Rate constants and the H atom branching ratio of the reactions of the methylidyne CH($X^2\Pi$) radical with C₂H₂, C₂H₄, C₃H₄ (methylacetylene and allene), C₃H₆ (propene) and C₄H₈ (*trans*-butene)

Jean-Christophe Loison*ab and Astrid Bergeatab

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The reactions of the CH radical with several unsaturated hydrocarbons C_2H_2 (acetylene), C_2H_4 (ethylene), C_3H_4 (methyl-acetylene and allene), C_3H_6 (propene) and C_4H_8 (*trans*-butene) were studied at room temperature, in a low-pressure fast-flow reactor. $CH(X^2\Pi, \nu = 0)$ radicals were obtained from the reaction of CHBr₃ with potassium atoms. The overall rate constants at 300 K are $CH + C_2H_2$: $(3.6 \pm 0.6) \times 10^{-10}$, $CH + C_2H_4$: $(3.1 \pm 0.6) \times 10^{-10}$, $CH + C_3H_4$ (methyl-acetylene): $(3.4 \pm 0.6) \times 10^{-10}$, $CH + C_3H_4$ (allene): $(3.6 \pm 0.6) \times 10^{-10}$, $CH + C_3H_6$ (propene): $(4.2 \pm 0.8) \times 10^{-10}$ and $CH + C_4H_8$ (*trans*-butene): $(4.0 \pm 0.80) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ (errors are cited at the level of $\pm 1\sigma$). Absolute atomic hydrogen production was determined by vacuum ultra-violet (VUV) resonance fluorescence, H production from the CH + CH₄ reaction being used as a reference. Observed H branching ratios for these CH reactions were: C_2H_2 : 0.90 ± 0.08 , C_2H_4 : 0.94 ± 0.08 , C_3H_4 (methyl-acetylene): 0.98 ± 0.08 , C_3H_4 (allene): 0.97 ± 0.08 , C_3H_6 (propene): 0.78 ± 0.10 , C_4H_8 (*trans*-butene): 0.69 ± 0.12 (errors are cited at the level of $\pm 1\sigma$). A compilation of the available kinetic data on these reactions has been made in order to propose rate coefficients for each possible channel of the different reactions for astrochemical models.

Introduction

The methylidyne radical, CH, is extremely reactive and plays a major role in various chemical environments ranging from hydrocarbon combustion,¹ dense interstellar clouds (ISCs)² and in the atmospheres of Titan,³ Neptune⁴ and Triton.⁵ The reactions of the CH radical provide a way to synthesize long hydrocarbons and complex organic molecules in dense interstellar clouds (ISCs)² and planetary atmospheres. The kinetics of CH reactions with unsaturated hydrocarbons have been previously studied for temperatures ranging from 300 K to 650 K,⁶⁻⁹ down to 23 K¹⁰ for CH + C_2H_2 , CH + C_2H_4 and $1-C_4H_8$ and down to 77 K¹¹ for CH + C₂H₂, C₃H₄ and C₃H₆. The experimental temperature dependence of the global rate constants of the CH + unsaturated hydrocarbon reactions suggest that these reactions proceed without any barrier. Although there is still debate about the exact mechanism of the CH + unsaturated hydrocarbons reactions, the intermediate results from the insertion of the CH radical into a C-H or single C-C bond, or addition to the double or triple C-C bond, leading to a triplet radical which then quickly evolves. The absence of any pressure dependence for the rate constant shows that stabilization is not competitive with dissociation of the intermediates. As the CH radical has a high enthalpy of formation $(\Delta_{\rm f} H_{298}({\rm CH}({\rm X}^2\Pi)) = 596.40 \text{ kJ mol}^{-1}),^{12}$ there are many thermodynamically accessible channels for the

CH + unsaturated hydrocarbon reactions. Identification of the final products and determination of branching ratios are particularly important for obtaining reliable modeling of complex chemistry such as interstellar chemistry and combustion. If the global rate constant of CH + hydrocarbons is quite well studied, there are only two previous experimental H branching ratio determinations for the CH + C_2H_2 reaction^{13,14} and one for the CH + C_2H_4 reaction.¹⁴ There are also theoretical studies for the CH + $C_2H_2^{15-19}$ and CH + $C_2H_4^{20,21}$ reactions and two coupled *ab initio*/RRKM studies on the evolution of the excited allyl radical $(C_3H_5)^{22,23}$ which is supposed to be the main intermediate of the CH + C_2H_4 reaction.

We have performed kinetics experiments using a selective source of CH radicals in a low-pressure fast-flow reactor at room temperature. The overall rate constants were obtained studying the decay of the CH radical by laser induced fluorescence or by OH chemiluminescence after addition of small amount of O₂ (CH + O₂ \rightarrow OH(A² Σ) + CO), the hydrocarbon being introduced in excess; corrections for radical loss by diffusion have been validated in previous studies.^{24–27} Absolute product branching ratios of the CH + hydrocarbons reactions were estimated for the channels yielding H atoms by comparison with the CH + CH₄ \rightarrow C₂H₄ + H (100%) ratio,²⁶ the H atoms were probed by resonance fluorescence in the VUV. Comparisons with previous experimental and theoretical studies are made for the CH + C₂H₂ and CH + C₂H₄ reactions.

Experimental measurement

The experimental setup has been described in detail previously $^{24-28}$ and only a brief summary is given here. The

^a Université de Bordeaux, UMR 5255, ISM, Groupe Astrochimie, 351 cours de la Libération, F-33405 Talence Cedex, France.

E-mail: jc.loison@ism.u-bordeaux1.fr; Fax: +33 (0)5 40 00 66 45^b CNRS, UMR 5255, ISM, Groupe Astrochimie, 351 cours de la

Libération, F-33405 Talence Cedex, France

setup consists of a fast-flow reactor, *i.e.*, a 36-mm Teflon[®] inner tube with four optical ports for detection. The CH radicals are produced in an "injector" which slides in the reactor. At the end of the injector, the CH radicals are mixed with the hydrocarbon flow. Then, the distance (*d*) between the end of the injector and the observation windows is directly proportional to the reaction time under plug flow conditions. The distance can be varied over the range 0–100 mm with 0.5 mm precision, allowing kinetic studies between 0 and 3.3 ms (the flow velocity is around 30 m s⁻¹). The pressure, is measured by a capacitance manometer (Barocel 0–10 Torr), and the flow rates are adjusted by thermal mass flow controllers.

