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Gas-phase reaction between $\text{CH}\cdot$ and CH_3OCH_3 at interstellar temperatures (25-100 K): Kinetics and astrochemical implications

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ABSTRACT

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The methylidyne radical ($\text{CH}\cdot$) and oxygen-bearing complex organic molecules (COMs), such as dimethyl ether (DME, CH_3OCH_3), are recognized to be of great importance in interstellar chemistry. However, despite its potential role in the growth and evolution of interstellar COMs, the reaction between $\text{CH}\cdot$ and DME has not yet been studied experimentally or theoretically. In this work, we measured the rate coefficients using the pulsed laser photolysis-laser induced fluorescence (PLP-LIF) technique, and characterized reaction product *via* vacuum ultraviolet (VUV) photoionization reflectron time-of-flight mass spectrometry (Re-TOFMS) under uniform supersonic low-temperature flow conditions. The rate coefficients were determined to range from $3.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to $1.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at temperatures of 25–100 K. By combining mass spectroscopy results and the newly calculated potential energy surface, we identified the dominate reaction pathway, which leads to the formation of $\text{CH}_3\text{O}\cdot + \text{C}_2\text{H}_4$. Astrochemical modelling further revealed that this reaction serves as a gas-phase reaction source for $\text{CH}_3\text{O}\cdot$ in the cold interstellar environments.

Complex organic molecules (COMs), defined in astrochemistry as carbon-containing molecules with six or more atoms [1], are extensively detected in the interstellar medium (ISM) [2], mainly toward dark clouds [3,4], low-mass [5,6] and high-mass [7,8] star-forming regions. Among these, oxygen-bearing complex organic compounds (O-COMs) have been extensively studied for decades because they serve as bridges between simple atoms/molecules and prebiotic species [9]. Molecular mass growth processes leading to prebiotic molecules in deep space could provide an exogenous source of vital biomolecules for early life evolution [10,11].

Dimethyl ether (DME, CH_3OCH_3) ranks among the most abundant and widely detected O-COMs in the ISM, with confirmed detections in cold molecular clouds including TMC-1 [4], L1689B [12], B1-b [13], L1544 [14], Barnard 5 [15], and L483 [16]. The ubiquity of DME suggests its active participation in diverse chemical networks governing COMs formation in these cold, dark interstellar environments. Multiple reaction pathways have been identified for DME conversion to formaldehyde (H_2CO) [17,18] and methyl formate (HCOOCH_3) [19,20], which are key intermediates to form more complex prebiotic molecules including sugars and nucleic acids [10,21,22]. This chemical evolution establishes DME as a crucial precursor in the astrochemical pathways to vital biomolecules necessary for the origins of life.

Methylidyne radical ($\text{CH}\cdot$) has been observed extensively in interstellar clouds with high abundance, *e.g.*, $(1.5 \pm 0.5) \times 10^{-8}$ relative to H_2 in TMC-1 [3,23]. $\text{CH}\cdot$ also serves as a proxy for the H_2 column density in the diffuse ISM [24]. Due to the unique molecular structure involving an unpaired electron and an empty molecular orbital, $\text{CH}\cdot$ is highly reactive and feasible to react with other molecules *via* barrierless insertion mechanism. Methylidyne radical has been revealed to play important roles in the chemical evolution of COMs in the cold interstellar medium and planetary atmospheres, especially in the growth of carbon chain and formation of unsaturated COMs [25–28]. Given high abundance of both $\text{CH}\cdot$ and DME in cold dark environments, it is necessary to study this title reaction theoretically and experimentally under cold conditions.

The bimolecular reaction kinetics of $\text{CH}\cdot$ with DME were investigated under low-temperature uniform flow conditions using a pulsed Laval nozzle supersonic flow apparatus (Fig. 1). A series of convergent–divergent Laval nozzles were utilized to produce stable and isentropic supersonic flows. These well-defined nozzles allow the generation of uniform gas flows at temperatures ranging from 25 K to 100 K, simulating interstellar or planetary environments where evolutions of chemical species are intriguing. Each nozzle configuration corresponds to a specific Mach number (between 3.2 and 6.0), resulting in distinct flow temperatures and densities. The characterization of these uniform flows was achieved by pitot measurements [29,30].

