High Temperature Shock Tube Experiments and Kinetic Modeling Study of Diisopropyl Ketone Ignition and Pyrolysis

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Abstract: Diisopropyl ketone (DIPK) is a promising biofuel candidate, which is produced using endophytic fungal conversion. In this work, a high temperature detailed combustion kinetic model for DIPK was developed using the reaction class approach. DIPK ignition and pyrolysis experiments were performed using UCF shock tube. The shock tube oxidation experiments were conducted between 1093 K and 1630 K for different reactant compositions, equivalence ratios ($\phi = 0.5-2.0$), and pressures (1-6 atm). In addition, methane concentration time-histories were measured during 2% DIPK pyrolysis in argon using cw laser absorption near 3400 nm at temperatures between 1300 and 1400 K near 1atm. To the best of our knowledge, current ignition delay times (above 1050 K) and methane time histories are the first such experiments performed in DIPK at high temperatures. Present data were used as validation targets for the new kinetic model and simulation results showed fair agreement compared to the experiments. The reaction rates corresponding to the main consumption pathways of DIPK were found to have high sensitivity in controlling the reactivity, so these were adjusted to attain better agreement between the simulation and experimental data. A correlation was developed based on the experimental data to predict the ignition delay times using the temperature, pressure, fuel concentration and oxygen concentration.

Keywords: Ignition delay time; Kinetic mechanism; Shock tube; Biofuel Oxidation; Diisopropyl Ketone.

1. Introduction

Use of biofuels, especially in automotive applications, is a growing trend due to their potential to reduce the greenhouse gas concentrations in atmosphere. Researchers have been exploring various methods - including endophytic fungal conversion of cellulose - to efficiently produce biofuels in order to decrease our dependence on fossil fuels. One example of a biofuel that is successfully blended with fossil fuels is ethanol, and as a result the focus of biofuel combustion research during last 3 decades mainly fell on ethanol blends. Experts have predicted that liquid biofuels will be a significant part of future energy portfolio[1] and recently, there have been many innovative methods to produce biofuels [2-5]. Even though, biofuels are a promising renewable alternative to conventional petroleum fuels that could lower greenhouse gas emissions[6], the products that are most efficiently produced from biomass may not have well-characterized combustion properties as they represent a wide range of chemical structures which have varying ignition, oxidation, and emission characteristics. Therefore, probing the fuel molecular effects on combustion is vital and critical kinetics knowledge is warranted for other oxygenated chemical classes, including ketones and aldehydes, which so far received rather scarce attention in the literature [7-9].

One of the most promising platforms for cellulosic biofuel generation is to harness the metabolic processes of endophytic fungi that directly convert lignocellulosic material into a variety of volatile organic compounds [10-13]. The biofuel co-development framework was initiated at Sandia National Labs [14-16], which is similar to the “Tailor-Made Fuels from Biomass” approach from Europe[17]. Here, the synthetic biologists[14, 18, 19] develop and engineer a new platform for drop-in fuel production from lignocellulosic biomass, using several endophytic fungi including *Hypoxylon CI-4A*, *EC-38*, *CO27-A*, and *Daldinia EC-12*. Fungal pathways are moreover particularly suited for synthetic bioengineering due to their relatively minimal genomes. Hence this process has the potential advantage that expensive pretreatment and fuel refining stages can be optimized thereby allowing scalability and cost reduction-two major considerations for widespread biofuel utilization. Large concentrations of ketones[20] along with other volatile organic compounds (VOC's) were produced by *Hypoxylon CO27-A* grown over

switchgrass media. The combustion and emission properties of these novel fungal biofuels (large ketones) are poorly known, and fundamental measurements of representative molecules are needed in order to provide feedback on their desirability in advanced combustion engines (e.g., HCCI: homogeneous, charge, compression and ignition engines) and their impact on emissions.

Most combustion studies in the literature focused on simple ketones such as, acetone[21-28] (simplest ketone), 3-pentanone[26, 29-31], and propanone[32]. Interesting to the current task are shock tube ignition investigations by Serinyel *et al.*[31, 33] for 3-pentanone and 2-butanone. Also, Black *et al.* [27] completed an experimental and numerical work on the ignition delay times, laminar flame speeds as well as a kinetic model for acetone using shock tube and spherical bomb. Pichon *et al.* [23] and Davidson *et al.* [34] have studied the ignition delay times of acetone at relatively high temperatures 1300-1900K. Recently, Hanson and co-workers [29, 35, 36] investigated ignition, pyrolysis, and oxidation of these ketones using shock tube and laser diagnostics technique. The premixed flames of three different C₃-oxygenated hydrocarbons (acetone, *n*-propanol, and *i*-propanol) were investigated at low pressure[37].

Very recently, ignition delay times of 2-butanone and 3-buten-2-one were measured using a shock tube to probe the effect of double bond. It is clear that combustion kinetics interests in ketones were mainly limited to small molecules due to their application as tracer-LIF species [24, 38] and critical ignition and oxidation data for realistic biofuel candidates are needed.

