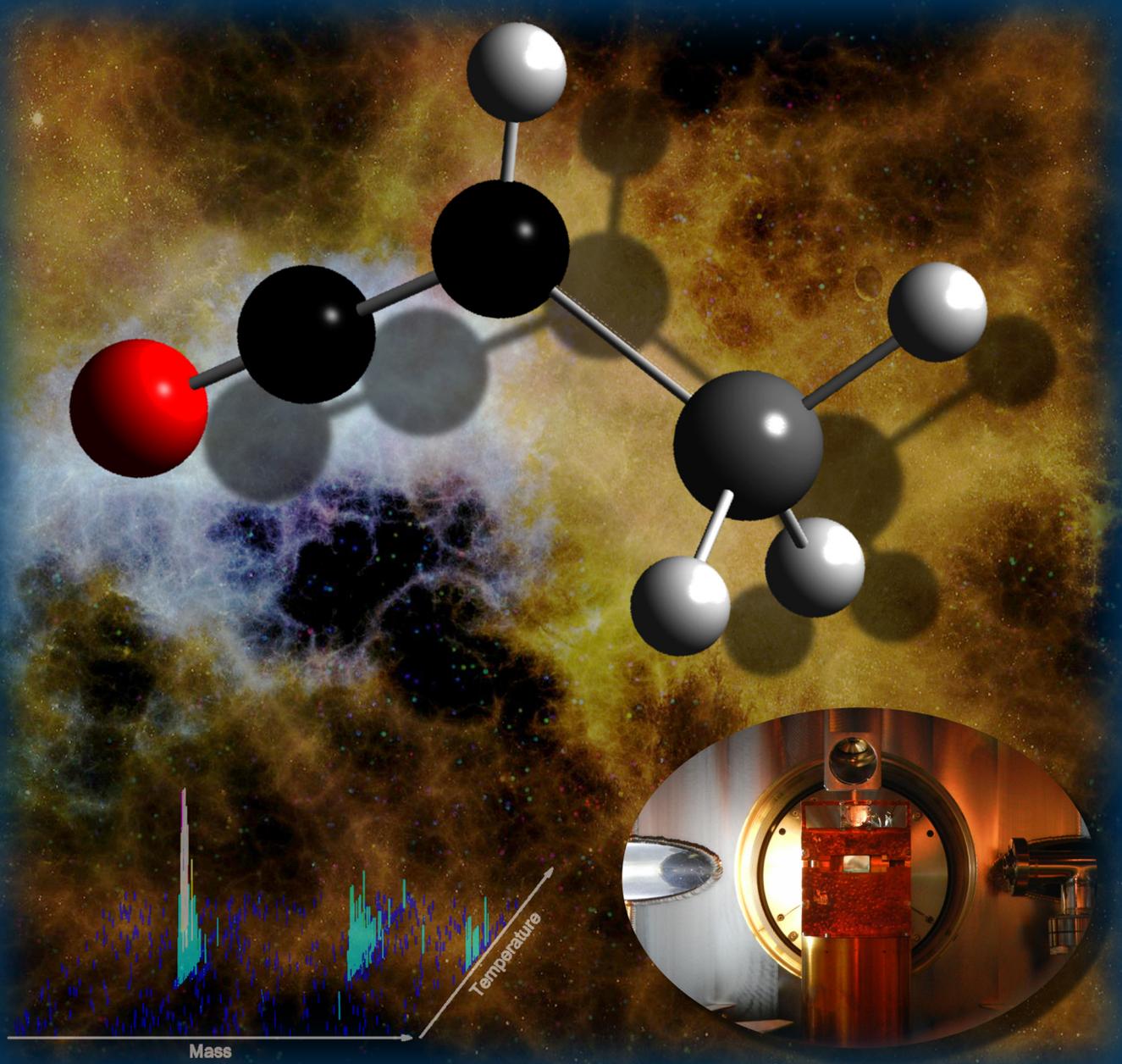


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Synthesis of the Smallest Member of the Silylketene Family:



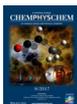
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Synthesis of the Smallest Member of the Silylketene Family: $\text{H}_3\text{SiC}(\text{H})=\text{C}=\text{O}$

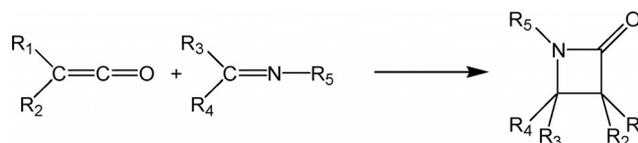
György Tarczay,^{*[a, b]} Marko Förstel,^[a, c] Sándor Góbi,^[a] Pavlo Maksyutenko,^[a] and Ralf I. Kaiser^{*[a]}

Exploiting photoionization reflectron time-of-flight mass spectrometry (PI-ReTOF-MS) combined with electronic structure calculations, it is shown that the hitherto elusive silylketene molecule ($\text{H}_3\text{SiC}(\text{H})=\text{C}=\text{O}$)—the isoivalent counterpart of the well-known methylketene molecule—is forming via interaction of energetic electrons with low-temperature silane–carbon monoxide ices. In combination with the infrared spectroscopically detected triplet dicarbon monoxide reactant, electronic structure calculations suggest that dicarbon monoxide reacts with silane via a de facto insertion of the terminal carbon atom into a silicon–hydrogen single bond. This is followed by non-adia-

batic reaction dynamics triggered by the heavy silicon atom intersystem crossing from the triplet to the singlet manifold, eventually leading to the formation of silylketene. The non-equilibrium nature of the elementary reactions within the exposed ices results in an exciting and novel chemistry which cannot be explored via traditional preparative chemistry. Since the replacement of hydrogen in silane can introduce side groups such as silyl or alkyl, the reaction of triplet dicarbon monoxide with silane represents the parent system for a previously disregarded reaction class revealing an elegant path to access the largely reactive group of silylketenes.

