Low temperature (39 K – 298 K) kinetics study of the reactions of C4H radical with various hydrocarbons observed in Titan’s atmosphere

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Running head: This paper presents an experimental kinetics study at low temperatures of reactions of C₄H radical with various hydrocarbons relevant to Titan’s atmosphere. Possible consequences of these results on the formation of large hydrocarbons are discussed as well as comparison with rate coefficients used in the various photochemical models.

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Abstract

The reaction kinetics of the butadynyl radical, C$_4$H, with various hydrocarbons detected in the atmosphere of Titan (methane, ethane, propane, acetylene, ethene and methylacetylene) are studied over the temperature range of 39 K – 298 K using the Rennes CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus. Kinetic measurements were made using the pulsed laser photolysis – laser induced fluorescence technique. The rate coefficients, except for the reaction with methane, all show a negative temperature dependence and can be fitted with the following expressions over the temperature range of this study: $k_{\text{C}_4\text{H}_4} = 0.29 \times 10^{-10} \exp(-25.6 / T) \times (T / 298 \text{ K})^{-1.24} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; $k_{\text{C}_4\text{H}_4} = 1.06 \times 10^{-10} \exp(-56.3 / T) \times (T / 298) ^{-1.35} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; $k_{\text{CH}_4} = 1.82 \times 10^{-10} \exp(65.8/T) \times (T / 298 \text{ K})^{-1.05} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{\text{C}_4\text{H}_4} = 1.94 \times 10^{-10} \exp(-9.5 / T) \times (T / 298 \text{ K})^{-0.40} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{\text{CH}_4\text{C}_2} = 3.21 \times 10^{-10} \exp(-47.2 / T) \times (T / 298 \text{ K})^{-0.82} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. These expressions are not intended to be physically meaningful but rather to provide an easy way to introduce experimental results in photochemical models. They are only valid over the temperature range of the experiments. Possible channels of these reactions are discussed as well as possible consequences of these results on the production of large molecules and hazes in the atmosphere of Titan. These results should also be considered for the photochemistry of Giant Planets.

Keywords: Titan, Atmospheres Chemistry, Organic chemistry, Experimental
Introduction

Polyynes are unsubstituted acetylene-like linear compounds with general formula $C_{2n}H_2$ [H–(C≡C)$_n$–H]. To date, only the simplest member of the series, $C_4H_2$ (H-C≡C-C≡C-H), diacetylene, has been detected in the atmosphere of some planetary objects of our Solar System: Jupiter (Gladstone et al., 1996), Uranus (Burgdorf et al., 2006), Saturn (de Graauw et al., 1997) and its moon Titan (Kunde et al., 1981; Shemansky et al., 2005). Triacetylene (H-C≡C-C≡C-C≡C-H), $C_6H_2$, has been identified in experimental simulations of Titan’s atmosphere (de Vanssay et al., 1995). Photochemically reactive in the UV range, polyynes are thought to be one of the possible precursors to the visible-absorbing haze materials present in many planetary environments (Allen et al., 1980). Such compounds may play, therefore, a key role in the chemistry of these planetary atmospheres.

Indeed in photochemical models of Jupiter (Gladstone et al., 1996; Lebonnois, 2005) (Moses and Greathouse, 2005), Saturn (Moses et al., 2000) (Ollivier et al., 2000) and Titan (Wilson and Atreya, 2004) (and references therein), polyynes are noteworthy for their role in the formation of solid organic materials present in the atmosphere of these objects. Current reaction networks modelling the chemistry involved in the evolution of such environments describe the formation via a polymerization process starting from $C_2H_2$:

\[
(C_2)_nH_2 + h\nu \rightarrow (C_2)_nH + H \quad \text{(R1)}
\]

\[
(C_2)_nH + (C_2)_mH_2 \rightarrow (C_2)_{(n+m)}H_2 + H \quad \text{(R2)}
\]

With the aim to refine the description of such mechanisms in models, polyynes have been the
subject of various studies. However, except for the simplest of them, acetylene C$_2$H$_2$, these compounds are not commercially available, and their synthesis and purification are more difficult to perform as the length of the carbon chain increases. Furthermore, there is an almost complete lack of quantitative data relating to larger polyynes due to their high thermal instability and their inclination to polymerize at anything but the lowest partial pressures.

Nevertheless, absolute photoabsorption cross sections of some of these species at relevant temperatures and over different ranges of wavelength have been determined in order to predict the fate of those compounds under irradiation. Such work is essential for the modelling of radiative transfer and photolysis rates. For example, for the two lightest polyynes, butadiyne (C$_4$H$_2$) and hexatriyne (C$_6$H$_2$), also called diacetylene and triacetylene respectively, absorption cross sections have been determined in the gas phase from 150 to 300 nm and at relatively low temperature (Benilan et al., 1995; Fahr and Nayak, 1994; Okabe, 1981; Shindo et al., 2003; Smith et al., 1998).

The reaction kinetics of the building up of complex long-chain carbon compounds has also been studied. Most of the experimental research however, has been undertaken in the context of combustion studies and, thus, has been conducted at temperatures of several thousands of degrees (Krestinin, 2000) (and references therein). Only a very few rate coefficients have been measured under conditions relevant for astrophysical environments, in particular at low temperatures (Smith, 2006).

Focussing on the case of Titan’s atmosphere, a complex photochemistry that involves polyynes among other hydrocarbons, takes place over a temperature range of 70—175 K, N$_2$ being the background gas. In such a medium, the formation of C$_4$H$_2$ is confirmed by its detection in the stratosphere from the analysis of the infrared spectra recorded by the Voyager mission (Hanel et al., 1981; Kunde et al., 1981). Thus, to describe the mechanisms involved,
rate coefficients are required for reactions involving these species at low temperatures. Relatively few data are available, being limited to the reactions of the C$_2$H radical with hydrocarbons with the work of Leone and co-workers employing laser photolysis and transient infrared absorption spectroscopy in cooled cells down to 150 K (Hoobler and Leone, 1997; Hoobler and Leone, 1999) (Opansky and Leone, 1996a; Opansky and Leone, 1996b; Pedersen et al., 1993), the work of Sims, Smith and co-workers employing laser photolysis – chemiluminescence detection in a CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme or Reaction Kinetics in Uniform Supersonic Flow) apparatus (Carty et al., 2001; Chastaing et al., 1998), and the work of Leone and co-workers using the latter detection technique in a pulsed CRESU apparatus (Goulay and Leone, 2006; Lee et al., 2000; Murphy et al., 2003; Nizamov and Leone, 2004a; Nizamov and Leone, 2004b; Vakhtin et al., 2001a; Vakhtin et al., 2001b).