Di-isopropyl ketone (DIPK), 2,4-dimethyl-3-pentanone (C₇H₁₄O), is a prototype for biofuels produced by endophytic fungi [14, 39]. DIPK is a branched ketone which is a potential candidate as a biofuel to be used in advanced homogeneous charge compression ignition (HCCI) engines [40]. A detailed study of DIPK was performed recently using experimental and modeling methods by Allen *et al.* [14] The detailed modeling of combustion phenomena is based on a comprehensive kinetic mechanism which includes details of several reactions and rate constants. In this regard, the smaller ketones such as, acetone and 2-butanone have been investigated theoretically and experimentally in terms of pyrolysis,

reaction rates, and ignition delay times at different ranges of temperature [27, 28, 30, 35] up to 2000K. However, due to a limited number of studies on larger ketones, their ignition characteristics and chemistry of oxidation are not well documented. For the larger straight-chained and branched ketones, there are some measurements at combustion temperatures for ketone +OH reactions using shock tube [41]. The detailed reaction mechanism developed by Allen *et al.* used an automated approach called reaction mechanism generator (RMG) for DIPK [14] and focused on temperatures below 1000K. The model was verified against various experiments; however, the ignition delay time measured by shock tube and rapid compression machine for the temperature range of 590-1023 K near 10 bar showed significant discrepancies comparing to predictions. The significant shift in the NTC suggests that more investigations should be performed to develop a model capable of predicting the combustion behavior of DIPK. This mechanism was slightly modified [39] to be able to predict Sandia's HCCI engine experimental data [40] for fuel reactivity, required bottom dead center temperature versus combustion timing. However, discrepancies were not completely resolved at high temperature. The "auto" option in RMG suggests that the user is not required to specify conversions at which the edge reaction fluxes are estimated. The user also does not need to decide whether to add a new species in the core reaction model. This option saves a lot of computational time and costs. However, it may result in missing of some important reactions.

The goal of this study is to investigate DIPK oxidation and pyrolysis characteristics at high temperature and to gain insights into branched ketones decomposition and oxidation pathways. A detailed high temperature kinetic reaction mechanism for DIPK was developed based on successful reaction classes approach adopted for other hydrocarbon fuels in the literature [42-44]. To validate DIPK kinetic mechanisms new high temperature experimental targets are needed. A shock tube is an ideal facility to measure the ignition delay time and species time histories due to the use of shockwaves being utilized to compress and heat the mixture on microsecond time scales compared to the hundreds of microsecond time scales of the experiments [27, 30, 41, 45, 46]. The ignition delay times were measured at 1093-1630 K in a shock tube for different reactant fractions, equivalence ratios ($\phi=0.5-2.0$), and pressures (1-6 atm). The ignition delay time, defined as the time it takes for a mixture to ignite under a certain pressure and

temperature is an important fundamental and design parameter for engine development. In addition, methane concentration time-histories were determined using laser absorption near 3400 nm during 2% DIPK pyrolysis (in argon) for temperatures between 1300 and 1400 K near 1atm. The agreement between current simulations and experimental data validates the model to be employed to interpret the oxidation pathway of DIPK.

2. Experimental Procedure

2.1. Shock Tube and Mixing Facility

The high purity kinetics shock tube located at the University of Central Florida (UCF) was used for all experiments (for details refer [47]). The UCF shock tube is made of electro-polished stainless steel with an ID=14.17cm and utilized lexan diaphragms (thickness 5-20 mm). The sidewall test section (located 2 cm from the driven end wall) has 8 ports for optical and pressure measurements. The test pressure was monitored by a piezoelectric pressure transducer (Kistler 603B1). Five PCB 113B26 transducers connected to four time-interval counters (Agilent 53220A) placed along the last 1.5 m of the driven section measured the incident shock velocities. Temperature (T_5) and pressure (P_5) in the reflected shock region were calculated based on the extrapolated end wall incident shock velocity with uncertainties estimated to be less than $\pm 1.5\%$ [47].

Mixtures of research grade gases from Air Liquide (O_2 , Ar, >99.999%) and DIPK (Acros Organics, 98%) were prepared in a heated (423 K), magnetically stirred, 33 L stainless steel mixing tank using the partial pressures of individual components and mixed for a minimum of 6 hours before experiments.

2.2. Ignition and Species Diagnostics

For this study, the ignition delay time was determined as the time between the midpoint of the pressure trace (caused by arrival of reflected shock wave), as recorded by the Kistler to the midpoint of the

emissions rise (during ignition), detected by a Thorlabs PDA25K photodetector with a 430 nm bandpass filter to isolate the CH* emission. the intensity of OH* or CH* chemiluminescence is used to measure the heat release in the flame. For this paper, the rise of CH was used as the start of ignition. The CH trace was normalized to the peak voltage measured.

An example of the ignition delay time is shown in Fig. 1 including normalized CH* emission detection as well as the pressure trace. A slit was placed in front of the detector to limit the spectral resolution of the emission trace and improve the accuracy of the measurement [47].

The methane time-histories during pyrolysis were measured using cw laser absorption spectroscopy. A distributed feedback interband cascade laser centered at 3403 nm from Nanoplus was used in conjunction with two Boston Electronic PVI-2TR-3.4 photodetectors (described in [47]). A differential peak-valley wavelength method (corresponds to the P(8) line of methane v3 band [48]) was used to eliminate the interfering species during the experiments. Using this absorbance line and the 4 nm tuning range of the laser, an interference-free peak-valley absorption scheme was developed.

