Rate Coefficients for the Reactions of $C_2(a^3\Pi_u)$ and $C_2(X^1\Sigma_g^+)$ with Various Hydrocarbons (CH_4, C_2H_2, C_2H_4, C_2H_6, and C_3H_8): A Gas-Phase Experimental Study over the Temperature Range 24−300 K[†]

Alejandra Páramo,[‡,§] André Canosa,[*,‡] Sébastien D. Le Picard,[‡] and Ian R. Sims[*,‡]

Institut de Physique de Rennes, UMR CNRS−Université n° 6251; Equipe "Astrochimie Expérimentale", Campus de Beaulieu, Bât. 11C, Université de Rennes 1, 35042 Rennes Cedex, France, and School of Chemistry, University of Birmingham, Edgbaston B15 2TT, Birmingham, U.K.

Received: March 23, 2008; Revised Manuscript Received: June 2, 2008

The kinetics of reactions of $C_2(a^3\Pi_u)$ and $C_2(X^1\Sigma_g^+)$ with various hydrocarbons (CH_4, C_2H_2, C_2H_4, C_2H_6, and C_3H_8) have been studied in a uniform supersonic flow expansion over the temperature range 24−300 K. Rate coefficients have been obtained by using the pulsed laser photolysis-laser induced fluorescence technique, where both radicals were produced at the same time but detected separately. The reactivity of the triplet state was found to be significantly lower than that of the singlet ground state for all reactants over the whole temperature range of the study. Whereas $C_2(X^1\Sigma_g^+)$ reacts with a rate coefficient close to the gas kinetic limit with all hydrocarbons studied apart from CH_4, $C_2(a^3\Pi_u)$ appears to be more sensitive to the molecular and electronic structure of the reactant partners. The latter reacts at least one order of magnitude faster with unsaturated hydrocarbons than with alkanes, and the rate coefficients increase very significantly with the size of the alkane. Results are briefly discussed in terms of their potential astrophysical impact.

1. Introduction

Understanding how molecular complexity may be generated and how far it can progress in gas-phase natural environments is a subject of current interest and debate. Such environments may display very different physical conditions and include interstellar clouds, circumstellar envelopes, protoplanetary disks, stellar atmospheres, comets, planetary atmospheres, plasmas, or combustion flames. Photochemical models simulating the chemistry taking place have been developed over several decades, and their evolution and improvement, in order to match the observed molecular and atomic concentrations, require a large number of physical and chemical parameters. Obviously, one must first infer the network of chemical reactions which could influence the concentration of species in the medium of interest. Then, the temperature and sometimes pressure dependence of individual rate coefficients and branching ratios must also be known. For example, the most recently updated astrochemical model[1] includes 4605 reactions and 420 species and requires data at temperatures as low as 10 K. Among these reactions, only about one-third can be constrained by available experimental data,[1] indicating how much still remains to be done.

Carbon-based molecules have been found to be ubiquitous in all the above-mentioned environments, and the understanding of the mechanisms permitting the growth of carbon chains is a special concern for modelers, theoreticians, and experimentalists. Even at the very cold temperatures of interstellar clouds, an incredibly rich chemistry is taking place, as clearly evidenced by the detection of about 150 interstellar molecules.[2] Among these, carbon-containing molecules are greatly dominant, the largest being the cyanopolyyne $HC_{11}N$ (cyanodecapentayne) which was detected in 1997. As is now well established, many neutral−neutral reactions are very fast at very low temperatures,[3] and reactions between neutral carbon-bearing radicals and hydrocarbons are expected to be potential processes that could significantly contribute to the increase of molecular complexity in cold space environments by insertion−elimination mechanisms leading to larger carbon-chain molecules. Motivated by these considerations, a considerable effort has been carried out in this direction during the past 15 years. Thanks to the development of new experiments[4–8] offering the possibility of measuring rate coefficients at temperatures as low as 13 K,[9] the reactivity of radicals such as CN, CH, $C(^3P)$, C_2, C_2H, and C_4H has been explored at temperatures below 300 K. An up-to-date list of references of experiments carried out in this matter can be found in ref. 10.

The dicarbon molecule which is the subject of this paper is a rather unusual species because its first excited electronic state, $a^3\Pi_u(v = 0)$, hereafter $^3C_2$, is only separated by 610 cm^{-1} (i.e., ∼880 K)[11] from the electronic ground state $X^1\Sigma_g^+(v = 0)$, hereafter $^1C_2$. From an experimental point of view, presently available techniques for the production of C_2 generate both states together offering the opportunity to compare the reactivity of the two states provided that no interferences occur resulting from collisional relaxation/excitation with the reactant partner or the buffer gas used in the experiment. In some cases, the presence of $^3C_2$ could act as a source of $^1C_2$ leading to underestimated measures for the reaction rate coefficients of the ground state with the reactant of interest. However, some methods based on the use of scavengers are available to eliminate either the singlet state[12–14] or the triplet state.[15]

Two classes of experimental device have been employed to study the kinetics of the dicarbon molecule. Flow reactors were initially used to measure the rate coefficients, whereas more recently, crossed beam experiments have been applied to the

---

[†] Part of the "Stephen R. Leone Festschrift".

[*] Corresponding author. Tel: +33 2 23 23 69 96. Fax: +33 2 23 23 67 86. E-mail: andre.canosa@univ-rennes1.fr (A.C). Tel: +33 2 23 23 69 18. Fax: +33 2 23 23 67 86. E-mail: ian.sims@univ-rennes1.fr (I.R.S.).

[‡] Université de Rennes 1.

[§] University of Birmingham.

10.1021/jp8025336 CCC: $40.75

investigation of the dynamics of the reactions involving both states $^1C_2$ and $^3C_2$. Interest in the reactivity of C_2 appeared in the late seventies and early eighties because it was discovered in the interstellar space just a few years before in 1977[16] and was thought to be an effective optical probe of kinetic temperatures of interstellar clouds at that time.[16] The large number of laboratory studies which followed this discovery provided measurements of the rate coefficients at room temperature and sometimes above for a variety of reactants among which hydrocarbons were largely dominant. Although many experimental studies have been carried out to measure the rate coefficients of the removal of $^3C_2$ with hydrocarbons,[17–21] data concerning the reactivity of $^1C_2$ were scarcer.[19,22,23] More recently, interest in this class of reactions has been rekindled, and new results have been published concerning the rate coefficients of the triplet state[14,24,25] and the singlet ground state[14,26] with hydrocarbons. For the first time, data have been obtained at temperatures below 300 K by using uniform supersonic flow reactors.[14,26] All these studies have demonstrated that $^1C_2$ reacts with hydrocarbons usually much faster than $^3C_2$. In most cases, $^1C_2$ was found to react at a rate close to the gas kinetic limit, whereas $^3C_2$ was more sensitive to the molecular and electronic structure of the reactant partners.

In parallel, a significant effort has been undertaken to understand the dynamics of these reactions from an experimental as well as theoretical point of view. Crossed molecular beam machines were used to study the products issuing from reactions of a mixture of $^1C_2$ and $^3C_2$ with several hydrocarbons, including C_2H_2,[27–32] C_2HD,[33] C_2H_4,[27,31,34–36] C_2H_3D,[36] $C_2H_2D_2$,[36] C_2D_4,[36] allene,[37] methylacetylene,[38] and benzene,[39] and potential energy surfaces were also explored to determine the suitable pathways leading from reactants to products.[27,28,30–34,36,37,39–44] Although crossed beam experiments were usually carried out at relative collision energies of several tens of kJ mol^{-1}, which is very high with respect to the conditions existing in interstellar clouds, the data obtained provide interesting additional information for the improvement of our understanding of these processes.

In this paper, we present the first ever measurements of the rate coefficient of the reaction of the triplet state $^3C_2$ with two alkanes C_2H_6 and C_3H_8 as well as C_2H_2 and C_2H_4 at temperatures as low as 24 K. Data are compared with those previously obtained for the singlet ground state over the same range of temperature,[26] and possible products are also discussed in light of the recent new results mentioned above. The reactivity of C_2 with CH_4 was also investigated, but in this case, data were obtained for the singlet ground state $^1C_2$ only (see below).

2. Experimental Technique

The work was carried out by using the CRESU (a French acronym standing for Cinétique de Réaction en Ecoulement Supersonique Uniforme or Reaction Kinetics in a Uniform Supersonic Flow) apparatus at the University of Rennes 1 (France). The fundamentals of this technique, which allows one to generate a wall-free ultracold gas reactor, have been explained in detail elsewhere,[9,45] and its adaptation to the study of reaction kinetics involving the dicarbon molecule has been described very recently.[15,26] Only a concise description will be given here, drawing attention to those aspects of the experiments which relate to measurements of the reactions involving $^1C_2$ and $^3C_2$ with CH_4, C_2H_2, C_2H_4, C_2H_6, and C_3H_8.

