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**A High Temperature Kinetic Study for the Thermal Unimolecular
Decomposition of Diethyl Carbonate**

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Abstract

Thermal unimolecular decomposition of diethyl carbonate (DEC) was investigated in a shock tube by measuring ethylene concentration with a CO₂ gas laser over 900 - 1200 K and 1.2 – 2.8 bar. Rate coefficients were extracted using a simple kinetic scheme comprising of thermal decomposition of DEC as initial step followed by rapid thermal decomposition of the intermediate ethyl-hydrogen-carbonate. Our results were further analysed using *ab initio* and master equation calculations to obtain pressure- and temperature- dependence of rate coefficients. Similar to alkyl esters, unimolecular decomposition of DEC is found to undergo six-center retro-ene elimination of ethylene in a concerted manner.

1. Introduction

In recent years, there has been an increasing interest of using fuel blends comprising of oxygenated organic compounds and conventional fuels to increase the oxygen content of the fuels. Such fuel blends can promote cleaner combustion and be environmentally friendly by reducing the emission of greenhouse gases and particulate matter, and they can be readily used in modern diesel engines and diesel-hybrids [1, 2]. The organic carbonates such as dimethyl carbonate (DMC) and diethyl carbonate (DEC) have potential to be good candidates for oxygenate additives to the diesel fuels due to their very high oxygen contents (53.3 and 40.6% by mass, respectively). These carbonates have high boiling points (363 K for DMC and 399-401 K for DEC) which can help reduce the Reid vapor pressure (RVP) of the blended fuels. These carbonates can be produced from biological sources and can thus help displace some of the conventional petroleum-based fuels. DEC is preferred over DMC due to its higher boiling point and due to the lower miscibility of DEC in groundwater. Diethyl carbonate (DEC) can be efficiently produced from the gas phase oxidative carbonylation of bioethanol over a heterogeneous $\text{CuCl}_2/\text{PdCl}_2$ catalyst supported on activated carbon [3].

Efficient utilization of these carbonates in compression ignition engines requires us to understand their combustion behavior to accurately predict combustion phasing and emissions such as CO, particulate matter, unburnt hydrocarbons and NO_x . There are several studies [4-19] rendered to understand the combustion behavior of carbonate esters of various chemical complexities. These studies showed that these carbonate esters and alkyl acetate esters containing a β hydrogen atom undergo alkene elimination via a concerted six-center retro-ene reaction. Alkene elimination from the carbonates was found to take place much faster than the reaction of the corresponding alkyl acetate esters. It appears that the additional alkoxy group destabilizes the carbonates and hence increases their reactivity compared to the corresponding

alkyl acetate esters. These reactions which fall under the class “pyrolytic *cis*-elimination” are now well known to the scientific community.

Only few experimental studies [4-8, 20] have been carried out to study the thermal decomposition of DEC. Most of these studies were confined to lower temperatures (550 – 710 K). The reported values of the rate coefficients from these low temperature studies are in good agreement except Gordon and Norris [20] values which are higher by a factor of 5-10. Herzler et al. [4] carried out experimental investigation on the thermal decomposition of ethoxy compounds using a single pulse shock tube, and this is the only high-temperature study in the literature. They reported an Arrhenius expression, $k(T) = 10^{13.03 \pm 0.11} \exp((-23290 \pm 267 \text{ K})/T) \text{ s}^{-1}$ for DEC decomposition over the temperature range of 955 – 1095 K. The extrapolated values of their rate coefficients agree reasonably well with the available experimental data at low temperatures. No pressure-dependence was observed by Herzler et al. [4] over the experimental pressure range of 1500 – 3000 Torr. All previous studies suggested that the thermal decomposition of DEC proceeds in two steps leading to the formation of equal amounts of C_2H_4 , CO_2 and $\text{C}_2\text{H}_5\text{OH}$. In the first step, DEC eliminates C_2H_4 to form ethoxy acid ($\text{C}_2\text{H}_5\text{OCO}_2\text{H}$), reaction R1, and in the second step, ethoxy acid rapidly dissociates to give ethanol and water, reaction R2.

