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# Rate coefficients for the reactions of Si($^3P_J$) with $C_2H_2$ and $C_2H_4$: Experimental results down to 15 K

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Rate coefficients for the reaction of ground-state silicon atoms Si($^3P_J$) with acetylene and ethylene have been measured at temperatures down to 15 K. The experiments have been performed in a continuous flow CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus using pulsed laser photolysis of $Si(CH_3)_4$ to generate Si($^3P_J$) atoms and laser-induced fluorescence to observe the kinetic decay of the atoms and hence determine the rate coefficients. Both reactions are found to be fast, and the reaction rates show a very mild dependence on temperature. The rate coefficients match the expressions $k(Si+C_2H_2)=(2.6\pm0.6)10^{-10}(T/300)^{-(0.71\pm0.24)}\exp(-(29\pm10)/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $k(Si+C_2H_4)=(3.7\pm0.3)10^{-10}(T/300)^{-(0.34\pm0.10)}\exp(-(16\pm4)/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ in the temperature range 15–300 K. The nature of the products and the similarities of the carbon and silicon chemistry are discussed. *© 2001 American Institute of Physics.* [DOI: 10.1063/1.1396855]

## I. INTRODUCTION

Silicon is one of the most abundant elements in the universe. It is second only to oxygen in its natural terrestrial abundance (≈28% of the earth's crust)[1] and occurs in a great variety of silicate minerals and as quartz. During the past decades, there has been considerable interest in the chemistry of organosilicon compounds, which have a wide variety of applications in the field of sensors,[2] electronics,[3,4] coatings,[5,6] biotechnologies,[7,8] and nanotechnologies.[9,10] More particularly, unsaturated hydrocarbons like ethylene or acetylene are used as precursor molecules in chemical vapor deposition (CVD) of silicon carbide films on silicon surfaces. In order to better understand the absorption–desorption mechanism, many experimental[11–14] and computational[15–17] studies have been made. Although the gaseous phase may influence the CVD process, the key step is the reaction of the $\pi$ bonds of the unsaturated hydrocarbons with the silicon surface.

Silicon is also present in space and its cosmic abundance is roughly twice that of sulfur. However, when compared to the 13 sulfur-bearing molecules detected in the interstellar medium, the silicon-containing molecules are found to be under-represented. So far, the detected molecules are SiO, SiS, SiC, c-$SiC_2$, $SiC_4$, $SiH_2$, $SiH_4$,[18–20] $SiC_3$,[21] and SiCN.[22] Atomic Si has been observed only recently[23] in the Orion-KL nebula, a region where $Si^+$ has already been detected. There are at least two reasons for this apparent under-representation.

The first one is that observational study of silicon-containing molecules relies on the accurate knowledge of rest frequencies of these species. The Merril–Sanford bands were assigned to $SiC_2$ more than 40 years ago,[24] and its spectrum and structure are now well known,[25–27] but only five other silicon compounds had a known rotational spectrum 10 years ago: SiN, SiO, SiC, SiS, and $SiC_4$.[20] Many experimental and theoretical studies, however, have been carried out in recent years, so that spectroscopic and structural data have become available on c-$SiC_3$,[28–31] linear silicon carbides $SiC_n$, $n$ ranging from 3 to 9 (Refs. 32–34) as well as the radio spectra of $SiC_2H$, SiNC, and SiCN,[35] the latter being detected in an astronomical source a few months later.[22] When considering hydrogenated silicon–carbon clusters ($Si_xC_yH_z$), very little is known from a spectroscopic point of view. Besides $SiC_2H$, the only radicals for which data are available are silicon methylidine SiCH[36–38] and silylidene $H_2CSi$.[39] Despite predictions that such clusters should be detectable[19] in circumstellar envelopes and in the molecular clouds, none of them has been detected yet.[39]

The second reason for the under-representation of silicon-containing molecules compared to its cosmic abundance is that, like other refractory elements, silicon is known to be heavily depleted from the gas phase due to its incorporation into silicate grains[19,40,41] or into nanoparticles.[42] It is possible that such aggregate grains could be responsible of the formation of complex molecules, among them silicon-bearing molecules.[43]

The form taken by the gas phase silicon varies greatly among the different components of the interstellar medium. Very few silicon compounds are detected in dense molecular clouds, as well as in photon dominated regions,[40] where silicon is expected to be mainly in the form of SiS or SiO.[19] Silicon–carbides and more generally, all relatively complex silicon-containing molecules (with the exception of silane), have been found in the circumstellar envelope of the carbon-rich star IRC+10 216. The mapping of silicon dicarbide in the envelope of this object[44,45] has revealed a shell-like dis-

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tribution which puts additional constraints on the chemistry responsible for the formation of this species. As hydrocarbons, many highly unsaturated, constitute a large part of the 121 molecules detected in space,[46] and since acetylene is one of the major species in IRC+10 216 with an abundance of a few $10^{-5}$ with respect to $H_2$,[47–49] it is necessary to measure the reaction rates of silicon atoms with hydrocarbons.

The chemistry and thermochemistry of silicon are not very well known. The reaction schemes that are invoked to account for the formation of the detected neutral organosilicon compounds in IRC+10 216 generally include ion–molecule reactions, with dissociative recombination as the ultimate step.[18,44,49–51] Some of these ion–molecule reactions have not been studied in the laboratory, but the temperature behavior and the 300 K rates can at least be evaluated using capture theories.[18,49] This is not the case for neutral–neutral reactions, for which their rates and temperature dependence cannot be predicted up to now. The importance of these reactions for astrochemical models has been highlighted,[47,52] however, and as it is admitted that they must be important for organosilicon chemistry,[44,49] they are included in some models.[18,53] When the rate constant of interest has not been measured, the value adopted in the model is estimated from results concerning the ''analogous'' reaction with a carbon-containing species, which is believed to be similar.[18,19,53]

Measurements of reactions rates of silicon atoms with acetylene and ethylene, together with other molecules, have been performed at 300 K[54–56] by Husain and co-workers, who employed time-resolved atomic resonance spectroscopy to monitor the $Si(^3P)$ concentration directly via the $(3p^2\,^3P-4s\,^3P)$ transition at 252 nm. Although a factor of 2 exists between the different sets of measurements, the authors report rapid room temperature rates, indicating that reactions proceed at close to unit collisional efficiency. As far as we know, the products of reactions of silicon with hydrocarbon have not been identified.

