A Mass Spectrometry Study of XCO^+, X = Si, Ge: Is $SiCO^+$ a Main Group Carbonyl? Comments on the Bonding in Ground State SiCO and the $[Si,C,O]^+$ Potential Energy Surface

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Dedicated to Professor Heindirk tom Dieck on the occasion of his 60th birthday

Abstract: The cation $[Si,C,O]^+$ has been generated by 1) the electron ionisation (EI) of tetramethoxysilane and 2) chemical ionisation (CI) of a mixture of silane and carbon monoxide. Collisional activation (CA) experiments performed for mass-selected $[Si,C,O]^+$, generated by using both methods, indicate that the structure is not inserted $OSiC^+$; however, a definitive structural assignment as Si^+-CO, Si^+-OC or some cyclic variant is impossible based on these results alone. Neutralisation–reionisation ($^+NR^+$) experiments for EI-generated $[Si,C,O]^+$ reveal a small peak corresponding to SiC^+, but no detectable SiO^+ signal, and thus establishes the existence of the Si^+-CO isomer. CCSD(T)//B3LYP calculations employing a triple-zeta basis set have been used to explore the doublet and quartet potential-energy surfaces of the cation, as well as some important neutral states. The results suggest that both Si^+-CO and Si^+-OC isomers are feasible; however, the global minimum is $^2\Pi$ $SiCO^+$. Isomeric $^2\Pi$ $SiOC^+$ is 12.1 kcal mol^{-1} less stable than $^2\Pi$ $SiCO^+$, and all quartet isomers are much higher in energy. The corresponding neutrals Si–CO and Si–OC are also feasible, but the lowest energy Si–OC isomer ($^3A''$) is bound by only 1.5 kcal mol^{-1}. We attribute most, if not all, of the recovery signal in the $^+NR^+$ experiment to $SiCO^+$ survivor ions. The nature of the bonding in the lowest energy isomers of $Si^+-(CO,OC)$ is interpreted with the aid of natural bond order analyses, and the ground state bonding of $SiCO^+$ is discussed in relation to classical analogues such as metal carbonyls and ketenes.

Keywords: ab initio calculations · carbonyl complexes · germanium · interstellar molecules · mass spectrometry · silicon

Introduction

Metal carbonyls represent a class of coordination complexes which are confined to the d-block elements of the periodic table. High coordination numbers and low oxidation states are characteristic of these species, which have been prepared for all but the early (Group 13) and late (Group 11/12) metals. In some cases, additional ligands are required for M–CO stabilisation. The unique metal-carbonyl bonding interaction is best represented by a σ M ← CO donation and M → CO back donation into the empty π*-orbital, so that overall there is no net change in the metal oxidation state. An important requirement for stability is undoubtedly the presence of suitably diffuse, occupied orbitals of the correct symmetry for the π-back donation. To the best of our knowledge, analogues of these species have not been prepared for any of the heavy main group elements under typical laboratory conditions, although recently there has been a proliferation of low temperature matrix studies in which carbonyl analogues have been synthesised.[1–4] Some examples of cationic alkali metal carbonyls have also been synthesised by Armentrout et al.,[5] but these species remain uncharacterised. The bonding is presumably electrostatic.

Herein, we report experimental results which confirm that $[Si,C,O]^+$ can be synthesised in the gas phase, and that the CO moiety is present in these ions as an intact ligand. We note in passing that the corresponding neutral, trapped in cryogenic

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matrices, has been thoroughly analysed,[6, 7] and has also formed the subject of several high-level theoretical investigations.[8, 9] The focus of these previous theoretical studies has clearly been the reproduction of measured spectroscopic values, and as such these studies were restricted to isomers with Si–CO connectivity. In this context, the recent observation of a 2-silaketene-like complex ($H_2Si \cdot CO$) [1] at low temperatures is noteworthy. We have also undertaken all-electron CCSD(T)(TZDP)//B3LYP(TZDP) calculations for doublet and quartet states of $SiCO^+$ and $SiOC^+$, and selected points on the neutral spin surfaces, in order to correctly assess the structure(s) of the ion(s) we have generated. The results suggest that a mixture of the isomers Si^+–OC and Si^+–CO might be generated in the gas phase under typical ionisation conditions.