In the CRESU technique, low temperatures are achieved via the isentropic expansion of a buffer gas through a Laval nozzle. At the exit of the Laval nozzle, because there is no further expansion downstream of the nozzle exit, the flow parameters (i.e., temperature, density, pressure, and velocity) do not exhibit any axial and radial variations at least in the center of the jet (typically 10−20 mm in diameter) where the flow is isentropic for several tens of centimeters corresponding to a hydrodynamic flow time of several hundreds of microseconds. This means that only rate coefficients greater than typically $\sim 10^{-12}$ cm^3 molecules^{-1} s^{-1} can be measured with a high level of confidence. The relatively high density of the supersonic flow ($10^{16}-10^{17}$ cm^{-3}) ensures frequent collisions, thus maintaining thermal equilibrium. The Laval nozzle was mounted on a reservoir kept at room temperature into which the buffer gas, the C_2 precursor molecule, and the reagent gases were injected.

In the current work, C_2 molecules have been obtained by pulsed laser photolysis (PLP) of C_2Cl_4 (Aldrich, 99.9% HPLC grade) by using an ArF excimer laser (Lambda-Physik, LPX 210i) working at 193 nm with repetition frequency of 10 Hz and an exit energy of ~200 mJ per pulse.

The $^1C_2$ radical was detected by laser-induced fluorescence (LIF) by exciting the ($D^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$) (0,0) transition at ~231 nm (Mulliken bands) and collecting the LIF signal on resonance by using an interference filter centered at 228 nm (band-pass: 11nm fwhm, Corion). Probe laser radiation was provided by a dye laser (Laser Analytical Systems, LDL 20505) operating with Coumarin 460 (Exciton) dye diluted in methanol. The dye was pumped by the third harmonic of a Nd:YAG laser (Spectra Physics, GCR 190, 10 Hz) at 355 nm, and frequency was doubled by using a BBO crystal to obtain the 231 nm wavelength. The $^3C_2$ population was probed by exciting the ($d\,^3\Pi_g \leftarrow a^3\Pi_u$) (0,0) band of the Swan system at ~516 nm and detecting LIF on the (0,1) band at ~563 nm which was isolated with an interference filter centered at 561.4 nm (band-pass: 9nm fwhm, Andover Corp.). The same dye laser was used to generate the appropriate green radiation by using Coumarin 307 (Exciton) dye diluted in methanol.

The probe and the photolysis beams were combined on a dichroic mirror and were directed along the axis of the supersonic flow, and LIF was collected at a known distance downstream of the Laval nozzle by using a UV-enhanced, optically fast telescope−mirror combination mounted inside the main vacuum chamber, focused through a slit, and directed onto the photocathode of a UV-sensitive photomultiplier tube (Thorn EMI, 9813 QSB) after passing through a narrow band filter to reduce the scattered light from the photolysis laser. The LIF signals as a function of time were accumulated, processed, and analyzed as described previously elsewhere,[9] leading to the determination of a first-order rate coefficient proportional to the hydrocarbon reagent concentration. A typical LIF decay for the triplet state $^3C_2$ at 83 K is shown in Figure 1. As can be seen, a significant risetime was observed for the $^3C_2$ LIF signal. This was taken as resulting from collisional relaxation of $^3C_2$ formed in rotationally excited states. This was also observed for the singlet state LIF decays (see Figure 2). In order to avoid contamination of the data, all nonlinear least-squares fits of the exponential decays of the $^{1,3}C_2$ LIF signals were commenced after this rise was complete. For a given temperature, LIF scans were then taken at differing reagent concentrations in order to construct a kinetic plot from which the second-order rate coefficient could be extracted. Figures 1 and 2 show second-order plots for $^3C_2 + C_2H_2$ at 83 K and $^1C_2 + C_3H_8$ at 49 K, respectively.

In the present experiment, both singlet and triplet states of C_2 were observed separately after photolysis took place. To avoid contamination in the $^1C_2$ LIF decay traces from possible intersystem crossing induced by collisions of $^3C_2$ with the

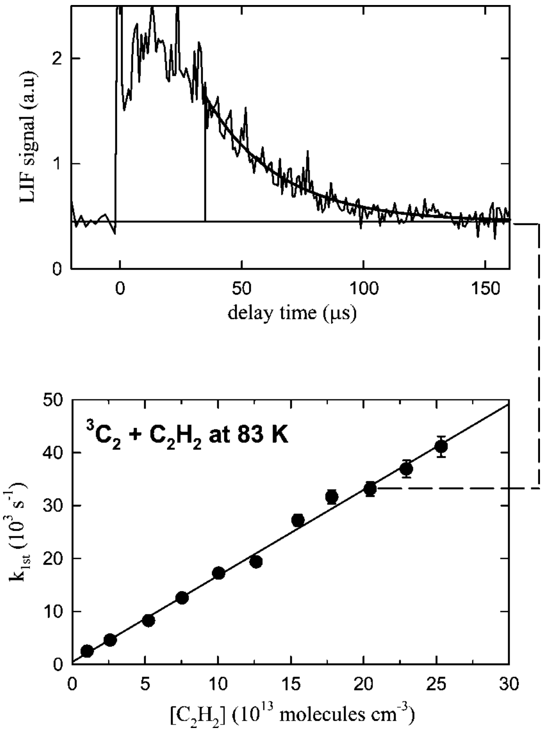

Figure 1. Upper panel: decay of $^3C_2$ LIF signal at 83 K in the presence of C_2H_2 ($[C_2H_2] = 2.0 \times 10^{14}$ molecules cm^{-3}) and N_2 buffer ($[N_2] = 4.9 \times 10^{16}$ molecules cm^{-3}), fit to a single exponential function. Lower panel: plot of pseudofirst-order rate coefficients for removal of $^3C_2$ as a function of C_2H_2 concentration yielding a value for the second order rate coefficient of $k = (1.62 \pm 0.18) \times 10^{-10}$ cm^3 $molecules^{-1}$ s^{-1}.

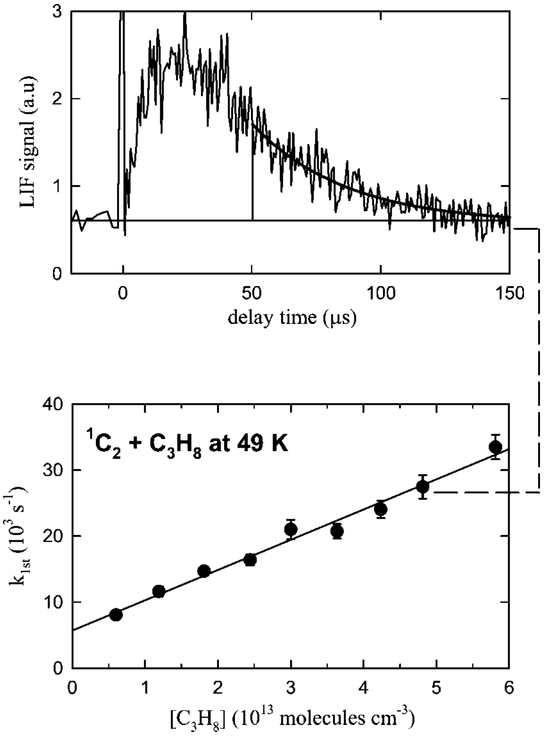

Figure 2. Upper panel: decay of $^1C_2$ LIF signal at 49 K in the presence of C_3H_8 ($[C_3H_8] = 4.8 \times 10^{13}$ molecules cm^{-3}) and He buffer ($[He] = 1.04 \times 10^{17}$ atoms cm^{-3}), fit to a single exponential function. Lower panel: plot of pseudofirst-order rate coefficients for removal of $^3C_2$ as a function of C_3H_8 concentration yielding a value for the second-order rate coefficient of $k = (4.58 \pm 0.63) \times 10^{-10}$ cm^3 $molecules^{-1}$ s^{-1}.

reagent or the buffer gas, molecular oxygen was introduced in order to quench the triplet state $^3C_2$. This process was found to be very efficient from 200 down to 50 K.[15] At lower temperatures (24 and 36 K), quenching by O_2 was no longer effective, and experiments were carried out for a mixture of $^1C_2$ and $^3C_2$, whereas at room temperature, O_2 was also introduced to obtain an equilibrated population of triplet and singlet states.[15] Possible consequences of this will be discussed below.

Hydrocarbon reagents were mixed with oxygen and the buffer gas before passing into the reservoir and expanding through the Laval nozzle. The flows of O_2 (99.998%), CH_4 (99.995%), C_2H_4 (99.95%), C_2H_6 (99.995%), C_3H_8 (99.95%), all from Air Liquide, C_2H_2 (99.6%, AGA), and carrier gas (N_2, He and Ar; Air Liquide, 99,995%) were taken directly from cylinders and regulated by means of calibrated Tylan mass flow controllers.