1. Introduction

During the last decade, ketenes ($\text{R}_1\text{R}_2\text{C}=\text{C}=\text{O}$) have received considerable attention from the organic chemistry community due to their role for example, in the preparation of β -lactams via a [2+2] cycloaddition reaction with imines ($\text{R}_3\text{R}_4\text{C}=\text{NR}_5$) (Scheme 1). The first ketene, diphenylketene ($\text{R}_1=\text{R}_2=\text{C}_6\text{H}_5$), was prepared by Staudinger as early as 1905.^[1] Two years later, in 1907, Wilsmore published the synthesis of the very reactive unsubstituted ketene: $\text{H}_2\text{C}=\text{C}=\text{O}$.^[2] This five-atom molecule plays a very important role not only in organic chemistry, it is also among the molecules best studied by high-resolution spectroscopy acting as a simple prototype of microwave-active cumulenes.^[3] Based on these spectroscopic studies, ketene was identified in the interstellar medium (ISM) toward the star forming region Sagittarius B2 via the $4_{13-3_{12}}$, $5_{15-4_{14}}$, and $5_{12-4_{13}}$



Scheme 1. [2+2] cycloaddition reaction of ketenes and imines yielding β -lactams.

transitions between 81 and 101 GHz.^[4] Its synthetic pathways in the ISM involve interaction of interstellar icy grains carrying methane and carbon monoxide with ionizing radiation at 10 K followed by sublimation of the ices in the hot core phase.^[5,6] It was suggested that ketene forms molecules with a peptide bond upon reaction with an amino acid; and in accordance with this, *N*-acetyl amino acids was identified in meteorites such as Murchison.^[7]

More than half a century later, silylketenes were discovered. The first representative of this class, trimethylsilylketene ($\text{Me}_3\text{SiC}(\text{H})=\text{C}=\text{O}$), was synthesized via the pyrolysis of ethoxy-(trimethylsilyl)acetylene.^[8] In contrast to ketene, trimethylsilylketene is stable and can be stored for extended periods of time (up to weeks) without undergoing dimerization. Since its discovery, more complex silylketenes were prepared via thermolysis, photolysis and even through classical synthetic organic chemistry methods.^[9] These silylketenes became popular as versatile reagents involved in cycloadditions, Wittig-reactions, diazomethane insertions, and nucleophilic additions of carbon along with heteroatomic nucleophiles.^[9,10] Organometallic ketene complexes are also known, in these compounds the ketene can form a π -d bond either via the $\text{C}=\text{C}$ or the $\text{C}=\text{O}$ groups.^[11]

Despite the ongoing interest in silylketenes from the preparative (in)organic and also physical chemical viewpoint as iso-

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valent systems of the carbon analogous molecules, the simplest unsubstituted silylketene, $\text{H}_3\text{SiC(H)=C=O}$, has never been identified so far. This is due to the fact that the formation of silylketene is thermodynamically much less favored than the synthesis of the trimethylated compound.^[12] Furthermore, the kinetic instability of the non-substituted silyl group toward oxygen and water also makes the synthesis of silylketene very challenging. Here we report the experimental detection of the hitherto elusive silylketene molecule ($\text{H}_3\text{SiC(H)=C=O}$) in the gas phase. Our experiments are combined with *ab initio* electronic structure calculations to verify the stability of silylketene and its isomers in the gas phase. The experiments were carried out in an ultra-high vacuum (UHV) surface science machine.^[13,14] Amorphous ices of silane (SiH_4) and carbon monoxide (CO) along with their isotopically substituted counterparts (D, ^{18}O , ^{13}C) were prepared in separate experiments with thicknesses of 750 ± 100 nm at 5.5 ± 0.2 K. While monitoring the processing of the ices via infrared spectroscopy *on line* and *in situ*, non-equilibrium chemical reactions were induced by irradiating these ices with energetic electrons. After the irradiation, the ices were heated at a rate of 0.5 K min^{-1} (temperature programmed desorption; TPD). The subliming neutral molecules were first ionized via single photon ionization (PI) in the vacuum ultraviolet (VUV) range as obtained by four-wave mixing, then mass resolved in a reflectron time-of-flight mass spectrometer (ReTOF-MS), and eventually identified by their arrival times through a multi-channel plate. Multiple VUV photon energies from 118.2 nm (10.49 eV) to 139.3 nm (8.90 eV) were used to discriminate the structural isomers based on their ionization energies which are obtained from electronic structure calculations. Additional information allowing for the discrimination of the structural isomers was obtained by measuring their sublimation temperatures.

Experimental Section

The experiments were carried out in a contamination-free ultrahigh vacuum stainless steel chamber evacuated to an ultra-high vacuum of a few 10^{-11} torr by using magnetically suspended turbomolecular pumps coupled with oil-free scroll backing pumps.^[15,16] Briefly, a rhodium-coated silver wafer is mounted onto a rotatable cold finger manufactured from oxygen-free high-conductivity copper (OFHC) cooled to 5.5 K by a closed-cycle helium refrigerator (Sumitomo Heavy Industries, RDK-415E). The substrate is freely rotatable within the horizontal plane via a differentially pumped rotational feedthrough (Thermoionics Vacuum Products, RNN-600/FA/MCO) and also translatable in the vertical axis through a UHV compatible bellows (McAllister, BLT106). Gas-phase silane (SiH_4 , Linde, 99.999%) or d_4 -silane (SiD_4 , Linde, 99% + D) was premixed with $^{12}\text{C}^{16}\text{O}$ (Matheson TRI-GAS, 99.9999%), $^{13}\text{C}^{16}\text{O}$ (Sigma-Aldrich, 99% ^{13}C , < 5% ^{18}O), or $^{12}\text{C}^{18}\text{O}$ (Sigma-Aldrich, 99.9% CO, 95% ^{18}O) in ratios of $1.0 \pm 0.1:5.0$. For mechanistic studies, we also prepared premixed gas mixtures of $\text{SiH}_4:\text{SiD}_4:\text{CO}$ at a ratio of $0.5 \pm 0.1:0.5 \pm 0.1:5.0$. Each mixture was condensed onto the substrate by introducing the gases into the main chamber through a glass capillary array at a pressure of 2.5×10^{-8} torr. Since the silane has a higher sticking coefficient than carbon monoxide on the cold surface, silane preferentially condensed on the cooled wafer (fractionated condensation). Considering the antisymmetric silicon-hydrogen

