Double imaging photoelectron photoion coincidence spectroscopy reveals the unimolecular thermal decomposition mechanism of dimethyl carbonate

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Abstract

We studied the thermal decomposition of dimethyl carbonate (DMC, C₃H₆O₃) in a flash vacuum pyrolysis reactor in the 1100–1700 K range. The reaction products and intermediates were probed by vacuum ultraviolet synchrotron radiation in a photoelectron photoion coincidence (PEPICO) spectrometer to record isomer-specific photoion mass-selected threshold photoelectron (ms-TPE) spectra. Reaction pathways were explored using quantum chemical calculations, which confirmed the experimental observation that intramolecular migration of a methyl group, yielding dimethyl ether (DME, C₂H₆O) and carbon dioxide, dominates the initial unimolecular decomposition chemistry. The role of a second, potentially important channel, namely C–O bond fission to yield methyl radicals, could not be determined experimentally due to the short lifetime of the ·C₂H₅O₃ radical and overlapping sequential decomposition products. However, potential energy surface and microcanonical rate constant calculations predict 2–3 orders of magnitude lower rates for this channel than for decarboxylation to yield DME. Consequently, DMC pyrolysis shows bewilderingly similar products and product abundances as DME pyrolysis. This coincides with DMC combustion modeling studies, which found that DME is a key intermediate in the mechanism. Furthermore, we have detected traces of methyl formate and formaldehyde, produced after hydrogen shift to the central carbon atom in DMC. Ethylene and acetylene could be established as bimolecular reaction products, because their abundance depended strongly on the DMC concentration. It is intriguing to compare the decomposition of DMC with that of the structurally similar methylal (dimethoxymethane, DMM). While methanol and formaldehyde are produced in similar quantities in DMM, thanks to low-energetic hydrogen transfer reactions, the methanol channel is almost fully suppressed in DMC due to the absence of hydrogens at the central carbon atom and the thermodynamically favored decarboxylation. These new mechanistic insights may help the development of predictive combustion models for fuel additives and biofuels.

Keywords: Threshold photoelectron spectroscopy, Synchrotron radiation, Flash vacuum pyrolysis, Dimethyl carbonate, Dimethyl ether, Ionization energy, Combustion, Intermediates
1. Introduction

Renewable fuels and additives can help reduce the carbon footprint of transportation. Dimethyl carbonate (DMC, \( \text{C}_6\text{H}_{12}\text{O}_3 \)) has been discussed in this context and promising routes have been explored for its synthesis from biological sources and from CO\(_2\).\(^1\)\(^-\)\(^2\) The molecular structure of DMC, in particular the high oxygen content and the lack of C–C bonds, facilitates clean combustion\(^3\)\(^-\)\(^4\) due to reduced smoke and soot emissions when blended into diesel\(^5\)\(^-\)\(^8\) and gasoline.\(^9\)\(^-\)\(^10\) DMC is biodegradable\(^2\) and of low toxicity, making it an ideal fuel additive.

Earlier DMC studies on its combustion behavior led to partially contradictory results regarding reaction pathways and products.\(^11\)\(^-\)\(^14\) This has changed with progress in computational quantum chemistry, allowing the development and continuous refinement of chemical kinetic mechanisms for DMC combustion.\(^15\)\(^-\)\(^18\) The most important unimolecular dissociation channel was found to be the loss of molecular CO to create dimethyl ether (DME), which lowers the effectiveness of DMC as oxygenate somewhat because two oxygen atoms are directly carried away in this process. Low-pressure flat flame studies concurred, as they revealed most of the CO\(_2\) to be formed early, via decomposition of the carbonate or ester functionalities rather than via CO oxidation.\(^17\) Consequently, DME chemistry must be taken into account when modeling combustion reactions of DMC. Another important decomposition pathway is the barrierless loss of a methyl radical. This is the energetically lowest bond fission, and it greatly influences the subsequent formation of H atoms through a sequence of \( \beta \) -scissions.\(^16\) The formation of H atoms and methyl radicals is crucial as these species influence further fuel reaction kinetics at high temperatures.\(^16\)