3. Results and discussion

3.1. General Considerations. The measured rate coefficients for both C_2 states in reactions with CH_4, C_2H_6, C_3H_8, C_2H_2, and C_2H_4 are summarized in Tables 1–5. Tables also detail the main flow conditions for each study. The quoted uncertainties include contribution from statistical and 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%.

The removal of $^3C_2$ by methane was not studied because for the triplet state, previous investigations[17,19,20,25] at room temperature and at higher temperatures showed that the rate coefficient was extremely low. Only upper limits were indicated by the authors with the exception of the study carried out by Pasternack et al.[20] which lead to an evaluation of the temperature dependence of the rate coefficient of $(1.65 \pm 0.2) \times 10^{-11}$ $\exp(-(2800 \pm 55)/T)$ cm^3 $molecules^{-1}$ s^{-1} in the temperature range 337−605 K. The high energy barrier revealed by this work and the very low rate coefficient that was inferred at room temperature strongly suggest that it will be even smaller at lower temperatures.[46,47] In view of this and the lower limit of 10^{-12} cm^3 $molecules^{-1}$ s^{-1} for measurable rate coefficients in the CRESU apparatus, it was decided not to attempt low-temperature measurements. For the same reason, measurements were only carried out at 200 and 300 K in the case of C_2H_6 (see Table 2). Figures 3–7 present the temperature dependence of the rate coefficients that we obtained for the five above-mentioned hydrocarbons along with previous experimental measurements.

As already specified, measurements at 24 and 36 K were carried out for a mixture of $^1C_2$ and $^3C_2$ because relaxation of the triplet state by oxygen becomes inefficient below 49 K.[15] Because it is not obvious whether $^3C_2$ will be removed by reaction or/and collisional relaxation by hydrocarbons, a case-by-case discussion is required here to decide whether or not the observed temporal evolution of $^1C_2$ at these two temperatures is purely due to reaction with the hydrocarbon reactant or also includes a contribution from the $^3C_2$ quenching. As mentioned earlier, for CH_4 and also C_2H_6, at room temperature, the removal of $^3C_2$ was found to be very slow or even not measurable in previous studies.[17,19,25] This is certainly still true at very low temperatures, leading to the conclusion that the rate coefficients measured at 36 and 24 K for $^1C_2$ are valid, and the decrease in reactivity observed in the case of the reaction $^1C_2 + C_2H_6$ (Figure 4) may then be due to the existence of a small energy barrier. Concerning C_3H_8, the reactivity for $^1C_2$ at 36 K was found to be two times less than at 49 K and about three times less at 24 K (Figure 5). This significant decrease might suggest that relaxation from the triplet state is taking place, causing the

TABLE 1: Results for the Kinetics of the Reaction $^1C_2 + CH_4$

			CH_4				
			$^1C_2$			$^3C_2$	
T/K	buffer gas	[buffer] 10^{16} molecules cm^{-3}	[O_2] 10^{16} molecules cm^{-3}	[CH_4] 10^{12} molecules cm^{-3}	k_{2nd} 10^{-11} cm^3 molecules^{-1} s^{-1}	[CH_4] 10^{12} molecules cm^{-3}	k_{2nd} 10^{-11} cm^3 molecules^{-1} s^{-1}
300	N_2	11.2	0.6	260−2475	0.9 ± 0.2[a]		
200	N_2	5.2	0.3	60−680	1.0 ± 0.2		
145	N_2	9.2	0.4	75−1475	1.1 ± 0.2		
83	N_2	4.9	0.1	60−630	1.2 ± 0.2		
49	He	10.4	0.3	120−1225	1.9 ± 0.3		
36	He	5.3		44−460	1.4 ± 0.6		
24	He	18.3		13−150	1.3 ± 0.5		

[a] Uncertainties include systematic errors estimated to be 10% and statistical errors $\pm t\sigma$ where σ is the standard error obtained from the fit of the second-order plot and t is the appropriate value of the Student′s t distribution for the 95% confidence interval.

TABLE 2: Results for the Kinetics of the Reaction of $^1C_2$ and $^3C_2$ with C_2H_6

			C_2H_6				
			$^1C_2$			$^3C_2$	
T/K	buffer gas	[buffer] 10^{16} molecules cm^{-3}	[O_2] 10^{16} molecules cm^{-3}	[CH_4] 10^{12} molecules cm^{-3}	k_{2nd} 10^{-11} cm^3 molecules^{-1} s^{-1}	[CH_4] 10^{12} molecules cm^{-3}	k_{2nd} 10^{-11} cm^3 molecules^{-1} s^{-1}
300	N_2	11.9−10.3	0.6	37−133	12.8 ± 3.1[a]	385−3850	1.2 ± 0.2
200	N_2	5.2	0.3	4−47	15.0 ± 3.8	210−1550	1.3 ± 0.3
145	N_2	9.2	0.4	11−100	17.7 ± 2.5		
83	N_2	4.9	0.1	2−44	23.1 ± 4.0		
49	He	10.4	0.3	8−82	34.3 ± 5.3		
36	He	5.3		3−33	26.6 ± 5.7		
24	He	18.3		10−95	20.5 ± 5.3		

[a] Uncertainties include systematic errors estimated to be 10% and statistical errors $\pm t\sigma$ where σ is the standard error obtained from the fit of the second-order plot and t is the appropriate value of the Student′s t distribution for the 95% confidence interval.

TABLE 3: Results for Kinetics of the Reaction of $^1C_2$ and $^3C_2$ with C_3H_8

			C_3H_8				
			$^1C_2$			$^3C_2$	
T/K	buffer gas	[buffer] 10^{16} molecules cm^{-3}	[O_2] 10^{16} molecules cm^{-3}	[C_3H_8] 10^{12} molecules cm^{-3}	k_{2nd} 10^{-11} cm^3 molecules^{-1} s^{-1}	[C_3H_8] 10^{12} molecules cm^{-3}	k_{2nd} 10^{-11} cm^3 molecules^{-1} s^{-1}
300	N_2	11−10.1	0.6	20−80	15.0 ± 4.1[a]	60−560	1.4 ± 0.2
200	N_2	5.2	0.3	3−35	25.9 ± 6.6	80−985	1.3 ± 0.2
145	N_2	9.2	0.4	6−75	29.4 ± 4.8	70−970	1.8 ± 0.2
83	N_2	4.9	0.1	3−57	34.0 ± 5.7	30−305	2.8 ± 0.3
53	Ar	20.2				10−100	1.8 ± 0.3
49	He	10.4	0.3	6−60	45.8 ± 6.3		
36	He	5.3		10−100	23.1 ± 2.8	80−310	0.8 ± 0.2
24	He	18.3		6−72	16.2 ± 5.1		

[a] Uncertainties include systematic errors estimated to be 10% and statistical errors $\pm t\sigma$ where σ is the standard error obtained from the fit of the second-order plot and t is the appropriate value of the Student′s t distribution for the 95% confidence interval.

measured rate coefficient for the singlet state to be depressed. Nevertheless, although the removal of $^3C_2$ by C_3H_8 was found to be quite rapid at room temperature ($\sim 10^{-11}$ cm^3 molecules^{-1} s^{-1}, Figure 5), our study showed that at 24 K, the rate coefficient was below the sensitivity of our experiment. This is at least two orders of magnitude lower than the measured rate coefficient of the removal of $^1C_2$ in the presence of C_3H_8 at this temperature (see Table 3), and therefore, it is unlikely that our results at temperatures below 49 K for $^1C_2$ have been influenced by cascading from $^3C_2$.

For the unsaturated hydrocarbons C_2H_2 and C_2H_4, the removal of the triplet state $^3C_2$ below 49 K was found to be fast. For acetylene, however, the rate coefficients obtained were at least three times lower than for $^1C_2$ at the same temperature, whereas in the case of ethylene, the measured rate coefficients were about a factor of 2 less. As it is here impossible to separate the contribution of relaxation from that of reactivity for this removal, it is not possible to state firmly that from our experiments, the rate coefficients for $^1C_2 + C_2H_2$ and C_2H_4 are not affected by the presence of $^3C_2$. We therefore recommend considering measurements below 49 K as being lower limits for the reactivity of $^1C_2$ with C_2H_2 and C_2H_4 (see Figures 6 and 7).

3.2. Reactivity of $^1C_2$. As can be appreciated in Figures 3–7, the rate coefficients for the reactivity of hydrocarbons with $^1C_2$ are close to the collisional limit in the gas phase with the exception of methane for which rate coefficients are found to be one order of magnitude lower than for other species. Both unsaturated species, C_2H_2 and C_2H_4, react faster than the saturated species CH_4, C_2H_6, and C_3H_8. In all cases, measured rate coefficients show slight increase as the temperature is decreased from 300 to 49 K.