In this paper, we present the first measurements of reactions rates of silicon atoms with acetylene and ethylene down to 15 K. The experimental work has been achieved using the CRESU technique (French acronym for ''reaction kinetics in a uniform supersonic flow''), which is now well established in the field of low temperature rate constant measurements.[57] This technique has been recently used in Birmingham (UK) to study the reaction rates of carbon atoms with molecules of astrochemical interest. $C(^3P)$ atoms were generated by photolysis of $C_3O_2$ at 193 nm, and their decay was followed either by chemiluminescence[58] or laser-induced fluorescence (LIF) in the VUV.[59] These sets of measurements will be compared to the results obtained for silicon atoms, and this comparison will be the basis of the discussion about the similarities of atomic carbon and atomic silicon reactions.

## II. EXPERIMENT

### A. The apparatus

Originally designed in the 1980's for ion–molecule studies at very low temperatures (down to 8 K),[60] the CRESU apparatus has been associated with the pulsed laser photolysis (PLP) laser-induced fluorescence (LIF) method for the studies of neutral–neutral reactions. The device is extensively described in Ref. 61, so the description below will focus on details specific to the work reported here.

In the CRESU technique, the low temperatures are achieved by the isentropic expansion of a gas mixture (consisting predominantly of a carrier gas, here helium, argon, or molecular nitrogen), through a Laval nozzle. A supersonic flow is generated in which the temperature, density, and velocity are uniform along the flow. This temperature is a true thermodynamic temperature as the density of the flow (typically $10^{16}$ to $10^{18}\,cm^{-3}$) is high enough to ensure thermal equilibrium by collisions. The nozzle is mounted on a movable reservoir kept at room temperature, into which the carrier gas, the reagent gas (ethylene or acetylene), and the precursor of the silicon atoms [tetramethylsilane: $Si(CH_3)_4$] are introduced, after passing through mass flow controllers (Tylan), and mixed together prior to expansion.

As in a previous study concerning the reaction of $Si(^3P)$ with $O_2$,[62] silicon atoms were produced in the supersonic flow by multiphoton photolysis of tetramethylsilane (TMS hereafter, Aldrich, 99% purity, used without further purification). TMS, which is a liquid at room temperature, has a high vapor pressure, however: 785 mbar at 296 K. A gas mixture containing about 500 mbar of TMS and 2 bar of argon was thus prepared and stored into a stainless-steel tank. A small concentration of this mixture, typically 0.1% of the carrier gas, was sufficient to generate a significant amount of silicon atoms. Photolysis of TMS was achieved using the fourth harmonic (266 nm) of a YAG pulsed laser beam (Spectra Physics, GCR 190, 10 Hz, 50 mJ) propagated along the flow and mildly focused at the nozzle exit by means of a converging lens (37 cm focal length) located inside the reservoir. A burst of silicon atoms was produced around the focal point, and flowed for several tens of microseconds before reaching the detection region. Here, a tunable pulsed laser (Spectra Physics, MOPO 730 with frequency doubling option, 10 Hz, ~10 $\mu$J) propagated perpendicularly to the flow and excited the $3p^2\,^3P_0-4s\,^3P_1$ transition of Si at 251.43 nm. The resonant fluorescence signal was collected using a UV-enhanced, optically fast telescope–mirror combination mounted inside the vacuum chamber and set at right angles to both the flow axis and the probe laser beam. It was then imaged through a slit, onto the photocathode of a UV-sensitive photomultiplier tube (Thorn EMI, 9813QSB) after passing through a narrowband interference filter (centered at 250 nm) to reduce the

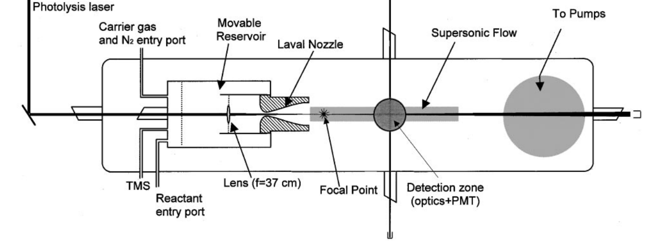


FIG. 1. Schematic diagram of the CRESU apparatus.

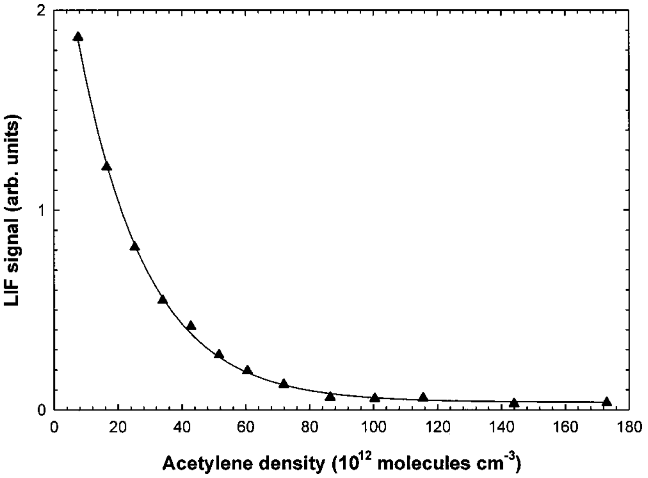


FIG. 2. Silicon atoms, Si($^3P_0$), fluorescence signal as a function of acetylene density at 15 K for a time delay set to 130 $\mu$s.

scattered light from the photolysis laser. A sketch of the apparatus is shown in Fig. 1.