stretching mode at 2181 cm^{-1} ($\approx 3 \times 10^2 \text{ kmol}^{-1}$) and the carbon monoxide stretching at 2137 cm^{-1} ($\approx 6 \times 10^1 \text{ kmol}^{-1}$),^[17,18] an approximate silane to carbon monoxide ratio in the ices between 1:1.5 and 1:3 was extracted. (The ratio in the ice was extremely sensitive to the deposition conditions.) The overall ice thickness was determined *in situ* via laser interferometry with a helium-neon (HeNe) laser (CVI Melles-Griot; 25-LHP-230) operating at 632.8 nm.^[19,20] With a refractive index of the ices of 1.4, a thickness of 750 ± 100 nm was derived. The ices were then isothermally irradiated for 60 minutes with 5 keV electrons at fluxes of $3 \times 10^{11} \text{ electrons s}^{-1} \text{ cm}^{-2}$ over an area of $1.0 \pm 0.1 \text{ cm}^2$ at an angle of incidence of 70° relative to the substrate normal. The averaged penetration depth of the energetic electrons was calculated via Monte Carlo simulations (CASINO)^[21] to be 310 ± 50 nm. This penetration depth is less than the thickness of the deposited ices to insure that the energetic electrons only interact with the ices, but not with the substrate. The dose deposited in the ice normalized by the number of irradiated molecules is estimated to be $4.5 \pm 0.5 \text{ V}$ per silane and $5.5 \pm 0.5 \text{ eV}$ per CO molecule, respectively.^[22] Note that during the irradiation, the ices were monitored with a Fourier-Transform Infrared Spectrometer (FTIR, Nicolet 6700) in the range of 6000 cm^{-1} to 500 cm^{-1} at 4 cm^{-1} resolution accumulating over 2 minutes for each spectrum.

After the irradiation, the sample was kept isothermal at 5.5 K for one hour. After this, a TPD experiment was conducted to sublime the ice and the products by warming up the irradiated samples to 300 K at a rate of 0.5 K min^{-1} . During the sublimation, the molecules were analyzed by a reflectron time-of-flight mass spectrometer (Jordan TOF Products, Inc.) after photoionization (PI-ReTOF-MS) at several wavelengths: including 118.2 nm (10.49 eV), 129.2 nm (9.60 eV), 131.2 nm (9.45 eV), 132.6 nm (9.35 eV), 134.0 nm (9.25 eV) and 139.3 nm (8.90 eV).^[15] The pulsed (30 Hz) coherent vacuum ultraviolet (VUV) light was generated via four-wave mixing using krypton (Speciality Gases, 99.999%) or xenon (Speciality Gases, 99.999%) as a nonlinear medium. The third harmonic (354.6 nm) of a high-power pulsed neodymium-doped yttrium aluminum garnet laser (Nd:YAG, Spectra Physics, PRO-250, 30 Hz) underwent a frequency tripling process ($\omega_{\text{uv}} = 3\omega_1$) to obtain the 118.2 nm photons at levels of a few $3 \times 10^{12} \text{ VUV photons s}^{-1}$.^[23] The 129.2 nm (9.60 eV) photons were generated by resonant four-wave mixing ($\omega_{\text{uv}} = 2\omega_1 - \omega_2$) in Krypton (2×10^{-4} torr). For this purpose, 202.3 nm (6.13 eV; ω_1) light was generated utilizing a dye laser (Sirah, Cobra-Stretch) containing a mixture of Rhodamine 640 and Rhodamine 610 dyes (Exciton), which was pumped by the second harmonic (532 nm; 2.33 eV) of the fundamental of a Nd:YAG laser (1064 nm; 1.17 eV; Spectra Physics, PRO-270-30) and frequency tripling of the dye laser output (606.9 nm; 2.04 eV) using $\beta\text{-BaB}_2\text{O}_4$ (BBO) crystals (44° and 77°). The ω_2 component, that is, the 466.7 nm (2.66 eV) light, was produced by using the third harmonic (354.6 nm; 3.49 eV) of the 1064 nm (1.17 eV) fundamental of a Nd:YAG laser (Spectra Physics, PRO-250-30) to pump a dye laser (Sirah, Precision Scan) containing Coumarin 460 dye. In case of the other photon energies (i.e., 9.45 eV, 9.35 eV, 9.25 eV, and 8.90 eV) 222.5 nm radiation (5.57 eV; ω_1) was generated by doubling the dye laser (Sirah, Cobra-Stretch, containing Coumarin 450 dye) output. The resonant four-wave mixing output was obtained by combining this beam with 441.2 nm (2.81 eV) or 426.1 nm (2.91 eV) or 411.9 nm (3.01 eV) or 369.0 nm (3.36 eV) photons (ω_1 , generated by Sirah, Precision Scan dye laser, using DCM, Pyridine 1 and 2 dyes) in xenon ($1\text{--}2 \times 10^{-4}$ torr). The VUV light was separated from the fundamental using a lithium fluoride (LiF) biconvex lens^[24] (ISP Optics) based on distinct refractive indices of the lens material for different wavelengths and then directed 1 mm above the ice sur-

face.^[23] The photoionized molecules were extracted to the direction of the focusing regions by an extraction plate (-190 V). Mass-to-charge ratios were determined on the basis of the arrival time of the ions at a multichannel plate; the signal was amplified with a fast preamplifier (Ortec 9305) and recorded using a bin width of 4 ns, which was triggered at 30 Hz (Quantum Composers, 9518).