Up to now, no data concerning the higher homologues were available in the literature as they are very unstable compounds. In these circumstances, the only way for modellers to include these reactions in their chemical schemes is to evaluate their rate coefficients from similar reactions for which rates are available in the literature. Thus, arguing that higher polyyne radicals are probably less reactive than C$_2$H, rate coefficients for (C$_2$)$_n$H + hydrocarbon reactions have been arbitrarily set to $k((C_2)_nH) = 3^{1-n} k(C_2H)$ by the authors of the first photochemical models of Titan’s atmosphere (Lara et al., 1996; Toublanc et al., 1995; Yung et al., 1984). More recently, the assumption adopted by (Wilson and Atreya, 2004) and (Burgdorf et al., 2006; Hébrard et al., 2007) is that all (C$_2$)$_n$H reaction rates are equal to their C$_2$H analogues.

In spite of the use of the updated laboratory low temperature data, and thus the subsequent improvement of the description of the chemistry of hydrocarbons, the mole fractions
estimated from the photochemical models do not well reproduce the observations (Hébrard et al., 2007; Vinatier et al., 2007). For example, Table 1 shows that C₄H₂ is either overestimated or underestimated compared to the concentration measured in Titan's atmosphere by ISO (Infrared Space Observatory) or CIRS (Composite InfraRed Spectrometer onboard the Cassini spacecraft orbiting Saturn) experiments at a given range of altitude (respectively 75—260 and 98—187 km). Moreover, the theoretical data for diacetylene, even those that take into account the error bars for the kinetic rate coefficients, do not fit the very last profile obtained from CIRS limb data (Vinatier et al., 2007). In fact, this is the case for the majority of unsaturated hydrocarbons detected in Titan’s stratosphere. Since mean concentrations appear to be controlled essentially by chemical rather than physical parameters (Lebonnois et al., 2001), this discrepancy is probably due to a deficiency in the estimation of kinetic parameters relating to the destruction or formation of C₄H₂ (Hébrard et al., 2007).

Another feature of Titan’s atmosphere is the presence of different layers of haze that give its orange-brown colour when observed in the visible. The sources and mechanisms leading to the formation of these hazes are still poorly understood. Photochemical formation of hazes has been explored for more than twenty years. Although laboratory simulations have shown that formation of aerosol particles could involve photolysis of acetylene (C₂H₂), ethylene (C₂H₄), and hydrogen cyanide (HCN), the difficulty of performing simulations of these processes under the conditions of the atmosphere of Titan makes those results quite speculative. The possible roles of polyynes (Yung et al., 1984), nitriles (Banaszkiewicz, 2000) and more recently aromatics (Lebonnois et al., 2002; Wilson and Atreya, 2003) have been studied in various models. The scarcity of kinetic measurements however, especially under the physical conditions of the atmosphere of Titan, makes these analyses uncertain.

We suggest that reactions of the type [R2] could play a role in the formation of long
polyacetylenic chains and large molecules. The kinetics study at low temperatures of C₄H radical reactions with various hydrocarbons among the most abundant observed in Titan’s atmosphere (CH₄, C₂H₂, C₂H₄, C₂H₆, CH₃C₂H and C₃H₈) that we present here should help modellers to assess this assumption.

2. Experimental technique

The CRESU technique which is now well established for the study of gas phase reaction kinetics at very low temperatures (Dupeyrat et al., 1985; Sims et al., 1994), has been used in the present study. CRESU is a French acronym standing for Cinétique de Réaction en Ecoulement Supersonique Uniforme which can be translated as Reaction Kinetics in Uniform Supersonic Flow. Here, we concentrate on those features of our experiments which are specific to kinetic experiments on the reactions of C₄H radicals.

In the CRESU technique, low temperatures are achieved via the isentropic expansion of a buffer gas through a Laval nozzle. Each nozzle employed provides an axially and radially uniform supersonic flow at a particular temperature, density and velocity for a given buffer gas. The relatively high density of the supersonic flow (10^{16}—10^{17} cm⁻³) ensures frequent collisions, thus maintaining thermal equilibrium. All these properties are conserved in the core of the supersonic flow over a typical distance of a few tens of centimetres along the flow corresponding to a hydrodynamic time of several hundreds of microseconds. The Laval nozzle is mounted on a reservoir kept at room temperature into which the buffer gas, the C₄H precursor molecule and the reagent gases were injected.

C₄H radicals were created by the pulsed laser photolysis of diacetylene, C₄H₂, using the 248 nm radiation of a KrF excimer laser (Lambda Physik, LPX 200). The beam from this laser entered the CRESU chamber through a Brewster angle window and propagated counter to the gas flow.
C₄H₂ was synthesized by dehydrochlorination of 1,4-dichloro-2-butyne (C₄H₄Cl₂)(Khlifi et al., 1995). Given the high instability of diacetylene, only small amounts were synthesized before a series of kinetic experiments. Once synthesized, C₄H₂ was mixed with helium gas in a 20 L glass vessel at a total pressure of ca. 1.2 bar. He-C₄H₂ mixture was injected into the reservoir of the CRESU chamber using very small flows of the order of a few standard cm³min⁻¹.

