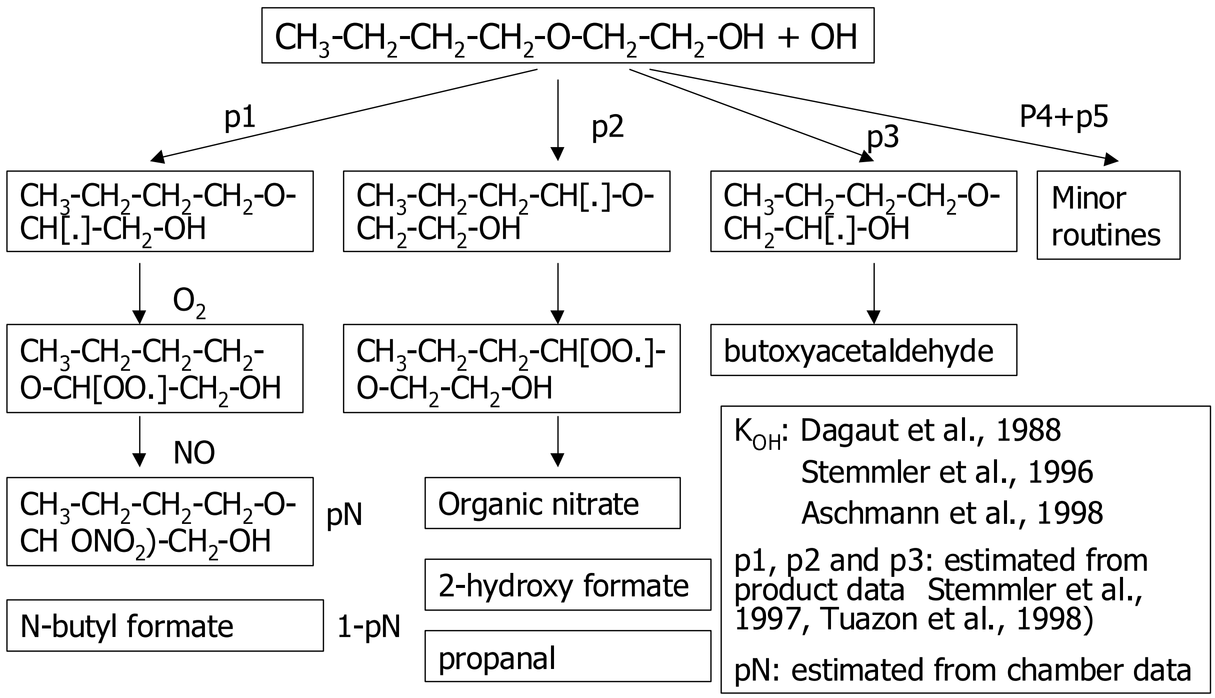


Figure 1. Key features of the 2-butoxy ethanol mechanism used in SAPRC.

0.503 MEK + 0.26 PROD2 + 1.136 RO2.

Here, RO2-R· represents NO to NO_2 conversions with HO_2 formation, RO2-N· represents formation of organic nitrates from peroxy + NO reactions, R2O2· represents extra NO to NO_2 conversions caused by multi-step mechanisms, HCHO, CCHO and RCHO represent formaldehyde, acetaldehyde and lumped higher aldehydes, respectively, MEK and PROD2 refer to lumped low and higher reactivity ketones, respectively, and RO2· refers to total alkyl peroxy radicals. Note that PROD2 is not in the SAPRC-97 mechanism, but was added to it for the purpose of representing the reactivities of these solvent species.

Table 1. Reaction mechanisms derived for 2-butoxy ethanol

Rxn No	Reactions			Est. Yield
1	CH3-CH2-CH2-CH2-O-CH2-CH2-OH + OH	->	H2O + CH3-CH2-CH2-CH2-O-CH[.]-CH2-OH	58%
2		->	H2O + CH3-CH2-CH2-CH[.]-O-CH2-CH2-OH	22%
3		->	H2O + CH3-CH[.]-CH2-CH2-O-CH2-CH2-OH	4%
4		->	H2O + CH3-CH2-CH[.]-CH2-O-CH2-CH2-OH	4%
5		->	H2O + CH3-CH2-CH2-CH2-O-CH2-CH[.]-OH	12%
	Radicals formed in Reaction 1			
6	CH3-CH2-CH2-CH2-O-CH[OO.]-CH2-OH + NO	->	CH3-CH2-CH2-CH2-O-CH(ONO2)-CH2-OH	7%
7		->	NO2 + CH3-CH2-CH2-CH2-O-CH[O.]-CH2-OH	50%
8	CH3-CH2-CH2-CH2-O-CH[O.]-CH2-OH	->	**CH3-CH2-CH2-CH2-O-CHO** + HO-CH2.	50%
9	HO-CH2. + O2	->	HCHO + HO2.	50%
	Radicals formed in Reaction 2			
10	CH3-CH2-CH2-CH[OO.]-O-CH2-CH2-OH + NO	->	CH3-CH2-CH2-CH(ONO2)-O-CH2-CH2-OH	3%
11		->	NO2 + CH3-CH2-CH2-CH[O.]-O-CH2-CH2-OH	19%
12	CH3-CH2-CH2-CH[O.]-O-CH2-CH2-OH	->	**HCO-O-CH2-CH2-OH** + CH3-CH2-CH2.	19%
13	CH3-CH2-CH2OO. + NO	->	NO2 + CH3-CH2-CH2O.	19%
14	CH3-CH2-CH2O. + O2	->	~~**CH3-CH2-CHO**~~ + HO2.	19%
	Radicals formed in Reaction 3			
15	CH3-CH[OO.]-CH2-CH2-O-CH2-CH2-OH + NO	->	CH3-CH(ONO2)-CH2-CH2-O-CH2-CH2-OH	0%
16		->	NO2 + (various minor products)	3%
	Radicals formed in Reaction 4			
17	CH3-CH2-CH[OO.]-CH2-O-CH2-CH2-OH + NO	->	CH3-CH2-CH(ONO2)-CH2-O-CH2-CH2-OH	1%
18		->	NO2 + (various minor products)	4%
	Radicals formed in Reaction 5			
19	CH3-CH2-CH2-CH2-O-CH2-CH[.]-OH + O2	->	CH3-CH2-CH2-CH2-O-CH2-CHO + HO2.	12%

[a] R. + O2 -> RO2. Reactions are not shown.
[b] Observed products whose yields have been quantified are in bold (Tuazon.et al, 1988)

Table 2 and Figure 1 show specific 2-butoxy ethanol product species that each of the SAPRC-97/98 model species are being used to represent, and how their overall yields are derived from the rate constant ratios in the mechanism. As indicated in Table 2 and Figure 1, the following mechanistic parameters are considered in our analysis: p1 is the fraction of the initial reaction forming the CH_3-CH_2-CH_2-CH_2-O-CH[.]-CH_2-OH radical, whose subsequent reactions result primarily in formation of n-butyl formate; p2 is the fraction of the initial reaction forming the CH_3-CH_2-CH_2-CH[.]-O-CH_2-CH_2-OH radical, whose subsequent reactions result primarily in the formation of 2-hydroxy formate and propanal; p3 is the fraction of the initial reaction forming the CH_3-CH_2-CH_2-CH_2-O-CH_2-CH[.]-OH radical, which is expected to react to form butoxyacetaldehyde (see Table 1); and pN is the fraction of the initially-formed peroxy radicals that form organic nitrates when they react with NO. Two pathways not shown, p4 and p5, are minor reaction routes that form CH_3-CH[.]-CH_2-CH_2-O-CH_2-CH_2-OH and CH_3-CH_2-CH[.]-CH_2-O-CH_2-CH_2-OH, respectively.

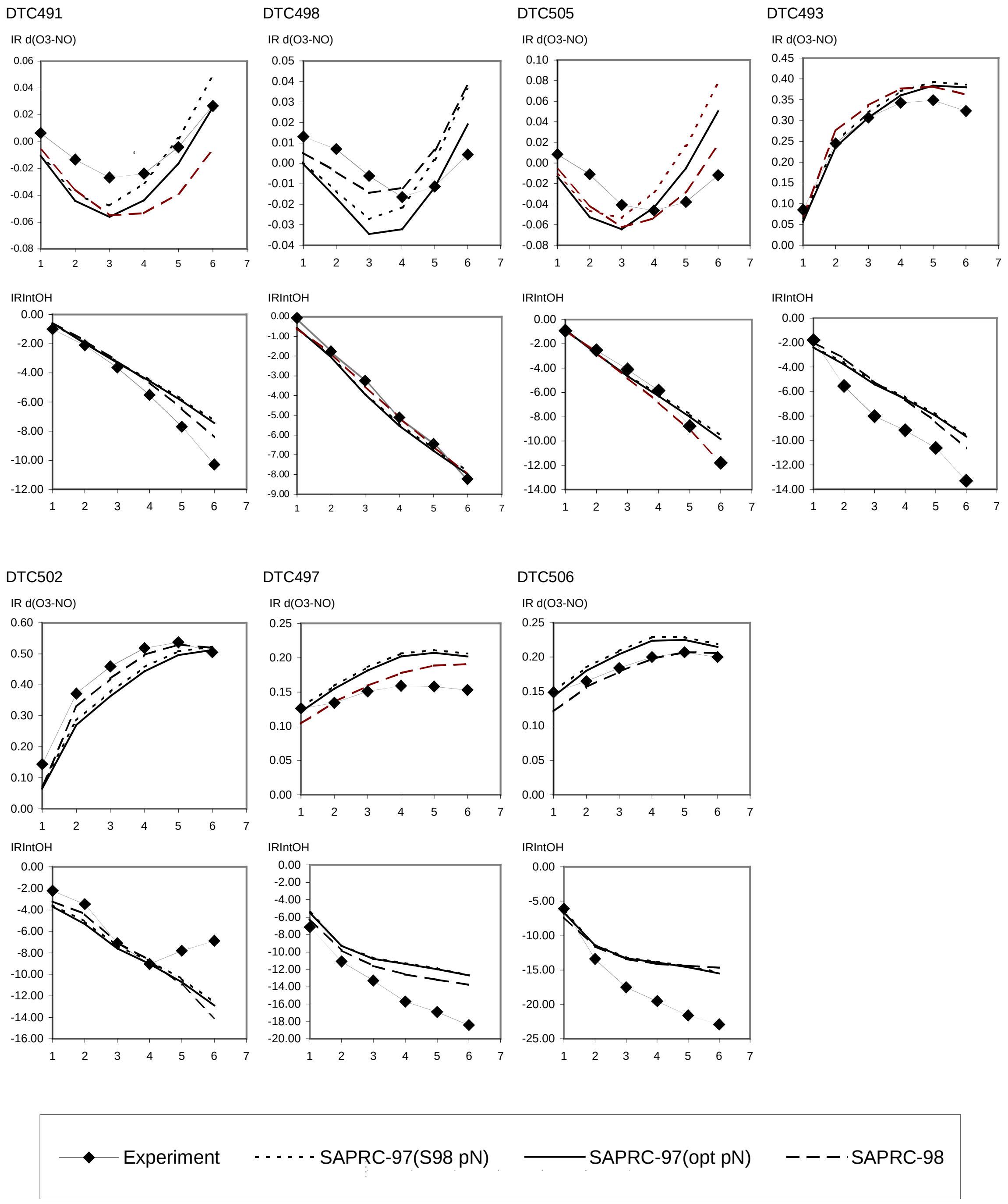
The value of the parameter p1 is derived based on observed 57 ± 5% yields of n-butyl formate from Tuazon et al. (1998). In contrast, Stemmler et al. (1997) observed only a 35 ± 11% yield of this product. The SAPRC mechanism relies on Tuazon et al.'s estimates because they obtained consistent data using both GC-FID and FT-IR. In addition, their data are consistent with the prediction that the propanal and 2-hydroxyethyl formate yields should be about the same. The value of p2 is derived based on observed 22 ± 2% yields of 2-hydroxy formate and 21 ± 2% yields of propanal from Tuazon et al. (1998). Stemmler et al. (1997) observed roughly similar yields of propanal, but higher (29 ± 18%) yields of 2-hydroxyethyl formate. The value of p3 is derived from the estimates for the other pathways, as indicated in Table 2. This is consistent with the data of Stemmler et al (1997), who observed a 12 ± 9% yield of butoxyacetaldehyde. Tuazon et al. (1998) did not observe this product, but were not able to account for 11% of the carbon converted in the reaction.

Table 2. Parameters and products used for 2-butoxy ethanol

Parm or Product	Represents	Computed Using	Default
Mechanistic Parameters [a]			
p1	k1 / Total kOH	Derived from product yield data	0.577
p2	k2 / Total kOH	Derived from product yield data	0.222
p3	k5 / Total kOH	p3 = 0.92 - (p1+p2)	0.123
pN	pN = k6/(k6+k7) = k10/(k10+k11) = k15/(k15+k16) = k17/(k17+k18)	Adjusted to fit chamber data	0.127
Product Yields used in Model			
RO2-R.	NO -> NO2 conversions with HO2 formation	Yield(RO2-R.) = p1*(1-pN) + p2*(1-pN) + 0.035*(1-pN)*0.5 + 0.035*(1-pN)*0.5*0.06 + 0.035*(1-pN)*0.5*0.94 + 0.043*(1-pN)*0.053 + 0.043*(1-pN)*0.026 + 0.043*(1-pN)*0.921*0.964 + p3	0.887
R2O2.	Additional NO -> NO2 conversions	Yield(R2O2.) = p1*(1-pN) + 2.0*p2*(1-pN) + 0.035*(1-pN) + 0.035*(1-pN)*0.5 + 0.035*(1-pN)*0.5*0.94 + 0.043*(1-pN) + 0.043*(1-pN)*0.026 + 0.043*(1-pN)*0.921*0.964 - Yield(RO2-R.)	0.136
RO2-N.	CH3-CH2-CH2-CH2-O-CH(ONO2)-CH2-OH, CH3-CH2-CH2-CH(ONO2)-O-CH2-CH2-OH, CH3-CH2-CH(ONO2)-CH2-O-CH2-CH2-OH, CH3-CH(ONO2)-CH2-CH2-O-CH2-CH2-OH, CH3-CH2-CH2-ONO2, and CH3-CH2-CH(OH)-CH2-O-CH(ONO2)-CH2-OH	Yield(RO2-N.) = p1*pN + p2*pN + 0.035*pN + 0.043*pN + 0.043*(1-pN)*0.921*0.036	0.113
HCHO	HCHO	Yield(HCHO) = p1*(1-pN) + 0.035*(1-pN)*0.5*0.94 + 0.043*(1-pN)*0.921*0.964	0.551
CCHO	CH3-CHO	Yield(CCHO) = 0.035*(1-pN)*0.5	0.015
RCHO	CH3-CH2-CHO, CH3-CH2-CH2-CH2-O-CH2-CHO, and HCO-CH2-O-CH2-CH2-OH	Yield(RCHO) = p2*(1-pN) + 0.035*(1-pN)*0.5*0.06 + 0.043*(1-pN)*0.026 + 0.043*(1-pN)*0.026 + p3	0.320
MEK	CH3-CH2-CH2-CH2-O-CHO	Yield(MEK) = p1*(1-pN)	0.504
PROD2	HCO-O-CH2-CH2-OH, CH3-CH2-CH(OH)-CH2-O-CHO, CH3-CO-CH2-CH2-O-CH2-CH2-OH, and CH3-CH2-CO-CH2-O-CH2-CH2-OH	Yield(PROD2) = 0.043*(1-pN)*0.053 + 0.043*(1-pN)*0.921*0.964	0.259
RO2.	Total peroxy radicals	Yield(RO2.) = Yield(RO2-R.) + Yield(RO2-N.) + Yield(R2O2.)	

[a] Rate constants refer to reactions on Table 1.

The final critical parameter is the overall yield of organic nitrates from the initially formed peroxy radicals (pN) which is estimated by fitting incremental reactivity estimates from environmental chamber experiments. The value of this parameter shown in Table 2 was derived using the SAPRC-98 mechanism, and was found not to be optimal when the SAPRC-97 mechanism is used. The performance of the fitted 2-butoxy ethanol mechanism in simulating incremental reactivity experiments is illustrated in Figure 2. Results are shown for both the SAPRC-97 and SAPRC-98 base mechanisms, with the SAPRC-97 calculations employing both



x-axis label: Time (hour)

Figure 2. Performance of the 2-butoxy ethanol mechanism for incremental reactivity experiments in the DTC chamber.

the pN value optimized using the SAPRC-98 mechanism, and the reoptimized value derived for SAPRC-97 in this work.

2.1.2 Butyl Acetate Mechanism

N-butyl acetate (CH_3-CH_2-CH_2-CH_2-O-CO-CH_3) is also assumed to react primarily with OH radicals. The rate constant used is 4.20×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, as recommended by Atkinson (1989). Two independent measurements of the rate constant are in good agreement, and the measured value is within 15% of the value estimated using the group-additivity method of Kwok and Atkinson (1995).

The mechanism for the subsequent reactions is generated using the same automated procedure and estimation methods as employed for 2-butoxy ethanol (Carter, 1999a). The major reactions derived for n-butyl acetate are summarized in Table 3 and are also shown in Figure 3, along with estimates of the relative contributions of each of these reactions. In terms of SAPRC-98 model species, the overall process is represented as follows.