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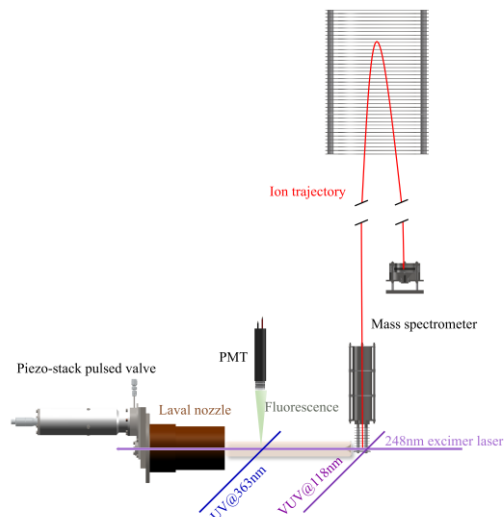


Fig. 1. The low-temperature kinetics apparatus based on pulsed *de* Laval nozzle, coupled with the LIF and the Re-TOFMS techniques. The uniform flow generated from the nozzle (pink), the laser lights for photolysis and detection, the collected fluorescence (green cone) and the ion trajectory (red break line) are also shown.

The reaction rate coefficients under various low-temperature conditions were measured employing the pulsed laser photolysis-laser induced fluorescence (PLP-LIF) technique [31-34]. The nascent CH radicals, initially generated with vibrational and rotational excitation, undergo rapid relaxation due to the high bath gas density in the uniform flow [30]. Consequently, exponential fits for extracting k_{obs} were applied starting at a delay time of 20 μs for N_2 flow (or 30 μs for Ar and He flow), following Eq. 1:

$$[\text{CH}]_t = [\text{CH}]_0 \cdot \exp(-k_{\text{obs}} t) \quad (1)$$

where $[\text{CH}]_0$ is the initial CH radical concentration, and $[\text{CH}]_t$ represents its instantaneous concentration at reaction time t . Fig. 2A displays representative time-resolved LIF traces of CH radical decay at 52.0 K for various DME concentrations. The CH $\cdot$ signal decay rate increases with higher [DME], indicating efficient bimolecular reaction under pseudo-first-order conditions ($[\text{DME}] \gg [\text{CH}]$). The pseudo first order reaction rate k_{obs} is expressed as:

$$k_{\text{obs}} = k_2 \cdot [\text{DME}] + k_{\text{other}} \quad (2)$$

where k_{other} accounts for the side reaction and diffusion losses of CH radicals. By plotting k_{obs} against [DME], the second-order rate coefficient k_2 for the title reaction was determined from the linear slope, as depicted in Fig. 2B.

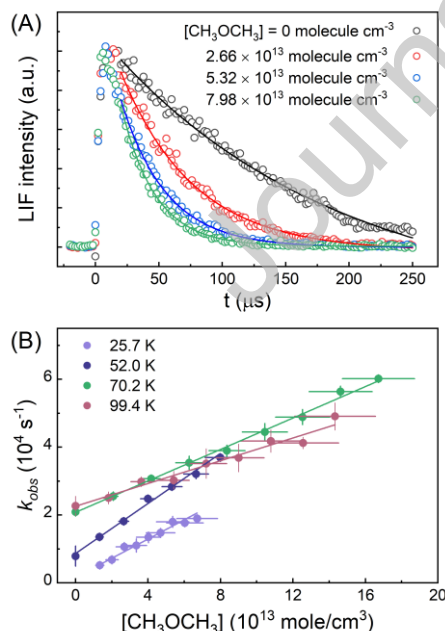


Fig. 2. (A) Time-resolved LIF traces of CH radical decay versus several DME concentrations within the N_2 Laval nozzle of 52.0 K, *pseudo*-first-order reaction rates of CH radical, k_{obs} , were obtained from single exponential fits. (B) k_{obs} versus $[\text{CH}_3\text{OCH}_3]$ at different temperatures, along with their linear fits whose slopes represent the reaction rate coefficients k_2 .

