



## An experimental and modeling study of diethyl carbonate oxidation



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### ABSTRACT

Diethyl carbonate (DEC) is an attractive biofuel that can be used to displace petroleum-derived diesel fuel, thereby reducing CO<sub>2</sub> and particulate emissions from diesel engines. A better understanding of DEC combustion characteristics is needed to facilitate its use in internal combustion engines. Toward this goal, ignition delay times for DEC were measured at conditions relevant to internal combustion engines using a rapid compression machine (RCM) and a shock tube. The experimental conditions investigated covered a wide range of temperatures (660–1300 K), a pressure of 30 bar, and equivalence ratios of 0.5, 1.0 and 2.0 in air. To provide further understanding of the intermediates formed in DEC oxidation, species concentrations were measured in a jet-stirred reactor at 10 atm over a temperature range of 500–1200 K and at equivalence ratios of 0.5, 1.0 and 2.0. These experimental measurements were used to aid the development and validation of a chemical kinetic model for DEC.

The experimental results for ignition in the RCM showed near negative temperature coefficient (NTC) behavior. Six-membered alkylperoxy radical (RÖ<sub>2</sub>) isomerizations are conventionally thought to initiate low-temperature branching reactions responsible for NTC behavior, but DEC has no such possible 6- and 7-membered ring isomerizations. However, its molecular structure allows for 5-, 8- and 9-membered ring RÖ<sub>2</sub> isomerizations. To provide accurate rate constants for these ring structures, *ab initio* computations for RÖ<sub>2</sub> = QOOH isomerization reactions were performed. These new RÖ<sub>2</sub> isomerization rate constants have been implemented in a chemical kinetic model for DEC oxidation. The model simulations have been compared with ignition delay times measured in the RCM near the NTC region. Results of the simulation were also compared with experimental results for ignition in the high-temperature region and for species concentrations in the jet-stirred reactor. Chemical kinetic insights into the oxidation of DEC were made using these experimental and modeling results.

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### 1. Introduction

Diethyl carbonate (DEC) is a bio-derived fuel that can be produced from bioethanol made from sugarcane and other agricultural crops. One promising way to produce DEC is to convert ethanol using carbon monoxide and oxygen over a copper-based catalyst [1,2]. One advantage of DEC over ethanol is that it can be mixed with diesel fuel for use in compression ignition engines. Adding DEC to diesel fuel has several additional advantages

including the potential for displacing petroleum-based fuel leading to a reduction in the emission of carbon dioxide (CO<sub>2</sub>), a greenhouse gas. Moreover, when DEC is mixed with diesel fuel, the particulate emissions from a diesel engine are reduced [3]. This is particularly important when it is desirable to reduce pollutant emissions from legacy fleets of diesel vehicles that do not have modern exhaust after-treatment systems. Finally, unlike other oxygenated fuels (e.g., alcohols), DEC has a gasoline/water distribution coefficient [4] that makes it less likely for DEC to transfer to the ground water after an accidental spill.

Another application for DEC is its use as a solvent for lithium-ion batteries. Under abusive conditions, lithium-ion batteries can release solvent, which poses a flammability hazard. A chemical

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kinetic model for DEC is valuable to help assess the risks associated with this type of use [5].

DEC has received attention in the literature. Kozak et al. [3] tested 11 different oxygenated fuels and found that DEC, dimethyl carbonate and diethyl maleate gave the greatest reduction in particulate emissions without adversely affecting NO<sub>x</sub> emissions. Ren et al. [6] found that a DEC–diesel blend reduced the production of smoke emissions by about 35% compared to neat diesel fuel in a direct injection diesel engine.

In order to obtain a better understanding on how the addition of DEC affects diesel engine performance and emissions, engine simulations with an accurate fuel combustion chemistry model need to be performed. The capability of multidimensional engine simulations to use detailed chemical kinetic models has recently seen much advancement through the use of faster chemistry solvers and mechanism reduction tools [7–9]. A detailed chemical kinetic model capable of reproducing the combustion characteristics of DEC is needed to facilitate these calculations. This DEC chemical kinetic model can also be used in less computer intensive zero-dimensional (0-D) calculations to explore DEC combustion chemistry under the pressure and temperature conditions found in an engine.

In the present work, a chemical kinetic mechanism for DEC has been developed for the first time. Composition profiles from a jet-stirred reactor (JSR) and ignition delay times from a shock tube and a rapid compression machine (RCM) were obtained, as these experimental data give targets for the kinetic model over a wide range of temperatures and equivalence ratios. This rich set of experimental targets ensures that the chemical kinetic model development is appropriately tested. The following sections present a description of the experimental method, the development of the chemical kinetic model, the experimental and modeling results, and a discussion of observations.

