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Decomposition Studies of Isopropanol in a Variable Pressure Flow Reactor

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Alternatives to traditional petroleum derived transportation fuels, particularly alcohols, have been investigated increasingly over the last 5 years. Isopropanol has received little attention despite bridging the gap between smaller alcohols (methanol and ethanol) and the next generation alcohols (butyl alcohols) to be used in transportation fuels. Previous studies have shown that decomposition reactions that dehydrate are important in the high-temperature oxidation of alcohols. Here we report new data on the dehydration reaction for isopropanol ($iC_3H_7OH \rightarrow C_3H_6 + H_2O$) in a Variable Pressure Flow Reactor at 12.5 atm pressure and temperatures from 976–1000 K. Pyrolysis experiments are performed in the presence of a radical trapper (1,3,5 trimethyl benzene or toluene) to inhibit secondary reactions of radicals with the fuel and product species. The recommended rate constant for the dehydration reaction is determined using an indirect method along with Latin Hypercube sampling to estimate uncertainties. Comparison of the rate constant data to previous works show that the reaction is considerably more rapid than the high level theoretical predictions of Bui et al. (Bui et al., J. Chem. Phys., 2002). The dehydration reaction rate for isopropanol is well described by k=8.52*10^6 T^2.12 exp(-30,667 / T) with an estimated uncertainty of $\sigma_{\ln z}^2 = 0.0195$.

The C-C bond fission reaction is also investigated, but the insensitivity of the decomposition data to this reaction results in an uncertainty in the determined rate constants to approximately 2 orders of magnitude. Theoretical estimates lie within these experimental uncertainties.

1. Introduction

Isopropanol, along with other alcohols[1–4], has garnered attention as a feedstock with which to supplement petroleum products used in ground transportation. The United States Congress has mandated that approximately 36 billion gallons of biofuels should be produced annually by 2022[5]. Already, ethanol (from corn) is used extensively as a supplement to gasoline. Unfortunately, ethanol's contribution as a gasoline supplement will reach its capped maximum of 15 billion gallons per year[6], exemplifying the urgent need for other renewable fuels to enter the market place. The European Union Renewable Energy Directive has similarly mandated that 10% of energy for transportation be derived from renewable sources by 2020[7]. Thus, integration of other alternative biofuels will be needed to fill the gap between the government mandates and the capped ethanol production.

The isomers of butanol have received considerable attention recently with regard to their combustion behaviors, but in relative terms, much less effort has been devoted to the interceding carbon number alcohols (i.e. three carbon atom alcohols). Propyl alcohols are the smallest molecular weight alcohols that have isomeric structures existing as *n*-propanol and isopropanol (2-propyl alcohol). Study of the combustion reaction kinetics of these interceding alcohols is important in terms of building a sound foundation for the pyrolysis and oxidation behaviors of alcohols in general.

Decomposition reactions are an important aspect of alcohol combustion chemistry. The inclusion of the alcohol moiety within a hydrocarbon imparts a character that distinguishes alcohol reaction kinetics from that of the analogous alkane (e.g. dehydration, enol tautomerization, and H-abstraction reactions). Typically, alcohol pyrolysis reactions are fast

enough to compete with radical chemistry as a significant process accounting for reactant consumption at the initial stages of reaction. Decomposition and pyrolysis occurs through dehydration and hydrogen elimination reactions, in addition to the usual simple C–C or C-H bond fissions typical of hydrocarbons. The relative significance of each of these processes affect the radical pool population that controls combustion behaviors, and therefore developing accurate reaction parameters for these processes is important.

Few previous studies on isopropanol decomposition have been conducted[8,9], despite recent interest in its combustion[10,11]. The experimental decomposition study of Trenwith did not recommend elementary rate constants, instead deriving global production rates for the formation of major products. The only study dedicated to determining rate parameters for the elementary decomposition reactions of isopropanol is the theoretical work of Bui *et al.*[8] However, no experimental data exist to compare with these theoretical estimations.

The decomposition of isopropanol proceeds through two dominant reaction channels: a molecular dehydration and a C–C bond fission, with other competing channels having much slower rates of reaction. As with similar studies of the decomposition of *tertiary*-butanol[2], the dehydration reaction of isopropanol forms an olefin (propylene) and water via a concerted four centered reaction complex[8]:

$$i\mathrm{C_3H_7OH} = \mathrm{H_2O} + \mathrm{C_3H_6}. \qquad \textbf{Reaction 1}$$

In direct competition with the dehydration reaction is the C–C bond fission reaction:

$$i\mathrm{C_3H_7OH} = \mathrm{CH_3\dot{C}HOH} + \dot{C}H_3. \qquad \textbf{Reaction 2}$$
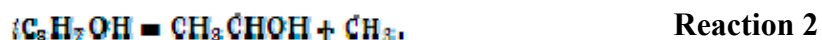
Previously, the dehydration rate of *tertiary*-butanol was determined by a direct technique where radical reactions could be neglected. Temporally resolved reactant and product species

measurements in an isothermal flow reactor were used to determine a reaction rate[2]. The data showed that in the case of *tertiary*-butanol, the dehydration reaction rate is approximately a factor of ten larger than the rate of the radical initiating C–C bond fission reaction. This attribute has been shown to be important in diffusively controlled combustion, where the dehydration reaction for *tertiary*-butanol was found to contribute as much as ~80% of the destruction of the fuel[12]. To further isolate the contributions of the dehydration reaction in experimental fuel pyrolysis studies, radical terminating components can be added to reduce the effects of the secondary radical chemistry. So-called "radical trapper" molecules operate by consuming reactive radicals (such as H, or OH, etc.) forming resonantly stabilized species that regenerate radical species at very long time scales in comparison to those over which reactant decomposition is observed.

By performing the pyrolysis of an alcohol in a mixture with a large excess of radical trapper species, the sum of the dehydration and C–C bond fission rates are equivalent to the rate of product formation, in the case of isopropanol pyrolysis, water and propylene. "Radical trappers" and the radical trapping technique have been applied frequently in pulsed shock tube decomposition studies[13] and in flow reactor studies of ethanol[14] and *tertiary*-butanol[2]. When the reactions targeted for study cannot be isolated from interferences experimentally, an indirect technique can be used to quantify the impact of secondary (radical) chemistry on the consumption of reactant and formation of product species. In such instances radical trappers can still be utilized to advantage, by varying the contributions of secondary reactions, thus giving higher moments for the determination of the dehydration and C–C bond fission channels[15].

This work reports new experimental pyrolysis profiles for isopropanol decomposition in a homogeneous, constant pressure flow reactor at four different reaction temperatures. Three of

the experiments are conducted in the presence of radical trappers. The dehydration and C–C bond fission rate constants are determined from the experimental measurements via both direct and indirect determination techniques. The results of these two different techniques are compared and contrasted along with the respective estimated uncertainty for each technique. Finally, the work of Bui et al.[9] is compared with the new experimental results. .

2. Experimental

The experimental measurements are conducted in the Variable Pressure Flow Reactor (VPFR) facility at Princeton University. The design, instrumentation, and experimental methodology of this apparatus have been discussed in detail previously[16,17] and are therefore only briefly summarized here.

Nitrogen carrier gas is heated by electric resistance heaters and homogeneously mixed with oxygen as it enters a 10.2 cm diameter quartz test section, see **Error! Reference source not found.**. The test section is surrounded by thermostatted electrical resistance heaters, which maintain the reactor wall temperatures at near-adiabatic conditions. Liquid isopropanol (99.0+%; Aldrich Chemical Co., Ltd.) and toluene (99.0+%, Aldrich Chemical Co.) or 1,3,5 trimethyl benzene, TMB, (99.0+%, Aldrich Chemical Co., Ltd.) is supplied to the reactor via a liquid evaporator system, where it is gas-blast vaporized and diluted by nitrogen gas at 548 K. Liquid fuel flow is metered using a volumetric syringe pump. The diluted reactant vapor is injected radially outward (through 32 small orifices in the central injector tube) into an opposed flow of nitrogen carrier gas at the entrance to a conical mixer/diffuser section. The reactant/carrier gas

mixture exits the mixer/diffuser section into the constant area test section downstream at Reynolds numbers where the reactor flow field is well characterized (Re > 6000).