Experimental Section

For a description of the experiment and the instrument used, the reader is directed to the recent review by Schalley et al.[10] In brief, the experiments were performed by using a four-sector modified HF-ZAB/AMD 604 mass spectrometer with BEBE configuration, where B and E represent magnetic and electric sectors respectively. $[^{28}Si,C,O]^+$ was generated by chemical ionisation (CI) of a mixture of SiH_4 (conc. sulfuric acid + solid Mg_2Si) and CO, with $p(CO) > 4 \times p(SiH_4)$. Previous tandem-MS experiments have established that SiH_2^+ reacts efficiently with CO to produce $[^{28}Si,C,O]^+$ in an addition–elimination reaction that evolves dihydrogen.[11] Another route to the formation of this ion, albeit inefficient, is via the adduct[12] and this may be important under the higher pressure conditions maintained for CI if Si^+ is generated during SiH_4 decomposition processes. In addition, $[^{28}Si,C,O]^+$ can be generated by the 100 eV electron ionisation (EI) of $Si(OCH_3)_4$ (Gelest). No isobaric interferences, other than from ^{29}Si-containing hydrocarbons, are expected to complicate the collisional activation (CA) spectra of EI-generated $[^{28}Si,C,O]^+$. Due to a preponderance of H-atom losses from these species, it is relatively simple to correct for their presence. On the other hand, several potential isobaric contaminants in the CA spectrum of CI-generated $[^{28}Si,C,O]^+$, such as $^{28}Si_2^+$ and $C_2O_2^+$, could lead to erroneous deductions concerning the ion structure. The CA spectra of the CI-generated contaminants, and the conditions under which they predominate, have been examined separately.[13, 14] Measures taken to eliminate or reduce their interference are discussed in the Results and Discussion. To further substantiate our claim that the observed fragmentations result from $[^{28}Si,C,O]^+$, we have also examined the CA spectrum of CI-generated $[^{70}Ge,C,O]^+$, which was synthesised from a mixture of GeH_4 (Union Carbide) and CO.

Typical CI source conditions are as follows: source temperature 200°C; repeller voltage 0.0–0.5 V; ion extraction voltage 8 kV; mass resolution $m/\Delta m \geq 1500$; source pressure $\leq 10^{-4.3}$ mbar. Typical EI source conditions are as follows: source temperature 200°C; trap current 100 μA; repeller voltage 15 V; ion extraction voltage 8 kV; $m/\Delta m \geq 1500$. Collisional activation of B(1)/E(1)-mass selected $[^{28}Si,C,O]^+$ was effected in collision cells, positioned between E(1) and B(2), using He as a target gas. The collision cell pressure (ca. 10^{-6} mbar) was maintained such that 80% of the parent ion beam was recovered after passing through this cell. This corresponds to an average of 1.1–1.2 collisions per ion.[15] CA products were recorded by scanning the second magnetic sector B(2).

Neutralisation–reionisation ($^+NR^+$) experiments were performed for B(1)/E(1)-mass selected $[^{28}Si,C,O]^+$, utilising the dual collision cells between sectors E(1) and B(2). Cation neutralisation was achieved by collision with Xe at 80% transmittance, while reionisation to cations was achieved by collision of the neutrals with O_2, again at 80% transmittance. Any ions remaining after the first collision event were deflected from the primary neutral beam using an electrode maintained at a high voltage (1.5 kV) positioned before the second collision cell. In order to detect a reionisation signal, the neutral species must be stable for approximately one microsecond. $^+NR^+$ spectra were averaged over 50–100 acquisitions in order to obtain sufficient S/N ratios, while CA spectra were averaged over 20–50 acquisitions.

Computational Methods

The theoretical calculations for $[Si,C,O]^{+/0}$ were performed using the Gaussian 94 software[16] on IBM RS/6000 computers running AIX 4.2.1. The all-electron 6–311G basis sets of McLean and Chandler[17, 18] were used throughout. The respective basis sets were supplemented with single s, p and d functions for each element.[19, 20] Geometry optimisations were performed using the 3-parameter hybrid density functional method of Becke (B3LYP).[21–23] The nature of each stationary point located at this level of theory was then established via subsequent frequency analysis. Single point energy calculations at the all-electron CCSD(T) level, which includes a perturbative estimation of the triples contribution, were then performed at the optimised B3LYP geometries. These energies are denoted CCSD(T)/TZDP)//B3LYP/TZDP in the ensuing sections. Finally, to ensure that basis set deficiencies do not present a misleading picture, all-electron single point CCSD(T) energies were calculated for the lowest energy exit channel ($^2Si^+ + {}^1CO$) and the two lowest energy isomers of Si^+–(C,O), using the correlation-consistent quadruple zeta basis sets of Dunning.[24, 25] Zero-point vibrational energy corrections to the potential-energy surfaces and reaction energies were calculated using the B3LYP/TZDP frequencies and scaled according to Wong.[26] The natural bond orbital analyses were performed at the optimised B3LYP geometries using version 3.0 of the NBO of Weinhold and co-workers.[27–29] These results establish both the bonding and Si-hybridisation in the ground states of the connectivity isomers.