The method utilized to measure the methane time-histories is based on the Beer-Lambert Law (Eqn. 1) which relates the ratio of transmitted light to a reference (I_{tr}/I_{ref}), to the absorption cross-section(σ), pressure (P_{tot}), temperature (T), mole fraction (X), and path length (L):

$$-\ln\left(\frac{I_{tr}}{I_{ref}}\right)_v = \sigma(\nu, T, P) \frac{P_{tot}}{RT} \chi L \quad (1)$$

In order to eliminate the interference, a peak (3403.40 nm)-valley (3403.56 nm) wavelength absorption scheme is used which refers to subtraction of the two transmission measurements obtained at two different wavelengths. Since the combustion products have constant absorption characteristics in the region around 3403 nm [35, 46, 49], the absorption of such species is removed by performing two sequential measurements, one at the peak absorbance of methane and the other one at its valley. Interfering species are then removed by subtracting the valley measurement from the peak to obtain the differential methane absorbance.

Figure 1- Ignition delay time data in 1%DIPK+20%O₂+79%Ar mixture (1196K, 0.97atm)

The ignition delay times were measured during the oxidation of DIPK for equivalence ratios between 0.5 and 2.0. Current experiments were conducted for temperature range of 1100-1600 K at pressures of 1 and 6 atm. Fuel concentrations for these experiments ranged between 1-2% with oxygen concentrations of 10-20%. For all mixtures the oxidation was performed in an argon bath. Methane time histories were measured during DIPK pyrolysis for temperatures at 1300 and 1400 K for 1 atm. Ignition delay measurements were taken for four mixtures covering the range of conditions which are summarized in Table 1. Guided by a design of experiments analysis, the broad test matrix was chosen to maximize the ranges of variations in parameters that affect ignition as it is impossible to conduct parametric studies covering all possible ranges.

Table 1- Experimental condition in shock tube

3. Chemical kinetic model development using reaction class approach

The reaction class approach was used to develop a kinetic mechanism for DIPK valid at high temperatures. A detailed high temperature (HT) reaction mechanism with the important reaction classes was created and then the rate constants were assigned based on analogy to the similar reactions or literature recommendations. This procedure was successfully applied for butanol combustion modeling by Sarathy *et al.*[42, 43] The DIPK submechanism was then integrated into a recently published AramcoMech-1.3 C₀-C₄ mechanism established by NUI-Galway [50]. The corresponding thermodynamic properties for the fuel and primary fuel radical species were calculated using the THERM [51] program. The high temperature oxidation submechanism includes unimolecular fuel decomposition, H-abstraction reactions and decomposition and isomerization of the resulting fuel radicals.

The ignition delay behind the reflected shock waves was simulated using a zero-dimensional model with constrained volume and adiabatic boundary, solving energy equation in CHEMKIN-PRO

[52]. This assumption is valid for short test times and for moderate heat release until ignition in shock tubes [53]. The HT reaction submechanism developed as well as the method of obtaining the rate constants through the reaction class approach for important reaction classes are explained in the following sections.

3.1. Unimolecular fuel decomposition reactions

The fuel unimolecular decomposition reactions are the fuel consumption reactions in high temperature region which are also denoted as initiation reactions. There are two possible classes of unimolecular decomposition for DIPK, including bond scission and H atom elimination which result in the formation of alkyl radicals or one hydrogen atom respectively (Scheme 1). The rate constants are considered for recombination reactions which are listed below

.....) to). The rate constants for) and for (R 2) are assumed as radical-radical recombination reaction based on Tsang recommendation for the recombination of n-propyl radical with methyl [54] and acetyl with isopropyl [55]. The former reaction rate constant for DIPK decomposition is assigned to be $6.0 \times 10^{15} T^{-0.32} s^{-1}$, with A-factor multiplied by 30 based on comparisons with present CH₄ time-histories data. Note that in the absence of experimental data, our estimation is justified because the reaction rate constants are all assigned based on analogy of the structures with the literature recommendations for alkanes (here we used Tsang's recommendation for a ketone with C=O functional group which can have a different decomposition reaction rate than alkanes).

The reaction rate can be rationalized by the presence of the carbonyl group which is polar compared to alkanes (The details are given in section 4.3). The rate constants for H-atom recombination with the fuel primary and tertiary radicals, namely (R3) and (R4) are assigned based on the radical recombination recommended by Allara and Shaw [56]. The modifications are made on the unimolecular decomposition rate constant according to the experimental data.

Scheme 1-DIPK decomposition

3.2. Fuel H-atom abstraction reactions

H atom abstraction takes place at primary (β) and tertiary sites (α) of DIPK which results in the formation of two different fuel radicals, denoted as R_{Pri} and R_{Tert} , (scheme 2). The hydrogen atom is abstracted from DIPK by different radicals ($\dot{\text{R}}$) including H, OH, HO_2 , CH_3 and C_2H_5 .

Scheme 2- DIPK radicals- tertiary and primary radicals

The rate constants of abstraction from β site by H, CH_3 and C_2H_5 , (namely R5, and R13) respectively), are considered to be analogous to twice of the corresponding reaction rates of abstraction from 3-pentanone and the rate constant for (R11) is assigned with A-factor of 4 times of the corresponding reaction in 3-pentanone [31]. The reaction rate for abstraction by HO_2 from DIPK primary β hydrogen, (R7), is obtained twice of isopropyl methyl ketone (iPMK) based on ab-initio and chemical kinetic study of abstraction reactions by Mendes et. al [57]. The schematic structure of iPMK is shown in Scheme 3.