To our knowledge, there have been no theoretical studies on the thermal decomposition of diethyl carbonates except that of Notario et al. [6] who employed MP2/6-311++G(2d,p)//MP2/6-31G(d) level of theory and classical transition-state theory to obtain kinetic

parameters. Their calculated values of the rate coefficients agree well with most of the low-temperature experimental data. However, their extrapolated values of the rate coefficients over-predict single-pulse shock tube data from Herzler et al. [4] by at least a factor of 2. Here, we have studied the initial pyrolytic steps of DEC experimentally and theoretically. The experiments were carried out in a shock tube behind reflected shock waves over $T = 900 - 1200$ K and $p = 900 - 2140$ Torr. Infrared (IR) laser absorption near $10.532\ \mu\text{m}$ was used to directly measure C_2H_4 during the chemical reaction. Absolute rate coefficients were obtained from the measured C_2H_4 time-histories and further analyses were carried out using *ab initio* / RRKM-master equation calculations to obtain the temperature and pressure dependence of the rate coefficients for reactions R1 and R2.

2. Experimental setup

The unimolecular decomposition of diethyl carbonate (DEC) was studied in the low-pressure shock tube (LPST) facility at King Abdullah University of Science and Technology (KAUST). The shock tube is briefly described here, while the details can be found elsewhere [21]. The stainless steel shock tube has an inner diameter of 14.2 cm, a 9 m long driven section and a variable length driver section. In this work, a 3 meter long driver section was used to achieve an observation time of about 1.5 ms. A polycarbonate diaphragm divided the driven section from the driver section. Prior to each experiment, the driven section of the shock tube was pumped down to less than 10^{-5} Torr using turbo-molecular pump, whereas the driver section was evacuated to 10^{-3} Torr. Thereafter, the driven and driver sections were filled with DEC/argon mixture and helium gas, respectively. Shock waves were generated by pressure bursting of the diaphragm and the shock waves propagated into the driven section heating and pressurizing the test gas mixture. The shock wave speed was measured by a series of five PCB 113B26 piezoelectric pressure transducers placed in the last 1.3 m of the driven section. Optical windows and a Kistler PZT pressure transducer were located at 2 cm from the

shock tube endwall. Temperatures and pressures behind the reflected shock wave were calculated using standard shock-jump relations [22] embedded in the Frosh code [23].

Figure 1: A schematic of the CO₂ laser set up for the detection of ethylene in the shock tube.

A schematic of the shock tube/laser diagnostic is shown in Fig. 1. Similar to our earlier works [24, 25], we employed a tunable CO₂ gas laser (10.3 -10.8 μm , Access Laser Co., Lasy-4G) to monitor ethylene formed from the thermal decomposition of diethyl carbonate. We utilized the P(14) emission line associated with the $(0\ 0\ 1) \rightarrow (1\ 0\ 0)$ vibrational transition of CO₂ to probe the the Q-branch of the ν_7 band of ethylene near 10.532 μm . The wavelength of the CO₂ laser emission was determined with high accuracy by using a mid-IR wavelength meter (Bristol 721). Intensity fluctuations of the CO₂ laser were corrected by transmitting a part of the beam to a reference photo-detector with the help of a ZnSe beam splitter (see Fig. 1). For light intensity measurements, two thermoelectric-cooled IR photovoltaic detectors (PVM-3TE-10.6, Vigo System) were employed. Barium fluoride (BaF₂) optical windows were installed on the sidewall of the shock tube to allow transmission of mid-IR laser light. A lens of 50 cm focal length placed before the shock tube helped reduce the effect of beam steering and a bandpass IR filter minimized thermal emission reaching the detector. Experimental data were recorded at a high sampling rate of 2.5 MHz using a 14-bit resolution data acquisition

board. The conversion of the measured absorption data into absolute concentrations of ethylene was achieved by using the well-known Beer-Lambert law. The absorption cross-sections, $\sigma(T, p)$, of ethylene were taken from the measurements of Ren et al. [26].

