Comprehensive Study of 1,1-Diethoxypropane Oxidation: Shock Tube Experiments, Laser Speciation, and Kinetic Model Development

Md Zafar Ali Khan[1], Chuangchuang Cao[2], Touqeer Anwar Kashif[1], Aamir Farooq[1]
[1]Mechanical Engineering Program, Physical Science and Engineering Division,
King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia
[2]Department of Chemical Engineering, Massachusetts Institute of Technology (MIT),
Cambridge, MA 02139, United States

1 Introduction and Motivation

Internal combustion engine (ICE) vehicles make up 99.8% of the global transportation fleet, making them major contributors to greenhouse gas emissions [1]. While electric vehicle (EV) adoption faces infrastructure and economic barriers, drop-in fuels offer a practical solution to reducing emissions without requiring major modifications to existing engines or refueling infrastructure. Among alternative fuels, 1,1-Diethoxypropane (1,1-DEP) stands out due to its oxygenated structure, which enhances combustion efficiency and reduces CO, NOx, and particulate emissions. As part of the oxymethylene ether (OME) family, it has high cetane numbers, making it suitable as a cetane booster for diesel fuel. Additionally, it can be synthesized from renewable sources, such as biomass and captured CO_2, making it a viable sustainable fuel option [2]. Despite its potential advantages, research on 1,1-DEP oxidation kinetics is

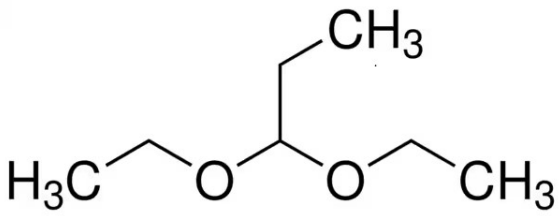

Figure 1: The molecular structure of 1,1-diethoxybutane with five carbon sites

limited, and no validated kinetic models exist. This study investigates the oxidation and ignition characteristics of 1,1-DEP using low-pressure (LPST) and high-pressure shock tubes (HPST) to measure IDTs at pressures from 1.2 to 30 bar and temperatures between 750 K–1300 K, see Figure 1. Laser diagnostics were used to monitor carbon monoxide (CO) and H_2O formation. Initial comparisons between experimental data and Reaction Mechanism Generator (RMG)-based models revealed discrepancies at high pressures, requiring sensitivity analysis to refine key reaction pathways. By modifying reaction rates to improve model accuracy, this research establishes the first comprehensive kinetic model for 1,1-DEP oxidation. This study provides valuable insights into 1,1-DEP combustion behavior, highlighting its role as a clean, drop-in fuel capable of supporting the transition toward sustainable transportation. The findings contribute to the development of advanced kinetic models and future fuel formulations aimed at decarbonizing internal combustion engine technologies.

Correspondence to: aamir.farooq@kaust.edu.sa

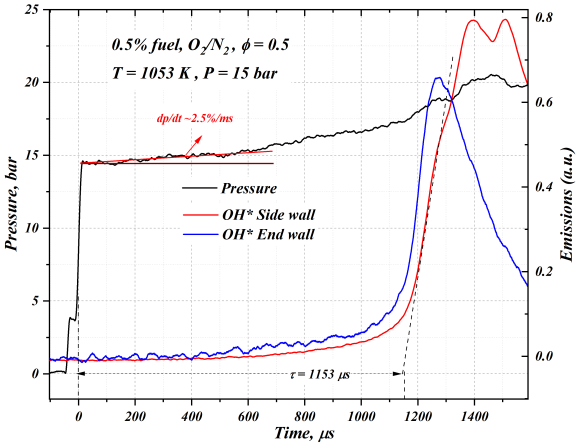

Figure 2: Sample pressure profile of the 1,1-DEP oxidation

2 Experimental and Simulation Methodologies

Experiments were carried out at King Abdullah University of Science and Technology (KAUST) using both Low-Pressure Shock Tube (LPST) and High-Pressure Shock Tube (HPST) facilities. The LPST, constructed from stainless steel (SS 316), consists of a 14.2 cm inner diameter driven section that extends 9 meters in length, while the HPST features a driven section with a 10.16 cm inner diameter and a length of 6.6 meters. Both facilities include modular driver sections that can be extended from 2.2 meters to match the length of the driven sections, enabling flexible experimental configurations. The driver and driven sections are separated by polycarbonate diaphragms in the LPST and pre-scored aluminum diaphragms in the HPST, both arranged in a double-diaphragm setup to improve control over post-reflected shock conditions. More details on the both facilities can be found elsewhere [3][4].