Results and Discussion

The CA spectrum of $[^{28}Si,C,O]^+$, synthesised in a CI source from a mixture of SiH_4 and CO, is presented in Figure 1. The fragmentations in the spectra obtained from the CA of EI-generated $[^{28}Si,C,O]^+$ (tetramethoxysilane) are essentially identical, so we assume that either the same isomer or isomeric mixture is generated using both methods. To eliminate any doubt regarding isobaric interferences from $C_2O_2^+$ and $^{28}Si_2^+$, we first analysed peak at m/z 56 for SiH_4 in the absence of CO. We noted that no cluster corresponding to Si_2^+ was formed, but a distribution of hydrogenated clusters including $Si_2H_n^+$, $n = 1–5$, were present with varying abundances at $m/z \geq 57$. Moreover, the CA spectra of species corresponding to $^{28}SiC_2H_4^+$ and $^{29}SiC_2H_3^+$ would invariably give rise to losses of hydrogen. Inspection of Figure 1 reveals that peaks attributable to losses of hydrogen are entirely absent for the mass-selected ion. This leaves only one other,

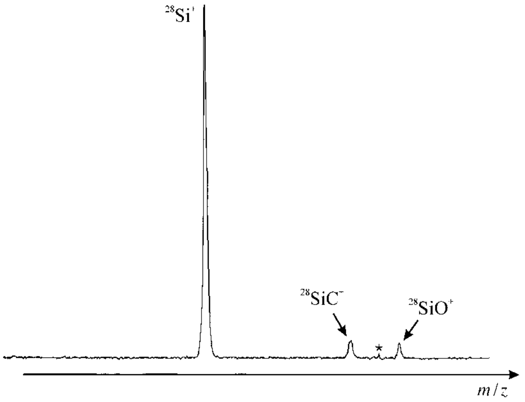

Figure 1. Collisional activation (CA) spectrum of $[^{28}Si,C,O]^+$ generated from a mixture of SiH_4 and CO using chemical ionisation. '*' denotes an artefact of the signal acquisition process.

potentially interfering ion, $C_2O_2^+$. Fortunately, this ion has also been comprehensively studied using CA and $^+NR^+$.[14] Inter alia, the CA spectrum of $C_2O_2^+$ exhibits a characteristic C_2^+ peak, which is not evident in Figure 1. Inspection of our CA spectrum reveals only three peaks, the most intense of which corresponds to loss of CO to yield $^{28}Si^+$. We attribute this peak to Si^+ due to the lower ionisation energy of this species with respect to CO (IE(Si) = 8.152 eV; IE(CO) = 14.014 eV [30]). Minor fragments correspond to loss of carbon (*m*/*z* 44) and loss of oxygen (*m*/*z* 40). The sharp peak between *m*/*z* 42–43, denoted '*' in Figure 1, is due to a minor electrical discharge from the source. If fragments corresponding to C^+ and O^+ are formed at all, their abundance is below the limit of detection for the yields of the parent ion formed in the source. To summarise, while we can unequivocally state that the ion possesses a CO ligand from the CA spectrum, no firm conclusions can be drawn from the results regarding the ion connectivity without recourse to computational results.

Owing to potential isobaric interferences in the various $[Si,C,O]^+$ spectra we have acquired, we have also studied the analogous $[Ge,C,O]^+$ system to establish that $[Si,C,O]^+$ is indeed synthesised. The CA spectrum of $[^{70}Ge,C,O]^+$ is presented in Figure 2. Unlike the CA spectrum of the ^{28}Si analogue, loss of oxygen is notably more intense than loss of carbon. Taking into consideration the base peak, which also corresponds to loss of CO from ionisation energy considerations, we can state that Ge^+–CO connectivity prevails in this case.

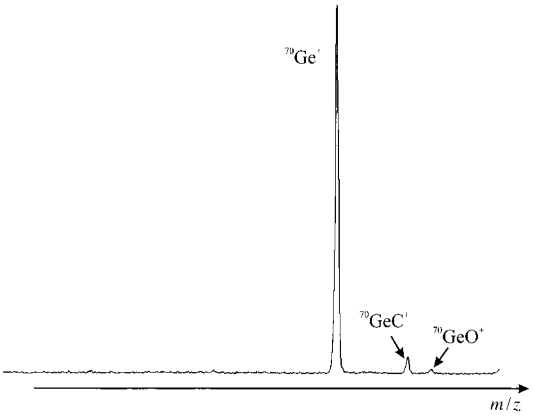

Figure 2. Collisional activation (CA) spectrum of $[^{70}Ge,C,O]^+$ generated from a mixture of GeH_4 and CO using chemical ionisation.