## 2. Experimental description

### 2.1. Jet-stirred reactor

The JSR facility used has been described previously [10,11]. It consists of a small spherical fused-silica reactor (4 cm O.D.) equipped with four nozzles of 1 mm I.D. each. High-purity reactants were used; oxygen (99.995% pure) and DEC (DEC anhydrous,  $\geq 99\%$  pure from Sigma–Aldrich; CAS 105-58-8, molecular structure in Fig. 1). The reactants were diluted with nitrogen (<100 ppm H<sub>2</sub>O) and quickly mixed before admission into the injectors. To minimize temperature gradients within the JSR, the reactants were preheated. A Shimadzu LC10 AD VP pump operating with an on-line degasser (Shimadzu DGU-20 A3) was used to distribute the fuel to an atomizer–vaporizer assembly thermally regulated at 473 K. A high degree of dilution (1000 ppm of fuel) was used to reduce heat release and temperature gradients inside the reactor. Temperature gradients of ca. 1 K/cm along the vertical axis of the reactor were measured by a 0.1 mm Pt–Pt/Rh-10% thermocouple located inside a thin-wall silica tube to avoid catalytic effects. A movable low-pressure fused silica sonic probe was used

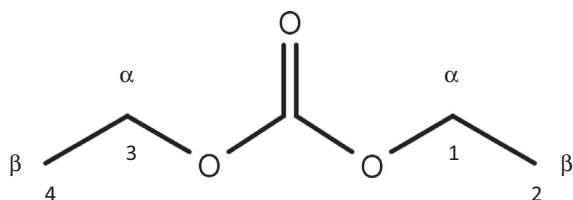


Fig. 1. Diethyl carbonate molecule with labels of the H-atom abstraction sites.

to sample the reacting mixtures inside the reactor. The samples were transferred to analyzers via a heated line (473 K). They were analyzed online by FTIR (200 mbar; 10 m path length; spectral resolution of 0.5 cm<sup>-1</sup>) and off-line, after collection and storage in 1 L Pyrex bulbs at ca. 50 mbar. Gas chromatographs (GC) equipped with capillary columns (DB-624 for oxygenates, CP-Al<sub>2</sub>O<sub>3</sub>-KCl for hydrocarbons, and CarboPlot-P7 for hydrogen and oxygen), a TCD (thermal conductivity detector), and an FID (flame ionization detector) were used for off-line analyses. The products were identified using a GC–MS (Varian V1200) operated with electron ionization (70 eV), wherein fragmentation patterns were compared to data obtained in previous work [11] for similar species.

The experiments were performed at steady state, at a constant pressure of 10 atm, a constant mean residence time of 0.7 s, using 1000 ppm of fuel and at three equivalence ratios ( $\phi = 0.5, 1, \text{ and } 2$ ), which were calculated including the oxygen in the fuel. The reactants flowed constantly into the JSR and the temperature of the gases inside the reactor was increased stepwise covering a range of temperatures between 500 and 1200 K. A good repeatability of the measurements and a reasonably good carbon balance (lower and upper bounds of 88% and 120%) were obtained in this series of experiments. The full experimental data is available as [Supplementary Material](#).

The species measured included the fuel (i.e., DEC), hydrogen (H<sub>2</sub>), oxygen (O<sub>2</sub>), water (H<sub>2</sub>O), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), ethanol (C<sub>2</sub>H<sub>5</sub>OH), ethane (C<sub>2</sub>H<sub>6</sub>), acetylene (C<sub>2</sub>H<sub>2</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>), ethylene oxide (C<sub>2</sub>H<sub>4</sub>O-12), ethane (C<sub>2</sub>H<sub>6</sub>), propene (C<sub>3</sub>H<sub>6</sub>), propane (C<sub>3</sub>H<sub>8</sub>), acetaldehyde (CH<sub>3</sub>CHO), and formaldehyde (CH<sub>2</sub>O). The uncertainty in these concentrations is ca.  $\pm 15\%$ , in reactor temperature is  $\pm 5$  K and in reactor residence time is  $\pm 0.02$  s.

### 2.2. Shock tube

Ignition delay times were measured at high-temperature using a high-pressure shock tube, details of which can be found in previous publications [12,13]. Briefly, the shock tube is 8.7 m long and 63.5 mm in the internal diameter. A double-diaphragm section divides the tube into a 3 m long driver section and a 5.7 m driven section. Aluminum plates of 1.5 mm thickness were used as the diaphragm material. A Helium (99.99% pure; BOC Ireland) and nitrogen (99.99% pure; BOC Ireland) mixtures were used as the driver gas, where the mixing ratio was varied from 90:10 to 100:0 (He:N<sub>2</sub>) to obtain the reflected shock pressure of 30 atm and the desired test duration. Six pressure transducers on the sidewall (PCB; 113A24) and one at the endwall (Kistler; 603B) were used to measure the velocity of the incident shock wave, which was used to calculate the temperature of the mixtures behind the reflected shock wave using the program Gaseq [14]. Pressures behind the reflected shock wave were measured using the pressure transducer in the endwall. The pressure rise before ignition is approximately 3%/ms in the present shock tube. The experiments were conducted for DEC/air mixtures of equivalence ratios of 0.5, 1.0 and 2.0. DEC was obtained from Tokyo Chemical Ltd. at over 98.0% purity (GC grade). Oxygen (99.5%) and nitrogen (99.99%) supplied by BOC Ireland were used to make air (O<sub>2</sub>:N<sub>2</sub> = 21:79). The initial temperature of the DEC/air mixture was 373 K for equivalence ratio of 0.5 and 383 K for equivalence ratios of 1.0 and 2.0. The reflected shock temperature ranged from approximately 940 K to 1240 K. The initial pressure of the DEC/air mixture was varied from 0.47 to 1.05 atm to obtain a reflected shock pressure of 30 atm. Estimated uncertainty limits of the measurements are  $\pm 1\%$  in reflected shock temperature,  $\pm 5\%$  in reflected shock pressure,  $\pm 2\%$  in mixture concentration and  $\pm 15\%$  in ignition delay time. All experimental data are available as [Supplementary Material](#).

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