Analysis of Chamber-Derived Incremental Reactivity Estimates for N-Butyl Acetate and 2-Butoxy Ethanol

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

William P.L. Carter
CE-CERT
University of California, Riverside, CA

Abstract

Incremental reactivity estimates for many high molecular weight organic compounds used in consumer products are viewed as uncertain because of limited data on their reaction mechanisms and products. This study performs a systematic uncertainty analysis of the calculated incremental reactivities of two such compounds: n-butyl acetate and 2-butoxy ethanol. 2-butoxy ethanol is a relatively well-studied compound for which incremental reactivity experiments have been performed and product data are available for most reaction pathways. In contrast, there are incremental reactivity experiments but essentially no product data for n-butyl acetate. The uncertainty analysis accounts for uncertainties in the environmental chamber experiments used to estimate key parameters of the 2-butoxy ethanol and n-butyl acetate mechanisms, as well as in the parameters of the base SAPRC-97 chemical mechanism used to calculate their incremental reactivities. Uncertainties in the 2-butoxy ethanol reactivity estimates are lower than those estimated previously for many other volatile organic compounds (VOCs). In contrast, the uncertainties in the n-butyl acetate reactivity estimates are at the upper end of the range of uncertainties estimated for other VOCs. The chamber-derived parameters of the n-butyl acetate and 2-butoxy ethanol mechanisms contribute at most about 7% of the uncertainty in their incremental reactivity estimates.

1. Introduction

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. In addition, incremental reactivities have been measured in environmental chambers for some of these compounds, with mechanistic parameters sometimes estimated by fitting the 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) 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 is product data for most 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-97 mechanism, the only parameter that is adjusted based on chamber data is the nitrate yield. N-butyl acetate is an example of a compound for which there is chamber reactivity data but essentially no product data. In this case, multiple parameters in the estimated mechanism are adjusted to fit the environmental 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. 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. Chamber experiments conducted by Carter et al. (1998) in the Dividable Teflon Chamber (DTC) at the University of California at Riverside (UCR) are used to estimate the mechanistic parameters. Finally, the estimates of uncertainty in the chamber-derived parameters, together with estimates of uncertainty in other SAPRC-97 parameters, are propagated through incremental reactivity calculations using Monte Carlo analysis with Latin hypercube sampling.

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). SAPRC-97 is used for consistency with past work on uncertainties in chamber-derived parameters for aromatic compounds (Wang et al., 1999). Comparisons between SAPRC-97 and the latest available update, SAPRC-98, are given below for parameters and incremental reactivities of 2-butoxy ethanol and n-butyl acetate.

2.1.1 2-Butoxy Ethanol Mechanism

The SAPRC-97 mechanism for 2-buxtoxy ethanol uses an OH reaction rate constant of 2.57×10^{-11} molecules cm^{-3} s^{-1} (Dagaut et al., 1988; Stemmler et al., 1997; Aschmann and Atkinson, 1998). An uncertainty of 25% is assigned for this rate constant (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, 1999). The major reactions derived for 2-butoxy ethanol are summarized in Figure 1. In terms of model species used in the SAPRC-97 mechanism, the overall process (with nominal parameter values) is represented as:

$$\begin{aligned}\text{OH} + \text{BUO-ETOH} \rightarrow\ & 0.887\ \text{RO2-R.} + 0.113\ \text{RO2-N.} + 0.136\ \text{R2O2.} + \\ & 0.55\ \text{HCHO} + 0.015\ \text{CCHO} + 0.32\ \text{RCHO} + \\ & 0.503\ \text{MEK} + 0.26\ \text{PROD2} + 1.136\ \text{RO2.}\end{aligned}$$

The reader is referred to Carter (1990) for definitions of the product species. Note that PROD2 is not in the SAPRC-97 mechanism, but was added here for the purpose of representing the reactivities of solvent species.

As indicated in 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, the fraction of the initial reaction forming the CH_3-CH_2-CH_2-CH[.]-O-CH_2-CH_2-OH radical and the formation of 2-hydroxy formate and propanal; p3, 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; and pN, the fraction of the initially formed peroxy radicals that form organic nitrates when they react with NO.

The value of p1 is derived based on observed 57 ± 5% yields of n-butyl formate from Tuazon et al. (1998). 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). The value of p3 is derived from the estimates for the other pathways. The overall yield of organic nitrates from the initially formed peroxy radicals (pN) is estimated by fitting incremental reactivity estimates from environmental chamber experiments. 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 repeated employing both the pN value optimized using the SAPRC-98 mechanism, and the reoptimized value derived for SAPRC-97 in this work.

2.1.2 N-Butyl Acetate Mechanism

The OH reaction rate constant used for n-butyl acetate is 4.20×10^{-12} molecules cm^{-3} s^{-1} (Atkinson et al, 1989). The mechanism for the subsequent reactions is generated using the same automated estimation methods as employed for 2-butoxy ethanol. The major reactions derived for n-butyl acetate are summarized in Figure 3. In terms of SAPRC-97 model species, the overall process is nominally represented as follows.

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

As indicated in Figure 3, five major parameters affecting product yields are considered in our uncertainty analysis for 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, 1999). 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.

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. The results using the SAPRC-97 mechanism are shown using best fit parameter values derived deterministically for SAPRC-98 as well as values derived in this work using stochastic parameter estimation.

2.2 Chamber Data and Chamber Effects Mechanism

As indicated, the values for some of the uncertain mechanistic parameters in the 2-butoxy ethanol and n-butyl acetate mechanisms are determined by optimization to fit chamber data. The chamber data employed consist of a series of incremental reactivity experiments carried out during 1996 and 1997 in the blacklight irradiated DTC (Carter et al, reports in preparation 1999). Seven pairs of experiments, for which inputs are summarized in Table 1, were conducted for both of these compounds. In each case, three of the pairs 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. For each experimental pair, the test compound was added to the base mixture in only one of the two bags of the dividable chamber.