Mixtures of 0.3 – 1% diethyl carbonate in argon were prepared manometrically in a 24-litre teflon-coated stainless steel vessel equipped with a magnetically-driven stirrer. The mixing vessel was turbo-pumped down to $< 10^{-5}$ Torr before mixtures were prepared. DEC was purchased from Sigma Aldrich with purity of $\geq 99\%$ and argon/helium (99.999%) were obtained from AH Gases. MKS Baratron pressure gauge of 0 – 20 Torr range was used to measure the partial pressure of DEC during mixture preparation. Prior to the shock tube experiments, the mixtures were stirred in the mixing vessel for at least an hour.

3. Computational details

We adopted a computational approach similar to that applied in our recent works on analogous systems [24, 25, 27]. Firstly, the global minimum (GM) of diethyl carbonate (DEC) in the conformational space was sampled systematically using the MMFF94x force field [28] as implemented in MOE 2009.1 program [29]. Secondly, this MMFF94x optimized GM geometry was then re-optimized at MP2/aug-cc-pVDZ level of theory [30, 31] within frozen core approximation by applying the ‘tight’ convergence criterion of Gaussian 09 program package [32]. In accord with recent findings [33, 34], the *cis-cis* conformer of DEC is found to represent the global minimum among the conformers. The barrier heights for DEC conformational changes are quite small compared to the decomposition reaction. This would mean that a rapid equilibration of these low lying conformers, *cis-cis* DEC and *cis-trans* DEC, is expected to precede decomposition at high temperatures. Hindered rotor treatment is used

to appropriately treat these conformers to obtain accurate partition functions for the calculation of rate coefficients of reactions R1 and R2. Thus, reactions originating from the global minimum of DEC are considered in this work. Similar to our previous works [24, 25, 35], the structures of all species (transition states, reaction intermediates and products) corresponding to the minimal energy pathways (MEP) were obtained at the MP2/aug-cc-pVDZ level of theory. Each stationary point on the potential energy surface was characterized by normal mode analysis. The MP2/aug-cc-pVDZ harmonic vibrational frequencies were scaled by a factor of 0.9615 [36] to improve accuracy of the computed thermodynamic properties. Each MEP was explored by intrinsic reaction coordinate (IRC) [37, 38] calculations using a step size of 0.06 a.u. in both directions of the reaction path.

For the quantitative energetic description, G3//MP2/aug-cc-pVDZ level of theory was employed. This variant of Gaussian-3 (G3) theory utilizes the geometries and scaled zero-point energies obtained at the MP2/aug-cc-pVDZ level of theory instead of using MP2(full)/6-31G(d) geometries and scaled HF/6-31G(d) zero-point energies [39, 40]. This variant of G3 was proven to provide quantitative kinetic descriptions of similar reactions investigated earlier [24, 25]. Similar to G3 protocol [39], a series of single-point calculations were carried out at QCISD(T)/6-31G(d), MP4/6-31+G(d), and MP4/6-31G(2df,p) level of theories within frozen core approximation [41] and MP2/G3Large level of theory including all electrons in correlation calculations. ‘Higher level correction’ (HLC) was also included *via* empirical term in the G3 energies, since HLC terms cannot cancel out each other while calculating the bond dissociation energies (BDE_0). Additional calculations at G3B3 (another variant of G3 theory) were also performed to ensure the accuracy of the energetics of the reaction. All electronic structure calculations were performed by using the Gaussian 09 program package[32].