We have also undertaken $^+NR^+$ studies of $[^{28}Si,C,O]^+$ synthesised by the EI of $Si(OCH_3)_4$ vapour. It is pertinent that the CA spectra of the $[^{28}Si,C,O]^+$ generated from CI and EI were essentially identical; however, the larger yields of the ion of interest from EI facilitated, whereas the lower yields from the CI mixture precluded, $^+NR^+$ studies. The $^+NR^+$ spectrum of this ion is presented in Figure 3. An intense recovery signal, and another large signal corresponding to Si^+ and/or CO^+ are evident in the spectrum.[31] A signal corresponding to loss of oxygen (cf. CA spectrum, Figure 1), and the absence of loss of carbon, are also noteworthy. Overall, we have confirmed with our $^+NR^+$ experiments that the neutral

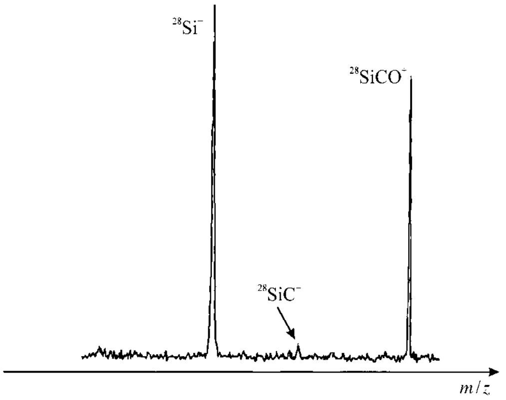

Figure 3. Neutralisation–reionisation ($^+NR^+$) spectrum of $[^{28}Si,C,O]^+$ generated by the electron ionisation of $Si(OCH_3)_4$.

[Si,C,O] is stable on a microsecond time scale, and that vertical transitions from the cation to the neutral, and back to the cation, do not result in gross geometric distortions. That is, due to favourable Franck–Condon factors, the transitions involve low vibrational levels of the neutral and cation, respectively.

The results for the various minima located using B3LYP/TZDP are presented in Table 1. Salient features of the respective potential-energy surfaces are presented in Figure 4. In the following discussions, relative energies refer to the zero-point corrected values calculated by using the CCSD(T)/TZDP//B3LYP/TZDP energies, unless stated otherwise. The ground state of the cation possesses Si-C-O connectivity (C-silicon carbonyl) and is 12.1 kcal mol^{-1} more stable than the lowest energy isomer with Si-O-C connectivity (O-silicon carbonyl). Single point all-electron CCSD(T) calculations at the optimised B3LYP/TZDP geometry, using the correlation-consistent quadruple-zeta basis sets, resulted in a calculated energy difference of 12.1 kcal mol^{-1} between the $SiCO^+$ and $SiOC^+$ ground states, which is in fair agreement with the previous value obtained by using the triple-zeta basis sets.[32]

The ground states of C- and O-silicon carbonyl ions are both linear $^2\Pi$ states. Bent isomers for both connectivities were also located, and the lowest of these is bent $^2A''$ $SiCO^+$, which lies only 0.5 kcal mol^{-1} above ground state $SiCO^+$. Similarly, $^2A''$ $SiOC^+$ lies only 0.9 kcal mol^{-1} above ground state $SiOC^+$. In accordance with these small energy differences, the π-bending modes of the ground states are very soft ($^2\Pi$ $SiCO^+$, ν_{bend} (π) = 225, 251 cm^{-1}; $^2\Pi$ $SiOC^+$, ν_{bend} (π) = 140, 148 cm^{-1}). Indeed, some of the minima located may be artefacts arising from a very flat PES.

Efforts were undertaken to locate cyclic minima on the doublet surface, but all cyclic starting geometries collapsed to either linear or low-lying bent structures. Though not unequivocal, we therefore rule out the existence of low-energy cyclic structures on this surface. Inspection of the relative energies of the quartet and doublet isomers suggests the high-spin states are relatively unstable with respect to their low-spin congeners, and it is presumed this is a manifestation of the inert pair effect for silicon.[31] Inserted isomers O-Si-C, or oxo silicon carbide cations were found to be high in energy with respect to isomers with intact CO

Table 1. Results for isomers and transition structures for [Si,C,O]$^+$ located by using density functional theory. Relative energetics (ΔE) have also been calculated by using the coupled cluster theory, and are zero-point energy corrected.