Using experimental data to estimate mechanism parameters requires consideration of the artifacts in the chamber. For this study, the most critical artifacts 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 → OH with reaction rate RSI × k_1 , where k_1, the NO_2 photolysis rate, is a measure of the light intensity in the experiment. HONO-F represents the fraction of initial NO_2 converted to HONO prior to irradiation. The radical sources are estimated from n-butane-NO_x or CO-NO $_x$ experiments conducted in the DTC at about the same time as the 2-butoxy ethanol and n-butyl acetate runs (Carter, 1996). Twelve n-butane-NO_x and two CO-NO_x experiments were used to estimate the radical source parameters for the n-butyl acetate experiments; 18 n-butane-NO_x experiments were used to estimate them for 2-butoxy ethanol.

Table 1. Chamber experiments used to estimate mechanism parameters for 2-butoxy ethanol and n-butyl acetate

				Char. Exp.[b]				Initial Concentrations			
Run ID	Test VOC	Type[a]	Date	A	B	k_1	T	NO	Unc.	NO2	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%

						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%

---

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

[b] Group of chamber characterization experiments used to estimate radical source parameters for the incremental reactivity experiments. See Wang (1999).

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 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., 1995a) is also used.

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

$$IR[D(O_3 - NO)]_t^{VOC} = \frac{D([O_3]-[NO])_t^{test} - D([O_3]-[NO])_t^{base}}{[VOC]_{test}} \qquad (1)$$

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., 1995b). The overall OH radical level is defined as the integrated OH radical concentration, INTOH:

$$INTOH_t = \int_0^t [OH]_\tau \, d\tau \qquad (2)$$

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

$$INTOH_t = \frac{\ln\left(\frac{[m-xylene]_0}{[m-xylene]_t}\right) - Dt}{KOH^{m-xylene}} \qquad (3)$$

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:

$$IR[INTOH]_t^{VOC} = \frac{INTOH_t^{test} - INTOH_t^{base}}{[VOC]_{test}} \qquad (4)$$

For this study, the subjective estimate was made that the experimental data for $D(O_3\text{-}NO)$ are three times as reliable as those for INTOH, so the two comparison criteria were weighted accordingly. The residuals are normalized by the maximum value in each experiment of the absolute value of the incremental reactivity. The n-butyl acetate and 2-butoxy ethanol parameters are optimized to give the best fits over the full duration of all of the applicable experiments.

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 separately for each characterization experiment and random sample of input parameter values. Then in estimating the parameters of the n-butyl acetate and 2-butoxy ethanol mechanisms, values of RSI and HONO-F for the kth Monte Carlo run are sampled from distributions that account for the invariability across the experiments. The same values of RSI and HONO-F are used for the test and base case of each experiment. The mean values and associated variances reported below for the estimated chamber characterization parameters are the average and variance of the experimentally averaged optimal values across all of the Monte Carlo samples.

Successive quadratic programming (SQP) (Han 1977, Powell 1977) is used to perform the optimization for the parameter estimation 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, 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 in SAPRC format are calculated according to the relationships prescribed in the mechanism generation program.

Monte Carlo analysis with Latin hypercube sampling (LHS) (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. Uncertainty estimates for mechanism parameters 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. Uncertainty estimates for experimental conditions were estimated for this study. M-xylene, a component of the base mixture used in the incremental reactivity experiments, has 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 light intensity (k_1), initial NO, NO_2 and VOC concentrations of the incremental reactivity experiments are listed in Table 1. 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, a first order sensitivity analysis was performed to identify the likely influential parameters. The sensitivity analysis was performed for both the base case and test case of each incremental reactivity experiment. First-order sensitivity coefficients indicating the response of O_3 concentrations to small variations in each of 207 input parameters or variables were calculated using the Decoupled Direct Method (Dunker, 1984). The variables considered included 183 reaction rate constants, 15 experimental conditions, 4 chamber-derived oxidation parameters for m-xylene and toluene, the 5 mechanistic parameters identified in Figure 2 for n-butyl acetate and the 4 mechanistic parameters identified in Figure 1 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 in Table 2 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.

Table 2. 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
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 did not find this parameter influential for ozone concentrations, it is treated as a random variable because it is thought to be influential for calculated incremental reactivities.

Among these influential parameters, the solvent parameters are treated as outputs, i.e., they are the parameters to be estimated. The other parameters identified in Table 2 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 n-butyl acetate or 2-butoxy ethanol parameters (Table 2). 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. 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 use of correlated LHS samples (Table 3). Further discussion of the treatment of the input uncertainties is provided by Wang (1999).

Table 3. Correlation among input parameters for chamber-derived parameter estimation

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 Variation

2.5 Incremental Reactivity Calculations

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 ($\Delta[VOC_j]$) to a base mixture of VOCs, in the presence of NO_x and sunlight:

$$IR_j = \lim_{\Delta[VOC_j]\to 0} \frac{[O_3]_{[base\ VOC]+\Delta[VOC_j]} - [O_3]_{[base\ VOC]}}{\Delta[VOC_j]} = \frac{\partial[O_3]}{\partial[VOC_j]} \qquad (5)$$

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 environmental conditions 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. The maximum ozone incremental reactivity scale (MOIR) is calculated for conditions that yield the maximum O_3 concentration with the base VOC mixture. The equal benefit incremental reactivity (EBIR) is defined for the conditions under which VOC and NO_x

reductions are equally effective in reducing ozone. The simulation conditions used for the MIR, MOIR and EBIR cases represent average conditions from 39 cities (Carter, 1994).