ChemRate master equation code [42] was used to compute pressure and temperature dependence for the unimolecular decomposition of diethyl carbonate (DEC) and ethyl hydrogen carbonate (EHC) which is the main decomposition product of DEC. Partition functions were calculated within the rigid rotor and harmonic oscillator (RRHO) approximations except for the low bending vibrational modes. These low lying bending torsional modes ($\text{C}_2\text{H}_5\text{—OC(O)OC}_2\text{H}_5$ and $\text{H}_3\text{C—CH}_2\text{OC(O)OC}_2\text{H}_5$ for DEC; $\text{C}_2\text{H}_5\text{—OC(O)OC}_2\text{H}_5$ for TS; $\text{OC(OH)—OC}_2\text{H}_5$ and $\text{C}_2\text{H}_5\text{—OC(OH)O}$ for EHC; $\text{O(O)C—O(H)C}_2\text{H}_5$ and $\text{C}_2\text{H}_5\text{—O(H)C(O)O}$ for TS) were treated as hindered rotors within the Pitzer-Gwinn approximations to appropriately obtain accurate partition function. All other rotors for reactants and transition states were assumed to cancel out.

4. Results and Discussion

4.1 Experimental Rate Coefficients

Carbonate esters containing a β -hydrogen atom fall under “pyrolytic cis-elimination” reaction class. Such reaction occurs via a concerted bond breaking and bond forming process to eliminate alkenes, and this is known to be a low activation energy process. For ethyl propionate (EP) [24], we showed earlier that C_2H_4 and propionic acid are the only products and no other radical producing channels are competitive to this molecular channel. Here, the presence of alkoxy group in the carbonate is expected to make alkene elimination reaction much faster than that of the corresponding alkyl acetate esters. This would mean that all probable reaction pathways other than the retro-ene elimination of C_2H_4 from DEC can be safely ruled out. Our experimental results also support the fact that unimolecular decomposition of DEC exclusively produces ethylene and ethyl hydrogen carbonate (EHC), where the ethylene yield reaches unity ($[\text{C}_2\text{H}_4]_{t \rightarrow \infty}/[\text{DEC}]_0 \sim 1$) at high temperatures and/or

long reaction times (see Fig. S1 in the Supplementary Material). This is in line with the results from earlier studies [4, 7, 8, 20] on DEC decomposition.

We recorded the evolution of C_2H_4 at a wavelength of $10.532 \mu m$ during the pyrolysis of DEC. At this wavelength, we also observed absorption interference caused by DEC (see Fig. S2 in the Supplementary Material). This interference should be corrected to reliably extract rate coefficients from the measured C_2H_4 time-histories. For the correction, we measured the absorption cross-sections of DEC in separate shock tube experiments carried out at temperatures below 900 K. At temperatures below 900 K, we did not observe any decomposition of DEC within our observation time of ~ 1.5 milliseconds. Above 900 K, the absorption cross-sections of DEC were obtained from the measured absorbance at time zero which is defined as the time of step rise in temperature by the arrival of reflected shock wave at the optical test section. These measurements resulted into the following equation for the absorption cross-section of DEC over our experimental conditions ($T = 900 - 1200$ K, $P = 900 - 2140$ torr):

$$\sigma (m^2 mol^{-1}) = 1.4 + 515 \times \exp\left(-\frac{6341 K}{T}\right) \quad (1)$$

The absorption cross-sections of DEC were found to be roughly 10% of the typical value of C_2H_4 absorption cross-section at $10.532 \mu m$. Our experiments further revealed that there are no residual absorptions caused by other products such as ethanol and carbon dioxide, which can be justified by their absorption spectra shown in Fig. S3a and S3b of Supplementary Material. Ethanol and carbon dioxide are formed by the decomposition of ethoxy acid, reaction R2. Consequently, the experimentally measured absorbance time-profiles, $A_{tot}(t)$, would be the sum of absorbances of C_2H_4 and DEC:

$$\begin{aligned} A_{tot}(t) &= A_{C_2H_4}(t) + A_{DEC}(t) \\ &= L[\sigma_{C_2H_4}(T, p)N_{C_2H_4}(T, p) + \sigma_{DEC}(T, p)N_{DEC}(T, p)] \quad (2) \end{aligned}$$

where $\sigma(T, p)$ is the absorption cross-section (cm^2/mol) at $10.532 \mu\text{m}$; $N(T, p)$ is the number density (cm^3/mol); L is the optical path length (14.2 cm). The values of the absorption cross-sections for C_2H_4 were adopted from Ren et al. [26], whereas $\sigma_{\text{DEC}}(T, p)$ were calculated using Eq. (1).