Kinetics combustion models and theoretical dissociation pathways of DMC were tested against several experimental observables, such as ignition delay times in shock tubes,\(^18\)\(^-\)\(^19\) H\(_2\), O\(_3\), and OH profiles behind reflected shock waves,\(^16\)\(^,\)\(^20\)\(^-\)\(^21\) and burning velocities in laminar flames.\(^22\) In addition, GC and HPLC analyses were carried out sampling the stable products in a diffusion flame and a flow reactor.\(^17\) Laminar flames were also probed with vacuum ultraviolet (VUV) photoionization and high-resolution mass spectrometry.\(^17\)\(^,\)\(^23\)

In all these studies, bimolecular reactions of decomposed DMC species, either with or without oxygen, contributed significantly. Nonetheless, pyrolysis and combustion of DMC is, in part, governed by unimolecular chemistry, which plays a significant role at high combustion temperatures and during ignition. This motivated us to investigate the thermal decomposition of DMC at very dilute — unimolecular — conditions.\(^17\)\(^,\)\(^23\)

The unimolecular decomposition of methylal (dimethoxymethane, \( \text{H}_2\text{CO}–\text{CH}_3\text{O}–\text{CH}_3 \), DMM), a structurally similar fuel additive candidate, was investigated only recently.\(^24\) Hydrogen-transfer reactions to yield methanol and methoxy methylene carbenes were found to be the dominant reaction channels and are favored over direct bond cleavage. These rearrangement reactions are often neglected in combustion models, which is why applying the same approach to DMC could provide new mechanistic insights to be considered in predictive kinetics models.\(^24\) Formally, DMC corresponds to DMM with the \( \text{H}_2 \) group at the methylene unit substituted by an oxygen atom. In practice, its unimolecular chemistry may be completely different from that of DMM. Thus, understanding the early dissociation and rearrangement reactions of DMC and their isomer-selective product identification is crucial to refine combustion models. This can be achieved by probing the molecular beam from a flash vacuum pyrolysis setup directly with vacuum ultraviolet synchrotron radiation in a photoelectron photoion coincidence (PEPICO) spectrometer. The same setup was used recently to measure the ionization energy of DMC and to decipher its dissociative photoionization (DPI) pathways between 10.3 and 12.5 eV.\(^25\) We rely on the DPI results in the present study to distinguish between fragments produced by the dissociation of the parent ion after photoionization and neutral pyrolysis decomposition products. The sensitivity of our setup even enables the detection of major and minor reaction pathways in reactive environments such as combustion,\(^16\) pyrolysis,\(^27\) catalysis,\(^28\)\(^-\)\(^30\) or during laser photolysis kinetics experiments.\(^31\) Thus, we can verify theoretical models for initial DMC pyrolysis by experimental, spectroscopic identification of the decisive reactive intermediates.

2. Methods

Double imaging photoelectron photoion coincidence (\( ^2 \)PEPICO) experiments were carried out using the CRF-PEPICO endstation at the VUV beamline of the Swiss Light Source. Detailed description of the beamline and the endstation are available elsewhere.\(^32\)\(^-\)\(^35\) Synchrotron radiation is collimated, dispersed by a 150 mm\(^1\) grating in grazing incidence, and focused on the exit slit, achieving an energy resolution of 6 meV at 8 eV. A differentially pumped noble gas filter (10 mbar; Ar:Ne:Kr \( = 3:6:1 \)) absorbs higher diffraction orders, and only the higher order free, monochromatic VUV beam enters the PEPICO setup. The photon energy was calibrated against argon autoionization lines in first and second order.

DMC (≥99%) was obtained from Sigma–Aldrich and used as delivered. It was diluted in Ar buffer gas (0.05–0.5 %), and a total of 20–40 standard ml/min of the gas mixture was expanded through a 100 \( \mu \)m pinhole into a resistively heated Chen-type SiC tubular pyrolysis microreactor\(^16\) with 1 mm inner diameter, 0.5 mm wall thickness, 15 mm heated zone, and 30 mm total length. A type C thermocouple attached to the outer wall measured the temperature of the reactor. In our study, the effective pressure and residence time in the reactor are tens of mbar and 10–100 \( \mu \)s, respectively.\(^17\) The gas sample leaving the reactor forms a continuous molecular beam at a background pressure of 10\(^-5\) mbar in the source chamber, which suppresses reactive collisions and preserves the original snapshot of the reaction mixture. The molecular beam was skimmed using a 2-mm skirted and entered the ionization region at a background pressure of ca. 10\(^-6\) mbar. Spectra were acquired at room temperature to discriminate between pyrolysis products and background impurities or DPI products. The temperature was then increased until reaction
products appeared in the mass spectra at about 1150 K. It was then raised further to improve signal levels for threshold photoelectron (TPE) spectroscopy scans of various intermediates to a maximum of 1700 K.