The CH radicals were produced from the CHBr₃ + 3 K \rightarrow CH + 3 KBr overall reactions which can be separated into three elementary bromine abstractions. As all of the $K + CHBr_x \rightarrow KH + CBr_x (x \ge 0)$ reactions are endoergic, this source can only produce CH radicals in their ground vibrational state which has also been checked experimentally. As a large excess of potassium is introduced in the injector compared to the CHBr3 concentration, the precursors (CHBr₃, CHBr₂, and CHBr) concentrations in the fast flow reactor are very small (as check in a previous study²⁵ by fitting the LIF time-dependent signals of CHBr and CH radicals with kinetic modelisation of the three bromine atoms stripping) and will not interfere in our study. The K atoms are not reactive with non-halogenated hydrocarbon molecules. The typical conditions in the reactor are the following: P = 2 Torr. [K] < 3.0×10^{12} molecule cm⁻³, [CHBr₃, CHBr₂, and CHBr] < 1.0×10^{10} molecule cm⁻³ and [CH] $\approx 1.0 \times 10^{12}$ molecule cm⁻³. the carrier gas being He with a stated purity of 99.995%. CHBr₃ (99%) was used without any further purification. The different hydrocarbons were used directly from the cylinder with a stated purity >99.995%.

The CH radicals were probed by laser-induced fluorescence (LIF) using a ND:YAG laser (Quantel YG 581C) pumped dye laser (around 100 μ J by pulse) and exciting the CH (A² $\Delta \leftarrow X^2\Pi$) near 431 nm or by OH (A² $\Sigma \rightarrow X^2\Pi$) chemiluminescence detection with an interference filter around 305 nm, with electronically excited OH being produced by introducing a very small concentration of O₂ for kinetics experiments (kinetic contribution of the CH + O₂ reaction was always inferior to 5% of the CH + hydrocarbons contribution).

Hydrogen atoms were detected by resonance fluorescence using the $2p^{1-2}P^{o} \rightarrow 1s^{1-2}S$ transition at 121.6 nm (L_{α}). Atom excitation was achieved with the microwave discharge lamp previously described.^{24–28} We also used the microwave discharge lamp in an absorption setup to check the absorption of H and hydrocarbons in the reactor. Typically the maximum H atom concentration attenuate the incident radiation by a few percent at the L_{α} (H atoms concentration range from 2–8 × 10¹¹ atom cm⁻³) and the light attenuation by hydrocarbons in this wavelength range is inferior to 0.1%. Thus, the conditions of the presently reported experiments ensure the linear dependence of the atomic fluorescence signal *versus* the lamp emission intensity and the H atom concentration, and also the negligible influence of hydrocarbon absorption.

Results

Overall rate constant

The pseudo-first-order decays of the CH radical fluorescence signal were measured at different concentrations of hydrocarbons introduced in large excess. To eliminate mixing effects at short reaction times, only the last stages of the decay (after 3 cm from the injector exit) have been taken to determine the pseudo-first-order rate constants. The measured rate constants were then corrected for radial and axial diffusion using Keyser's formula,²⁹ as done previously with good results.²⁶

A typical measurement of the second-order rate constant is displayed in Fig. 1, for the $CH + C_2H_2$ reaction, where axial and radial corrected pseudo-first-order rate constants are plotted versus the hydrocarbon concentration. The main source of errors in our measurements was the important radial and axial diffusion correction. Moreover, the high wall removal rate constant, due to wall deposit of potassium, associated with these diffusional processes, leads to the limit conditions of the plug-flow approximation and the errors quoted take into account these uncertainties. The secondorder rate constants of the CH reaction with the various hydrocarbons concerned by this study are summarized in Table 1 and are compared with previous measurements. The present results are in relatively good agreement with previous measurements, considering the variety of experimental setups. There are fairly substantial scatters in the measurements of the rate coefficients for the CH + C_2H_2 and CH + C_2H_4 reactions. However, no systematic deviation can be identified in the various studies, even for the lowest values of Butler *et al.*⁶ In fact, the measurements of the other reactions they have studied are in better agreement with those of others groups. We thus propose to adopt, at 298 K, the average value (fit by weighted least squares analysis) of (3.4 ± 0.4) and $(3.0 \pm 0.3) \ 10^{-10} \ cm^3 \ molecule^{-1} \ s^{-1}$ for the CH + C₂H₂ and C₂H₄ rate coefficients, respectively.

Product branching ratios

Hydrogen atom production from the CH + hydrocarbon reactions was measured relative to the H atom production



Fig. 1 Pseudo-first-order rate constant of the $CH + C_2H_2$ reaction *versus* the C_2H_2 concentration.

Reactions	$k_{298 \text{ K}}/10^{-10} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$	References
$CH + C_2H_2$	3.2 (±0.2)	Thiesemann et al. ⁸
	4.0	Canosa <i>et al.</i> ¹⁰
	4.2 (±0.4)	Berman <i>et al.</i> ⁷
	$2.2(\pm 0.4)$	Butler <i>et al.</i> ⁶
	$3.6(\pm 0.6)$	This work
$CH + C_2H_4$	2.85 (±0.02)	Thiesemann et al.9
	3.2	Canosa <i>et al.</i> ¹⁰
	$3.65 (\pm 0.3)$	Berman et al. ⁷
	$2.1(\pm 0.8)$	Butler <i>et al.</i> ⁶
	$3.1(\pm 0.6)$	This work
$CH + C_3H_4 (H_3C-C \equiv CH)$	$4.6(\pm 1.5)$	Butler <i>et al.</i> ⁶
	$3.4(\pm 0.6)$	This work
	4.03 (±0.13) (170 K)	Daugey et al. ¹¹
$CH + C_3H_4$ (H ₂ C=C=CH ₂)	3.6 (±0.6)	This work
5 . (2 2)	4.01 (±0.16) (170 K)	Daugey et al. ¹¹
$CH + C_3H_6 (H_3C-CH=CH_2)$	4.2 (±0.8)	This work
5 6 (5 2)	3.86 (±0.20) (170 K)	Daugey et al. ¹¹
$CH + C_4H_8$ (trans-Butene)	4.0 (±0.8)	This work
$CH + C_4H_8$ (1-Butene)	3.70 (±0.25)	Canosa <i>et al.</i> ¹⁰