C₄H radicals were detected by laser induced fluorescence (LIF) using a ^2Σ⁺ − ^2Σ⁺ vibronic band type of the ^2Πᵢ − ^X ^2Σ⁺ electronic system. Laser radiation at a wavelength of ca. 408 nm was generated using the frequency doubled output of a Nd:YAG laser (Continuum, Powerlite Precision II) to pump a dye laser (Laser Analytical Systems, LDL 20505) operating with Styryl 9M dye (Sigma Aldrich) in methanol, the output of which was frequency doubled in a BBO crystal. The linewidth of the UV laser was measured with a wavemeter (HighFinesse/Angstrom, WS-7R) to be 0.24 cm⁻¹. This probe laser entered the CRESU chamber and gas reservoir through two quartz Brewster angle windows and passed through the Laval nozzle throat and down the gas flow along its axis counter to the direction of the photolysis beam. Fluorescence from C₄H (^2Πᵢ) was collected at right angle to the laser propagation direction using an optically fast collection system, and detected with a photomultiplier tube (Thorn EMI, 9813 QSB) through a low-pass glass filter (Schott, GG 435). The signal from the PMT was recorded by a gated integrator and a boxcar averager (Stanford Research Systems) and transferred to a PC via an IEEE interface (Stanford Research Systems, SR 245) controlled by data acquisition software. The time delay between the pump and probe beams, which was scanned to generate decay traces, was controlled by a four-channel delay/pulse generator (Stanford Research Systems, DG535), which was also controlled by the same data acquisition software via an IEEE interface.
A typical LIF decay trace for C$_4$H at 52 K is shown in Fig. 1. As can be seen, a finite rise time was observed for the C$_4$H LIF signal. This was taken as resulting from collisional relaxation of C$_4$H formed in electronic and/or rotationally excited states. Indeed, the first excited electronic state of C$_4$H, $\tilde{A}^2 \Pi$, is predicted to lie very close to the ground state, with theoretical estimations varying from 70 cm$^{-1}$ to 565 cm$^{-1}$ (Woon, 1995). Photoelectron spectroscopy experiments of C$_4$H$^-$ anions allowed the authors to give an upper limit for the energy of the $\tilde{A}^2 \Pi$ state: Neumark and co-workers (Taylor et al., 1998) gave an upper value of 468 cm$^{-1}$, while more recent experiments by Pino et al. (Pino et al., 2002) were consistent with an $\tilde{A}^2 \Pi$ state lying at a lower energy of ca. 160 cm$^{-1}$ above the $\tilde{X}^2 \Sigma^+$ ground state, which is a value cited as a private communication by Endo and co-workers in the paper by Neumark and co-workers (Taylor et al., 1998). In order to avoid contamination of the data, all nonlinear least-squares fits of the exponential decays of the LIF signals were started after this rise corresponding to electronic and/or rotational relaxation of C$_4$H was complete, and pseudo-first-order decay times were kept at least ten times longer than this rise time. For a given temperature, LIF scans were then taken for different reagent concentrations in the usual way in order to construct a kinetic plot from which the second-order rate coefficient could be extracted. Fig. 2 shows a second-order plot for C$_4$H + C$_2$H$_6$ at 52 K. Measurements at room temperature were performed in the CRESU apparatus as previously described (Sims et al., 1994).

Hydrocarbon reagents were mixed with the buffer gas before passing into the reservoir and expanding through the Laval nozzle. CH$_4$ (99.995%), C$_2$H$_4$ (99.95%), C$_2$H$_6$ (99.995%), C$_3$H$_4$ (methyl acetylene) (96%) and C$_3$H$_8$ (99.95%), all from Air Liquide, C$_2$H$_2$ (99.6%, AGA) and carrier gas (N$_2$ and Ar; Air Liquide, 99.995%) were taken directly from cylinders and regulated by means of calibrated MKS mass flow controllers. Knowledge of the total gas
density along the flow, and of the individual gas flow rates, allowed the hydrocarbon
concentrations in the supersonic flow to be calculated.

3. Results

3.1 C\textsubscript{4}H spectra

To our knowledge the most recent spectroscopic work on neutral C\textsubscript{4}H was published by Endo
and co-workers (Hoshina et al., 1998; Pino et al., 2002). In their paper, (Hoshina et al., 1998)
present and analyse twenty vibronic bands of C\textsubscript{4}H observed by laser induced fluorescence
(LIF) in the 24000 – 25000 cm\textsuperscript{-1} region, corresponding to the range of wavelengths 400 to 416
nm. Figure 3 shows a survey spectrum obtained in our experiment at 52 K for a time delay
between the photolysis laser and the probe laser of 20 µs over the same wavelength range.
Most of the vibronic bands observed by Endo and co-workers (Hoshina et al., 1998) are also
present in our spectrum, only the weakest of them are absent. We did not, however, see any of
the C\textsubscript{3} features which were observed by Endo and co-workers probably as a result of their use
of a discharge source, in contrast to the more specific photolytic source of C\textsubscript{4}H radical used in
this study. We have performed a theoretical simulation of the entire band system using the
spectroscopic parameters determined by (Hoshina et al., 1998). Some bands also present in
the spectra of Endo and co-workers clearly show up here. They cannot be attributed to C\textsubscript{3}
since it is not present in detectable amount in our spectra (less than 1% relative to C\textsubscript{4}H). A
complete reanalysis of the C\textsubscript{4}H band system will be presented elsewhere. To perform our
kinetic measurements we used the band at 24490.8 cm\textsuperscript{-1} referred to as the [J] band
(corresponding to a transition from the ground state to the \(\tilde{B}^2\Pi\text{, }3\nu_5\text{, }\Sigma^+\) excited state) by
Endo and co-workers, as this band is one of the most intense and suffers least from overlap
with other bands. Figure 4 shows this band observed in our experiment at 52 K, as well as a
simulation calculated using the spectroscopic parameters determined by (Hoshina et al., 1998)
except for a rotational constant of the upper state $B'_{\text{eff}} = 0.1512(1) \text{ cm}^{-1}$ and spin splitting constant $\Gamma' = 0.009(1) \text{ cm}^{-1}$. The band is quite well reproduced, apart from the perturbed lines as already noticed by (Hoshina et al., 1998), with a Voigt profile using a resolution of 0.08 cm$^{-1}$.

To obtain the kinetic measurements presented in the next section, we used the $R$-band head of the transition, which is the most intense part of this spectrum, as can be seen in Fig. 4.

### 3.2 Kinetic measurements

Our experimentally measured rate coefficients are summarized in Table 2 which also reports the main flow conditions for each study. The quoted uncertainties comprise statistical errors calculated as the standard error obtained from the fit of the second-order kinetic plot multiplied by the appropriate Student’s $t$ factor for the 95% confidence limit combined with an estimate of possible systematic errors. The latter are essentially due to flow control inaccuracies or inaccuracies in the determination of the buffer gas total density. Every effort was made to minimize these and we estimate that they do not exceed 10%.

In Figures 5 to 9, the rate coefficients $k(T)$ that we obtained are displayed as a function of the temperature on log-log plots. Results of the fittings of the data are presented in Table 3, using the equation $k(T) = A \exp(-\theta / T)(T / 298 \text{ K})^n$ and the resulting values of $A$, $\theta$ and $n$ are given with their associated statistical uncertainties. We emphasise that these expressions are only valid over the temperature range 39–300 K. They are not intended to be physically meaningful but rather to provide an easy way to introduce experimental results in photochemical models with a good level of confidence, as these fits do not generally deviate too much from our measurements.

In every case, with the exception of methane, the rate coefficients for the reactivity of
hydrocarbons with C₄H are close to the collisional rates and show slight negative temperature dependences. In the case of methane, which reacts much more slowly, we were not able to obtain any rate coefficient below 200 K. The measurements are limited by both the length and therefore the duration of the supersonic flow, as well as the maximum concentration of hydrocarbon possible without either perturbing the supersonic flow, or causing condensation. These limitations preclude the determination of rate coefficients slower than ~ 5 × 10⁻¹³ cm³ molec⁻¹s⁻¹.