Small quantities of the reacting mixture are sampled at incremental axial positions downstream of the mixer/diffuser using a hot-water-cooled, stainless steel sampling probe. The sampled stream is continuously extracted and convectively quenched by wall heat transfer. The centerline temperature of the reacting flow is measured at the same axial location as the sampling probe tip using a silica-coated R-type thermocouple. With all flows established except the reactant flow, the temperature at the sampling location varies by less than ±1.5 K independent of the location of the mixer/diffuser in the test section and is known to have a relative uncertainty of ±1.5 K and has an absolute accuracy (2σ) better than ±7.5 K. Recent experimental studies have shown a negligible effect of radiative coupling between the water cooled sampling probe body and the thermocouple bead[18]. Estimated absolute uncertainty in the reported pressure is ±0.2 atm.

The sampling configuration inside the test section is altered by positioning the mixer/diffuser relative to the fixed sampling location. This procedure is employed at various mixer/diffuser positions to obtain stable species and temperature measurements as a function of reaction time for a given set of initial test section conditions. Residence times for specific sampling locations along the test section are calculated using a Reynolds number correlation of experimental axial velocity profile information determined for the test section under cold flow conditions. Uncertainty in residence time is less than ±1.6% of the reported value. In each experiment, the concentration of radical trapper (TMB or toluene) in comparison to that of isopropanol is held constant. The test conditions are summarized in Table 1 and span 976-999 K always at 12.5 atm.

2.1. Sample Analysis

The continuously sampled gas flow is transferred through heated Teflon lines (373 K) to a Fourier transform infrared (FTIR) spectrometer with a heated sample cell. Water is quantified using FTIR spectroscopy, calibrated using known standards of water concentration in nitrogen. The estimated uncertainties (2σ) are ± 50 ppm of the reported value. The average of thirty-two individual FTIR spectra taken at each axial sampling location is recorded. The specific wavelengths used for quantification have no overlap with isopropanol, 1,3,5 trimethyl benzene (TMB), toluene, or the intermediate/product species that result from their reaction.

Discrete volumes of the sample flow at each axial sampling location are also stored for subsequent offline analysis using a heated (400 K) sample storage unit composed of a 32 port multi-position stainless steel valve (MPV) with fifteen stainless steel sample storage loops (VICI Valco Inc., 10 ml volume). A gas chromatograph (GC, Agilent 7890A) equipped with a capillary column (J&W HP-PLOT Q, 30 m length, 535 μm diameter, 40 μm film thickness) is utilized for chemical analysis of each of the stored samples using a flame ionization detector (FID). Using nitrogen carrier gas and appropriate temperature programming from -50 to 250 C, the particular column and detector combination provides excellent separation and quantification of hydrocarbons and oxygenates, with detection limits of better than 0.5 part-per-million (ppm) molar fraction. Identification of species is performed by retention time comparisons against those of pure substances for the same chromatographic conditions.

Water and oxygenate (acetone, isopropanol, and acetaldehyde) calibrations are performed by vaporizing a known flow rate (by volumetric displacement) into a constant hot nitrogen carrier flow in the VPFR. The liquid flow rate of the material to be calibrated is varied to produce different vapor/nitrogen mixtures, which are then sampled and analyzed in the same manner as

used in the experiments. Standard calibration gases (Airgas and Air Liquide) are flowed through the sampling system to calibrate the GC-FID analyses for all other species (permanent gases, and hydrocarbons with carbon number <6). The analyses of a standard gas mixture of known composition (Airgas and Air Liquide) are interspersed among those of the experimental tests to check calibration fidelity. The maximum estimated uncertainties (2σ) on the species quantifications using the GC-FID are ±5%.

Three of the reported experiments are performed in the presence of a radical trapper (TMB or toluene). Two different radical trappers are used here to effectively observe the impact of radical trapper type and concentration on the determined dehydration rates. Radical reactions with isopropanol are inhibited through competition of the radical trapper for very reactive radicals (such as H, CH_3 or OH), resulting in the production of metastable benzylic-type intermediates and molecular products that reduce the regeneration rate of the active radical pool relative to that produced found for the pyrolysis of pure isopropanol.

Toluene has one third the methyl sites available for H-abstraction as compared to 1,3,5 trimethyl benzene. Thus changing the radical trapper from TMB to toluene while maintaining the same molar concentrations of each, reduces the radical trapping potential by approximately one third. The TMB concentrations used here represent the upper limit of trapper concentration as a result of vaporization and sampling system configurations. The toluene concentration used in the 976 K experiment was chosen to reduce the radical trapping potential by approximately a factor of four in comparison to that achieved using TMB at the same experimental conditions, thus characterizing the effectiveness of the radical trapping concept.

3. Results and Discussion

3.1. Experimental Results for Isopropanol Decomposition

Five decomposition experiments of isopropanol are reported, three of which are conducted in the presence of the radical trapper and used to determine elementary rate constants (Table 1). For all experiments, the decomposition of isopropanol results in the formation of propylene, water, acetone, methane, acetaldehyde, and ethylene.

Previous experimental pyrolysis studies of *tertiary*-butanol, ethanol and methylformate[2,14,19] have shown that a heterogeneous reaction processes of these species occurs in the mixer/diffuser section of the flow reactor. At early reaction times corresponding to flow within the mixer/diffuser section, isopropanol is also found to react heterogeneously on the mixer surfaces. Figure 2 shows that the initial concentration of isopropanol entering the reactor section downstream of the mixer/diffuser remains essentially unchanged at the longer reaction times. The result of the heterogeneous processes is in evidence at the first sampling location in the high temperature pyrolysis experiments shown in Figure 3 (a) and (b).

It has been shown both experimentally and computationally that heterogeneous chemistry has no effect on measurements in the test section of the VPFR, other than having modified the composition of the entering reactive mixture. Experimentally, species profiles at low temperatures illustrate, see Figure 2, no additional conversion of oxygenate[2,14,19] to olefin and water occurs within the test section of the VPFR. Computationally, Large Eddy Simulations (LES), at very similar flow conditions utilized here, have shown that the timescale required for radial diffusion to the centerline of heterogeneously converted species is much larger than experimentally sampled timescales. Thus, any catalytic occurrence at the test section wall has no

appreciable impact the centerline gas phase measurement[20]. Therefore, the heterogeneous processes noted within the mixer/diffuser region only affects the initial conditions of the flow entering the downstream constant-diameter, test section of the flow reactor. These initial conditions are inconsequential to determination of rate constants when the chemical composition of the initial flow entering the test section is fully characterized and the data treated appropriately (i.e. initial conditions are mathematically irrelevant).

The atom balances for the data sets used to determine rate constants show no less than a 6/9/9 % deficiency of total carbon/oxygen/hydrogen presented to the experiments. The determined atom balance for carbon lies well within the experimental uncertainty (~5%) of the analytical technique. The atomic balance of oxygen averaged a deficit of 4.5/3.6/1.4/6.6/7.2 % for the 976/978/999/981/800 K experiments respectively, while the experimental uncertainty of the oxygen balance is no better than 5 %. The 981 and 800 K experiments are used only for model comparison purposes, not for the determination of rate constants, since no radical trappers were used in the 981 K experiment and insufficient conversion was observed in the 800 K experiment to determine a rate constant.

The dominant products observed in all experiments with radical trappers are propylene and water at a molar ratio very near one, consistent with both being formed almost exclusively through the molecular dehydration (Reaction 1) of isopropanol. In the absence of radical trappers, the absolute concentrations and rates of formation for water and propylene are different, when comparing experimental results at 981 K with the other experiments where radical trappers are present, see Figure 3 (b). This feature indicates a significant occurrence of radical orientated secondary chemistry.