Photoelectrons (PE) and -ions (PI) were both velocity map imaged (VMI) using a constant extraction field of 230 V cm$^{-1}$. Position sensitive delay line anode detectors were utilized (Roentdek DLD40), and electron and ion events were correlated in a multiple start/multiple stop scheme to plot mass spectra.$^{38}$ In order to suppress sampling effects and to increase the radical detection sensitivity, PI velocity map images were used to align the source and maximize the molecular beam signal. They can also be used to distinguish between dissociative ionization and direct ionization as the former is often accompanied by large kinetic energy release.$^{39}$

Threshold electrons were selected with a resolution of 5–8 meV by discriminating for the central part of the PE image and subtracting the hot electron background from the center signal.$^{39}$ Photoion mass-selected TPE (ms-TPE) spectra were acquired by scanning the photon energy in steps of 5–100 meV and plotting the threshold photoelectron signal in coincidence with the m/z channel of interest. Due to the mild expansion conditions from the microreactor into vacuum, the vibrational and rotational degrees of freedom are not efficiently cooled, leading to hot and sequence band transitions in the ms-TPE spectrum. Typical vibrational and rotational temperatures of 500 K were observed using these type of reactors.$^{40}$ Nevertheless, these transitions do not affect the isomer-selective assignment in this work.$^{39}$

Quantum chemical calculations, i.e., geometry optimizations, potential energy surface calculations, adiabatic ionization energies (IEs), and Franck–Condon simulations were performed using the Gaussian16 software package in the harmonic approximation using density functional theory (DFT) and the CBS-QB3 as well as the G4 composite methods.$^{42-43}$ 

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3. Results and Discussion

Figure 1 compares time-of-flight mass spectra obtained at room temperature and at a pyrolysis temperature of 1300 K. The most prominent mass peaks appearing in the high temperature data are at m/z 15, 28, 29, 30, 31, 33, 45, 46, and 59–62. However, not all of these are due to thermal decomposition. DMC photoionization was investigated at room temperature and m/z 29, 31, 33, 45, and 59–62 could be assigned to dissociative photoionization.$^{25}$ At elevated temperatures, the DPI appearance energies shift markedly to lower photon energies, because the elevated thermal energy of the neutral can also be utilized in fragmentation.$^{46}$ Thus, it is inevitable that contributions of dissociative ionization are present in our mass spectra, especially at higher reactor temperatures.$^{40}$ Ion velocity map imaging is a versatile tool to distinguish whether the detected ions stem from neutral pyrolysis products or from DPI. The mass-selected ion images of the molecular beam (Fig. 2) appear narrow only if the respective molecule (e.g., m/z 46 on the right) was created before ionization, i.e., upon pyrolysis.$^{29}$ Fragmentation due to DPI in the ionization region of the spectrometer will broaden the ion momentum distribution due to isotropic kinetic energy release, 

![Fig. 1. Ion time-of-flight mass spectra at two photon energies and pyrolysis temperatures. The high temperature data (in red) has been scaled by a factor of 5.](image)

![Fig. 2. Ion images at 11 eV photon energy for two selected masses. The red ellipse marks the molecular beam. The diffuse ion cloud at the bottom is due to thermalized species.](image)
especially if the ion loses a significant portion of its mass in fragmentation or dissociates impulsively.\textsuperscript{46} For instance, the \textit{m/z} 45 fragment can thus be ascribed to DPI from DMC at a photon energy of 11 eV (Fig. 2), 0.47 eV below its 0 K appearance energy and 0.3 eV below its onset in the room temperature breakdown diagram of DMC.\textsuperscript{25} The same kinetic energy release signature is detected for mass signals at \textit{m/z} 31, 33, 59, 61, and 62, which can thus be assigned to dissociative ionization. A second indication for a DPI process is an asymmetric ion mass peak (see \textit{m/z} 62) with a tail towards longer flight times. This indicates that the precursor ion is metastable and dissociates in part during its several \(\mu\)s long residence time in the acceleration region of the mass spectrometer.\textsuperscript{44} This strategy was utilized to clearly identify the pyrolysis products at \textit{m/z} 14, 15, 26, 28, 30, 32, 44, and 46. In the following, species created in pyrolysis are divided into major or minor decomposition products based on the intensity of their mass spectral peaks and their ms-TPE signal and as discussed below.