For the HPST experiments, OH* chemiluminescence signals were recorded at both the endwall and sidewall ports using photomultiplier tubes (PMTs) equipped with narrow bandpass filters centered at 309 nm. The focus of these experiments was the oxidation behavior of 1,1 DEP mixed with O_2 and diluents (N_2) under a range of thermodynamic conditions. Specifically, experiments were conducted at temperatures between 750 K and 1300 K, pressures of 1.2 bar, 15 bar, and 30 bar, and equivalence ratios of 0.5, 1.0, and 2.0, as summarized in Table 1. Figure 2 shows a typical pressure trace profile and OH* chemiluminescence signal for 1,1-DEP in O_2 and N_2 as diluent. The IDT is measured as the time interval between the passage of the reflected shock wave (time zero) and the point where the steepest pressure rise intersects a horizontal reference line at P5. The uncertainty associated with IDT measurements was estimated to be below 20%.

Table 1: Experimental conditions for shock tube experiments

Equivalence Ratio (ϕ)	**Mixture Concentration**	**Device/Pressure**
1	0.5% fuel, 5% O_2, 94.5% N2	HPST / 15 bar and 30 bar
0.5	0.5% fuel, 10% O_2, 89.5% N2	HPST / 15 bar and 30 bar
2	0.5% fuel, 2.5% O_2, 97% Ar	HPST / 15 bar and 30 bar
1	0.5% fuel, 5% O_2, 94.5% Ar	LPST/ 1.3 bar
0.5	0.5% fuel, 10% O_2, 89.5% Ar	LPST/ 1.3 bar
2	0.5% fuel, 2.5% O_2, 97% Ar	LPST / 1.3 bar

Initial experiments in this study revealed that 1,1-DEP exhibited high reactivity under air-diluted condi-

tions, particularly in HPST experiments at elevated pressures,and in most cases leading to ignition with the incident shock wave - inhibiting any IDT extraction. To mitigate this, fuel mixtures were prepared at higher dilution levels than an air mixture, reducing reactivity and improving experimental control. At $\phi = 2$, the low OH* due to insufficient oxygen made IDT measurements difficult. To resolve this, argon (Ar) was used as a diluent instead of N_2, which minimized the quenching of OH^* radical giving a more pronounced OH emission signal. A combination of LPST and HPST experiments, along with precise diagnostics, enabled a comprehensive analysis of 1,1-DEP oxidation kinetics under varying conditions. The findings provide valuable insights for model development and validation of the fuel's behavior across a wide range of pressures and temperatures.

For mechanism generation, RMG is a widely adopted software tool to automate the development of chemical kinetic models. It employs a rate-driven iterative approach to model expansion, incorporates a comprehensive library of reaction templates for systematically enumerating potential reactions from a given set of chemical species, and offers a database with parameter estimation methods based on group additivity [5] and rate rules [6]. Using these capabilities, RMG can autonomously navigate chemical space using reaction rules, determines which species and reactions to incorporate into the model, and the most accurate parameters. With minimal user input, specifically the initial conditions of the system investigated, RMG can generate detailed chemical kinetic models effectively.