TABLE 4: Results for the Kinetics of the Reaction of $^1C_2$ and $^3C_2$ with C_2H_2

			C_2H_2				
			$^1C_2$			$^3C_2$	
T/K	buffer gas	[buffer] 10^{16} molecules cm^{-3}	$[O_2]$ 10^{16} molecules cm^{-3}	$[C_2H_2]$ 10^{12} molecules cm^{-3}	k_{2nd} $10^{-11} cm^3$ molecules^{-1} s^{-1}	$[C_2H_2]$ 10^{12} molecules cm^{-3}	k_{2nd} 10^{-11} cm^3 molecules^{-1} s^{-1}
300	**N_2**	11.2−10.6	0.6	40−140	24.4 ± 5.1[a]	45−380	8.7 ± 1.1
200	**N_2**	5.2	0.3	8−40	25.6 ± 5.8	55−535	9.9 ± 1.1
145	**N_2**	9.3	0.4	15−60	43.9 ± 5.9	120−1060	12.2 ± 1.4
83	**N_2**	4.9	0.1	5−55	48.5 ± 6.0	10−255	16.2 ± 1.8
49	He	10.4	0.3	10−50	48.2 ± 8.7	35−450	14.9 ± 2.4
36	He	5.3	-	6−35	47.7 ± 7.9	35−355	9.2 ± 1.8
24	He	18.3	-	11−130	27.4 ± 4.4	20−120	8.1 ± 1.7

[a] Uncertainties include systematic errors estimated to be 10% and statistical errors ±*tσ* where *σ* is the standard error obtained from the fit of the second-order plot and *t* is the appropriate value of the Student′s *t* distribution for the 95% confidence interval.

TABLE 5: Results for the kinetics of the reaction of $^1C_2$ and $^3C_2$ with C_2H_4

			C_2H_4				
			$^1C_2$			$^3C_2$	
T/K	buffer gas	[buffer] 10^{16} molecules cm^{-3}	$[O_2]$ 10^{16} molecules cm^{-3}	$[C_2H_4]$ 10^{12} molecules cm^{-3}	k_{2nd} $10^{-11} cm^3$ molecules^{-1} s^{-1}	$[C_2H_4]$ 10^{12} molecules cm^{-3}	k_{2nd} 10^{-11} cm^3 molecules^{-1} s^{-1}
300	**N_2**	11−10.9	0.6	30−120	18.2 ± 3.9[a]	40−400	9.7 ± 1.2
200	**N_2**	5.2	0.3	5−30	32.4 ± 5.5	45−285	9.5 ± 1.6
145	**N_2**	9.3	0.4	11−126	38.0 ± 5.2	24−240	18.2 ± 2.4
83	**N_2**	4.9	0.1	5−53	36.3 ± 5.5	20−63	28.7 ± 3.7
49	**He**	10.4	0.3	7−56	45.1 ± 7.1	35−135	20.8 ± 3.6
36	**He**	5.3	-	8−77	34.9 ± 4.4	20−190	21.7 ± 3.4
24	**He**	18.3	-	12−125	34.3 ± 5.5	13−90	15.9 ± 3.0

[a] Uncertainties include systematic errors estimated to be 10% and statistical errors ±*tσ* where *σ* is the standard error obtained from the fit of the second-order plot and *t* is the appropriate value of the Student′s *t* distribution for the 95% confidence interval.

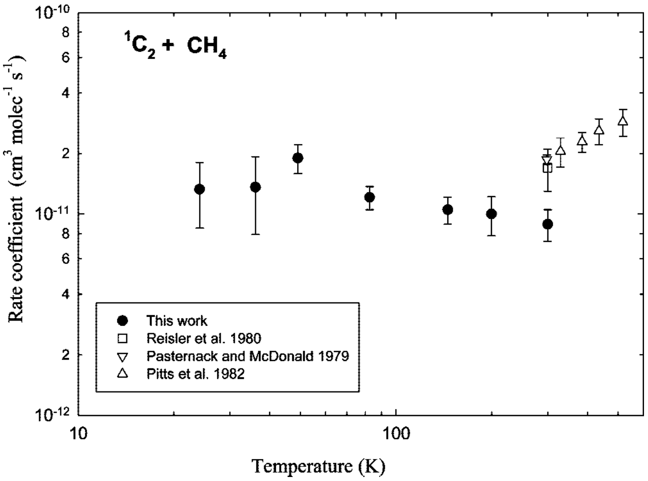

Figure 3. Rate coefficients for the reaction of $^1C_2$ with CH_4 as a function of temperature, displayed on a log−log scale.

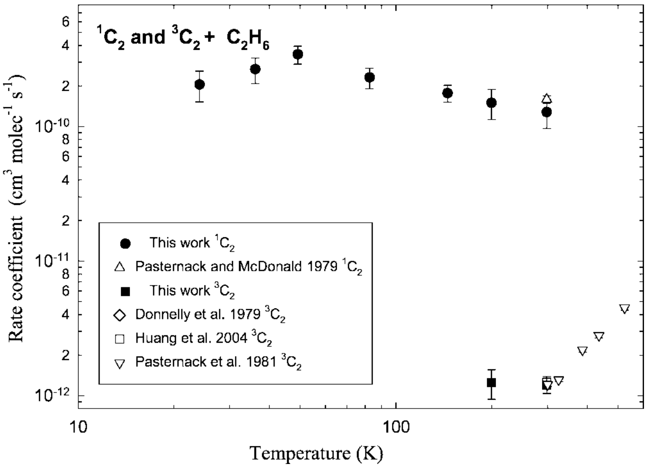

Figure 4. Rate coefficients for the reaction of $^1C_2$ and $^3C_2$ with C_2H_6 as a function of temperature, displayed on a log−log scale.

Data from previous studies are also included in Figures 3–7. In the case of methane, the temperature dependence displays a change in its evolution. At temperatures higher than 300 K, a positive dependence was observed,[23] whereas our data show a very slight negative dependence down to 24 K. This behavior has been observed previously for other reactions[47,48] and has been explained theoretically in terms of a two-transition state model.[47,49,50]

Very recently, a low-temperature study was undertaken by Daugey et al.[14] by using the mini CRESU apparatus available at the Université de Bordeaux 1 (France). They studied the reactivity of $^{1,3}C_2$ with four hydrocarbons: acetylene, methylacetylene, allene, and propene over the temperature range 77−296 K. On the basis of standard PLP-LIF methods for the production (from C_2Br_4 photolysis at 266 nm) and detection of the radical, a feature of this work was the simultaneous detection of the two states of the dicarbon radical. Results for C_2H_2 are plotted in Figure 6, showing a very good agreement with our measurements below 200 K. At higher temperatures, however, our data for $^1C_2$ are somewhat smaller. This difference was also observed for C_3H_8, C_2H_4, and, to a less extent, C_2H_6 when comparing our measurements to previous experimental studies. Our room temperature data, however, were always in good agreement with the general trend observed at lower temperatures, giving a reasonable level of confidence to these sets of measurements. Several additional experiments were undertaken in the case of the $^1C_2 + C_2H_4$ reaction which was, perhaps, the

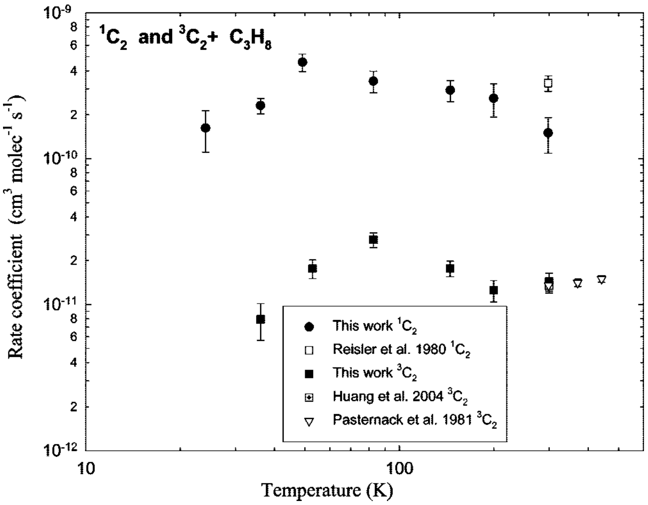

Figure 5. Rate coefficients for the reaction of $^1C_2$ and $^3C_2$ with C_3H_8 as a function of temperature, displayed on a log−log scale.