### B. Measurement of the rate constant

The time delay between the photolysis pulse and the probe laser pulse was set equal to the time required for the silicon atoms to flow from the focal point to the detection zone. During this time, the silicon atoms react with the hydrocarbon molecules according to the reaction

$$Si + C_nH_m \rightarrow \text{products},$$

with a rate constant $k$. The LIF signal of the silicon atoms was recorded and averaged over several hundreds of laser shots, and the measurement was repeated for different hydrocarbon flow rates. The decrease of the LIF signal as a function of hydrocarbon density $[C_nH_m]$ was well fitted by the exponential function $\exp(-k'[C_nH_m])$, where $k'$ is expressed in cm$^3$/molecule. (Fig. 2). As the nozzle can be moved, the delay $\Delta t$ between production and detection of Si($^3P$) can be varied using a delay generator, and since $k' = k \times \Delta t$, the plot of $k'$ versus $\Delta t$ is a straight line whose slope is the rate constant $k$, at the temperature and density of the nozzle used (Fig. 3).

### C. State of the Si atoms

As discussed in Ref. 62, because of laser focusing, photolysis of Si(CH$_3$)$_4$ generates silicon atoms in a non-Boltzmann spin–orbit distribution, and the first excited electronic state Si($^1D_2$) which lies 0.78 eV above the ground state has been detected together with the ($^3P$) states of interest. The efficiency of the quenching of the $^1D_2$ state depends, however, on the nature of the carrier gas. The relative population of this state was measured by exciting the $3p^2\,{}^1D_2 - 4s\,{}^1P_1$ transition at 288.16 nm with the probe laser; resonant photons were collected through the previously described optical system in which a narrow-band filter centered at 289 nm was used. When the carrier gas was argon, and in the absence of any reactant gas, measurements indicated that quenching of $^1D_2$ was always completed within about 30 $\mu$s. On the other hand, using helium as a carrier gas, the Si($^1D_2$) state turned out to relax slowly on the time scale of the experiment. For all Laval nozzles working in helium, it was therefore necessary to inject a quencher into the flow to electronically deexcite the silicon atoms. N$_2$ was a good candidate for this purpose, as its reaction with Si ($^3P_J$ and $^1D_2$) to yield SiN is endothermic. Its quenching efficiency, moreover, was found to be high so that addition of a small amount of N$_2$, corresponding to about 1% of the total density, ensured complete deexcitation of the electronic state within 50 $\mu$s. Although higher electronic states were not probed in this study, it is likely that they are also produced and we assume that they are relaxed efficiently by argon or nitrogen.

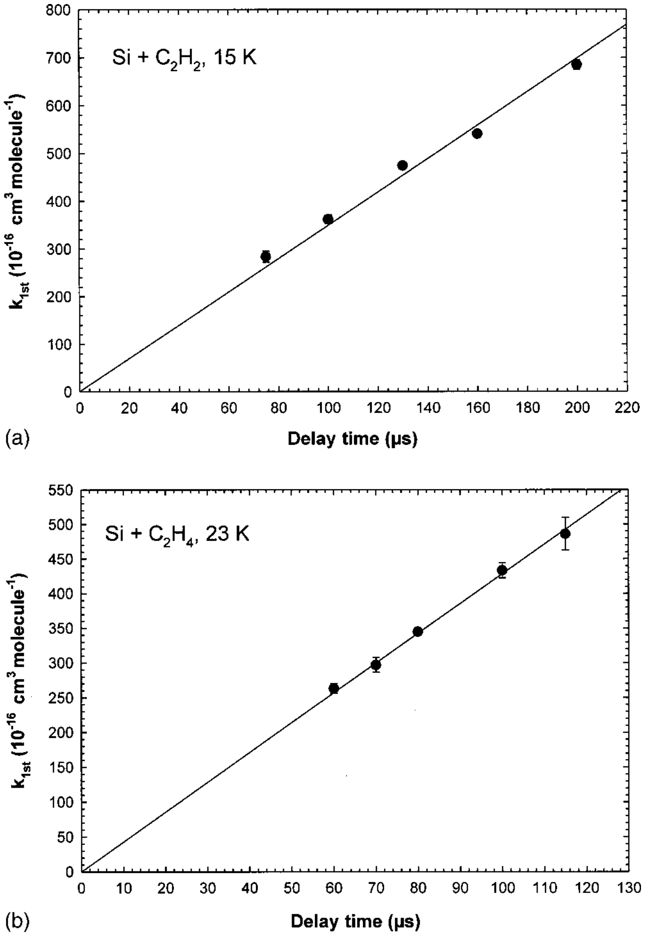


FIG. 3. First-order rate coefficients, $k_{1st}$, as a function of the time delay for (a) Si($^3P_J$) + acetylene at 15 K and (b) Si($^3P_J$) + ethylene at 23 K.

The spin–orbit relaxation of the Si($^3P$) states was checked by probing the three levels ($J = 0,1,2$) by exciting the transitions $3p^2\,{}^3P_0 - 4s\,{}^3P_1$ (251.43 nm), $3p^2\,{}^3P_1 - 4s\,{}^3P_2$ (250.69 nm), $3p^2\,{}^3P_2 - 4s\,{}^3P_2$ (251.61 nm), respectively. For all nozzles, the relative intensities of these transitions were found to be constant after about 40 $\mu$s, indicating that an equilibrium had been reached.