Computational Details

The equilibrium geometries of various C_2OSiH_4 structural isomers (singlets) along with their ions (doublets) were optimized at the B3LYP^[25,26]/cc-pVTZ^[27,28] level of theory. Using these structures, single-point energy computations were performed at the frozen-core (fc) CCSD(T)^[29]/cc-pVTZ level. For the neutral singlet species, the reference electronic wave functions were obtained by the single-configuration restricted Hartree–Fock (RHF) method, while in the case of doublet ions and triplet species unrestricted Hartree–Fock (UHF) reference wave functions were used. Adiabatic ionization potentials were obtained as the difference of the CCSD(T)/cc-pVTZ/B3LYP/cc-pVTZ energies of the neutral and the ionized species corrected by the difference of the unscaled harmonic zero-point vibrational energies (ZPVE) determined at the B3LYP/cc-pVTZ level. All the computations were performed with the Gaussian09^[30] program package. For the determination of the geometry of the singlet-triplet intersystem crossing (ISC) along the reaction path, intrinsic reaction coordinate (IRC) computations were performed for the triplet surface at the B3LYP/cc-pVTZ level of theory. Along this IRC path single-point electronic energies and ZPVE corrections were computed at the fc CCSD(T)/cc-pVTZ and B3LYP/cc-pVTZ levels, respectively. The ISC geometry along the IRC path was located at the geometry, where the energy difference between the triplet and singlet energies is closest to zero. To test the accuracy of the computations, the adiabatic ionization energy was computed at the same level of theory at the CCSD(T)/cc-pVTZ/B3LYP/cc-pVTZ energies plus B3LYP/cc-pVTZ harmonic zero-point vibrational energy (ZPVE) corrections for trimethylsilylketene ($Me_3Si(H)C=O$),

for which the adiabatic ionization energy was determined experimentally to be 8.55 eV.^[31] The computational result of 8.64 eV suggests errors of at least 0.1 eV. This conclusion also gains support from previous studies suggesting computational uncertainties of ± 0.2 eV.^[32] In addition, the electric field of the Re-TOF-MS setup lowers the experimental ionization energies of the subliming molecules by about 0.04 eV.^[15]

2. Results and Discussion

The mass spectra of the subliming molecules released from the irradiated silane–carbon monoxide ices are shown as a function of temperature in Figure 1 recorded at a photon energy of 9.60 eV. These spectra in the displayed mass region are essentially dominated by three groups of ion counts covering the mass-to-charge, m/z of 72–76, 92–94 (for SiH_4 ; 100–103 for SiD_4 ices), and 102–104. With respect to silylketene ($H_3SiC(H)=C=O$; 72 u), an intense peak was observed at the prospective parent ion at $m/z=72$ in the temperature range from 110 to 170 K for the $SiH_4-^{12}C^{16}O$ system. It should be noted that ions with this mass-to-charge ratio do not appear when irradiating pure silane^[17] or neat carbon monoxide ices^[18] under otherwise identical experimental conditions. Therefore, the molecule at $m/z=72$ cannot consist solely of silicon–hydrogen or carbon–oxygen, respectively.

Considering the atomic weight of the silicon (28 u), hydrogen (1 u), carbon (12 u), and oxygen (16 u), the molecular weight of 72 u is consistent with the formation of numerous molecules holding the molecular formula C_5H_{12} , C_4OH_8 , SiC_3H_8 , SiC_2OH_4 , $SiCO_2$, Si_2O , and Si_2CH_4 . To untangle the molecular formula of the product formed, experiments were carried out exploiting ^{13}C , ^{18}O , and D substituted reactants (Figures 1 & 2)

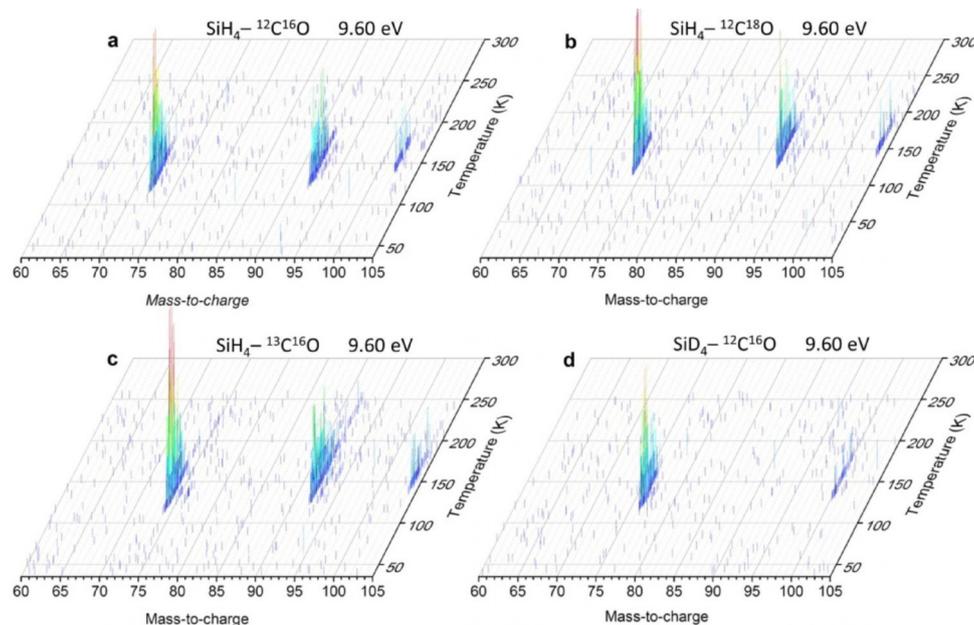


Figure 1. 3D visualization of the PI-ReTOF-MS TPD data for $m/z=60$ to 105. The photon energy was 9.60 eV. Irradiated $SiH_4-^{12}C^{16}O$ ice (a), $SiH_4-^{12}C^{18}O$ ice (b), $SiH_4-^{13}C^{16}O$ ice (c), $SiD_4-^{12}C^{16}O$ ice (d). (The intense peak at $m/z=92$ for SiH_4 -containing ice and at $m/z=100$ SiD_4 -containing ice belong to Si_3H_8/Si_3D_8 . Si_2H_6 is not ionized at 9.60 eV. See details in Ref. [17]).