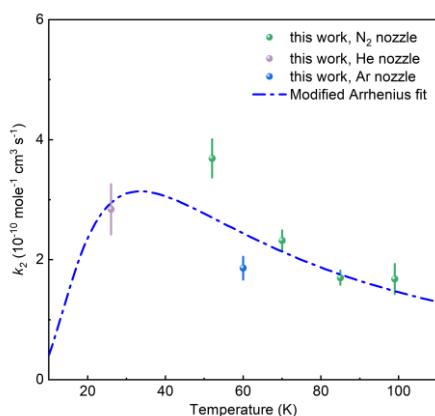
A summary of the measured rate coefficients for the $\text{CH}\cdot + \text{DME}$ reaction at different temperatures is listed in Table 1. The values range from $3.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to $1.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over 50-100 K, exhibiting a moderate negative temperature dependence. This trend is consistent with reactions involving a submerged barrier [35]. As the temperature decreases from 50 K to 25 K, the rate coefficients decline slightly from $3.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to $2.8 \times 10^{-10} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$. To describe the temperature dependence of $k_2(T)$ and extrapolate to lower temperatures, a modified Arrhenius formula (Eq. 3) was fitted to the data, as shown in Fig. 3:

$$k_2(T) = (3.72 \pm 4.47) \times 10^{-10} \times \left(\frac{T}{300}\right)^{(-1.79 \pm 1.51)} \times \exp\left[-\frac{60.0 \pm 70.0}{T}\right], 25 \text{ K} \leq T \leq 100 \text{ K}$$

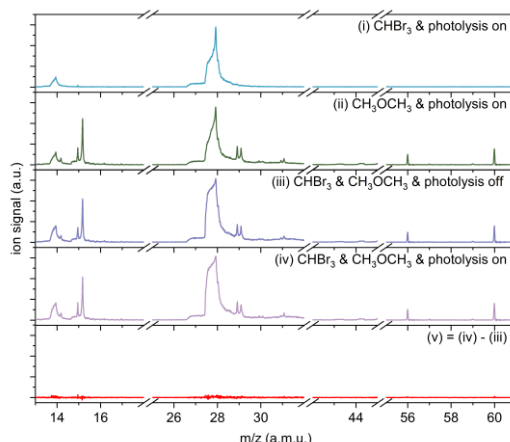
(3)

Table 1 Experimental conditions and corresponding rate coefficients for $\text{CH}^\bullet + \text{CH}_3\text{OCH}_3$ reaction.

T (K)	Bath gas	N_{total}^a (10^{16} molecule/ cm^3)	[DME] (10^{13} molecule/ cm^3)	k_2 (T) (10^{-10} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
25.7 ± 2.8	He	2.39 ± 0.40	$1.34 - 6.71$	2.84 ± 0.42
52.0 ± 2.2	N_2	1.26 ± 0.13	$0 - 7.98$	3.69 ± 0.32
60.1 ± 5.4	Ar	13.3 ± 1.8	$0 - 9.31$	1.86 ± 0.19
70.2 ± 3.4	N_2	4.29 ± 0.51	$0 - 16.7$	2.32 ± 0.17
85.1 ± 4.8	N_2	4.50 ± 0.62	$0 - 9.90$	1.70 ± 0.20
99.4 ± 6.2	N_2	6.62 ± 1.03	$0 - 14.3$	1.68 ± 0.25
<i>52.0 ± 2.2^b</i>	<i>N_2</i>	<i>1.26 ± 0.13</i>	<i>$0 - 7.68$</i>	<i>4.30 ± 0.25</i>

^a Total density of the supersonic low-temperature uniform flow, error represents the non-uniformity along the flow axis.^b Experimental condition and rate coefficient for $\text{CD}^\bullet + \text{CH}_3\text{OCH}_3$ reaction, distinguished in italics.**Fig. 3.** Comparison of second order reaction rate coefficients (solid dots), k_2 , for the $\text{CH}^\bullet + \text{CH}_3\text{OCH}_3$ reaction versus temperatures and the modified Arrhenius fit (dash dotted blue line).