A simple chemical kinetic model comprising of reactions R1 and R2 was constructed to account for non-isothermal effects while extracting the rate coefficients. The kinetic model was used to obtain concentration-time-profiles of C_2H_4 and DEC which were then converted into absorbance-time-profiles according to Eq. (2). The rate coefficient for R1 is iteratively varied until the kinetic model delivers the best fit with the experimentally measured absorbance-time-profiles. We kept the rate coefficients for R2 unaltered during the kinetic modelling. For reaction R2, we obtained the rate parameters from our ab initio/RRKM-master equation calculations. Some representative measured C_2H_4 profiles and the best-fit kinetic simulations are shown in Fig. 2.

Figure 2: Representative absorbance time-profiles for the formation of C_2H_4 from the unimolecular decomposition of diethyl carbonate (DEC). Solid red lines are the results of the best fit of our kinetic simulations at the specified conditions (see Table 1 for further experimental information).

Figure 3: Arrhenius plot for the experimental and theoretical rate coefficient comparison. (●) this work at $P \sim 1100$ Torr, (●) this work at $P \sim 1875$ Torr. Open symbols are for previous studies; (□) Cross et al. [8], (△) Bigley et al. [7], (◇) Gordon and Norris [20], (☆) Herzler et al. [4]. Black lines from top to bottom are the results of our *ab initio*/master equation calculations at pressures $P = \infty$, 900, and 10 Torr for 6-center C_2H_4 elimination from DEC via TS1.

The extracted rate coefficients are plotted in Fig. 3 alongside our *ab initio*/master equation results and compiled in Table 1. As can be seen, our measured rate coefficients showed no discernible pressure dependence indicating that our data are close to the high-pressure limit. This observation is in line with Herzler et al. [4] data which did not exhibit any pressure dependence for $p = 1500 - 3000$ Torr. Our values of the rate coefficients show excellent agreement with those of Herzler et al. [4]. Both data sets match within an absolute average deviation (AAD) of 11% for overlapping temperatures. The low-temperature rate constant data of Godron and Norris [20] are larger than Cross et al. data [8], and this discrepancy increases as temperature increases. Comparison of the experimental rates with our theoretical calculations will be discussed in the next section.

The decomposition of diethyl carbonate (DEC) showed increased reactivity when compared to ethyl propionate (EP) decomposition from our earlier work [24]. For a given temperature, the rate coefficients for DEC decomposition are found to be at least 3 times faster than that of EP. We derived an activation energy of ~ 190 kJ/mol and a pre-exponential factor of $10^{12.85} \text{ s}^{-1}$ from our DEC experiments. While the pre-exponential factors compare well, we find a significant drop in the activation energy by almost ~ 14 kJ/mol for DEC decomposition as opposed to that of EP [24]. This lowering of activation energy and hence increased reactivity of DEC can be attributed to the destabilizing effect of ethoxy group present in DEC. Comparing the reactivity of alkyl esters [8, 11, 24, 25, 43], we can conclude that the acid group (R') forming the alkyl esters ($R'COOR$) has little effect on the rate coefficients for alkene elimination from $R'COOR$. However, the replacement of R' with alkoxy ($R'O$) group affects the decomposition rates of these esters by severalfold increase.

Table 1. Measured rate coefficients with the experimental conditions. The uncertainty associated with the rate coefficients is $\sim \pm 20\%$.