Most of the rates were obtained using nitrogen as a buffer gas, with the exception of the measurements at 50 K and some of the measurements at 300 K that were obtained using argon as a buffer gas. Considering the temperature dependences k(T), results derived in argon are fully consistent with those obtained in nitrogen, showing no effect of the nature of the buffer gas (N₂ or Ar) on the rate coefficients measured. In addition, at 50 K we performed kinetic experiments for all gases with nozzles giving two different densities: 0.52 × 10¹⁷ cm⁻³ and 1.01 × 10¹⁷ cm⁻³. In both cases the rates obtained were the same, within the uncertainty of our experiments. At 300 K, measurements with methane were also performed at two densities, 0.68 × 10¹⁷ cm⁻³ and 2.07 × 10¹⁷ cm⁻³ respectively, and the rate coefficients were found to be similar. These results indicate that either all these reactions are bimolecular or that they were obtained in the high pressure limit of a termolecular process, the third body being the buffer gas (N₂ or Ar).

4. Discussion

4.1 Temperature dependences and possible products of the reactions

In this subsection, we comment the temperature dependences observed in our experiments and give some insights on the possible products formed by these reactions. More details on the
chemistry of these reactions, and others involving C₄H with a larger number of hydrocarbons will be given elsewhere (Berteloite et al., in preparation).

**Reaction of C₄H with methane (CH₄), ethane (C₂H₆) and propane (C₃H₈)**

The rate coefficients of the reaction of C₄H with methane (Fig. 5) show a slightly positive temperature dependence as observed by (Opansky and Leone, 1996a) in the case of the reaction of C₂H with methane, with almost the same rate coefficients. This behaviour indicates the presence of a small barrier along the minimum energy path for the reaction. Fitting their results with an Arrhenius type function, Opansky and Leone were able to derive an activation energy of 4 kJ mol⁻¹ for the reaction C₂H + CH₄. As we only have data at two temperatures, 298 K and 200 K, it would be too risky to derive such a barrier in our case. By analogy with the reaction of C₂H with methane, we believe this reaction to proceed more likely via hydrogen abstraction, C₄H₂ and CH₃ being the two subsequent products. Given the high mixing ratio of CH₄ in the stratosphere of Titan, ca. 1.4%, this reaction would represent an important way of recycling diacetylene. The production of the methyl radical, CH₃, is also worthy of note, as the recombination of two methyl radicals will form ethane, the second most abundant hydrocarbon in the atmosphere of Titan.

In the cases of ethane and propane (Fig. 6 and 7), the rate coefficients present negative temperature dependences, the rate coefficient being larger for propane than for ethane. This negative temperature dependence is consistent with reactions proceeding through potential energy surfaces with no or very small energy barriers. The increase of the reactivity with the number of carbons in the alkanes has already been observed in other studies (Murphy et al., 2003; Sims et al., 1993) and is probably due to the increasing number of primary and secondary hydrogen available in the co-reactant of C₄H. As in the case of methane, we believe the hydrogen abstraction to be the most probable channel, forming C₄H₂ and C₂H₅ in the
reaction with ethane, and C₄H₂ and C₃H₇ in the reaction with propane. All the reactions with alkanes presented here are therefore likely to recycle C₄H₂ and produce alky radicals.

**Reaction of C₄H with acetylene (C₂H₂)**

As for reactions involving large alkanes, we found the rate coefficient for C₄H + C₂H₂ to increase when the temperature is lowered (Fig. 8), with rate coefficients larger than those for the reactions with alkanes. This indicates the absence of an energy barrier along the minimum energy path for the reaction. The higher reactivity of acetylene compared to the alkanes is probably due to the presence of π electrons in C₂H₂. The most likely mechanism could be the addition of the electrophilic C₄H to the π orbital of C₂H₂, thus forming a C₆H₃ intermediate which could subsequently undergo a C-H bond fission. This reaction mechanism would be quite similar to those of the analogous C₂H + C₂H₂ (Stahl et al., 2002) and CN + C₂H₂ (Huang et al., 2000) reactions. Interestingly, the structures of some C₆H₃ isomers have been recently calculated at the B3LYP/6-311G(d,p) level of calculations (Guo et al., 2007). The isomer identified as p3 in that paper has the correct properties to be the addition intermediate: according to the above mentioned calculations, the formation of the C₆H₃ addition intermediate from C₄H and C₂H₂ would be exothermic by ca. 250 kJ mol⁻¹, thus reinforcing the suggestion that an addition mechanism is possible.

The main products would be therefore, C₆H₂ and H. This is obviously a very interesting channel for the atmospheric photochemistry of Titan, as it forms the next polyyne after C₄H₂, triacetylene (C₆H₂), so increasing the chain length of the hydrocarbon. The formation of other products however, following the dissociation of the short-lived intermediate complex, C₆H₃‡, cannot be completely excluded. Furthermore, the possibility of an abstraction process, leading to the formation of C₄H₂ and C₂H can not be ruled out as this channel is exothermic by ca. 100 kJ mol⁻¹. It is worth noting that this abstraction channel was not open at low temperature.
in the case of \( C_2H + C_2H_2 \) and \( CN + C_2H_2 \) as these reactions are thermoneutral and endothermic respectively.

**Reactions of \( C_4H \) with ethene (\( C_2H_4 \)) and methylacetylene (\( C_3H_4 \))**

For these two reactions we found a similar temperature dependence (Fig. 9 and 7) as for the reaction with acetylene, with slightly larger rate coefficients. Again, these reactions are likely to proceed through the addition of the electrophilic \( C_4H \) radical to the multiple bond of ethene, \( C_2H_4 \), or methylacetylene, \( CH_3C_2H \), immediately followed by the formation of fragments. The hydrogen displacement channel, giving the radical \( C_6H_4 \) in the case of ethane, and \( C_7H_4 \) in the case of methylacetylene, seems the most probable reaction mechanism, especially if we consider the results of (Stahl et al., 2002) on the dynamics of \( C_2H \) with hydrocarbons in crossed beam experiments. Other channels however, in particular an H abstraction mechanism similar to that occurring with saturated hydrocarbons, cannot be ruled out.