Additionally, the product information is of great importance to unravel the reaction mechanism between $\text{CH}^\bullet$ and DME. Selected experiments were conducted using vacuum ultraviolet (VUV, 118.27 nm) photoionization reflectron time-of-flight mass spectrometry (Re-TOFMS) to identify reaction products at reaction time of 200 μs . To discriminate the source of all the ions, several parallel experiments of variable controlling were implemented by introducing only either of the reactants or setting the on/off of the photolysis laser (Fig. 4).

**Fig. 4.** VUV photoionization mass spectra under different conditions at kinetic time of 200 μs , $T = 52.0 \text{ K}$, $[\text{CH}_3\text{OCH}_3] = 7.98 \times 10^{13} \text{ molecule}/\text{cm}^3$. Mass spectrum of (i) only CHBr_3 with photolysis laser on, (ii) only CH_3OCH_3 with photolysis laser on, (iii) both CHBr_3 and CH_3OCH_3 present with photolysis laser off, (iv) both CHBr_3 and CH_3OCH_3 present with photolysis laser on, and (v) subtraction of (iii) from (iv).

The broad peaks at mass-to-charge ratio (m/z) of 14 and 28 (Fig. 4(i)-(iv)) originate from the bath gas N_2 , likely due to the multiphoton ionization by the VUV laser. A comparison of Fig. 4(ii), (iii) and (iv) reveals a high degree of similarity, suggesting that most ion signal peaks arise from sample impurities ($m/z = 56$ and 60) and the dissociative ionization of DME ($m/z = 15$ and 29) [36]. Since no direct reaction product was discernible in the mass spectra, potential energy surface (PES) calculations were performed to explore possible reaction pathways (Fig. 5).

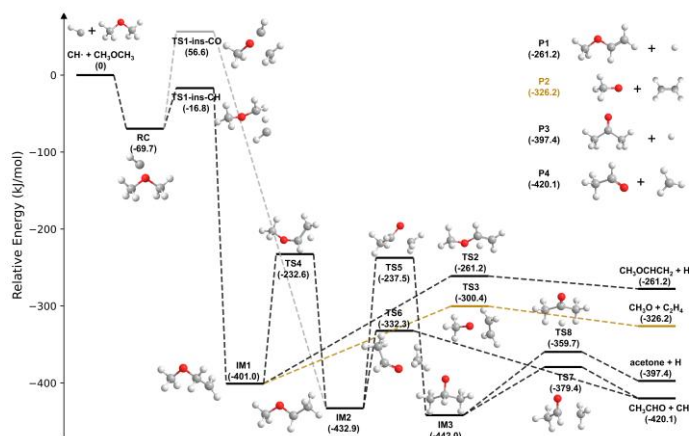


Fig. 5. Potential energy surfaces of $CH\cdot + CH_3OCH_3$ reaction obtained at the CCSD(T)/aug-cc-pVTZ//B2PLYP-D3/aug-cc-pVTZ level of theory. All energy values are in kJ/mol with the ZPE corrections relative to the reactants. The brown golden line indicates the most probable reaction route.

The interaction between the two reactants forms a complex in the entrance channel (RC, -69.7 kJ/mol) with a bond length of approximately 1.67 Å between the central O and the incoming C atom. This complex then evolves through two pathways, the C-H insertion and C-O insertion. In the C-H insertion pathway, $CH\cdot$ inserts into a C-H bond of DME, forming the intermediate $CH_3OCH_2CH_2$ (IM1, -401.0 kJ/mol), via transition state (TS1-ins-CH) with a submerged barrier (-16.8 kJ/mol). In contrast, the C-O insertion pathway proceeds through a positive barrier transition state (TS1-ins-CO, 56.6 kJ/mol), forming CH_3OCHCH_3 (IM2) via $CH\cdot$ insertion into the C-O bond of DME. The substantial barrier in the C-O insertion pathway renders this route thermally inaccessible at the studied temperatures unless quantum tunneling occurs. To investigate this possibility, the reaction rate coefficient for the deuterated methylidyne radical ($CD\cdot$) and DME was measured at 52.0 K. The obtained value of $4.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ matches that of the $CH\cdot + CH_3OCH_3$ reaction under same conditions, demonstrating a negligible kinetic isotope effect (KIE) [37,38]. This finding reveals that the title reaction proceeds exclusively through the C-H insertion mechanism to form IM1.