### 3.1 Major Decomposition Channels

We used mass-selected threshold photoelectron spectra, depicted in Figure 3, to isomer-selectively assign the intermediates and products emerging from the pyrolysis micro reactor by comparison with literature photoelectron spectra.\textsuperscript{47,56} Major components are CO\(_2\) (44 amu), CO (28 amu), formaldehyde (\(\text{H}_2\text{CO}\), 30 amu), methyl (\(\cdot\text{CH}_3\), 15 amu) and dimethyl ether (DME, \(\text{C}_2\text{H}_6\text{O}\), 46 amu). Excellent agreement with the literature photoelectron spectra confirms the assignment of methyl, formaldehyde and CO\(_2\) respectively, as presented in Figure 3. The fundamental transition of the ionization into the CO\(^+\) ground state is at 14.01 eV,\textsuperscript{57} which is absorbed by the gas filter. Due to the formation of vibrationally hot CO in our pyrolysis micro reactor, the hot band transitions \(\nu(1,2\rightarrow0)\), are significantly populated, which proves the production of CO. In addition, water (18 amu) and methane (16 amu) were observed but ascribed mainly to background signal in the detector chamber (verified by ion VMIs) or secondary reactions of radicals via bimolecular chemistry of DMC (vide infra). Additional minor products are the methylene carbene (\(\cdot\text{CH}_2\), 14 amu), acetylene (\(\text{C}_2\text{H}_2\), 26 amu), ethylene (\(\text{C}_2\text{H}_4\), 28 amu), methanol (\(\text{CH}_3\text{OH}\), 32 amu) and methyl formate (\(\text{HCO(O)CH}_3\)). A discussion of reactions leading to these species follows hereafter.

\textbf{Fig. 3.} Mass-selected TPE spectra of DMC pyrolysis products (black) identified by comparison with literature PE spectra (red).
Oxygen detected in the ms-TPE spectrum of m/z 32 is exclusively due to background gas in the ionization chamber without a molecular beam component, as confirmed by the ion velocity map image. The ms-TPE spectrum of hot DMC (m/z 90), surviving the pyrolysis reactor (see Figure 3), and that of pyrolytically generated DME differ largely from the literature PE spectra. They peak at 0.1–0.3 eV lower photon energy and converge to zero soon afterwards. This is due to their parent ions being relatively unstable and prone to fragmentation. Prominent daughter ions of DMC are CH$_2$OH$^+$ (31 amu at 0 K appearance energy of 11.14 eV), CH$_2$CHOH$^+$ (45 amu, 11.46 eV), CH$_3$COO$^+$ (59 amu, 11.47 eV), OHCH$_2$CH$_2$OH$^+$ (62 amu, 11.16 eV), CH$_3$OH$_2$$^+$ (33 amu, 11.54 eV) as well as C$_2$O$_2$H$_4$(60 amu). The DME cations also fragment into C$_2$H$_2$O$^+$ (45 amu) + H already below 11.2 eV. As mentioned before, the DPI onsets are further shifted significantly, by up to 2 eV, to the red due to the high temperature in the microreactor and inefficient cooling afterwards.

To rationalize the observed pyrolysis products, we explored the potential energy surface of DMC along several reaction coordinates with CBS-QB3 theory. Fig. 4 depicts seven unimolecular decomposition pathways. C–O bond cleavage creating a methyl radical (R1) is the energetically lowest direct bond fission calculated at 3.81 eV (3.72 eV, G4). The resonantly stabilized C$_2$H$_2$O$_2$ radical decomposes to methoxy (-OCH$_3$) and CO$_2$ after surmounting a low-lying barrier of only 0.62 eV relative to OCH$_3$. This is easily accessible in pyrolysis. The thermolabile OCH$_3$ intermediate can either lose an -H to create H$_2$CO or H$_2$ and -H in series to form CO. The hydrogen (R2) or methoxy radical (R3) formation from DMC are energetically more demanding and require activation energies of 4.30 and 4.48 eV, respectively at CBS-QB3 level of theory (4.22 and 4.34 using G4), as summarized in Figure 4.

