Thermal Decomposition-induced Multi-stage Reaction of Diethyl Carbonate Examined by a Micro Flow Reactor with a Controlled Temperature Profile

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1   Introduction

The combustion process that uses carbonate esters, such as diethyl carbonate (DEC), have been studied principally aiming to reduce emissions of particulate and smoke from engines [1]. Besides, the reactivity of carbonate esters becomes one of the significant concerns due to their use as electrolytes of lithium-ion batteries [2]. Since there are only a few studies on the fundamental combustion characteristics of DEC [3–5] to the best of the authors' knowledge, further understanding is highly required.

In this study, the oxidation and pyrolysis characteristics of DEC are investigated using a micro flow reactor with a controlled temperature profile (MFR) [6]. MFR consists of a quartz tube whose inner diameter is smaller than the ordinary quenching diameter and an external heat source that forms a stationary temperature profile on the tube inner wall surface. At low inlet flow velocity conditions (~ a few cm/s) in MFR, weak flame that is a stable flame accompanying a very small heat release is formed [7]. The gas temperature profile in the flow direction is strongly governed by the wall temperature (T_w) profile at the weak flame conditions due to a small Peclet number. By giving a gradual T_w profile, a series of reaction steps can be spatially separated in the tube axis direction. Species measurements at an arbitrary temperature region and observations of multi-stage oxidation (low-temperature oxidation (LTO), oxidation of LTO products to CO and oxidation of CO to CO_2) [8,9] were successfully performed applying this method.

The aim of this study is to obtain further understanding of oxidation and pyrolysis characteristics of DEC. Species measurements, weak flame observation and reaction analysis were conducted using MFR.

2   Experimental Setup and Computational Method

Figure 1 shows a schematic of the experimental setup for species measurements and weak flame observation. A quartz tube whose inner diameter of 2 mm was employed as the reactor channel. Liquid
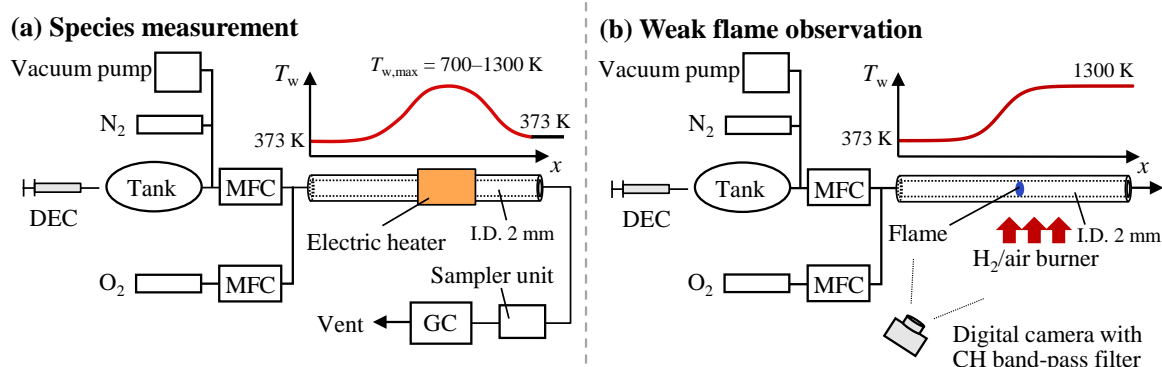
Figure 1: Experimental setup for (a) species measurement and (b) weak flame observation.

DEC was vaporized and mixed with N_2 in a heated tank (373 K). The composition of DEC/N_2 mixtures in the tank were controlled by the partial pressure method. All the lines from tank to the reactor were heated to 373 K to avoid the fuel condensation. The flow rate of DEC/N_2 was controlled by a mass flow controller applicable to high temperature gases. The inlet flow velocity of mixtures was set to 2 cm/s. Experiments were conducted at atmospheric pressure.

For the species measurements, an electric heater was used as an external heat source. The maximum wall temperature ($T_{w,max}$) was varied between 700 and 1300 K. Stoichiometric 1.5%DEC/9.0%O_2/N_2 mixtures at oxidation conditions and 1.5%DEC/N_2 mixtures at pyrolysis conditions were supplied to the reactor. Exhaust gases from the downstream of the reactor were sampled online and directly introduced into a gas chromatograph (GC). The sampling lines were heated to 373 K to avoid the condensation of unburnt fuel and water vapor. As a detector of GC, a barrier ionization detector was employed. Although O_2, H_2, CO, CO_2, CH_4, C_2H_4 and C_2H_6 were measured and quantified, only the results of CO, CO_2 and C_2H_4 are shown in this paper. Further explanation of the experimental method and the results of O_2, H_2, CH_4 and C_2H_6 can be found in our recent work [10].