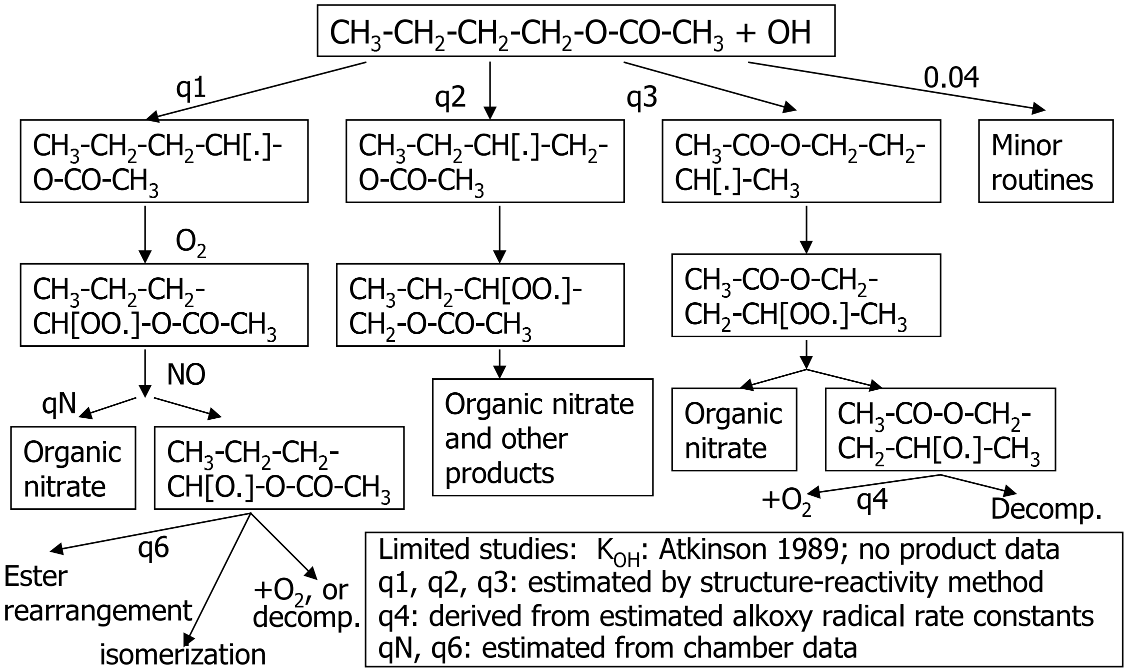
$$\begin{aligned} \text{HO. + BU-ACET} \rightarrow\ & \text{0.694 RO2-R. + 0.106 RO2-N. + 0.553 R2O2. + 0.2 C2CO-O2. +} \\ & \text{0.019 CO + 0.011 CO2 + 0.011 HCHO + 0.143 CCHO + 0.199 RCHO +} \\ & \text{0.462 MEK + 0.254 PROD2 + 1.353 RO2. + 0.2 RCO3} \end{aligned}$$

Here, C2CO-O2· refers to the lumped higher acyl peroxy radical, RCO3· refers to total acyl peroxy radicals, and the other model species are as indicated above. The derivation of this overall mechanism from the detailed mechanism shown in Table 3 and the n-butyl acetate mechanistic parameters considered in this work is summarized in Table 4 and Figure 3.

Table 3. Reaction mechanism derived for n-butyl acetate

Rxn No	Reactions [a]			Est. Yield
1	CH3-CH2-CH2-CH2-O-CO-CH3 +	->	H2O + CH3-CO-O-CH2-CH2-CH2-	4%
2		->	H2O + CH3-CO-O-CH2-CH2-CH[.]-	25%
3		->	H2O + CH3-CH2-CH[.]-CH2-O-CO-	31%
4		->	H2O + CH3-CH2-CH2-CH[.]-O-CO-	40%
	Radicals formed in Reaction			
5	CH3-CO-O-CH2-CH2-CH2-CH2OO. +	->	CH3-CO-O-CH2-CH2-CH2-CH2-	0%
6		->	NO2 + (various minor	3%
	Radicals formed in Reaction			
7	CH3-CO-O-CH2-CH2-CH[OO.]-CH3 +	->	CH3-CH(ONO2)-CH2-CH2-O-CO-	2%
8		->	NO2 + CH3-CO-O-CH2-CH2-CH[O.]-	23%
9	CH3-CO-O-CH2-CH2-CH[O.]-CH3 +	->	CH3-CO-CH2-CH2-O-CO-CH3 +	12%
10	CH3-CO-O-CH2-CH2-CH[O.]-	->	CH3-CHO + CH3-CO-O-CH2-CH2.	12%
11	CH3-CO-O-CH2-CH2OO. +	->	CH3-CO-O-CH2-CH2-ONO2	1%
12		->	NO2 + CH3-CO-O-CH2-CH2O.	11%
13	CH3-CO-O-CH2-CH2O. +	->	CH3-CO-O-CH2-CHO + HO2.	11%
	Radicals formed in Reaction			
14	CH3-CH2-CH[OO.]-CH2-O-CO-CH3 +	->	CH3-CH2-CH(ONO2)-CH2-O-CO-	3%
15		->	NO2 + CH3-CH2-CH[O.]-CH2-O-CO-	28%
16	CH3-CH2-CH[O.]-CH2-O-CO-CH3 +	->	CH3-CH2-CO-CH2-O-CO-CH3 +	23%
	CH3-CH2-CH[O.]-CH2-O-CO-	->	(various minor	5%
	Radicals formed in Reaction			
17	CH3-CH2-CH2-CH[OO.]-O-CO-CH3 +	->	CH3-CH2-CH2-CH(ONO2)-O-CO-	4%
18		->	NO2 + CH3-CH2-CH2-CH[O.]-O-CO-	37%
19	CH3-CH2-CH2-CH[O.]-O-CO-CH3 +	->	CH3-CH2-CH2-CO-O-CO-CH3 +	1%
20	CH3-CH2-CH2-CH[O.]-O-CO-	->	CH3-CH2-CH2-CHO + CH3. +	1%
21		->	CH3-CO-O-CH(OH)-CH2-CH2-	15%
22		->	CH3-CO-OH + CH3-CH2-CH2-CO.	20%
24	CH3-CO-O-CH(OH)-CH2-CH2-CH2OO. +	->	CH3-CO-O-CH(OH)-CH2-CH2-CH2-	1%
25		->	NO2 + CH3-CO-O-CH(OH)-CH2-CH2-	14%
26	CH3-CO-O-CH(OH)-CH2-CH2-	->	CH3-CO-O-C[.](OH)-CH2-CH2-CH2-	14%
27	CH3-CO-O-C[.](OH)-CH2-CH2-CH2-OH +	->	CH3-CO-O-CO-CH2-CH2-CH2-OH +	14%

[a] R. + O2 -> RO2. Reactions are not shown.



Limited studies: K_{OH}: Atkinson 1989; no product data
q1, q2, q3: estimated by structure-reactivity method
q4: derived from estimated alkoxy radical rate constants
qN, q6: estimated from chamber data

Figure 3. Key features of the n-butyl acetate mechanism used in SAPRC.

Table 4. Parameters and products used for n-butyl acetate

Parm or Product	Represents	Computed Using	Default
Mechanistic Parameters [a]			
q1	k4 / Total kOH	Estimated using structure-reactivity method of Kwok and Atkinson (1995)	0.40
q2	k3 / Total kOH	Estimated using structure-reactivity method of Kwok and Atkinson (1995)	0.31
q4	k9 / k10	Derived from estimated alkoxy radical rate constants (Carter, report in preparation, 1999)	0.50
q6	k22 / (k20+k21+k22)	Adjusted to fit chamber data	0.54
qN	k5/(k5+k6) = k7/(k7+k8) = k14/(k14+k15) = k17/(k17+k18)	Adjusted to fit chamber data	0.09
Product Yields used in Model			
RO2-R.	NO -> NO2 conversions with HO2 formation	Yield(RO2-R.) = 0.0006*(1-qN) + 0.0306*(1-qN) + (0.963-(q1+q2))*(1-qN)*q4 + (0.963-(q1+q2))*(1-qN)*(1-q4)*0.96 + q2*(1-qN)*0.823 + q2*(1-qN)*0.102 + q2*(1-qN)*0.0062 + q2*(1-qN)*0.0688 + q1*(1-qN)*0.031 + q1*(1-qN)*0.029 + q1*(1-qN)*(0.94-q6)*0.95	0.70
R2O2.	Additional NO -> NO2 conversions	Yield(R2O2.) = 0.037*(1-qN) + 0.0321*(1-qN) + (0.963-(q1+q2))*(1-qN) + (0.963-(q1+q2))*(1-qN)*(1-q4)*0.96 + q2*(1-qN) + q2*(1-qN)*0.102 + q2*(1-qN)*0.075 + q1*(1-qN) + q1*(1-qN)*0.029 + q1*(1-qN)*(0.94-q6)*0.95 - Yield(RO2-R.)	0.55
RO2-N.	CH3-CH2-CH2-CH(ONO2)-O-CO-CH3, CH3-CH2-CH(ONO2)-CH2-O-CO-CH3, CH3-CH(ONO2)-CH2-CH2-O-CO-CH3, CH3-CO-O-CH(OH)-CH2-CH2-CH2-ONO2, CH3-CO-O-CH2-CH2-ONO2, CH3-CO-O-CH2-CH2-CH2-CH2-ONO2, and CH3-CO-O-CH(ONO2)-CH2-CH2-CH2-OH	Yield(RO2-N.) = 0.037*qN + 0.0043*(1-qN) + (0.963-(q1+q2))*qN + (0.963-(q1+q2))*(1-qN)*(1-q4)*0.04 + q2*qN + q1*qN + q1*(1-qN)*(0.94-q6)*0.05	0.11
C2CO-O2.	CH3-CH2-CH2-CO[OO.]	Yield(C2CO-O2.) = 0.0015*(1-qN) + q1*(1-qN)*q6	0.20
CO	CO	Yield(CO) = q2*(1-qN)*0.0688	0.02
CO2	CO2	Yield(CO2) = q1*(1-qN)*0.029	0.01
HCHO	HCHO	Yield(HCHO) = q1*(1-qN)*0.029	0.01
CCHO	CH3-CHO	Yield(CCHO) = (0.963-(q1+q2))*(1-qN)*(1-q4) + q2*(1-qN)*0.102	0.14
RCHO	CH3-CO-O-CH2-CHO, CH3-CO-O-CH(OH)-CH2-CH2-CHO, CH3-CH2-CH2-CHO, and CH3-CH2-CHO	Yield(RCHO) = 0.0006*(1-qN) + 0.0306*(1-qN) + (0.963-(q1+q2))*(1-qN)*(1-q4)*0.96 + q2*(1-qN)*0.102 + q2*(1-qN)*0.075 + q1*(1-qN)*0.029	0.20
MEK	CH3-CH2-CO-CH2-O-CO-CH3, CH3-CO-OH, and CH3-CH2-CH2-CO-O-CO-CH3	Yield(MEK) = 0.0015*(1-qN) + q2*(1-qN)*0.823 + q2*(1-qN)*0.0688 + q1*(1-qN)*0.031 + q1*(1-qN)*q6	0.46
PROD2	CH3-CO-CH2-CH2-O-CO-CH3, and CH3-CO-O-CO-CH2-CH2-CH2-OH	Yield(PROD2) = (0.963-(q1+q2))*(1-qN)*q4 + q1*(1-qN)*(0.94-q6)*0.95	0.26
RO2.	Total peroxy radicals	Yield(RO2.) = Yield(RO2-R.) + Yield(RO2-N.) + Yield(q2O2.)	1.35
RCO3.	Total acyl peroxy radicals	Yield(RCO3.) = Yield(C2CO-O2.)	0.20

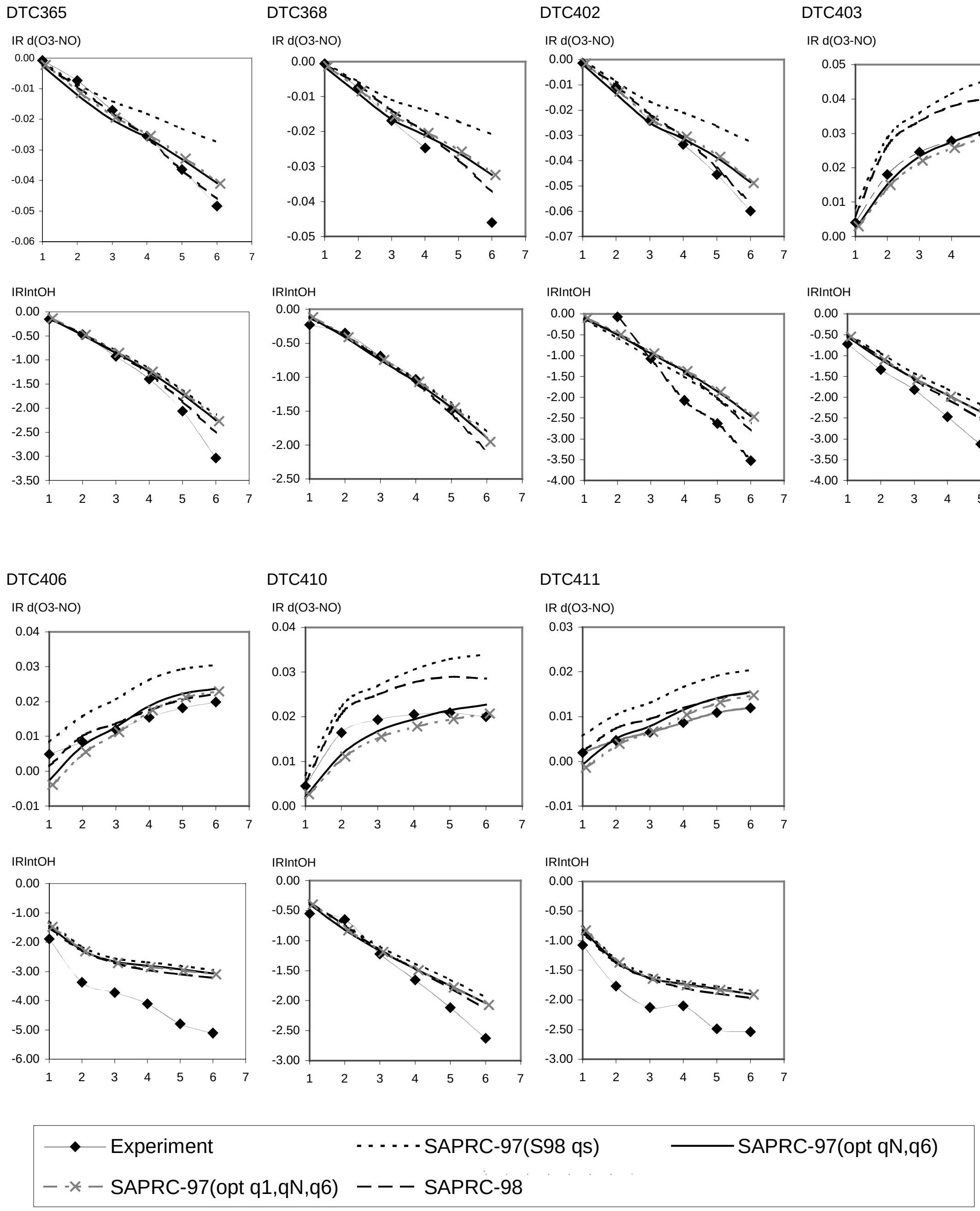
[a] Rate constants refer to reactions on Table 3.

As indicated in Table 4 and Figure 3, five major parameters affecting product yields are considered in our uncertainty analysis for n-butyl acetate. Branching ratios of the initial OH reaction step for CH_3-CH_2-CH_2-CH[.]-O-CO-CH_3 (q1) and CH_3-CH_2-CH[.]-CH_2-O-CO-CH_3 (q2) are estimated based on the structure-reactivity estimation methods given by Kwok and Atkinson (1995). As in the 2-butoxy ethanol reaction, the overall organic nitrate yield from the initially formed peroxy radicals (qN) is estimated from fitting incremental reactivity estimates from environmental chamber experiments. The fraction of the alkoxy radical CH_3-CO-O-CH_2-CH_2-CH[O.]-CH_3 that reacts with O_2 (q4) rather than decomposing to CH_3-CHO + CH_3-CO-O-CH_2-CH_2 is estimated using the alkoxy radical rate constant estimates incorporated in the mechanism generation system (Carter, 1999a). Finally, the fraction of CH_3-CH_2-CH_2-CH[O.]-O-CO-CH_3 undergoing ester rearrangement (q6) instead of isomerizing to CH_3-CO-O-CH(OH)-CH_2-CH_2-CH_2 is also adjusted to fit chamber experimental results. Table 4 shows the formulas for calculating the yields of model species in the overall reaction from the values of these parameters.

Figure 4 shows how the n-butyl acetate mechanism performs with the SAPRC-97 and SAPRC-98 base mechanisms, with values of q6 and qN adjusted to fit the incremental reactivity experiments. As with 2-butoxy ethanol, the parameter values that gave best fits to the data using the SAPRC-98 mechanism were found not to be optimal for SAPRC-97, so the results using the SAPRC-97 mechanism are also shown using best fit parameter values derived in this work.

2.1.3 Chamber Effects Mechanism

As indicated above, the values for some of the uncertain mechanistic parameters in the 2-butoxy ethanol and n-butyl acetate mechanisms were determined by optimization to fit chamber data. The chamber data employed consisted of a series of incremental reactivity experiments



x-axis label: Time (hour)

Figure 4. Performance of the n-butyl acetate mechanism for incremental reactivity experiments in the DTC chamber.

carried out during 1996 and 1997 in the blacklight irradiated DTC (Dividable Teflon Chambers) at the University of California at Riverside (Carter et al., 1998). Carter et al. (1998) estimated the parameters for each reaction by informally fitting the incremental reactivity of the test organic compound across the corresponding sets of experiments, as shown in Figures 2 and 4.

Using experimental data to estimate mechanism parameters requires consideration of the artifacts in the chamber. These artifacts include differences in intensity and spectral distribution between artificial lights and sunlight; artificial radical sources; loss of O_3 and N_2O_5 to the chamber walls; and heteorogeneous conversion of N_2O_5 to HNO_3 and NO_2 to HONO (Carter et al., 1995a). As assumed by Wang et al. (1999), the most critical artifacts in this study are thought to be the chamber-dependent radical sources. Two radical source parameters, RSI and HONO-F, are considered here. RSI represents a NO_2 independent, continuous light-induced release of radicals from the chamber walls (Carter, 1996; Carter et al., 1997). This radical source is described by the reaction $hv \rightarrow OH$ with reaction rate $RSI \times k_1$, where k_1, the NO_2 photolysis rate, is a measure of the light intensity in the experiment. RSI thus has units of concentration, and is given here in ppb units. HONO-F represents the fraction of initial NO_2 converted to HONO prior to irradiation (Carter, 1996; Carter et al., 1997), with results given here in percentage units. The radical sources are estimated from chamber experiments in which the compounds added have insignificant radical sources in their mechanisms. N-butane-NO_x experiments conducted in the DTC at about the same time as the 2-butoxy ethanol and n-butyl acetate runs are used for this purpose (Carter, 1996).