Table 1 Overall rate constants at room temperature in 10^{-10} cm⁻³ molecule⁻¹ s⁻¹

from the CH + CH₄ reaction by resonance fluorescence in the VUV. As the H atom branching ratio is known to be equal to 1 for the CH + CH₄ reaction²⁶ in our conditions, these relative determinations of the branching ratio for the CH + hydrocarbon reactions can be converted to absolute values.

In order to measure the relative H atom production, the fluorescence signal is recorded successively for the $CH + CH_4$ and the CH + hydrocarbon reactions. The CH₄ and hydrocarbon concentrations were adjusted in order to have equivalent global first-order rate constants, the CH production being constant during a period of more than one hour. This operation was repeated several times, alternately for different CH₄ and hydrocarbon concentrations, under different pressures and different CHBr3 concentrations. In our experimental conditions we have to be aware that secondary reactions occur. (i) We checked that the molecules and radicals produced by the CH + hydrocarbon reactions do not react with the reactant hydrocarbon (the radical products are mainly H or CH₃, both of them presenting a barrier towards reaction with unsaturated hydrocarbons). (ii) There are two other sources of H atoms: one is the CH + CH \rightarrow C₂H + H reaction and the second source is the C_2H + hydrocarbon reactions. These two sources have to be taken in account as they could produce H atoms. To determine the H atom production of CH + hydrocarbon reactions, we performed simulations of H production, including the CH + CH \rightarrow C₂H + H reaction, the C_2H + hydrocarbon reaction, the mixing effect and wall reactions for each experimental condition: CH alone, $CH + CH_4$ and CH + hydrocarbon. The kinetic parameters used in the simulation are listed in Table 2. The H atoms branching ratio for the C₂H + hydrocarbons reactions are not known and are estimated in the following way. Ab initio calculations for the $C_2H + C_2H_2^{30}$ shown that H production is equal to 100% for this reaction. The $C_2H + C_2H_4$ leads to the HC₃H₂CH₂³¹ radical which should mainly evolve toward HC3HCH3 and so leading to 100% of $HC_3HCH_2 + H$ (see discussion on $CH + C_3H_4$ reactions). For the others reactions, H atom abstraction can become important³²⁻³⁵ as well as others exit channel such as CH₃

production. We used the Wu and Kern estimation for $CH + C_3H_4^{33}$ reactions and arbitrary H atom productions for the others reactions. As the C_2H + hydrocarbon reaction produces a maximum of 10% of the total H atoms present in the experiment, the uncertainties of these branching ratios are included in the total uncertainty of the H product branching ratios of the CH + hydrocarbon reactions. Typical traces of H atom concentrations, deduced from the fluorescence signals, *versus* the distance (*i.e.* the reaction time) are shown in Fig. 2 for the CH + CH₄ and CH + C₂H₂ reactions. In the experimental conditions of Fig. 2, the contribution from CH + CH \rightarrow C₂H + H in the presence of CH₄ or C₂H₂ is close to 10% and the contribution to the H atom concentration from C₂H + C₂H₂ \rightarrow C₄H + H is also close to 10%.

The two total H atom concentration traces during $CH + CH_4$ and $CH + C_2H_2$ are very similar. As the $C_2H + CH_4$ reaction gives $C_2H_2 + CH_3$ and no H atom, the $CH + C_2H_2$ reaction has a smaller H branching ratio than the $CH + CH_4$ reaction. The total uncertainty in the H atom branching ratio is estimated to be 8% in this case. As the H atom production from the CH + CH reaction is the same when CH_4 and hydrocarbons are added with equivalent global first-order rate constants, the uncertainty comes mainly from the amount of C_2H radical formed and the subsequent C_2H + hydrocarbons reactions.

We have performed simulations for all the experimental H branching ratios for the CH + hydrocarbon reactions. The results are presented in Table 3.

Discussion

Overall rate constant

The high values of the rate constants for these reactions suggest that there are no barriers on the potential-energy surfaces for these reactions. This absence of a barrier is confirmed by low temperature kinetics studies performed with the CRESU technique, down to 23 K for the CH + C_2H_2 , CH + C_2H_6 and CH + 1-butene reactions¹⁰ and down to 77 K

Table 2 Reaction mechanism used in simulations of atomic H production $(k_{298 \text{ K}} \text{ in cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$