For the weak flame observation, a H_2/air flat-flame burner was used as the external heat source. A stationary temperature profile of 373–1300 K was given on the reactor inner wall surface. A stoichiometric DEC/O_2/N_2 (O_2:N_2 = 21:79) mixture was supplied to the reactor. A weak flame was optically observed by a digital still camera installing a CH band-pass filter (transparent wavelength of 431.2 nm and half bandwidth of 6.4 nm) with the exposure time of 30 s.

To perform weak flame analysis, one-dimensional steady-state computations modeling the MFR system were conducted. The flow field in the MFR at low inlet flow velocity conditions can be modeled as a reactive flow without a boundary layer. A PREMIX-based code whose gas-phase energy equation includes an additional term of convective heat transfer between gas and the reactor inner wall [6] was used. Computational conditions (mixture compositions, inlet flow velocity, T_w profiles and pressure) were set to the same as those in the experiments. A detailed chemical reaction model for linear carbonate esters (dimethyl carbonate (DEC), ethyl methyl carbonate (EMC) and DEC) [11] was used. The chemical reaction model consists of 371 species and 2076 reactions. Its model performance of the species evolutions for DMC, EMC and DEC oxidation was validated in [12].

3   Results and Discussion

Figure 2 shows measured and computed mole fractions of CO, CO_2 and C_2H_4 for oxidation and pyrolysis of DEC at varied $T_{w,max}$ and atmospheric pressure. In the oxidation case (Fig. 2a), the measured CO mole fraction starts increasing at $T_{w,max}$ = 900 K, having a peak at around $T_{w,max}$ = 1000–1050 K. While the measured CO_2 and C_2H_4 mole fractions increase at low temperatures ($T_{w,max}$ = 750–850 K). At the low temperature region, measured O_2 mole fraction showed little decrease. The measured CO_2 mole fraction
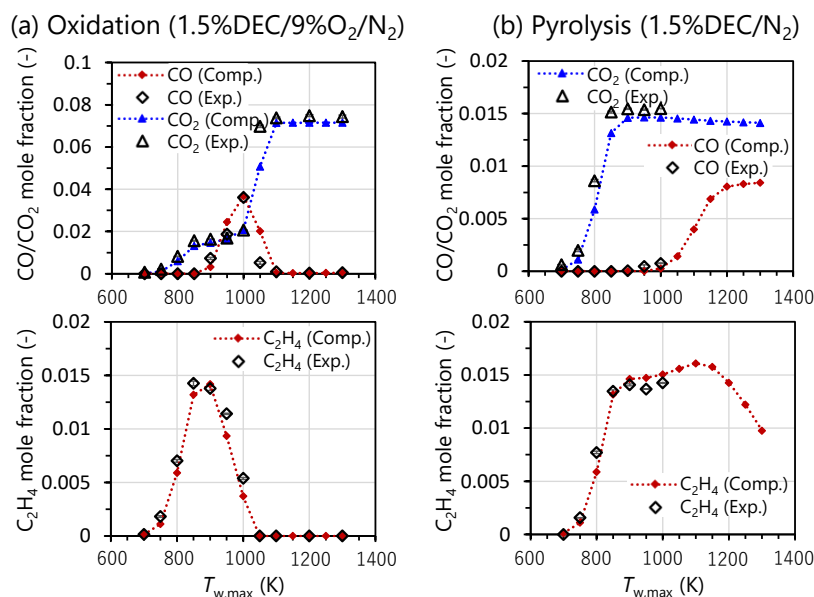
Figure 2: Experimental and computational species mole fractions of CO, CO_2 and C_2H_4 for (a) oxidation (1.5%DEC/9%O_2/N_2 mixtures) and (b) pyrolysis (1.5%DEC/N_2 mixtures) at $T_{w,max}$ = 700–1300 K and atmospheric pressure.