Scheme 3- Isopropyl methyl ketone iPMK

The OH reaction rate constants for four hexanone isomers were compared. In this study Badra *et al.* [58] showed that the carbonyl group position in the hexanone isomers has negligible effect on the rate constants. In the current study, we tried to use this concept to estimate the rate constants for $\text{DIPK} + \text{OH} \rightarrow \text{products}$, along with Cohen's method [59, 60] of next-nearest-neighbor (NNN) to specify the site specific rate constants for primary and tertiary abstracted H. For this purpose, as our first approach, according to Badra *et al.* [58] conclusion for hexanone isomers, we assumed that the overall reaction rate of OH with isopropyl methyl ketone (iPMK) is approximately the same as its isomer, 3-pentanone. Now DIPK, iPMK and 3-pentanone are defined using NNN method.

$$k_{\text{DIPK}+\text{OH}} = 12P_{2,\text{CO}} + 2T_{100,\text{CO}} \quad (2)$$

$$k_{\text{iPMK}+\text{OH}} = P_{1,\text{CO}} + 6P_{2,\text{CO}} + T_{100,\text{CO}} \quad (3)$$

$$k_{\text{3-pentanone}+\text{OH}} = 6P_1 + 4S_{10,\text{CO}} \quad (4)$$

where $P_{1,\text{CO}}$ is the rate constant for the primary site H abstraction by OH next to the carbonyl group, the same as in acetone; $P_{2,\text{CO}}$ and $T_{100,\text{CO}}$ refers to are the rate constants for primary and tertiary H abstraction by OH from CH and methyl groups next to to the carbonyl group, respectively; $S_{10,\text{CO}}$ is the rate constant for secondary H-abstraction by OH from CH_2 nearby the carbonyl group and P_1 is the rate constant for primary H-abstraction by OH from the methyl group at the site adjacent to the CH_2 group based on Badra *et al.* [58] definitions. First, the compound isopropyl methyl ketone (iPMK) is used as a reference to estimate the rate constant for H- abstraction reaction from DIPK by OH and forming tertiary radical as a result. The reason to pick this species was due to the similar structure of tertiary carbon in iPMK with DIPK. In a recent quantum chemical calculations on ketones H abstraction reactions by OH studied by Zhou et al [61]., the rate constants for the

reaction of iPMK with OH was estimated and the overall and the site specific reaction rate were given. We used this rate to estimate the H abstraction reaction for DIPK. The similar structure of the tertiary carbon in iPMK (scheme 3 in the paper) to that of DIPK was used with the corresponding branching ratio and number of tertiary sites and the reaction rate was estimated (1st approach).

Second, since Zhou et al rate constants were based on calculations, they should be verified. For that purpose, our rate estimation second approach, according to a recent study by Badra et al [58] in which the effects of the position of the carbonyl group (C=O) and methyl (CH₃) branching on the overall rate constant with OH are studied, we used the overall rate constant for 3-pentanone+OH instead of iPMK+OH. Therefore, the overall rate constant of DIPK+OH based on our estimation (equations 5.1 & 5.2) was presented.

$$\begin{aligned} k_{\text{DIPK+OH}} &= 2(6P_{2,CO} + T_{100,CO}) = 2(k_{\text{iPMK+OH}} - P_{1,CO}) \approx 2(k_{\text{3-pentanone+OH}} - P_{1,CO}) \\ k_{\text{DIPK+OH}} &= 6P_1 + 4S_{10,CO} - P_{1,CO} \end{aligned} \quad (5.1, 5.2)$$

The comparison which was based on next-nearest-neighbor (NNN) to specify the site specific rate constants for primary and tertiary abstracted H showed similar trends. Therefore, the rate constants for DIPK is first being calculated based on similar structure to 3-pentanone with NNN method as well as the analogy of the tertiary carbon with that of iPMK.

Badra *et al.* [58] estimated 3-pentanone+OH reaction rate based on their calculation of $S_{10,CO}$ and $P_{1,CO}$ and verified their result by Lam *et al.* [36] experimental data. DIPK rate constant with OH can be estimated by analogy approach, (2nd approach) which is based on using the *ab initio* calculation of iPMK+OH→products, calculated in terms of overall and site specific rates by Zhou *et al.* [61]. In order to estimate the rate constants for H-abstraction reactions of DIPK with O, resulting in primary radical, 3-pentanone reaction with O was considered as a reference. In order to obtain the rate for the resulting tertiary radical branching ratios for +O and +H radicals were assumed to be same. The rate constants for H abstraction reaction by different radicals are summarized in Table 2.

Table 2- DIPK estimated rates for H abstraction reactions by H, OH, HO₂, CH₃, O and C₂H₅ radicals

3.3. Ketonyl radical decomposition

The rate constants for H atom addition to C₇H₁₂O producing R_{pri} and R_{tert} C₇H₁₂O+H⇌R_{pri} (R 5) C₇H₁₂O+H⇌R_{tert} (R 6) are assigned to have the same A-factor of $1.0 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ with the activation energy of 2.9 kcal/mol and 1.2 kcal/mol respectively based on Curran et al recommendation [44]. Also the rate constants corresponding to the addition of methyl to C₆H₁₀O to form R_{pri} C₆H₁₀O+CH₃⇌R_{pri} (R 7) as well as the addition of isopropyl radical to dimethyl ketene (DMK) to produce R_{tert} DMK+iC₃H₇⇌R_{tert} (R 8) are estimated to be $8.5 \times 10^{10} \exp(-5334/T) \text{ s}^{-1}$. C₆H₁₁O is another radical formed by a methyl group removal from the fuel. The reaction rate constants for C₆H₁₀O+H⇌C₆H₁₁O (R 9) and $1.0 \times 10^{13} \exp(-1459/T) \text{ s}^{-1}$ and $8.5 \times 10^{10} \exp(-5334/T) \text{ s}^{-1}$ respectively.