Reactions	$k_{298 \text{ K}}{}^a$	References
$CH + CH \rightarrow C_2H + H$	$3.0 imes10^{-10}$	Dean <i>et al.</i> ³⁶
		Bergeat et al. ²⁸
$CH + C_2H \rightarrow C_3H + H$	$3.0 imes 10^{-10}$	Ь
$CH + CH_4 \rightarrow C_2H_4 + H$	$0.9 imes10^{-10}$	Blitz <i>et al.</i> ³⁷
		Fleurat-Lessard et al. ²⁶
$CH + C_2H_2 \rightarrow C_3H_2 + H$	$3.4 imes 10^{-10}$	This work
$CH + C_2H_2 \rightarrow C_3H + H_2$	$0.2 imes 10^{-10}$	This work
$CH + C_2H_4 \rightarrow C_3H_3 + H$	$3.0 imes 10^{-10}$	This work
$CH + C_2H_4 \rightarrow C_2H_2 + CH_3$	6.0×10^{-12}	This work
$CH + CH_3CCH \rightarrow C_4H_3 + H$	$3.3 imes 10^{-10}$	This work
$CH + CH_3CCH \rightarrow C_4H_2 + H_2$	7.0×10^{-12}	This work
$CH + CH_2CCH_2 \rightarrow C_4H_3 + H$	$3.5 imes 10^{-10}$	This work
$CH + CH_2CCH_2 \rightarrow C_4H_2 + H_2$	1.0×10^{-11}	This work
$CH + C_3H_6 \rightarrow C_4H_6 + H$	$3.3 imes 10^{-10}$	This work
$CH + C_3H_6 \rightarrow C_4H_4 + CH_3$	$0.9 imes 10^{-10}$	This work
$CH + C_4H_8 \rightarrow C_4H_8 + H$	$2.6 imes 10^{-10}$	This work
$CH + C_4H_8 \rightarrow C_4H_6 + CH_3$	$1.1 imes 10^{-10}$	This work
$C_2H + CH_4 \rightarrow C_2H_2 + CH_3$	3.0×10^{-12}	Opansky et al. ³⁸
$\tilde{C_2H} + \tilde{C_2H_2} \rightarrow \tilde{C_4H_2} + H$	$1.3 imes 10^{-10}$	Ceursters et al. ³⁰
$C_2H + C_2H_4 \rightarrow \text{products}$	$1.2 imes 10^{-10}$	Opansky et al. ³⁹
$C_2H + C_2H_4 \rightarrow C_4H_4 + H$	$1.2 imes 10^{-10}$	Estimation
$C_2H + CH_3CCH \rightarrow products$	$1.9 imes10^{-10}$	Hoobler et al. ³²
$C_2H + CH_3CCH \rightarrow C_2H_2 + CH_2CCH$	$1.7 imes 10^{-11}$	Wu and Kern ³³
$C_2H + CH_3CCH \rightarrow C_5H_4 + H$	$1.7 imes10^{-10}$	Hoobler et al. ^{32,33}
$C_2H + CH_2CCH_2 \rightarrow products$	$1.7 imes10^{-10}$	Hoobler et al. ³²
$C_2H + CH_2CCH_2 \rightarrow C_2H_2 + CH_2CCH$	$1.7 imes 10^{-11}$	Wu and Kern ³³
$C_2H + CH_2CCH_2 \rightarrow C_5H_4 + H$	$1.5 imes 10^{-10}$	Hoobler et al. ^{32,33}
$C_2H + C_3H_6 \rightarrow \text{products}$	$2.4 imes 10^{-10}$	Vaktin et al. ⁴⁰
$C_2H + C_3H_6 \rightarrow C_5H_6 + H$	$1.4 imes 10^{-10}$	Estimation
$C_2H + C_4H_8 \rightarrow \text{products}$	2.1×10^{-10}	Vakhtin et al. ^{41,42}
$C_2H + C_4H_8 \rightarrow C_6H_8 + H$	$0.8 imes10^{-10}$	Estimation
^{<i>a</i>} In cm ³ molecule ⁻¹ s ⁻¹ . ^{<i>b</i>} Assumed to be equal to CH +	CH.	



 $H(ms) = \frac{t(ms)}{t(ms)}$

Fig. 2 H atom concentrations, for the CH + CH₄ and CH + C_2H_2 reactions. The open squares are the experimentally measured H atom concentrations during the CH + CH₄ reaction and the continuous line is the simulation, the filled circles are the total experimental measured H atom concentrations during the CH + C_2H_2 reaction and the dashed line is the simulation, the filled stars are the H atom concentrations from the CH + CH reaction in the absence of CH₄ or C_2H_2 and the dashed-point line is the simulation.

 Table 3 Branching ratio of atomic hydrogen production

Reactions	H atom yields	References
$\overline{CH + C_2H_2}$	0.90 ± 0.08	This work
	$0.85 + {}^9_{-15}$	Boullart et al.13
	1.05 ± 0.09	McKee et al. ¹⁴
	0.98 (RRKM)	Nguyen et al. ¹⁹
$CH + C_2H_4$	0.94 ± 0.08	This work
	1.09 ± 0.14	McKee et al. ¹⁴
	0.98 ± 0.01 (RRKM)	Davis et al. ^{22,23}
$CH + C_3H_4$ (methylacetylene)	0.98 ± 0.08	This work
$CH + C_3H_4$ (allene)	0.97 ± 0.08	This work
$CH + C_3H_6$	0.78 ± 0.10	This work
$CH + C_4H_8$ (<i>trans</i> -butene)	0.69 ± 0.12	This work

for CH + methylacetylene, CH + allene and CH + propene.¹¹ Ab initio calculations on the CH + C_2H_2 ,^{15–19} CH + $C_2H_4^{20,21}$ and CH + $C_2H_6^{27}$ reactions show that the first step without a potential energy barrier is (i) the insertion of the CH radical into a C–H bond or eventually a single C–C bond, or (ii) the addition to the double or triple C–C bond, resulting in a chemically-activated radical. As for all of the reactions studied here, there are several open exothermic exit channels, thus stabilization of any adduct cannot compete with dissociation and the transient radical rapidly decomposes. Therefore the rate-limiting process is the CH insertion and/or addition. The same argument can be applied to the CH radical reacting with larger alkenes or alkynes. The similarity in the overall rate constants for the reactions studied here, where the overall rate constants at room temperature are equal to $3-4 \times 10^{-10}$ cm⁻³ molecule⁻¹ s⁻¹, could be qualitatively explained by the dominance of the dispersion interaction, as well as the quite large contribution from the dipole-induced dipole term, as shown by Georgievskii and Klippenstein.⁴³

Products

CH + **C**₂**H**₂. Detailed *ab initio* calculations from Vereecken *et al.*¹⁶ and Nguyen *et al.*¹⁹ indicate that the first step of this reaction is the CH insertion into one C–H bond, leading to propargyl, or the CH addition to the triple bond, leading to cyclic C₃H₂. As there are several open exothermic exit channels, stabilization of any adduct cannot compete with dissociation.^{17,19} A simplified representation of the minimum energy paths (MEP) from their calculations is presented in Fig. 3.