Four distinct reaction product channels were calculated through isomerization and decomposition pathways originating from the highly energetic intermediate IM1 (-401.0 kJ/mol relative to reactants). Product channel **P1** ($CH_3OCH=CH_2 + H$, -261.2 kJ/mol) is generated through direct H elimination via transition state TS2. Product channel **P2** ($CH_3O\cdot + C_2H_4$, -326.2 kJ/mol) is yielded via C-O bond cleavage through TS3. IM1 can also isomerize through TS4 to form IM2 (-432.9 kJ/mol), which further isomerize to IM3 (-442 kJ/mol) via TS5 (involving a side methyl transfer from the central O atom). IM3 then leads to two product channels: **P3** (acetone + H, -397.4 kJ/mol) by H loss via TS8, and **P4** ($CH_3CHO + CH_3\cdot$, -420.1 kJ/mol) by CH_3 loss via TS7. Alternatively, **P4** could also be generated directly from IM2 by losing a methyl moiety via TS6. Complete computational details, including optimized geometries and harmonic vibrational frequencies for all stationary points, are provided in Supporting information.

The calculated product pathways include two H elimination channels, **P1** and **P3**, producing $H + CH_3OCH=CH_2$ and $H + \text{acetone}$, respectively. Both products have adiabatic ionization energies (8.95 eV for $CH_3OCH=CH_2$ [39] and 9.7 eV for acetone [40]) below the photon energy of VUV ionization laser (10.48 eV), making them theoretically detectable under our experimental conditions. However, the absence of any signal at $m/z = 58$ indicates that neither $CH_3OCH=CH_2$ (58 amu) nor acetone (58 amu) is formed under the uniform supersonic low-temperature flow conditions.

The most exothermic channel **P4**, yielding $CH_3\cdot + CH_3CHO$ (-420.1 kJ/mol), involves products with ionization energies of 9.84 eV [41] (methyl) and 10.23 eV [42] (acetaldehyde), both within the present VUV detection range. However, Fig. 4(v) shows no evident mass peaks at $m/z = 15$ or 44. The observed bimodal features around $m/z = 15$ in Fig. 4(ii) and (iv) likely originate from dissociative ionization of DME, as they persist in DME-only experiments. The complete disappearance of these signals after subtracting Fig. 4(iv) from (iii) provides conclusive evidence against methyl radical and acetaldehyde formation in the title reaction. Therefore, we exclude the $CH_3\cdot$ elimination pathway (**P4**) under present experimental conditions.

The calculated product channel **P2** yields $CH_3O\cdot + C_2H_4$ (-326.2 kJ/mol). Both products have high ionization energies (10.72 eV [43] for $CH_3O\cdot$ and 10.51 eV [44] for C_2H_4), exceeding the photon energy of the VUV photoionization laser. Consequently, neither product of **P2** can be detected in our current setup. Nevertheless, the stationary point calculations indicate that product channel **P2** is the most favorable reaction pathway. Unlike **P3** and **P4** product channels, which involve multiple transition states and complex wells, **P2** products ($CH_3O\cdot + C_2H_4$) can be generated via direct cleavage of the C-O bond in intermediate IM1 ($CH_3OCH_2CH_2\cdot$). Although product channel **P1** can also form directly from IM1, it has a larger barrier and reaction enthalpy than **P2**. Given that **P1**, **P3** and **P4** were not detected experimentally in the present Re-TOFMS study and secondary reactions are negligible under current uniform flow conditions, we suggest that $CH_3O\cdot + C_2H_4$ is the main product channel for the $CH\cdot + CH_3OCH_3$ reaction under low-temperature conditions investigated here, with the measured reaction rate coefficient described as Eq. 3.