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:

$$R\_IRj = \frac{IR_j}{IR_{base\ VOC}} \tag{6}$$

The base VOC mixture used in this study is the mixture of reactive organic gases initially present or emitted in the scenarios, excluding biogenic VOCs and VOCs present aloft.

The methods used to estimate uncertainties in incremental reactivities and the uncertain input parameters considered in the analysis are presented below.

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. The same method is used to identify the major sources of uncertainty in the incremental reactivity estimates. 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. For the chamber characterization experiments conducted concurrently with the n-butyl acetate experiments, the average optimal values are 0.087 ppb for RSI and 0.272 % for HONO-F. Across these experiments, the average uncertainties (Iσ) in the optimal values are about 33% of the mean for RSI and 78% for HONO-F. Similar values were obtained for the chamber characterization experiments conducted along with the 2-butoxy ethanol experiments. The average optimal values for this set of experiments are 0.057 ppb for RSI and 0.604% for HONO-F, with corresponding uncertainties of about 35% for both RSI and HONO-F. Results for individual experiments are given in Wang (1999). The mean values estimated by stochastic programming are similar to those estimated deterministically by Carter (1999). A regression analysis was not performed for RSI and HONO-F in this study, but 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 (i.e., 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

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 here as the parameters to be estimated from the chamber experiments. In the SAPRC-98 mechanism, the value of q1 was estimated from structure-activity relationships. The only influential chamber-derived parameter in the 2-butoxy ethanol mechanism is the nitrate yield, pN.

With the random variables listed in Table 2, 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 (Wang, 1999) 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 and the initial NO_2 concentrations.

For n-butyl acetate, stochastic optimization results in values of 0.720 ± 0.223 for q6 and 0.127 ± 0.050 for qN. The mean values are about 34% and 41% higher than those used in SAPRC-98. Regression analysis of the stochastic optimization results shows that the influential sources of uncertainty for all of 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. Uncertainties in the rate constants for HNO_4 decomposition, n-butyl acetate oxidation, HCHO and NO_2 photolysis, 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 sources of the 31% uncertainty in the optimal value for q6.

3.3 Incremental Reactivity Estimates

In the next step of the analysis, uncertainties in the rate parameters of the SAPRC-97 chemical mechanism, including the estimated uncertainties in qN and q6 for n-butyl acetate and pN for 2-butoxy ethanol, were propagated through incremental reactivity calculations using Monte Carlo analysis with Latin hypercube sampling. The input random variables used in the Monte Carlo analysis are given in Table 4. Correlations between n-butyl acetate and 2-butoxy ethanol parameters and other SAPRC parameters incorporated in the analysis are shown in Table 6. Correlations between the rate constants for CCOO2+NO and CCOO2+NO_2 and between aromatics mechanistic parameters and the rate constants for NO_2+OH and the aromatic +OH reactions were also included. A complete list is given by Wang (1999). Due to the limitations of the LHS program, only the correlations higher than 0.3 are preserved in the incremental reactivity calculations.

The results of deterministic incremental reactivity calculations with nominal values of SAPRC-97 parameters are listed in Table 6 for comparison with incremental reactivities calculated with SAPRC-98 (Carter, 1998). The mean values and the associated uncertainties for the calculated incremental reactivities for n-butyl acetate and 2-butoxy ethanol obtained from 460 LHS samples are listed in Table 7 for absolute and relative incremental reactivities.

Table 4. Input Random Variables for Incremental Reactivity Calculations

Reaction or Coefficients	**Coefficient of Variance ($\sigma_i/\kappa_{i\ nominal}$)**	**Reaction or Coefficients**	**Coefficient of Variance ($\sigma_i/\kappa_{i\ nominal}$)**
O_3 + NO ->	0.10 (2)[a]	ethene + OH ->	0.11 (2)
O^1D + H_2O ->	0.18 (2)	propene + OH ->	0.14 (3)
O^1D + M ->	0.18 (2)	isopene + OH ->	0.19 (3)
NO_2 + OH ->	0.27 (1)	1,3-butadiene + OH ->	0.19 (3)
CO + OH ->	0.27 (2)	2-m-1-butene + OH ->	0.18 (3)
HO_2 + NO ->	0.18 (1)	2-m-2-butene + OH ->	0.18 (3)
HO_2 + HO_2 ->	0.27 (2)	224-TM-C5 + OH ->	0.18 (3)
HO_2 + HO_2 + H_2O ->	0.27 (1)	MTBE + OH -> [b]	0.18 (7)
RO_2 + NO ->	0.42 (2)	ETBE + OH -> [b]	0.18 (7)
RO_2 + HO_2 ->	0.75 (2)	ethene + O_3 ->	0.23 (2)
CRES + NO_3 ->	0.75 (3)	propene + O_3 ->	0.18 (1)
HCHO + OH ->	0.23 (2)	isoprene + O_3 ->	0.35 (3)
CCHO + OH ->	0.18 (2)	1,3-butadiene + O_3 ->	0.42 (3)
RCHO + OH ->	0.35 (3)	2-m-1-butene + O_3 ->	0.35 (3)
CCOO2 + NO ->	0.34 (2)	2-m-2-butene + O_3 ->	0.42 (3)
CCOO2 + NO_2 ->	0.16 (1)	ALK2 + OH ->	0.27 (3)
CCOO2 + HO_2 ->	0.75 (2)	ARO1 + OH ->	0.27 (3)
CCOO2 + RO_2 ->	0.75 (3)	ARO2 + OH ->	0.27 (3)
C2COO2 + NO_2 ->	0.75 (3)	OLE2 + OH ->	0.18 (3)
PPN ->	0.66 (4)	OLE2 + O3 ->	0.42 (3)
PAN ->	0.40 (4)	OLE3 + OH ->	0.23 (3)
NO_2 + hv -> (action spectra)[i]	0.18 (2)	OLE3 + O3 ->	0.42 (3)
NO_3 + hv ->[i]	0.42 (1)	P1U1 [c]	0.40 (5)
O_3 + hv -> [i]	0.27 (2)	SC(AFG1,benzene) [d]	0.33 (5)