2.2 Chamber Experiments

In this study, incremental reactivities determined from pairs of organic compound-NO_x experiments are used to estimate oxidation parameters for 2-butoxy ethanol and n-butyl acetate. Seven pairs of experiments, for which inputs are summarized in Table 5, were conducted for both of these compounds. In each case, three of the pairs were conducted with relatively high NO_x levels and utilized a three-compound base mixture including n-hexane, ethene and m-xylene. The other four pairs used an eight compound base mixture with n-butane, n-octane, ethene, propene, trans-2-butene, toluene, m-xylene and formaldehyde. One of these pairs was conducted for high NO_x and three for low NO_x conditions. For each experimental pair, the test compound was added to the base mixture in only one of the two bags of the dividable chamber.

N-butane-NO_x and CO-NO_x experiments conducted at about the same time as the n-butyl acetate and 2-butoxy ethanol experiments are used to estimate the radical source parameters. The optimizations were done by minimizing the ratio of the residual between measurements and model results to the maximum value of the measurements.

As listed in Table 6, 12 n-butane-NO_x and two CO-NO_x experiments were used to estimate the radical source parameters for the butyl acetate experiments; 18 n-butane-NO_x experiments were used to estimate them for butoxy ethanol. The sets designated in Table 6 as sets 11, 14 and 15, refer to groups of experiments conducted at about the same time. The values shown for RSI and HONO-F were deterministically adjusted to fit the chamber experiments, using the SAPRC-97 mechanism.

Table 5. Chamber experiments used to estimate mechanism parameters for 2-butoxy ethanol and n-butyl acetate

				Char. Exp.[c]				Initial Concentrations			
Run ID[a]	Test VOC	Type[b]	Date	A	B	k_1	T	NO	Unc.	NO_2	Unc.
DTC365A	BU-ACET	MR3	6/6/96	11	11	0.199	298	0.23	3%	0.08	11%
DTC368B	BU-ACET	MR3	6/11/96	11	11	0.198	299	0.25	3%	0.08	11%
DTC402B	BU-ACET	MR3	8/23/96	11	11	0.190	299	0.26	3%	0.10	11%
DTC403A	BU-ACET	MR8	8/27/96	11	11	0.189	299	0.23	3%	0.06	11%
DTC410B	BU-ACET	MR8	9/10/96	11	11	0.188	298	0.21	3%	0.06	11%
DTC406A	BU-ACET	R8	8/30/96	11	11	0.189	299	0.08	4%	0.04	12%
DTC411A	BU-ACET	R8	9/11/96	11	11	0.187	297	0.06	5%	0.02	14%
DTC491B	BUO-ETOH	MR3	5/20/97	14	15	0.221	298	0.28	3%	0.10	11%
DTC498B	BUO-ETOH	MR3	5/30/97	14	15	0.219	299	0.27	3%	0.11	11%
DTC505B	BUO-ETOH	MR3	6/11/97	14	15	0.217	298	0.28	3%	0.10	11%
DTC493B	BUO-ETOH	MR8	5/22/97	14	15	0.221	297	0.23	3%	0.07	11%
DTC502A	BUO-ETOH	MR8	6/5/97	14	15	0.218	299	0.23	3%	0.07	11%
DTC497A	BUO-ETOH	R8	5/29/97	14	15	0.219	299	0.09	4%	0.04	11%
DTC506A	BUO-ETOH	R8	6/12/97	14	15	0.217	298	0.08	4%	0.04	12%

		Initial Concentrations									
Run ID	Test VOC	Test VOC	Unc.	N-C4	Unc.	N-C6	Unc.	N-C8	Unc.	Ethene	Unc.
DTC365A	BU-ACET	5.88	5%			0.48	13%			0.79	5%
DTC368B	BU-ACET	6.30	5%			0.49	13%			0.80	5%
DTC402B	BU-ACET	3.79	27%			0.43	38%			0.75	5%
DTC403A	BU-ACET	5.15	27%	0.35	5%			0.09	25%	0.06	5%
DTC410B	BU-ACET	7.60	27%	0.33	5%			0.09	15%	0.05	5%
DTC406A	BU-ACET	3.69	27%	0.34	5%			0.09	15%	0.06	5%
DTC411A	BU-ACET	7.72	27%	0.32	5%			0.09	15%	0.05	5%
DTC491B	BUO-ETOH	1.72	12%			0.47	10%			0.87	12%
DTC498B	BUO-ETOH	1.15	12%			0.46	10%			0.26	12%
DTC505B	BUO-ETOH	1.08	12%			0.41	10%			0.84	12%
DTC493B	BUO-ETOH	1.11	12%	0.34	11%			0.10	7%	0.06	12%
DTC502A	BUO-ETOH	0.53	12%	0.34	11%			0.09	12%	0.06	12%
DTC497A	BUO-ETOH	0.86	12%	0.36	11%			0.10	12%	0.07	12%
DTC506A	BUO-ETOH	0.57	12%	0.35	11%			0.10	12%	0.06	12%

[a] A and B refer to different sides of the dual teflon chamber.

[b] MR3 stands for mini surrogate experiment; MR8 full surrogate experiment; R8 full surrogate, low NO_x experiment.

[c] Group of chamber characterization experiments used to estimate radical source parameters for the incremental reactivity experiments. See Table 6.

Table 5. Chamber experiments used to estimate mechanism parameters for 2-butoxy ethanol and n-butyl acetate (continued)

		Initial Concentrations									
Run ID	Test VOC	Propene	Unc.	T-2-Bute	Unc.	Toluene	Unc.	M-Xyle	Unc	HCHO	Unc.
DTC365A	BU-ACET							0.13	16%		
DTC368B	BU-ACET							0.13	16%		
DTC402B	BU-ACET							0.13	20%		
DTC403A	BU-ACET	0.05	5%	0.05	5%	0.08	16%	0.08	30%	0.06	40%
DTC410B	BU-ACET	0.05	5%	0.05	5%	0.08	25%	0.10	14%	0.08	30%
DTC406A	BU-ACET	0.05	5%	0.05	5%	0.08	25%	0.10	14%	0.07	30%
DTC411A	BU-ACET	0.04	5%	0.04	5%	0.07	25%	0.09	14%	0.09	30%
DTC491B	BUO-ETOH							0.14	9%		
DTC498B	BUO-ETOH							0.14	9%		
DTC505B	BUO-ETOH							0.14	9%		
DTC493B	BUO-ETOH	0.05	7%	0.05	9%	0.09	8%	0.09	9%	0.07	30%
DTC502A	BUO-ETOH	0.05	7%	0.05	9%	0.09	10%	0.09	9%	0.07	30%
DTC497A	BUO-ETOH	0.05	7%	0.05	9%	0.09	10%	0.09	9%	0.07	30%
DTC506A	BUO-ETOH	0.05	7%	0.05	9%	0.09	10%	0.09	9%	0.06	30%

Other than the radical source parameters, the most important chamber artifacts are expected to be the intensity and spectral distribution of the artificial lights used in indoor chambers such as the DTC. Blacklights, as used in the DTC, have an unnatural spectrum above about 320 nm. Their relative intensity is too high in the range from 320 - 360 nm and is negligible above 400 nm. Differences between artificial lights and sunlight can be compensated for if the spectral distribution of the light source is characterized and the action spectra of significant photolyzing species are known. The light intensity in the DTC experiments is measured as k_1, using the quartz tube actinometry method of Zafonte et al. (1977). A constant spectral distribution based primarily on measurements made with a LiCor Li-1800 spectroradiometer (Carter et al., 1995b) is also used.

Table 6. Chamber experiments used to estimate radical source parameters for the DTC chamber at the time of the 2-butoxy ethanol and n-butyl acetate experiments

Run	Type	NO_x (ppm)	T (K)	k_1 (min^{-1})	Carter RS-I	Carter HONO-F
DTC Set 11 (Around time of BU-ACET runs)						
DTC347A	N-C4	0.29	298	0.203	0.109	0.5%
DTC347B	N-C4	0.30	298	0.203	0.111	0.6%
DTC357A	N-C4	0.24	298	0.201	0.134	0.2%
DTC357B	N-C4	0.24	298	0.201	0.130	0.1%
DTC373A	N-C4	0.25	298	0.197	0.081	0.3%
DTC373B	N-C4	0.24	298	0.197	0.090	0.2%
DTC383A	CO	0.06	298	0.194	0.058	-
DTC383B	CO	0.06	298	0.194	0.052	-
DTC384A	N-C4	0.25	298	0.194	0.059	0.3%
DTC384B	N-C4	0.25	298	0.194	0.069	0.1%
DTC416A	N-C4	0.25	297	0.186	0.073	0.3%
DTC416B	N-C4	0.25	297	0.186	0.071	0.1%
DTC434A	N-C4	0.25	295	0.180	0.125	-
DTC434B	N-C4	0.25	295	0.180	0.102	0.1%
DTC Set 14 (Around time of BUO-ETOH runs)						
DTC473A	N-C4	0.29	297	0.227	0.105	0.9%
DTC482A	N-C4	0.27	298	0.224	0.093	-
DTC494A	N-C4	0.27	298	0.220	0.094	-
DTC518A	N-C4	0.28	299	0.213	0.087	-
DTC545A	N-C4	0.27	299	0.205	0.078	0.0%
DTC555A	N-C4	0.24	299	0.202	0.076	-
DTC566A	N-C4	0.23	299	0.199	0.084	0.6%
DTC571A	N-C4	0.26	298	0.197	0.073	0.4%
DTC587A	N-C4	0.27	297	0.193	0.078	-
DTC Set 15 (Around time of BUO-ETOH runs)						
DTC473B	N-C4	0.29	297	0.227	0.073	1.1%
DTC482B	N-C4	0.27	298	0.224	0.062	0.1%
DTC494B	N-C4	0.27	298	0.220	0.068	0.2%
DTC518B	N-C4	0.28	299	0.213	0.068	-
DTC545B	N-C4	0.27	299	0.205	0.063	0.4%
DTC555B	N-C4	0.24	299	0.202	0.076	-
DTC566B	N-C4	0.23	299	0.199	0.049	1.2%
DTC571B	N-C4	0.26	298	0.197	0.051	0.8%
DTC587B	N-C4	0.27	297	0.193	0.024	0.5%

2.3 Stochastic Programming

Determining optimal estimates with uncertainties for chamber characterization and organic compound mechanism parameters is a stochastic parameter estimation problem (Figure 5). The inner loop is used to provide optimal parameter estimates for a given sample of random mechanism and experimental variables. The outer loop provides the samples. The procedure terminates when the probability distribution functions of the optimal parameter values are determined. Regression analysis is then used to identify the major sources of uncertainty in the parameter estimates and thus provide guidance for designing new experiments.

The parameter estimation problem is defined in this study as minimizing the weighted squares of the differences between the model results and experimental measurements (Bard, 1974):

$$\begin{aligned} &\min \; f\left(\underline{\kappa},\underline{\theta},\underline{P};t\right)=\sum_{i=1}^{NC}\underline{X}^{(i)T}\,\underline{W}^{(i)}\,\underline{X}^{(i)} \\ &s.t. \quad \underline{P_L} \le \underline{P} \le \underline{P_U} \end{aligned} \qquad (1)$$

where f is the objective function; $\underline{P}$ is the vector of parameters to be estimated; $\underline{\kappa}$ is the vector of other model parameters and experimental conditions with uncertainty; $\underline{\theta}$ is the vector of parameters and experimental conditions treated as fixed; and t is time. $\underline{P}_L$ and $\underline{P}_U$ are the lower and upper bounds for $\underline{P}$, respectively. In the right-hand-side of eqn. 1, NC is the number of criteria, $C^{(i)}$, used to compare model and experimental results; $\underline{X}^{(i)} = \underline{C_s}^{(i)}(\underline{\kappa}, \underline{\theta}, \underline{p}; t) - \underline{C}_e^{(i)}(t)$ is the vector of residuals; and $\underline{W}^{(i)}$ is the diagonal matrix of weight factors applied for criterion i.

In this study, the primary comparison criterion used is the incremental reactivity with respect to $D(O_3\text{-}NO)$ of the test compound, $IR[D(O_3\text{-}NO)]$. The quantity $D(O_3\text{-}NO)_t$ is defined as the amount of ozone formed plus the amount of NO consumed at time t, that is $D(O_3\text{-}NO)_t$ =

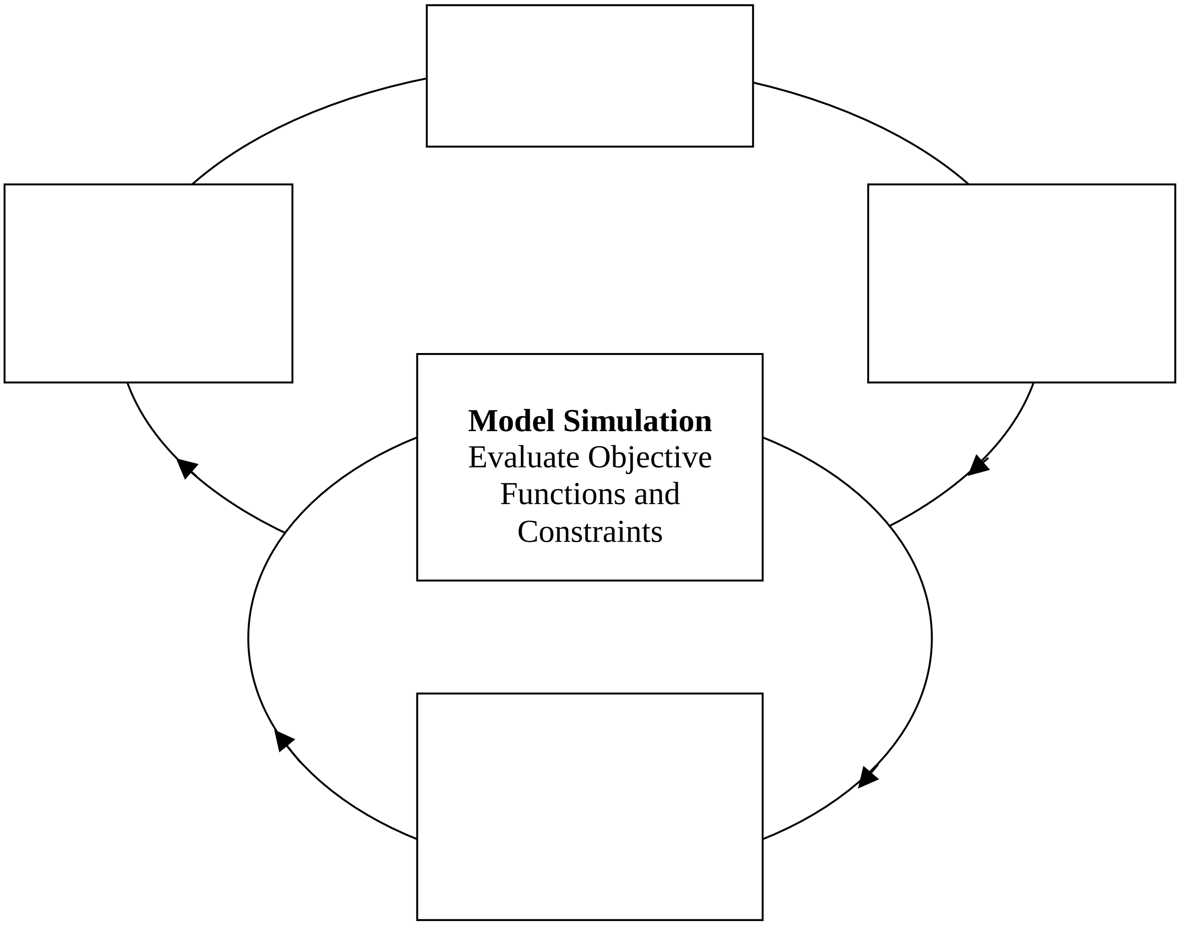


Figure 5. Schematic diagram of the study approach using stochastic programming.

$[O_3]_t$ – ($[NO]_t$ - $[NO]_0$). The incremental reactivity with respect to D(O_3-NO) at time t is determined from pairs of experiments or simulations as:

$$IR[D(O_3 - NO)]_t^{VOC} = \frac{D([O_3]-[NO])_t^{test} - D([O_3]-[NO])_t^{base}}{[VOC]_{test}} \qquad (2)$$

where the differences are between the experiment or simulation with the base mixture of organic compounds and the experiment or simulation with the test compound added. A second comparison criterion is incremental reactivity with respect to OH radical levels, which is an important factor because radical levels affect how rapidly all VOCs present, including the base VOC components, react to form ozone (Carter et al., 1995c). The overall OH radical level is defined as the integrated OH radical concentration, INTOH:

$$INTOH_t = \int_0^t [OH]_\tau \, d\tau \qquad (3)$$

Estimates of INTOH are derived from the rate of consumption of m-xylene:

$$INTOH_t = \frac{\ln\left(\frac{[m-xylene]_0}{[m-xylene]_t}\right) - Dt}{KOH^{m-xylene}} \qquad (4)$$

where D is the dilution rate and $KOH^{m\text{-}xylene}$ is the rate constant for the reaction m-xylene+OH. Then similarly the incremental reactivity with respect to INTOH at time t is calculated from pairs of experiments or simulations as:

$$IR[INTOH]_t^{VOC} = \frac{INTOH_t^{test} - INTOH_t^{base}}{[VOC]_{test}} \qquad (5)$$

For this study, the subjective estimate was made that the experimental data for D($[O_3]$-[NO]) are three times as reliable as those for INTOH, so the objective function used is:

$$f(\kappa,\theta,P;t)=\sum_{i=1}^{N}\sum_{j=1}^{Tend}\left(\begin{array}{l} 0.75\left(\dfrac{IR[D(O3-NO)]e_{i,j}-IR[D(O3-NO)]s_{i,j}}{\underset{over\ \ j}{MAX}[ABS(IR[D(O3-NO)]e_{i,j})]}\right)^2 \\ +0.25\left(\dfrac{IR[INTOH]e_{i,j}-IR[INTOH]s_{i,j}}{\underset{over\ \ j}{MAX}[ABS(IR[INTOH]e_{i,j})]}\right)^2 \end{array}\right) \tag{6}$$

where i=1,…,N is the ith pair of experiments, j=1,…,T_{end} is the jth time interval from a given experiment, e denotes an experimental observation and s a simulation result. As indicated in eqn. 6, the residuals are normalized by the maximum value in each experiment of the absolute value of the incremental reactivity.