Our experimental H production for this reaction has been determined to be equal to $90 \pm 8\%$. There are two previous experimental measurements: one from Boullart et al.13 at 600 K equal to 85^{+9}_{-15} % for the C₃H₂ + H channel and $15^{+15}_{-9}\%$ for the C₃H + H₂ channel, and one another from McKee *et al.*¹⁴ equal to $105 \pm 9\%$ for the C₃H₂ + H channel. There is also one study of the unimolecular dissociation of the propargyl radical by McCunn et al.44 with identification of H and H₂ products, without a branching ratio determination but with dissociation onset for the various channels. The study of the photodissociation of propargyl radicals at 248 nm⁴⁵ (leading to a propargyl radical with a similar energy to that obtained from the CH + $C_2H_2 \rightarrow C_3H_3$ reaction) gives 97.6% for the C_3H_2 + H (HCCCH + H) channel and 2.4% for the C₃H + H₂ channel. Combined *ab initio* and RRKM calculations predict the yield of H atoms to be 97% according to Vereecken et al.¹⁷ and 98% according to Nguyen et al.;¹⁹ in good agreement with the results of McKee et al.14 and Goncher et al.45 and within the error bars of the data of Boullart et al.¹³ and our result. Despite the greater exothermicity of the $C_3H + H_2$ channel, the low H_2 yield comes from the tight transition state for H₂ elimination. Ab initio calculations on such transition state energies have a precision of 4 to 10 kJ mol^{-1} , and as the energy location of this transition state



H H+

<u>_____</u> H₂ + C•C≡C-H is only 60 kJ mol⁻¹ below the entrance channel, a change of -4 kJ mol⁻¹ will lead to a higher H₂ production in better agreement with the two last experimental results. Furthermore, the dissociation onsets for propargyl determined by McCunn *et al.*⁴⁴ are significantly lower than the *ab initio* predictions, indicating that the *ab initio* predictions could be too high, so the RRKM predictions could underestimate the H₂ channel. Considering all the experimental data and theoretical calculations, there is no doubt that the C₃H₂ + H channel is the major one, the overlap of the experimental data leading to the value of 95%. Considering the various experimental data and RRKM calculations, we propose the following branching ratios:

 $CH + C_2H_4$. There are some theoretical calculations on the initial step of the CH + C_2H_4 reaction, ^{9,20,21} and detailed theoretical calculations on the evolution of the subsequent C_3H_5 isomers,^{22,23} evolution related to the unimolecular dissociation of the allyl radical. The most recent and reliable calculations^{9,21} have predicted that the insertion of CH in one C-H bond leading to allyl radical, and the addition of CH to the double C=C bond, leading to cyclo-propyl, do not possess any potential energy barrier in the entrance valley. Detailed quantum chemical calculations at various levels by Thiesemann et al.9 strongly suggest that the initial step of the reaction is dominated by the addition. However, because of the much lower energy of the allyl radical compared to the cyclo-propyl radical, associated to high isomerization rates, this allyl radical will be the dominant isomer and the relative product yields will not be sensitive to the initial branching. A simplified representation of the calculated MEP is presented in Fig. 4.

Our experimental H production for this reaction has been determined to be equal to $94 \pm 8\%$, in relatively good agreement (within error bars) with the previous experimental measurement from McKee *et al.*¹⁴ of 109 \pm 14%. There are also several photodissociation studies of the allyl radical at 248 nm (leading to an excited allyl radical with a similar



Fig. 4 Simplified representation of the lowest MEP of the CH + C_2H_4 reaction (energies in kJ mol⁻¹ from Davis *et al.*²² and Stranges *et al.*²³).

H-C-C≡C-H

Relative Energy (kJ mol-1)

 $CH + C_2H$ 0.00

-100

-200

-300

400

energy to the CH + $C_2H_4 \rightarrow C_3H_5$ reaction): two of them^{46,47} were only able to detect H (or D) atom (associated to allene production and not to cyclo-propene), and two other studies in 1998^{48} and 2008^{23} detect H as the main channel (84 and 95%) respectively) but also 16% and 5% respectively, for the $CH_3 + C_2H_2$ channel. Furthermore, two RRKM calculations studies^{22,23} on the excited allyl dissociation branching ratio give similar conclusions. They predict 98% of H atom production (mainly allene + H) and 2% of CH₃ + C₂H₂. Among those calculations, Davis et al.²² have estimated RRKM error limits by varying the transition state energy between \pm 4 kJ mol⁻¹, and they get a variation of \pm 1% for the H atom production, this small effect being due to the large amount of energy above the transition state (typically $\sim 220 \text{ kJ mol}^{-1}$). Considering the various experimental data and the reliability of the RRKM calculations, there is no doubt that the $H_2C = C = CH_2 + H$ atom channel is the major one, with a small contribution from the $CH_3 + C_2H_2$ channel. We propose the following branching ratio:

> CH + C₂H₄ → H₂C==CH₂ + H 98 ± 2% → CH₃ + C₂H₂ 2 ± 1%

CH + C_3H_4 (methylacetylene). Our measurement clearly shows that H atom production is the main exit channel (0.98 ± 0.08) . There is no theoretical work on this reaction. Based on our knowledge of the CH reactivity and the theoretical calculations on the C₄H₅ system,^{31,49-54} we propose a mechanism for this reaction and a schematic representation of our proposed MEP is presented in Fig. 5. From experimental and theoretical works,^{9,16,21,26,55} we know that the CH radical can insert into a sigma C-H bond and eventually into a sigma C-C bond, or add to double and triple C-C bonds. So the first step of this reaction can be either CH insertion into one C-H bond leading to $CH_2-CH_2-C\equiv CH$ or to $CH_3-C\equiv C-CH_2$, insertion into the sigma C–C bond leading to CH_3 –•CH–C \equiv CH, or addition to the triple bond, leading to cyclo-C₄H₅ (methyl cvclo-propenvl). However this addition leads to a much less stable isomer: if methyl cyclo-propenyl is formed, it is likely to be

Fig. 5 Simplified representation of the lowest MEP of the CH + methylacetylene reaction (energies in kJ mol⁻¹ from Parker and Cooksy³¹).