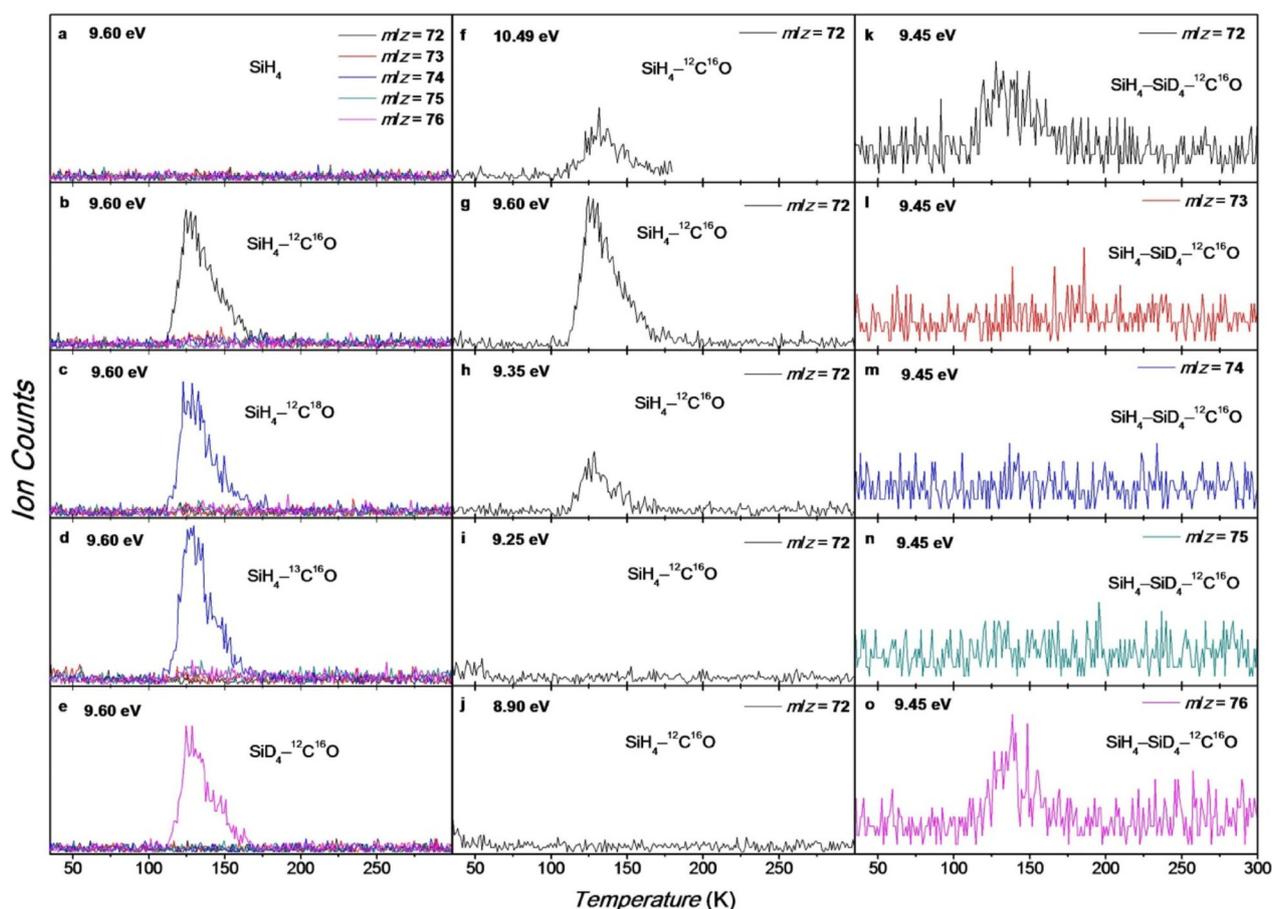


Figure 2. a–e) PI-ReTOF-MS TPD curves for $m/z = 72$ to 76 using photon energy of 9.60 eV. Irradiated pure SiH_4 ice (a), $\text{SiH}_4\text{-}^{12}\text{C}^{16}\text{O}$ ice (b), $\text{SiH}_4\text{-}^{12}\text{C}^{18}\text{O}$ ice (c), $\text{SiH}_4\text{-}^{13}\text{C}^{16}\text{O}$ ice (d), $\text{SiD}_4\text{-}^{12}\text{C}^{16}\text{O}$ ice (e). f–j) PI-ReTOF-MS TPD curves for $m/z = 72$ of the irradiated $\text{SiH}_4\text{-}^{12}\text{C}^{16}\text{O}$ ice as recorded by using different photon energies for ionization as given on the panels in eV. (In the case of 10.49 eV photon energy (panel f) the experiment was terminated at 180 K.) k–o) PI-ReTOF-MS TPD curves for $m/z = 72$ to 76 of the irradiated $\text{SiH}_4\text{-SiD}_4\text{-}^{12}\text{C}^{16}\text{O}$ ice using ionizing photon energy of 9.45 eV.

while monitoring the sublimation profiles during the TPD phase. Considering the TPD profiles of the $\text{SiH}_4\text{-}^{12}\text{C}^{18}\text{O}$ and $\text{SiH}_4\text{-}^{13}\text{C}^{16}\text{O}$ systems, the sublimation profile shifts from $m/z = 72$ to $m/z = 74$ (Figure 2). The overlapping TPD profiles at $m/z = 72$ and 74 reveal that the product carries one oxygen atom, but two carbon atoms. For the $\text{SiD}_4\text{-}^{12}\text{C}^{16}\text{O}$ ice, the TPD profile shifts from $m/z = 72$ to $m/z = 76$ indicating that the newly formed molecule holds four hydrogen atoms. Accounting for these findings (one oxygen atom, two carbon atom, four hydrogen atom), a molecular mass of 44 u is obtained, which is 28 u below the molecular mass of 71 u of the product. The mass difference of 28 u indicates that a single silicon atom is incorporated. It should be noted that silicon has two more natural isotopes, ^{29}Si and ^{30}Si , with natural abundances of 4.7% and 3.1% , respectively. However, these abundances are below our detection limit in these experiments. In conclusion, the product detected at $m/z = 72$ holds the molecular formula of SiOC_2H_4 .