The bond fissions (R1)-(R3) eventually yield the same products at high temperatures, i.e., -CH$_3$ + CO$_2$ + H$_2$CO + -H, due to &-scissions of the radicals formed, which offers a tentative explanation for most of the major products. Furthermore, our microcanonical rate constants (Fig.4, right) indicate that (R2) and (R3) are more than hundred times slower than R1, in agreement with master equation calculations of Peukert et al. However, the energetically lowest-lying decomposition channel is not CH$_3$ loss but CH$_3$ transfer in the cis-trans rotamer of DMC to generate DME and CO$_2$ (see Figure 4, R4).

The transition state barrier is only 3.09 eV at CBS-QB3 level of theory (3.11 eV at G4), thus, this pathway is expected to dominate the dissociation at low temperatures although the transition state of R4 is tighter and its activation entropy is lower than that of R1. This suggests that the rates for R1 may overtake R4 at high enough energies, although not below 5–6 eV (Fig. 4). The product of the methyl-transfer initiated decarboxylation is DME, which can then further decompose as discussed later. Our calculations are in excellent agreement with the most prominent species observed in our experiment and confirm previous theoretical studies. Overall, R4 is the dominant unimolecular decomposition channel of DMC, even at high temperatures, as confirmed by microcanonical
rate-constant calculations depicted in Figure 4 (right). Thus, molecular CO$_2$ loss is predicted to be $10^7$–$10^9$ times more frequent than $\cdot$CH$_3$ production in R1. It is therefore questionable whether the observation of methyl is due to pathway R1 in Fig. 4. Instead, $\cdot$CH$_3$ is also produced by the unimolecular dissociation of DME, which is its likely source. While the $\cdot$C$_2$H$_3$O$_3$ intermediate, the other product of R1, could not be detected, this is also explained by its low, 0.62 eV barrier to CO$_2$ loss. This implies a very short $\cdot$C$_2$H$_3$O$_3$ lifetime in the pyrolysis microreactor and rapid conversion to methoxy radicals and CO$_2$. Methoxy radicals are also unstable and decompose rapidly into $\cdot$H and H$_2$CO, formaldehyde. However, formaldehyde is a dominant peak at m/z 30, anyway, as it is also formed in further decomposition of the main primary DMC pyrolysis product, DME and in R5 (see below).

3.2 Minor reaction pathways

While hydrogen-transfer reactions played a major role in the fragmentation of the DMC cation$^{24}$ and the thermal decomposition of methylal,$^{24}$ methyl transfer (R4) is the most important process in the unimolecular thermal decomposition of DMC. The detection of minor products, such as :CH$_2$, C$_2$H$_2$, C$_2$H$_4$, CH$_3$OH and methyl formate (C$_2$H$_5$O$_2$), hints at further unimolecular decomposition pathways of DMC, with potential hydrogen-transfer reactions at their origin. Due to their small abundance in the product stream, the molecularity of these products requires further attention: they may be formed in bi- or unimolecular processes. These products may be the result of a reaction between indirectly produced radicals with another DMC molecule, or stem from recombination reactions between two radicals producing, e.g., new carbon–carbon bonds. To address the role of bimolecular chemistry, we investigated the DMC concentration dependence of intermediate and product abundances (see Figure 5). While the :CH$_2$ (14 amu), CH$_3$OH (32 amu), and C$_2$H$_5$O$_2$ (60 amu) peaks are minor ones across the board, the m/z 26 and 28 peaks depend strongly on the DMC concentration and are almost fully suppressed below ca. 0.05 %. Thus, the formation of ethylene (28 amu) is assigned to dimerization of methyl radicals (15 amu) and subsequent dehydrogenation and is not a unimolecular reaction channel of the DMC decomposition.

Even at low DMC concentrations, m/z 60 persists at a constant, low abundance and two origins can be found for this product. It is formed in part in the dissociative ionization of DMC, as pointed out recently,$^{25}$ but its TPE spectrum also contains vibrational features at 10.85, 11.05 and 11.20 eV, which are indicative of methyl formate (see Figure 3). Peukert et al. also found methyl formate as minor decomposition product of DMC.\textsuperscript{16}

We found an initial barrier of 4.15 eV (CBS-QB3, 4.16 eV at G4), as depicted in Figure 4 (R5), which compares well with the Peukert et al. energetics at 4.14 eV:

![Microcanonical rate constants](image-url)

Microcanonical rate constants show, however, that R5 only plays a subordinate role. Furthermore, methyl formate is prone to further decomposition at elevated temperatures, yielding (1) two equivalents of formaldehyde, (2) methane and CO$_2$, or (3) CO and methanol at 3.33, 2.96 and 3.61 eV, respectively, according to Metcalf et al.$^{60-61}$ Kinetic modeling predicts that channel (3) is the most prominent one. Nevertheless, we can assign methyl formate (60 amu) in our ms-TPE spectrum in Figure 3 and thus confirm this minor reaction pathway, notwithstanding its low abundance due to the slow rates of R5 when compared with the dominant R4. Note that computed rates do not include quantum tunneling, which may enable H-scrambling even below the transition state barrier.