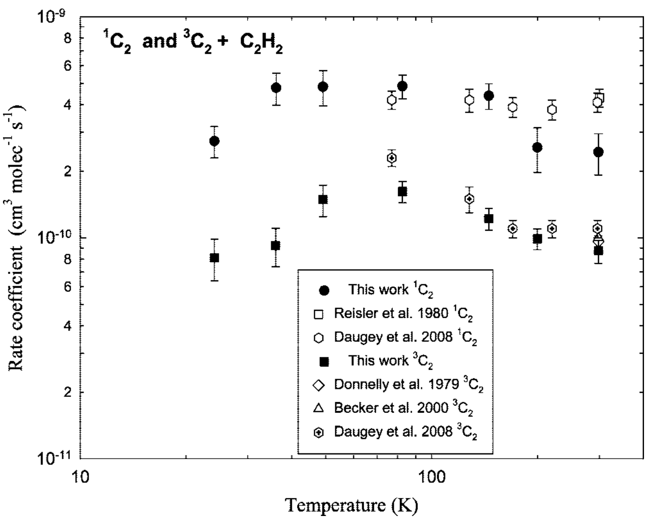

Figure 6. Rate coefficients for the reaction of $^1C_2$ and $^3C_2$ with C_2H_2 as a function of temperature, displayed on a log−log scale.

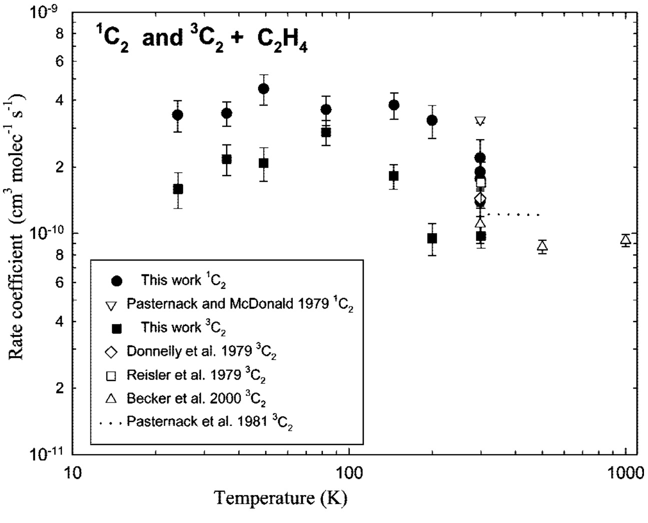

Figure 7. Rate coefficients for the reaction of $^1C_2$ and $^3C_2$ with C_2H_4 as a function of temperature, displayed on a log−log scale.

hardest to understand, because the previous measurement by Pasternack and McDonald[22] at room temperature (3.3×10^{-10} cm^3 molecules^{-1} s^{-1}) is in good agreement with an extrapolation of our measurements in the range 24−200 K, whereas at 300 K, we obtained a lower value (2.2 ± 0.4) $\times 10^{-10}$ cm^3 molecules^{-1} s^{-1}. Because in their work Pasternack and McDonald did not use O_2 in contrast to our study, we made an experiment in nitrogen without addition of O_2 and found a rate of (1.9 ± 0.2) $\times 10^{-10}$ cm^3 molecules^{-1} s^{-1}. Another experiment, carried out for a nitrogen density which was lowered by a factor of 2, lead to a rate coefficient of (1.4 ± 0.2) $\times 10^{-10}$ cm^3 molecules^{-1} s^{-1}, consistent with the other experiments. Finally, changing nitrogen to argon led to a rate coefficient still in agreement with the first three measurements, (1.8 ± 0.4) $\times 10^{-10}$ cm^3 molecules^{-1} s^{-1}. These rate coefficients are all presented in Figure 7, but only the mean value of these four experiments is indicated in table 5 for clarity. No additional experiments were carried out for the $^1C_2 + C_2H_2$ reaction.[26] For this reactant, Daugey et al.[14] explored the possibility of interferences between the two states of the dicarbon radical resulting from intersystem crossing induced by the hydrocarbon reactant. They measured the rate coefficient of the reaction $^1C_2 + C_3H_6$ at 77 and 220 K with and without O_2 and did not observe any differences in the results obtained as we also have not seen for C_2H_4 at room temperature. They concluded that intersystem crossing was not operating for the reaction of $^1C_2$ with propene and generalized this conclusion to the other coreactants studied. It is presently rather difficult to reconcile other studies undertaken at room temperature with our work, and no obvious explanation can be proposed to elucidate this discrepancy.

3.3. Removal of $^3C_2$ and Comparison with $^1C_2$.

The most fascinating aspect of the reactivity of the C_2 molecule is the large difference in reactivity of the $^1C_2$ and $^3C_2$ species. Unlike the ground state, the reactivity of the triplet state shows significant differences as a function of temperature and with respect to the nature of the reactants. For all hydrocarbons, $^3C_2$ reactivity was found to be significantly smaller than that of $^1C_2$. This is especially striking for alkanes for which the rate coefficients, when measurable, were found to be at least one order of magnitude lower than for the corresponding reaction with $^1C_2$ in the whole temperature range. It is also interesting here to note that the reactivity increases considerably with the carbon chain length of the reactant molecule. Whereas the reactivity for $^3C_2 + CH_4$ is expected to be (much) lower than 3×10^{-14} cm^{-3} molecules^{-1} s^{-1} below 300 K according to previous studies,[17,19,20,25] it is at least two orders of magnitude higher for $^3C_2 + C_2H_6$ and three orders of magnitude higher for $^3C_2 + C_3H_8$. This agrees with previous experimental studies of the reactivity of $^3C_2$ with alkanes up to octane C_8H_{18}[21,24,25] and with alcohols as well.[51] At room temperature, Huang et al.[25] derived a positive linear dependence of the removal rate coefficient for reactions $^3C_2 + C_nH_{2n+2}$ ($3 \leq n \leq 8$) as a function of the number of CH_2 groups and concluded that these reactions may proceed via the hydrogen abstraction mechanism, as has been assumed by others.[21] Becker et al.[24] proposed that this behavior is the result of the increasing inductive electron effect of larger alkyl groups.

Our results are plotted in Figures 4 and 5 for C_2H_6 and C_3H_8, respectively, along with previous measurements from Donnelly and Pasternack,[17] Pasternack et al.,[21] and Huang et al.[25] Our rate coefficient obtained for $^3C_2 + C_2H_6$ at room temperature agrees with previous experimental studies. However, the value at 200 K seems to break with the trend of positive dependence of the rate coefficient on temperature displayed at higher temperatures in the investigation of Pasternack et al.[21] An experiment was then performed at 145 K, but no observable decay of $^3C_2$ was detected when the concentration of C_2H_6 was varied, indicating that the rate coefficient is certainly lower than 10^{-12} cm^{-3} molecules^{-1} s^{-1} and therefore that the process probably possesses an energy barrier. Pasternack et al.[21] estimated an activation energy of 7.66 kJ mol^{-1} over the limited temperature range 300−524 K. Concerning C_3H_8, our results at room temperature are in very good agreement with those from Pasternack et al.[21] and Huang et al.[25] The result obtained by Reisler et al.[19] is surprisingly very different because they reported a rate coefficient for the reactivity of $^3C_2$ with C_3H_8 which is an order of magnitude larger (1.66×10^{-10} cm^3 molecules^{-1} s^{-1}) than that measured by others. For clarity, this data was not included in Figure 5. The temperature dependence that is now available from 24 to 441 K presents a behavior that may suggest that the mechanisms involved in the reaction are different according to the range of temperature. The rate coefficient is found to decrease slightly from 441 to 200 K, then to increase by a factor of 2 down to ~80 K, and finally to decrease significantly so that no measurements were possible at 24 K, probably indicating that a very small barrier is present along the reactive pathway.

For the unsaturated hydrocarbons C_2H_2 and C_2H_4, our measured rate coefficients were at least one order of magnitude higher than those for alkanes. Data were found to be close to the collisional limit, although they were still significantly lower than those obtained for $^1C_2$: typically a factor of 2 for C_2H_4 and 3 for C_2H_2 over the temperature range of this study. In this regard, Becker et al.[24] pointed out that the reactivity of $^3C_2$ displays a strong positive dependence on the electron density of the reactive center of the reagent molecule. In other words, the number of π bonds in the reactant molecule increases significantly the reactivity of $^3C_2$, indicating that it is strongly electrophilic. In our present study, however, this rule does not appear to hold for C_2H_4 and C_2H_2, especially when the temperature is below 200 K. Although the rate coefficients are very similar at 300 and 200 K, they significantly deviate from each other below 200 K, with C_2H_4 being more reactive than C_2H_2.

For C_2H_4, our data at room temperature are in good agreement with those from Becker et al.[24] and Pasternack et al.,[21] whereas results from Reisler et al.[18] and Donnelly and Pasternack[17] are somewhat higher (see Figure 7). For C_2H_2, the agreement is very good with data from Becker et al.[24] and Donnelly and Pasternack[17] at room temperature as well as with the very recent study from Daugey et al.,[14] who measured the rate coefficient of the removal of $^3C_2 + C_2H_2$ between 296 and 77 K. A slight deviation is observed however at ~80 K, where we measured a rate coefficient of $(1.62 \pm 0.18) \times 10^{-10}$ cm^3 molecules^{-1} s^{-1}, which is 30% lower than the value obtained by Daugey et al., $(2.30 \pm 0.20) \times 10^{-10}$ cm^3 molecules^{-1} s^{-1}.