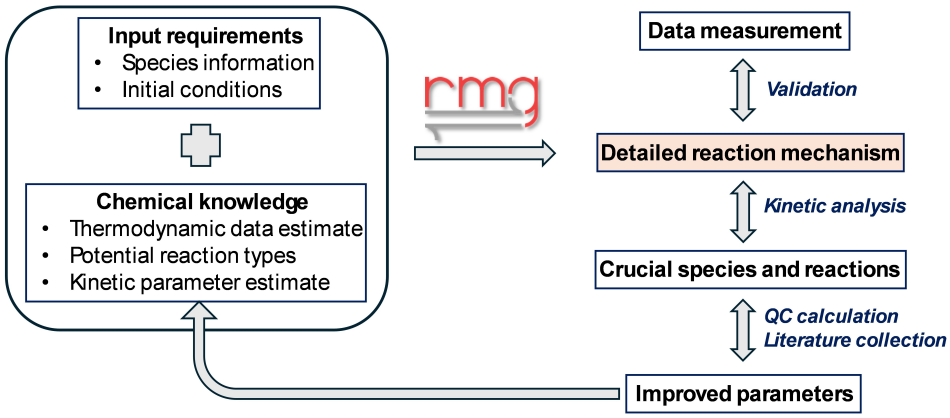

Figure 3: Reaction mechanism generation workflow using RMG.

Figure 3 presents the workflow for chemical reaction mechanism generation using RMG . The workflow prioritizes the refinement of parameters for key chemical species and reactions, aiming to expand RMG's chemical insight during model development. The necessity for this refinement stems from multiple aspects:

- The precision of individual parameter heavily determines the accuracy of model simulations through the uncertainty propagation;
- The identification of crucial species and reactions is guided by the reaction flux simulated, which is influenced by parameter accuracy;
- New investigated system requires exploring chemical spaces that extend beyond well-characterized conditions with reliable database;
- RMG gains improved access to high-quality data as training inputs by refining parameters, leading to the development of more accurate models.

3 Result and Discussion

Experimental Results from Shock Tube

To investigate the oxidation of 1,1-DEP at three different pressure, experiment was performed using 1,1-DEP+O_2 in (N_2/Ar) mixture from fuel-lean to fuel-rich conditions; the results of variations of IDT with temperature are shown in Figure 4. Across all tested mixtures and conditions, IDTs consistently decreased as temperature increased. No evidence of negative temperature coefficient (NTC) behavior was detected within the investigated temperature range. It is evident that at low pressure, 1,1-DEP exhibits a strong dependence on the equivalence ratio. However, as the pressure increases, this dependence becomes less pronounced.

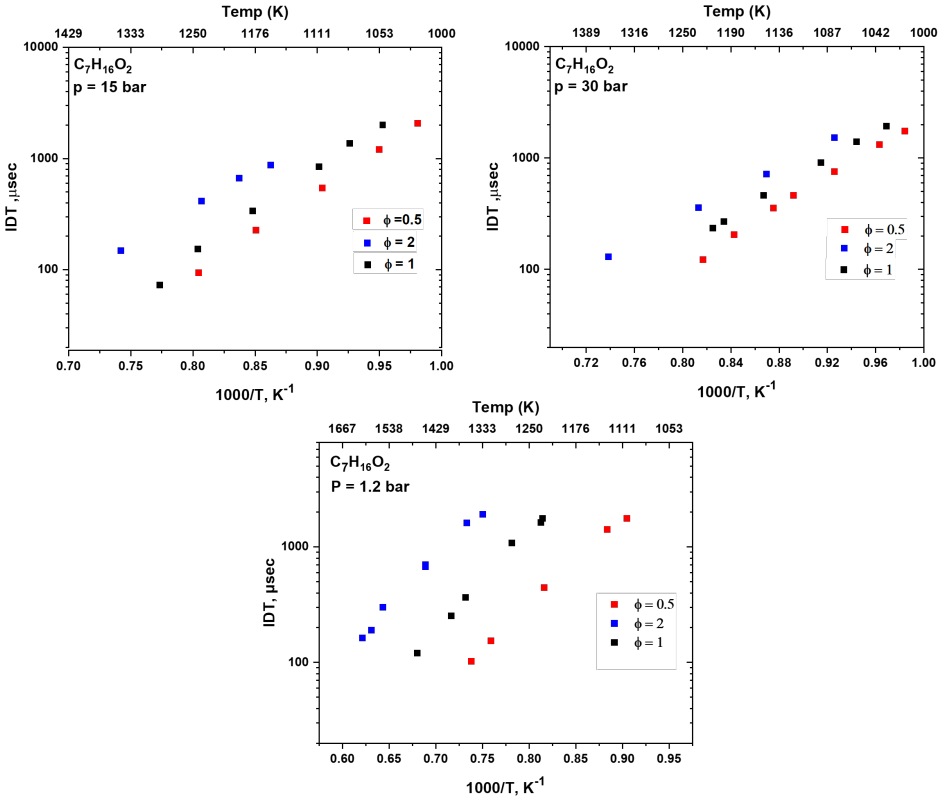

Figure 4: IDT plots of 1,1-DEP oxidation at three pressures.