Other unimolecular reaction channels are H$_2$ loss, forming a carbene species (R6) with a rate-limiting barrier of 4.13 eV (G4 and CBS-QB3), as depicted in Figure 4. R6 was also found by Peukert et al. computationally:

![Carbene formation](image-url)

This carbene is likely unstable at pyrolysis temperatures and decomposes to products, such as HCO, CH$_4$, and CO$_2$, also observed in the primary reaction channels R1–R5. Thus, R6 is difficult to observe experimentally.
The appearance of :CH₂ is puzzling, as a hydrogen needs to migrate from a CH₂ group towards the oxygen of the other methoxy group. We found a loose transition state on the singlet potential energy surface, where methanol, :CH₂, and CO₂ are bound by long-range interaction (see Figure 4 R7), after passing a transition state at ca. 3.82 eV, but we could not find a clear transition state yielding the triplet or singlet methylene carbene. The latter is probably owing to the intersystem crossing from the singlet to the triplet methylene potential energy surface. We estimated the barrier to be at least > 4.09 eV (4.05 eV @ G4), the reaction energy to form the singlet methylene carbene, ranking this reaction pathway in similar rates as compared to the direct methyl loss (R1):

Due to the large abundance of radicals (H, CH₃) formed in DMC decomposition, it may also be possible that the detection of the methylene carbene is owing to hydrogen abstraction from the methyl radical occurring at combustion relevant conditions.

3.3 Secondary Decomposition Reactions

![Mass spectra of the dimethyl ether (DME) decomposition in our microtubular reactor at 11 eV.](image)

Fig. 6 Mass spectra of the dimethyl ether (DME) decomposition in our microtubular reactor at 11 eV. The methyl radical (15 amu) and formaldehyde (30 amu) dominate the decomposition products.

The strong dimethyl ether (DME, 46 amu) signal in Figure 1 and its temperature dependence indicates that DME is subject to further decomposition in the pyrolysis reactor. Just as DMC, it has long been featured in the combustion literature as a non-toxic, eco-friendly fuel or fuel additive with superior laboratory performance in diesel engines and as an ignition enhancer for methanol in diesels. Most studies on the pyrolysis of DME were performed in denser media, with bimolecular reactions contributing significantly. Thus, we decided to investigate the thermal decomposition of DME in our microtubular reactor at similar conditions as for DMC. The mass spectra at 11 eV are presented in Figure 6 and show only peaks at m/z 45 and 46, which correspond to DME and DME-H, the latter from dissociative ionization. Upon increasing the pyrolysis temperature, methyl radicals (m/z 15) and formaldehyde (m/z 30) appear, while the DME peak decreases and completely disappears at temperatures above 1600 K. At 11 eV photon energy, the mass spectra are virtually identical with the ones from DMC confirming that the decarboxylation is the most important primary reaction of DMC. Mass spectra taken at 13 and 13.95 eV show presence of CO and CH₄, but only to a small extent.

A decomposition reaction initiated by a •CH₃ loss characterizes the pyrolysis of DME at an initial barrier of 3.62 eV according to our CBS-QB3 calculations. The complementary •OCH₃ radical rapidly decomposes at a 0.99 eV (CBS-QB3) threshold to yield formaldehyde (H₂CO, m/z 30) after hydrogen loss. Other unimolecular dissociation routes have much lower reaction rates and are usually not included in the description of the DME pyrolysis and combustion chemistry in dense media. Notably, a roaming mechanism exists yielding CH₄ + H₂O, where the detached •CH₃ remains close to the bigger fragment due to van der Waals interactions, moves around at long range and finally removes another hydrogen without further (or with very low) activation energy. This pathway may contribute to only 1–2% to the overall unimolecular dissociation according to calculations, and could be responsible for the traces of methane found in our experiments, too. Roaming radical mechanisms have been shown to also play a role in the dissociation of formaldehyde (to form CO through a roaming H atom) and in acetaldehyde (with a roaming methyl radical). However, methane could also originate from an CH₃ radical abstracting hydrogen from DME or recombination with abundant hydrogen atoms, making it difficult to prove the roaming pathway at our experimental conditions.