4. The Determination of Rate Constants from Experimental Isopropanol Decomposition Profiles

Similar to previously published work[2], rate constants for the dehydration and C–C bond fission reactions are determined from the experimentally measured decomposition profiles by objectively comparing modeling predictions with experimental observables. Nominally, the indirect determination of these rate constants from experimental profiles requires a physical model and a numerical procedure to evaluate the determined rate constant uncertainties. The physical model utilized here is comprised of a zero-dimensional kinetic solver and a chemical kinetic model. This model is reported in the Supplemental Material. The experimental VFFR apparatus has been carefully designed, and computationally and experimentally characterized, to very closely approximate homogeneous, constant pressure adiabatic reaction conditions when operated in the configuration of the present set of experimental tests. Thus the experimental data are properly interpretable as being a zero-dimensional adiabatic constant pressure system. With regard to the chemistry submodels used in the analyses, each serves a specific purpose:

1) The isopropanol submodel includes the hydrogen abstraction reactions from oxygenated and non-oxygenated radicals, and the decomposition of the alkyl and alkoxy radicals that are formed, in addition to the isopropanol decompositions reactions that are the targets of the study[9,21].

2) The H_2/O_2, C_1-C_4 hydrocarbon "small" species submodel describes the reactions of radical initiated "secondary" chemistry, including the consumption of the products of the molecular elimination reactions, propylene, acetone, hydrogen etc.

3) The radical trapper submodel describes the consumption of toluene and 1,3,5 trimethyl benzene, both uni-molecularly and by hydrogen abstraction by small radical species. It additionally describes the lifetimes and the consumption products of the radicals formed by these processes. Both the toluene and 1,3,5 trimethyl benzene submodels have been developed by the authors in previous works[22]. Importantly, both models have been developed with data obtained in the same VPFR facility at similar test conditions to those probed here, and also with a host of data available in the literature.

Comparisons of the model simulations with experiment require an optimization technique/algorithm to minimize the distance between experiments and predictions. Here a differential evolution algorithm and an iterative optimization technique, are used to optimize the rate constant determinations of interest. In addition, a computational initialization procedure is utilized to numerically account for the very well understood heterogeneous non-idealities that if left untreated could result in a significant error in zero-dimensional prediction comparisons with experiment. Finally, the uncertainties of the rate determinations are estimated via a Latin Hypercube sampling. Below, the kinetic sub-model, the simulation/experimental comparison approach, and the rate constant uncertainty estimation methods are discussed in more detail.

4.1. Kinetic Mechanism Sub-Models

As noted above, the kinetic model used in the indirect determination of rate constants is composed of three sub-models to represent the small species, radical trapper, and isopropanol chemistry. For the small species chemistry, the model of Sheen *et al.*[23] is chosen. Sheen *et al.* carefully documented the uncertainty factors (UF), for all small species of interest, thus supplying information pertinent to evaluating rate constant determination uncertainties resulting

from kinetic model parameter uncertainties. Moreover, Sheen *et al.* extensively compared their modeling results with experimental observations over a wide range of conditions that encompass the present experimental conditions[23].

A radical trapper sub-model for 1,3,5 trimethyl benzene is used to investigate the radical termination effectiveness in the present experiments and to determine the resulting uncertainties in the extracted rate constants. The radical termination submodel kinetics are developed from the work of Metcalfe *et al.*[24] for toluene, that were later extended by Diévart *et al.*[22] to describe the reactions of TMB. The reactions with O_2 addition, ring opening of aromatic species, large radical (MW>26 gm/mol) - radical reactions present in the model of Diévart *et al.*, are not considered as molecular oxygen is absent in the experiments, and reactions duplicating those already present in the model of Sheen *et al.* are also discarded. The removal of these reactions facilitated computationally solving the problems at a reasonable timescale (The complete model of Diévart *et al.* contains several thousand reactions.). A computational comparison of predicted results using the detailed model of Diévart *et al.* and the skeletal model results in inconsequential differences in computed product profiles for water and propylene (<1-2% differences), but may slightly affect confidence intervals of the uncertainty analyses.

The isopropanol sub-model controls the radical initiation and simulates the decomposition of isopropanol via channels in addition to those occurring through the subject reactions of the current optimization scheme (e.g. $iC_3H_7OH + O_2$ and $iC_3H_7OH + OH$). The model reported in the thesis of Serinyel[21] is utilized to describe all radical reactions involving isopropanol and its subsequent reaction intermediates. For the decomposition reactions of isopropanol (e.g. the H_2 and CH_4 elimination reactions), the results of Bui *et al.* are employed. No work has yet appeared from which to estimate the parameter uncertainties associated with

this submodel, and there are insufficient experiments in the literature to comprehensively study the veracity of the propanol kinetic submodel components.

The three aforementioned sub-models are combined to form the kinetic model used to determine the dehydration and C–C bond fission rate constants of isopropanol. Collectively, the model is composed of 575 reactions and 121 species, and is available in the Supplemental Material.

4.2. Non-Ideal Chemical Approximations for Isopropanol

Similar to the prior pyrolysis studies of ethanol, methyl formate, and *tertiary*–butanol in the Variable Pressure Flow Reactor[2,17,19], isopropanol decomposes heterogeneously at early mixer diffuser times in the VPFR, modifying the composition entering the constant diameter reactor section downstream. In the case of *tertiary*-butanol, we conclusively showed that the heterogeneous effects were only significant in the silica foam, mixer/diffuser section. The processes contributed only to the formation of isobutene and water, the products also characteristic of the gas phase dehydration reaction channel. Downstream, the reactor test section measurements showed that the observed production rate of isobutene and water were almost entirely a result of the gas phase dehydration reaction. Radical trappers were found to fully suppress secondary reactions of radicals with *tertiary*-butanol, thus assuring that the local destruction rate of the *tertiary*-butanol contributed greater than 98% of the observed dehydration reaction product formation rates, with the net fuel destruction occurring only from the dehydration and C-C bond fission channels. The C–C bond fission rate of destruction produces different reaction products than the dehydration reaction and was observed to be a much slower reaction. The measurements in the test section could therefore be directly applied to determine the dehydration rate and C-C bond rate constants by considering the local destruction of *tertiary*-

butanol and respective product evolution rates. In this scenario, comparisons with model simulations are not required to extract rate constant information.

In the case of isopropanol, however, the dehydration and C–C bond fission reaction rates are more similar in magnitude (at the selected flow reactor conditions), and their respective contributions are more difficult to distinguish directly from experimental measurements alone. In fact, some C-C bond fission products are noted to be evolved within the mixer diffusion region, upstream of the first sampling point in the reactor test section. Thus, an "indirect" determination technique that involves comparison of computational simulations with experimental data is applied. To initialize such comparisons in the reactor test section requires a more complex consideration of the processes occurring within the diffuser/mixer in order to in interpret the downstream results[25].

In the earlier work of Scire *et al.*[15] to determine the rate constants for $CH_3 + HO_2$ and $CH_3 + O_2$ from the oxidation of trace amounts of methane in a reacting bath of carbon monoxide and oxygen, the initialization of the model simulations to compare against the experimental data could be adequately accomplished using "time shifting" optimization[26]. Similar "time-shifting" methods have been used extensively in this laboratory for many years, with the procedure documented and tested in each specific application[25,27]. However, in the presence of heterogeneous non-idealities such as those found in the cases of ethanol, methyl formate, and isopropanol decomposition, simple time shifting cannot be applied. In their study of ethanol decomposition, Li *et al.* [14,17] developed and evaluated an alternative initialization approach based upon computational methods. The "computational re-initialization" method of Li *et al.* has been further discussed in more general terms recently by Dryer *et al.*[25]. A modification of the Li *et al.* methodology is applied here and is described in more detail below.