Uncertainty estimates for RSI and HONO-F used in estimating the n-butyl acetate and 2-butoxy ethanol parameters must reflect how the radical source parameters vary from experiment to experiment as well as how they respond to input uncertainties. RSI and HONO-F are thus optimized for each characterization experiment listed in Table 6, as:

$$\min \sum_{t=0}^{tend^i}\left(D([O_3]-[NO])^i{}_{e(t)}-D([O_3]-[NO])^i{}_{s(t)}\right)^2 \tag{7}$$

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

Then in estimating the parameters of the solvent mechanisms, values of RSI and HONO-F for the kth Monte Carlo run are sampled from distributions with averages and standard deviations given by:

$$\overline{P}_k=\frac{\sum_{i=1}^{N}W^iP_k{}^i}{\sum_{i=1}^{N}W^i} \tag{8}$$

$$\sigma_{\overline{P}_k} = \sqrt{\frac{\sum_{i=1}^{N} W^i (P_k{}^i - \overline{P}_k)^2}{\sum_{i=1}^{N} W^i}} \tag{9}$$

where P_k^i is the estimated value for parameter P for the kth sample and ith experiment and W^i is the weight factor for the ith experiment. The same values of RSI and HONO-F are used for the test and base case of each incremental reactivity experiment. The mean values and associated variances reported below for the estimated chamber characterization parameters are the average and variance of $\overline{P}_k$ across all of the Monte Carlo samples.

The incremental reactivities for the test compounds depend in a strongly nonlinear manner on the parameters to be estimated, so eqn. 6 and 7 represent nonlinear programming (NLP) problems. Successive quadratic programming (SQP) (Han 1977, Powell 1977) is used to solve these problems because of its fast convergence rate and widespread use for chemical process applications (Biegler et al. 1983). In the SQP 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 subproblem is solved for each step to obtain the next trial point. This cycle is repeated until the optimum is reached. The decision variables in this study are parameters such as pN and qN and q6 for the reactions of 2-butoxy ethanol and n-butyl acetate. These parameters determine the product yields of the compounds' reactions with OH, but do not show up directly in the mechanism. So, each time the parameters being estimated are changed during the optimization routine, the corresponding product yields for the reactions are calculated according the relationships given in Tables 2 and 4.

Monte Carlo analysis with Latin hypercube sampling (LHS; Yang et al., 1995; Iman et al. 1984) is used for the uncertainty analysis loop in Figure 5. Before performing the Monte Carlo simulations, first order uncertainty analysis is used to identify the most influential parameters.

The number of input random variables can then be limited without neglecting significant sources of uncertainty (Yang et al., 1995). Given a specified number of uncertain input parameters, LHS further reduces the Monte Carlo computational requirements through selective representative sampling.

2.4 Input Parameter Uncertainties for Stochastic Programming

The sources of uncertainty considered in this study include the parameters of the SAPRC-97 mechanism and the conditions of the incremental reactivity experiments. The uncertainty estimates for mechanism parameters shown in Tables 7 and 17 are compiled primarily from expert panel reviews (Atkinson, 1989; DeMore et al., 1994; DeMore et al., 1997; Stockwell et al., 1994). The compilation provided by Stockwell et al. (1994) for the SAPRC-90 mechanism was updated for this study. Specific updates for influential parameters are identified below.

Uncertainty estimates made by Carter (1999b) for the mechanistic parameters for 2-butoxy ethanol and n-butyl acetate are given in Appendix A. Two sets of estimates are given in Appendix A for 2-butoxy ethanol, one accounting for the available experimental product data and one assuming these data do not exist. The uncertainty estimates that account for the available experimental data were used in the stochastic programming calculations to estimate 2-butoxy ethanol parameters from the chamber data.

M-xylene, a component of the base mixture used in the incremental reactivity experiments, has key mechanistic parameters that are estimated from chamber experiments in a manner similar to the n-butyl acetate and 2-butoxy ethanol parameters considered here. Uncertainty estimates calculated by Wang et al. (1999) using stochastic programming were used for the chamber-derived parameters of the m-xylene mechanism.

Uncertainty estimates for experimental conditions were estimated for this study. Uncertainty estimates for light intensity (k_1), initial NO, NO_2 and VOC concentrations of the incremental reactivity experiments are listed in Table 5. The light intensity uncertainty estimates are based on the reproducibility of the quartz tube actinometry measurements. The uncertainties in the initial NO_x concentrations reflect the span and zero calibration errors of the Teco Model 14B chemiluminescent NO/NO_x monitor and the converter efficiency for NO_2. Uncertainties in the initial hydrocarbon concentrations primarily reflect calibration errors in the GC FID detectors. Uncertainties in temperature were also considered but found to be negligible. Wang et al. (1999) examined uncertainties in the spectral distribution of the chamber light source but found them to be small compared to the action spectra uncertainties for the photolyzing species.

Before the stochastic programming runs to estimate the 2-butoxy ethanol and n-butyl acetate parameters, a first order sensitivity analysis was performed to identify the parameters likely to be influential for the stochastic programming. The sensitivity analysis was performed for both the base case and test case of each incremental reactivity experiment performed for n-butyl acetate and 2-butoxy ethanol. First-order sensitivity coefficients indicating the response of O_3 concentrations to small variations in each of 208 input parameters or variables were calculated using the Direct Decoupled Method (Dunker, 1984). The variables considered included 183 reaction rate constants, 15 experimental conditions, 4 chamber-derived oxidation parameters for m-xylene and toluene, 5 mechanistic parameters for n-butyl acetate and 4 mechanistic parameters for 2-butoxy ethanol. 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 38 parameters shown below in Table 7 account for more than 95% of the uncertainty in the simulated O_3 concentrations for all of the incremental reactivity experiments used in this study.

Among these influential parameters, the solvent parameters are treated as outputs, i.e., they are the parameters that are to be estimated. The other potential influential parameters identified in Table 7 are treated as random input variables with lognormal distributions for the reaction rate constants and chamber-derived aromatics parameters, and normal distributions for the initial concentrations.

Several uncertain input variables are influential for both the radical source parameters and the butyl acetate or butoxy ethanol parameters (Table 7). The relationship found between these input variables and the radical source parameters must be maintained in estimating the parameters for the solvents. To accomplish this, LHS samples are generated including all of the random variables for both stages of the analysis, except for the values of RSI and F-HONO. For use in the solvent parameter estimation, the values for RSI and HONO-F are drawn from the distributions determined in the first stage for each run in the Monte Carlo sample. Expressions for the mean and standard deviation of these distributions are given in eqns. 8 and 9. The chamber-derived aromatics oxidation parameters for m-xylene were estimated in a previous study (Wang et al., 1999) and found to be highly correlated with reaction rate constants for NO_2+OH and m-xylene+OH. These correlations are maintained in this study through LHS samples. Table 8 gives detailed information on the correlations between the input parameters.

Table 7. Influential parameters identified by first order sensitivity analysis

Parameter[a]	Uncertainty Reference	Coefficient of Variance (σ/κ)	Radical Source Parameters	BU-ACET	BUO-ETOH
NO_2 + hv (light intensity)	Wang et al. (1999)	0.12	X [b]	X	X
O_3 + NO	DeMore et al 1997	0.10	X	X	X
O_3 + NO_2	DeMore et al 1997	0.14	X	X	X
HONO + hv (action spectra)	DeMore et al 1997		X		
NO_2 + OH	DeMore et al. 1994	0.27	X	X	X
HO_2 + NO	DeMore et al. 1994	0.18	X	X	X
HNO_4	DeMore et al. 1994	2.40	X	X	X
HO_2 + O_3	DeMore et al 1997	0.27			X
RO2 + NO	DeMore et al 1997	0.42			X
RO_2+HO_2	DeMore et al 1997	0.75		X	X
HCHO + hv	DeMore et al 1997	0.34		X	X
CCHO + OH	DeMore et al 1997	0.18		X	X
CCOO2 + NO	DeMore et al 1997	0.34		X	X
CCOO2 + NO_2	DeMore et al. 1994	0.16		X	X
PAN	Bridier et al. 1991 Grosjean et al. 1994	0.40		X	X
C2COO2+NO_2	Stockwell et al. 1994	0.75		X	
PPN	Grosjean et al. 1994	0.66		X	
CRES + NO_3	Stockwell et al. 1994	0.75		X	
NC_4 + OH	Stockwell et al. 1994	0.18	X	X	X
PROPENE + OH	Stockwell et al. 1994	0.14			X
T2BUTE + OH	Stockwell et al. 1994	0.18		X	X
T2BUTE + O_3	Stockwell et al. 1994	0.42		X	X
MXYLENE + OH	Stockwell et al. 1994	0.23		X	X
PROD2 + OH	Carter 1999	1.33		Y[c]	X
BU-ACET + OH	Carter 1999	0.25		X	
BUO-ETOH + OH	Carter 1999	0.25			X
SC(AFG2, MXYLENE)	Wang et al. (1999)	0.31		X	X
SC(MGLY, MXYLENE)	Wang et al. (1999)	0.29		X	X
Initial NO_2	This Study	~ 11%		X	X
Initial NO	This Study	~ 10%		X	X
Initial HCHO	This Study	30% - 40%		X	X
Initial ETHE	This study	12%			X
Initial TOLUENE	This Study	16% - 25%		X	
Initial MXYLENE	This Study	9% - 30%		X	X

Table 7. (Cont'd.) Influential parameters identified by first order sensitivity analysis

Parameter[a]	Uncertainty Reference	Coefficient of Variance (σ/κ)	Radical Source Parameters	BU-ACET	BUO-ETOH
Initial BU-ACET	This Study	10% - 27%		X	
Initial BUO-ETOH	This Study	12%			X
RSI	This Study			X	X
HONO-F	This Study			X	X
Solvent parameters	Carter 1999			q1, qN, q6	pN

[a] When a reaction label is shown, the parameter is the rate constant for that reaction. SC indicates the stochiometric coefficient for the product of the OH reaction of the identified organic compound SC(product,reactant)

[b] X indicates the parameter is treated as a random variable in stochastic parameter estimation

[c] Although first order sensitivity analysis finds the parameters noninfluential for ozone concentrations in the chamber experiments, it is treated as a random variable in stochastic estimation, since it is thought to be influential for calculated incremental reactivities.

Table 8. Correlation among input parameters for chamber-derived parameters

Parameter	COV[a]	Correlated Parameter	COV[a]	Correlation
CCOO2 + NO ->	0.34	CCOO2 + NO_2 ->	0.16	0.7
SC(AFG2, m-xylene)	0.33	m-xylene + OH ->	0.23	-0.63
SC(AFG2, m-xylene)	0.33	NO_2 + OH ->	0.27	0.55
SC(MGLY, m-xylene)	0.31	m-xylene + OH ->	0.23	-0.55
SC(MGLY, m-xylene)	0.31	NO_2 + OH ->	0.27	0.50

[a] COV = Coefficient of Variance

The first order analysis identified three different types of uncertainty as influential. The treatment of random (e.g., random experimental errors), systematic (e.g., calibration errors) and global (e.g., rate parameter) uncertainties in the Latin hypercube sampling procedure is discussed in detail by Wang et al. (1999). Briefly, the uncertainty in the chamber light intensity is considered to be systematic, and so is perfectly correlated across all of the experiments carried out at about the same time . Likewise, the initial concentrations listed in Table 7 are assumed to have systematic uncertainties. For a given species, e.g., NO_2, the initial concentrations used in the experiments conducted at about the same time are perfectly correlated. Although slightly different optimal values of RSI and HONO-F have been found for the two sides of the DTC in pairs of chamber characterization experiments, the same LHS sample values of RSI and HONO-F are used for the base and test case members of each incremental reactivity experimental pair. The differences in RSI and HONO-F found between sides of the DTC are small compared to the variability across separate experiments (see Table 6). Except for photolysis rates, the rate parameters of the SAPRC-97 mechanism are treated as global random variables, i.e. in a given sample they are assigned the same value for all of the experiments.

2.5 Incremental Reactivity Calculations

The experimental incremental reactivities are calculated based on concentration measurements and according to eqns. 2 and 5. For each sample, the SAPRC-97 mechanism is used to simulate the base VOC mixture-NO_x experiment and the corresponding experiment with the test VOC added to the base mixture. Then according to eqns. 2 and 5, the simulated incremental reactivities are calculated by taking the difference of the calculated concentrations.

The atmospheric incremental reactivity (IR) of compound j is defined as the change in ozone associated with the addition of a small amount of the compound j ($\Delta[VOC_j]$) to a base mixture of volatile organic compounds, in the presence of NO_x and sunlight:

$$IR_j = \lim_{\Delta[VOC_j]\to 0} \frac{[O_3]_{[base\ VOC]+\Delta[VOC_j]} - [O_3]_{[base\ VOC]}}{\Delta[VOC_j]} = \frac{\partial[O_3]}{\partial[VOC_j]} \qquad (10)$$

In this study, the atmospheric incremental reactivities are estimated as the local sensitivity of the predicted ozone concentration to the initial concentrations of each organic compound in a mixture (Yang et al., 1995).

Three incremental reactivity scales (Carter, 1994) representing different conditions of NO_x availability are evaluated in this study. The maximum incremental reactivity (MIR) scale is calculated using NO_x levels adjusted to maximize the overall incremental reactivity of the base VOC mixture. MIRs are typically observed at relatively low VOC/NO_x ratios (~ 3-6 ppmC/ppm). The maximum ozone incremental reactivity scale (MOIR) is calculated for NO_x conditions that yield the maximum O_3 concentration with the base VOC mixture, which occurs at higher VOC/ NO_x ratios (~ 5-8 ppmC/ppm). The equal benefit incremental reactivity (EBIR) is defined for the NO_x conditions where VOC and NO_x reductions are equally effective in reducing ozone. The simulation conditions used for the MIR, MOIR and EBIR cases are given in Table 9 and represent average conditions from 39 cities (Carter, 1994). The incremental reactivities of selected organic compounds including n-butyl acetate and 2-butoxy ethanol are calculated as local sensitivities to initial conditions using the Direct Decoupled Method (Dunker, 1984) as described by Yang et al. (1995).

For control strategy analyses, the relative reactivity, R_IR, of a given VOC compared to that of a base mixture may be of greater relevance than the absolute incremental reactivity:

$$R\_IRj = \frac{IR_j}{IR_{base\ VOC}} \qquad (11)$$

The base VOC mixture used in this study is the mixture of reactive organic gases initially present or emitted in the scenarios (Table 9), excluding biogenic VOCs and VOCs present aloft. The scenarios are the same as those used by Wang et al. (1999).

Table 9 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) [a]	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	α–pinene	1.0×10^{-4}	0.0
NO (MIR)	1.29×10^{-1}	0.0	Unknown biogenic	1.0×10^{-4}	0.0
HONO (MIR)	3.50×10^{-3}	0.0	HCHO	6.48×10^{-3}	2.25×10^{-3}
NO_2 (MOIR)	2.85×10^{-2}	0.0	CCHO [d]	3.90×10^{-3}	3.23×10^{-4}
NO (MOIR)	8.55×10^{-2}	0.0	RCHO [e]	2.30×10^{-3}	0.0
HONO (MOIR)	2.33×10^{-3}	0.0	ACET	2.52×10^{-3}	0.0
NO_2 (EBIR)	1.94×10^{-2}	0.0	MEK	8.98×10^{-4}	0.0
NO (EBIR)	5.82×10^{-2}	0.0	BALD	1.34×10^{-4}	0.0
HONO (EBIR)	1.58×10^{-3}	0.0	ALK1 [f]	5.53×10^{-2}	3.55×10^{-3}
O_3	0.0	7.04×10^{-2}	ALK2 [f]	1.64×10^{-2}	1.64×10^{-4}
CO	2.03	0.5	ARO1 [g]	1.11×10^{-2}	2.22×10^{-4}
CO_2 [c]	330	330	ARO2 [g]	1.34×10^{-2}	1.11×10^{-4}
H_2O	$1.99\times10^{+4}$	0.0	OLE1 [h]	1.10×10^{-2}	4.67×10^{-4}
methane [c]	1.79	1.79	OLE2 [h]	8.86×10^{-3}	8.09×10^{-5}
isoprene	1.26×10^{-3}	1.09×10^{-4}	OLE3 [h]	1.03×10^{-2}	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 10h 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

[e] Propionaldehyde and higher aldehydes

[f] Lumped classes of alkanes

[g] Lumped classes of aromatics

[h] Lumped classes of alkenes

2.6 Linear Multivariate Regression Analysis

Linear multivariate regression analysis is applied to the stochastic parameter estimation results to identify the influence of the random variables on the optimal values of the parameters. As explained by Wang et al. (1999) the standardized regression model is used for this analysis unless the variance inflation factor (VIF) is greater than 3.0, indicating the presence of multi-collinearity between the explanatory random variables. In that case, ridge regression is used.