converted to CH₃-•CH–C≡CH with a 1,2-H migration by comparison with the C–C₃H₃ \rightarrow H₂C–C≡CH case. There are several other stable C₄H₅ isomers, mainly *i*-C₄H₅ (H₂C•–CH=CCH₂) and *n*-C₄H₅ (H•C=CH–CH=CH₂), with the possibility of interconversion through isomerization by 1,2 H transfer⁵¹ and with another open exit channel (C₂H₃ + C₂H₂: –248 kJ mol⁻¹ relative to the reactants energy). However, isomerization between the *i*-C₄H₅ or *n*-C₄H₅ isomers and the CH₃–•CH–C≡CH or CH₃–C≡C–•CH₂ isomers seems to be impossible:⁵¹ it has already dissociated before isomerization can occur. So the reaction can lead to

CH + C₃H₄ → •CH₂-CH₂-C≡CH
$$\Delta_{\rm r}H$$
 = -380 kJ mol⁻¹
→ CH₃-C≡C-•CH₂ $\Delta_{\rm r}H$ = -486 kJ mol⁻¹
→ CH₃-•CH-C≡CH $\Delta_{\rm r}H$ = -474 kJ mol⁻¹

The $^{\circ}CH_{2}-CH_{2}-C\equiv CH$ and $CH_{3}-^{\circ}CH-C\equiv CH$ can directly evolve to an H atom loss, which leads to $H_2C = HC - C \equiv CH + H$ $(\Delta_r H = -280 \text{ kJ mol}^{-1})$ without or with a very small barrier, or to H₂ elimination, which leads to •CH=CH-C=CH + H₂ ($\Delta_r H = -279$ kJ mol⁻¹) and $H_2C = C - C = CH + H_2 (\Delta_r H = -239 \text{ kJ mol}^{-1})$. The other intermediate, CH3-C=C-•CH2, can only convert to $CH_2 = C = CH_2 + H (\Delta_r H = -249 \text{ kJ mol}^{-1}/CH + C_3H_4)$ as 1,3 H transfer leading to CH₃-•CH-C=CH seems impossible.⁵¹ The H₂ loss, either 1,1-H₂ loss where the hydrogen atoms come from the same carbon atom or 1,2-H₂ loss where the hydrogen atoms come from two neighboring carbon atoms, always have a substantial activation barrier versus the exit channel, for example 40 kJ mol⁻¹ calculated for $H_2 + C^{\bullet}-C \equiv CH$ and 200 kJ mol⁻¹ for $H_2 + HC^{\bullet}=CH_2$. H atom loss from the radical does not possess any barrier in the exit channel. In the case of CH + C_2H_2 ,^{17,19} the RRKM calculations show that the H_2 formation could play a role only if the H₂ channel is much lower than the other channels, which is not the case here. As for the CH + C₂H₂ reaction, the H₂ branching ratio will only play a minor role, and our observation (2%) may be even too high as H elimination leads to the very stable H₂C=CH-C=CH molecule. Considering our experimental data and the exothermicity of the reaction, we can consider that the H atom production is equal to 100%.

 $CH + C_3H_4$ (allene). As with the other reactions, our measurement of 0.97 ± 0.08 clearly shows that H atom production is the main exit channel. There is no theoretical work on this system although it is a different part of the potential energy surface of the CH + CH₃-CCH reaction. A simplified representation of the MEP, taken from Miller et al.,⁵¹ for this reaction is presented in Fig. 6. There are only two different first steps for this reaction: CH insertion into one C-H bond leading to H_2C^{\bullet} -CH=CCH₂ (*i*-C₄H₅) or addition to one of the double bonds of the allene leading to a quite unstable cyclo-C₄H₅, in fact a less stable cyclic isomer than for $CH + C_2H_2$, $CH + C_2H_4$ and CH + methylacetylene. If this addition occurs, this cyclic isomer is likely to be rapidly converted to $H_2C^{\bullet}-CH = C = CH_2$ (*i*-C₄H₅). Thus we have only to consider the i-C₄H₅ adduct formation. The i-C₄H₅ evolution has been studied in detail by Miller et al.⁵¹ The





Fig. 6 Simplified representation of the lowest MEP of the CH + allene reaction (energies in kJ mol⁻¹ from Miller *et al.*⁵¹).

H₂C[•]-CH=C=CH₂ adduct mainly evolves through C-H bond dissociation to $H_2C = C = CH_2 + H (\Delta_r H)$ -258 kJ mol⁻¹/CH + allene) with a very minor part to $n-C_4H_5$ (H[•]C=CH-CH=CH₂). This in turn yields mainly $H_2C = C = C = CH_2 + H$ and a very minor production of $C_2H_3 + C_2H_2$. Considering the relative stability of *i*- C_4H_5 and $n-C_4H_5$ isomers associated to the tight transition state for the isomerization, the $C_2H_3 + C_2H_2$ exit channel can only be a very minor one. As in the case of the $CH + C_2H_2$ and the $CH + C_2H_4$ reactions, the stability gain for the H₂ elimination channel is too low (HC \equiv C-•C=CH₂ + H₂ $\Delta_r H =$ $-278 \text{ kJ mol}^{-1}/\text{CH}$ + allene) to overcome the tightness of the transition state, and the H₂ elimination exit channel can only be a very minor one. These conclusions are in good agreement with our experimental results, and we can consider thet CH + allene leads only to H formation, likely associated with the $H_2C = C = C = CH_2$ formation.