HCHO + hv ->[i]	0.34 (2)	SC(AFG2,toluene) [e]	0.34 (5)
CCHO + hv ->[i]	0.34 (3)	SC(MGLY,toluene) [f]	0.31 (5)
RCHO + hv ->[i]	0.34 (3)	SC(AFG2,ethylbenzene)	0.44 (5)
MEK + hv ->[i]	0.42 (3)	SC(MGLY,ethylbenzene)	0.63 (5)
benzene + OH ->	0.27 (3)	SC(AFG2,123-TMB)	0.39 (5)
toluene + OH ->	0.18 (3)	SC(MGLY,123-TMB)	0.36 (5)
ethylbenzene + OH	0.31 (3)	SC(AFG2,124-TMB)	0.40 (5)
1,2,3-trimethylbenzene + OH ->	0.31 (3)	SC(MGLY,124-TMB)	0.49 (5)
1,2,4-trimethylbenzene + OH ->	0.31 (3)	SC(AFG2,135-TMB)	0.40 (5)
1,3,5-trimethylbenzene + OH ->	0.31 (3)	SC(MGLY,135-TMB)	0.29 (5)
p-xylene + OH ->	0.31 (3)	SC(AFG2,p-xylene)	0.45 (5)
o-xylene + OH ->	0.23 (3)	SC(MGLY,p-xylene)	0.71 (5)
m-xylene + OH ->	0.23 (3)	SC(AFG2,o-xylene)	0.30 (5)
NC_4 + OH ->	0.18(3)	SC(MGLY,o-xylene)	0.43 (5)
NC_6 + OH ->	0.18 (3)	SC(AFG2,m-xylene)	0.33 (5)
NC_8 + OH ->	0.18 (3)	SC(MGLY,m-xylene)	0.31 (5)
$CYCC_6$ + OH ->	0.27 (3)	SC(AFG1,ARO1) [g]	0.33 (5)
2-methylpentane + OH ->	0.23 (3)	SC(AFG2,ARO1) [g]	0.29 (5)
m-cyclopentane + OH ->	0.27 (3)	SC(MGLY,ARO1) [g]	0.29 (5)
methanol + OH -> [b]	0.18 (7)	SC(AFG2,ARO2) [h]	0.23 (5)
ethanol + OH -> [b]	0.18 (7)	SC(MGLY,ARO2) [h]	0.20 (5)
BU-ACET+OH ->	0.25 (7)	BUO-ETOH+OH->	0.25 (7)
qN for BU-ACET	0.40 (6)	q6 for BU-ACET	0.31 (6)
pN for BUO-ETOH	0.18 (6)	PROD2 + OH ->	1.33 (7)

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) This study
(7) estimated from Carter 1998

[b] uncertainty is estimated for this study according to the uncertainty classes described by (47)

[c] quantum yield for photolysis of model species AFG1

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

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

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

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

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

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

Table 5 Correlated Parameters Used in Incremental Reactivity Calculations

Parameter	COV	Correlated Parameter	COV	Correlation
qN for BU-ACET	0.40	C_2COO_2 + NO_2 ->	0.75	-0.43
qN for BU-ACET	0.40	NO_2 + OH ->	0.27	0.31
qN for BU-ACET	0.40	PPN ->	0.0.66	0.31
q6 for BU-ACET	0.31	C_2COO_2 + NO_2 ->	0.75	-0.34
pN for BUO-ETOH	0.18	HCHO + hv ->	0.34	0.34
pN for BUO-ETOH	0.18	NO_2 + OH ->	0.34	0.40

Table 6 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	0.344	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.

Table 7 Stochastic Incremental Reactivities for 2-Butoxy Ethanol and n-Butyl Acetate [a]

VOC	MIR	MOIR	EBIR	R_MIR[b]	R_ MOIR[b]	R_EBIR [b]
2-butoxy ethanol	1.12 (24%)	0.59 (24%)	0.40 (28%)	0.90 (16%)	1.10 (15%)	1.20 (16%)
n-butyl acetate	0.414 (37%)	0.29 (34%)	0.20 (41%)	0.34 (38%)	0.53 (31%)	0.60 (30%)
Base Mixture	1.25 (21%)	0.56 (24%)	0.33 (22%)			

[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 6 shows incremental reactivity values for n-butyl acetate and 2-butoxy ethanol calculated using nominal values of SAPRC-97 parameters together with the best estimates of the chamber-derived mechanism parameters pN, qN and q6. MIR values calculated here are close to those calculated with SAPRC-98 (Carter, 1998), about 1.4 ppmO_3/ppmC for 2-butoxy ethanol and 0.5 ppmO_3/ppmC for n-butyl acetate. The deterministic estimates of the MOIR and EBIR, respectively, are 0.66 ppmO_3/ppmC and 0.46 ppmO_3/ppmC for 2-butoxy ethanol and 0.32 ppmO_3/ppmC and 0.23 ppmO_3/ppmC for n-butyl acetate. The mean values from the Monte Carlo simulations shown in Table 7 are generally slightly lower than the nominal estimates given in Table 6.

The uncertainty level for the estimated incremental reactivities for 2-butoxy ethanol is about 25% in the MIR, MOIR and EBIR cases. For n-butyl acetate, the uncertainty level ranges from 34 to 41% across the three 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.