Formaldehyde (H₂CO), as second major product in DMC and DME pyrolysis can decompose further, either via two sequential H loss reactions (mainly at high pressures) or via molecular H₂ loss (at pressures below 1 bar) and may be responsible for the CO formation. According to Zhang et al. the barriers for the H loss and H₂ loss are 4.12 and 3.75 eV respectively. Thus, both reactions may contribute to the observed CO signal at m/z 28.

4. Conclusion

The decomposition intermediates and products of dimethyl carbonate (DMC) in a pyrolysis microreactor could be clearly identified by photon mass-selected threshold photoelectron spectroscopy, velocity map ion imaging and mass spectrometry, utilizing vacuum ultraviolet synchrotron radiation.

We found that the main decomposition channel is initiated by a methyl shift between the two methoxy groups, yielding dimethyl ether (DME) and carbon dioxide in an almost isoenergetic thermal decomposition reaction. Potential energy surface and microcanonical rate calculations, in agreement with Peukert et al., revealed that the methyl transfer reaction channel is favored by two orders of magnitude compared to the direct methyl, hydrogen or methoxy abstraction reactions or the formation of
methyl formate via a hydrogen shift. Consequently, the major peaks in the mass spectrum of the DMC decomposition are virtually identical with the decomposition of DME, which deliver mostly methyl and -OCH₃ radicals. Methoxy species are thermally labile and decompose to formaldehyde, which represents the most abundant product in our study.

The second most important channel, according to current knowledge, is the direct methyl fission from DMC. However, this pathway could not be proven unequivocally in our experiments due to the short lifetime of the -C₂H₅O₃ radical intermediate and because the other products are identical to the DME decomposition channels. Thanks to the vibrational transitions in the TPES of methyl formate (m/z 60), we could identify it as a decomposition product, although m/z 60 is also a dissociative ionization product of DMC. An intramolecular hydrogen-transfer from the methyl group to the carbonyl C in DMC is responsible for this reaction, which also yields formaldehyde as second product. Traces of methanol were also identified, which were assigned to the decomposition of methyl formate, in agreement with literature calculations. Ethylene and acetylene could unequivocally be assigned to bimolecular chemistry, as their abundance depends strongly on the DMC concentration in the reactor.

In view of their structural similarity, it is worth comparing the thermal decomposition of dimethyl carbonate (DMC) with that of methylal (dimethoxymethane, H₂CO–CH₂–OCH₃, DMM), another promising biofuel additive, in similar conditions. In DMM, the central carbon contains two hydrogen atoms, making it more reactive towards methanol formation. Methyl alcohol can be produced in three hydrogen-transfer reactions yielding cis- and trans-methoxy methylene carbene (R8), respectively, at rate-limiting barriers of less than 3.5 eV. The carbenes then rapidly decompose towards methyl radicals and CO. In an alternative DMM decomposition channel, formaldehyde is produced along with dimethylether (DMM) and methyl radicals (R9).

Consequently, DMM decomposition yields similar amounts of methanol and formaldehyde at our experimental conditions. In DMC, the high selectivity towards DME and, sequentially, formaldehyde formation is explained by the lack of a central hydrogen atom that could transfer to the methoxy groups to yield methanol. Furthermore, H transfer from the terminal CH₃ group to the oxygen of the methoxy group to yield the methylene carbene (:CH₂), methanol and CO₂ is energetically more demanding in DMC (see Figure 4 R7), in agreement with the low observed :CH₂ concentration. Thus, upon substituting the two hydrogens in DMM by an oxygen to yield DMC, the methanol formation channel is effectively blocked, and dimethylether is produced in R10 almost exclusively thanks to the large thermodynamic stabilization of CO₂. Due to isoenergetic decarboxylation and DME formation, the latter species is generated vibrationally hot and thus subject to further decomposition either unimolecularly or in an oxidizing environment, such as flames. Our study confirms the importance of DME as key-species in DMC combustion models and may serve as mechanistic starting point for combustion studies utilizing PEPICO as detection technique.

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