	E_{SCF}(Ha)		Bond lengths [Å]			Angle [°]	ΔE
	B3LYP	CCSD(T)	r_{Si-C}	r_{Si-O}	r_{C-O}	θ	[kcal mol^{-1}]
$^2\Pi$ SiCO$^+$	– 402.487777	– 401.917030	2.030		1.124	180.0	0.0
$^2A''$ SiCO$^+$	– 402.487256	– 401.916308	2.016		1.124	169.6	0.2
$^2A''$ SiCO$^+$	– 402.486531	– 401.915399	2.004		1.124	164.2	0.7
$^4A''$ SiCO$^+$	– 402.395782	– 401.829568	1.754		1.136	173.7	55.1(5)
$^4\Sigma$ SiCO$^+$	– 402.396333	– 401.830270	1.760		1.137	180.0	55.2(4)
$^2\Sigma$ SiCO$^+$	– 402.346702	– 401.770248	1.742		1.147	180.0	93.8
$^4A''$ SiCO$^+$	– 402.317479	– 401.746225	1.838	2.064	1.209	62.0	107.5
$^2A''$ (^{2}TS)	– 402.393900	– 401.820853		1.637	1.365	126.6	58.6
$^4A''$ (^{4}TS)	– 402.289519	– 401.733899		1.930	1.170	109.2	114.9
$^2\Pi$ SiOC$^+$	– 402.462917	– 401.896703		2.255	1.146	180.0	12.1
$^2A''$ SiOC$^+$	– 402.461586	– 401.895040		2.212	1.146	156.1	13.0
$^4\Sigma$ SiOC$^+$	– 402.317479	– 401.741292		1.636	1.274	180.0	109.9
$^4\Sigma$ SiOC$^+$ (TS)	– 402.266648	–		2.070	1.217	180.0	137.5[a]
^{4} SiOC$^+$ (TS)	– 402.189107	–		2.304	1.482	180.0	184.9[a]
$^2A''$ OSiC$^+$	– 402.292531	–	2.065	1.507		176.3	120.9[a]

[a] B3LYP/TZDP relative energies, including zero-point corrections.

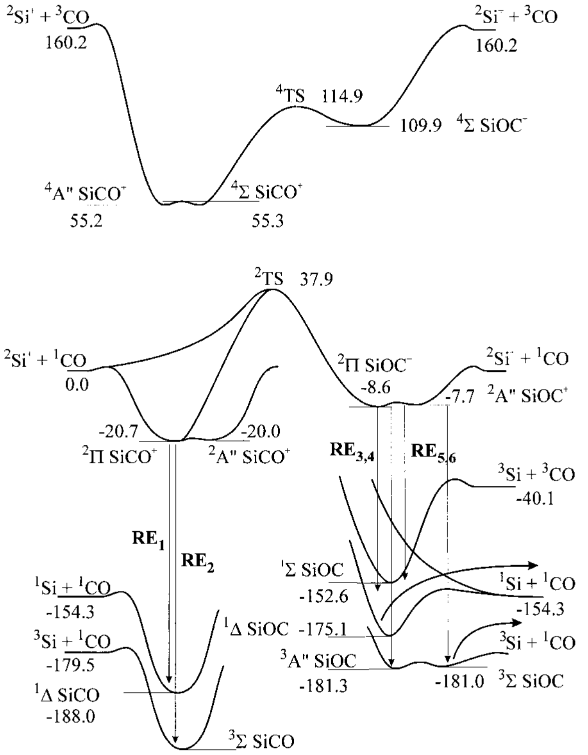

Figure 4. Important features of the potential-energy surfaces of [Si,C,O]$^{+/0}$ derived from CCSD(T)/TZDP//B3LYP/TZDP calculations.

ligands, and were not investigated further. As expected, the lowest lying dissociation asymptote corresponds to ^2P Si$^+$ + $^1\Sigma$ CO, and according to our calculations, the ground state of the cation is bound by 20.7 kcal mol^{-1}.

We have also calculated the ground state for the neutral ($^3\Sigma$ SiCO), and a comparison of our calculated results with those from other theoretical studies are presented in Table 2. We calculate the neutral is bound by 25.0 kcal mol^{-1} with respect to the ^3P Si and $^1\Sigma$ CO asymptote, which is larger than the binding energy of the cation even though there is no ion-dipole bonding stabilisation in the neutral. This suggests that the extra binding energy contributed by the π back-bonding, as is evident in the C–O bond elongation in the neutral, compensates for the additional electrostatic bonding contribution in the cation. Further evidence for π-stabilisation in the neutral is the much shorter Si–C bond length compared with the cation. The bonding schemes for both these species are discussed further below.