As shown in Wang (1999) 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 and the HCHO photolysis rate 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 RCHO photolysis rate 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 O_3 photolysis, and the chamber-derived parameters qN and q6. The organic nitrate yield qN is also influential for the MOIR and EBIR of n-butyl acetate. However, the MOIR and EBIR of 2-butoxy ethanol are not sensitive to its 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 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 MIR, the relative MIR 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 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 less sensitive than the absolute MIR to the rate parameters for NO_2 photolysis, PAN and PPN chemistry. The influential parameters for the relative MOIR and EBIR of 2-butoxy ethanol include the rate constants for its reaction with OH, PROD2+OH, O_3 photolysis and PAN and PPN chemistry.

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. O_3 and HCHO photolysis rates are also influential in the MIR and MOIR cases. Parameters related to PAN and PPN chemistry are very influential in the

MOIR and EBIR cases. 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.

4. Summary and Conclusions

Through formal uncertainty analysis, this study examined the uncertainties in calculated incremental reactivities for 2-butoxy ethanol and n-butyl acetate. 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 chamber-derived parameters of the 2-buxtoxy ethanol and n-butyl acetate mechanisms 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 stochastically estimated value of pN for 2-butoxy ethanol is close to that 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 from n-butyl acetate 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 from 2-butoxy ethanol is influenced most by uncertainty in the radical source parameters estimated for the DTC.

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 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.

The MIR, MOIR and EBIR values estimated for n-butyl acetate 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 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 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 most of the uncertainty in the incremental reactivity estimates for n-butyl acetate and 2-butoxy ethanol is attributable to parameters of the base SAPRC mechanism. The uncertainties in the chamber-derived mechanistic parameters specific to their reactions and in turn the conditions of the experiments used to estimate these parameters contribute at most 7% of the total uncertainty in the reactivity estimates.

Acknowledgments

Support for this research was provided by the California Air Resources Board, under CARB contract no.95-331. The authors appreciate the nonlinear optimization programs provided by Professor Urmila Diewkar at University of Carnegie Mellon.

References

Aschmann S.M. and Atkinson R. (1998): Kinetics of the gas-phase reactions of the OH radical with selected glycol ethers, glycols and alcohols. *International Journal of Chemical Kinetics*. 30:(8) 553-540. August.

Atkinson, R., Baulch, D.L., Cox, R.A., Hampson, R.F.Jr., Derr, A., Troe, J.(1989): Evaluated kinetic and photochemical data fro atmospheric chemistry: supplement III. IUPAC subcommittee on gas kinetic data evalution for atmospheric chemistry, *Journal of Phyical and Chemical Reference Data*, 13:1259- 1380.

Biegler, L.T. and Hughes R.R.(1983): Process optimization: a comparative study. *Computers and Chemical Engineering*, 7:645-661.

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

Carter, W.P.L.(1994): Development of ozone reactivity scales for volatile organic compounds. *Journal of the Air and Waste Management Association*, 44:881-899.

Carter, W.P.L., Luo, D., Malkina, I.L. and Pierce, J.A.(1995a): Environmental chamber studies of atmospheric reactivities of volatile organic compounds: effects of varying ROG surrogate and NO_x. Final report to Coordinating Research Council, Inc., Project ME-9, California Air Resources Board, Contract A032-0692, and South Coast Air Quality Management District, Contract C91323, March.

Carter, W.P.L., Pierce, J. A., Luo, D. and Malkina, L. (1995b): Environmental chamber study of maximum incremental reactivities of volatile organic compounds. May.

Carter W.P.L.(1996): Development and application of an updated photochemical mechanism for VOC reactivity assessment. Quarterly Report to the California Air Resources Board, Contract N0. 92-329.

Carter,W.P.L. Luo, D., and Malkina, I.L.(1997): Environmental chamber studies for development of an updated photochemical mechanism for VOC reactivity assessment, Final report to California Air Resources Board, contract 92-345; coordinating Research Council, Inc., Project M- 9; National Renewable Energy Laboratory, contract ZF-2-12252-07.

Carter, W.P.L. (1998) Updated maximum incremental reactivity scale for regulatory applications, preliminary report to California Air Resources Board, Contract No. 95-308, August.

Carter, W.P.L., Luo, D., Malkina, I.L. (1998) Investigation of atmospheric reactivities of selected stationary source VOCs, Final Report for CARB Contract 95-308.

Carter (1999): personal communication

Dagaut, P.T., J. Wallington, R. Liu and M.J. Kurylo (1988) 22nd international symposium on combustion, Seattle, August 14 – 19DeMore, W.B., Sander, S.P., Golden, D.M., Molina, M.J., Hampson, R.F., Kurylo, M.J., Howard, C.J., Ravishankara, A.R., Kolb, M.J., and Molina M.J.(1994): Chemical kinetics and photochemical data for use in stratospheric modeling, Evaluation No. 11, JPL Publ., 94-26 .

DeMore, W.B., Golden, D.M., Hampson, R.F., Howard, C.J., Ravishankara, A.R., Kolb, M.J., and Molina, M.J.(1997): Chemical kinetics and photochemical data for use in stratospheric modeling, Evaluation 12, JPL Publ. 97-4.

Dunker, A.M.(1984): The direct decoupled method for calculating sensitivity coefficients in chemical kinetics. *Journal of Chemical Physics*, 81: 2385-2393.

Grosjean, D., E. Grosjean and E.L. Williams II (1994). Thermal decomposition of PAN, PPN and Vinyl-PAN. *Air and Waste Management Association* 44, 391-396.

Han, S.P. (1977). A globally convergent method for nonlinear programming. *Journal of Optimization Theory and Applications* 22(3), 297-309.