4 Kinetic Modelling

Reaction Mechanism Generator (RMG)

RMG v3.1.0 was employed to generate the 1,1-DEP combustion model. RMG is described in detail [7]. In this study, the RMG database was utilized to construct a detailed kinetic model for the oxidation of the target fuel. The RMG database consists of several libraries that store thermodynamic, kinetic, and transport data, which are essential for automated mechanism generation. The thermodynamic properties of species were primarily sourced from libraries such as `BurkeH2O2`, `DFT_QCI_thermo`,

`CBS_QB3_1dHR`, `thermo_DFT_CCSDTF12_BAC`, and `primaryThermoLibrary` [8], which contain high-accuracy quantum chemistry calculations and experimental data. These libraries ensure accurate representation of thermophysical properties, which are crucial for predicting reaction pathways and equilibrium compositions.

For reaction kinetics, several well-established reaction libraries were incorporated, including a `C0-C4` library based on Aramco Mech 2.0 [9], `BurkeH2O2inArHe`, `ERC-FoundationFuelv0.9`, and `CurranPentane` [8]. These reaction libraries contain experimentally validated reaction rate parameters, allowing RMG to efficiently construct reaction networks for hydrocarbon and oxygenated fuel oxidation. Unlike traditional mechanism development approaches that rely solely on literature data, RMG expands the reaction network iteratively, ensuring comprehensive coverage of all possible reaction pathways, see Figure 5.

Additionally, seed mechanisms were not explicitly used in this study, meaning that the kinetic model was developed entirely based on rate rules and training data. The kinetics depositories were set to training, allowing RMG to refine rate predictions using existing kinetic training data. The kinetics families were defined as default, enabling the inclusion of all available reaction families to ensure a complete and consistent reaction network. The kinetics estimator was set to rate rules, where reaction rates were determined using a hierarchical approach based on known reaction trends. As a result, out of all the fuel-specific reactions automatically generated by RMG, five key reactions that significantly influence the ignition of 1,1-DEP were retained. The details of these five critical reactions are presented in Table 2.

The final output of RMG is a reaction network comprising hundreds of species and thousands of reactions, along with thermodynamic and kinetic data stored in Chemkin or Cantera formats. In this study, the Chemkin format was selected for subsequent numerical simulations due to its compatibility with computational fluid dynamics (CFD) solvers and its ability to efficiently handle large reaction mechanisms.