3.4. Fuel radical isomerization reaction

The isomerization reaction of fuel radicals $\text{R}_{\text{pri}} \rightleftharpoons \text{R}_{\text{tert}}$ (R 11)

based on 1,2 H-Shift (Scheme 4) rate rule used in the calculations by Matheu et al [62] is assigned to be $3.56 \times 10^{10} \times T^{0.88} \exp(-14897/T) \text{ s}^{-1}$.

Scheme 4- H atom migration in 1,2 H-Shift

3.5. Olefin unimolecular decomposition reactions

The radical decomposition through β -scission rule produces unsaturated species with carbon atoms double bond for which the decomposition and abstraction rate constants are to be determined. DIPK

radicals β -scission results in the formation of $C_7H_{12}O$. The unimolecular decomposition reaction of DIPK by removing a methyl group also yields $C_6H_{11}O$ radical which undergoes β -scission to produce $C_6H_{10}O$ and H radical. The rate constants of decomposition for $C_7H_{12}O$ are considered in reverse direction as recombination reaction of isopropyl radical with C_4H_5O as well as sC_3H_5 and C_4H_7O . The rate constant for the former is estimated to be $9.033 \times 10^{12} \times T^{-0.35} s^{-1}$ based on Tsang recommendation [54] found in NIST web book [63] for recombination of isopropyl to acetyl group. Similarly, the rate constant for C_3H_5 and acetyl radical recombination is used to estimate the $sC_3H_5 + C_4H_7O \rightleftharpoons C_7H_{12}O$ (R 13 rate constant [55]). $iC_3H_7 + C_3H_3O \rightleftharpoons C_6H_{10}O$ (R 14) rate constant is estimated to be the same as $iC_3H_7 + C_4H_5O \rightleftharpoons C_7H_{12}O$ (R 12).

3.6. Olefin H-abstraction reaction

The H abstraction from large olefins ($>C_4$) formed during DIPK oxidation are assumed to occur either in paraffinic side or double bond carbon side, although the latter has smaller effects on the large molecule [64]. Therefore, in $C_7H_{12}O$, the H abstraction reactions are from allylic and vinyl sites as well as primary and tertiary positions (see

Scheme 5). The rate constants for the H abstraction reactions from $C_7H_{12}O$ paraffinic side by all the

radicals considered here $C_7H_{12}O + H \rightleftharpoons C_7H_{11}O + H_2$ (R 15) to (R 17)

are half of that of DIPK in order to form primary and tertiary radicals.

The rate constant for the H abstraction by H atom from vinyl site is assigned to be

$5.06 \times 10^7 \times T^{1.98} \exp(-5910/T) s^{-1}$ based on group additivity rate calculation by Sumathi *et al.* [65]

for $R_2C = CH_2 + H \rightarrow R_2C = \dot{C}H + H_2$. Similarly, from the same reference, the rate of abstraction

from allylic site is assumed to be $1.299 \times 10^6 \times T^{2.38} \exp(-1410/T) s^{-1}$ predicted for

$R_2C = CRCH_3 + H \rightarrow R_2C = CR\dot{C}H_2 + H_2$. The H abstraction reaction rate of $C_7H_{12}O$ by

OH to from vinyl site is estimated by similarity to that of 2-butene-2-one reaction measured by Badra *et*

al. [41] to be $8.513 \times 10^{12} \times \exp(-4666/T) s^{-1}$. The rest of the rate constants including the abstraction

reactions by CH_3 and HO_2 are assumed to be similar to isobutene H abstraction, [66] resulting in vinyl

and allylic radicals, as found in the latest version of isooctane reaction mechanism [67]. In the reactions

$C_7H_{12}O + H \rightleftharpoons C_7H_{11}O + H_2$ (R 15) to $C_7H_{12}O + CH_3 \rightleftharpoons C_7H_{11}O + CH_4$ (R 18),

$C_7H_{11}O$ stands for the general representation of all radicals (allylic, vinyl, primary and tertiary).

Scheme 5- H abstraction from $C_7H_{12}O$

3.7. Olefin radical isomerization reaction

As mentioned in the previous section, there are four different radicals formed from $C_7H_{12}O$ in H abstraction reactions. The isomerization rate constants are estimated for 1,3 H-shift from vinyl to form allylic radical (v→a) as well as 1,2 H-shift from primary to form tertiary radical (p→t) to be $3.80 \times 10^{10} \times T^{0.67} \exp(-19476/T) s^{-1}$ and $3.56 \times 10^{10} \times T^{0.88} \exp(-14897/T) s^{-1}$ respectively based on Matheu *et al.* [62] calculations.

3.8. Olefin radical decomposition reaction

The decomposition rate constants for radicals are estimated in reverse direction. It is assumed that all the radicals decompose to smaller species for which the rate constants are all $2.5 \times 10^{13} \times \exp(-22647/T) s^{-1}$ based on Curran *et al.* [64].

3.9. Keto-enol tautomerization

Ketones are often in rapid equilibrium with their tautomeric form, known as an enol. The isomerization called keto-enol tautomerization in which the hydrogen in α position (next to the carbonyl group) moves to form the hydroxyl group by shifting the double bond from the carbonyl group to the carbon atoms bond next to the OH moiety. As the concerted keto-enol tautomerization is constrained by the transition state geometry requirements, an acid or a base catalysis is required for tautomerization to take place. This kind of reaction usually occurs in favor of ketone formation which is more stable species. Sarathy *et al.* [43] estimated the rate constant for butanol isomers enol-keto tautomerization catalyzed by H, HO₂ and formic acid. In order to estimate the rate constant for this type of reaction, supplementary information is required which is not available at the moment.