The interactions of R$_3$Si$^+$ (R = H, CH$_3$) with CO have previously been studied using Møller–Plesset perturbation theory, in conjunction with double and triple zeta basis sets, and using the G2 method.[34, 35] For these systems, the barriers for the interconversions of C- and O-silylated carbon monoxide are predicted to be very close in energy to the respective 'R$_3$Si$^+$ + CO' entrance channels, and it was argued that a non-interconverting mixture of these isomers might be formed upon chemical ionisation.[34] For the [Si,C,O]$^+$ system, the transition state (TS) on the doublet surface for the endothermic SiCO$^+$ → SiOC$^+$ interconversion lies 58.6 kcal mol^{-1} above ground state SiCO$^+$. The TS is a first order saddle point, that is, it exhibits one imaginary frequency (a', bend, 2022i cm^{-1}). The unusually large magnitude of the imaginary frequency is due to the involvement of C–O stretching. In order to examine the relationship between the TS and the two connecting minima, the imaginary mode was followed downhill from the TS towards the SiCO$^+$ structure. Dissociation was observed, which is not an unreasonable outcome considering the height of the barrier with respect to the 'Si$^+$ + CO' asymptote. On the other hand, downhill searching in the reverse direction linked the TS with the two lowest SiOC$^+$ states. It is, however, doubtful that unimolecular interconversion is possible on the doublet surface due to the barrier height with respect to the '^{2}Si$^+$ + ^{1}CO' channel. This does not preclude formation of either or both of the silicon carbonyl cation isomers upon ionisation because both are stable minima accessible from this asymptote.

A much lower imaginary frequency is associated with the TS on the quartet surface (307i cm^{-1}), and thus involves less CO bond stretching and more concerted CO rotation. Overall, the quartet surface is quite similar to the doublet surface, aside from the position of the TS with respect to the exit channels. The most striking difference is that both ^{4}[Si,C,O] isomers are strongly bound with respect to the lowest energy spin-allowed dissociation asymptote '$^4Si^+ + {}^1CO$' ($D(^4Si^+$-$CO) = 82.6$ kcal mol^{-1}, $D(^4Si^+-OC) = 28.3$ kcal mol^{-1} cf. $D(^2Si^+-CO) = 20.7$ kcal mol^{-1}, $D(^2Si^+-OC) = 8.6$ kcal mol^{-1}). The TS for the interconversion lies 59.7 kcal mol^{-1} above the most stable $^4A''$ $SiCO^+$ isomer, but only 5.0 kcal mol^{-1} above the most stable $^4\Sigma$ $SiOC^+$ isomer, which is 54.7 kcal mol^{-1} less stable than the aforementioned $^4A''$ $SiCO^+$. The contrast between our results for the interconversion barriers for $Si^+-(C,O)$ and the previous results for the $R_3Si^+-(C,O)$ probably belies fundamental differences between the interactions of CO with R_3Si^+, which represents high-valent Si^{IV}, and Si^+, which represents low-valent Si^I. The interaction in the high-valent species can be classified as predominantly electrostatic with some σ donation from CO, particularly as the Si^{IV} centre has no electrons remaining for further bonding interactions. In contrast, Si^+ is a low-valent Si^I cation capable of σ-bond formation and some π-bonding.

We have also investigated SiOC structures to examine the feasibility of this neutral, and in particular to see if the analogous cation can be expected to survive a $^+NR^+$ event. Interestingly, the ground state of the neutral, $^3A''$ SiOC, resides in a very shallow well, 1.5 kcal mol^{-1}, with respect to the $^3Si + {}^1CO$ asymptote, at the CCSD(T)/TZDP//B3LYP/TZDP + ZPE level of theory, and might be detectable in matrix experiments at extremely low temperatures. Given that the ground state triplet is bound by only 1.5 kcal mol^{-1} and that rotational barriers to dissociation are usually small, vertical recombination onto the triplet surface should invariably lead to dissociation, particularly if the neutral is hyperthermal.

Vertical recombination of $^2\Pi$ $SiOC^+$ to $^1\Delta$ SiOC (147.0 kcal mol^{-1}) imparts more than 20 kcal mol^{-1} rovibrational energy to the neutral. Our results indicate that this energy is sufficient to cause dissociation via the spin-allowed $^1Si + {}^1CO$ exit channel. Even if $^1\Delta$ SiOC remains bound with the additional rovibrational energy imparted by recombination, there is still the possibility of internal conversion to the shallow triplet minimum prior to the followup collision event. In view of the shallowness of the ground state SiOC minima, and the weak binding of $^2\Pi$ $SiOC^+$, it is unlikely that any state of neutral SiOC would survive the $^+NR^+$ process. Details and energies of the various neutral structures are presented in Table 2, together with vertical and adiabatic energies for selected ionisation and recombination events. These last values were used to estimate rovibrational excitation energies for the transition products, which are also compiled in Table 3, and are expressed as the difference between the adiabatic and vertical transition values.