4.2.1. Computational Re-initialization

The computational re-initialization for the simulation of isopropanol experiments employs the constrained equilibrium approximation to determine the species concentrations of fast reacting species, given a chemical kinetic model and thermochemistry. This constrained equilibrium technique calculates a solution for

$$\dot{X}^n \left(T, P, X^m, X^n, X_{N_2} \right) = 0$$

where $\dot{X}^n$ is the vector composed of the concentration production rates for all unknown (unmeasured-fast reacting) species at an early experimental observation location in the reactor test section downstream of the mixer/diffuser, where T/P is the experimental temperature/pressure, X^m is the concentration matrix composed of known (experimentally measured slow reacting) species, X^n is the concentration matrix composed of all unknown (unmeasured fast reacting) species, X_{N_2} is the concentration of molecular nitrogen, and 0 is the null or zero matrix. The matrix of known species and experimental conditions are the solver inputs, and the matrix of unknown species and nitrogen concentration are solver outputs. The outputs are approximated via a "steady-state" solution obtained from a series of transient calculations using a stiff ordinary differential equation solver[17,28]. The execution of the constrained equilibrium technique is as described in Dryer et al.[25]. We found that the convergence of the computational re-initializations applied in this work was well behaved. The rates of production, $\dot{X}$, are repeatedly checked to confirm convergence of the approximation. Typical values for the molar production rate of species are $<10^{-7}$ ppm/s absolute. In order to estimate the uncertainty of this technique, all the input parameters are varied independently for each sample and the statistical significance of their cross correlation is numerically evaluated.

4.3. Uncertainty Estimation Methodology

The uncertainties considered in the indirect determination of Reaction 1 and Reaction 2 can be broken down into three main sources: kinetic model uncertainty, measurement uncertainty, and initialization uncertainty. These three sources are collectively considered using Latin Hypercube sampling to span the kinetic model, measurement, and initialization uncertainties so as to determine the global uncertainties for the dehydration and C–C bond fission rate constants. In this section, the probability density functions (PDFs), means, and variances for each of these three sources of uncertainty are discussed.

4.3.1. Kinetic Model Uncertainty

The kinetic modeling uncertainty is estimated using the method of uncertainty factors. Uncertainty factors have been used historically to describe the upper and lower limits of probable rate constant values for a reaction[29], and this characterization has been adopted recently to produce a distribution of possible rate constant values for specific reactions[23,30]. It has been shown previously[31] that the distribution definition used by Sheen *et al.* best describes the determined rate constant distribution, and this approach is applied here to evaluate the impacts of all kinetic model uncertainties.

The uncertainty factor, UF_i, values for the kinetic parameters of each reaction *i* are categorized into reaction submodel considerations for the small species, radical trapper, and isopropanol kinetic submodel sources, as reported in Table 2. The UF_i values for the Sheen *et al.*, small species, and Diévart *et al.*, radical trapper, submodels are taken from recommendations attributable to the respective works[21,22,30]. In the radical trapper submodel, an *UF* of 5 is used for

reactions of H atom and OH plus radical trapper, and a *UF* of 10 is used for all other reactions

based upon the recommendation of Diévart[32]. As no prior recommendations are available for the isopropanol sub-model reactions, the uncertainty factors are estimated as $UF_i =$ 5, based upon similar work in this laboratory[33]. Specific exceptions to this general rule are the assignment of a UF_i value of 10 for the tautomerization of propylene-2-ol and the beta-scission reactions of propyl-oxy radicals to form H atom and acetone. The tautomerization reactions of alcohols remain an active research field in combustion, making the estimation of these reactions particularly uncertain, and the beta scission rate constants of propyl-oxy radicals are believed to be significantly underestimated as the formation rates of acetone (by the kinetic model) are many orders slower than experimentally observed here. The assignment of uncertainty factors that result in a uniform distribution over the smallest and largest rate constant values having equal probability is most likely not the case. In similar uncertainty work[31], we found that the distributions more closely resemble a normal- rather than uniform-distribution. The fact that the distributions used here are uniform rather than normal yields a conservative uncertainty evaluation for the determined rate constant values.

4.3.2. Measurement and Initialization Uncertainty

The experimental and model initialization parameters are also considered as sources of uncertainty for the determination of the dehydration and C–C bond fission rate constants. The uncertainties of these experimental parameters are reported in Table 3, and a normal distribution

is assumed to describe their PDFs. Measured species are varied normally about their reported value. Uncharacterized species that may have been present (e.g. no isobutene was observed in the experiments), are varied for each sample calculation about a defined threshold measurement. The threshold value is the estimated concentration below which a particular species could not be detected (~0.5-25 ppm depending on the species). A normal distribution is also used to describe those species that were not characterized experimentally.

An exception to this approach is the case of molecular oxygen initialization. Previous decomposition studies in the VPFR have shown that trace quantities of molecular oxygen in the nitrogen diluent[17]. Here, up to 100 ppm of molecular oxygen is considered as a trace contaminant in simulating the experimental results. The trace molecular oxygen value assumed in the numerical predictions are treated as a parameter and varied with each Latin Hypercube sample. Trace oxygen perturbations were analyzed by considering the reactions involving O_2 in the isopropanol and small species chemistry submodel constructs. Most notably, the objective function analysis required O_2 plus isopropanol to remain in the model in order to account for the potential additional production of water and destruction of isopropanol. The simulations of the complete Diévart *et al.* model with O_2 at these conditions produced < 10 ppm of water and < 0.3 ppm of propylene confirming the neglect of molecular oxygen reactions in the radical trapper submodel construct.

4.3.3. Sample Generation for Latin Hypercube Sampling

The Latin Hypercube sampling technique is employed to generate an expectation value for a rate constant at each condition for the dehydration and C-C bond fission reaction. Perhaps more importantly, Latin Hypercube sampling is used to determine the uncertainties for these rate constants as a function of the experimental, modeling, and initialization uncertainties. The use of

Latin Hypercube sampling requires that the cumulative distribution function be known or estimated. The cumulative distribution function (CDF) is sub-divided into N equi-probable bins (where N is the number of samples), and a number is selected between the lower and upper limits in each bin with respect to the probability of each bin. The sequence of each independent variable sample set is randomized and combined with the remaining independent variables. Finally, these uncertainties and distributions are used to generate 14,000 sample simulations for each of the reported 976, 978, and 999 K decomposition experiments. From these sample simulations, the expectation value and variance were found to converge to better than 1% over all of the determined dehydration reaction rate constant values. All told, approximately 900 variables are altered in each Latin Hypercube sample.

4.3.4. Weighting the Experimental Measurements

All experimental data are given a weighting factor of one, for the 15 chemical sample analyses used to determine the chemical profiles for each experiment. The fractional extent of conversion observed in each experiment implies that all data have sensitivities of similar order to reaction parameters.

4.4. Numerical Results for Isopropanol Decomposition

The experiments at 976, 978, and 999 K are used to determine the dehydration and C–C bond fission rate constants at each of the respective reaction conditions. The cumulative and histogram results of the Latin Hypercube sampling are given in Figure 4 (a) and Supplemental Material. The experimental data are found to well constrain the determination of the dehydration reaction rate for all reported experiments. In all cases, the data and simulation comparisons poorly constrain the determination of rate constant values for the C–C bond fission. The average

percent uncertainty for the dehydration reaction is 6%, while that for the C–C bond fission reaction is the order of a factor of two. The large uncertainty for the C–C bond fission results is due to the ill-conditioning of the objective function to the experimental data (i.e. the simulations show that the measured species profiles are relatively insensitive to the C–C bond fission reaction rate). In contrast, the relatively small uncertainties of the dehydration reaction are due to the high sensitivities of the isopropanol, water, and propylene profiles to the dehydration rate constant. Table 4 reports the expectation values for the determined rate constants and their respective confidence intervals.

The rate constant values determined here and the high-pressure-limit theoretical predictions of Bui *et al.* are compared in Figure 5. The determined values are approximately four times faster than the theoretical predictions of Bui *et al.* Of the 42,000 sample values determined, none are in parity with the dehydration reaction rate reported by Bui *et al.* In contrast, the much larger uncertainty in the determined C–C bond fission reaction rates is in reasonable accord with the theoretical results of Bui *et al.* It is not possible to draw more precise information from the comparison of the C-C bond fission results.