3. Results

3.1 Parameter Estimation for Chamber Characterization Parameters

In the first stage of this study, radical source parameters were estimated for the DTC chamber for the time periods during which the n-butyl acetate and 2-butoxy ethanol incremental reactivity experiments were conducted. Eqn. 7 was used as the objective function for these calculations. The input random variables considered were those identified by Wang et al. (1999) as influential for predicting ozone concentrations in the chamber characterization runs and are listed in Table 7. The optimal radical source parameters and associated uncertainties for the individual experiments are shown in Table 10. For the chamber radical source experiments conducted at about the same time as the n-butyl acetate experiments, the average optimal values are 0.087 ppb for RSI and 0.27% for HONO-F. The average uncertainties in the optimal values across these experiments are about 33% of the mean for RSI and 78% for HONO-F. Similar values were obtained for the set of chamber characterization experiments conducted at about the same time as the 2-butoxy ethanol experiments. The average optimal values for the third set of experiments are 0.057 ppb for RSI and 0.60% for HONO-F. The average uncertainties in the

Table 10. Mean and standard deviation of the stochastic parameter estimation results for RSI and HONO-F, for individual chamber characterization experiments

Run	Opt. RSI (ppb)			Opt. HONO-F (%)		
	Mean	Std. Dev	COV (%)	Mean	Std. Dev.	COV (%)
DTC347A	0.114	0.038	33.0	0.578	0.306	52.8
DTC347B	0.115	0.038	32.8	0.672	0.321	47.8
DTC357A	0.139	0.042	30.4	0.374	0.386	103.0
DTC357B	0.135	0.041	30.2	0.272	0.308	113.1
DTC373A	0.084	0.029	34.6	0.362	0.259	71.7
DTC373B	0.094	0.031	32.9	0.264	0.263	99.7
DTC383A	0.067	0.029	43.1	0.073	0.291	397.2
DTC383B	0.061	0.026	43.1	0.001	0.012	946.2
DTC384A	0.061	0.020	33.4	0.395	0.238	60.4
DTC384B	0.072	0.023	31.6	0.177	0.181	102.3
DTC416A	0.075	0.026	34.3	0.448	0.273	61.1
DTC416B	0.074	0.024	31.8	0.198	0.191	96.4
DTC434A	0.131	0.034	25.6	0.063	0.131	207.0
DTC434B	0.107	0.029	26.6	0.181	0.211	116.6
Weighted Average	**0.087**	**0.028**	**32.5**	**0.272**	**0.212**	**78.1**
DTC473A	0.112	0.045	39.9	0.976	0.194	19.8
DTC482A	0.096	0.029	30.1	0.119	0.195	163.7
DTC494A	0.097	0.028	29.3	0.146	0.236	161.4
DTC518A	0.090	0.025	28.2	0.082	0.174	211.4
DTC545A	0.080	0.023	29.1	0.164	0.247	150.2
DTC555A	0.078	0.022	28.9	0.146	0.229	156.3
DTC566A	0.087	0.028	32.4	0.660	0.350	53.0
DTC571A	0.077	0.028	37.0	0.412	0.221	53.5
DTC587A	0.081	0.024	29.4	0.091	0.196	215.5
Weighted Average	**0.087**	**0.028**	**31.7**	**0.314**	**0.212**	**67.6**
DTC473B	0.078	0.035	45.6	1.216	0.260	21.4
DTC482B	0.065	0.021	32.8	0.185	0.191	103.2
DTC494B	0.071	0.022	31.3	0.238	0.244	102.3
DTC518B	0.071	0.020	28.5	0.036	0.104	288.6
DTC545B	0.064	0.021	32.5	0.549	0.328	59.7
DTC555B	0.079	0.023	29.7	0.102	0.190	186.4
DTC566B	0.050	0.019	38.1	1.335	0.358	26.8
DTC571B	0.053	0.020	38.5	0.854	0.229	26.8
DTC587B	0.025	0.012	47.0	0.521	0.222	42.6
Weighted Average	**0.057**	**0.020**	**35.6**	**0.604**	**0.212**	**35.2**

optimal values for this third set of experiments are about 35% of the mean for both RSI and HONO-F.

The mean values estimated by stochastic programming are similar to those estimated deterministically by Carter (Table 6). A regression analysis was not performed for RSI and HONO-F in this study, but a previous study (Wang et al., 1999) showed that optimal values of RSI for the DTC chamber are sensitive to uncertainties in the rate parameters for NO_2+OH, n-butane+OH or CO+OH, and NO_2+hv (or light intensity). The most influential parameters for the average HONO-F values in the DTC chamber are the rate parameters for HONO+hv (action spectra), n-butane+OH, NO_2+OH and NO_2+hv.

3.2 Parameter Estimation for Solvent Parameters

As discussed above, in the first-order sensitivity analysis qN, q1 and q6 were found to be influential to ozone formation in the n-butyl acetate experiments. Two parameters, qN and q6 are treated as the primary parameters to be estimated from the chamber experiments. In the SAPRC-98 mechanism, the value of q1 has been estimated from structure-activity relationships. The effect of this estimate on the optimal values of qN and q6 is tested here by also considering a case in which all three parameters are estimated from the experimental data. The only influential parameter in the 2-butoxy ethanol mechanism found by the first-order analysis was the nitrate yield, pN.

With the random variables listed in Table 7 and the objective function given in eqn. 6, the optimal value of pN for 2-butoxy ethanol was calculated to be 0.134±0.024. In comparison, the value used by Carter in SAPRC98 is 0.127. Ridge regression results shown in Table 11 indicate that the 18% uncertainty calculated for the nitrate yield results primarily from uncertainty in the radical source parameters estimated for the DTC, the formaldehyde action spectra, the NO_2

photolysis rate or experimental light intensity, and the initial NO_2 concentrations. Of the total uncertainty, approximately 40% is due to the chamber radical effects.

Table 11 Ridge regression analysis for the optimal organic nitrate yield from 2-butoxy ethanol (pN = 0.134 ± 0.024; Adjusted R^2 = 0.85)

Parameter	COV(σ/μ)[a]	Std. Reg. Coef.[a]	UC (%)[a]
RSI for Set 15	0.36	0.4840	23.4
HONO-F for Set 15	0.35	0.3792	14.4
HCHO + hv ->	0.34	0.2905	8.5
NO_2 + hv ->	0.12	0.2290	5.3
HONO-F for Set 14	0.68	-0.2190	4.8
RSI for Set 14	0.32	-0.2180	4.8
Initial NO_2	0.11 – 0.12	0.2039	4.2
SC(MGLY, MXYL)	0.29	0.2038	4.2
Initial MXYL	0.10	-0.1440	2.1
NO_2 + OH ->	0.27	0.1376	1.9
HNO_4 ->	2.40	0.1308	1.7
			(SUM > 75%)

[a] COV = Coefficient of Variance
Std. Reg. Coef. = Standardized Regression Coefficient
UC = uncertainty contribution, calculated as the square of the standardized regression coefficient.

Table 12 shows the optimal values for the butyl acetate mechanism parameters calculated using the random variables identified in Table 7. Three sets of estimates are given. First, estimates were obtained for qN and q6 using the objective function shown in eqn. 6. In this case, q1 was set to its nominal value, which was estimated for SAPRC-98 from structure-activity relationships. The two-parameter estimation problem was then repeated, but omitting the IR[INTOH] values from the objective function, to test their influence. Finally, values for q1, q6 and qN were estimated simultaneously using the objective function as given in eqn. 6.

Table 12 Mean and standard deviation of the stochastic parameter estimates for n-butyl acetate parameters.

Parameter	Default Values for SAPRC98	2-parameter estimation with IR[INTOH]	2-parameter estimation without IR[INTOH]	3-parameter estimation with IR[INTOH]
q1	0.402	0.402	0.402	0.538 ± 0.132
q2	0.309	0.309	0.309	0.309
q4	0.500	0.500	0.500	0.500
q6	0.539	0.720 ± 0.223	0.715 ± 0.227	0.644 ± 0.218
qN	0.090	0.127 ± 0.050	0.126 ± 0.050	0.118 ± 0.051
Obj. Fnc. (eqn. 6)	5.380	0.938	0.953	0.891

The estimation results indicate that including IR[INTOH] in the objective function gives slightly lower values of q6 and qN. However, the differences are small compared to the uncertainties in the parameter values. The two parameter estimation approach results in mean values for q6 and qN that are about 34% and 41% higher than those used in SAPRC-98. The mean values for q6 and qN obtained through the three parameter estimation approach are about 10% lower than those obtained with the two parameter estimation approach, while the mean value for q1 is about 34% higher than that used in SAPRC-98. The estimated uncertainties for the three parameters are about 25% for q1, 34% for q6 and 43% for qN. Note that the two-parameter estimation results for q6 and qN (calculated with IR[INTOH] included in the objective function) are used in the incremental reactivity calculations presented below. For q1, the nominal SAPRC-98 value is used in the incremental reactivity calculations.

The distributions of the solvent parameter estimates are shown in Figure 6, which indicates that for many of the Monte Carlo/LHS samples, the optimal mechanistic parameter values for n-butyl acetate reach their lower boundary to make their distribution more like a discrete uniform distribution than a lognormal distribution. On the other hand, pN for 2-butoxy ethanol has a lognormal distribution.

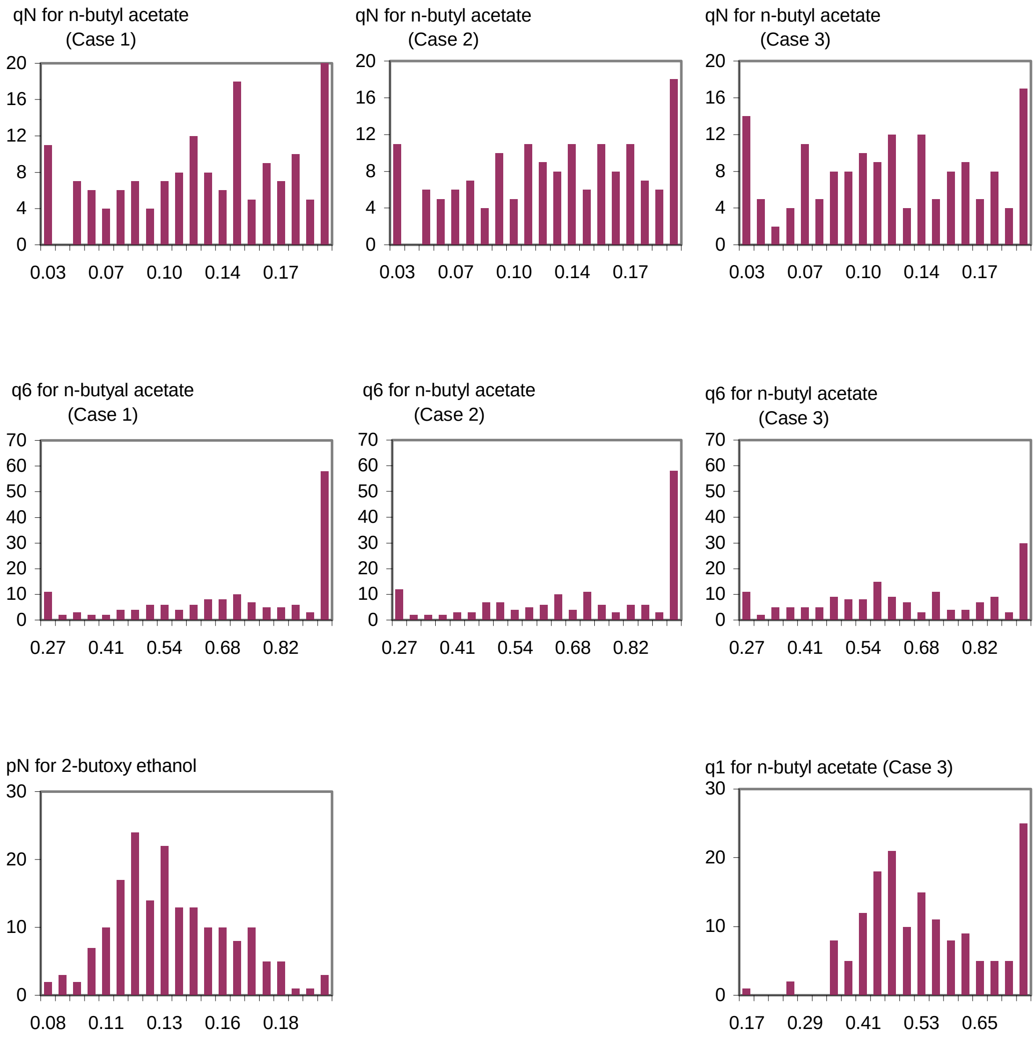


Figure 6. Distribution of the optimal estimates for mechanistic parameters for 2-butoxy ethanol and n-butyl acetate (the x-axis is the values for the mechanistic parameters, the y-axis is the frequency).

Regression analysis was conducted for the two-parameter estimation and three-parameter estimation results that included IR[INTOH] in the objective function. Tables 13 and 14 show that the common influential uncertainty sources for all the estimated parameters include the rate constants for PPN formation and decomposition and PAN formation, the m-xylene initial concentration and the methyl glyoxal yield from m-xylene. The ~40% uncertainty in the optimal value for qN is also due to uncertainties in the rate constants for NO_2+OH and trans-2-butene+O_3, and the initial concentrations of NO_2 and HCHO used in the experiments. The uncertainties in the initial n-butyl acetate concentration and rate constant for HNO_4 decomposition appear influential for qN in the three-parameter estimation problem. Uncertainties in the rate constants for HNO_4 decomposition, n-butyl acetate oxidization, HCHO and NO_2 photolysis (light intensity), RO_2+HO_2, HO_2+NO and CRES+NO_3, and uncertainties in the initial n-butyl acetate concentration are also among the influential uncertainty sources causing the 31% uncertainty in the optimal value for q6. The 25% uncertainty in q1 in the three-parameter estimation problem is also due to uncertainties in the rate constant forO_3+NO and uncertainties in initial concentrations of HCHO, NO and n-butyl acetate.

Table 13 Ridge regression analysis for 2 parameter estimation results for n-butyl acetate parameters (qN = 0.127 ± 0.050, adjusted R^2 = 0.82; q6 = 0.720 ± 0.223, adjusted R^2 = 0.70).

Parameter	COV[a] (σ/μ)	Std. Reg. Coef. [a]	UC (%) [a]
qN			
C2COO2 + NO_2 ->	0.75	-0.4834	23.4
Initial MXYL	0.14 – 0.16	-0.4228	17.9
PPN ->	0.66	0.2591	6.7
NO_2 + OH ->	0.27	0.1941	3.8
SC(MGLY, MXYL)	0.29	0.1809	3.3
T2BUTE+O_3 ->	0.42	0.1735	3.0
CCOO2 + NO ->	0.34	0.1667	2.8
Initial NO_2	0.11 – 0.14	0.1056	1.1
Initial HCHO	0.30 – 0.40	0.1000	1.0
			(SUM > 63%)
q6			
Initial BUACET	0.10 – 0.27	-0.4394	19.3
C2COO2 + NO_2 ->	0.75	-0.3581	12.8
HNO4 ->	2.40	0.2463	6.1
Initial MXYL	0.14 – 0.16	0.2202	4.9
BUACET+OH ->	0.25	0.1621	2.6
NO_2 + hv ->	0.12	0.1561	2.4
RO_2 + HO_2	0.75	-0.1418	2.0
Initial NO	0.10	0.1412	2.0
PAN	0.40	-0.1390	1.9
HCHO + hv ->	0.34	0.1314	1.7
PPN ->	0.66	0.1192	1.4
HO_2 + NO ->	0.18	0.1171	1.4
CRES + NO_3 ->	0.75	0.1125	1.3
$CCOO_2$ + NO ->	0.34	0.1101	1.2
			(SUM > 61%)

[a] COV = Coefficient of Variance
Std. Reg. Coef. = Standardized Regression Coefficent
UC = Uncertainty Contribution

Table 14 Ridge regression analysis for 3 parameter estimation results for n-butyl acetate parameters (q1 = 0.538 ± 0.132, adjusted R^2 = 0.65; qN = 0.118 ± 0.050, adjusted R^2 = 0.82; q6 = 0.644 ± 0.218, adjusted R^2 = 0.75)

Parameter	**COV[a] (σ/μ)**	**Std. Reg. Coef. [a]**	**UC (%) [a]**
q1			
C2COO2 + NO_2 ->	0.75	-0.5478	30.0
Initial BU-ACET	0.10 – 0.27	-0.3072	9.5
Initial NO	0.10	0.2332	5.4
Initial HCHO	0.30 – 0.40	-0.2023	4.1
CCOO2 + NO ->	0.34	0.1677	2.8
PPN ->	0.66	0.1302	1.7
O_3 + NO ->	0.10	-0.1262	1.6
SC(MGLY, MXYL)	0.29	0.1003	1.0
			(SUM > 56%)
qN			
Initial MXYL	0.14 – 0.16	-0.4358	19.0
C2COO2 + NO_2 ->	0.75	-0.4144	17.2
NO_2 + OH ->	0.27	0.2450	6.0
PPN ->	0.66	0.2243	5.0
SC(MGLY, MXYL)	0.29	0.2211	4.9
Initial NO_2	0.11 – 0.14	0.1646	2.7
T2BUTE + O_3 ->	0.42	0.1628	2.7
CCOO2 + NO ->	0.34	0.1472	2.2
HNO4 ->	2.40	-0.1338	1.8
Initial HCHO	0.30 – 0.40	0.0989	1.0
Initial BU-ACET	0.10 – 0.27	0.0952	0.9
			(SUM > 63%)
q6			
Initial BU-ACET	0.10 – 0.27	-0.4407	19.4
HNO_4 ->	2.40	0.3130	9.8
C2COO2 + NO_2 ->	0.75	-0.2789	7.8
BUACET+OH ->	0.25	0.2377	5.7
Initial MXYL	0.14 – 0.16	0.2238	5.0
NO_2 + hv ->	0.12	0.2041	4.2
PPN ->	0.66	0.1553	2.4
CCOO2 + NO ->	0.34	0.1327	1.8
HCHO + hv ->	0.34	0.1348	1.8
CRES + NO_3 ->	0.75	0.1245	1.6
RO_2 + HO_2 ->	0.75	0.1096	1.2
HO_2 + NO ->	0.18	0.1084	1.2
			(SUM > 64%)

[a] COV = Coefficient of Variance
Std. Reg. Coef. = Standardized Regression Coefficent
UC = Uncertainty Contribution

3.3 Incremental Reactivity Estimates

3.3.1 Deterministic Incremental Reactivity Estimates

In the next step of the analysis, incremental reactivities and associated uncertainties for 2-butoxy ethanol and n-butyl acetate under MIR, MOIR and EBIR conditions are estimated with the SAPRC-97 mechanism. First, deterministic incremental reactivities for 2-butoxy ethanol and n-butyl acetate are estimated using nominal values of SAPRC-97 parameters together with the best estimates of the chamber-derived mechanism parameters from section 3.2, including pN for 2-butoxy ethanol, and qN and q6 for n-butyl acetate ((from the two-parameter estimation with IR[INTOH], see Table 12). The results are listed in Table 15 for comparison with incremental reactivities calculated with SAPRC-98 (Carter, 1998).