In all cases, therefore, the kinetics of the reactions of Si with ethylene and acetylene was carried out in conditions where both deexcitation reactions were completed ($\Delta t > 50\,\mu$s; see Table I). As a consequence, the rate coefficients obtained in our experiment are for Si($^3P_J$) atoms displaying

TABLE I. Rate coefficients for the reaction of Si($^3P_J$) atoms with acetylene. For each temperature the main experimental conditions are also given and more particularly the acetylene density range. The number of measurements represents the number of time delays $\Delta t$ for which an LIF decay signal was recorded as a function of the acetylene density.

| $T$ (K) | Buffer gas | Number of measurements | Total density ($\times 10^{16}$ cm$^{-3}$) | [$C_2H_2$] ($\times 10^{13}$ cm$^{-3}$) | $\Delta t$ range ($\mu$s) | Rate constant ($\times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) |
|---|---|---|---|---|---|---|
| 15 | He | 5 | 5.05 | 1–27 | 75–200 | $3.49 \pm 0.15$[a] |
| 23 | He | 5 | 4.73 | 1–23 | 60–115 | $4.17 \pm 0.12$ |
| 36 | He | 5 | 5.28 | 1–22 | 60–190 | $4.53 \pm 0.28$ |
| 49 | He | 5 | 10.0 | 1–81 | 75–105 | $5.69 \pm 0.26$ |
| 52 | Ar | 5 | 10.3 | 1.5–71 | 100–400 | $4.90 \pm 0.17$ |
| 72 | $N_2$ | 6 | 5.79 | 1–40 | 50–150 | $5.18 \pm 0.25$ |
| 97 | Ar | 5 | 15.45 | 0.1–8.9 | 100–450 | $4.20 \pm 0.32$ |
| 168 | Ar | 6 | 9.01 | 0.1–27 | 100–500 | $3.10 \pm 0.25$ |
| 295 | Ar | 5 | 9.23 | 0.4–16 | 100–500 | $2.26 \pm 0.22$ |

[a] Errors quoted are $\pm t\sigma$ errors, where $t$ is the value of the student's $t$-distribution for the 95% point.

the Boltzmann-type spin–orbit distribution at the temperature of the flow. Determination of the individual state-to-state relaxation rate coefficients will be the subject of a forthcoming article.

Si($^3P_1$) and Si($^3P_2$) lie at 111 and 321 K above Si($^3P_0$), respectively, so that at 15 K, only the $^3P_0$ level is populated (Fig. 4). This was obvious on the LIF spectra, on which at 15 K only the signal of the $J=0$ state was present and at 23 K, the signal arising from the $J=1$ state was hardly detectable (Fig. 5). Incidentally, the measurements at 15 and 23 K are relative to the single ($J=0$) state.

## III. RESULTS

Our experimental results are listed in Tables I and II, and log(*k*) is plotted as a function of log(*T*) in Fig. 6 for both reactions. Only statistical errors are quoted. Some systematic errors due to flow control inaccuracies or inaccuracies in the determination of the total buffer gas density should, however, also be taken into account. Every effort was made to minimize these, and we estimate that the additional error does not exceed 10%.

These results concern the $^3P$ states of Si, the $^1D$ state being quenched by the addition of $N_2$. It is worth noting that in the case of ethylene, the addition of $N_2$ led to rate constants that were not significantly higher than the rate constants measured without $N_2$. This is interpreted by the fact that ethylene is an efficient quencher of the $^1D$ state. A similar behavior was noted for $O_2$.[62] At the opposite, as acetylene seems to be a poor quencher for the $^1D$ state, the reaction rate constants obtained with $N_2$ have been found to be about 30% higher than without $N_2$.

The reaction rates were fitted by the relations

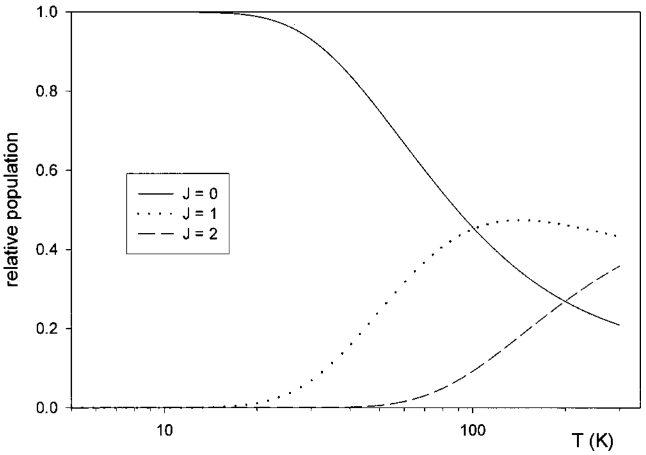


FIG. 4. Relative spin–orbit populations (calculated) as a function of *T*.

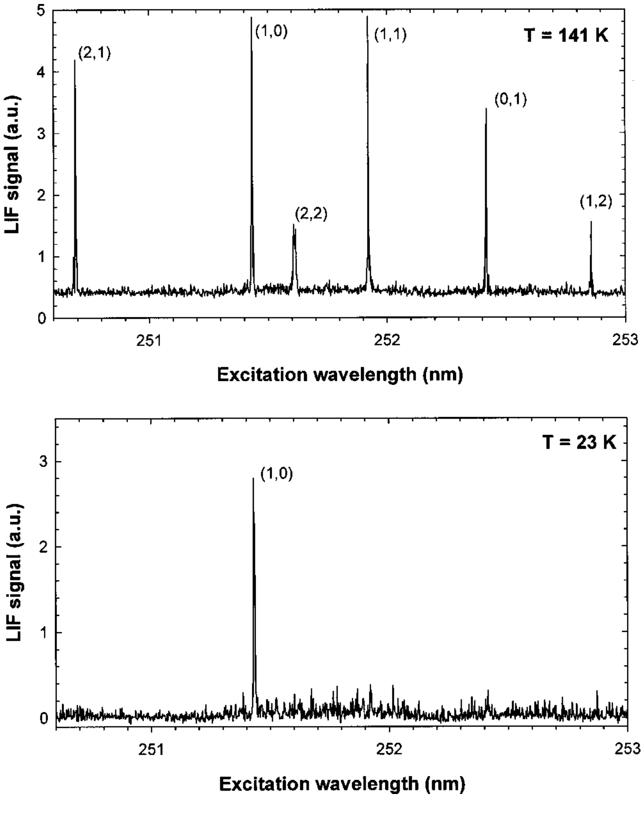


FIG. 5. LIF spectra of the Si [$4s(^3P_J)-3p^2(3P_J)$] transitions recorded in the CRESU apparatus at two different temperatures: 141 K (upper spectrum) and 23 K (lower spectrum). The transitions are labeled according to the upper and lower spin–orbit levels involved ($J', J''$). In both cases, the delay times between the photolysis and probe laser pulses were made sufficiently long (290 and 95 $\mu$s, respectively) to allow total spin–orbit relaxation.