4.5. Functional form of the Reported Isopropanol Dehydration Reaction Distributions

Statistics for six different functions are calculated for the reported dehydration distributions of isopropanol, with the resulting statistics reported in Table 5. A log-normal distribution outperformed the five other reported distributions[31]. In fact, the average R^2 value for the log-normal distribution is found to be 0.9999, indicating that the log-normal distribution is the preferred description.

4.6. Comparison to Direct Determination Methodology

As noted above, an indirect determination approach is more appropriate for the analysis of data for the isopropanol pyrolysis tests in the presence of radical trapper, given the relatively competitive nature of dehydration and C-C bond fission reactions. However, the indirect method results provide an opportunity to assess differences yielded by applying a direct method to quantitatively determine the dehydration reaction rates.

The direct determination of the dehydration rate constant and its uncertainties for each experiment are reported in Table 6. In comparing these results with the numbers produced from the indirect determination, the direct and indirect approaches are found to be in good agreement with the expectation values for each, differing between 6 and 11 %, respectively. In fact, the upper (97.5%) and lower (2.5%) confidence intervals for the indirect method lie completely within the upper and lower confidence intervals for the direct method. The somewhat larger expectation values and smaller uncertainties for the indirect method are at first glance unexpected, as radical chemistry is neglected from a direct determination, implying rate constants could be skewed to faster reaction rates. Further, the indirect approach also considered many more uncertainties. However, the direct method largely determines the rate constant directly from the formation rates of product species. The decomposition rate of the reactant is only used to normalize the production rates. The production rate of water will increase as it is an inert product species, while that of the propylene will decrease in the presence of radicals as it may be reacted further, giving a mean very near the indirect determination.

An explanation for the smaller estimated uncertainties associated with the indirect method is less clear. Most data used in the determination only change the recommended rate constant by less than 0.25%. However, in a select small set of cases, the deviation of a

measurement by one sigma can change the determined rate constant by as much as 7% (see discussion below). Furthermore, when the measured values are randomly perturbed about their measured value, there is only a 1 in 8192 chance that all the values of a specific species profile will be above/below their mean. In those select cases, the rate constant determination for these particular simulations will be systematically skewed. The propagation of errors approach used in the uncertainty analysis of a direct determination effectively skews all the data systematically by one sigma and removes the sign of the derivative (i.e. depends on the square of the derivative values). As a result, the uncertainty produced is very nearly a root-mean-square analysis. Correspondingly, it can be shown that the root-mean-square of the standardized regression coefficients reproduces uncertainties near those determined via the simple propagation of errors technique developed in Heyne *et al* [2]. Thus, in this case the uncertainty of the isopropanol dehydration rate constant is over-estimated when a direct approach is employed.

4.7. Standardized Regression Coefficient Analysis

The root sources of uncertainty for the dehydration and C–C bond fission reaction are investigated by using standardized regression coefficient analysis. This analysis normalizes the dependent variables, the kinetic, experimental, and initialization parameters in this case, and statistically correlates the independent variables (determined rate constants for each sample) to the dependent variables (model parameters such as initial conditions and rate constants). In this analysis, a linear regression is performed for all dependent variables versus both the dehydration and C–C bond fission reaction rate values. If a regression returns a p-value above 0.05, the variable is said to have returned a "null hypothesis," i.e. it is assumed that the independent variable is not significantly correlated with the dependent variables. The results of this analysis are reported in Figure 4 (b).

Figure 4 (b) plots the R^2 value of a regression versus the number of parameters used in the regression for the dehydration reaction of isopropanol, broken down into the three main categories of uncertainty in the determination of the rate constants (kinetic model, experimental, and initialization uncertainties). Each symbol represents a parameter with a p-value less than 0.05, and each symbol to the left of another symbol represents the inclusion of an additional parameter used in the regression. The R^2 value is chosen as the metric in this analysis as it is directly related to the "goodness-of-fit" for a regression. Thus with a constant set of samples, the R^2 value is directly related to the sum of the residuals squared and approximates how well a regression model captures the dependent variable. Figure 4 (b) shows that a regression composed of only experimental independent variables (squares) describes the distribution of the dehydration reaction better than the initialization (triangles) and kinetic model (circles) parameters. Further, Figure 4 (b) shows the relative insensitivity of the dehydration rate constant distribution to kinetic model parameters. In all experiments, more experimental parameters failed to return a null hypothesis, and resulted in a better fit as compared to the model parameters.

On average, a change in an experimental measurement is correlated to approximately a 0.26% change in the determined rate constant value. Only a few experimental measurements (2–7 per experiment) are correlated to more than a 1% change in the determined rate constant when the experimental measurement is changed by one standard deviation. The water profile data show the greatest effect in altering the determined rate constant. For example, in the 999 K experiment a change in the water measurement at 1.12 s by one sigma is correlated with a 7% decrease in the determined dehydration rate constant. This specific measurement of water concentration has the largest effect on the determined rate constant over all other water

measurements and experiments, the next greatest being < 3% for the water measurement at 0.59 s in the 976 K experiment.

Only one initialization parameter is correlated with an effect greater than 1% of the determined rate constant. Xylene (2,4 dimethyl benzene) is measured in trace quantities in the 999 K experiment, and is a consumption product owing to the radical trapping process. The measurement of xylene at the first measured point in the 999 K experiment is correlated with changing the determined rate constant by approximately 8%. In investigating why xylene has such a strong influence on this particular case, the derivatives and sensitivities of initial species concentrations with-respect-to xylene concentration are evaluated. The derivative of molecular hydrogen simulation to xylene initialization was the largest as molecular hydrogen supplies a source of radical hydrogen atoms. Furthermore, the concentrations of other reactive species, CH_3O_2 and CH_3O_2H , formed from methyl radicals are also among the most sensitive to the initialization of xylene. Both the derivative of molecular hydrogen and the sensitivities of initial CH_3O_2 and CH_3O_2H concentrations are positive. Thus, an increase in the concentration of xylene causes an increase in the concentrations of molecular hydrogen, CH_3O_2 , and CH_3O_2H . These dependencies result in proportional changes in the radical destruction rate of isopropanol to produce water, thus resulting in a decrease in the determined dehydration reaction rate. At lower temperatures the initial xylene concentrations are found to be much less important.

Similar to Figure 4 (b), the R^2 values combining the experimental, kinetic model, and initialization parameters are shown for all experiments and literature rate constant determinations in the Supplemental Material. The dehydration reaction rate distribution is well described by the regression analysis, returning cumulative R^2 values of 0.898/0.861/0.961 for the 976/977/999 K experiment. On the other hand, the C–C bond fission rate distribution is poorly described by the

regression analysis, returning cumulative R^2 values of 0.027/0.144/0.063 for the 976/977/999 K experiment. Finally, it should be noted that the total number of parameters varied in the analysis is approximately 900. In referencing the R^2 value plots, only the order of 70–90 parameters fail to return a null hypothesis. Of those 70-90 variables, less than a quarter of the dependent variables significantly relate to the "goodness-of-fit."

4.8. Rate Parameter Recommendation

Experimentally, the study of the dehydration reaction in the VPFR is instrumentally limited to the temperature range of 950 to 1000 K, precluding an accurate determination of the curvature (*n*) and slope (*Ea*) of the dehydration rate constant. Thus, we have taken the approach of adopting these parameters as recommended by Bui *et al*. The pre-exponential factor (A) is then adjusted in order to align experimental and numerical simulated results. On this basis, the recommended rate correlation for the dehydration reaction of isopropanol is:

$$k = 8.32 \times 10^6 \text{ s}^{-1} \, T^{2.12} \exp\left(-30{,}667\frac{K}{T}\right).$$

The method to determine this value and the uncertainty value prescribed to it are detailed in the Supplemental Material. The recommended uncertainty for the pre-exponential value is estimated to be $\sigma_{\ln A}^2 = 0.0195$. Figure 5 plots the determined rate constants, the previous high pressure limit of Bui *et al*., and updated rate constant recommendations with their respective uncertainties. This uncertainty neglects the uncertainties inherent in the slope and curvature recommendations of Bui *et al*., and as such, may under-represent the total uncertainty in the dehydration rate. The analysis also effectively assumes that the measurements here described are at the high pressure limit. Nonetheless, the updated rate constant description agrees well with the newly reported experimental and numerical results.