Having established the molecular formula of the newly formed molecule at 72 u as SiOC_2H_4 , we switch our attention to the actual identification of the structural isomer. Here, our electronic structure calculations reveal the existence of 14 closed-shell structural isomers, whose relative energies and

adiabatic ionization energies are presented in Figure 3; Cartesian coordinates and vibrational modes are compiled in the Supporting Information. Considering the range of ionization energies of the SiOC_2H_4 isomers from 10.52 eV to 7.39 eV, the PI-ReTOF data of the subliming molecules in the $\text{SiH}_4\text{-}^{12}\text{C}^{16}\text{O}$ ices were recorded at photon energies of 8.9 eV, 9.25 eV, 9.35 eV, 9.60 eV and 10.49 eV in an attempt to identify the molecule formed. The TPD profiles recorded at $m/z = 72$ are compiled in Figure 2 for distinct photon energies. At 8.90 eV and 9.25 eV, no ion counts were observed at $m/z = 72$; after scaling, the TPD profiles recorded at 9.35 eV, 9.60 eV, and 10.49 eV are identical; the lower intensity of the ion counts of the 10.49 eV experiment compared to that of the 9.60 eV experiment is explained by the fragmentation of the parent ion observed at $m/z = 42$ (most likely ionized ketene and SiH_2). These data reveal an ionization energy of the SiC_2OH_4 isomer(s) of 9.30 ± 0.05 eV. Taking into account the computational and experimental uncertainties, an uncertainty of $0.1\text{--}0.2$ eV of the computed adiabatic ionization energies, our data limit possible structures of the SiOC_2H_4 isomers to **1**, **6** and **10**. All possible structures reveal common building blocks: the CCO moiety, the SiH_3 group, and hydrogen. In **1** and **10** the whole CCO unit is formally inserted into the Si–H bond of the silane molecule, while

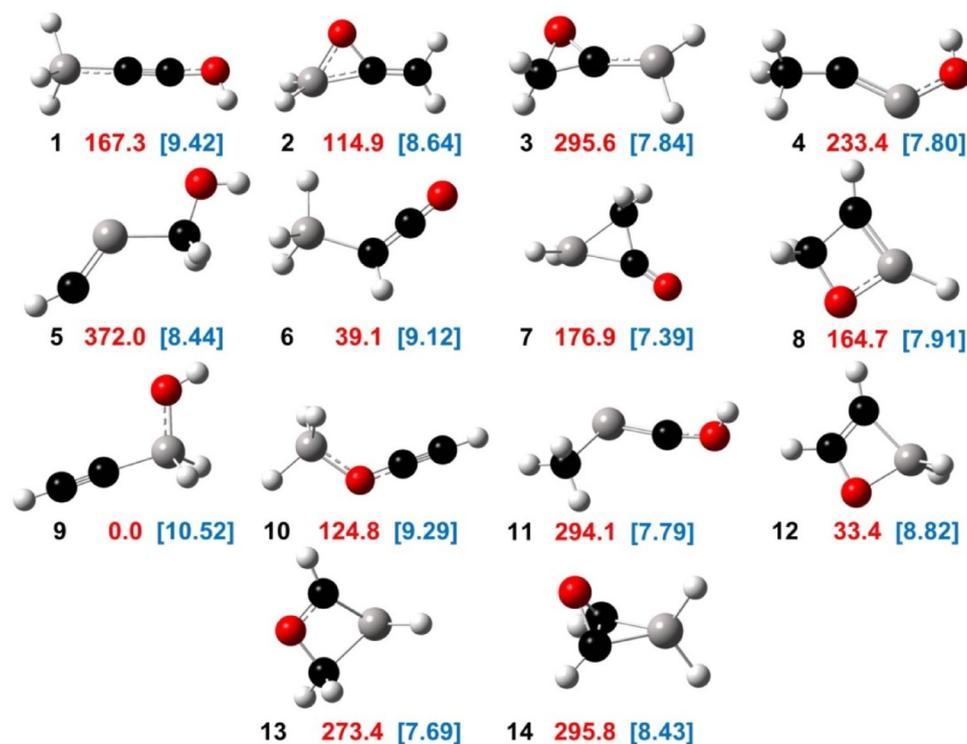


Figure 3. Singlet structures of SiC_2OH_4 with computed relative energies (in kJ mol^{-1} ; red numbers) adiabatic ionization energies (in eV; blue numbers in square brackets).

in **6** the terminal carbon atom of the CCO unit is inserted into the Si–H bond of the silane molecule. Which isomer(s) is(are) eventually formed in our study?

An inspection of the infrared spectra reveals additional information (Figure 4). Here, the infrared spectra are dominated by the fundamentals of silane (antisymmetric degenerate stretching mode, 2181 cm^{-1} ; degenerate deformation mode, 912 cm^{-1}) and by the stretching fundamental of the carbon monoxide reactant ($^{12}\text{C}^{16}\text{O}$, 2137 cm^{-1}). Carbon dioxide ($^{12}\text{C}^{16}\text{O}_2$; antisymmetric stretching mode, 2346 cm^{-1}) and triplet dicarbon monoxide ($^{12}\text{C}_3^{16}\text{O}$; 1988 cm^{-1})—the central building block of isomers **1**, **6**, and **10**—are the most prominent reaction products emerging in the infrared spectra during the radiation exposure.^[18] Both species have been shown to be prominent radiation products in pure carbon monoxide ices exposed to energetic electrons at 10 K.^[18] Furthermore, the infrared spectra suggest that the isomers **1** and **10** are likely absent. Our quantum chemical calculations predict intense carbon–carbon stretching modes of **1** and **10** at 2271 cm^{-1} and 2232 cm^{-1} , respectively; computed frequencies were scaled with a recommended scaling factor of 0.98.^[33] However, only two peaks at 2242 cm^{-1} and 2281 cm^{-1} could be monitored; they are associated with carbon suboxide ($^{12}\text{C}_3^{16}\text{O}_2$; ν_3) and ^{13}C -substituted carbon dioxide ($^{13}\text{C}^{16}\text{O}_2$; ν_3), respectively.^[18] Unfortunately, a direct infrared spectroscopic identification of **6** is not feasible as the most intense fundamental of $\text{H}_3\text{Si}^{12}\text{C}(\text{H})=^{12}\text{C}=\text{O}$ overlaps with the fundamental of the carbon monoxide reactant. This also holds for $\text{H}_3\text{Si}^{13}\text{C}(\text{H})=^{13}\text{C}=\text{O}$ and $\text{H}_3\text{Si}^{12}\text{C}(\text{H})=^{12}\text{C}=\text{O}$.