4.2 Destruction of \( C_4H \) radical by hydrocarbons in the atmosphere of Titan

In order to evaluate the efficiency of each reactant as a destruction route of \( C_4H \) the ratio of the characteristic time, \( \tau_X \), for the reactions of \( C_4H \) with these hydrocarbons relative to that of \( CH_4 \), \( \tau_{CH_4} \), can be calculated using the observed abundances and the rate coefficients obtained in our study. We can easily show that:

\[
\frac{\tau_{CH_4}}{\tau_X} = \frac{n_X}{n_{CH_4}} \frac{k_X}{k_{CH_4}}
\]

where \( n_X / n_{CH_4} \) is the relative abundance of hydrocarbon X with respect to \( CH_4 \) and \( k_X \) and \( k_{CH_4} \) are the rate coefficients for the reaction of \( C_4H \) with hydrocarbon X and \( CH_4 \) respectively. Values greater than say 0.1 for this ratio of characteristic times will indicate that
hydrocarbon X will play a significant role in the destruction of C₄H and therefore must be taken into account in the photochemical scheme.

The Cassini-Huygens mission is providing very interesting new data with respect to the composition of the atmosphere of Titan (Flasar et al., 2005; Niemann et al., 2005; Shemansky et al., 2005; Teanby et al., 2006; Teanby et al., 2007; Vinatier et al., 2007; Waite et al., 2005) from which it is possible to obtain a new description of the concentration profiles with respect to the altitude.

Figure 10 is an attempt to summarize these data over the altitude range 120 – 1200 km for the hydrocarbons of interest here. Data in the stratosphere were taken from (Flasar et al., 2005) and (Vinatier et al., 2007). Flasar et al. measured abundances of several species in the stratosphere as a function of latitude using the CIRS apparatus of the Cassini orbiter during fly-bys T0 and Tb. Methane abundance (1.6±0.5 %) was obtained over the altitude range 80—140 km whereas other hydrocarbon abundances were derived between 140 and 180 km (Flasar et al., 2005; Waite et al., 2005). Mean abundances with respect to latitude were derived from their data and plotted in Figure 10 at ~180 km. Another study by (Niemann et al., 2005) based on the GCMS instrument (Gas Chromatograph Mass Spectrometer) show that methane was uniformly mixed with a mole fraction of 1.41±0.07 % in the stratosphere. More recently, (Vinatier et al., 2007) analysed spectra obtained with CIRS during fly-bys Tb (15° S) and T3 (80° N) from which vertical profiles were derived for a series of hydrocarbons in the altitude range 100-460 km (Tb fly-by) and 170-495 km (T3 fly-by). For clarity, in Figure 10 we have only included their results corresponding to the low latitudes Tb fly-by. Data from 450 km to 1000 km were derived from the measurements by (Shemansky et al., 2005) who obtained the densities of a variety of molecules using the Cassini UVIS (Ultraviolet Imaging Spectrometer) experiment. Finally, data at ~1200 km were extracted from the work by (Waite et al., 2005)
who derived abundances from the INMS (Ion Neutral Mass Spectrometer) apparatus. Note that the abundance taken for propane is an upper limit whereas for ethene we chose the lowest value indicated in their paper.

In the altitude range that we are considering here, the temperature varies from about 150 to 200 K. Over this range our rate coefficients do not vary significantly with temperature and therefore we made our analysis taking a mean value for each hydrocarbon: 

\[ k_{\text{C}_2\text{H}_2} = 2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}; \]

\[ k_{\text{C}_2\text{H}_4} = 3.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}; \]

\[ k_{\text{C}_2\text{H}_6} = 0.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}; \]

\[ k_{\text{CH}_2\text{C}_2\text{H}} = 3.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ and } k_{\text{C}_2\text{H}_4} = 1.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \]

For methane, as already mentioned, we were not able to study its reactivity below 200K. Considering that this process is very slow and that our data indicate a reduction of the rate coefficient when the temperature is lowered from 300 K to 200 K, we have arbitrarily chosen to take a rate coefficient slightly lower (and probably too high at 150 K) than our measurement at 200 K for the present analysis: 

\[ k_{\text{CH}_4} = 6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \]

Using these assumptions it is then possible to calculate for every altitudes the ratio \( \tau_{\text{CH}_4}/\tau_X \) and therefore to analyze the possible impact of each hydrocarbon in the destruction process of \( \text{C}_4\text{H} \). As can be seen in Figure 11, at altitudes greater than 600 km, excepting propane and methyl acetylene for which no data are presently available, the ratio \( \tau_{\text{CH}_4}/\tau_X \) is much greater than 1 indicating that the destruction of \( \text{C}_4\text{H} \) by \( \text{C}_2\text{H}_2, \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_6 \) is more efficient than that by methane. This is especially striking in the ionosphere within 800 and 1000 km. These conclusions were also drawn in a recent study of the reactivity of the \( \text{C}_2 \) radical with hydrocarbons (Canosa et al., 2007). In that study however, the effect was not as striking as in the present work because reactivity of \( \text{C}_2 + \text{CH}_4 \) was found to be about 20 times higher than that of \( \text{C}_4\text{H} + \text{CH}_4 \). At 1200 km, reactions with \( \text{C}_2\text{H}_2 \) and \( \text{C}_2\text{H}_4 \) are still dominant.
whereas the reaction with ethane becomes less efficient than methane although still significant ($\tau_{\text{CH}_4}/\tau_{\text{C}_2\text{H}_6} \sim 0.5$). It is also worth stressing that the contributions of propane and methyl acetylene increase significantly with respect to lower altitudes ($\tau_{\text{CH}_4}/\tau_{\text{C}_3\text{H}_8} \sim 0.06$ and $\tau_{\text{CH}_4}/\tau_{\text{C}_3\text{H}_4} \sim 0.1$ respectively) although their reaction with $\text{C}_4\text{H}$ still remains much less efficient than that of $\text{C}_2\text{H}_2$ and especially $\text{C}_2\text{H}_4$ as a destruction source of $\text{C}_4\text{H}$.