In Figure 3 (b), the updated and original Bui *et al.* rate parameters are used to simulate the experimental water, propylene, and isopropanol profiles for the 981 K experiment. All experimental profiles are better represented with the updated rate parameters. Particularly, the propylene profile is well characterized by the new rate parameters of the dehydration reaction. The predicted water and isopropanol profiles, although better represented, are not completely captured by the updated dehydration rate. Improvements to these profiles can be made by further considering the consumption of isopropanol by radical reactions, which is beyond the scope of the present work.

5. Conclusions

The decomposition of isopropanol was studied in a flow reactor facility to determine the reaction rate for the dehydration and C-C bond dissociation reactions. The importance of heterogeneous reactions of isopropanol on silica surfaces was experimentally noted and shown to be unimportant in affecting the measured experimental reaction profiles used to extract rate information. Three different decomposition experiments in the presence of a radical trapper were conducted to determine the rate constants and the results were compared with an additional experiment without the presence of a radical trapper. In all experiments, isopropanol was observed to decompose to form water, propylene, acetaldehyde, ethylene, methane, and acetone. Both the dehydration and C–C bond fission reaction rates of isopropanol were determined via an indirect technique through comparison of model simulations with the experimental data. The dehydration reaction rate was additionally estimated via the analytical direct determination technique outlined in Heyne *et al.*[2] It is shown that the obtained experimental profiles are

insufficiently sensitive to the C–C bond fission reaction to determine the rate constant to better than an uncertainty of approximately a factor of two. However, results were sufficiently sensitive to the dehydration rate constant to determine its values much more precisely. The direct and indirect determinations of the dehydration reaction rate were found to be in good agreement, and the difference in the estimated uncertainties was explained as the difference between random sampling and systematic root-mean-square uncertainty estimation.

The categorical and individual sources of uncertainty in the dehydration rate determinations were systematically analyzed via standardized regression coefficient methods. The experimental uncertainty was found to be the major categorical source of uncertainty for all rate constant determinations. Specifically, the water profile measurement uncertainties are the most significant contributor.

Finally, the theoretical results of Bui *et al.* were compared to the elaborated analysis. The dehydration rate constants determined from the reported experimental profiles were shown to be approximately a factor of four faster than the recommendation of Bui *et al.* To produce a rate correlation reconciled with this information, the pre-exponential factor of Bui *et al.* was adjusted, and an estimated uncertainty for the pre-exponential factor for the modified rate correlation was determined. The reported rate constants and correlation represent the first experimental dehydration rate constant results determined by suppressing secondary radical effects using radical trappers, produced using both indirect and direct determination techniques, with detailed uncertainty estimations of the results.
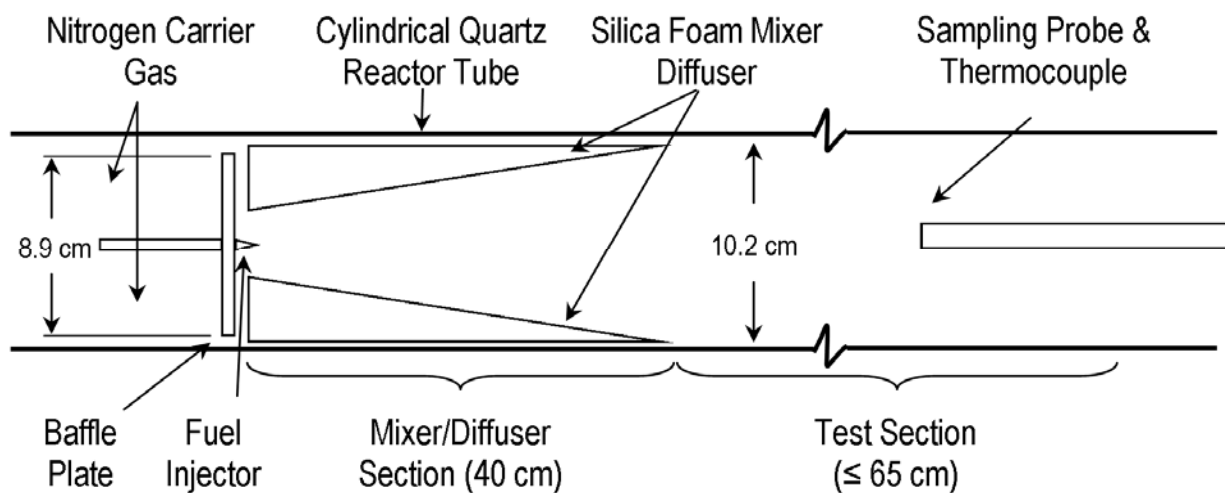
6. Acknowledgment