The reaction mechanism for high temperature region is developed and presented. Some of the reaction rates are modified based on the experimental validation which is explained in the Result and discussions section.

4. Results and discussion

4.1. Ignition delay times

The ignition delay time data points for each of these conditions are illustrated in Fig. 2. The proposed kinetic model was used to simulate the ignition delay time and the results are compared to the experimental data from UCF's shock tube. The effect of reactants various fractions on the reactivity of DIPK is studied by comparing the ignition delay time versus temperature inverse at different equivalence ratios and at the pressures of 1 and 6 atm. The shock tube experimental conditions are presented in Table 1 and the results of the experiments are summarized in Table 3. The results displayed in Fig. 3 show good agreement between the simulation (solid lines) and experiment (markers) for the given temperature ranges. The results are also compared with the reaction mechanism developed by Allen *et al.* [14] (dashed lines). The discrepancies are observed between the simulation based on their mechanism and the

experimental data. In comparison, the model used in the current work improved the prediction by about an order of magnitude.

Figure 2- Current ignition delay time results for DIPK oxidation

In addition to the comparisons to the updated kinetic model, a correlation was developed to predict the ignition delay times using the temperature, pressure, fuel concentration and oxygen concentration, with $R^2 = 0.979$. Equation (6) shows the correlation:

$$\begin{aligned}\tau_{ign}[\mu s] &= A \exp\left(\frac{E[cal/mol]}{R[cal/mol \cdot K]T[K]}\right) P^b [DIPK]^c [O_2]^d \\ &= 1.97 \cdot \exp\left(\frac{28196.2}{RT}\right) P^{-1.08} [DIPK]^{-0.29} [O_2]^{-1.93}\end{aligned}\quad (6)$$

where A had an uncertainty of ± 0.63 , E had an uncertainty of ± 1262.82 , the uncertainty of b was ± 0.08 , the uncertainty of c was ± 0.09 and the uncertainty of d was ± 0.14 . From the correlation and the uncertainty in the various measurements, the overall uncertainty in the ignition delay time was determined to be less than 18%.

The uncertainty was determined using a combination of the correlation presented above and the uncertainty of the pressure and temperature in the test section. Using the linear regression analysis described in Bevington and Robinson, the velocity at the end wall was determined from the four timer-counters [68]. From this analysis, the end wall velocity was determined to be less than 1%. The next part in determining the uncertainty in the ignition delay times is to calculate the uncertainty in the pressure and temperature. From the Nishida *et al.*, the pressure and temperature for the test section can be written in terms of the initial pressure and temperature and the end wall velocity [69]. The uncertainty in the temperature and the pressure can then be determined to be 2% for each value. The uncertainty in ignition delay times was calculated from the uncertainty analysis on the ignition delay time correlation and factoring in the values for the uncertainty for each measurement from the specs

and the uncertainties from the nonlinear regression analysis from the correlation as well as the linear regression analysis used to calculate the uncertainty in the pressure and temperature of the system.

Figure 3- Simulated (solid lines, present mechanism) and experimental (markers) ignition delay times for different mixtures (Table 1) of DIPK oxidation; the results are compared to Allen et al mechanism [14] (dashed lines).

Figure 4- Current ignition delay times (experimental and simulations) as a function of pressures for DIPK oxidation in Ar bath at $\phi=1$ (reactants percentages are given in Table 1). Note: 10atm data are from [14].

Table 3- The experimental ignition delay time results for different mixtures

The pressure effects on ignition delay time is shown at the different reactants ratios and at pressures of 1, 6 and 10 atm in Fig. 4. In order to simulate the ignition delay time at high pressure, the experimental pressure trace profile was used in CHEMKIN-PRO.

Figure 4 shows the experimental ignition delay time at different pressures compared to the present model. Pressure increases reactivity significantly (1 to 6 atm) and this compensates for reduced reactivity caused by decreasing O_2 concentration (the mixture fractions are also changed from 20% O_2 to 10%). This

shows that the oxidizer concentration effects are significant such that the increased reactivity due to the increased pressure is compensated by the reduced amount of O_2 concentration.

4.2. DIPK oxidation path analysis

The model based on the reaction class approach was validated by experimental data; therefore, it has been used to describe DIPK high temperature oxidation pathways (Fig. 5). The pathways are presented based on the CHEMKIN-PRO zero-dimensional model for 2% DIPK oxidation in Ar at 1300 K at time at which 20% of the fuel is consumed. The consumption of DIPK is initiated through H-abstraction reactions resulting in the formation of primary and tertiary radicals. Furthermore, DIPK is consumed through the unimolecular decomposition reactions. The decomposition pathway resulting in methyl radical and $C_6H_{11}O$ is considered as a dominant reaction controlling the fuel reactivity. In addition, due to the formation of CH_3 which is a source of methane, it is also important in CH_4 sensitivity analysis.

The fuel radicals from the H-abstraction reactions decompose to propene (from the R_{pri}) and dimethyl ketene (from R_{tert}). The radicals decomposition also results in formation of an important intermediate, $C_7H_{12}O$ which can further decompose through unimolecular decomposition or participate in H-abstraction reactions which forms four different radicals. The isomerization reactions between these radicals are also considered within the pathway.