P_5 (Torr)	T_5 (K)	$[\text{DEC}]/10^{-7}$ (mol/cm ³)	$[\text{Ar}]/10^{-5}$ (mol/cm ³)	k (s ⁻¹)
1800	918	3.1	3.1	91
1875	970	3.1	3.1	408
938	971	0.5	1.5	279
2138	1001	1.0	3.4	881
1050	1002	1.7	1.7	1053
1140	1005	1.8	1.8	1131
2100	1029	1.0	3.3	1697
2025	1062	0.9	3.0	3512
1080	1071	1.6	1.6	5311
1943	1084	0.9	2.9	5563
1875	1120	0.8	2.7	6623
1140	1130	0.5	1.6	10298
1223	1175	0.5	1.7	20672
1800	1187	0.7	2.4	57189
1860	1187	0.8	2.5	31772
1058	1195	0.4	1.4	25466
1058	1204	0.4	1.4	29594

4.2 Potential Energy Surface and Theoretical Rate Coefficients

Various possible reaction pathways were explored at the G3//MP2/aug-pVDZ level of theory to understand the reaction kinetics of diethyl carbonate (DEC). The computational results are compiled in Tables 2 and S1 – S3 of the Supplementary Material. Figure 4 depicts the main reaction path. As can be seen in Table 2, the radical producing channels via simple bond fission reactions are energetically highly unlikely due to their high reaction threshold. Even the weakest bond in DEC ($\text{H}_3\text{C}-\text{CH}_2\text{OC}(\text{O})\text{OC}_2\text{H}_5$) has a large threshold energy of ~ 373 kJ/mol. This value of the bond dissociation energy (BDE) compares very well with the corresponding bond in ethyl propionate ($\text{BDE}_0 = 375.8$ kJ/mol in Ref [24]). We further exclude other reaction pathways of DEC decomposition leading to bimolecular products, such as ketene, enol and aldehyde. This judgement is reasonable when these reactions are taken analogous to those of ethyl propionate (EP). For EP, these reactions occur via high lying

transition states [44] and cannot compete with the energetically efficient 6-center C_2H_4 elimination channel. Similar to

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Table 2: G3//MP2/aug-cc-pVDZ values for the bond dissociation energies (BDE) of DEC in kJ mol⁻¹

Bond Type	BDE ₀	BDE (298 K)
CH-H	405.4	412.4
CH ₂ -H	423.9	430.9
C-CH ₃	372.8	380.2
O-C ₂ H ₅	386.0	391.3
C-OC ₂ H ₅	431.8	435.4

EP reaction system, DEC can also eliminate C₂H₄ through a low lying 4-center transition state ($\Delta E_0^\ddagger$ of 269 kJ/mol) which comes next to the most favourable six-centered C₂H₄ elimination channel. However, the 4-center transition state lies about ~ 69 kJ/mol higher in energy than the 6-center transition state. Therefore, as in our EP work [24], this channel seems highly unlikely to be competitive. This allows us to conclude that the reaction pathway shown in Fig. 4 is the only kinetically relevant pathway for the thermal decomposition of DEC under our experimental conditions. Figure 4 shows that DEC eliminates C₂H₄ in a similar fashion to that seen in retro-ene reactions of other esters [11, 24, 25]. The characteristics of the transition states are also found to be similar. In each case, the breaking C-H bond length in the TS comes close (~1.3 Å) to the forming O-H bond while the O-C bond being broken is elongated to about 2 Å. However, a noticeable drop in the barrier height was observed for C₂H₄ elimination from DEC as compared to that from EP [24]. Again, we note here that the nature of the alkyl group (R') of R'COOC₂H₅ does not seem to alter the barrier height for C₂H₄ elimination. The replacement of R' with an alkoxy group (R'O) is found to markedly lower the barrier height by several kJ/mol, and, hence, increasing the reactivity of carbonates compared to alkyl esters.

Figure 4: G3//MP2/aug-cc-pVDZ energy profile (zero-point corrected) for the most preferable decomposition pathway of diethyl carbonate (DEC). G3B3 energies are shown in parentheses.

Table 3. Modified Arrhenius parameters obtained from the fit* of the calculated values for the pressure-dependent rate coefficients over the temperature range of 500 to 1300 K.