TABLE II. Rate coefficients for the reaction of Si($^3P_J$) atoms with ethylene. For each temperature the main experimental conditions are also given and more particularly the ethylene density range. The number of measurements represents the number of time delays $\Delta t$ for which an LIF decay signal was recorded as a function of the ethylene density.

| $T$ (K) | Buffer gas | Number of measurements | Total density ($\times 10^{16}$ cm$^{-3}$) | [$C_2H_4$] ($\times 10^{13}$ cm$^{-3}$) | $\Delta t$ range ($\mu$s) | Rate constant ($\times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) |
|---|---|---|---|---|---|---|
| 15 | He | 5 | 5.05 | 1–24 | 80–200 | $3.52 \pm 0.10$[a] |
| 23 | He | 5 | 4.73 | 1–27 | 60–120 | $4.29 \pm 0.07$ |
| 52 | Ar | 7 | 10.3 | 0.1–12.9 | 50–350 | $4.77 \pm 0.19$ |
| 72 | $N_2$ | 5 | 5.79 | 1–50 | 50–125 | $5.08 \pm 0.18$ |
| 97 | Ar | 6 | 15.45 | 0.2–5.6 | 200–450 | $4.45 \pm 0.22$ |
| 141 | Ar | 5 | 9.01 | 0.6–6.7 | 200–400 | $4.30 \pm 0.20$ |
| 295 | Ar | 6 | 9.23 | 0.4–12.4 | 100–800 | $3.46 \pm 0.32$ |

[a] Errors quoted are $\pm t\sigma$ errors, where $t$ is the value of the Student's $t$-distribution for the 95% point.

$$k(\mathrm{Si}+\mathrm{C_2H_2}) = (2.6 \pm 0.6)10^{-10}\left(\frac{\mathrm{T}}{300}\right)^{-(0.71\pm0.24)} \times \exp\left(-\frac{(29\pm10)}{T}\right)\mathrm{cm^3\,molecule^{-1}\,s^{-1}},$$

and

$$k(\mathrm{Si}+\mathrm{C_2H_4}) = (3.7 \pm 0.3)10^{-10}\left(\frac{\mathrm{T}}{300}\right)^{-(0.34\pm0.10)} \times \exp\left(-\frac{(16\pm4)}{T}\right)\mathrm{cm^3\,molecule^{-1}\,s^{-1}},$$

where errors are quoted as $\pm 2\sigma$, $\sigma$ being the standard error.

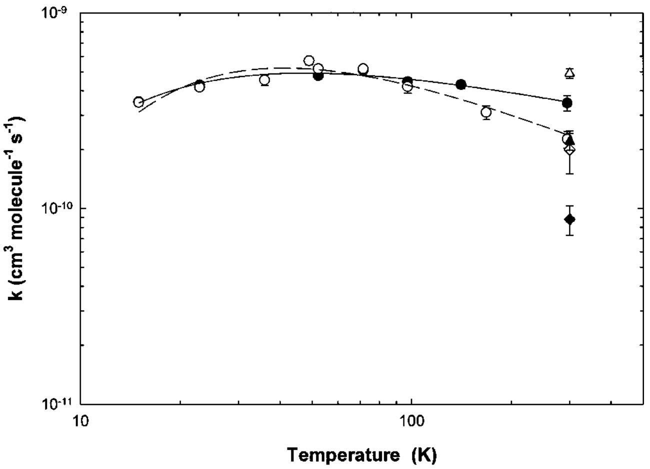


FIG. 6. Rate constants for the reaction of Si($^3P_J$) with acetylene and ethylene as a function of temperature plotted on a log–log scale. The open circles (○) show the results from the present work for Si($^3P_J$)+$C_2H_2$ and the filled circles (●) for Si($^3P_J$)+$C_2H_4$. The results of other workers at room temperature for Si($^3P_J$)+$C_2H_2$ are shown as an open triangles (Ref. 56) (△) and an open diamond (Ref. 54) (◇). The results of other workers at room temperature for Si($^3P_J$)+$C_2H_4$ are shown as a filled triangle (Ref. 56) (▲) and a filled diamond (Ref. 55) (◆). The dashed line is a fit to all the CRESU data for for Si($^3P_J$)+$C_2H_2$, yielding $k=(2.6\pm0.6)\times10^{-10}\,(T/300)^{-(0.71\pm0.24)}\exp(-(29\pm10)/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The continuous line is a fit to all the CRESU data for Si($^3P_J$)+$C_2H_4$, yielding: $k=(3.7\pm0.3)\times10^{-10}(T/300)^{-(0.34\pm0.10)}\exp(-(16\pm4)/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

## IV. DISCUSSION

### A. What are the products?

Our experimental technique does not allow us to determine the nature of the products, so the following discussion is based on energetic considerations. Heats of formation of a number of organosilicon compounds are available in the litterature,[63] but most of the data are for saturated stable compounds such as methylsilanes, and few data are available for unsaturated molecules. Among the compounds of interest, only the heat of formation of cyclic silicon dicarbide c-$SiC_2$ has been determined experimentally[64] and theoretically (see Ref. 27 and references therein), all other heats of formation are calculated.[27,64–67] The available thermochemical data are summarized in Table III.