Hartmann, D., A. Gedra, D. Rhasa and R. Zellner (1986) Proceedings, 4th European Symposium on the Physico-Chemical Behavior of Atmospheric Pollutants, 1986; D. Riedel Publishing Co., Dordrecht, Holland, 1987, p.225

Iman, R.L. and M.J. Shortencarier (1984). A FORTRAN77 program and user’s guide for the generation of Latin Hypercube and random samples for use with computer models, Rep. SAND83-2365, U.S. Dep. of Energy, Sandia National Laboratory, Albuquerque, N.M, 1984.

McBride, S.J., Oravetz, M.A. and Russell, A.G.(1997): Cost-benefit and uncertainty issues in using organic reactivity to regulate urban ozone. *Environmental Science & Technology/News,* 31:238A- 244A.

Powell, M.J.D.(1977):A fast algorithm for nonlinear constrained optimization calculations. *Dunde Conf. Numerical Anal.*, Dundee, Scotland.

Stemmler K., Mengon W., Kinnison, D. and Kerr, J.A.(1997): OH radical-initiated oxidation of 2-butoxyethanol under laboratory conditions related to the troposphere: product studies and proposed mechanism. *Environmetal Science Technol*ogy 31:1496-1504.

Stockwell, W.R., Yang, Y.J. and Milford, J.B.(1994): A compilation of estimated uncertainty factors for rate constants in W.P.L. Carter’s detailed mechanism. Prepared for the Automotive Emissions Cooperative Research Program under Coordinating Research Council, Inc. Contract No. AQIRP-19-92.

Tuazon , E. C., Aschmann S. M. and Atkinson R. (1998): Products of the gas-phase reactions of the OH radical with 1-methoxy-2-propanol and 2-butoxyethanol. *Environmental Science Technol*ogy 32: 3336-3345.

Yang, Y.J., Stockwell, W.R., and Milford, J.B.(1995): Uncertainty in Incremental reactivities of volatile organic compounds, *Environmental Science Technology,* 23:1336-1345.

Wang, L. (1999): Stochastic parameter estimation and uncertainty analysis applied to photochemical air quality models, Ph.D. Thesis, Department of Mechanical Engineering, University of Colorado.

Wang L., Milford, J.B. and Carter, W.P.L. (1999): Reactivity estimates for aromatics compounds. Draft Report to the California Air Resources Board. Contract No. 95-331.

Zafonte, L., Rieger, P.L. and Holmes, J.R.(1977): Nitrogen dioxide photolysis in the Los Angeles atmosphere. *Environmental Science Technol*ogy, 11: 483-387.

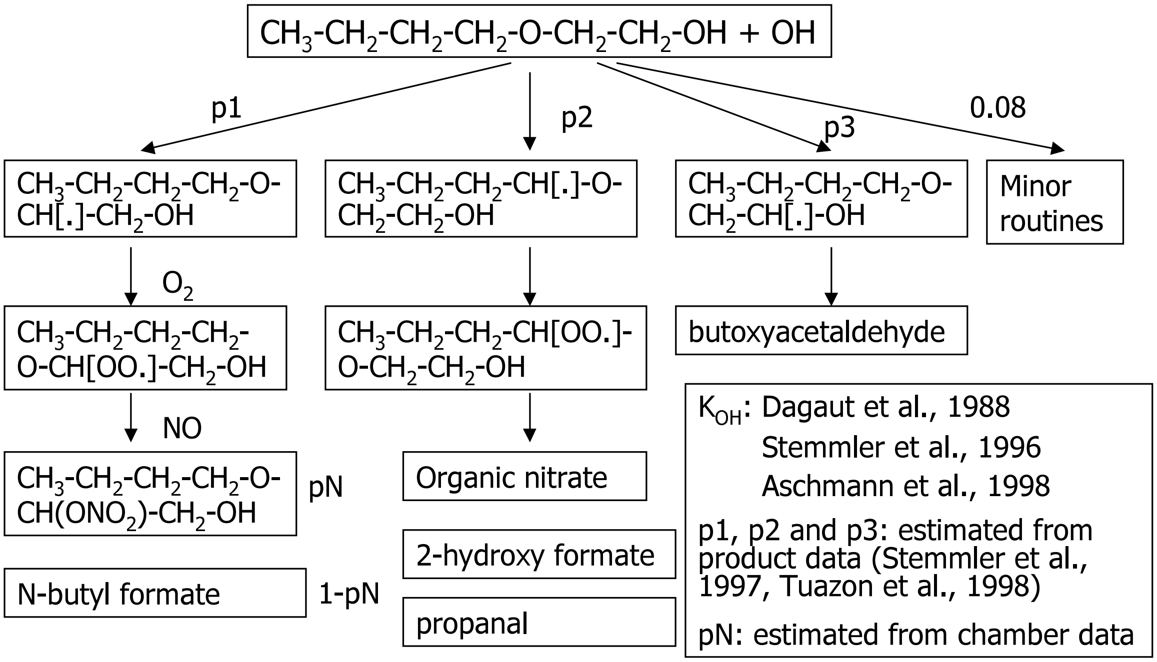


Figure 1. Key Features of the 2-Butoxy Ethanol Mechanism Used in SAPRC.