In Titan's stratosphere, abundances of hydrocarbons are much smaller and therefore destruction reactions of $\text{C}_4\text{H}$ by hydrocarbons are no longer dominant with respect to methane. It is worth noting however that $\tau_{\text{CH}_4}/\tau_X$ is close to 0.1 for $\text{C}_2\text{H}_2$ and $\text{C}_2\text{H}_6$ which are then significant destruction sources of $\text{C}_4\text{H}$ in this zone. On the other hand, propane, ethene and methyl acetylene will play a minor role as the ratio $\tau_{\text{CH}_4}/\tau_X$ is only a few % or even less for these species. As mentioned above the choice of the rate coefficient $k_{\text{CH}_4}$ may be too high at 150 K. A rough extrapolation of our measurements down to 150 K would give a rate coefficient of about $k_{\text{CH}_4}(150\text{K}) = 4 \times 10^{-13} \text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ which is not significantly different from the adopted value. Furthermore, a lower value would even more emphasize the impact of other hydrocarbons than the present analyses and will not change our conclusions. Considering the data obtained during the T3 fly-by, one can observe that the derived abundances were generally found to be larger than those obtained from the Tb fly-by. This essentially reflects the polar enrichment in these high latitudes conditions resulting from circulation in winter time. Although they are far from common in Titan's atmosphere it is interesting to point out that the efficiency of $\text{C}_2\text{H}_2$ in the destruction of $\text{C}_4\text{H}$ is significantly greater than in the equatorial area and increases with altitude. At ~460 km the ratio $\tau_{\text{CH}_4}/\tau_{\text{C}_2\text{H}_2}$ becomes close to 0.5. The effect of these peculiar atmospheric conditions for other molecules is either insignificant ($\text{C}_2\text{H}_6$, $\text{C}_3\text{H}_8$) or not sufficient ($\text{CH}_3\text{C}_2\text{H}$, $\text{C}_2\text{H}_4$) to modify the conclusions that we indicated for the Tb fly-by data.
4.3 Comparison with rate coefficients used in various photochemical models

Since the pioneer model of the atmosphere of Titan by Yung and coworkers in 1984 (Yung et al., 1984), various photochemical models have been developed, incorporating the chemistry, some of them also adding the transport of species in the atmosphere. The choice of the chemical scheme, and the quality of the rate coefficients used have been improved over the years, often taking into account the latest laboratory measurements when available. Figures 5 to 9 show the rate coefficients used in the various photochemical models (Lara et al., 1996; Lebonnois et al., 2001; Toublanc et al., 1995; Wilson and Atreya, 2004; Yung et al., 1984) for the reactions of C₄H with hydrocarbons. It can be seen that differences between predictions used and the measurements we made can reach several orders of magnitude, especially at the lowest temperatures. It is worth noting that in some of these models (Yung et al., 1984),(Lara et al., 1996),(Toublanc et al., 1995), authors followed the recommendation by (Yung et al., 1984) to adjust arbitrarily the rate coefficients of reactions involving polyacetylene radicals to those involving C₂H using the following formula: k((C₂)nH) = 3¹⁻ⁿ k(C₂H). In the most recent of these models however (Wilson and Atreya, 2004), the authors used the experimental results obtained at low temperatures by Leone and co-workers (Hoobler and Leone, 1997; Hoobler and Leone, 1999; Lee et al., 2000; Murphy et al., 2003; Nizamov and Leone, 2004a; Vakhtin et al., 2001a; Vakhtin et al., 2001b) and Smith and co-workers (Carty et al., 2001; Chastaing et al., 1998) for the analogous reactions with C₂H in order to derive an upper limit for the production of polyacetylene polymers. It is worth noting that if the temperature dependence is about the same as for the reactions with C₄H, the absolute rate coefficients we measured are always larger by a factor of two to four, with the exception of reactions with methane.
4.4 The role of C$_4$H radical for the formation of big molecules and haze

As mentioned in the Introduction, photochemical sources of hazes have been explored in various models and recently Wilson et al. (Wilson and Atreya, 2003) have considered the role of polymerization of pure polyacetylenes in the formation of the hazes as suggested in 1980 by Allen et al. (Allen et al., 1980). In their photochemical model, the first step for the growth of polyacetylenic chains is given by the reaction

$$C_2H + C_2H_2 \rightarrow C_4H_2 + H$$

whose rate coefficient has been measured at low temperatures by Chastaing et al. (1998). The chain-lengthening process is therefore considered to be continued through the photolysis of C$_4$H$_2$ forming polyacetylene radicals: C$_4$H, C$_6$H and C$_8$H. As mentioned in section 4.2, the reaction of C$_4$H with acetylene is very likely to form efficiently triacetylene, C$_6$H$_2$. Reactions of polyacetylene radicals with C$_4$H$_2$, C$_6$H$_2$ and C$_8$H$_2$ are proposed by Wilson and Atreya (Wilson and Atreya, 2003) to lead to the formation of polyacetylene polymers. In their model, the rate coefficients for all these reactions were taken as equal to that of C$_2$H + C$_2$H$_2$ as measured by Chastaing et al. (Chastaing et al., 1998) and Leone and co-workers (Vakhtin et al., 2001a). Our results show however that the rates constants for C$_4$H + C$_2$H$_2$ are actually about two times faster. Finally, Wilson et al. (Wilson and Atreya, 2003) found the contribution of polyacetylenes to be insignificant compared to the channel involving aromatics for the formation of hazes and it would be worth to know how our new results could affect their conclusions. It has to be mentioned however, that most of the kinetics of aromatics considered in this photochemical model have not been studied experimentally at low temperature so far, making these results still quite speculative.
The role of metastable states of diacetylene, C₄H₂*, in the formation of large molecules in Titan’s atmosphere has also been explored in the 1990’s by Zwier and co-workers ((Zwier and Allen, 1996)and reference therein). More specifically, Zwier and Allen (Zwier and Allen, 1996) compared the efficiency of C₄H₂* reactions with free radicals as routes for forming large hydrocarbons and nitriles. The main reactions involved in their chemical scheme were the reactions of C₄H₂* with unsaturated hydrocarbons, the reactions of C₂H with C₄H₂, CH₄ and C₂H₂ and the reactions of C₄H with C₂H₂ and CH₄. At that time however, none of these reactions had been studied at low temperatures, and the rate constants for C₂H and C₄H reactions were taken from the photochemical model of (Toublanc et al., 1995) and reference therein. As can be seen on Fig. 8, our experimental results differ from those used by (Toublanc et al., 1995) by an order of magnitude considering for instance the reaction C₄H + C₂H₂. The role of the metastable states of C₄H₂* in the formation of large molecules in Titan’s atmosphere should be therefore, reconsidered.