The variation of the Gibbs energy of reaction $\Delta G^\circ_R$ tells us if a reaction proceeds or not. Such data are scarce for organosilicon compounds, and when the entropy of formation of a compound is not available, we shall consider that the reaction must be at least exothermic. Endothermic reactions are ruled out as our measurements are carried out at low temperatures. It should be noted that the lower the temperature, the closer $\Delta G^\circ_R$ and $\Delta H^\circ_R$.

According to these constraints, two main routes are open for the reaction of silicon with acetylene or ethylene

$$\mathrm{Si}+\mathrm{C_2H}_n \rightarrow \mathrm{SiC_2H}_n$$
$$\rightarrow \mathrm{SiC_2H}_{n-2}+\mathrm{H_2}.$$

For the Si($^3P$) + acetylene reaction, their energetics at 298 K are the following:

$$\mathrm{Si}+\mathrm{C_2H_2} \rightarrow \text{c-Si(CH)}_2 \quad \Delta H^\circ_1 = -320\ \mathrm{kJ/mol}, \tag{1}$$

$$\rightarrow \mathrm{HSiCCH} \quad \Delta H^\circ_{1'} = -238\ \mathrm{kJ/mol}$$

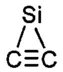
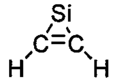
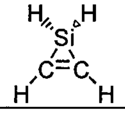
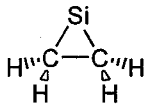
$$\Delta G^\circ_{1'} = -208\ \mathrm{kJ/mol}, \tag{1'}$$

$$\rightarrow \text{c-SiC}_2+\mathrm{H_2} \quad \Delta H^\circ_2 = -61.7\ \mathrm{kJ/mol}$$

$$\Delta G^\circ_2 = -61.2\ \mathrm{kJ/mol}, \tag{2}$$

and for Si($^3P$) + ethylene

TABLE III. Thermochemical data for organosilicon compounds.

| Formula | Developed formula | | Common name | $\Delta_f H°(0K)$ (kJ/mol) | $\Delta_f H°(298K)$ (kJ/mol) | $S_f°$ (298K) ($J\ mol^{-1}\ K^{-1}$) |
|---|---|---|---|---|---|---|
| Si | | $^3P$ | | $445.7^g$ | $450^a$ | $168^a$ |
| H | | $^2S_{1/2}$ | | $216.0^g$ | $218^a$ | |
| $H_2$ | | $^1\Sigma_g^+$ | | 0 | 0 | $130.7^a$ |
| $C_2H_2$ | | $^1\Sigma_g^+$ | Acetylene | $235.7^g$ | $226.7^a$ | $201^a$ |
| $C_2H_4$ | | $^1A_g$ | Ethylene | $61.0^g$ | $52.5^a$ | $219.3^a$ |
| $SiC_2$ |  | $^1A_1$ | Silicon dicarbide | $648^b$ | $615^a$ | $236.7^a$ |
| $SiC_2H$ | $Si{-}C{\equiv}CH$ | $^2\Pi$ | | $523^d$ | $539^c$ | |
| $SiC_2H_2$ |  | $^1A_1$ | | | $359.5^c$ | |
| | $H{-}Si{-}C{\equiv}CH$ | | | $439^d$ | $439^d$ | $269.2^d$ |
| $SiC_2H_3$ | | $^2A'$ | | $413.8^d$ | $397^c$-$409^d$ | |
| $SiC_2H_4$ | $H_3Si{-}C{\equiv}CH$ | $^1A_1$ | Silylacetylene | $229.9^d$ | $214.8^c$-$253^e$ | $268^d$ |
| |  | | Silacyclopropene | | $284.3^f$-$301.4^e$ | |
| |  | $^1A_1$ | silacyclopropylidene | | $285.8^f$ | |
| | | $^3B_1$ | silacyclopropylidene | | $430.4^f$ | |
| | $H_2C{=}\underset{H}{C}{-}SiH$ | | vinylsilylene | $316^d$ | $307^d$-$329^e$ | $278.8^d$ |
| | $H_2C{=}Si{=}CH_2$ | $^1A_1$ | 2-silaallene | | $406^f$ | |
| | $H_3C{-}Si{\equiv}CH$ | | 2-silapropyne | | $468.7^f$ | |

[a] Reference 63.
[b] Reference 27.
[c] Reference 64.
[d] Reference 67.
[e] Reference 66.
[f] Reference 65.
[g] Reference 79.

$$Si+C_2H_4 \rightarrow SiC_2H_4 \quad -287.7 \leqslant \Delta H_3^\circ \leqslant -33.8\ \text{kJ/mol} \quad \text{(depending upon the isomer)}, \tag{3}$$

$$\Delta G_3^\circ = -214\ \text{kJ/mol for } H_3SiCCH,$$

$$\rightarrow c\text{-}Si(CH)_2+H_2 \quad \Delta H_4^\circ = -143\ \text{kJ/mol}, \tag{4}$$

$$\rightarrow HSiCCH+H_2 \quad \Delta H_{4'}^\circ = -63\ \text{kJ/mol}$$

$$\Delta G_{4'}^\circ = -67\ \text{kJ/mol}. \tag{4'}$$

From a mechanistic point of view, reactions (1), (1′), and (3) are three-body associations whose apparent second-order rate constant is measured. In the conditions of our experiment, only the buffer gas can play the role of the third body, and in this case, the calculated three-body association rates are greater than $10^{-27}\ cm^6\ molecule^{-2}\ s^{-1}$. Such a calculated rate could correspond to a saturated reaction, but its fairly

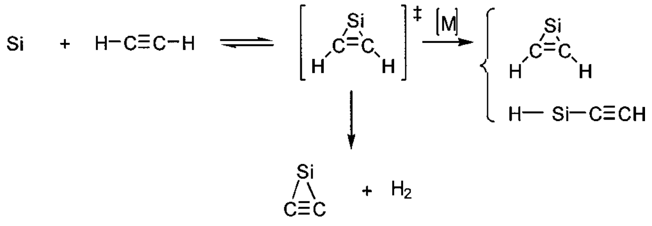


FIG. 7. Reaction scheme for $Si(^3P_J)+C_2H_2$.