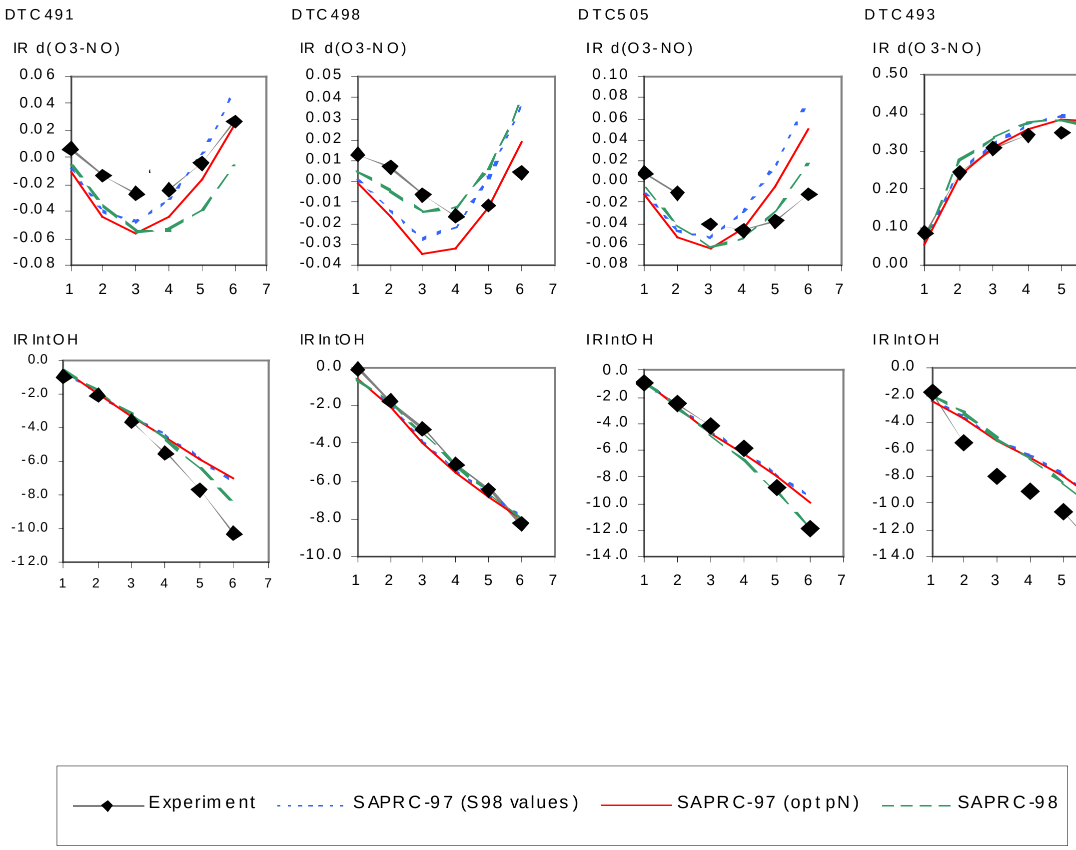
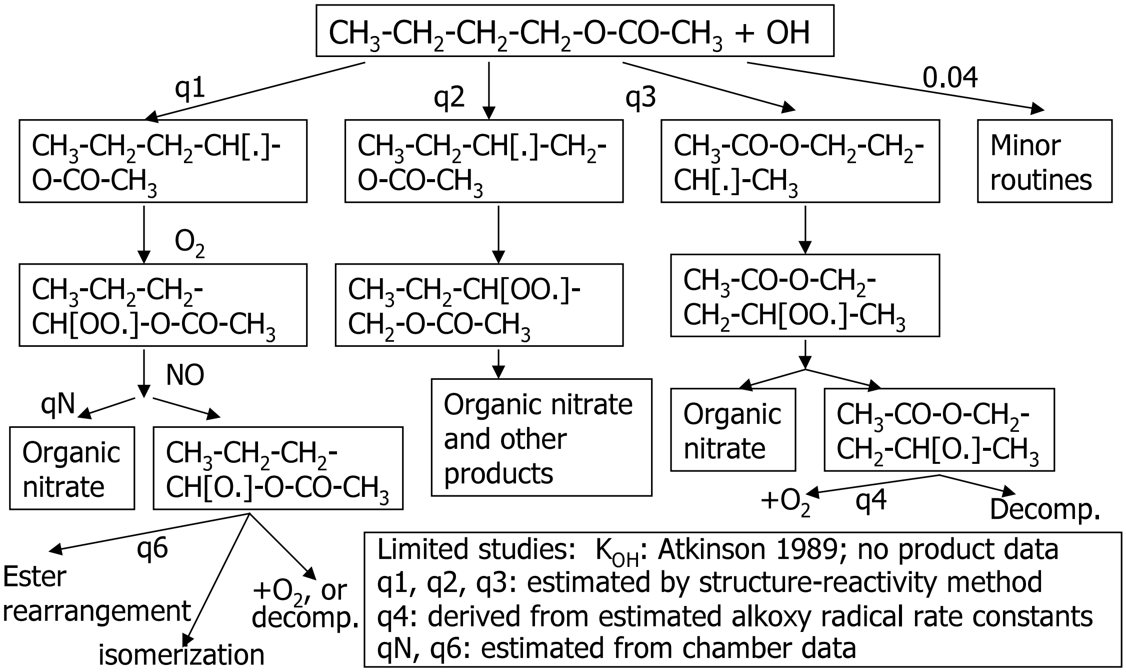


Figure 2. Simulation Performance for 2-Butoxy Ethanol Incremental Reactivity Experiments (4 of 7)



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.