Finally, for C_3H_8, C_2H_2, and C_2H_4, our data show a slight negative temperature dependence rising to a maximum as the temperature is lowered between 100 and 50 K depending on the system. The decrease in reactivity may be compatible with the existence of a small energy barrier in all cases.

3.4. Possible Reaction Products. The experiments described here do not permit the determination of product branching ratios for the reactions studied. Nevertheless, thermodynamic and kinetic considerations can give considerable insight into the likely products, and for almost all the reactions reported here, there have been prior theoretical and/or experimental studies which, although neither numerous nor always pertinent, do provide some insight into these systems and will now be summarized.

The significant variations in overall reactivity between $^1C_2$ and $^3C_2$ toward CH_4, C_2H_2, C_2H_4, C_2H_6, and C_3H_8 serve as a reminder that product branching ratios may also vary strongly as a function of the electronic state of the C_2 reagent, a fact that is not always taken into account in experimental studies of such ratios for these two species.

3.4.a. $C_2 + CH_4$. Only $^1C_2$ shows significant reactivity toward CH_4, and Pitts et al.,[23] in their early temperature-dependent study of the kinetics reaction concluded, by comparing mechanisms of reactions of similar species, that the reaction proceeds by insertion of C_2 into the C−H bond. In the mid-1990s, two theoretical studies were published on this reaction. Horner et al.[41] performed ab initio calculations at the MP2/6-31G* level and found that $^1C_2$ and CH_4 can react together by an insertion mechanism to yield the methylvinylidene intermediate, on a potential which, after optimization at the G2 level and inclusion of zero-point energy, showed no barrier above the reagent energy. They further showed that the methylvinylidene intermediate can isomerize to form methyl acetylene through a transition state lying below the energy of methylvinylidene. However, they did not consider further bond fission to yield bimolecular products, because their main interest was in modeling C_2 addition to hydrogen-terminated diamond surfaces. In what appears to have been a parallel study, Richardson and Francisco[40] performed ab initio calculations at the UMP2/6-311G(2df,2p) level by using the QCISD(T) wave function to investigate the full reaction

$$^1C_2 + CH_4 \rightarrow C_2H + CH_3 \qquad \Delta_r H^{\ominus} = -61.1 \text{ kJ mol}^{-1} \tag{1}$$

(where the estimated experimental heat of reaction is given as by Richardson and Francisco). They found that this reaction proceeds via a methylvinylidene intermediate (as predicted by Horner et al.[41]) over an almost barrierless potential. It would seem likely, therefore, that the products of the $^1C_2 + CH_4$ reaction are the radical species $C_2H + CH_3$. This, combined with the relatively rapid low-temperature rate coefficients measured in this study, has important implications for the growth of hydrocarbons in low-temperature environments such as Titan's atmosphere.

3.4.b. $C_2 + C_2H_6$, C_3H_8. To our knowledge, no experimental or theoretical studies have been undertaken which relate directly to the products of reactions of $^1C_2$ and $^3C_2$ with the saturated species C_2H_6 and C_3H_8. Pasternack and McDonald[22] suggest for the reaction of $^1C_2$ with C_2H_6 a hydrogen abstraction mechanism

$$^1C_2 + C_2H_6 \rightarrow C_2H + C_2H_5 \qquad \Delta_r H^{\ominus} = -103.8 \text{ kJ mol}^{-1} \tag{2}$$

(where the estimated experimental heat of reaction is as given by Pasternack and McDonald).

Huang et al.[25] propose on the basis of the relative reactivity of primary, secondary, and tertiary hydrogens the equivalent mechanism for the reaction of $^3C_2$ with alkanes

$$^3C_2 + RH \rightarrow C_2H + R \tag{3}$$

with heats of reaction from −84 to −126 kJ mol^{-1} for ground state $C_2H(X^2\Sigma^+)$ product and from −42 to −84 kJ mol^{-1} for $C_2H(A^2\Pi)$.

3.4.c. $C_2 + C_2H_2$, C_2H_4. The products of the reactions of $^1C_2$ and $^3C_2$ with C_2H_2[27–31,33] and C_2H_4[27,31,34–36,42,44] have been studied both experimentally and theoretically in a series of joint studies by the groups of Kaiser and Mebel. In addition, Casavecchia and co-workers have recently studied the reactions with C_2H_2 by the crossed molecular beams technique.[32] The main conclusions of these studies will be briefly discussed below.

The crossed molecular beams experiments of Kaiser and co-workers and Casavecchia and co-workers are incapable of distinguishing the products resulting from reactions of $^1C_2$ and $^3C_2$ which are both present in their dicarbon beams in unknown but no doubt differing proportions according to the method of C_2 generation (laser ablation for Kaiser and co-workers and discharge for Casavecchia and co-workers). The main findings for the reaction of $^1C_2$ and $^3C_2$ with C_2H_2 are that the only products detected (at the relatively high collision energies employed in these experiments of 10–50 kJ mol^{-1}) are the 1,3butadiynyl radical plus a hydrogen atom

$$^1C_2 + C_2H_2 \rightarrow C_4H + H \qquad \Delta_r H^\ominus = -33.3 \text{ kJ mol}^{-1} \quad (4)$$

$$^3C_2 + C_2H_2 \rightarrow C_4H + H \qquad \Delta_r H^\ominus = -41.9 \text{ kJ mol}^{-1} \quad (5)$$

(where the estimated experimental heats of reaction are as given by Gu et al.[30]). No evidence was found for the pathway leading to $C_4 + H_2$. This addition–elimination pathway is consistent with what has been observed in other types of product branching studies for reactions of carbon-containing radicals with unsaturated hydrocarbons, for example, for the reactions of C_2H_2 with CH and CN.[52–54] Theoretical potential energy surface calculations performed by Mebel and co-workers[27,28,30,31,33] support this conclusion for the case of both $^1C_2$ and $^3C_2$ with C_2H_2, confirming the existence of a barrierless pathway leading to these products.

Kaiser, Mebel, and co-workers have also performed a combined crossed molecular beam and ab initio investigations for the reactions of $^1C_2$ and $^3C_2$ with C_2H_4. The most recent crossed beam experimental studies[31,36] at collision energies of 10–40 kJ mol^{-1} indicate that the major products of the reaction of $^1C_2$ and $^3C_2$ with C_2H_4 are the *i*-C_4H_3 radical and a hydrogen atom

$$^1C_2 + C_2H_4 \rightarrow i\text{-}C_4H_3 + H \qquad \Delta_r H^\ominus = -156.1 \text{ kJ mol}^{-1} \quad (6)$$

$$^3C_2 + C_2H_4 \rightarrow i\text{-}C_4H_3 + H \qquad \Delta_r H^\ominus = -164.7 \text{ kJ mol}^{-1} \quad (7)$$

(where the estimated experimental heats of reaction are as given by Gu et al.[31]). RRKM calculations on an ab initio potential energy surface performed by Mebel et al.[44] indicate roughly equal formation of *i*-C_4H_3 + H (41.3% at zero collision energy) and $C_2H_2 + CCH_2$ (48.6% at zero collision energy) from the reaction $^1C_2 + C_2H_4$, with a significant formation of $H_2CCCC + H_2$ (6.1%). However, no experimental evidence is forthcoming to support the presence of these other product channels, and the detection of C_4H_3 in $C_2H_4/O_2/Ar$ flames (where both C_2 and C_2H_4 are abundant) by Westmoreland et al.[55] and specifically of *i*-C_4H_3 in fuel rich flames by Hansen et al.[56] serve to support this conclusion.

Earlier theoretical work of Mebel and co-workers[27,34,42] for the reaction of $^3C_2$ with C_2H_4 had indicated the presence of a small entrance barrier of 15.5 kJ mol^{-1}. The present low-temperature kinetics results indicate that rate coefficients for this reaction remain close to the collisional rate even at the lowest temperatures, confirming the conclusion of Kaiser et al.[27] themselves who admit that their calculation of a 15.5 kJ mol^{-1} entry channel barrier is probably an overestimate. This is supported by later calculations[31,36,42] by the same group showing no barrier on the $^3C_2 + C_2H_4$ surface.