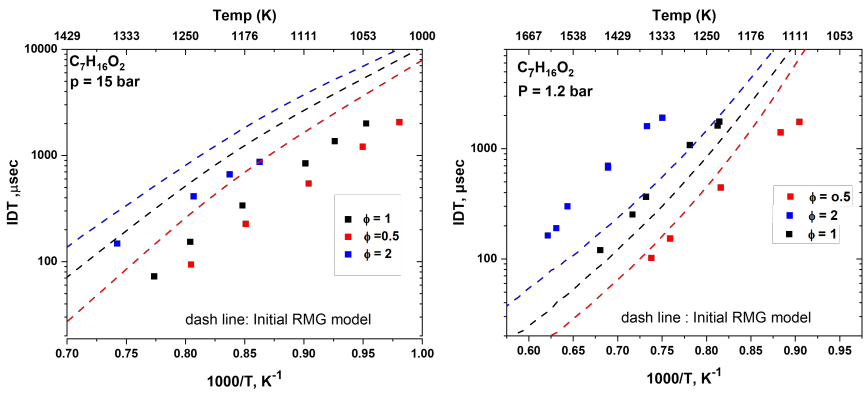

Figure 5: Inital model genererated by RMG

Table 2: Important reaction kinetic parameters

No.	Reactions	A (s^{-1}, cm^3mol^{-1})	n	Ea (kcal/mol)
1	C_2H_4 + CCOC(O)CC $\leftrightarrow$ $C_7H_{16}O_2$	9.46×10^{1}	3.000	47.000
2	HO_2 + $C_7H_{15}O_2$ $\leftrightarrow$ O_2 + $C_7H_{16}O_2$	2.6419×10^{-3}	4.194	2.536
3	CH_3 + $C_7H_{16}O_2$ $\leftrightarrow$ CH_4 + $C_7H_{15}O_2$	4.00×10^{1}	3.370	7.630
4	OH + $C_7H_{16}O_2$ $\leftrightarrow$ H_2O + $C_7H_{15}O_2$	9.00×10^{2}	3.110	-2.666
5	H + $C_7H_{16}O_2$ $\leftrightarrow$ H_2 + $C_7H_{15}O_2$	1.76×10^{4}	2.680	2.913

5 Conclusions and Future Work

IDT of 1,1-DEP oxidation is measured using LPST and HPST facility at a pressure of 1.2, 15 and 30 bar, equivalence ratio 0.5-2.0 and a temperature range of 1000 - 1600 K. CO and H_2O were also measured using laser diagnostics in the shock tube. RMG is utilized for model generation due to unavailability of any model. Following this, the next phase will involve refining the model by incorporating reactions with experimentally validated or more accurately measured rate constants. Additionally, any reactions missing from the RMG database will be sourced from the literature and integrated into the model to enhance its predictive accuracy

References

[1] Khan, M.Z.A., H.A., Ravi, S.S., Turner, J.W. and Aziz, M., 2023. Potential of clean liquid fuels in decarbonizing transportation–An overlooked net-zero pathway?. Renewable and Sustainable Energy Reviews, 183, p.113483.

[2] Zeng, M., Li, Y., Yuan, W., Zhang, Y., Yang, J. and Qi, F., 2019. Exploration of the pyrolysis chemistry of 1, 1-diethoxybutane: A flow reactor and kinetic modeling study. Fuel, 236, pp.437-444.

[3] Kashif, T.A., AlAbbad, M., Figueroa-Labastida, M., Chatakonda, O., Kloosterman, J., Middaugh, J., Sarathy, S.M. and Farooq, A., 2023. Effect of oxygen enrichment on methane ignition. Combustion and Flame, 258, p.113073.

[4] Kashif, T.A., Subburaj, J., Khan, M.Z.A. and Farooq, A., 2024. Insights into shock velocity variation in double-diaphragm shock tubes. Physics of Fluids, 36(5).

[5] Benson, S.W., 1976. Thermochemical kinetics: methods for the estimation of thermochemical data and rate parameters. (No Title).

[6] Johnson, M.S., Dong, X., Grinberg Dana, A., Chung, Y., Farina Jr, D., Gillis, R.J., Liu, M., Yee, N.W., Blondal, K., Mazeau, E. and Grambow, C.A., 2022. RMG database for chemical property prediction. Journal of Chemical Information and Modeling, 62(20), pp.4906-4915.

[7] Liu, M., Grinberg Dana, A., Johnson, M.S., Goldman, M.J., Jocher, A., Payne, A.M., Grambow, C.A., Han, K., Yee, N.W., Mazeau, E.J. and Blondal, K., 2021. Reaction mechanism generator v3. 0: advances in automatic mechanism generation. Journal of Chemical Information and Modeling, 61(6), pp.2686-2696.

[8] Gao, C.W., Allen, J.W., Green, W.H. and West, R.H., 2016. Reaction Mechanism Generator: Automatic construction of chemical kinetic mechanisms. Computer Physics Communications, 203, pp.212-225.

[9] Li, Y., Zhou, C.W., Somers, K.P., Zhang, K. and Curran, H.J., 2017. The oxidation of 2-butene: A high pressure ignition delay, kinetic modeling study and reactivity comparison with isobutene and 1-butene. Proceedings of the Combustion Institute, 36(1), pp.403-411.