 $CH + C_3H_6$ (propene). Our measurement clearly shows that H atom production is an important channel (78 \pm 10%) but much less abundant than for the previous reactions in this

Relative Energy (kJ mol⁻¹) CH + H₃C-CH=CH₂ 0.0 -100 1,2-butadiene + H -200 -239 H2 + n-C4H allene + CH, -300 1,3-butadiene + H CH, HCCH 400 CH2-CH2-CH=CH2 CH₃CH-CH=CH, ÇH, CH. H,C

Fig. 7 Simplified representation of the lowest MEP of the $CH + C_3H_6$ reaction (energies in kJ mol⁻¹ from Miller *et al.*⁵⁶).

study. There is no theoretical work for this reaction but there is a detailed theoretical study of C_4H_7 isomers and their isomerizations or dissociation transition states.⁵⁶ A schematic representation of their theoretical calculations relevant for the CH + propene reaction is presented in Fig. 7. The first step of this reaction can be either (i) CH insertion into one C–H bond leading to $^{\circ}CH_2$ –CH₂–CH=CH₂ or to the most stable isomers CH₃–C($^{\circ}CH_2$)=CH₂ and CH₃–CH=CH- $^{\circ}CH_2$, (ii) CH insertion into the sigma C–C bond leading to CH₃– $^{\circ}CH$ –CH=CH₂ \leftrightarrow CH₃–CH=CH= $^{\circ}CH_2$, or (iii) CH addition to the double bond, leading to *cyclo*-C₄H₇ (2-methyl *cyclo*-propyl). This addition leads to a much less stable isomer which will convert to CH₃– $^{\circ}CH$ –CH=CH₂ \leftrightarrow CH₃–CH=CH– $^{\circ}CH_2$ and not to CH₃–C($^{\circ}CH_2$)=CH₂ as isomerization happens through ring opening without H transfer.⁵⁷ So the reaction can lead to:

CH + C₃H₆ → •CH₂-CH₂-CH=CH₂
$$\Delta_{\rm r}H$$
 = -395 kJ mol⁻¹
→ CH₃-C(•CH₂)=CH₂ $\Delta_{\rm r}H$ = -461 kJ mol⁻¹
→ CH₃-•CH-CH=CH₂ $\Delta_{\rm r}H$ = -463 kJ mol⁻¹

Among these three isomers, two of them will lead mainly to $H+H_2C=CH-CH=CH_2$ formation and the $CH_3-C(^{\bullet}CH_2)=CH_2$ isomer only to $CH_3 + H_2C = C = CH_2$ formation (we neglect H_2 formation in this case). As the isomerization between $CH_3-CH-CH=CH_2$ (or $^{\circ}CH_2$ -CH₂-CH=CH₂) and $CH_3-C(^{\bullet}CH_2)=CH_2$ isomers needs a rearrangement of the C skeleton through a tight cyclic structure of three carbon atoms,⁵⁶ it is non-competitive with C-H or C-CH3 bond dissociation which proceeds through a small barrier.⁵⁶ So for this reaction, the relative product branching ratios are very sensitive to the initial CH attack. Our experimental H production for this reaction is measured to be equal to $78 \pm 8\%$ and clearly shows that the CH_3 -C($^{\bullet}CH_2$)=CH₂ isomer is formed in the CH attack as the two other isomers which cannot isomerize to $CH_3-C(^{\bullet}CH_2)=CH_2$ lead unambiguously to H atom production.

 $CH + C_4H_8$ (*trans*-butene). This case is close to the CH + propene reaction, where H atom production is still an

important channel (69 \pm 12%) but far from being the only one. There is no theoretical work for this reaction to the best of our knowledge. The first step of this reaction can be either (i) CH insertion into one C–H bond leading to •CH₂–CH₂–CH=CH–CH₃ or to the most stable CH₃–C(•CH₂)=CH–CH₃, (ii) CH insertion into the sigma C–C bond leading to CH₃–•CH–CH=CH–CH₃, or (iii) CH addition to the double bond, leading to *cyclo*-C₅H₉ (dimethyl-1,2-*cyclo*-propyl). As for CH + C₂H₄, this addition leads to a much less stable isomer and is likely to be converted to CH₃–•CH–CH=CH–CH₃ (as isomerization happens through ring opening without H transfer⁵⁷). So the reaction leads to:

$$CH + C_4H_8 \rightarrow {}^{\bullet}CH_2 - CH_2 - CH = CH - CH_3$$
$$\Delta_r H = -457 \text{ kJ mol}^{-1}$$
$$\rightarrow CH_3 - C({}^{\bullet}CH_2) = CH - CH_3$$
$$\Delta_r H = -535 \text{ kJ mol}^{-1}$$
$$\rightarrow CH_3 - {}^{\bullet}CH - CH = CH - CH_3$$
$$\Delta_r H = -540 \text{ kJ mol}^{-1}$$

Among these three isomers two of them will lead only to $H + H_2C = CH - CH = CH - CH_3 (-322 \text{ kJ mol}^{-1}/CH + trans$ butene) and the last one, CH₃-C(•CH₂)=CH-CH₃ will only produce $CH_3 + H_2C = C = CH - CH_3 (-304 \text{ kJ mol}^{-1}/CH +$ trans-butene) (H₂ formation can be neglected in this case). However 1,4-H and 1,5-H migrations should be quick in this case, even if they involve one double C-C bond. This should allow the isomerization to CH3-CH2-CH2CH2 and leads to the most stable CH₃ + H₂C=CH-CH=CH₂ $(-360 \text{ kJ mol}^{-1}/\text{CH} + trans-\text{butene})$ exit channel. The relative product yields are thus eventually sensitive to the initial branching and coupled ab initio/RRKM calculations are needed to estimate the influence of the isomerization. Our experimental H production for this reaction is measured equal to $69 \pm 7\%$ and clearly shows that other channels are open, likely mainly CH₃ formation.