Calculation of the low-lying neutral states also permits determination of the adiabatic recombination energy of

Table 3. Adiabatic and vertical one-electron transition energies for $[Si,C,O]^+$. 'RE' and 'IE' represent recombination (neutralisation) and ionisation events, respectively. Those transitions highlighted are incorporated in Figure 4. 'E_{int}' is the zero-point corrected rovibrational energy imparted to the product after the transition.

Transition	Transition type	Adiabatic energy [kcal mol^{-1}]	Vertical Energy [kcal mol^{-1}]	E_{int}
$^2\Pi$ $SiCO^+ \rightarrow {}^3\Sigma$ SiCO	**RE_2**	185.4	180.2	5.5
$^2\Pi$ $SiCO^+ \rightarrow {}^1\Delta$ SiCO	**RE_1**	168.7	161.3	7.7
$^2A''$ $SiCO^+ \rightarrow {}^3\Sigma$ SiCO	RE	186.1	186.7[a]	5.7
$^2A''$ $SiCO^+ \rightarrow {}^1\Delta$ SiCO	RE	168.7	162.4	7.7
$^2\Pi$ $SiOC^+ \rightarrow {}^3\Sigma$ SiOC	**RE_4**	174.2	169.4	4.7
$^2\Pi SiOC^+ \rightarrow {}^1\Delta$ SiOC	**RE_3**	168.1	143.4	24.5
$^2\Pi SiOC^+ \rightarrow {}^1\Sigma$ SiOC	**RE_3**	145.5	143.4	1.9
$^2A''$ $SiOC^+ \rightarrow {}^1\Sigma$ SiOC	**RE_5**	146.4	143.2	3.2
$^2A''$ $SiOC^+ \rightarrow {}^1\Delta$ SiOC	**RE_5**	169.0	143.2	25.8
$^2A''$ $SiOC^+ \rightarrow {}^3A''$ SiOC	**RE_6**	174.7	169.0	5.7
$^3\Sigma$ SiCO $\rightarrow {}^2\Pi$ $SiCO^+$	IE	185.4	192.1	6.5
$^1\Delta$ SiCO $\rightarrow {}^2\Pi$ $SiCO^+$	IE	168.7	171.1	2.0
$^1\Delta$ SiOC $\rightarrow {}^2\Pi$ $SiOC^+$	IE	168.1	169.6	1.7
$^3\Sigma$ SiOC $\rightarrow {}^2\Pi$ $SiOC^+$	IE	174.2	176.0	1.9
$^3A''$ SiOC $\rightarrow {}^2A''$ $SiOC^+$	IE	174.8	176.0	1.3

[a] A vertical value slightly larger than the adiabatic value is a manifestation of the neglect of zero-point energies for both the ion and neutral structures.

Table 2. Comparison of computational results from this work (CCSD(T)/TZDP//B3LYP/TZDP) with experimentally derived values and previous theoretical results for some states of neutral SiCO, plus results for some neutral states of SiOC.

Method	E_{SCF} [Ha]	ω_e [cm^{-1}]	Bond lengths [Å] r_{Si-C}	r_{C-O}	Angle [°] θ	$D(Si-CO)$ [kcal mol^{-1}]
B3LYP/TZDP[a]	– 402.80148	1955, 572, 322 (π)	1.818	1.160	180.0	
CCSD/TZ2P//B3LYP/TZDP[a]	– 402.21036					25.0
CISD/TZ2P[b]	– 402.01373	2058, 541, 342 (π)	1.876	1.127	180.0	11.2[c]
CASSCF/DZP[b]	– 401.70966		1.886	1.145	180.0	
MRSDCI/DZP[d]	– 401.99399	873, 2105	1.835	1.167	180.0	
Expt.[e]		1899, 803				
$^1\Delta$ SiCO, B3LYP/TZDP[a]	– 402.77241	266(π_a), 374(π_b), 576, 1958	1.824	1.162	180.0	
CCSD/TZ2P//B3LYP/TZDP[a]	– 402.18415					33.7[f]
			SiOC			
			r_{Si-O}	r_{C-O}	θ	$D(Si-CO)$
$^3\Sigma$ SiOC	– 402.17175		2.837	1.130	180.0	1.8
$^3A''$ SiOC	– 402.17111		2.763	1.130	151.2	1.5
$^1\Delta$ SiOC[g]	– 402.16213		2.798	1.130	180.0	20.8
$^1\Sigma$ SiOC[g]	– 402.12638		2.392	1.139	180.0	112.5