The methoxyl radical ($CH_3O\cdot$) is a reactive and transient species that plays a critical role in astrochemical environments, particularly within cold dense molecular clouds. As a pivotal intermediate in chemical networks, $CH_3O\cdot$ contributes to the formation and destruction of O-bearing COMs like formaldehyde (CH_2O) [45], methyl hydroperoxide (CH_3OOH) and methyl formate ($HCOOCH_3$) [46]. And it is regarded as a central intermediate for CO hydrogenation [47]. Observationally, $CH_3O\cdot$ has long posed a challenge for spectroscopists

detected in the ISM toward the B1-b cold core [13], four prestellar cores [49] and the L483 dense core [16]. Since these cold sources share similar environmental conditions with TMC-1, *e.g.*, a rotational temperature of 10 K and comparable levels of chemical evolution, they exhibit a common upper limit of fractional abundance of $\text{CH}_3\text{O}\cdot$, 10^{-10} relative to H_2 [50].

Astrochemical models have been developed to include extensive network of molecular species and chemical reactions to explore the chemical evolution of cold molecular clouds. However, current models underestimate the abundance of $\text{CH}_3\text{O}\cdot$ by several orders of magnitude [45,51]. In this work, we performed a homogeneous astrochemical modeling of a dark molecular cloud (with a density of $2 \times 10^4 \text{ cm}^{-3}$ and a temperature of 10 K) using the RATE22 database [45], supplemented by the reaction $\text{CH}\cdot + \text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_3\text{O}\cdot + \text{C}_2\text{H}_4$ from our study. DME is a well-documented molecule in TMC-1 with a typical fractional abundance of 2.5×10^{-10} relative to H_2 [4]. Since known gas-phase formation pathways for DME are insufficient to explain its observed abundance under cold conditions, current astrochemical models significantly underestimate the abundance of CH_3OCH_3 , thereby reducing the contribution from the $\text{CH}\cdot + \text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_3\text{O}\cdot + \text{C}_2\text{H}_4$ reaction. Several attempts have been made by other groups to replicate observed CH_3OCH_3 abundance in the model by involving surface chemistry on icy grain mantles followed by non-thermal, like chemical, UV, cosmic ray, desorption processes [19,52,53]. Consequently, our model assumed an initial DME relative abundance of 2.5×10^{-10} to account for these non-thermal desorption processes.

The model yielded intriguing insights, as illustrated in Fig. 6A. The fractional abundances of $\text{CH}\cdot$ and DME remained nearly unchanged regardless of whether our kinetic measurements were included, as the title reaction represents only a minor loss pathway compared to reactions with more abundant species (*e.g.*, O, N, and H). Although the predicted $\text{CH}_3\text{O}\cdot$ abundance at all times remains below the observed value, the predicted abundance in the early stage (10^2 - 10^5 years) increases by nearly an order of magnitude due to the inclusion of the title reaction. This highlights the significance of including of the title reaction—unless the fractional abundance of DME drops below 5×10^{-12} . This finding underscores the importance of the $\text{CH}\cdot + \text{CH}_3\text{OCH}_3$ reaction in producing $\text{CH}_3\text{O}\cdot$ when DME abundance reaches observed levels.

The UMIST Database includes several $\text{CH}_3\text{O}\cdot$ formation pathways, which were categorized into five groups by us (see Supporting information). To assess their relative contributions, we tested each category in the astrochemical model while setting all other reaction rates to zero. As shown in Fig. 6B, both $\text{CH}\cdot + \text{CH}_3\text{OCH}_3$ and $\text{He}^+ + \text{CH}_3\text{OCH}_3$ contribute significantly at early times due to the high DME abundance, with the title reaction dominating—confirming its role as a key gas-phase $\text{CH}_3\text{O}\cdot$ source. At later stages ($>10^5$ y), as DME abundance declines in the model, dissociative recombination (DR) reactions and CH_3OH involved reactions become increasingly important and eventually dominate. These results further confirms that the $\text{CH}\cdot + \text{CH}_3\text{OCH}_3$ reaction dominates the gas-phase formation to $\text{CH}_3\text{O}\cdot$ at low temperatures when CH_3OCH_3 reaches its observed abundance.