Figure 5- Oxidation path analysis for 2% DIPK in Ar/ O_2 ($\phi = 1$) at 1300K, 1 atm.

4.3. Methane time-histories

Methane is one of the main products in ketones oxidation. The laser absorption spectroscopy was performed using a differential absorption scheme. The peak wavelength (3403.40 nm) for methane was determined by Pyun *et al.* [49]. In this study, we noticed that the valley wavelength of 3403.7 that was used in the previous paper had more interference than previously measured in our lab [47]. Therefore, a new valley wavelength was chosen in order to reduce the noise and increase the accuracy of the measurement. A new wavelength was chosen of 3403.56 nm that is closer to the original wavelength and has a smaller differential absorption cross section as shown in Fig. 6. Possible interfering species and their cross section is also provided in Fig. 6.

Methane time-histories were measured at 1300 and 1400 K. Because of the smaller differential absorption cross section of methane, the measurement window was limited to a narrow temperature region. During the breakdown of DIPK, methane is produced as an intermediate specie (Fig. 7). Thus, these time-histories serve as a secondary method for the validation of chemical kinetic modeling and help to optimize the DIPK decomposition reaction rates [45].

Figure 6- Methane, H₂O, OH and DIPK Absorptions at the peak and valley measurements and most common interfering species.

Figure 7- Measured CH₄ concentration profiles during DIPK pyrolysis in Ar at 1300 and 1400 K.

Figure 8- CH₄ Absorption at both the peak and the valley wavelengths at 1300 K. Absorbance (left axis) and pressure (right axis).

To calculate the methane mole fractions, the absorption at the peak and valley were subtracted from each other to determine the differential absorbance. For the new wavelength, the differential cross section was measured for the range of temperatures considered. Equation 7 shows how the methane mole fraction was calculated from the Beer-Lambert Law and the differential absorbance:

$$\chi_{\text{CH}_4} = \frac{(\alpha_{\text{CH}_4,\text{peak}} - \alpha_{\text{CH}_4,\text{valley}})}{\frac{(\sigma_{\text{CH}_4,\text{peak}} - \sigma_{\text{CH}_4,\text{valley}})P_{\text{tot}}L}{RT}} \quad (7)$$

An example of the peak and valley absorbance measurements is shown in Figure 8. It shows that without eliminating the interference, the methane concentration would not be determined as the measured profiles at these wavelengths differ significantly.

Figure 9- CH₄ concentration profiles during 2% DIPK pyrolysis in Ar at 1300 K (top) and 1400 K (bottom) compared to the present HT mechanism as well as Allen et al. mechanism [14] at 0.9 bar.

The current HT DIPK reaction mechanism is used to simulate CH₄ concentration time-histories (results for 2% DIPK pyrolysis in argon are shown in Fig. 9). At 1400K, there is rapid formation of methane compared to the slower rise at 1300K which is captured by the present mechanism. Also, one can see a decent quantitative agreement with current mechanism simulation at 1300K, while the Allen *et al.* [14] mechanism (dashed lines) slightly under-predicts current data during all times. At 1400K, the present model reasonably predicts the measured profile up to 650 μs , and underpredicts the data for later times. The predicted profiles by the Allen *et al.* shows a reverse trend: good agreement at later times and underprediction the early-time rise. A temperature sensitivity analysis for CH₄ profiles (using CHEMKIN PRO, see equation 8) identified the most sensitive reaction under these conditions to be the primary radical β -scission, which results in the formation of CH₃ and C₆H₁₀O-1. In addition, the tertiary radical β -scission turned out to be the second most sensitive reaction. In the absence of experimental data for the rate constants of DIPK main reactions, better agreement between predictions and experiment can be achieved by detailed investigations based on quantum chemical calculations on the rate constants of the reactions R11, R12, the group of the reaction associated with R28 and the reaction of C₃H₄O+CH₃→C₃H₃O+CH₄, all of which also appear in the temperature sensitivity analysis.

4.4. Sensitivity analysis

The OH concentration ignition delay time sensitivity analysis has been performed to identify the most sensitive reactions in the oxidation of DIPK using CHEMKIN-PRO, where the sensitivity coefficient (S) for i^{th} reaction rate (k_i) for a species is defined as,

$$S(X_{\text{species}}, k_i, t) = \left\{ \frac{dX_{\text{species}}(t)}{dk_i} \right\} \left\{ \frac{k_i}{X_{\text{species}}(t)} \right\} \quad (8)$$

The analysis is based on OH radical concentration and implemented for 2% DIPK with 20% O₂ in Ar bath at 1100 K and 1 atm. The result is illustrated in Fig. 10 where the two important reactions are shown with red arrows. These reactions are H-abstraction reaction from DIPK by H atom resulting in the formation of tertiary radical, as well as DIPK unimolecular decomposition to methyl group and C₆H₁₁O. Both reactions are considered as the main consumption pathways of DIPK and found to have high sensitivity in controlling the reactivity. These reaction rates were adjusted such that improved agreement between the simulation and experimental data was attained.

Figure 10- Ignition delay time sensitivity analysis for 2% DIPK in Ar/O₂ ($\phi=1$) at 1100 K and 1 atm using the CHEMKIN-PRO tool at the time of 20% fuel consumption.

Figure 11- CH₄ sensitivity analysis at 1400 K and 0.9 for 2% DIPK in Ar.