7. Figures

Figure 1. **Schematic of VPFR. Preheated nitrogen carrier gas flows around baffle and mixes with pre-vaporized isopropanol and toluene/TMB. The mixture reacts along a quasi-adiabatic flow tube. Gas is sampled via water cooled probe (~353 K). The sampled gas then goes to online (FTIR) and offline (GC-FID) analysis equipment. The mixer/diffuser section is composed of silica foam. The test section is made of fused silica.**
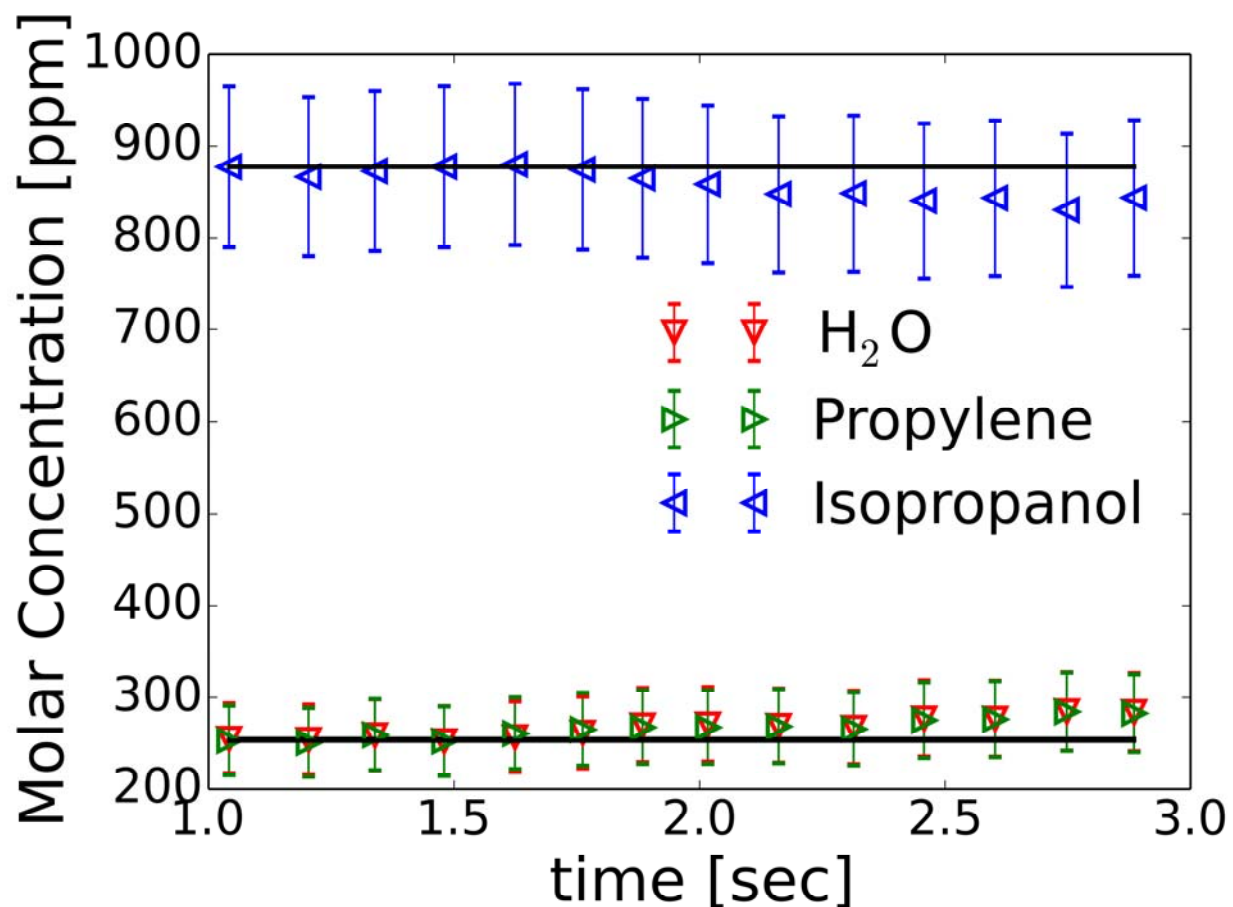
Figure 2: Illustration of heterogeneous conversion outside the mixer/diffuser section at lower a lower temperature (800 K) in the VPFR[21]. At early times within the mixer/diffuser region (< 1 s) approximately 250 ppm of isopropanol is converted to water and propylene. Outside this region, in the test section, isopropanol is largely unreactive and heterogeneously produced water and propylene do not have time to diffuse to the centerline sampling location. The species profiles of isopropanol, water, and propylene are within the estimated measurement uncertainties for this particular experiment. Estimation of the apparent rate constant for conversion in the mixer/diffuser is ~10^4 times faster than expected based upon the gas phase dehydration rate at 800 K.
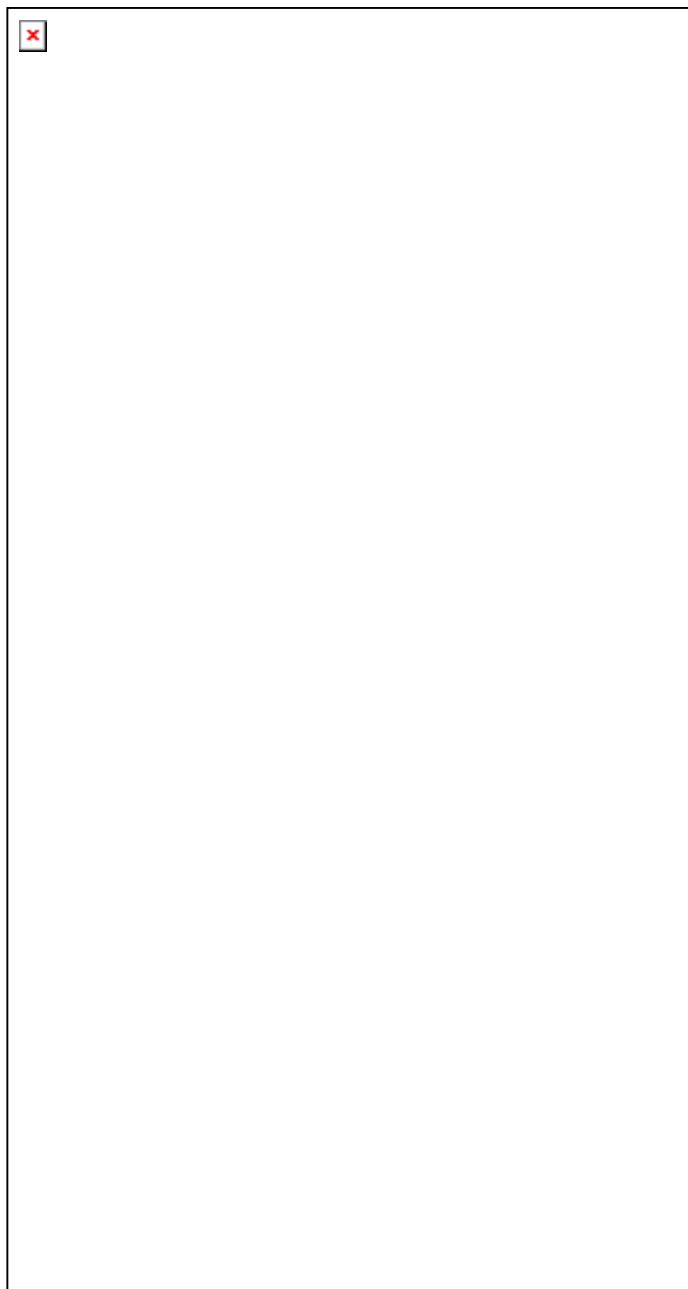
Figure 3. Experimental results and computational predictions of isopropanol decomposition. (a) Speciation profile of isopropanol with TMB in the flow reactor at 978 K, 12.5 atm, 1750/4550/993700 isopropanol/TMB/N_2. (b) Major and minor species profiles for the 981 K decomposition experiment. The dashed lines are the species profiles with the initial dehydration rate constant recommendation of Bui *et al.* The solid lines are the species profiles using the recommended dehydration rate parameters. All experimental profiles are better captured with the dehydration reaction rate recommended by this study. Discrepancies between the water, isopropanol, and minor species profiles can be improved by updating radical plus isopropanol reactions and additional isopropanol submodel reactions.
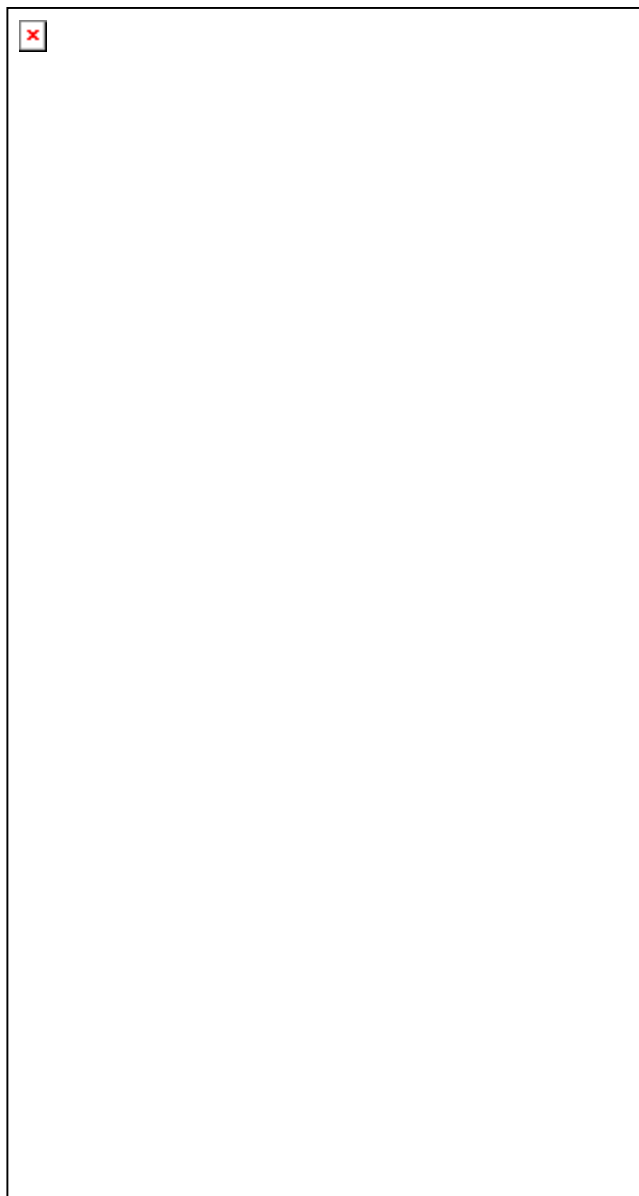
Figure 4. Numerical results from Latin Hypercube sampling: (a) PDFs of the dehydration rate constant determination for two experimental conditions, 976 K and 978 K. The two experiments used different radical trappers and radical trapper concentrations. Nonetheless, there is agreement between the experiments. (b) R^2 value of a linear regression for each source of rate constant uncertainty via model, experimental, and initialization parameters. At the far left hand side of the plot only one parameter is used in the regression. With each subsequent point, an additional parameter is added to the regression. Here the parameters are grouped as model, experimental, and initialization parameters. The experimental parameters induce the largest source of uncertainty in the determination. Model parameter uncertainty induces the least amount uncertainty. The initial Xylene concentration for the 999 K experiment is the only initialization parameter that has a statistically significant effect on the determination of the dehydration rate constant.
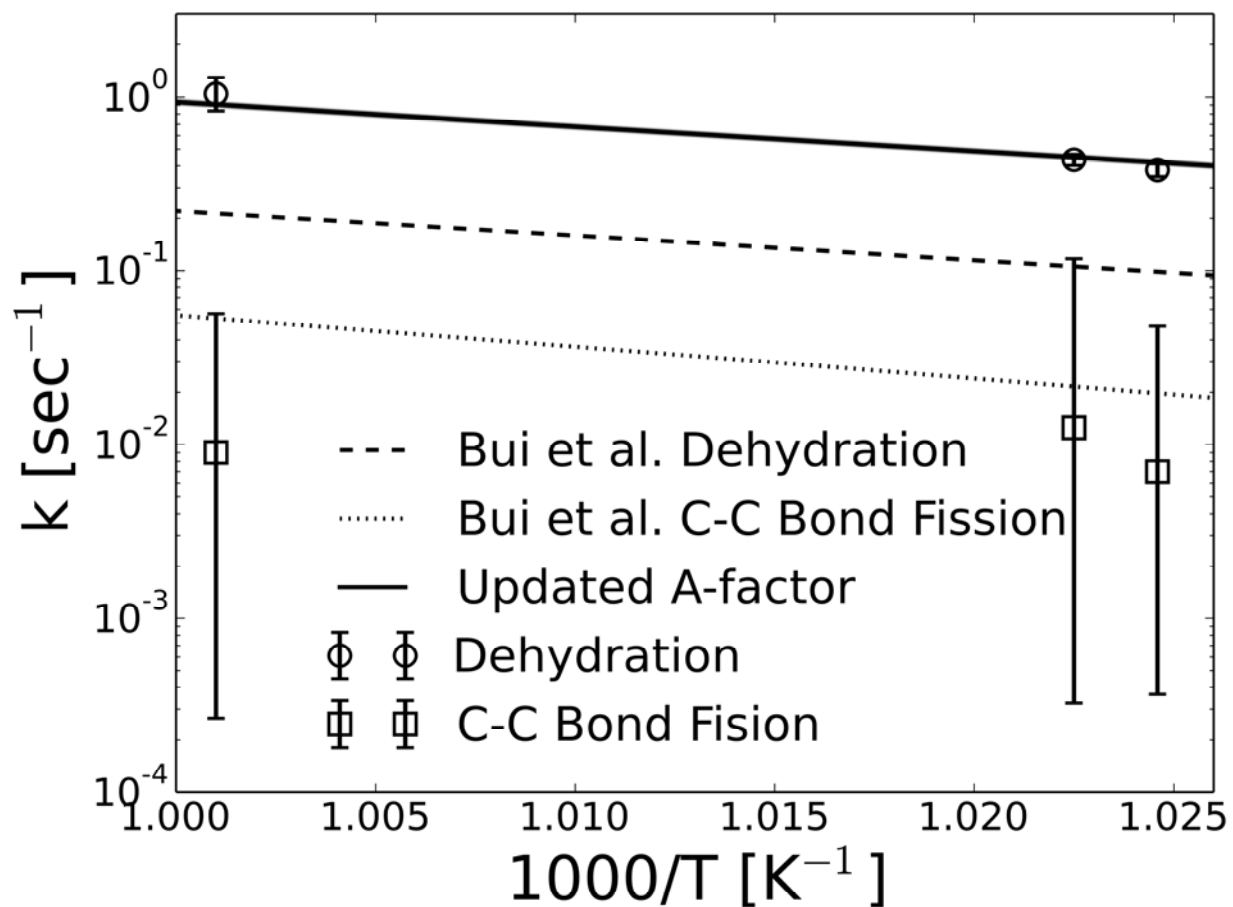
Figure 5. Comparison of this work's experimental results (open symbols) vs. computational determinations of Bui *et al.*(dashed and dotted lines) for the dehydration (circle) and C–C bond fission (square) reaction of isopropanol, and the updated rate using the reported experimental profiles (solid line). The error bars are the 95% confidence intervals for experimental predictions. There is poor agreement between the experimental and computational results for the dehydration reaction. There is good agreement between the experimental and computational results for the C–C bond fission reaction. The experimenal data are much more contraining in the determination of the dehydration reaction of isopropanol, and ill-conditioned to accurately determine the C–C bond fission reaction. The thickness of the updated prediction represents the 95% confidence intervals for the adjusted pre-exponential term. The total uncertainty for the rate constant is likely much larger when the theoretical uncertainties for *n* and *Ea* are considered.