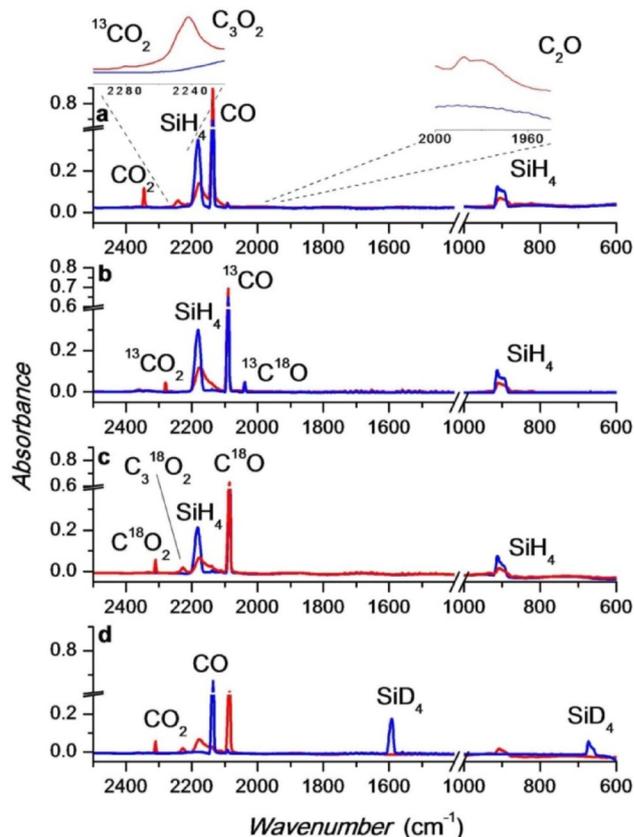


Figure 4. IR spectra of silane–carbon monoxide ices recorded before (blue traces) and after 1 h electron irradiation (red traces); $\text{SiH}_4\text{-}^{12}\text{C}^{16}\text{O}$ ice (a); $\text{SiH}_4\text{-}^{13}\text{C}^{16}\text{O}$ ice (b); $\text{SiH}_4\text{-}^{12}\text{C}^{18}\text{O}$ ice (c); $\text{SiD}_4\text{-}^{12}\text{C}^{16}\text{O}$ ice (d). (^{12}C and ^{16}O are denoted simply by C and O on the Figure.)

To gain further information on the reactivity of the triplet dicarbon monoxide (C_2O) molecule with the silane forming **1**, **6**, and/or **10**, we focus our attention on the species formed in the SiH_4 - SiD_4 -CO system (Figure 2). This experiment was designed to probe if dicarbon monoxide (C_2O) reacts with silane in one step or in two steps. A one-step reaction via insertion should result only in $H_3Si^{12}C(H)=^{12}C=^{16}O$ (72 u) and $D_3Si^{12}C(D)=^{12}C=^{16}O$ (76 u). However, a two-step pathway via cleavage of the silicon-hydrogen bond followed by free hydrogen atoms adding to dicarbon monoxide and subsequent reaction of SiH_3/SiD_3 with HCCO/DCCO should result in both, the partially deuterated products $H_3Si^{12}C(D)=^{12}C=^{16}O$ (73 u) and $D_3Si^{12}C(H)=^{12}C=^{16}O$ (75 u) along with $H_3Si^{12}C(H)=^{12}C=^{16}O$ (72 u) and $D_3Si^{12}C(D)=^{12}C=^{16}O$ (76 u). The TPD profiles clearly reveal that only the fully hydrogenated ($H_3Si^{12}C(H)=^{12}C=^{16}O$) and fully deuterated products ($D_3Si^{12}C(D)=^{12}C=^{16}O$) are detected via $m/z = 72$ and 76 (Figure 2); mixed isotopomers are not formed. This observation is consistent with the one-step reaction of dicarbon monoxide with silane likely via insertion of dicarbon monoxide into a silicon-hydrogen bond of silane.

Possible reaction pathways were explored computationally for the gas phase reaction of triplet dicarbon monoxide with silane (Figure 5). Here, triplet dicarbon monoxide was found to

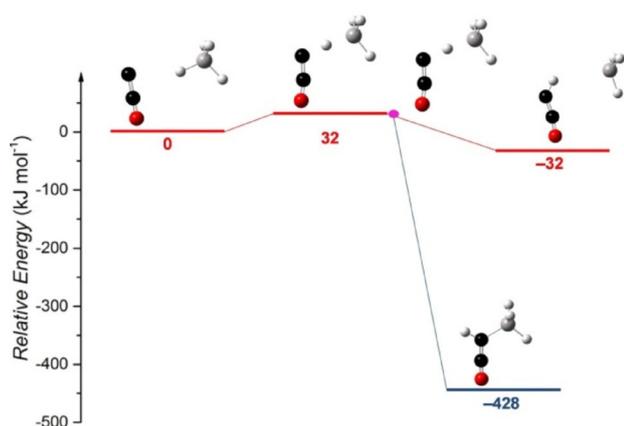


Figure 5. A possible reaction mechanism leading to the formation of singlet silylketene from triplet dicarbon monoxide and silane. (The triplet surface shown in red, the singlet surface in blue, the singlet-triplet intersystem crossing is visualized by a purple circle. The energies were obtained at the CCSD(T)/cc-pVTZ//B3LYP/cc-pVTZ energies level with B3LYP/cc-pVTZ harmonic ZPVE corrections.)