shows a two-stage increase that includes the first increase at the low temperatures followed by a plateau ($T_{w,max}$ = 850–1000 K) and the second increase at $T_{w,max}$ = 1000–1050 K. The second CO_2 increase is a completion of oxidation because it occurs at which the measured CO mole fraction rapidly decreases. The measured CO_2 mole fractions at higher than $T_{w,max}$ = 1050 K are approximately 0.07, implying that 100% of fuel converts to CO_2 based on the carbon-balance. The measured C_2H_4 mole fraction shows a peak at around $T_{w,max}$ = 850–900 K. The C_2H_4 peak value is approximately 0.015, which corresponds to the initial mole fraction of DEC. The molecular structure of DEC consists of one carbonate ester group and two ethyl groups; therefore, the increases in CO_2 and C_2H_4 mole fractions at the low temperatures would be delivered by thermal decomposition of DEC. In the pyrolysis case (Fig. 2b), the measured CO mole fraction starts slightly increasing at $T_{w,max}$ = 950 K. The measured CO_2 and C_2H_4 mole fractions, however, increase at the lower temperatures ($T_{w,max}$ = 750–850 K), reaching approximately 0.015 at $T_{w,max}$ = 850 K. This tendency of CO_2 and C_2H_4 at the low temperature is similar to the oxidation case. The computational results quantitatively reproduce the experimental results of both oxidation and pyrolysis cases. Based on the rate of production analysis of DEC, dominant reactions at the low temperatures were the thermal decomposition reactions of DEC in both cases. The thermal decomposition reaction produces C_2H_4 and ethoxy formic acid (EFA), which rapidly decomposes into CO_2 and C_2H_5OH through four-center elimination reaction [13]. Consequently, CO_2 and C_2H_4 are produced at the low temperature region where still little CO is produced even for the oxidation case.

Figure 3 shows a weak flame image, experimental luminosity profile, computational heat release rate (HRR) profile and species profiles of a stoichiometric DEC/air mixture. The computational weak flame position (the maximum peak location of HRR profile) agrees well with the experimental weak flame position (the maximum peak location of luminosity profile). The computational HRR profile shows a three-stage reaction: Stage I at around $T_{w,max}$ = 800–950 K (x = 4.3–4.6 cm) where the negative HRR region appears; Stage II at around $T_{w,max}$ = 950–1100 K (x = 4.6–5.0 cm) where HRR turns into positive and shows the second largest peak; and Stage III at $T_{w,max}$ > 1100 K (x > 5.0 cm) where the largest HRR peak appears. These three stages are depicted in the species profiles at the corresponding regions. At Stage I, DEC is completely consumed and CO_2 and C_2H_4 are produced. At Stage II, CO mole fraction has a peak followed by the rapid decrease at Stage III with the remarkable increase in CO_2 mole fraction.

The HRR and species profiles indicate that the three-stage reaction of DEC consists of the thermal decomposition of DEC, which is an endothermic reaction, at the low temperature region (Stage I), oxidation of the decomposition products to CO at the intermediate temperature region (Stage II) and the completion of oxidation, CO to CO_2, at the high temperature region (Stage III). This three-stage reaction is distinctive from the ones observed in our past studies on multi-stage oxidation of *n*-heptane [8] and dimethyl ether [9], which were initiated by LTO.

Figure 4 shows reaction pathways of DEC oxidation at Stage I ($T_{w,max}$ = 830 K) and Stage II ($T_{w,max}$ = 1030 K). At the low temperature condition ($T_{w,max}$ = 830 K), the major intermediates, C_2H_4 and C_2H_5OH, and the final product, CO_2, are produced from a sequence of thermal decomposition of DEC via EFA
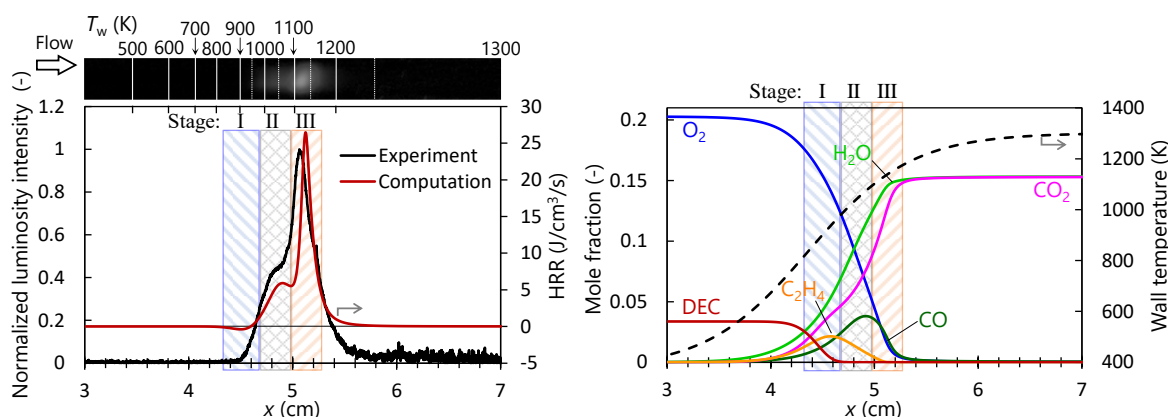