Astrochemical importance

As CH, C₂H₂, C₂H₄, allene, methylacetylene and very recently propene⁵⁸ have been detected in cold interstellar clouds, it is necessary to provide detailled rate constant at 298 K and formulae expressing how these detailled rate coefficients vary with temperature for astrochemical models. For the branching ratio at 298 K we propose speculative values ("educated guess") based on our H atoms production and theoritical data from litterature presented in the discussion on the products. For the reactions of CH with C₂H₂ and C₂H₄ we used the RRKM estimations.^{17,19,22,23} For the CH + methylacetylene reaction, we neglect CH insertion into a CH bond of the methyl group, as it leads to a less stable isomer, and CH insertion into the sigma C-C bond, because of the hindrance. That means that we consider only $H_2C = C = C = CH_2 + H$ formation and not $H_2C = CH - C \equiv CH + H$. Moreover, contrary to the CH + C_2H_2 case, the presence of a low energy exit channel, associated with a quick isomerization of the first methyl cyclo-propenyl adduct, should avoid the methyl-cyclopropyl formation. So we consider only $H_2C = C = CH_2 + H$

production. For the CH + allene reaction there is less ambiguity: we consider also only $H_2C=C=C=CH_2 + H$ formation. For the CH + propene reaction, considering our experimental data and the fact that there are only two available exit channels, we propose the following branching ratio: $78 \pm 10\%$ for $H_2C=CH-CH=CH_2 + H$ and $22 \pm 10\%$ for $H_2C=C=C=CH_2 + CH_3$. The three last branching ratios should be used with care as they are highly speculative.

For the temperature dependence we use the modified Arrhenius form $k = A (T/300)^{\beta} \exp(-\gamma/T)$. For the reaction of CH with unsaturated hydrocarbons, the kinetic behavior is similar to that observed for the reactions of CH with C_2H_2 and C_2H_4 , with high values for the rate constants and non pronounced maxima near 50-100 K. The origin of these maxima is still unknown, but with the exception of the $CH + C_2H_4$ reaction, the variation of the rate constant between 23 and 600 K is very small and within the experimental errors. We propose the use of a constant value for all of these reactions with the exception of the $CH + C_2H_4$ reaction for which we use a temperature-dependent rate coeffi*cient* expression fitted to the experimental values (A = $3.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \beta = -0.33 \text{ and } \gamma = 14 \text{ K}$ as shown in Fig. 8. For this fit we add extra points at 10 and 15 K to force a value of 3.0×10^{-10} cm³ molecule⁻¹ s⁻¹ at 10 K to get a reasonable value in the 10-20 K range. It can be seen that even for the CH + C_2H_4 reaction, the constant value of $k = 3.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in the 23–800 K range is very close (within 50%) to the 3.5 \times 10⁻¹⁰ $(T/300 \text{ K})^{-0.33} \exp(-14 \text{ K}/T)$ expression.

The extrapolation of the H branching ratio measurements at 300 K to low temperature is somewhat hazardous. However, we can use the *ab initio* calculations on the $CH + C_2H_2^{16}$ and $CH + C_2H_4^{9}$ systems. When isomerization between the various intermediates is quick, the lowest intermediate radical



Fig. 8 Temperature dependence of the rate coefficient for the CH + C₂H₄ reaction. Open circles are the measurements from Canosa *et al.*,¹⁰ filled circles are from Thiesemann *et al.*,⁹ open squares are from Berman *et al.*⁷ and the present measurements as well as the ones of Butler *et al.* at 296 K⁶ are shown as filled stars. The continuous line is the fit with the expression $k = 3.5 \times 10^{-10} (T/300)^{-0.33} \exp(-14/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and the dashed line is the average value $k = 3.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

will be the dominant isomer, and the relative product yields are not sensitive to the initial branching and so to the temperature. Furthermore, as the exit barrier or exit channel is well below the energy of the reactants and as RRKM calculations give reliable results indicating good energy distribution in the adducts, the energy variation of the reactants in the 300-10 K range is negligible versus the intermediate energy formation. The only critical case is when the cyclic radical from CH addition to double or triple CC bonds converts to an isomer with a different carbon skeleton than that from CH insertion. In this case, as isomerization involving carbon skeleton reorganization could not be competitive with C-H or C-C bond dissociation, the relative product yields can be sensitive to the initial branching between addition and insertion if these processes have not the same temperature dependence as suggested by Thiesemann et al. for the CH + C_2H_4 reaction,⁹ where insertion could be a temperature-dependent process. However, this is only the case for CH + methylacetylene where the main exit channel is $H + C_4H_4$ with formation of the two isomers (CH₂=CH-C=CH and H₂C=C=C=CH₂) with unknown branching ratio and for CH + propene where addition leads only to H₂C=CH-CH=CH₂ + H and insertion leads to $H_2C = CH - CH = CH_2 + H$ and $H_2C = C = CH_2 + CH_3$. However, for the CH + methylacetylene reaction, we neglect CH insertion into a CH bond of the methyl group and CH insertion into the sigma C-C bond. For CH + propene we increased the uncertainties to take in account the eventual branching ratio evolution with the temperature.

In the 15–300 K range and in units of cm³ molecule⁻¹ s⁻¹ we propose an "educated guess" for the rate constants of the CH + C₂H₂, C₂H₄, C₃H₄ (methylacetylene and allene) and C₃H₆ (propene), using the various values for the rate constants (see Table 1) and neglecting the small branching ratios when their values are within the uncertainties.

CH + C₂H₂ → HCCCH + H (2.9 ± 0.4) × 10⁻¹⁰
→
$$c$$
-C₃H₂ + H (0.3 ± 0.2) × 10⁻¹⁰
→ HCCC + H₂ (0.2 ± 0.1) × 10⁻¹⁰

CH + H₂C=CCCH₂
$$\rightarrow$$
 H₂C=CCCH₂ + H
(4.0 ± 1.0) × 10⁻¹⁰

CH + H₃C-CH=CH₂
$$\rightarrow$$
 H₂C=CH-CH=CH₂ + H
(3.1 ± 1.8) × 10⁻¹⁰

Ab initio and RRKM calculations on these systems, particularly for the evolution of the *cyclic* radical formed after

addition of the CH radical to the double or triple bond will be required to verify our proposed branching ratios. However, as astrochemical, combustion and planetary atmospheric models use rate constants and branching ratios, we think it is important to propose branching ratios associated with a critical discussion. For this purpose, we are currently engaged in the creation of a new database, KIDA: kinetic database for astrochemistry (http://kida.obs.u-bordeaux1.fr/), which is an international project to create an interactive database for reaction rate coefficient useful in the chemical modeling of the interstellar chemistry and in planetary atmospheres with author-submitted discussion on the quality of the data.

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