Table 15 Deterministic Incremental Reactivites for 2-Butoxy Ethanol and n-Butyl Acetate[a]

VOC	MIR	MOIR	EBIR	R_MIR [b]	R_ MOIR [b]	R_EBIR [b]
SAPRC-97 (This Study)						
2-butoxy ethanol	1.41	0.66	0.46	0.94	1.19	1.34
n-butyl acetate	0.50	0.32	0.23	0.33	0.58	0.67
Base Mixture	1.50	0.55	0.34	1.0	1.0	1.0
SAPRC-98 (Carter 1998)						
2-butoxy ethanol	1.35	0.55	0.35	1.12	1.29	1.42
n-butyl acetate	0.47	0.26	0.17	0.39	0.61	0.71
Base mixture	1.21	0.42	0.24	1.0	1.0	1.0

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

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

The results indicate that the absolute incremental reactivities calculated using SAPRC-97 are generally higher than those calculated using SAPRC-98, while the corresponding relative incremental reactivities calculated using SAPRC-97 are generally lower than those calculated using SAPRC-98. The MIR values calculated here are close to those calculated with SAPRC-98

(Carter, 1998), within a 5% difference. However, the differences in the MOIRs and EBIRs are about 17% and 25% respectively.

3.3.2 Stochastic Incremental Reactivity Estimates

The reliability of the incremental reactivity estimates for 2-butoxy ethanol and n-butyl acetate under MIR, MOIR and EBIR conditions is then investigated using Monte Carlo analysis with Latin hypercube sampling. In the first case, referred to as Case 1 in the following discussion, the uncertainties in the rate parameters of the SAPRC-97 chemical mechanism, including the estimated uncertainties in chamber-derived solvent parameters qN and q6 for n-butyl acetate and pN for 2-butoxy ethanol, were propagated through incremental reactivity calculations. Case 1 represents the condition where the incremental reactivities of 2-butoxy ethanol and n-butyl acetate are constrained by the existing measurements of their rate constants for reaction with OH, their observed product yields and by the chamber experiments used to estimate other product yields.

In order to investigate the effects of the experimental data on the uncertainties of the incremental reactivity estimates, 2-butoxy ethanol and n-butyl acetate incremental reactivities and associated uncertainties are also calculated for two other cases. In Case 2, it is assumed that there are experimental data for the hydroxyl radical reaction rate constants, but no observed product yields or chamber experiments to derive the mechanistic parameters. In Case 3, it is assumed that there are no experimental data for the rate constants or the mechanistic parameters. In cases 2 and 3, estimates from structure-activity relationships are substituted for the observed or experimentally derived parameter values. Associated uncertainty estimates were subjectively made by Carter (1999b).

The parameter values and assigned uncertainties for the three cases are listed in Table 16. The input random variables for the Monte Carlo incremental reactivity calculations are given in Table 17 while their correlations are presented in Table 18. The correlation coefficients used were calculated from standard regression (not ridge regression) including only reaction rate constants as explanatory variables. Due to the limitations of the LHS program, only the correlations higher than 0.3 are preserved in the incremental reactivity calculations.

For each of the three cases described above, 460 LHS Monte Carlo samples were used to estimate the mean values and the associated uncertainties for the absolute and relative MIRs, MOIRs and EBIRs for n-butyl acetate and 2-butoxy ethanol. Incremental reactivities of the base VOC mixture listed in Table 9 are also shown. The results are listed in Table 19. In Case 1, the incremental reactivities are constrained by the experimental data for the key reaction rate constants and mechanistic parameters for 2-butoxy ethanol and n-butyl acetate. The results for Case 2 are constrained by the experimental data for the OH reaction rate constants, while unconstrained by the experimental data for the key mechanistic parameters. The results for Case 3 show the uncertainties in incremental reactivities in the absence of experimental data for the rate constants and the mechanistic parameters. The regression analysis results for the uncertainty in the MIRs and relative MIRs calculated for the three cases are presented in Tables 20 and 21. Regression results for absolute and relative MOIRs and EBIRs calculated for Case 1 are shown in Tables 22 and 23.

Table 16 Cases used for Monte Carlo incremental reactivity calculations [a]

	Case 1	Case 2	Case 3
2-Butoxy Ethanol			
K_{OH} [b]	Based on measurements 2.57×10^{-11} (25%)	Based on measurements 2.57×10^{-11} (25%)	Estimated 2.61×10^{-11} (59%)
Mechanistic parameters	Systematically estimated from measurements and chamber experiments pN: 0.134 (18%) [c, d] p1: 0.58 (fixed) p2: 0.22 (fixed) p3: 0.12 (fixed) p4: 0.04 (fixed) p5: 0.04 (fixed)	Estimated without measurements or chamber experiments pN: 0.096 (60%) [d] p1: 0.366 (39%) [g] p2: 0.365 (39%) [g] p3: 0.162 (54%) [g] p4: 0.048 (58%) [g] p5: 0.059 (58%) [g]	Estimated without measurements or chamber experiments pN: 0.096 (60%) [d] p1: 0.366 (39%) [g] p2: 0.365 (39%) [g] p3: 0.162 (54%) [g] p4: 0.048 (58%) [g] p5: 0.059 (58%) [g]
Correlations between mechanistic parameters and influential rate constants	PN with HCHO+hv 0.34 [c] PN with NO_2+OH 0.40 [c] (see Table 16)	None	None
n-Butyl Acetate			
K_{OH} [b]	Based on measurements 4.20×10^{-12} (25%)	Based on measurements 4.20×10^{-12} (25%)	Estimated 4.20×10^{-12} (59%)
Mechanistic parameters	Systematically estimated from chamber experiments qN: 0.127 (40%) [c,e] q6: 0.720 (31%) [c,e] q1: 0.402 (fixed) q2: 0.309 (fixed) p4: 0.50 (fixed)	Estimated without chamber experiments qN: 0.09 (35%) [d] q6: 0.470 (58%) [f] q1: 0.402 (fixed) q2: 0.309 (fixed) p4: 0.50 (fixed)	Estimated without chamber experiments qN: 0.09 (35%) [d] q6: 0.470 (58%) [f] q1: 0.402 (fixed) q2: 0.309 (fixed) p4: 0.50 (fixed)
Correlations between mechanistic parameters and influential rate constants	qN with $C2COO_2$+NO_2 -0.43 [c] NO_2+OH 0.31 [c] PPN 0.31 [c] q6 with $C2COO_2$+NO_2 -0.34 [c] (see Table 16)	None	None

[a] The values in this table are presented as nominal value (coefficient of variance)

[b] The units for the reaction rate constant are cm^3 $molecule^{-1}$ s^{-1}. These reaction rate constants are treated as lognormally distributed random variables.

[c] Estimated from section 3.2

[d]. Treated as lognormally distributed random variables.

[e]. Treated as discrete uniformly distributed random variables with frequency as shown in Figure 6.

[f]. Treated as uniformly distributed random variables

[g]. These values are the final sample values used for the incremental reactivity calculations. They are produced by the following procedures. First, p1, p2, p3 and (p4+p5) are treated as independently lognormal distributed random variables with about 60% coefficient of variance. Then they are normalized for each sample so that p1+p2+p3+(p4+p5)=1, and p4 = 0.45×(normalized (p4+p5)), p5 = 0.55 × (normalized (p4+P5)).

Table 17 Input random variables for incremental reactivity calculations

Reaction or Coefficients	Coefficient of Variance $(\sigma_i/\kappa_{i\ \mathrm{nominal}})$	Reaction or Coefficients	Coefficient of Variance $(\sigma_i/\kappa_{i\ \mathrm{nominal}})$
O_3 + NO	0.10 (2)[a]	ARO2 + OH	0.27 (3)
O^1D + H_2O	0.18 (2)	OLE2 + OH	0.18 (3)
O^1D + M	0.18 (2)	OLE2 + O_3	0.42 (3)
NO_2 + OH	0.27 (1)	OLE3 + OH	0.23 (3)
CO + OH	0.27 (2)	OLE3 + O_3	0.42 (3)
HO_2 + NO	0.18 (1)	P1U1[d]	0.40 (5)
HO_2 + HO_2	0.27 (2)	SC(AFG1,benzene)[e]	0.33 (5)
HO_2 + HO_2 + H_2O	0.27 (1)	SC(AFG2,toluene)[f]	0.34 (5)
RO_2 + NO	0.42 (2)	SC(MGLY,toluene)[g]	0.31 (5)
RO_2 + HO_2	0.75 (2)	SC(AFG2,ethylbenzene)	0.44 (5)
CRES + NO_3	0.75 (3)	SC(MGLY,ethylbenzene)	0.63 (5)
HCHO + OH	0.23 (2)	SC(AFG2,123-TMB)	0.39 (5)
CCHO + OH	0.18 (2)	SC(MGLY,123-TMB)	0.36 (5)
RCHO + OH	0.35 (3)	SC(AFG2,124-TMB)	0.40 (5)
$CCOO_2$ + NO	0.34 (2)	SC(MGLY,124-TMB)	0.49 (5)
$CCOO_2$ + NO_2	0.16 (1)	SC(AFG2,135-TMB)	0.40 (5)
$CCOO_2$ + HO_2	0.75 (2)	SC(MGLY,135-TMB)	0.29 (5)
$CCOO_2$ + RO_2	0.75 (3)	SC(AFG2,p-xylene)	0.45 (5)
$C2COO_2$ + NO_2	0.75 (3)	SC(MGLY,p-xylene)	0.71 (5)
PPN	0.66 (4)	SC(AFG2,o-xylene)	0.30 (5)
PAN	0.40 (4)	SC(MGLY,o-xylene)	0.43 (5)
NO_2 + hv (action spectra)[b]	0.18 (2)	SC(AFG2,m-xylene)	0.33 (5)
NO_3 + hv[b]	0.42 (1)	SC(MGLY,m-xylene)	0.31 (5)
O_3 + hv[b]	0.27 (2)	SC(AFG1,ARO1)[h]	0.33 (5)
HCHO + hv[b]	0.34 (2)	SC(AFG2,ARO1)[h]	0.29 (5)
CCHO + hv[b]	0.34 (3)	SC(MGLY,ARO1)[h]	0.29 (5)
RCHO + hv[b]	0.34 (3)	SC(AFG2,ARO2)[i]	0.23 (5)
MEK + hv[b]	0.42 (3)	SC(MGLY,ARO2)[i]	0.20 (5)
benzene + OH	0.27 (3)	PROD2 + OH	1.33 (7)
toluene + OH	0.18 (3)	BU-ACET+OH [j]	varied
Ethylbenzene + OH	0.31 (3)	BUO-ETOH+OH [j]	varied
1,2,3-trimethylbenzene + OH	0.31 (3)	q6 for BU-ACET [j]	varied
1,2,4-trimethylbenzene + OH	0.31 (3)	qN for BU-ACET [j]	varied

Table 17. (Cont'd.) Input random variables for incremental reactivity calculations

Reaction or Coefficients	Coefficient of Variance ($\sigma_i/\kappa_{i\ nominal}$)	Reaction or Coefficients	Coefficient of Variance ($\sigma_i/\kappa_{i\ nominal}$)
1,3,5-trimethylbenzene + OH	0.31 (3)	pN for BUO-ETOH [j]	varied
p-xylene + OH	0.31 (3)	p1 for BUO-ETOH [j]	varied
o-xylene + OH	0.23 (3)	p2 for BUO-ETOH [j]	varied
m-xylene + OH	0.23 (3)	p3 for BUO-ETOH [j]	varied
NC_4 + OH	0.18(3)	p4 for BUO-ETOH [j]	varied
ALK2 + OH	0.27 (3)	p5 for BUO-ETOH [j]	varied
ARO1 + OH	0.27 (3)		

[a] The references for the uncertainty estimates are:
(1) DeMore et al. 1994; (2) DeMore et al. 1997; (3) Stockwell et al. 1994;
(4) Grosjean et al. 1994, Brider et al. 1991; (5) Wang et al., 1999 (6) Section 3.2 (qN and q6 for n-butyl acetate are treated as uniform distribution); (7) estimated from Carter 1998

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

[c] Uncertainty is estimated for this study according to the uncertainty classes described by Carter, 1998

[d] Quantum yield for photolysis of model species AFG1

[e] Product yield for model species AFG1 from reaction benzene+OH

[f] SC(AFG2, aromatics) represents the chamber-derived aromatics oxidation parameter B1U2 (the product yield for model species AFG2) from reaction aromatics+OH

[g] SC(MGLY, aromatics) represents the chamber-derived aromatics oxidation parameter B1MG (the product yield for model species MGLY) from reaction aromatics+OH

[h] 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.

[i] 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, 123-trimethylbenzene and 135-trimethylbenzene.

[j] These variables are varied for the three studied cases. (see Table 16).

Table 18 Correlated parameters used in incremental reactivity calculations [a]

Parameter	COV	Correlated Parameter	COV	Correlation
CCOO2 + NO ->	0.34	CCOO2 + NO_2 ->	0.16	0.7
P1U1	0.35	Benzene + OH ->	0.27	-0.58
P1U1	0.35	NO_2 + OH ->	0.27	0.40
SC(AFG1, benzene)	0.26	Benzene + OH ->	0.27	-0.40
SC(AFG1, benzene)	0.26	NO_2 + OH ->	0.27	0.30
SC(AFG2, toluene)	0.33	Toluene + OH ->	0.18	-0.55
SC(AFG2, toluene)	0.33	NO_2 + OH ->	0.27	0.68
SC(MGLY, toluene)	0.28	Toluene + OH ->	0.18	-0.57
SC(MGLY, toluene)	0.28	NO_2 + OH ->	0.27	0.45
SC(AFG2, ethylbenzene)	0.39	Ethylbenzene + OH ->	0.31	-0.73
SC(AFG2, ethylbenzene)	0.39	NO_2 + OH ->	0.27	0.37
SC(MGLY, ethylbenzene)	0.62	Ethylbenzene + OH ->	0.31	-0.43
SC(MGLY, ethylbenzene)	0.62	NO_2 + OH ->	0.27	0.36
SC(AFG2, 123-TMB)	0.37	123-TMB + OH ->	0.31	-0.73
SC(AFG2, 123-TMB)	0.37	NO_2 + OH ->	0.27	0.35
SC(AFG2, 124-TMB)	0.36	124-TMB+OH ->	0.31	-0.72
SC(AFG2, 124-TMB)	0.36	NO_2 + OH ->	0.27	0.36
SC(MGLY, 124-TMB)	0.50	124-TMB+OH ->	0.31	-0.51
SC(MGLY, 124-TMB)	0.50	NO_2 + OH ->	0.27	0.38
SC(AFG2, 135-TMB)	0.38	135-TMB + OH ->	0.31	-0.69
SC(AFG2, 135-TMB)	0.38	NO_2 + OH ->	0.27	0.38
SC(AFG2, p-xylene)	0.41	p-xylene + OH ->	0.31	-0.73
SC(AFG2, p-xylene)	0.41	NO_2 + OH ->	0.27	0.37
SC(MGLY, p-xylene)	0.73	p-xylene + OH ->	0.31	-0.55
SC(MGLY, p-xylene)	0.73	NO_2 + OH ->	0.27	0.31
SC(AFG2, o-xylene)	0.28	o-xylene + OH ->	0.23	-0.70
SC(AFG2, o-xylene)	0.28	NO_2 + OH ->	0.27	0.45
SC(MGLY, o-xylene)	0.43	o-xylene + OH ->	0.23	-0.50
SC(MGLY, o-xylene)	0.43	NO_2 + OH ->	0.27	0.44
SC(AFG2, m-xylene)	0.31	m-xylene + OH ->	0.23	-0.63
SC(AFG2, m-xylene)	0.31	NO_2 + OH ->	0.27	0.55
SC(MGLY, m-xylene)	0.29	m-xylene + OH ->	0.23	-0.55
SC(MGLY, m-xylene)	0.29	NO_2 + OH ->	0.27	0.50
SC(AFG2, ARO1)[b]	0.26	ARO1 + OH ->	0.27	-0.61
SC(AFG2, ARO2) [c]	0.28	ARO2 + OH ->	0.27	-0.73
qN for BU-ACET [d]	varied	C_2COO_2 + NO_2 ->	0.75	varied
qN for BU-ACET [d]	varied	NO_2 + OH ->	0.27	varied
qN for BU-ACET [d]	varied	PPN ->	0.66	varied
q6 for BU-ACET [d]	varied	C_2COO_2 + NO_2 ->	0.75	varied
pN for BUO-ETOH [d]	varied	HCHO + hv ->	0.34	varied
pN for BUO-ETOH [d]	varied	NO_2 + OH ->	0.34	varied

[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.

[b] 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 emissions mass.

[c] The sample values of B1U2 and B1MG for ARO2 are calculated as the emissions mass-weighted average of the corresponding sample values for o-xylene, p-xylene, m-xylene, 123-trimethylbenzene and 135-trimethylbenzene.