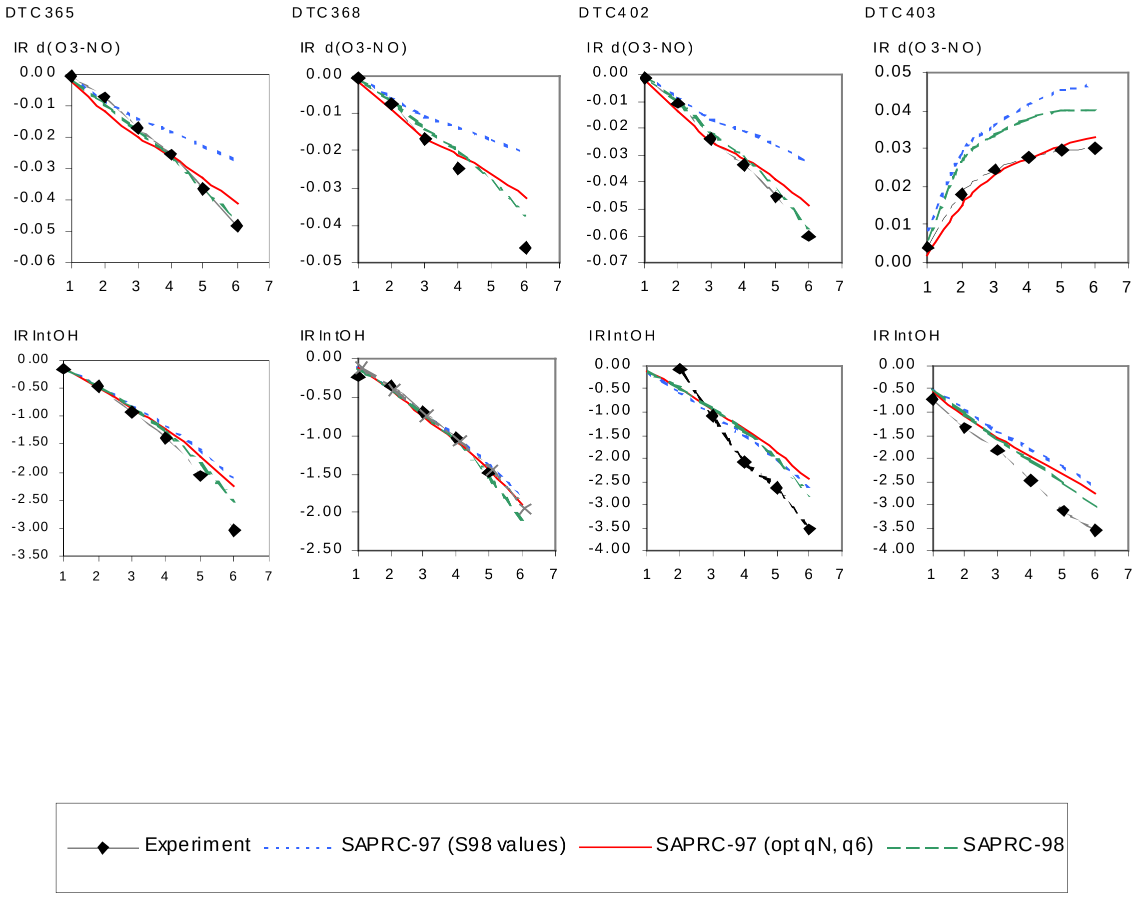


Figure 4. Simulation Performance for n-Butyl Acetate Incremental Reactivity Experiments (4 of 7)

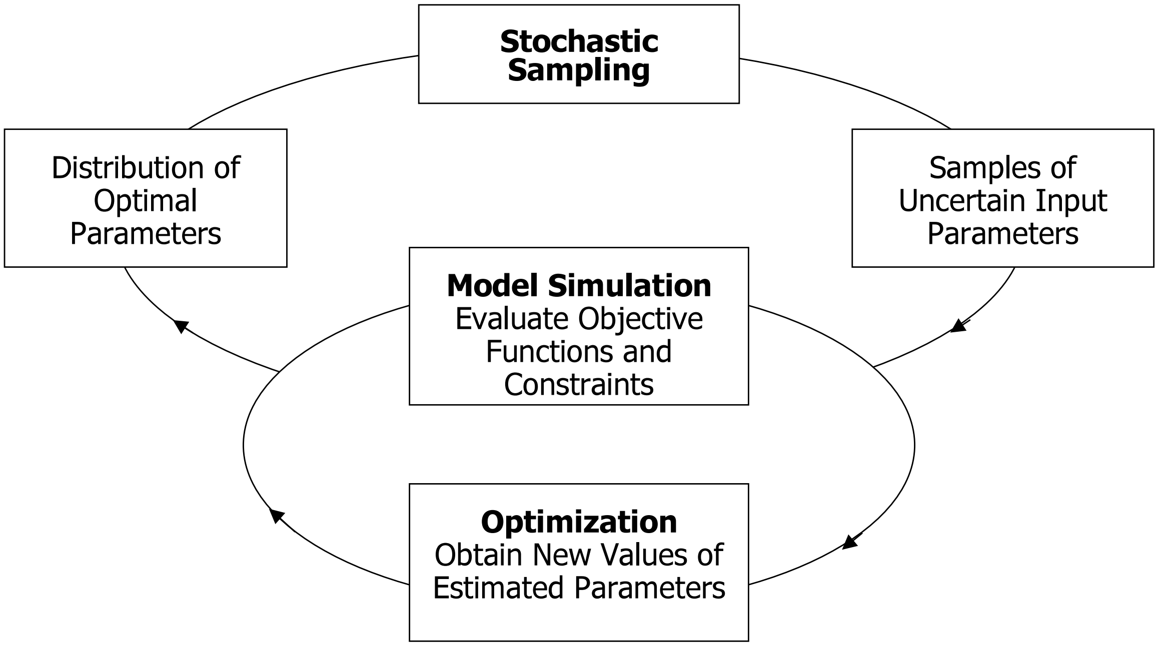


Figure 5. Stochastic Programming Approach Using Monte Carlo/Latin Hypercube Sampling and Successive Quadratic Programming.