In previous experimental studies of the reactivity of small carbon containing radical species such as C(^{3}P),[57] CH,[58] and C_2H[59] with unsaturated hydrocarbons, it has been argued that a significant reaction mechanism probably involves the incorporation of one, in the case of C(^{3}P) and CH, or two, in the case of C_2H, more carbon atoms into the molecule and the elimination of a hydrogen atom,

$$C(^3P) + C_nH_m \rightarrow C_{n+1}H_{m-1} + H \quad (8)$$

$$CH + C_nH_m \rightarrow C_{n+1}H_m + H \quad (9)$$

$$C_2H + C_nH_m \rightarrow C_{n+2}H_m + H \quad (10)$$

thereby forming molecules containing a larger number of carbon atoms. Taking into account the above discussion, we propose that reactions of C_2 with unsaturated molecules can also be a source of long chain hydrocarbons via the following types of rapid, barrierless addition–elimination reactions.

$$C_2 + C_nH_m \rightarrow C_{n+2}H_{m-1} + H \quad (11)$$

In view of the rapidity of these reactions down to very low temperatures as demonstrated in this study, this has important implications for the growth of carbon chains in low-temperature environments such as dense interstellar clouds and planetary atmospheres.

3.5. Astrophysical Interest. As mentioned in the Introduction, the C_2 radical is involved in the chemistry of astrophysical environments either in the Solar system or in the interstellar medium. Only the ground state is considered however. We have recently discussed in detail the possible consequences of our measurements on $^1C_2$ for the photochemistry of Titan and Giant Planets,[26] and more particularly, we drew several conclusions about the destruction routes of $^1C_2$ in the atmospheres of these bodies. Until now, $^1C_2$ was expected to be destroyed by CH_4 and H_2 in all models. Data which are presently used for the $^1C_2 + CH_4$ reaction have been extrapolated to low temperatures from the investigation by Pitts et al.[23] (see Figure 3), leading to notable differences with our measurements. Furthermore, our work shows that reactions of $^1C_2$ with C_2H_2, C_2H_4, and C_2H_6 are significant destruction routes of the dicarbon radical that must be taken into account as well. Although the abundances of these hydrocarbons are substantially smaller than that of CH_4 in Titan's atmosphere, their reactivity is significantly higher. As a consequence, these processes become major destruction pathways at altitudes greater than 600 km, whereas the reaction involving H_2 has no appreciable impact.[26] This is not the case for Giant Planets where H_2 is the main gas. For Saturn and Uranus, however, reactions with C_2H_2 and C_2H_6 should be taken into account as well.[26]

In interstellar clouds and more precisely in the so-called dark clouds, where the more complex interstellar molecules have been discovered, the destruction route for $^1C_2$ is assumed to be via the reaction with oxygen atoms. In recent models,[60] the rate coefficient for this reaction is taken as $\sim 10^{-10}$ cm^3 molecules^{-1} s^{-1}, which seems rather reasonable when considering a recent study by Becker et al.[24] who measured this value for the reaction involving the triplet state $^3C_2$ which is expected to be less reactive than $^1C_2$. As the abundance of oxygen atoms is several orders of magnitude higher than that of the hydrocarbons studied here, it is unlikely that reactions of $^1C_2$ with hydrocarbons will play a major role in the chemistry. We cannot discount the possibility, however, that they can be minor pathways to the formation of more complex carbon-based radicals.

In the case of circumstellar envelopes (CSEs) of carbon-rich stars, the reactivity of $^1C_2$ is expected to play an important role in the hydrocarbon growth. In the model of Millar and Herbst,[61] several reactions of $^1C_2$ with different hydrocarbons are considered, but among them, only C_2H_2 has been studied here. The rate coefficient used in this model for the reaction $^1C_2 + C_2H_2$ (a potential source of C_4H) was considered to be constant with temperature and of magnitude $\sim 1.0 \times 10^{-10}$ cm^3 molecules^{-1} s^{-1}. Very recently however, this value has been updated by using our new measurements, leading to an increase of the rate coefficient by at least a factor of 4[1] (see also The UMIST Database for Astrochemistry Web site).[62] Reactions with C_2H_4 and CH_4, which were absent in the chemical scheme, have also been added. To our knowledge, no specific consequences of this upgrading have been published till now.

Finally, it is also worth mentioning that the triplet state is at present completely ignored in photochemical models, although it has been observed in CSEs.[63] The current investigation demonstrates that its reactivity can be significant even so and especially for unsaturated species.

4. Conclusions

This study has shown that the reactivity of $^1C_2$ and $^3C_2$ with simple saturated (CH_4, C_2H_6, and C_3H_8) and unsaturated (C_2H_2 and C_2H_4) hydrocarbons can be very efficient in the temperature range 24−300 K. Between 49 and 200 K, experiments involving the ground state $^1C_2$ have been carried out in the presence of oxygen to remove completely $^3C_2$. At lower temperatures, the removal of $^1C_2$ was studied in the presence of the triplet state $^3C_2$. Our analysis, however, indicates that the rate coefficients observed for reactions of $^1C_2$ with saturated hydrocarbons should not be affected by the presence of $^3C_2$ because its removal by these hydrocarbons is very slow or not measurable below 49 K. On the other hand, the rate coefficients obtained for unsaturated hydrocarbons should be taken as lower limits below 49 K because the removal of the triplet state by C_2H_2 and C_2H_4 remains fast in this temperature range.

The reactivity of the triplet state has been found to be somewhat lower than that of the ground state. Furthermore, it is very dependent on the nature of the molecule and more specifically the number of π bonds, indicating that the triplet state is strongly electrophilic. This is less striking for the singlet state. The reactivity of the triplet state with the first three lighter alkanes increases by several orders of magnitude when the size of the alkane augments, confirming observations of previous works at room temperatures for heavier species. Finally, the temperature dependences of the rate coefficients for C_3H_8, C_2H_2, and C_2H_4 display a maximum in the temperature range 50−100 K and then decrease at lower temperatures, which is compatible with the existence of very small energy barriers.

These results have been analyzed in terms of potential destruction sources of $^1C_2$ in astrophysical environments. Although a significant impact has been demonstrated for the atmospheres of the giant planets and their satellites, quantitative conclusions cannot yet be drawn for interstellar environments. Because these processes are expected to generate new radicals as suggested above, it would be of great interest to see what kind of consequences our new data may have on the chemical models of these environments.

Acknowledgment. We thank the Programme National Physique et Chimie du Milieu Interstellaire, the Programme National Planétologie, and the European Union (RTN Network Molecular Universe, Contract MRTN-CT-2004-512302) for support. A.P. thanks the European Union for support under Contracts FMRX-CT97-0132 (DG12-MIHT) and HPRN-CT-2000-00142, and she is also grateful to the University of Rennes 1 for support. I.R.S. gratefully acknowledges support for this work from the European Union via the award of a Marie Curie Chair (Contract MEXC-CT-2004-006734, Chemistry at Extremely Low Temperatures).

References and Notes

(1) Woodall, J.; Agundez, M.; Markwick-Kemper, A. J.; Millar, T. J. *Astron. Astrophys.* **2007**, *466*, 1197.

(2) Woon, D. E. www.astrochymist.org/astrochymist_ism.html, 2008.

(3) Canosa, A.; Goulay, F.; Sims, I. R.; Rowe, B. R. Gas Phase Reactive Collisions at very Low Temperature: Recent Experimental Advances and Perspectives In *Low Temperatures and Cold Molecules*; Smith, I. W. M. , Ed.; World Scientific:Singapore,2008.

(4) Sims, I. R.; Queffelec, J. L.; Defrance, A.; Rebrion-Rowe, C.; Travers, D.; Rowe, B. R.; Smith, I. W. M. *J. Chem. Phys.* **1992**, *97*, 8798.

(5) James, P. L.; Sims, I. R.; Smith, I. W. M. *Chem. Phys. Lett.* **1997**, *272*, 412.

(6) Atkinson, D. B.; Smith, M. A. *Rev. Sci. Instrum.* **1995**, *66*, 4434.

(7) Daugey, N.; Caubet, P.; Retail, B.; Costes, M.; Bergeat, A.; Dorthe, G. *Phys. Chem. Chem. Phys.* **2005**, *7*, 2921.

(8) Spangenberg, T.; Kohler, S.; Hansmann, B.; Wachsmuth, U.; Abel, B.; Smith, M. A. *J. Phys. Chem. A* **2004**, *108*, 7527.

(9) Sims, I. R.; Queffelec, J. L.; Defrance, A.; Rebrion-Rowe, C.; Travers, D.; Bocherel, P.; Rowe, B. R.; Smith, I. W. M. *J. Chem. Phys.* **1994**, *100*, 4229.

(10) Canosa, A. *Russ. Chem. Rev.* **2007**, *76*, 1093.

(11) Ballick, E. A.; Ramsay, D. A. *Astrophys. J.* **1963**, *137*, 84.

(12) Mangir, M. S.; Reisler, H.; Wittig, C. *J. Chem. Phys.* **1980**, *73*, 829.