[d] These correlations are varied for the three cases (see Table 16)

Table 19 Stochastic incremental reactivities for 2-butoxy ethanol and n-butyl acetate [a]

VOC	MIR	R_MIR[b]	MOIR	R_ MOIR[b]	EBIR	R_EBIR [b]
SAPRC-97 (Case 1)						
2-butoxy ethanol	1.12 (24%)	0.90 (16%)	0.59 (24%)	1.10 (15%)	0.40 (28%)	1.20 (16%)
n-butyl acetate	0.41 (37%)	0.34 (38%)	0.29 (34%)	0.53 (31%)	0.20 (41%)	0.60 (30%)
Base Mixture	1.25 (21%)	1.0	0.56 (24%)	1.0	0.327 (22%)	1.0
SAPRC-97 (Case 2)						
2-butoxy ethanol	1.33 (27%)	1.07 (21%)	0.72 (29%)	1.30 (21%)	0.49 (33%)	1.47 (23%)
n-butyl acetate	0.42 (37%)	0.34 (37%)	0.29 (35%)	0.54 (31%)	0.21 (41%)	0.62 (30%)
SAPRC-97 (Case 3)						
2-butoxy ethanol	1.27 (31%)	1.03 (26%)	0.69 (31%)	1.25 (24%)	0.48 (35%)	1.42 (26%)
n-butyl acetate	0.40 (51%)	0.33 (49%)	0.28 (46%)	0.51 (43%)	0.20 (52%)	0.59 (43%)

[a] Mean and (coefficient of variation). The units for absolute incremental reactivity are ppmO_3/ppmC.
The units for relative incremental reactivity are (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 20 Apportionment of uncertainty in MIRs for 2-butoxy ethanol[a]

Parameter	σ/μ[b]	Std. Reg. Coef.[b]	UC [b] (%)	Parameter	σ/μ[b]	Std. Reg. Coef.[b]	UC [b] (%)
Absolute Incremental Reactivities				**Relative Incremental Reactivities**			
Case 1 (adjusted R^2 = 0.58)				**Case 1 (adjusted R^2 = 0.90)**			
NO_2 + hv ->	0.18	0.29	8.5	2-butoxy ethanol + OH	0.25	0.41	16.4
2-butoxy ethanol + OH	0.25	0.24	6.0	PROD2 + OH ->	1.33	0.36	12.8
PROD2 + OH ->	1.33	0.23	5.4	solvent parameter pN	0.18	-0.18	3.4
CCOO2 + NO ->	0.34	0.21	4.5	NO_2 + OH ->	0.27	-0.18	3.2
O_3 + NO ->	0.10	-0.18	3.3	O_3 + hv ->	0.27	0.17	2.8
NO_2 + OH ->	0.27	-0.16	2.7	SC(MGLY, ARO2)	0.20	-0.16	2.5
PAN ->	0.40	0.15	2.3	HCHO + hv ->	0.34	0.15	2.4
HO_2 + NO ->	0.18	0.13	1.6	SC(AFG2, ARO2)	0.23	-0.14	2.1
RCHO + hv ->	0.34	0.13	1.6	RCHO + hv ->	0.34	0.14	1.9
C2COO2 +NO_2 ->	0.75	-0.12	1.5	O^1D + M ->	0.18	-0.12	1.4
HCHO + hv ->	0.34	0.12	1.4	O^1D + H_2O ->	0.18	0.12	1.4
PPN ->	0.66	0.11	1.2	C2COO_2 +NO_2 ->	0.75	-0.11	1.3
SC(MGLY, ARO2)	0.20	-0.11	1.2	SC(MGLY, ARO1)	0.29	-0.10	1.0
solvent parameter pN	0.18	-0.10	1.0				
Case 2 (adjusted R^2 = 0.64)				**Case 2 (adjusted R^2 = 0.86)**			
NO_2 + hv ->	0.18	0.28	7.6	PROD2 + OH ->	1.33	0.38	14.6
PROD2 + OH ->	1.33	0.27	7.3	2-butoxy ethanol + OH	0.25	0.29	8.5
2-butoxy ethanol + OH	0.25	0.22	4.7	pN	0.60	-0.26	6.7
pN	0.60	-0.21	4.4	P2	0.39	0.23	5.4
CCOO2 + NO ->	0.34	0.18	3.1	P1	0.39	-0.20	4.1
P2	0.39	0.17	3.0	NO_2 + OH ->	0.27	-0.20	4.0
C2COO_2 +NO_2 ->	0.75	-0.17	2.8	RCHO + hv ->	0.34	0.18	3.4
PAN ->	0.40	0.16	2.7	SC(MGLY, ARO2)	0.20	-0.15	2.3
PPN ->	0.66	0.16	2.4	O_3 + hv ->	0.27	0.13	1.8
P1	0.39	-0.13	1.7	C2COO_2 +NO_2 ->	0.75	-0.11	1.2
RCHO + hv ->	0.34	0.13	1.5	PPN ->	0.66	0.10	1.0
SC(AFG2, ARO2)	0.23	-0.12	1.4				

Table 20 (Cont'd.) Apportionment of uncertainty in MIRs for 2-butoxy ethanol[a]

Parameter	σ/μ[b]	**Std. Reg. Coef.**[b]	**UC** [b] **(%)**		**Parameter**	σ/μ[b]	**Std. Reg. Coef.**[b]	**UC** [b] **(%)**
Case 3 (adjusted R^2 = 0.73)					**Case 3 (adjusted R^2 = 0.89)**			
2-butoxy ethanol + OH	0.59	0.46	20.8		2-butoxy ethanol + OH	0.59	0.55	30.5
NO_2 + hv ->	0.18	0.24	5.8		PROD2 + OH ->	1.33	0.31	9.9
PROD2 + OH ->	1.33	0.24	5.7		pN	0.60	-0.20	4.2
pN	0.60	-0.18	3.3		P2	0.39	0.19	3.5
CCOO2 + NO ->	0.34	0.15	2.4		NO_2 + OH ->	0.27	-0.18	3.2
P2	0.39	0.15	2.2		P1	0.39	-0.16	2.5
$C2COO_2$ +NO_2 ->	0.75	-0.15	2.1		RCHO + hv ->	0.34	0.15	2.1
PAN ->	0.40	0.14	2.0		O_3 + hv ->	0.27	0.12	1.4
PPN ->	0.66	0.14	1.9		SC(MGLY, ARO2)	0.20	-0.12	1.3
P1	0.39	-0.11	1.3		$C2COO_2$ +NO_2 ->	0.75	-0.10	1.0
RCHO + hv ->	0.34	0.11	1.2					
SC(AFG2, ARO2)	0.23	-0.10	1.0					

[a] Ridge regression for normalized predictors

[b] COV = Coefficient of Variance
Std. Reg. Coef. = Standardized Regression Coefficient
UC = Uncertainty Contribution

Table 21 Apportionment of uncertainty in MIRs of n-butyl acetate[a]

Parameter	σ/μ[b]	**Std. Reg. Coef.**[b]	**UC** [b] **(%)**	**Parameter**	σ/μ[b]	**Std. Reg. Coef.**[b]	**UC** [b] **(%)**
Absolute Incremental Reactivities				**Relative Incremental Reactivities**			
Case 1 (adjusted R^2 = 0.82)				**Case 1 (adjusted R^2 = 0.89)**			
n-butyl acetate + OH	0.25	0.42	18.0	n-butyl acetate + OH	0.25	0.44	19.0
NO_2 + OH ->	0.27	-0.30	9.3	O_3 + hv ->	0.27	0.29	8.4
NO_2 + hv ->	0.18	0.28	7.8	NO_2 + OH ->	0.27	-0.28	7.9
CCOO2 + NO ->	0.34	0.19	3.7	solvent parameter qN	0.40	-0.22	4.8
solvent parameter qN	0.40	-0.19	3.4	O^1D + H_2O ->	0.18	0.19	3.7
O_3 + NO ->	0.10	-0.17	2.8	O^1D + M ->	0.18	-0.17	2.9
PAN ->	0.40	0.16	2.6	NO_2 + hv ->	0.18	0.15	2.1
$C2COO_2$ +NO_2 ->	0.75	-0.13	1.7	HCHO + hv ->	0.34	0.12	1.4
PPN ->	0.66	0.12	1.4	PROD2 + OH ->	1.33	0.11	1.2
ARO2 + OH ->	0.27	0.11	1.2	$C2COO_2$ +NO_2 ->	0.75	-0.11	1.1
HCHO + hv ->	0.34	0.11	1.1				
Case 2 (adjusted R^2 = 0.83)				**Case 2 (adjusted R^2 = 0.89)**			
n-butyl acetate + OH	0.25	0.43	18.1	n-butyl acetate + OH	0.25	0.43	18.5
NO_2 + hv ->	0.18	0.28	7.9	NO_2 + OH ->	0.27	-0.37	13.4
NO_2 + OH ->	0.27	-0.27	7.5	O_3 + hv ->	0.27	0.30	8.9
CCOO2 + NO ->	0.34	0.18	3.3	O^1D + H_2O ->	0.18	0.18	3.3
$C2COO_2$ +NO_2 ->	0.75	-0.17	2.8	PROD2 + OH ->	1.33	0.17	3.0
PAN ->	0.40	0.16	2.7	O^1D + M ->	0.18	-0.17	3.0
PROD2 + OH ->	1.33	0.15	2.2	NO_2 + hv ->	0.18	0.13	1.8
O_3 + NO ->	0.10	-0.13	1.8	solvent parameter qN	0.35	-0.12	1.4
PPN ->	0.66	0.13	1.7	CCOO2 + NO ->	0.34	0.11	1.2
HCHO + hv ->	0.34	0.12	1.5	$C2COO_2$ +NO_2 ->	0.75	-0.11	1.2
O_3 + hv ->	0.27	0.12	1.4	HCHO + hv ->	0.34	0.11	1.1
solvent parameter qN	0.35	-0.12	1.4	PPN ->	0.66	0.10	1.0

Table 21 (Cont'd.) Apportionment of uncertainty in MIRs of n-butyl acetate[a]

Parameter	**σ/μ**[b]	**Std. Reg. Coef.**[b]	**UC**[b] **(%)**	**Parameter**	**σ/μ**[b]	**Std. Reg. Coef.**[b]	**UC**[b] **(%)**
Case 3 (adjusted R^2 = 0.85)				**Case 3 (adjusted R^2 = 0.90)**			
n-butyl acetate + OH	0.59	0.66	44.0	n-butyl acetate + OH	0.59	0.68	46.1
NO_2 + hv ->	0.18	0.21	4.2	NO_2 + OH ->	0.27	-0.25	6.5
NO_2 + OH ->	0.27	-0.19	3.6	O_3 + hv ->	0.27	0.22	4.8
CCOO2 + NO ->	0.34	0.13	1.8	PROD2 + OH ->	1.33	0.13	1.8
$C2COO_2$ +NO_2 ->	0.75	-0.13	1.7	O^1D + H_2O ->	0.18	0.13	1.8
PAN ->	0.40	0.12	1.5	O^1D + M ->	0.18	-0.12	1.5
PROD2 + OH ->	1.33	0.12	1.5	NO_2 + hv ->	0.18	0.10	1.1
O_3 + NO ->	0.10	-0.10	1.0	$C2COO_2$ +NO_2 ->	0.75	-0.10	0.9
PPN ->	0.66	0.10	1.0	CCOO2 + NO ->	0.34	0.10	0.9

[a] Ridge regression for normalized predictors

[b] COV = Coefficient of Variance

Std. Reg. Coef. = Standardized Regression Coefficient

UC = Uncertainty Contribution

Table 22 Apportionment of uncertainty in MOIRs for Case 1[a]

Parameter	σ/μ[b]	Std. Reg. Coef.[b]	UC [b] (%)	Parameter	σ/μ[b]	Std. Reg. Coef.[b]	UC [b] (%)
Absolute Incremental Reactivities				**Relative Incremental Reactivities**			
2-butoxy ethanol (adjusted R^2 = 0.90)				**2-butoxy ethanol (adjusted R^2 = 0.91)**			
NO_2 + hv	0.18	0.35	12.4	PROD2 + OH	1.33	0.37	13.6
O_3 + hv	0.27	-0.33	10.8	O_3 + hv	0.27	0.33	11.0
CCOO2 + NO	0.34	0.25	6.2	2-butoxy ethanol + OH	0.25	0.28	7.6
PROD2 + OH	1.33	0.23	5.1	CCOO2 + NO	0.34	0.21	4.5
PAN	0.40	0.23	5.1	O^1D + M	0.18	-0.20	4.2
C2COO2 +NO_2	0.75	-0.20	4.1	C2COO2 +NO_2	0.75	-0.20	3.8
O^1D + M	0.18	0.19	3.5	HCHO + hv	0.34	0.18	3.3
O^1D + H_2O	0.18	-0.18	3.2	O^1D + H_2O	0.18	0.18	3.3
2-butoxy ethanol + OH	0.25	0.17	2.9	PPN	0.66	0.18	3.1
PPN	0.66	0.18	2.8	solvent parameter pN	0.18	-0.14	2.1
n-butyl acetate (adjusted R^2 = 0.89)				**n-butyl acetate (adjusted R^2 = 0.93)**			
n-butyl acetate + OH	0.25	0.43	18.2	n-butyl acetate + OH	0.25	0.45	19.9
NO_2 + hv	0.18	0.36	13.1	O_3 + hv	0.27	0.32	10.2
CCOO2 + NO	0.34	0.27	7.4	NO_2 + OH	0.27	-0.22	4.9
PAN	0.40	0.26	6.6	CCOO2 + NO	0.34	0.20	4.2
C2COO2 +NO_2	0.75	-0.22	4.7	O^1D + M	0.18	-0.20	3.9
PPN	0.66	0.20	3.9	solvent parameter qN	0.40	-0.19	3.8
NO_2 + OH	0.27	-0.17	3.0	O^1D + H_2O	0.18	0.19	3.7
solvent parameter qN	0.40	-0.16	2.7	C2COO2 +NO_2	0.75	-0.19	3.5
CO + OH	0.27	-0.16	2.6	NO_2 + hv	0.18	0.17	2.9
O_3 + NO	0.10	-0.14	1.9	PPN	0.66	0.16	2.5

[a] Ridge regression for normalized predictors

[b] COV = Coefficient of Variance
Std. Reg. Coef. = Standardized Regression Coefficient
UC = Uncertainty Contribution

Table 23 Apportionment of uncertainty in EBIRs for Case 1[a]

Parameter	σ/μ[b]	Std. Reg. Coef.[b]	UC [b] (%)	Parameter	σ/μ[b]	Std. Reg. Coef.[b]	UC [b] (%)
Absolute Incremental Reactivities				**Relative Incremental Reactivities**			
2-butoxy ethanol (adjusted $R^2 = 0.89$)				**2-butoxy ethanol (adjusted $R^2 = 0.85$)**			
NO_2 + hv	0.18	0.40	15.9	PROD2 + OH	1.33	0.35	12.3
PAN	0.40	0.35	12.3	C2COO2 +NO_2	0.75	-0.29	8.5
CCOO2 + NO	0.34	0.35	12.0	2-butoxy ethanol + OH	0.25	0.27	7.5
C2COO2 +NO_2	0.75	-0.24	5.7	CCOO2 + NO	0.34	0.26	6.7
PPN	0.66	0.22	4.9	PPN	0.66	0.25	6.4
PROD2 + OH	1.33	0.20	3.9	O_3 + hv	0.27	0.20	4.1
2-butoxy ethanol + OH	0.25	0.15	2.4	CRES + NO_3	0.75	0.18	3.4
O_3 + NO	0.10	-0.15	2.2	solvent parameter pN	0.18	-0.17	2.7
CO + OH	0.27	-0.14	2.0	SC(MGLY, ARO2)	0.20	-0.12	1.4
O_3 + hv	0.27	-0.13	1.6	O^1D + M	0.18	-0.11	1.1
n-butyl acetate (adjusted $R^2 = 0.89$)				**n-butyl acetate (adjusted $R^2 = 0.89$)**			
NO_2 + hv	0.18	0.36	13.3	n-butyl acetate + OH	0.25	0.48	23.1
n-butyl acetate + OH	0.25	0.36	13.2	C2COO2 +NO_2	0.75	-0.28	7.6
PAN	0.40	0.34	11.5	CCOO2 + NO	0.34	0.26	6.8
CCOO2 + NO	0.34	0.33	10.7	solvent parameter qN	0.40	-0.25	6.5
C2COO2 +NO_2	0.75	-0.25	6.1	PPN	0.66	0.24	5.8
PPN	0.66	0.23	5.5	PAN	0.40	0.18	3.3
solvent parameter qN	0.40	-0.17	2.7	O_3 + hv	0.27	0.18	3.2
CO + OH	0.27	-0.16	2.6	NO_2 + hv	0.18	0.16	2.7
O_3 + NO	0.10	-0.13	1.7	NO_2 + OH	0.27	-0.15	2.2
NO_2 + OH	0.27	-0.10	0.9	O^1D + M	0.18	-0.10	1.1

[a] Ridge regression for normalized predictors
[b] COV = Coefficient of Variance
Std. Reg. Coef. = Standardized Regression Coefficient
UC = Uncertainty Contribution

Compared with the deterministic incremental reactivity estimates in Table 15, the mean values from the Monte Carlo simulations for the corresponding case with uncertainty (Case 1) are generally slightly lower than the nominal estimates. Given the available measurements or experimental estimates of the OH rate constants and key mechanistic parameters, the uncertainty level for the estimated incremental reactivities for 2-butoxy ethanol is around 25% in the MIR, MOIR and EBIR cases. For n-butyl acetate, the uncertainty level ranges from 34 to 41% in the MIR, MOIR and EBIR cases. As found previously for most VOCs (Wang et al., 1999), the uncertainty in the relative incremental reactivities is less than that in the corresponding absolute incremental reactivities. For 2-butoxy ethanol, the uncertainty for the relative incremental reactivities is about 15% for the three cases studied. The uncertainty for the relative incremental reactivity for n-butyl acetate ranges from 30 to 38% for the three cases.