8. Tables

Table 1. Experimental conditions of isopropanol decomposition experiments. "TMB" is 1,3,5, trimethylbenzene, balance is nitrogen.

Test [#]	Temperature [K]	Pressure [atm]	[isopropanol] [ppm]	Radical Trapper	Radical Trapper: isopropanol ratio
1	976	12.5	2478	Toluene	1.9:1
2	978	12.5	1750	TMB	2.6:1
3	999	12.5	1500	TMB	2.6:1
4	981	12.6	2700	-	-
5	800	12.5	1200	TMB	2:1

Table 2: Uncertainty Factors used for Latin Hypercube sampling to estimate the uncertainty in the determined rate constant

Submodel / Reaction Class	UF
Small Species	Recommendations by Sheen et al.[23]
$\frac{H}{OH} + TMB$ /toluene	5^{32}
Radical Trapper	10^{32}
Propylene-2-ol tautomerization	10
Propyl-oxy Reactions	10
Isopropanol Submodel	5

Table 3. Uncertainties used in the determination of the isopropanol decomposition rate constants.

Parameter	Uncertainty [1 σ]
Species [%] (measured)	2.5
Species [ppm] (unmeasured)	2.5-12.5
Temperature [K]	3.75
Time [%]	1.5
Pressure [atm]	0.1

Table 4. Determined rate constants and confidence intervals for reported experiments. The upper and lower limits reported are the 95% confidence intervals based on the Latin Hypercube sampling. Thus, 95% of all the samples fall between the lower and upper limits reported here.

Test [#]	Temperature [K]	Dehydration Reaction			C–C Bond Fission Reaction		
		k [s^{-1}]	Lower Limit (2.5 %)	Upper Limit (97.5 %)	k [s^{-1}]	Lower Limit (2.5 %)	Upper Limit (97.5 %)
1	976	0.379	0.347	0.412	0.00699	0.36	48.22
2	978	0.434	0.403	0.467	0.001251	0.32	116.71
3	999	1.043	0.834	1.294	0.00902	0.27	56.70

Table 5. R^2 values, χ^2 tests, and Kolmogorov-Smirnov test results averaged over all three reported distributions for the dehydration reaction of isopropanol.

Distribution Form	R^2 value	χ^2 Test	Kolmogorov-Smirnov Test
Normal	0.9989	0.000187	0.01346
Log-normal	0.9999	0.0000244	0.004968
Uniform	0.5938	0.069095	0.2565
Log-uniform	0.5762	0.06292	0.2030
Logistic	0.9984	0.000257	0.01740
Log-logistic	0.9995	0.0000855	0.01393

Table 6. Direct determination of dehydration rate constant for isopropanol, and the values given by the Bui *et al.* recommendation for the dehydration reaction of isopropanol.

Experiment	k (2σ) [s^{-1}]	Lower Limit (2.5 %)	Upper Limit (97.5 %)	Bui *et al.* dehydration k [s^{-1}]
976 K	0.339 (0.060)	0.280	0.400	0.0983
978 K	0.410 (0.065)	0.345	0.475	0.105
999 K	0.971 (0.358)	0.613	1.329	0.213

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