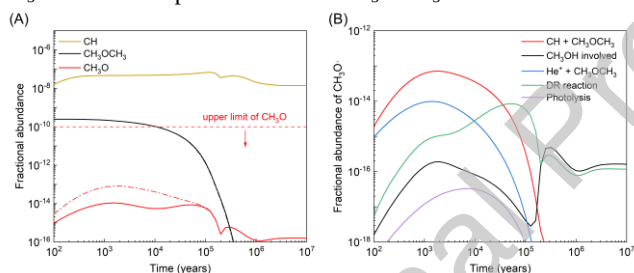


Fig. 6. (A) Abundances of key reagents and products of the title reaction relative to abundance of molecular hydrogen *versus* time in the cold cloud model of TMC-1. The solid lines show evolution of those key species without our kinetic measurements, while the dash dotted lines represent the species evolution considering the $\text{CH}\cdot + \text{CH}_3\text{OCH}_3$ kinetic results. The red dotted line at fractional abundance of 10^{-10} marks the upper relative abundance limit of $\text{CH}_3\text{O}\cdot$ in TMC-1. (B) $\text{CH}_3\text{O}\cdot$ evolution contribution of all possible reactions from the UMIST model. These reactions are sorted into five categories. CH_3OH involved: reactions between radical (*e.g.*, $\cdot\text{CN}$, O, F, Cl, $\cdot\text{OH}$) and CH_3OH . DR: dissociative recombination reactions. Photolysis: CH_3OCH_2 photolysis process. For further information, see SI.

In this work, we measured the rate coefficients of the reaction between $\text{CH}\cdot$ and DME (CH_3OCH_3) using a Laval nozzle apparatus coupled with PLP-LIF method. Additionally, mass spectroscopy of the reaction was performed under 52.0 K N_2 flow conditions with VUV photoionization to reveal product information. Although PES calculations suggest four possible reaction pathways, no direct reaction products were observed in the Re-TOFMS study. The comparable reaction rate coefficients between $\text{CH}\cdot + \text{DME}$ and $\text{CD}\cdot + \text{DME}$ indicate that the reaction proceeds *via* $\text{CH}\cdot$ insertion into the C-H bond of the methyl group, which features a submerged barrier. We ruled out three possible product channels (two H-loss pathways and one $\text{CH}_3\cdot$ loss pathway) due to their absence in the mass spectra. Instead, the $\text{CH}_3\text{O}\cdot + \text{C}_2\text{H}_4$ channel is identified as the most likely product pathway. The measured rate coefficients and reaction mechanism for the title reaction may serve as a benchmark for $\text{CH}\cdot$ reaction with ethers and other O-bearing COMs. Astrochemical modelling suggests that this reaction could be a gas-phase source of $\text{CH}_3\text{O}\cdot$, feeding into larger networks of O-bearing COMs formation. Investigating this reaction may also enhance our understanding of the chemical evolution of organic complexity in cold molecular clouds and star-forming regions, with direct implications for molecular inventories in pre-stellar cores and protoplanetary disks.

Declaration of competing interest

The authors declare no competing financial interests.

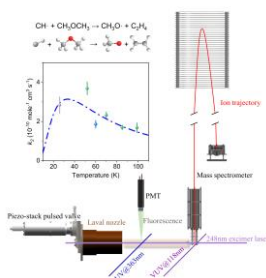
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Graphical Abstract



Gas-phase kinetics of methylidyne radical ($\text{CH}\cdot$) and dimethyl ether (DME, CH_3OCH_3) have been investigated at low interstellar temperatures using our Laval-nozzle-based apparatus, from which astrochemical relevance of this reaction as a source of the interstellar $\text{CH}_3\text{O}\cdot$ was discussed.

Declaration of Interest Statement

- ☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
- ☐ The author is an Editorial Board Member/Editor-in-Chief/Associate Editor/Guest Editor for this journal and was not involved in the editorial review or the decision to publish this article.
- ☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: