

Reactions of the methylidine radical with CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , and but-1-ene studied between 23 and 295 K with a CRESU apparatus

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Received 15 July 1996 / Accepted 19 September 1996

Abstract. The temperature dependences of the reactions of the methylidine radical (CH) with several hydrocarbons were studied in the temperature range 23–295 K using the Rennes CRESU apparatus coupled with the pulsed laser photolysis (PLP), laser induced fluorescence (LIF) technique. All the reactions remain very fast at low temperature. For the reactions of CH with olefins, a maximum rate is obtained at about 70 K and then the rate coefficients slightly decrease at lower temperatures. A similar effect is observed in the data for $\text{CH}+\text{CH}_4$ and $\text{CH}+\text{C}_2\text{H}_6$ with a maximum rate being obtained at about 40 K. The results are compared with previous studies where available, and the nature of the possible products is also discussed, although this study does not enable their detection. Consequences of these new results for the chemistry of planetary atmospheres and interstellar clouds are stressed.

Key words: molecular data – molecular processes – methods: laboratory – ISM: molecules – planets: atmospheres – rate constant

1. Introduction

One of the most fascinating challenges in contemporary astrophysics is the understanding of the origin and evolution of the solar system, especially of planetary atmospheres, beginning with the collapse of an interstellar cloud and the formation of a presolar nebula (Lewis 1989). Clearly it would be of great significance to track the chemical history of planetary atmospheres from this early stage, but the relationships between pre-planetary materials and present planetary atmospheres are still poorly understood, even if, in the last three decades, with the considerable development of spatial probes and of infrared and radio observations, much knowledge has been gathered on their respective chemical compositions.

Although evidence for the presence of extraterrestrial complex organic molecules was found a long time ago in some meteorites (Sagan et al. 1992), it is only with the increasing body of spectroscopic and other data that the presence of a rich and complex organic chemistry throughout large parts of the Galaxy has been widely recognized. Cold and ultracold media, partly or totally shielded from harsh radiation fields, provide the most favorable environment for the appearance of this chemistry. Such conditions are found in particular in dense and diffuse interstellar clouds, in circumstellar envelopes and in the planetary atmospheres of the outer solar system, including some large moons, notably Titan and Triton. Hydrocarbons are pervasive in these systems, methane being the most abundant. Therefore, in the atmospheres of the outer planets and of their satellites, the hydrocarbon photochemistry is initiated by methane photolysis, mainly by the Lyman- α solar flux. It follows that the significance of the methylidine (CH) radical in these atmospheres is directly linked to the quantum yield for its formation in the photodissociation of methane at 121.6 nm, a quantity which is not yet firmly established. The measurements of Rebbert & Ausloos (1972) indicated a rather small value (close to 0.08). However Mordaunt et al. (1993) have shown recently that a much larger value of about 0.5 is likely. A low value would imply a barrier to the formation of $\text{CH}+\text{H}_2$ in the unimolecular decay of the superexcited CH_3^* fragments which are formed in photolysis of CH_4 , which is unlikely on the bases of both ab-initio calculations (Aoyagi et al. 1990) and kinetic results for the reactions and relaxation of $\text{CH}(v=0)$ and $\text{CH}(v=1)$ in collisions with H_2 and D_2 at ultralow temperatures (Brownsword et al. 1996b). It should be noted that a large quantum yield for production of CH in the photolysis of CH_4 had earlier been deduced from the experimental work of Braun et al. (1966). It follows that the methylidine radical could have a central place in the chemistry of several planetary atmospheres.

It might also be noted that CH was one of the first molecules detected in the interstellar medium (Dunham & Adams 1937;

Swings & Rosenfeld 1937), in diffuse clouds where it plays a vital role in the gas phase chemistry (Smith 1992; Lequeux & Roueff 1991; Dalgarno & Fox 1994). In dense clouds, although certainly of much less importance than the corresponding reactions with neutral and ionized atomic carbon, reactions of hydrocarbons with the methylidine radical can lead to the accretion of carbon to produce a larger carbon skeleton, opening the way to the formation of large organic molecules (Winniewisser & Herbst 1993).

The database on the kinetics of neutral-neutral reactions is quite sparse at low temperatures. However, it has been improved recently, especially at ultralow temperatures where virtually no data were previously available, with the development of a CRESU facility at the University of Rennes I devoted to such measurements (CRESU is a French acronym for “Kinetics of Reactions in Uniform Supersonic Flows”). Several reactions of the CN, CH and OH radicals with various molecules have already been studied (Sims et al. 1993; Sims et al. 1994a; Bocherel et al. 1996; Sims et al. 1994b; Sims et al. 1994c; Sharkey et al. 1994; Sims & Smith 1995). In this paper we briefly present the experimental method and then outline the results obtained for the temperature dependence of the rate coefficients for reactions of the methylidine radical with various hydrocarbons (CH_4 , C_2H_2 , C_2H_4 , C_2H_6 and but-1-ene C_4H_8). All these reactions exhibit a maximum of the rate coefficient value around 40–70 K although the 23 K value remains large, close to gas kinetic, an observation which appears to be in agreement with current theories based on adiabatic capture (Clary 1990, 1994). We think that these results are relevant to the astrochemical problems outlined above. The knowledge of the nature of the products would also be of vital importance but will be only discussed below, since our experiment does not yet allow reaction products to be determined.

2. Experimental

The results presented in this paper were obtained by using the CRESU apparatus that is available at the University of Rennes I. The fundamentals of the technique have been widely reported in the literature (see for example: Sims et al. 1994a) so a concise description will be given here.

Low temperatures were achieved in the CRESU apparatus via the isentropic expansion of a buffer gas through a suitably designed Laval nozzle. The resulting supersonic flow was found to be axially and radially uniform in temperature, density and velocity. Due to the relatively high density of the supersonic flow ($10^{16} - 10^{17} \text{ cm}^{-3}$), thermal equilibrium is maintained all along the flow (i.e. for 5–50 cm depending on the particular nozzle which was in use). Several nozzles were employed in the present work, each providing a particular temperature and density for the selected buffer gas.

The Laval nozzle was mounted on a reservoir into which the buffer gas as well as reagent gases were injected. The CH radical was produced by multiphoton pulsed laser photolysis of bromoform CHBr_3 (Aldrich, 99+ % or 96 %) which was placed in a glass vessel outside the CRESU chamber. The CHBr_3 vapour

was entrained into the buffer gas flow by bubbling a controlled flow of He through liquid CHBr_3 . The resultant mixture was passed through a stainless steel tube whose walls were temperature controlled and then this small precursor flow was introduced into the reservoir by means of a PTFE line.

The UV photolysis pulse was provided by either a Questek 2740 Excimer laser with a typical pulse energy of 200 mJ at $\lambda = 248 \text{ nm}$ or a Nd:Yag laser (GCR 190, Spectra Physics) with a pulse energy of 75 mJ at $\lambda = 266 \text{ nm}$. CH radicals were detected by off-resonance LIF, (Butler et al. 1981) exciting the (0,0) band of the $\text{CH}(A^2\Delta - X^2\Pi)$ system at $\sim 430 \text{ nm}$, and detecting fluorescence from the (0,1) band at $\sim 490 \text{ nm}$. Kinetic data were gathered using the strongest available rotational line, usually the $R_{22\text{ee}}(1)$ line at 430.03 nm (Moore & Broida 1969). Probe laser radiation was provided by a MOPO 730 laser (Spectra-Physics) pumped by frequency-tripled radiation from a Nd:YAG laser (Spectra Physics, GCR 230) and then frequency doubled by means of an autotracker (Inrad AT-II). The typical pulse energy was about 1 mJ.

The photolysis and probe laser beams were mildly focused by means of quartz lenses (2 m and 4 m focal lengths), combined on a dichroic mirror, and directed along the axis of the supersonic flow. They entered the CRESU apparatus through a Brewster angle window, passed through another such window mounted on the back of the reservoir, and co-propagated out through the throat of the Laval nozzle and along the axis of the flow, before leaving the vacuum chamber *via* a third Brewster angle window. LIF was gathered at a known distance downstream of the Laval nozzle (usually 10–30 cm) by a UV-enhanced, optically fast telescope-mirror combination mounted inside the main vacuum chamber, focused through a slit to reduce scattered light and directed onto the photocathode of a UV-sensitive photomultiplier tube (Thorn EMI 9124 B) after passing through a narrow band interference filter centred at 490 nm (band pass 10 nm FWHM; Corion). The signals were accumulated, processed and analysed by the same procedures as before (Sims et al. 1994a). For the interested reader, more details concerning the production and detection of CH radicals can be found in a previous paper by Bocherel et al. (1996).

The flows of reagent gases (CH_4 99.995%, Air Liquide; C_2H_2 99.6%, AGA; C_2H_4 99.5%, Air Liquide; C_2H_6 99.95%, Air Liquide; and C_4H_8 but-1-ene 99%, Union Carbide) and carrier gases (He, Ar or N_2 ; Air Liquide, 99.995%) were taken directly from the cylinders and regulated by means of mass flow controllers (Tylan). Knowledge of the total gas density all along the flow from impact pressure measurements using a Pitot tube (Sims et al. 1994a) and the individual gas flows enabled the calculation of the reagent concentration in the supersonic flow, essential for the kinetic measurements.

3. Results

The rate coefficients for the reactions of CH with hydrocarbons which have been obtained in the present study are shown at the bottom of Table 1 which also reports the main flow conditions for each measurement. Only statistical errors are quoted. However,

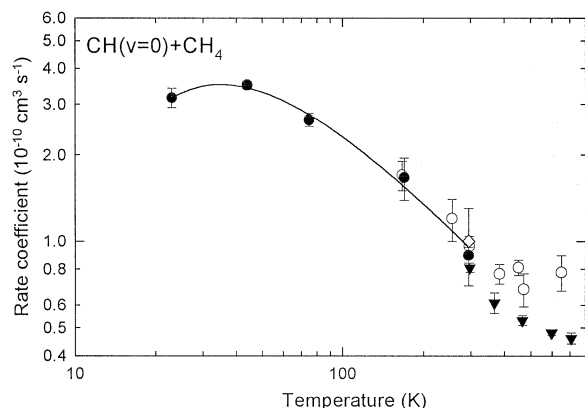


Fig. 1. Rate coefficients for the reaction of CH with CH_4 as a function of temperature, displayed on a log-log scale. The filled circles show the results obtained in the CRESU apparatus while the open circles show those obtained by Berman & Lin (1983), the filled triangles those obtained by Herbert (1995) and the open diamond the measurement of Butler et al. (1981). The solid line shows the fit to the CRESU data only, as described in the text and in Table 3.

some systematic errors from mis-calibration of flow controllers or inaccuracies in the determination of the total gas density and temperature should also to be taken into account. We estimated these additional errors to be $\leq 10\%$.

In Figs. 1-5 our results and how they depend on temperature are shown along with previous results. In Fig. 1, our measurements for the reactions of CH with CH_4 are presented and compared to the data of Butler et al. (1981), Berman & Lin (1983) and Herbert (1995). In Figs. 2 and 3, our data are plotted along with the results of Butler et al. (1981) and Berman et al. (1982) for the reactions of CH with C_2H_2 and C_2H_4 . Fig. 4 shows our results for the reaction of CH with C_2H_6 , as well as the data of Butler et al. (1981) and Berman & Lin (1983). Finally, our results involving but-1-ene, C_4H_8 , are displayed in Fig. 5. To our knowledge, no previous data are available for the reaction of CH with C_4H_8 . Where our results overlap with the temperature-dependent data of Berman & Lin (1983) and Berman et al. (1982), the agreement is excellent, except in the case of $\text{CH}+\text{C}_2\text{H}_4$ where the rate constants reported by Berman & Lin (1983) are approximately 40% larger than our values.

4. Discussion

4.1. Reaction mechanisms

Neither our experiments nor those of Lin and coworkers (Butler et al. 1981, Berman & Lin 1983, Berman et al. 1982) provide any direct information about the products of the reactions for which the rate constants have been measured. However, the magnitude of the rate constants, implying reaction at nearly every collision, and their independence on total pressure show that reaction does not proceed via collisionally-stabilised association, unless such a reaction is at its high pressure limit. It is generally believed that the reactions of CH with hydrocarbons proceed by initial insertion or addition of the radical. However, according

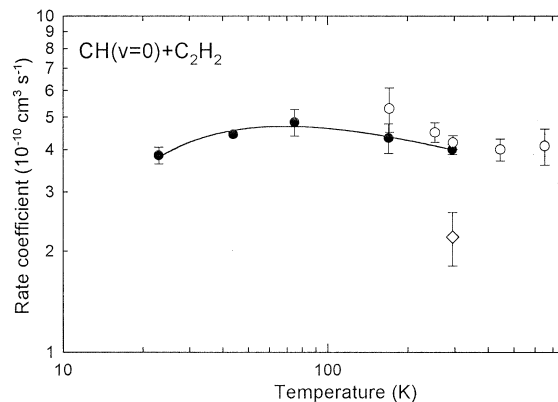


Fig. 2. Rate coefficients for the reaction of CH with C_2H_2 as a function of temperature, displayed on a log-log scale. The filled circles show the results obtained in the CRESU apparatus while the open circles show those obtained by Berman et al. (1982) and the open diamond the measurement by Butler et al. (1981). The solid line shows the fit to the CRESU data only, as described in the text and in Table 3.

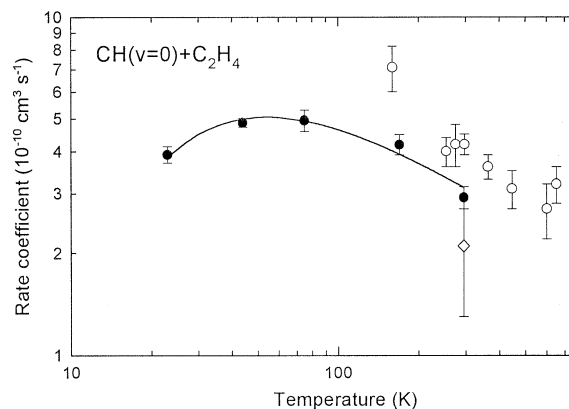


Fig. 3. Rate coefficients for the reaction of CH with C_2H_4 as a function of temperature, displayed on a log-log scale. See Fig. 2 for symbols description.

to RRKM considerations and with the possible exception of the C_5H_9 radical formed from $\text{CH} + \text{C}_4\text{H}_8$, the energised radicals formed by this initial associative process would be too short-lived with respect to decomposition - even in the absence of highly exothermic fragmentation processes - for these associations to be in their high pressure limit at the total pressures employed in our experiments. Therefore it must be concluded that reaction proceeds via facile insertion or addition over a potential with no potential energy barrier to the formation of the energised intermediate, followed by the fragmentation of this addition complex to one or more sets of products.

The possible non-associative reaction channels for the reactions of CH with CH_4 , C_2H_6 , C_2H_2 and C_2H_4 and the thermochemistry of these channels are listed in Table 2. The products listed in the second column of this table can be formed by simple fission of a single bond in the energised adduct, whereas those given in the fourth column require more complicated reorganisations of the intermediate radical.

Table 1. Rate coefficients obtained for reaction of CH with CH₄, C₂H₂, C₂H₄, C₂H₆ and but-1-ene C₄H₈.

Temperature (K)	23	44	75	170	295
Carrier gas	He	Ar	N ₂	N ₂	Ar
Total Density (10 ¹⁶ molec cm ⁻³)	4.73	2.90	1.67	0.57	30-40 ^a
Range of reagent gas (10 ¹⁴ molec cm ⁻³)					
CH ₄	0.07 - 0.67	0.09 - 0.46	0.07 - 0.35	0.08 - 0.35	0.47 - 2.85
C ₂ H ₂	0.05 - 0.52	0.07 - 0.37	0.06 - 0.29	0.07 - 0.41	0.45 - 2.70
C ₂ H ₄	0.06 - 0.56	0.08 - 0.38	0.04 - 0.31	0.07 - 0.42	0.41 - 2.43
C ₂ H ₆	0.09 - 0.47	0.06 - 0.32	0.04 - 0.26	0.06 - 0.35	0.33 - 1.98
C ₄ H ₈	0.06 - 0.28	0.03 - 0.20	0.02 - 0.16	0.04 - 0.21	0.20 - 1.19
Rate constant (10 ⁻¹⁰ cm ³ molec s ⁻¹)					
CH ₄	3.16±0.25 ^b	3.50±0.11	2.65±0.14	1.67±0.28	0.89±0.06
C ₂ H ₂	3.85±0.23	4.44±0.07	4.83±0.44	4.33±0.44	4.00±0.14
C ₂ H ₄	3.92±0.22	4.87±0.15	4.94±0.36	4.19±0.29	2.92±0.22
C ₂ H ₆	2.47±0.27	4.63±0.08	4.27±0.18	3.65±0.56	2.26±0.19
C ₄ H ₈	3.95±0.65	5.49±0.12	5.68±0.32	5.02±1.02	3.70±0.25

^a At room temperature, measurements were not carried out at the same pressure for all hydrocarbons so that only the density range is given here.^b Errors quoted are $\pm t\sigma$ statistical error where t is the appropriate value of the Student's t-distribution for the 95% point.**Table 2.** Pathways and thermochemistry^a for the reactions of CH with saturated and unsaturated hydrocarbons

Reagent	Products ^a	$-\Delta_r H_{298}^\circ/\text{kJ mol}^{-1}$	Products ^b	$-\Delta_r H_{298}^\circ/\text{kJ mol}^{-1}$
CH ₄	(C ₂ H ₅)	-404		
	C ₂ H ₄ +H	-251	C ₂ H ₃ +H ₂	-245
	CH ₃ +CH ₂	+17	C ₂ H ₂ +H ₂ +H	-75
			C ₂ H+2H ₂	+44
C ₂ H ₆	(<i>n</i> -C ₃ H ₇)	-417		
	(<i>i</i> -C ₃ H ₇)	-413		
	C ₃ H ₆ +H	-274	CH ₂ CHCH ₂ +H ₂	-351
	C ₂ H ₄ +CH ₃	-314	CH ₃ CCH+H ₂ +H	-108
			CH ₂ CCH+2H ₂	-169
C ₂ H ₄	(CH ₂ CHCH ₂)	-487		
	CH ₃ CCH+H	-244	CH ₃ +C ₂ H ₂	-275
	CH ₂ CCH ₂ +H	-240	CH ₄ +C ₂ H	-158
	CH ₂ +C ₂ H ₃	+20	C ₃ H+2H ₂	91
			CH ₂ CC+H ₂ +H	135
			CHCCH+H ₂ +H	139 ^c
			CH ₂ CCH+H ₂	-306 ^c
			<i>c</i> -C ₃ H ₃ +H ₂	-209
			CH ₃ CCH+H	-244
C ₂ H ₂	(CH ₂ CCH)	-481		
	CH ₂ CC+H	-37 ^{b,c}	CH ₃ +C ₂	+153
	CHCCH+H	-41 ^{b,c}	C ₂ H ₃ +C	+158
	CH ₂ +C ₂ H	+133	C ₃ H+H ₂	-85
			C ₃ +H ₂ +H	+231

^a sources of thermodynamic data: Atkinson et al. 1989, Lias et al. 1988^b theoretical values from: Walch, 1995 and from Bettens and Herbst 1995^c see also Clauberg et al. 1992

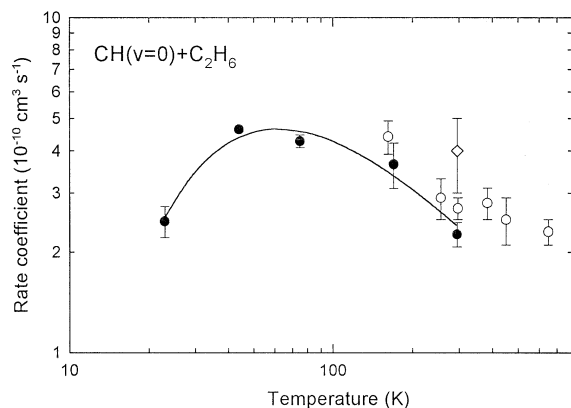


Fig. 4. Rate coefficients for the reaction of CH with C_2H_6 as a function of temperature, displayed on a log-log scale. See Fig. 1 for symbols description

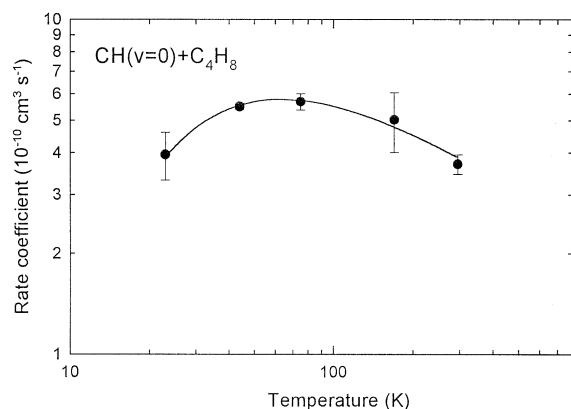


Fig. 5. Rate coefficients obtained in the CRESU apparatus for the reaction of CH with but-1-ene, C_4H_8 as a function of temperature, displayed on a log-log scale. The solid line shows the fit as described in the text and in Table 3.

The possible mechanisms of the reactions of CH with CH_4 , C_2H_6 , C_2H_2 and C_2H_4 have been discussed in some detail by Berman et al. (1982) and Berman & Lin (1983). Like Berman & Lin, we begin by considering the reaction between CH and CH_4 . Formation of a C_2H_5 radical is strongly exothermic, and the energised radical which is initially formed will have approximately 153 kJ mol^{-1} more energy than that associated with thermal $C_2H_4 + H$. Moreover, from measurements of the rate of addition of H atoms to C_2H_4 which yield an activation energy in the limit of high pressure of 9 kJ mol^{-1} (Lightfoot & Pilling 1987), it is known that the threshold energy for dissociation of C_2H_5 radicals to $C_2H_4 + H$ is only slightly greater than the endothermicity of the process and that the transition state is quite loose. Consequently, the lifetime of the chemically activated C_2H_5 radical formed from $CH + CH_4$ with respect to this process will be extremely short (from an RRKM calculation, Berman & Lin (1983) estimate a lifetime of 0.4 ps) and other processes such as less exothermic dissociations via tighter transition states (e.g. $C_2H_5 \rightarrow C_2H_3 + H_2$) or collisional stabilisation will not be able to compete. Our conclusion, agreeing with that

of Berman & Lin (1983) is that the reaction of CH with CH_4 must lead exclusively to the formation of $C_2H_4 + H$.

For $CH + C_2H_6$, the situation is less clear cut than for $CH + CH_4$. Addition of CH to C_2H_6 will lead to the formation of a *n*-propyl or *i*-propyl radical according to whether the CH inserts into a CH or CC bond. The fact that the reaction between $CH + CH_4$ (which contains no CC bonds) is almost as fast as that between $CH + C_2H_6$ suggests strongly that insertion into CH bonds is facile and probably the first step in both these reactions. Subsequent loss of an H-atom from either isomeric form of the propyl radical can lead to $C_3H_6 + H$ whereas cleavage of a CC bond in the *n*-propyl radical results in $C_2H_4 + CH_3$. These two channels have comparable exothermicities, -274 kJ mol^{-1} for $C_3H_6 + H$ and -314 kJ mol^{-1} for $C_2H_4 + CH_3$. The activation energies for the association of $C_3H_6 + H$ and $C_2H_4 + CH_3$ to *n*-propyl are 14 kJ mol^{-1} (Tsang 1991) and 31 kJ mol^{-1} (Baulch et al. 1992), respectively. Consequently, *n*-propyl radicals formed from the association of CH with C_2H_6 will have internal energies of $\sim 260 \text{ kJ mol}^{-1}$ above the threshold for fragmentation to $C_3H_6 + H$ and $\sim 283 \text{ kJ mol}^{-1}$ above the threshold for fragmentation to $C_2H_4 + CH_3$. Clearly, the *n*-propyl radical will be short-lived. Furthermore, these two product channels are likely to be competitive and to be the dominant ones in the reaction of CH with C_2H_6 , although other products, such as $C_2H_3 + CH_4$, which can be reached by relatively simple reaction pathways cannot be entirely ruled out.

The mechanism of the reactions of CH radicals with unsaturated hydrocarbons has been discussed by Berman et al. (1982). They suggest that the most likely initial step is addition of CH to the carbon-carbon double or triple bond to form a three-membered ring followed by rapid ring opening. In the case of $CH + C_2H_4$ this mechanism would lead to formation of the allyl radical. In the reactions of CH with unsaturated hydrocarbons, the products formed by fission of CC bonds are energetically less favoured than in those of CH with saturated hydrocarbons and the products obtained by elimination of an H atom again seem most likely. For the particular instance of $CH + C_2H_4$, such a process would yield $C_3H_4 + H$, although the most stable isomer of C_3H_4 , methyl acetylene ($CH_3C \equiv CH$), requires the internal transfer of an H-atom before loss of another H-atom. For $CH + \text{but-1-ene}$, the similar mechanism would yield $C_5H_8 + H$, where $CH_3C \equiv CC_2H_5$ is the most stable form of C_5H_8 .

The reaction of CH with C_2H_2 has recently been the subject of high quality quantum chemical calculations by Walch (1995). The initial formation of a $CHCHCH$ radical adduct can be followed either by loss of the central H atom to yield $CHCCH + H$ or by the formation and subsequent fragmentation of the propargyl radical (CH_2CCH) to yield $CH_2CC + H$. Along the latter pathway, there is no energy barrier; that is, no point of higher energy than that associated with the $CH + C_2H_2$ reagents. On the other hand, Walch (1995) does find a saddlepoint between $CHCHCH$ and $CHCCH + H$ which, including zero-point energies, has an energy 31 kJ mol^{-1} higher than the energy of the reagents. These calculations would suggest that the main products at low temperature and pressure will be $CH_2CC + H$. The large values of the rate constants for the reactions which

Table 3. Values of the parameters A , n and θ obtained by non-linear least-squares fitting of the rate coefficients $k(T)$ obtained in the CRESU apparatus to the form $k(T) = A(T/K)^n \exp(\theta/T)$. Valid *only* in the temperature range $T=23$ – 295 K.

Reaction	A ($\text{cm}^3 \text{s}^{-1}$)	n	θ (K)
$\text{CH} + \text{CH}_4$	3.96×10^{-8}	-1.04	-36.1
$\text{CH} + \text{C}_2\text{H}_2$	1.59×10^{-9}	-0.233	-16.0
$\text{CH} + \text{C}_2\text{H}_4$	7.74×10^{-9}	-0.546	-29.6
$\text{CH} + \text{C}_2\text{H}_6$	3.80×10^{-8}	-0.859	-53.2
$\text{CH} + \text{but-1-ene, C}_4\text{H}_8$	8.78×10^{-9}	-0.529	-33.5

we have studied, as well as their dependence on temperature, indicate clearly that the reactions proceed across surfaces with no potential energy barrier and that their rates are determined by adiabatic capture (Clary 1990, Smith 1995). Berman & Lin (1983) attributed the increase in rate constant for reactions of CH along the sequence CH_4 , C_2H_6 and $n\text{-C}_4\text{H}_{10}$ to ‘increased statistical factors’. An alternative explanation, which we prefer, is that the relatively small changes in the rate constants for the reactions of CH with all the hydrocarbons whose reactions have been studied, as well as their mild dependences on temperature, are attributable to subtle differences in the long-range potentials between the reagents (Smith 1995).

For the reactions of CH with unsaturated hydrocarbons, the kinetic behaviour is very reminiscent of that observed for the reactions of CN with C_2H_2 and C_2H_4 (Sims et al. 1994b) and of OH with the butenes (Sims et al. 1993). The rate constants increase below room temperature but then appear to reach a limiting value determined by the long-range electrostatic forces between the reagents. At still lower temperatures, the rate constants might actually decrease slightly, as any increase in reaction cross-section at low energies is more than compensated for by the decrease in relative velocity, and hence the collision rate decreases as the temperature falls (Smith 1995). In the reactions of CH with saturated hydrocarbons, the long-range attractive forces are somewhat weaker and the rate constants continue to increase until ‘saturation’ occurs at lower temperatures.

For the purposes of astrochemical modeling, it is useful to provide formulae expressing how the rate coefficients, $k(T)$, for particular reactions vary with temperature. Since the temperature-dependence is often expressed in the form $k(T) = A(T/K)^n \exp(\theta/T)$, we have fitted our data to this form yielding the values of A , n and θ listed in Table 3. The quality of the fits is shown in Figs. 1 to 5 where the line on each diagram represents the functional form of $k(T)$. It should be stressed that this fitting is entirely empirical, no theoretical meaning should be attached to the values derived for the parameters n and θ . As a consequence of this limitation, we *strongly discourage* the use of these formulae outside the range of the measurements, $T = 23$ – 295 K. In the absence of measurements down to 10 K, we would advise the use of the rate coefficients obtained at 23 K for this region.

4.2. Astrochemical implications

What are the implications of the present results for interstellar and planetary chemistry? Conventional diffuse cloud chemistry assumes that the sources of small hydrocarbons do not compensate their fast destruction by the harsh radiation field. For example the calculation of Viala (1986) yields for acetylene a typical abundance (relative to total hydrogen) lower than 10^{-11} in the case of a hot diffuse cloud ($T = 100$ K) with a visual extinction of 0.1. Using such a low value, the characteristic time of the reaction of acetylene with the methyldine radical would be much longer than the lifetime of the cloud and therefore certainly negligible either as a loss of CH or as a source of C_3H_2 . The same conclusion would apply for the other reactions studied here but could be changed if, as suggested by Hall & Williams (1995), a significant population of carbon chain molecules might be maintained as a result of the erosion of carbonaceous grains at the edge of the cloud.

In dense clouds the abundances of the various hydrocarbons are certainly much larger but are apparently still too low for their reactions with CH to generate significant loss of CH radicals in comparison with their destruction by reactions with ionized carbon or with neutral oxygen, carbon and nitrogen atoms, although such reactions have not yet been studied in the laboratory at the relevant temperatures (though see Brownsword et al. 1996a). However, the reactions of CH which have been studied here could be a source of some larger hydrocarbons in dense clouds. For example, if we consider C_3H_2 , the route of formation in conventional models (e.g. Adams and Smith 1987) was ionic and involved reaction of C^+ with acetylene:



followed by radiative association of C_3H^+ with H_2 :



and then dissociative recombination of C_3H_3^+ to yield C_3H_2 .

Very recently an alternative route has been proposed (Herbst 1996) in which the first step is the neutral-neutral reaction:



which has not yet been studied at low temperature, although the reaction is known to be fast at room temperature (Clary et al. 1994b) and to yield $\text{C}_3\text{H} + \text{H}$ at low collision energies (Kaiser et al. 1995). C_3H can then be converted into C_3H_2 either by the slow reaction with H_2 or by charge transfer:



followed by hydrogenation (association) to form C_3H_3^+ (reaction 2) which recombines dissociatively as previously specified. Another alternative is the proton transfer of H_3^+ to C_3H leading to C_3H_2^+ which may react with H_2 to yield again C_3H_3^+ . Although the CH radical is less abundant than ionized or neutral atomic carbon, its reaction with acetylene provides yet a direct route to C_3H_2 with a production rate which could be larger than that of

the slow radiative association C_3H^+ with H_2 , despite the very large abundance of molecular hydrogen. It would therefore be interesting to include the studied reactions in current models in order to evaluate their importance in the hydrocarbon chemistry.

The methylidene radical plays a major role in several planetary atmospheres. For example, in the upper stratosphere of Jupiter, where the typical temperature is in the range 180–300 K, it has been found that the CH radical is of key importance in the primary synthesis of higher hydrocarbons through insertion reactions such as those studied in the present work (Gladstone et al., 1996). More particularly, they are strongly involved in the set of reactions leading to the loss of C compounds.

In a recent model of Triton's atmosphere (Krasnopolsky & Cruikshank, 1995) it has been recognized that the methylidene radical is probably one of the main products of the photolysis of methane by Lyman- α (Mordaunt et al., 1993). As the density is low even in the lower layer of the atmosphere, solar radiation in the 100–400 nm range (of which 80% of the flux is Lyman- α) can produce CH with a large rate in the lowest 50 km where the typical temperature is 40–50 K (Krasnopolsky & Cruikshank, 1995, Strobel et al. 1990). Once it is formed, CH reacts readily with methane to provide C_2H_4 . The other reactions which we have studied could be a source of some minor hydrocarbons. The present study therefore provides results for the modeling of Triton's atmosphere in the relevant temperature range which were not previously available.

In the much denser atmospheres of Titan and Neptune, photolysis of methane occurs in the upper and warmer layers. The bulk of the photolysis occurs for an altitude higher than 400 km in both cases and therefore at temperatures higher than 130 K for Titan (Yung et al., 1984, Toubanc et al., 1995) and 180 K for Neptune (Yelle et al., 1993). The peak of the destruction rate is at around 800 km altitude for Titan and 500 km altitude for Neptune, with typical temperatures of 160 and 180 K, respectively. The reactions of CH are then a potential source of various hydrocarbons especially ethylene in these upper layers. These hydrocarbon species would then be transported downward to the lower layers of the atmospheres. The present study confirms the results of Berman et al. (1982) and Berman & Lin (1983), and extends the temperature range to values relevant for Titan's atmosphere.

Finally, we note that in around fifteen years the planned Rosetta mission (Schwehm, 1994) toward the inner coma of a comet will considerably improve our knowledge of the chemical composition of the coma very close to the kernel, at distances where the flow regime is still mainly collisional. The understanding of the chemistry in this region will certainly require knowledge of the rate coefficients of many reactions at low temperatures and this is a further reason for extending the kinetic data base far beyond what is presently available.

Acknowledgements. We are grateful for funding from the Groupement De Recherche: 'Physicochimie des Molécules et des Grains Interstellaires', from the 'Programme National de Planétologie', from the British Council under its Alliance programme and from the EPSRC. The excimer laser was borrowed from the EPSRC Laser Loan Pool at the Rutherford-Appleton Laboratory, for which we express thanks.

We thank Dr. L.B. Herbert for permission to quote his results on the $\text{CH}+\text{CH}_4$ reaction.

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