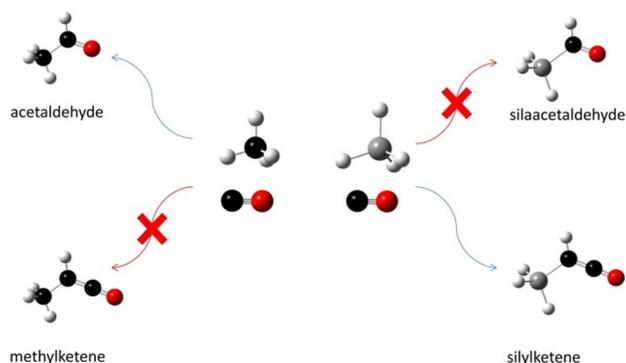
abstract a hydrogen atom from silane via a transition state located 32 kJ mol^{-1} above the separated reactants. On the triplet surface, both the ketylenyl (HCCO) and silyl (SiH_3) radicals are formed in an overall exoergic reaction (-32 kJ mol^{-1}). In the gas phase, the products of this bimolecular reaction fly apart under single collision conditions; in the condensed phase (ices), the doublet radicals can recombine to silylketene ($H_3Si^{12}C(H)=^{12}C=^{16}O$) within the matrix. However, in the isotopically mixed SiH_4 - SiD_4 -CO system, this also should result in the formation of d_1 -ketylenyl (DCCO) and d_3 -silyl (SiD_3) radicals, which in turn can recombine to d_4 -silylketene ($D_3Si^{12}C(D)=^{12}C=^{16}O$) and also react with ketylenyl (HCCO) and silyl (SiH_3) to d_1 -

and d_3 -silylketene ($H_3Si^{12}C(D)=^{12}C=^{16}O$, $D_3Si^{12}C(H)=^{12}C=^{16}O$). Since neither d_1 - nor d_3 -silylketene was observed experimentally, we can disregard a multi-step reaction to silylketene from free ketylenyl and silyl radicals formed via abstraction. However, a detailed look at the potential energy surface reveals the possibility to form silylketene by intersystem crossing (ISC) from the triplet to the singlet surface. The seam of crossing (MSX) between the triplet and the singlet surface almost perfectly coincides both in geometry and in energy with those of the transition state (Figure 5); the energy difference of the singlet and the triplet state at the transition structure is only 0.3 kJ mol^{-1} (CCSD(T)/cc-pVTZ//B3LYP/cc-pVTZ energies plus B3LYP/cc-pVTZ harmonic ZPVE corrections). Therefore, the computations predict an efficient insertion pathway of triplet dicarbon via its terminal carbene-type carbon atom into the Si-H bond of silane forming the methylketene (isomer **6**). No pathways could be exposed connecting the reactants via insertion of dicarbon monoxide to isomers **1** or **10**. This is most likely due to the favorable insertion geometry of dicarbon monoxide via a single terminal carbon atom resulting in a significantly larger cone-of-acceptance of the Si-H bond compared to the geometrically unfavorable and eventually computationally not verified insertion of dicarbon monoxide via carbon and oxygen atoms into the Si-H bond of silane. Recall that the insertion to form methylketene has a small barrier of 32 kJ mol^{-1} (2700 cm^{-1}); thermally, the reaction of dicarbon monoxide with silane is forbidden at 5 K as present in our experiment. However, the necessary energy to overcome the transition state can be imparted from vibrationally excited dicarbon monoxide formed upon reaction of two carbon monoxide molecules with dicarbon monoxide reacting instantaneously upon its generation with a neighboring silane molecule to silylketene. Alternatively, the impinging energetic electrons can deliver the excess energy necessary to overcome the transition state via non-equilibrium chemistry.^[34]

3. Conclusions

Exploiting single vacuum ultraviolet photoionization reflectron time-of-flight mass spectrometry (PI-ReTOF-MS), the present study provides compelling evidence that the interaction of ionizing radiation in the form of energetic electrons with low temperature silane-carbon monoxide ices leads to the formation of the hitherto elusive silylketene ($H_3SiC(H)=C=O$)—the isovalent counterpart of the well-known methylketene molecule. Utilizing isotopically labeled reactants, this method allowed the extraction of the molecular formula of the newly formed molecule based on the isotopic shifts along with the fragment-free nature and inherent stability of the molecular ion upon ionization of the neutral parent molecule. In comparison with computed ionization energies, the variation of the photon energy allowed to narrow down the possible product isomers to **1**, **6**, and **10**. In combination with the infrared spectroscopically detected triplet dicarbon monoxide reactant, electronic structure calculations suggest that dicarbon monoxide reacts with silane via a de facto insertion of the terminal carbon atom into a silicon-hydrogen single bond following non-adiabatic

reaction dynamics and as triggered by the heavy silicon atom intersystem crossing from the triplet to the singlet manifold eventually synthesizing silylketene (**6**); this isomer is more stable by 128 kJ mol^{-1} and 87 kJ mol^{-1} compared to **1** and **10**, respectively. The non-equilibrium nature of the elementary reactions within the exposed ices results in an exciting and novel chemistry which cannot be explored utilizing traditional preparative chemistry. The comparison of the chemical behavior of silicon relative to carbon in form of the methane (CH_4)-carbon monoxide (CO) system is fundamental to our understanding of chemistry and will affect how we explain chemical bonding involving silicon atoms and how we think about chemical structure in the future. A recent experimental study reveals that upon radiation exposure, methane decomposes to methyl (CH_3) plus atomic hydrogen, which in turn reacts with carbon monoxide to the formyl radical (HCO); formyl and methyl recombine yielding acetaldehyde (CH_3CHO).^[34] No insertion of triplet dicarbon monoxide into a carbon-hydrogen bond of methane leading to methylketene was observed ($\text{H}_3\text{SiC(H)=C=O}$). On the other hand, in the silane-carbon monoxide system, silane was not observed to fragment to silyl plus atomic hydrogen, with the latter reacting with carbon monoxide to the formyl radical. Therefore, the replacement of a single carbon atom by silicon in methane leads to a fascinating change in chemical reactivity even under non-thermal (non-equilibrium) conditions even at a temperature as low as 5 K (Scheme 2). Considering that the hydrogen atoms in silane can be substituted by side groups such as silyl or alkyl groups, the reaction of triplet dicarbon monoxide with silane represents the parent system for a previously disregarded reaction class potentially revealing an elegant path to synthesize the largely obscure group of silylketenes.



Scheme 2. Distinct reactivities in the isovalent systems silane-carbon monoxide and methane-carbon monoxide via radical intermediates (left) and non-adiabatic reaction dynamics following insertion of triplet dicarbon monoxide (right).

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Conflict of interest

The authors declare no conflict of interest.

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