5. Conclusion

The work presented here is, to our knowledge, the first ever experimental reaction kinetics investigation involving the radical C₄H. Rates of the reactions between C₄H and methane were found to be very close to those of C₂H with methane, with a small energy barrier along the minimum energy path for the reaction. For all the other reactions studied here, the rate coefficients are very fast (k \geq 10^{-10} \text{ cm}^3\text{ molecule}^{-1}\text{s}^{-1}) with k increasing when the temperature is lowered. These reactions are therefore dominated by long range dispersion forces and proceed on a potential energy surface with no barrier or a small barrier in the entrance channel. The rate coefficients are all larger than those found for reactions of C₂H with the same hydrocarbons. These new rate coefficients should therefore be included in future
photochemical models of the atmosphere of Titan and of other planets containing methane. Reactions with alkanes are likely to recycle C\textsubscript{4}H\textsubscript{2} while other reactions could form various products of interest as for instance triacetylene, C\textsubscript{6}H\textsubscript{2} in the case of the reaction involving acetylene. For the other reactions involving unsaturated hydrocarbons (C\textsubscript{2}H\textsubscript{2}, C\textsubscript{2}H\textsubscript{4}, CH\textsubscript{3}C\textsubscript{2}H), a short-lived addition complex is likely to be formed, that decomposes to give various products with H-atom elimination being probably the dominant channel. The high enthalpy of formation of C\textsubscript{4}H offers however, many possibilities for the products, more than is the case for C\textsubscript{2}H or CN radicals, and therefore the formation of radicals leading to larger molecules, such as PAHs for instance. The role of these products in the formation of big particles and hazes should be further explored. These kinetics results therefore, even measured at low temperatures (40 K – 298 K), could be also of interest for chemical schemes leading to the formation of soot in combustion (Krestinin, 2000).

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Chastaing, D., James, P. L., Sims, I. R., Smith, I. W. M., 1998. Neutral-neutral reactions at the temperatures of interstellar clouds - Rate coefficients for reactions of C\textsubscript{2}H radicals with O\textsubscript{2}, C\textsubscript{2}H\textsubscript{2}, C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{6} down to 15 K, Faraday Discuss., 165-181.


Huang, L. C. L., Asvany, O., Chang, A. H. H., Balucani, N., Lin, S. H., Lee, Y. T., Kaiser, R. I., Osamura, Y., 2000. Crossed beam reaction of cyano radicals with hydrocarbon molecules. IV. Chemical dynamics of cyanoacetylene (HCCCN; X (1)Sigma(+)) formation from reaction of CN(X (2)Sigma(+)) with acetylene, C_2H_2(X (1)Sigma(+)(g)). 113, 8656-8666.


**TABLE 1.** Comparison between mixing ratios observed by ISO (2003) and the Cassini CIRS instrument (2005) with various photochemical models.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Altitude (km)</th>
<th>Model</th>
<th>Observation</th>
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<td>C$_2$H$_6$</td>
<td>125</td>
<td>Yung et al. (1984)</td>
<td>2.0x10$^{-5}$</td>
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<td></td>
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<tr>
<td></td>
<td></td>
<td>Wilson &amp; Atreya (2004)</td>
<td>5.8x10$^{-6}$</td>
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<tr>
<td></td>
<td></td>
<td>ISO Alt. 75-260 km</td>
<td>3.0x10$^{-6}$</td>
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<tr>
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<td></td>
<td>Flasar et al. (2005)</td>
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<td></td>
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(a) mixing ratio at 130 km, (b) mixing ratio at 105 km, (c) mixing ratio at 125 km.
TABLE 2. Rate coefficients measured at different temperatures for the reactions of 
C₄H with CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₈ and CH₃C₂H.

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<th>83</th>
<th>145</th>
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<td>Total density (10¹⁶ molec cm⁻³)</td>
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<td>10.3</td>
<td>4.9</td>
<td>9.2</td>
<td>5.83</td>
<td>25</td>
<td>21.5</td>
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Range of reactant gas density (10¹² molec cm⁻³)

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<td>C₂H₂</td>
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<td>13-77</td>
<td>2.5-47.5</td>
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<td>4-26</td>
<td>10-110</td>
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<td>25-386</td>
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<td>C₂H₆</td>
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<td>89-448</td>
<td>215-1039</td>
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<tr>
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<td>7-79</td>
<td>8-7</td>
<td>13-66</td>
<td>78-728</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃C₂H</td>
<td>2-14</td>
<td>5-33</td>
<td>3-34</td>
<td>8-79</td>
<td>14-164</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Rate coefficient (10⁻¹⁰ cm³ molec⁻¹ s⁻¹)

<table>
<thead>
<tr>
<th></th>
<th>CH₄</th>
<th>C₂H₂</th>
<th>C₂H₄</th>
<th>C₂H₆</th>
<th>C₃H₈</th>
<th>CH₃C₂H</th>
<th>0.77±0.12 × 10⁻²</th>
<th>2.13 ± 0.2 × 10⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₂</td>
<td>2.57 ± 0.24</td>
<td>3.88 ± 0.14</td>
<td>2.74 ± 0.08</td>
<td>2.54 ± 0.20</td>
<td></td>
<td>1.54 ± 0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₄</td>
<td>5.57 ± 0.32</td>
<td>4.84 ± 0.08</td>
<td>3.19 ± 0.43</td>
<td>3.27 ± 0.12</td>
<td></td>
<td>1.8 ± 0.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₆</td>
<td>1.75 ± 0.04</td>
<td>1.81 ± 0.02</td>
<td>0.78 ± 0.04</td>
<td>0.58 ± 0.03</td>
<td></td>
<td>0.41 ± 0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₃H₈</td>
<td>3.70 ± 0.22</td>
<td>4.15 ± 0.07</td>
<td>2.72 ± 0.3</td>
<td>1.88 ± 0.19</td>
<td></td>
<td>1.03 ± 0.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃C₂H</td>
<td>4.93 ± 0.58</td>
<td>5.66 ± 0.21</td>
<td>5.04 ± 0.61</td>
<td>4.13 ± 0.33</td>
<td></td>
<td>2.80 ± 0.25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Uncertainties (here and throughout the tables) are calculated using the statistical error evaluated on the second order plot via the Student’s t factor (95%). A systematic error of 10% was added to take into account contribution from possible systematic errors.
TABLE 3. Fit parameters \((A, \theta, n)\) of our kinetic data according the following equation

\[
k_{2nd} = A \exp\left(-\frac{\theta}{T}\right)\left(\frac{T}{298 \text{ K}}\right)^n
\]

for each reagent \(\text{C}_2\text{H}_2, \text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \text{C}_3\text{H}_8\) and \(\text{CH}_3\text{C}_2\text{H}\), in the range \(T = 39\text{–}300 \text{ K}\).