* $k(T) = A T^n \exp(-E/RT)$ in the units of cm^3 , mol, s, J and K.

a) Rate parameters for reaction R1: $\text{C}_2\text{H}_5\text{OC}(\text{O})\text{OC}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_5\text{OCO}_2\text{H}$

S. No.	P (Torr)	Log(A)	n	E
1.	0	65.05	-20.72	232856
2.	0.1	78.53	-20.33	298701
3.	1	63.26	-15.41	279701
4.	10	43.96	-9.363	251097
5.	900	15.21	0.487	204505
6.	∞	9.244	1.345	194438

b) Rate parameters for reaction R2: $\text{C}_2\text{H}_5\text{OCO}_2\text{H} \rightarrow \text{CO}_2 + \text{C}_2\text{H}_5\text{OH}$

S. No.	P (Torr)	Log(A)	n	E
1.	0	42.02	-14.56	191296
2.	0.1	63.00	-16.34	214413
3.	1	63.28	-16.05	222155
4.	10	59.96	-14.69	224616

5.	900	37.20	-7.278	197802
6.	∞	12.76	0.286	158771

In the first step of DEC decomposition, C_2H_4 elimination occurs via a 6-membered cyclic transition state (TS1) by overcoming an energy barrier of 199.6 kJ/mol at G3//MP2/aug-cc-pVDZ level of theory. This value is very close to that computed at G3B3 level of theory ($\Delta E_0^\ddagger = 196.2$ kJ/mol). In the second step, the ethoxy acid, ethyl hydrogen carbonate (EHC), decomposes to produce ethanol (ETOH) and CO_2 . The transition state for this step (TS2) is a 4-membered cyclic structure which lies about 157.5 kJ/mol higher in energy than EHC. The overall reaction is an endothermic process ($\Delta H_{r,0K}^0 = 59$ kJ/mol) according to the G3//MP2/aug-cc-pVDZ level of theory. As in our previous works [24, 25], we used G3//MP2/aug-cc-pVDZ *ab initio* results to compute the pressure- and temperature- dependent rate coefficients for reactions R1 and R2. The molecular parameters used for these computations are compiled in Table S1 of Supplementary Material. The optimized geometries of the stationary points in Cartesian coordinates are provided in Table S3 (Supplementary Materials).

We obtained the pressure- and temperature-dependent rate coefficients, $k(T, p)$, for the thermal decomposition of DEC and EHC by employing thermal steady-state master equation calculations using ChemRate code [42]. Again, the parameters required for those calculations are compiled in Table S1. We used the exponential-down model for the collisional energy transfer parameter, $\langle \Delta E \rangle_d$, which is taken as: $\langle \Delta E \rangle_d = 0.370 \times (T/K) \text{ cm}^{-1}$. We note here that the same expression for $\langle \Delta E \rangle_d$ reproduced our experimental data on EP [24] and ethyl levulinate [25] decomposition. As can be seen in Fig. 3, the computed values of the rate coefficients for C_2H_4 elimination from DEC display no discernible pressure dependence in our experimental pressure range ($p = 900 - 2140$ Torr). In view of the size of DEC molecule,

this observation of negligible pressure dependence is not surprising. For reactions involving large molecules with more than eight heavy atoms, $k(T, p)$ becomes approximately equal to $k_{\infty}(T)$, *i.e.*, $k(T, p) \approx k_{\infty}(T)$ [45, 46]. This is because the density of states, $\rho(E)$, of molecules undergoing reactions increases exponentially with increasing the size of the molecule. Consequently, microcanonical rate constant, $k(E)$, drops rapidly below the collisional stabilization rate, $\beta k_s[M]$, *i.e.*, $\beta k_s[M] \gg k(E)$, with the bath gas M making the pressure dependence irrelevant. Here, k_s and $k(E)$ are the collisional rate and collisional efficiency, respectively. As a cautionary note, we state here that the validity of the assumption $k(T, p) \approx k_{\infty}(T)$ depends strongly on temperature and may not hold at high temperatures even for heavy molecules. The observation of negligible pressure effect for DEC decomposition agrees well with our experiments (see Fig. 3). Moreover, our calculated values of the high-pressure limiting rate coefficients agree well with all available experimental data ($p \sim \text{few Torr} - 3000 \text{ Torr}$ and $T = 550 - 1200 \text{ K}$) except the one from Gordon and Norris [20]. This indicates that our experimental data are already at the high-pressure limit and the calculated barrier height for C_2H_4 elimination from DEC is quite accurate. Gordon and Norris [20] data underpredict our theoretical rates and all the other low-temperature data by at least a factor of 5, suggesting that their data are likely in error.