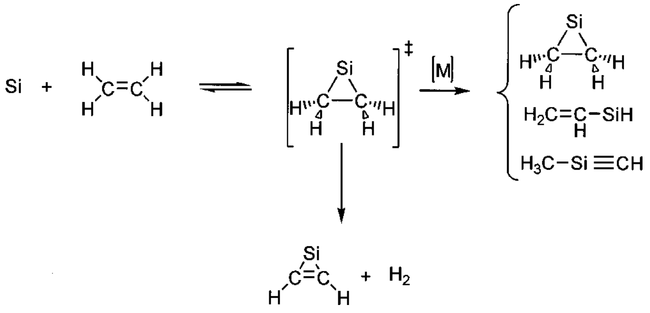


FIG. 8. Reaction scheme for $Si(^3P_J)+C_2H_4$.

high value suggests that if three-body associations occur, they are competing with bimolecular channels.

The reaction of sillylene $(SiH_2)$ with acetylene has been studied experimentally[68,69] and theoretically.[66,70] This reaction could have some similarities with $Si+C_2H_4$, as products are isomers with the formula $SiC_2H_4$. Experimentally, it was found that the pressure dependence of this reaction was such that it suggested the coexistence of a bimolecular and a termolecular channel.[69] *Ab initio* calculations coupled with kinetic analysis have been performed on the association channel, and have suggested a reaction scheme, where the reaction intermediate is excited silacyclopropene $(c\text{-}H_2SiC_2H_2)$, which can be either collisionally stabilized, or undergo isomerization to silylacetylene $(HCCSiH_3)$ or vinylsilylene $(H_2CCHSiH)$. These rearrangements have an activation barrier of 172 and 154 kJ/mol respectively, which is less than the exothermicity of the reaction, and do not require more than two chemical bonds to be broken and reformed.

If a cyclo-addition of Si to ethylene occurred in our experiment, then the adduct would be silacyclopropylidene $c\text{-}Si(CH_2)_2$. This reaction is rather exothermic if the adduct is formed in its ground electronic state, but if one considers the possibility of forming $c\text{-}Si(CH_2)_2$ in the first excited $(^3B_1)$ state, a reaction which is spin-allowed, the energy excess is much less,

$$Si+C_2H_4 \rightarrow c\text{-}Si(CH_2)_2(^1A_1) \quad \Delta H^\circ_5=-216\ \text{kJ/mol}, \tag{5}$$

$$\rightarrow c\text{-}Si(CH_2)_2(^3B_1) \quad \Delta H^\circ_6=-72\ \text{kJ/mol}. \tag{6}$$

This adduct could be collisionally stabilized, or could undergo isomerization. Direct rearrangement of silylacetylene or vinylsilylene would need four chemical bonds to be broken or reformed, and thus is highly improbable. However, $c\text{-}Si(CH_2)_2$ is very close in energy to the adduct formed by the reaction of $SiH_2$ with acetylene, and the isomerization of silacyclopropylidene to silacyclopropene requires the 1–2 shift of two hydrogen atoms. Silacyclopropene could then rearrange further to form more stable products. As far as we know, no studies have been made on the rearrangements of silacyclopropylidene, and the fate of the adduct depends on the height of its isomerization barriers, among other parameters.

Channels (2), (4), and (4′) correspond to the dissociation of the adduct, forming molecular hydrogen and a reaction product. The energy excess removal is then ensured by hydrogen ejection. Reactions (2) and (4) are spin-forbidden, and the intermediate adduct has to be sufficiently long lived to allow time for intersystem crossing to a singlet surface.

The termolecular channels cannot be eliminated on the basis of our measurements. The only indication we have that we measure true bimolecular rate constants is the insensitivity of the rate constants to the nature of the carrier gas, which is required to stabilize the adduct.

The possible reaction schemes are summarized in Figs. 7 and 8.

## B. Comparison with $C(^3P_J)$+acetylene or ethylene

### 1. Reaction rate constants

The reactions of $C(^3P_J)$ atoms with hydrocarbons, among them acetylene and ethylene, have been studied recently by Chastaing *et al.*[58,59] The reaction kinetics was measured in the same temperature range as this work.

The reaction rates for carbon atoms are quite similar to those obtained for silicon, and can be fitted by the relations: $k(T)=(2.9\pm0.3)10^{-10}(T/298)^{-(0.12\pm0.10)}$ for acetylene, and $k(T)=(3.0\pm0.4)10^{-10}(T/298)^{-(0.11\pm0.07)}$ for ethylene. The measurements and their fits are represented in Figs. 9 and 10, together with the corresponding results for silicon.

The main difference is the slight decrease of the rate constant that is observed below 50 K in the case of silicon. This could be attributed to a dependence of the reactivity on the spin–orbit state of the atom, as the relative spin–orbit

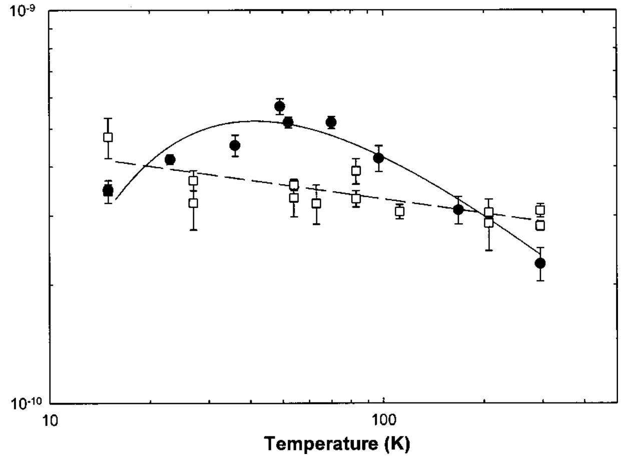


FIG. 9. Rate constants for the reaction of $Si(^3P_J)$ with acetylene (●, this work) and $C(^3P_J)$ with acetylene (Ref. 59) (□), as a function of temperature plotted on a log–log scale. The continuous line is a fit to the data for $Si(^3P_J)+C_2H_2$, yielding $k=(2.6\pm0.6)\times10^{-10}\,(T/300)^{-(0.71\pm0.24)}\times\exp(-(29\pm10)/T)\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$. The dashed line is a fit to the data for $C(^3P_J)+C_2H_4$, yielding $k=(2.9\pm0.3)\times10^{-10}(T/298)^{-(0.12\pm0.10)}\ \text{cm}^3\text{molecules}^{-1}$.