(13) Huang, C. S.; Li, Z. X.; Zhao, D. F.; Xin, Y.; Pei, L. S.; Chen, C. X.; Chen, Y. *Chin. Sci. Bull.* **2004**, *49*, 438.

(14) Daugey, N.; Caubet, P.; Bergeat, A.; Costes, M.; Hickson, K. M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 729.

(15) Páramo, A.; Canosa, A.; Le Picard, S. D.; Sims, I. R. *J. Phys. Chem. A* **2006**, *110*, 3121.

(16) Souza, S. P.; Lutz, B. L. *Astrophys. J.* **1977**, *216*, L49.

(17) Donnelly, V. M.; Pasternack, L. *Chem. Phys.* **1979**, *39*, 427.

(18) Reisler, H.; Mangir, M.; Wittig, C. *J. Chem. Phys.* **1979**, *71*, 2109.

(19) Reisler, H.; Mangir, M. S.; Wittig, C. *J. Chem. Phys.* **1980**, *73*, 2280.

(20) Pasternack, L.; Baronavski, A. P.; McDonald, J. R. *J. Chem. Phys.* **1980**, *73*, 3508.

(21) Pasternack, L.; Pitts, W. M.; McDonald, J. R. *Chem. Phys.* **1981**, *57*, 19.

(22) Pasternack, L.; McDonald, J. R. *Chem. Phys.* **1979**, *43*, 173.

(23) Pitts, W. M.; Pasternack, L.; McDonald, J. R. *Chem. Phys.* **1982**, *68*, 417.

(24) Becker, K. H.; Donner, B.; Dinis, C. M. F.; Geiger, H.; Schmidt, F.; Wiesen, P. *Z. Phys. Chem. (Muenchen)* **2000**, *214* (4), 503.

(25) Huang, C. S.; Zhu, Z. Q.; Xin, Y.; Pei, L. S.; Chen, C. X.; Chen, Y. *J. Chem. Phys.* **2004**, *120*, 2225.

(26) Canosa, A.; Páramo, A.; Le Picard, S. D.; Sims, I. R. *Icarus* **2007**, *187*, 558.

(27) Kaiser, R. I.; Le, T. N.; Nguyen, T. L.; Mebel, A. M.; Balucani, N.; Lee, Y. T.; Stahl, F.; Schleyer, P. V.; Schaefer, H. F. *Faraday Discuss.* **2001**, *119*, 51.

(28) Kaiser, R. I.; Balucani, N.; Charkin, D. O.; Mebel, A. M. *Chem. Phys. Lett.* **2003**, *382*, 112.

(29) Gu, X. B.; Guo, Y.; Kaiser, R. I. *Int. J. Mass Spectrom.* **2005**, *246*, 29.

(30) Gu, X. B.; Guo, Y.; Mebel, A. M.; Kaiser, R. I. *J. Phys. Chem. A* **2006**, *110*, 11265.

(31) Gu, X. B.; Guo, Y.; Zhang, F. T.; Mebel, A. M.; Kaiser, R. I. *Faraday Discuss.* **2006**, *133*, 245.

(32) Leonori,F.; Petrucci, R.; Hickson, K. M.; Segolini, E.; Le Picard, S. D.; Balucani, N.; Foggi, P.; Casavecchia, P. *Planet. Space Sci.* In press.

(33) Guo, Y.; Kislov, V. V.; Gu, X.; Zhang, F.; Mebel, A. M.; Kaiser, R. I. *Astrophys. J.* **2006**, *653*, 1577.

(34) Balucani, N.; Mebel, A. M.; Lee, Y. T.; Kaiser, R. I. *J. Phys. Chem. A* **2001**, *105*, 9813.

(35) Guo, Y.; Gu, X. B.; Kaiser, R. I. *Int. J. Mass Spectrom.* **2006**, *249*, 420.

(36) Gu, X. B.; Guo, Y.; Zhang, F. T.; Mebel, A. M.; Kaiser, R. I. *Chem. Phys.* **2007**, *335*, 95.

(37) Guo, Y.; Gu, X. B.; Zhang, F. T.; Mebel, A. M.; Kaiser, R. I. *J. Phys. Chem. A* **2006**, *110*, 10699.

(38) Guo, Y.; Gu, X. B.; Balucani, N.; Kaiser, R. I. *J. Phys. Chem. A* **2006**, *110*, 6245.

(39) Gu, X. B.; Guo, Y.; Zhang, F. T.; Mebel, A. M.; Kaiser, R. I. *Chem. Phys. Lett.* **2007**, *436*, 7.

(40) Richardson, S. L.; Francisco, J. S. *Mol. Phys.* **1994**, *83*, 1041.

(41) Horner, D. A.; Curtiss, L. A.; Dieter, D. M. *Chem. Phys. Lett.* **1995**, *233*, 243.

(42) Mebel, A. M.; Kaiser, R. I.; Lee, Y. T. *J. Am. Chem. Soc.* **2000**, *122*, 1776.

(43) Mebel, A. M.; Kislov, V. V.; Kaiser, R. I. *J. Phys. Chem. A* **2006**, *110*, 2421.

(44) Mebel, A. M.; Kislov, V. V.; Kaiser, R. I. *J. Chem. Phys.* **2006**, *125*, 133113.

(45) Dupeyrat, G.; Marquette, J. B.; Rowe, B. R. *Phys. Fluids* **1985**, *28*, 1273.

(46) Smith, I. W. M.; Sage, A. M.; Donahue, N. M.; Herbst, E.; Quan, D. *Faraday Discuss.* **2006**, *133*, 137.

(47) Sabbah, H.; Biennier, L.; Sims, I. R.; Georgievskii, Y.; Klippenstein, S. J.; Smith, I. W. M. *Science* **2007**, *317*, 102.

(48) Sims, I. R.; Queffelec, J. L.; Travers, D.; Rowe, B. R.; Herbert, L. B.; Karthaüser, J.; Smith, I. W. M. *Chem. Phys. Lett.* **1993**, *211*, 461.

(49) Klippenstein, S. J.; Georgievskii, Y. Theory of low Temperature Gas-Phase Reactions. In *Low Temperatures and Cold Molecules*; Smith, I. W. M. , Ed.; World Scientific: Singapore, 2008.

(50) Georgievskii, Y.; Klippenstein, S. J. *J. Phys. Chem. A* **2007**, *111*, 3802.

(51) Huang, C. S.; Zhu, Z. Q.; Wang, H. L.; Pei, L. S.; Chen, Y. *J. Phys. Chem. A* **2005**, *109*, 3921.

(52) Gannon, K. L.; Glowacki, D. R.; Blitz, M. A.; Hughes, K. J.; Pilling, M. J.; Seakins, P. W. *J. Phys. Chem. A* **2007**, *111*, 6679.

(53) Choi, N.; Blitz, M. A.; McKee, K.; Pilling, M. J.; Seakins, P. W. *Chem. Phys. Lett.* **2004**, *384*, 68.

(54) McKee, K.; Blitz, M. A.; Hughes, K. J.; Pilling, M. J.; Qian, H. B.; Taylor, A.; Seakins, P. W. *J. Phys. Chem. A* **2003**, *107*, 5710.

(55) Westmoreland, P. R.; Law, M. E.; Cool, T. A.; Wang, J.; McIlroy, A.; Taatjes, C. A.; Hansen, N. *Combust. Explos.* **2006**, *42*, 672.

(56) Hansen, N.; Klippenstein, S. J.; Taatjes, C. A.; Miller, J. A.; Wang, J.; Cool, T. A.; Yang, B.; Yang, R.; Wei, L. X.; Huang, C. Q.; Wang, J.; Qi, F.; Law, M. E.; Westmoreland, P. R. *J. Phys. Chem. A* **2006**, *110*, 3670.

(57) Chastaing, D.; Le Picard, S. D.; Sims, I. R.; Smith, I. W. M. *Astron. Astrophys.* **2001**, *365*, 241.

(58) Canosa, A.; Sims, I. R.; Travers, D.; Smith, I. W. M.; Rowe, B. R. *Astron. Astrophys.* **1997**, *323*, 644.

(59) Chastaing, D.; James, P. L.; Sims, I. R.; Smith, I. W. M. *Faraday Discuss.* **1998**, *109*, 165.

(60) Smith, I. W. M.; Herbst, E.; Chang, Q. *Mon. Not. R. Astron. Soc.* **2004**, *350*, 323.

(61) Millar, T. J.; Herbst, E. *Astron. Astrophys.* **1994**, *288*, 561.

(62) Woodall, J.; Agundez, M.; Markwick-Kemper, A. J.; Millar, T. J. http://www.udfa.net/, 2008.

(63) Bakker, E. J.; van-Dishoeck, E. F.; Waters, L. B. F. M.; Schoenmaker, T. *Astron. Astrophys.* **1997**, *323*, 469.

JP8025336