As for ethyl hydrogen carbonate (EHC), its lifetime ($t_{1/2} \leq 3 \mu\text{s}$ above 1000 K) is very brief under our experimental conditions. The decomposition of EHC (R2) to eliminate CO_2 occurs very rapidly as compared to reaction R1. For instance, our calculations predict that EHC decomposes four order of magnitude faster than DEC at 600 K, whereas it reacts about 65 times faster at 1200 K. There are no available literature data for EHC decomposition except a recent theoretical study by Notario et al. [6] where they calculated rate coefficients for EHC and MHC (methyl hydrogen carbonate) decomposition. They reported a value of 0.37 s^{-1} at

600 K for the decomposition rate coefficient of methyl hydrogen carbonate (MHC). Taking the reaction analogy, their value for MHC compares well with our value ($\sim 0.5 \text{ s}^{-1}$) for EHC decomposition (R2) at the same temperature. However, their reported value for R2 at 600 K overpredicts our theoretical prediction by almost a factor of 30. This discrepancy may be attributed to the calculated value of the free energy of activation ($\Delta G^\ddagger$). Their reported $\Delta G^\ddagger$ value (136.9 kJ/mol at 600 K) obtained at the MP2/6-311++G(2d,p)//MP2/6-31G(d) level of theory for R2 underpredicts our value from G3 methods by almost 20 kJ/mol. Our G3 value for $\Delta G^\ddagger$ (~ 156 kJ/mol for R2), however, compares very well with their value ($\Delta G^\ddagger = \sim 155.4$ kJ/mol) for methyl hydrogen carbonate (MHC) decomposition which occurs via a similar 4-centered cyclic transition state. Comparing $\Delta G^\ddagger$ values obtained at the similar level of theory for reaction R2, we find that our calculated value of ~ 137.5 kJ/mol at MP2/aug-cc-pVDZ level of theory closely matches to that (136.9 kJ/mol) of Notario et al. [6]. This clearly indicates that MP2 level of theory is inadequate to quantitatively predict the energetics of carbonate ester decomposition. Our calculated values of the rate coefficients, $k(T, p)$, are compiled in Table 3 and are recommended for combustion modelling over the temperature range of 500 – 1300 K.

5. Conclusions

The thermal decomposition of diethyl carbonate behind reflected shock waves was investigated over $T = 900 - 1200$ K and $p = 900 - 2140$ Torr. Our experimental data did not exhibit noticeable pressure dependence. Our measured data showed excellent agreement with the only available high-temperature rate coefficient data from Herzler et al. [4]. The temperature and pressure dependence of the rate coefficients were computed using G3//MP2/aug-cc-pVDZ *ab initio* method combined with master equation calculations. Like other alkyl esters having a β hydrogen atom, C_2H_4 elimination from DEC was found to occur

via six-centre retro-ene reaction in a concerted manner forming ethyl hydrogen carbonate (EHC) and C_2H_4 . Decomposition of DEC was found to be faster than alkyl esters as the presence of ethoxy group in DEC lowered the barrier height significantly for C_2H_4 elimination compared to that of alkyl esters. The alkoxy intermediate (EHC) was found to decompose several orders of magnitude faster than DEC under our experimental conditions. The computed rate coefficients agree very well with our experimental results and are recommended for combustion modelling.

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Graphical Abstract

Highlights

- Unimolecular thermal decomposition of diethyl carbonate studied at high temperatures
- Measured rates do not exhibit noticeable fall off over 1 – 3 bar
- Diethyl carbonate decomposition proceeds through ethyl hydrogen carbonate
- Decomposition process results in six-centered retro-ene elimination of ethylene
- Ab-initio/master equation calculations agreed very well with experimental rates