<table>
<thead>
<tr>
<th></th>
<th>(A/10^{10} \text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1})</th>
<th>(\theta/\text{ K})</th>
<th>(n)</th>
<th>estimated uncertainty (a/10^{10}) (\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_2\text{H}_2)</td>
<td>1.82</td>
<td>65.79</td>
<td>-1.06</td>
<td>0.75</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_4)</td>
<td>1.95</td>
<td>-9.52</td>
<td>-0.40</td>
<td>0.65</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_6)</td>
<td>0.29</td>
<td>25.58</td>
<td>-1.24</td>
<td>0.37</td>
</tr>
<tr>
<td>(\text{C}_3\text{H}_8)</td>
<td>1.06</td>
<td>56.27</td>
<td>-1.35</td>
<td>0.48</td>
</tr>
<tr>
<td>(\text{CH}_3\text{C}_2\text{H})</td>
<td>3.21</td>
<td>47.20</td>
<td>-0.82</td>
<td>0.29</td>
</tr>
</tbody>
</table>

\(a\) Corresponds to \(2\sigma\) with \(\sigma = \sqrt{\frac{\sum (k_{2nd \exp} - k_{2nd \text{ fit}})^2}{\text{number of experimental points}}}\)
Figure captions

Figure 1. Decay of C₄H (\(^{2}\Sigma^{+} \rightarrow ^{2}\Sigma^{+}\)) LIF signal at 52.3K in the presence of C₂H₆ ([C₂H₆] = 0.43 \times 10^{14} \text{ molecule cm}^{-3}) and Ar buffer ([Ar] = 10.3 \times 10^{16} \text{ molecule cm}^{-3}), fit to a single-exponential function.

Figure 2. Second order plot for the reaction of C₄H + C₂H₆ at 52.3K in Ar, leading to a value for the second-order rate coefficient of \(k = (1.81 \pm 0.02) \times 10^{-10} \text{ molecule}^{-1} \text{ cm}^{3} \text{ s}^{-1}\).

Figure 3. LIF spectrum survey at 52.3K of products of C₄H₂ photolysis at 248 nm. Simulation was calculated using a temperature of 50 K, a Voigt profile of 0.08 cm\(^{-1}\) (FWHM) and spectroscopic parameters derived by (Hoshina et al., 1998). Transitions [A-W] belong to the C₄H radical according (Hoshina et al., 1998).

Figure 4. LIF spectrum of a \(^{2}\Sigma^{+} \rightarrow ^{2}\Sigma^{+}\) [J] band of C₄H. Observed spectrum is obtained at 52.3 K, simulation was calculated using a temperature of 50 K and a Voigt profile of 0.08 cm\(^{-1}\) (FWHM).

Figure 5. Rate coefficients for the reaction of C₄H with CH₄ as a function of temperature, displayed on a log-log scale. The filled circles show the experimental results obtained in this work. The dashed lines represent equations used for this reaction in various photochemical models of the atmosphere of Titan. The long dashed line represents data from (Wilson and Atreya, 2004), the medium dashed line from (Toublanc et al., 1995), the dotted line from (Lara et al., 1996) and the dash-dotted line from (Yung et al., 1984).

Figure 6. Rate coefficients for the reaction of C₄H with C₂H₆ as a function of temperature, displayed on a log-log scale. The filled triangles down show the experimental results obtained in this work and the bold solid line shows the fit to these data. The other dashed lines represent equations used for this reaction in various photochemical models of the atmosphere of Titan. The long dashed line represents data from (Wilson and Atreya, 2004), the medium dashed line from (Toublanc et al., 1995), the dotted line from (Lara et al., 1996) and the dash-dotted line from (Yung et al., 1984).

Figure 7. Rate coefficients for the reaction of C₄H with respectively C₃H₈ and CH₃C₂H as a function of temperature, displayed on a log-log scale. The filled squares show the experimental results obtained in this work for C₃H₈ and the bold solid line shows the fit to these data. The filled triangle down show the experimental results obtained in this work for CH₃C₂H and the solid line shows the fit to these data.
**Figure 8.** Rate coefficients for the reaction of C₄H with C₂H₂ as a function of temperature, displayed on a log-log scale. The filled circles show the experimental results obtained in this work and the bold solid line shows the fit to these data. The other dashed lines represent equations used for this reaction in various photochemical models of the atmosphere of Titan. The long dashed line represents data from (Wilson and Atreya, 2004), the medium dashed line from (Toublanc et al., 1995), the dotted line from (Lara et al., 1996) and the dash-dotted line from (Lebonnois et al., 2001).

**Figure 9.** Rate coefficients for the reaction of C₄H with C₂H₄ as a function of temperature, displayed on a log-log scale. The filled squares show the experimental results obtained in this work and the bold solid line shows the fit to these data. The other dashed lines represent equations used for this reaction in various photochemical models of the atmosphere of Titan. The long dashed line represents data from (Wilson and Atreya, 2004), the medium dashed line from (Toublanc et al., 1995) and the dotted line from (Lara et al., 1996).

**Figure 10.** Relative abundances of C₂H₂, C₂H₄, C₂H₆, CH₃C₂H and C₃H₈ with respect to CH₄ as a function of altitude in the atmosphere of Titan. Data in the stratosphere are taken from (Flasar et al., 2005) and (Vinatier et al., 2007) (flyby Tb only). Between 600 and 1000 km, data are from (Shemansky et al., 2005) and at 1200 km they are derived from (Waite et al., 2005).

**Figure 11.** Characteristic reaction time τCH₄ of the reaction C₄H + CH₄ relative to the characteristic reaction time τX of the reaction C₄H + X with X= C₂H₂, C₂H₄, C₂H₆, CH₃C₂H and C₃H₈ as a function of altitude in the atmosphere of Titan. Lines between data are added only for clarity.
FIGURE 1 Berteloite et al.
FIGURE 2 Berteloite et al.

\[
\begin{align*}
\text{[C}_2\text{H}_6\text{]} \ (10^{14} \text{ molecule cm}^{-3}) & \quad 0.0 \quad 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \quad 1.0 \\
\text{k}_{1,\text{st}} \ (10^4 \text{ s}^{-1}) & \quad 0.0 \quad 0.5 \quad 1.0 \quad 1.5 \quad 2.0 \quad 2.5
\end{align*}
\]
FIGURE 3 Berteloite et al.
FIGURE 4 Berteloite et al.
FIGURE 6 Berteloite et al.
FIGURE 7 Berteloite et al.
FIGURE 8 Berteloite et al.

![Graph showing rate coefficient (cm$^3$ molec$^{-1}$ s$^{-1}$) vs. temperature (K)](image-url)
FIGURE 9 Berteloite et al.

![Figure 9](image_url)
FIGURE 10 Berteloite et al.

The figure shows the abundance of various hydrocarbons relative to CH$_4$ as a function of altitude. The graph includes data points for C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_8$, and CH$_3$C$_2$H. The x-axis represents the abundance of hydrocarbons relative to CH$_4$, while the y-axis shows altitude in kilometers. The data points are plotted on a log-log scale.
FIGURE 11 Berteloite et al.