The parameters identified as most influential for the absolute incremental reactivities of 2-butoxy ethanol and n-butyl acetate include the rate constants for their reactions with OH, the NO_2 photolysis rate and rate constants for PPN and PAN chemistry and O_3+NO. The rate constant for lumped higher ketone (PROD2)+OH is highly influential to the absolute incremental reactivities for 2-butoxy ethanol, which are also sensitive to the chamber derived methyl glyoxal yield from the lumped aromatic species ARO2 in the MIR and MOIR conditions. Moreover, the MIR of 2-butoxy ethanol is also sensitive to the rate constant of HO_2+NO, the HCHO and RCHO photolysis rates and the chamber-derived organic nitrate yield pN. The MIR of n-butyl acetate is also sensitive to the rate constants for ARO2+OH and NO_2+OH, the HCHO photolysis rate, and the chamber-derived parameters qN. In the MOIR and EBIR cases, the uncertainties in the PPN, PAN and CO+OH rate constants become more influential with a corresponding decrease in the importance of the NO_2 + OH rate constant for both 2-butoxy ethanol and n-butyl acetate. As in the MIR case, the chamber-derived organic nitrate yield qN is influential for the MOIR and EBIR of n-butyl acetate. However, the MOIR and EBIR of 2-butoxy ethanol are not sensitive to its chamber-derived organic nitrate yield pN. Instead, uncertainty in the O_3

photolysis rate and O^1D reaction rate constants appear relatively important for the MOIR for 2-butoxy ethanol. With the exception of the PROD2 + OH rate constant and the mechanistic parameters for the two compounds, the influential parameters shown for Case 1 in Tables 20-23 are similar to those for most compounds that react at average or slower than average rates (Yang et al., 1995; Wang et al., 1999).

Compared with the absolute maximum incremental reactivity, the relative maximum incremental reactivity for 2-butoxy ethanol is more sensitive to the rate parameters for its reaction with OH, PROD2+OH and NO_2+OH, and to the chamber-derived parameter pN. The rate parameters for O_3, HCHO and RCHO photolysis and O^1D reactions and the chamber-derived aromatics parameters for the lumped species ARO2 are also more influential for the relative MIR than the absolute MIR. On the other hand, the relative MIR of 2-butoxy ethanol is not sensitive to the rate parameters for NO_2 photolysis, PAN and PPN chemistry. The same influential parameters are found for the relative MOIR and EBIR of 2-butoxy ethanol, with the increased importance of rate parameters for PAN and PPN reactions and PROD2+OH. The rate constants for 2-butoxy ethanol + OH and the value of pN are also more influential for the relative MOIR and EBIR estimates than for their absolute values.

The influential parameters for the relative incremental reactivities of n-butyl acetate include the rate constants for n-butyl acetate+OH, NO_2+OH, O^1D chemistry, NO_2 photolysis, and the chamber-derived parameter qN. Parameters related to PAN and PPN chemistry are very influential in the MOIR and EBIR cases. In particular, rate constants for O_3 photolysis and O^1D reactions are more influential for the relative MIR and MOIR of n-butyl acetate than for the absolute MIR and MOIR values. The relative EBIR is especially sensitive to the rate constant for n-butyl acetate+ OH and the value of qN, compared to the absolute EBIR.

3.3.3 Effects of Measurements and Chamber Experiments on Uncertainty in Incremental Reactivity Estimates

Cases 2 and 3 show the effects of measurements and chamber data on the reliability of the incremental reactivity estimates. The results for 2-butoxy ethanol in Table 19 indicate that the uncertainty (1σ relative to the mean) for the relative MIR is about 26% when there are no experimental data for the rate constant of its reaction with OH and there are no chamber experiments to constrain its key mechanistic parameters. The available experimental data for the reaction of 2-butoxy ethanol+OH are estimated to reduce the uncertainty of the relative MIR from 26% to 21%. Product yield data and chamber experiments further decrease the estimated uncertainty of the relative MIR to about 16%. Combined, the rate constant and product yield studies and chamber experiments thus reduce the uncertainty in the relative MIR by almost 40%. Similar trends are seen across the three cases in the relative MOIRs and EBIRs.

The most influential factors for the absolute MIRs under the three cases are generally the same, including the NO_2 photolysis rate, the rate constants of 2-butoxy ethanol+OH, PROD2+OH, PPN and PAN chemistry, the product yield of methyl glyoxal from ARO2 and the solvent parameter pN. These parameters, except NO_2 photolysis rate, are generally also influential for the relative MIRs of 2-butoxy ethanol under all three cases. The rate constants for NO_2+OH, O_3 and RCHO photolysis are also influential to the relative MIRs. When relatively high uncertainties are assumed for the mechanistic parameters in the absence of measurements, p2 and p1 are also found to be influential to the absolute and relative MIR estimates, but their effects are less than the organic nitrate yield pN. This is somewhat different from the results obtained in our previous first order sensitivity analysis in section 3.2, which concluded that p1 and p2 are not influential for the incremental reactivity of 2-butoxy ethanol. The reason is that the estimated uncertainty levels for p1 and p2 are only about 8% in Case 1, which is the case used for the first order sensitivity analysis (see Appendix A) in contrast to the 39% uncertainty assumed for Cases 2 and 3. The mechanistic parameter pN is also found to be more influential to the incremental reactivity estimates for 2-butoxy ethanol under Cases 2 and 3 than in Case 1. This is probably because correlations between pN and other reaction rates in Case 1 lead to decreased influence of pN and increased effects of the HCHO photolysis parameter.

The incremental reactivity estimates in Table 19 and the regression results in Table 21 indicate that the incremental reactivities of n-butyl acetate are most sensitive to the rate constant of its reaction with OH. The uncertainty in the relative MIR of n-butyl acetate is about 49% when there are no experimental measurements for that rate constant. The available rate constant measurements reduce the uncertainty in the relative MIR to 37%, which is almost a 25% reduction. The improved rate constant estimate reduced the uncertainties in the relative MOIR and EBIR by 28% and 30%, respectively. The most influential parameters for the absolute MIRs of n-butyl acetate include the rate constants of n-butyl acetate+OH, NO_2+OH, NO_2 photolysis, PAN and PPN chemistry and O_3+NO. The key mechanistic parameter qN is also influential in Cases 1 and 2. The rate constant for PROD2+OH is also influential in Cases 2 and 3. The generally influential parameters for the relative MIRs of n-butyl acetate under the three cases are almost the same as those for the absolute MIRs. However, the O_3 photolysis rate and the rate constants of O^1D chemistry and PROD2+OH are also influential to the relative MIRs of n-butyl acetate. The correlations considered in Case 1 increase the influence of qN on the absolute and relative MIRs.

4. Summary and Conclusions

Through formal uncertainty analysis, this study examines the uncertainties in calculated incremental reactivities for two compounds used in consumer products: 2-butoxy ethanol and n-butyl acetate. The study extends our previous analysis of the influence of chamber-derived parameters on incremental reactivity estimates for aromatic compounds (Wang et al., 1999). The analysis considers uncertainties in the initial conditions, radical source parameters and light intensity of the incremental reactivity experiments used to estimate mechanistic parameters for the two compounds, and in the other parameters of the SAPRC-97 mechanism.

The uncertainty in the estimated chamber-derived solvent parameters ranges from 18% for the organic nitrate yield (pN) from 2-butoxy ethanol to 40% for the organic nitrate yield (qN) from n-butyl acetate. The mean stochastically estimated value of pN for 2-butoxy ethanol is close to the value used in SAPRC-98, while the values of qN and q6 for n-butyl acetate are about 40% and 35% higher than the SAPRC-98 values. The uncertainty in the optimal value for qN is primarily due to uncertainties in the initial concentrations of m-xylene used in the experiments and the rate constants for PPN formation and decomposition. The uncertainty in the optimal value for pN is influenced most by uncertainty in the radical source parameters estimated for the DTC.

Uncertainty estimates for the incremental reactivities of 2-butoxy ethanol and n-butyl acetate were calculated using Monte Carlo analysis with Latin hypercube sampling. Uncertainties in almost 100 parameters of the SAPRC-97 mechanism were propagated through the Monte Carlo calculations. These parameters included the rate constants and mechanistic parameters of the 2-butoxy ethanol and n-butyl acetate reactions.

Taking into account the available kinetic and product yield data for 2-butoxy ethanol reactions and the chamber-derived mechanistic parameter estimates (Case 1), the absolute incremental reactivities estimated in this study for 2-butoxy ethanol are 1.12 ± 0.27, 0.59 ± 0.14 and 0.40 ± 0.11 ppm O_3/ppmC, respectively, under MIR, MOIR and EBIR conditions. For 2-butoxy ethanol, the estimated uncertainties of about 25% relative to the mean are comparable to those calculated previously for most VOCs with no chamber-derived parameters in their mechanisms (Yang et al., 1995; 1996; Wang et al., 1999). The relative MIR, MOIR and EBIR of 2-butoxy ethanol in Case 1 are 0.90 ± 0.14, 1.08 ± 0.16 and 1.20 ± 0.19, respectively. Uncertainties in these relative reactivities, which are about 15% of the mean estimates, are comparable to or lower than those estimated for many other VOCs including relatively well-studied light alkanes. Measurements of the 2-butoxy ethanol + OH rate constant and product yields and chamber-derived estimates of key mechanistic parameters reduce the uncertainty in the relative MIR by 40%, compared to the uncertainty level that was estimated assuming they were not available.

The MIR, MOIR and EBIR values estimated for n-butyl acetate in Case 1 are 0.41 ± 0.16, 0.29 ± 0.10 and 0.20 ± 0.08 ppm O_3/ppmC, respectively. The uncertainties in these values, which range from 34 to 41% relative to the mean estimates, are comparable to those calculated by Wang et al. (1999) for aromatic compounds with chamber-derived parameters, and somewhat higher than incremental reactivity uncertainty estimates for many other VOCs. The respective relative incremental reactivities for n-butyl acetate are 0.34 ± 0.13, 0.53 ± 0.16 and 0.60 ± 0.18. The 30 to 38% uncertainties in these estimates are at the upper end of the range of estimates obtained by Wang et al. (1999) for other VOCs without chamber-derived parameters in their mechanisms. The availability of data on the n-butyl acetate + OH rate constant is estimated to have reduced the uncertainty in the relative MIR for n-butyl acetate by about 25%.

The absolute incremental reactivities for 2-butoxy ethanol and n-butyl acetate are sensitive to the rate constants for their reactions with OH, NO_2 and O_3 photolysis, and PAN and PPN chemistry. For the MIR and MOIR of 2-butoxy ethanol, the uncertainty in the rate constant for PROD2+ OH is also influential. The organic nitrate yield from 2-butoxy ethanol, pN, contributes at most 1% to the uncertainty in its absolute incremental reactivities. About 3% of the uncertainty in the absolute incremental reactivities of n-butyl acetate is attributable to its organic nitrate yield, qN. The relative reactivity estimates for 2-butoxy ethanol are strongly influenced by uncertainty in the rate constants for 2-butoxy ethanol + OH, and for PROD2 + OH. Uncertainties in the rate parameters for n-butyl acetate + OH, O_3 photolysis and NO_2 + OH are most influential for n-butyl acetate relative reactivity estimates. Uncertainty in pN contributes about 2 to 3% of the total uncertainty in the relative reactivities of 2-butoxy ethanol. About 4 to 7% of the uncertainty in the n-butyl acetate relative reactivities is attributable to qN. With the exception of the PROD2 + OH rate constant, their OH rate constants and the chamber-derived mechanistic parameters for the two compounds, the parameters that contribute most to the uncertainty in both the absolute and relative reactivities of 2-butoxy ethanol and n-butyl acetate are similar to those identified for other VOCs in previous studies (Yang et al., 1995; Wang et al., 1999).

A significant finding of this study is that the uncertainties in the chamber-derived mechanistic parameters specific to their reactions and in turn the conditions of the chamber experiments used to estimate these parameters contribute relatively little of the uncertainty in current relative reactivity estimates for 2-butoxy ethanol and n-butyl acetate. At most about 7%

of the total uncertainty is attributable to the chamber-derived parameters.   From 8 to 23% of the uncertainty in the 2-butoxy ethanol and n-butyl acetate relative reactivities is due to their hydroxy radical rate constants, with the remaining uncertainty attributable to parameters of the base SAPRC mechanism.

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Appendix A Uncertainty Information for the Mechanistic Parameters in 2-Butoxy Ethanol Mechanism and in n-Butyl Acetate Mechanism

The uncertainties of the mechanistic parameters in 2-butoxy ethanol mechanism and n-butyl acetate mechanism in SAPRC-97 are estimated by the observed product yields or expert review, and are listed in Tables A.1 and A.2, respectively.

Table A.1 Uncertain Mechanistic Parameters in the Butoxy Ethanol (BUO-ETOH) Mechanism

Parameter	ID	Nominal	Min	Max	Uncertainty Treatment	Discussion
Total reaction rate constant	K	2.57e-11			Standard deviation of average (one sigma) is 13%. Use uncertainty based on that or standard treatment for recommended rate constant, whichever is greater.	Average of 2.31 (Dagaut et al, 1988a), 2.45 (Stemmler et al, 1996) and 2.94 x 10^{-11} (Aschmann and Atkinson, 1998). Anomalously low value of Hartmann et al (1986) is rejected.
Initial OH reaction branching ratios						
CH3-CH2-CH2-CH2-O-CH[.]-CH2-OH	p1	57.7%	30.0%	65.0%	The appropriate treatment depends on how much weight is given to the data of Stemmler et al (1997) compared to Tuazon et al (1998). I would recommend basing it on the data of Tuazon et al (1998), since consistent data were obtained using GC-FID and FT-IR, and the data are consistent with the prediction that the propanal and 2-hydroxyethyl formate yields should be about the same. If this approach is used, the uncertainty would be based on the experimental error limits of product yield data of Tuazon et al (1998). Note that their stated error limits include calibration uncertainties as well as scatter in the data.	Branching ratio based on observed 57+/-5% yields of n-butyl formate from Tuazon et al (1998). Note, however, that Stemmler et al (1997) observed this product in only 35+/-11% yield.
CH3-CH2-CH2-CH[.]-O-CH2-CH2-OH	p2	22.2%	20.0%	30.0%		Branching ratio based on observed 22 +/-2% yields of 2-hydroxy formate and 21+/-2% yields of propanal from Tuazon et al (1998). Stemmler et al (1997) observed roughly similar yields of propanal, but higher (29+/-18%) yields of 2-hydroxyethyl formate.
CH3-CH[.]-CH2-CH2-O-CH2-CH2-OH		3.5%				The branching ratios for the minor routes are held fixed, for simplicity.

Table A.1 (continued)

Parameter	ID	Nominal	Min	Max	Uncertainty Treatment	Discussion
Initial OH Reaction Branching Ratios (continued)						
CH3-CH2-CH[.]-CH2-O-CH2-CH2-OH		4.3%				
CH3-CH2-CH2-CH2-O-CH2-CH[.]-OH	p3	12.3%	0	20.0%	Constrain p3 = 0.92 - (p1+p2)	This route is expected to involve formation of butoxyacetaldehyde, which was not observed by Tuazon et al (1998) but which would account for their unaccounted-for 11% of the reaction. This is consistent with the 12+/-9% yield observed by Stemmler et al (1997).
Overall Nitrate yield for initially formed peroxy radicals						
	pN	12.7%	3%	20%	Use factor of 2 uncertainty in rate constant for nitrate formation, log-normal distribution, assuming total rate constant is constant.	Adjusted to fit chamber data
OH Reactivity of major reactive products						
OH + PROD2 rate constant					Factor of 3 uncertainty in rate constant, log-normal distribution	PROD2 OH rate constant

Table A.2 Uncertain Mechanistic Parameters in the n-Butyl Acetate (BU-ACET) Mechanism

Parameter	ID	Nominal	Min	Max	Uncertainty Treatment	Discussion
Total reaction rate constant	K	4.20e-12			Use standard uncertainty treatment for Atkinson (1989) recommended rate constants.	Atkinson (1989) recommendation. Two independent measurements in good agreement, and measured rate constant within 15% of estimate.
Initial OH reaction branching ratios						
Fraction of CH3-CH2-CH2-CH[.]-O-CO-CH3 formed.	q1	40.2%	15.0%	75.0%	Use 75% standard deviation, normal distribution, subject to the constraints of the minimum and maximum values shown.	Estimated using Atkinson's group-additivity methods.
Fraction of CH3-CH2-CH[.]-CH2-O-CO-CH3 formed.	q2	30.9%	15.0%	75.0%		Estimated
Fraction of CH3-CH[.]-CH2-CH2-O-CO-CH3 formed.	-	25.2%			R3 = 96.3% - (R1 + R2)	Fraction for minor pathways kept at estimated values, and not varied.
Overall Nitrate yield for initially formed peroxy radicals						
	qN	9%	3%	20%	Use factor of 2 uncertainty in rate constant for nitrate formation, log-normal distribution, assuming total rate constant is constant.	Adjusted to fit chamber data

Table A.2 (continued)

Parameter	ID	Nominal	Min	Max	Uncertainty Treatment	Discussion
OH Reactivity of major reactive product						
OH + PROD2 rate constant	K	9.60e-12			Factor of 3 uncertainty in rate constant, log-normal distribution	PROD2 OH rate constant
Alkoxy reactions for CH3-CO-O-CH2-CH2-CH[O.]-CH3 (22.9%)						
Fraction reacting with O2	q4	50.0%	0.0%	100%	Use factor of 3 uncertainty in each rate constant (k4 and k5), with log normal distribution, with R4=k4/(k4+k5).	Estimate using estimated alkoxy + O2 and decompositon rate constants.
Fraction decomposing to CH3-CHO + CH3-CO-O-CH2-CH2.	-	50.0%			R5 = 1 - R4	
Alkoxy reactions for CH3-CH2-CH2-CH[O.]-O-CO-CH3 (36.6%)						
Fraction undergoing ester re-arrangement	q6	53.9%	25.0%	94.0%	Assume R6 is equally likely to take on any value between 0% and 94%.	Adjusted, though rate can’t be below a certain amount to be consistent with data for other VOCs.
Fraction isomerizing to CH3-CO-O-CH(OH)-CH2-CH2-CH2.	-	40.1%			R7 = 94% - R6	