Figure 3: Experimental weak flame image (top), experimental luminosity and computational HRR profiles (left) and computational species profile (right) of a stoichiometric DEC/air mixture at $T_{w,max}$ = 1300 K and atmospheric pressure.
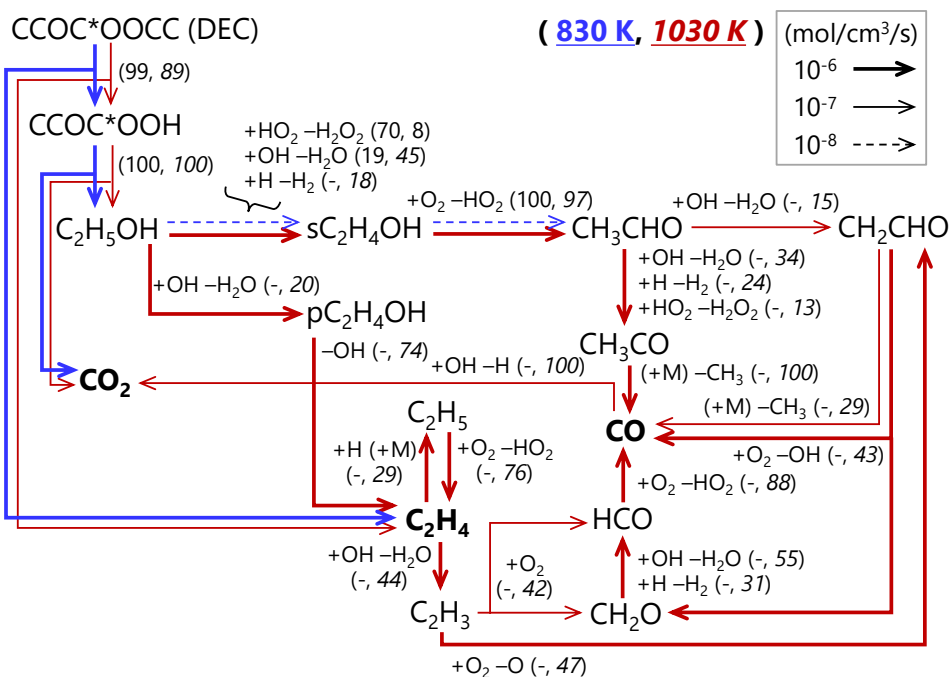

Figure 4: Main reaction pathways of DEC oxidation at $T_{w,max}$ = 830 K (blue) and 1030 K (red). The number shown in the parenthesis is a contribution percentage of each reaction to consumption of the parent species at (830 K, *1030 K*). Measured species are denoted in bold. "*" implies double bond.

(denoted as CCOC*OOH). The decomposition products are, however, relatively stable, promoting the further reactions little. At the intermediate temperature condition ($T_{w,max}$ = 1030 K), oxidation reactions proceed via C2 pathways to CO. At the following temperature region corresponding to Stage III, the CO oxidation to CO_2 became stronger.

4   Conclusions

Characteristics of oxidation and pyrolysis of diethyl carbonate (DEC) were investigated using a micro flow reactor with a controlled temperature profile. A multi-stage reaction was experimentally and computationally observed.

Species measurements for the oxidation and pyrolysis of DEC indicated the productions of CO_2 and C_2H_4 at the low temperatures ($T_{w,max}$ = 750–850 K). In the oxidation case, CO_2 mole fraction showed a two-stage increase: the first increase at the low temperatures followed by a plateau ($T_{w,max}$ = 850–1000 K), and then the second increase at $T_{w,max}$ = 1000–1050 K. Based on the heat release rate profile of DEC/air weak flame, a three-stage reaction appeared. The three-stage reaction consists of thermal decomposition of DEC, oxidation of the decomposition products to CO and oxidation of CO to CO_2. This thermal decomposition-induced multi-stage reaction is distinctive from the ones observed in our past studies on oxidation of n-heptane [8] and dimethyl ether [9], which were initiated by low-temperature oxidation. The thermal decomposition of DEC at the low temperatures were driven by the existence of ethyl ester group in its molecular structure.

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