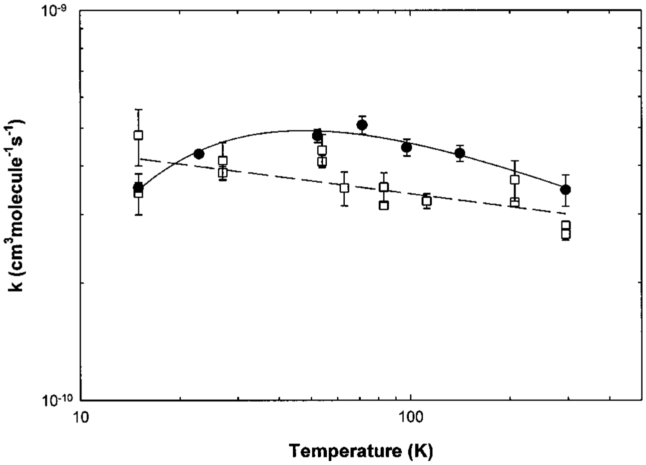


FIG. 10. Rate constants for the reaction of Si($^3P_J$) with ethylene (●, this work) and C($^3P_J$) with ethylene (Ref. 59) (□), as a function of temperature plotted on a log–log scale. The continuous line is a fit to the data for Si($^3P_J$)+$C_2H_4$, yielding $k=(3.7\pm0.3)\times10^{-10}(T/300)^{-(0.34\pm0.10)}\times\exp(-(16\pm4)/T)$ cm$^3$ molecule$^{-1}$. The dashed line is a fit to the data for C($^3P_J$)+$C_2H_4$, yielding $k=(3.0\pm0.4)\times10^{-10}(T/298)^{-(0.11\pm0.07)}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

populations change dramatically between 295 K (where $N_{J=0}:N_{J=1}:N_{J=2}=1.0:2.7:1.72$) and 15 K (where $N_{J=0}:N_{J=1}:N_{J=2}=1.0:0.001:<10^{-4}$).

### *2. The products*

Although Si and C belong to the group IVA(14) of the periodic classification, their chemical behavior is very different.[1,71] The chemistry of carbon is characterized by the ability of this element to form single, double, or triple bonds with itself and with other atoms. On the other hand, silicon leads to form multidirectional single bonds.[72] The best illustration of the difference existing between the carbon and silicon "analogs" is provided by $CO_2$ and $SiO_2$: carbon dioxide is a gas, properly written O═C═O, whereas $SiO_2$ is a network substance, with each Si atom singly bonded to four oxygen atoms. In fact, while stoichiometric similarities exist between carbon and silicon compounds, there is no structural or chemical similarity between them. This difference is not limited to the multiplicity of chemical bonds in neutral molecules, but also concerns the maximum coordination number[71] and the structure of the ions.[72–74]

With regard to silicon–carbon bonds, before a stable compound containing a doubly bonded silicon atom was synthesized less than 30 years ago, it was thought that silicon [and the remainder of the Group IVA(14)] could not form stable multiple bonds with either carbon or another atom.[1] A variety of stable compounds containing silicon–carbon double bonds have now been synthesized, but the first silicon–carbon triple bond has been reported only recently in an excited state of silicon methylidine (SiCH).[36] These multiple bonds are weaker, however, than multiple bonds involving only carbon atoms,[71] so that when an alternative structure is possible (see the isomers of formula $SiC_2H_2$), silicon is rather involved in single bonds.[65]

It is therefore not surprising that the products of the reaction of carbon atoms with hydrocarbons are not the same as the products of the reaction of silicon atoms with the same hydrocarbons. The reaction of C with $C_2H_4$ leads mainly to $C_3H_3$+H (Ref. 75) and the corresponding channel is endothermic for silicon. H ejection is also observed in the C+$C_2H_2$ reaction,[76,77] leading to $C_3H$, but in a recent experimental study, Loison *et al.*[78] have shown that the ratio of H atom detected per C atom consumed is only about 50%. They suggest that the other products for this reaction are $C_3$+$H_2$. The corresponding channel for silicon is the formation of silicon carbide $SiC_2$. The structures of the products are, however, not the same, as $C_3$ is linear and $SiC_2$ cyclic.

## V. CONCLUSION

We present the first kinetics measurements of gas-phase reactions of silicon atoms with ethylene and acetylene below 300 K. These reactions have been found to be fast, proceeding at close to the collisional limit. From an energetic point of view, Si+$C_2H_n$ can form $SiC_2H_n$ and/or $SiC_2H_{n-2}$+$H_2$. Our experiment does not allow us to determine the nature of the products, nor to distinguish between a termolecular saturated reaction and a true bimolecular reaction. These results, however, and especially the results concerning acetylene, will have consequences for astrochemical models of IRC +10 216, where the abundance and the spatial distribution of $SiC_2$ remain to be explained.

The analogy between reactions of carbon and silicon atoms has been discussed. The main conclusion that can be drawn is that reaction rates (at least their order of magnitude) may be guessed for silicon reactions, from their analogs for carbon. This is true namely when the reactions are driven by long-range forces as is the case here, where the first step is the formation of an adduct between the silicon and the $\pi$ orbitals of the unsaturated hydrocarbon. The analogy fails, however, with the products of the reaction, which are very different according to the nature of the reactants.

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