The CH₄ sensitivity analysis (Fig. 11) was performed to show the most sensitive reactions for pyrolysis. The H-abstraction from DIPK by CH₃ radical which results in the formation of CH₄ and fuel radicals, were two of the most sensitive reactions. The A-factor sensitivity also reveals that DIPK decomposition reaction to CH₃ + C₆H₁₁O was one of the most sensitive reactions. In addition, C₆H₁₁O decomposition to C₃H₄O + iC₃H₇ was an important reaction. As mentioned previously, Curran's recommendation [44] for (CH₃+alkyl= fuel) to estimate the rate constant for CH₃+C₆H₁₁O = DIPK is apparently too low. This reaction is also very important source of methane since it produces methyl radical which is a source of methane production (current experiments). Also the rate constant for this specific reaction was found to

play a crucial role in determination of ignition time. In the absence of direct experimental or theoretical study, present experimental data has been used as a validation method and these sensitive reaction rates were adjusted (as we described in earlier sections).

Detailed quantum chemical and experimental investigations of fuel specific decomposition and abstraction reactions of large ketones are recommended for future study.

5. Conclusion

A high-temperature (HT) chemical kinetic model was developed and validated against new shock tube experimental data for di-isopropyl ketone. The HT model developed using the reaction class approach showed significant improvements over that developed by Allen *et al.* [14] using an automated approach. Specifically shock tube ignition delay time and methane concentration from DIPK pyrolysis were accurately captured by the present model. The new mechanism shows reasonable agreement with the ignition delay times at high temperatures. The reaction path analysis as well as the OH sensitivity were performed and the oxidation of DIPK were discussed along with the most sensitive reactions which control the fuel reactivity. A correlation was developed based on the experimental data to predict the ignition delay times as a function of reactants concentration, temperature, and pressure. To the best of our knowledge, current ignition delay times (above 1050 K) and methane time-histories are the first such experiments performed in DIPK- an important biofuel candidate.

In order to further validate and optimize the new mechanism, additional experiments are planned over a greater range of experimental conditions and extending time-histories to different intermediate species (e.g., CO, C₂H₄, CO₂). Also, direct experimental and theoretical studies of key abstraction and decompositions reactions of DIPK are recommended for future study. The experimental data and mechanism presented in this paper could greatly improve the decision making required for using DIPK as a biofuel in advanced engines.

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Mixture	Pressure (atm)	φ	DIPK %	mole	O ₂ mole %	Ar mole %	Temperature range [K]
1	1	1		2	20	78	1093-1505
2	1	2		2	10	88	1285-1630
3	1	0.5		1	20	79	1128-1394
4	6	1		1	10	89	1178-1459

Reaction	$A \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	n	$E_a(\text{kcal mol}^{-1})$	No.
$\text{DIPK} + \text{H} \leftrightarrow \text{R}_{\text{pri}} + \text{H}_2$	2.660×10^6	2.450	6756	(R 25)
$\text{DIPK} + \text{H} \leftrightarrow \text{R}_{\text{tert}} + \text{H}_2$	1.505×10^6	2.41	2556	(R 26)
$\text{DIPK} + \text{OH} \leftrightarrow \text{R}_{\text{pri}} + \text{H}_2\text{O}$	3.108×10^1	3.540	-2909	(R 27)
$\text{DIPK} + \text{OH} \leftrightarrow \text{R}_{\text{tert}} + \text{H}_2\text{O}$	9.840×10^3	2.700	-4036	(R 28)
$\text{DIPK} + \text{HO}_2 \leftrightarrow \text{R}_{\text{pri}} + \text{H}_2\text{O}_2$	4.760×10^{-3}	4.560	15184	(R 29)
$\text{DIPK} + \text{HO}_2 \leftrightarrow \text{R}_{\text{tert}} + \text{H}_2\text{O}_2$	1.696×10^0	3.53	11375	(R 30)
$\text{DIPK} + \text{CH}_3 \leftrightarrow \text{R}_{\text{pri}} + \text{CH}_4$	12.24×10^0	3.650	7150	(R 31)
$\text{DIPK} + \text{CH}_3 \leftrightarrow \text{R}_{\text{tert}} + \text{CH}_4$	4.68×10^3	2.71	3710	(R 32)
$\text{DIPK} + \text{C}_2\text{H}_5 \leftrightarrow \text{R}_{\text{pri}} + \text{C}_2\text{H}_6$	2.000×10^{11}	0.0	13400	(R 33)
$\text{DIPK} + \text{C}_2\text{H}_5 \leftrightarrow \text{R}_{\text{tert}} + \text{C}_2\text{H}_6$	2.646×10^{10}	-0.19	10216	(R 34)
$\text{DIPK} + \text{O} \leftrightarrow \text{R}_{\text{pri}} + \text{OH}$	3.920×10^6	2.43	4750	(R 35)
$\text{DIPK} + \text{O} \leftrightarrow \text{R}_{\text{tert}} + \text{OH}$	2.214×10^6	2.30	550	(R 36)

Mixture	Pressure (bar)	Temperature (K)	Ignition delay time (μ s)
1	0.912	1093	2330
	0.934	1160	1170
	0.948	1234	5841
	0.903	1280	333
	0.868	1344	216
	0.845	1442	92
	0.838	1505	48
2	0.730	1285	1584
	0.836	1412	734
	0.842	1446	534
	0.791	1535	242
	0.756	1630	112
3	1.012	1128	1867
	0.968	1196	808
	0.958	1243	453
	0.899	1342	155
	0.851	1394	83
4	6.304	1178	506
	5.948	1217	373
	5.857	1299	193
	5.670	1392	92
	5.490	1459	40