[a] This work. [b] From reference [8]. [c] Calculated at the SCF/TZ2P level. [d] From reference [9]. [e] From reference [6]. [f] Spin-allowed dissociation can only occur to $^1Si + {}^1CO$, or $^3Si + {}^3CO$. The first of these asymptotes is lowest in energy according to CCSD(T)/TZDP//B3LYP/TZDP. Binding energy (zero-point corrected) value is with respect to the spin-allowed $^1Si + {}^1CO$ asymptote. [f] Binding energy (zero-point corrected) value with respect to the spin-allowed $^1Si + {}^1CO$ asymptote, [g] Binding energy (zero-point corrected) value with respect to the spin-allowed $^3Si + {}^3CO$ asymptote.

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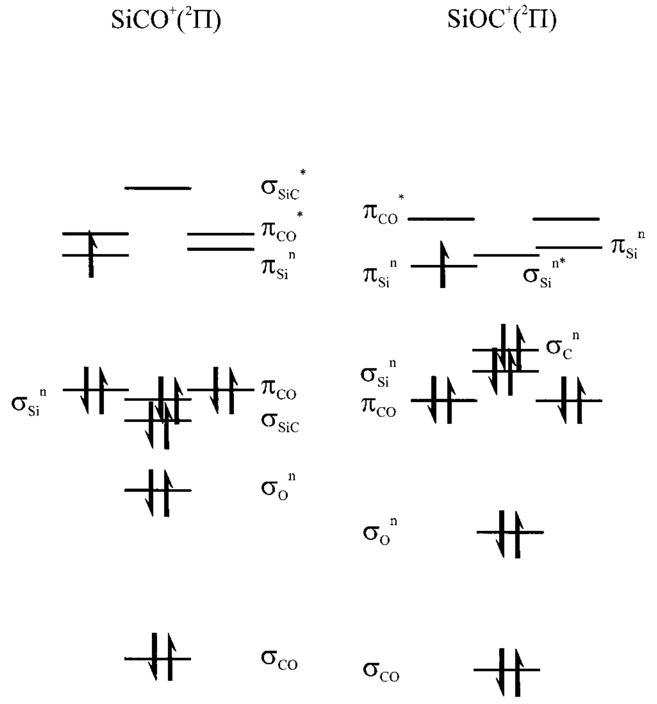
$^2\Pi$ SiCO$^+$, which is 185.4 kcal mol^{-1}. The vertical recombination energy is calculated to be 180.2 kcal mol^{-1}, so the first collision in the $^+$NR$^+$ sequence deposits 5.5 kcal mol^{-1} rovibrational energy into the triplet neutral that is formed, assuming vertical transitions from the cation ground state. The reionisation of this neutral, which according to our calculations deposits 6.5 kcal mol^{-1} internal energy into the resulting cation, should be survived by at least a fraction of the parent beam even if these ions are hyperthermal, as $^2\Pi$ SiCO$^+$ is bound by 20.7 kcal mol^{-1}. To summarise, a fraction of the SiCO$^+$ ions that are in the ground vibrational state are expected to survive $^+$NR$^+$ experiments. In order to detect a recovery signal for SiOC$^+$, population of low vibrational states of the $^1\Sigma$ SiOC surface is required, say $v' = 0{,}1$. Even if under exceptional circumstances some $^1\Sigma$ SiOC is formed, it is likely to be formed in a higher vibrational state and thus possess the requisite energy to dissociate via the ^{1}Si + ^{1}CO exit channel. Consideration of the experimental data in view of the theoretical findings thus suggest that the CA results are therefore representative of a mixture of SiCO$^+$ and SiOC$^+$ isomers, whereas the $^+$NR$^+$ survivor ion signal is very likely to be exclusively indicative for the SiCO$^+$ isomer.

The MO diagrams for the ground states of SiCO$^+$ and SiOC$^+$ are presented in Scheme 1. High energy virtual orbitals and core orbitals are omitted for simplicity, and the energy separations between the MOs are approximately to scale. A discussion of the bonding in $^3\Sigma$ SiCO appears in reference [8].



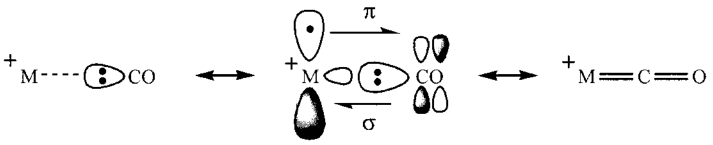
Scheme 1.

Inspection of the character of the MOs for the ground states of both C- and O-silicon carbonyl ions reveals firstly, that the Si 3p orbitals with the correct symmetry for the π-interaction do not mix with the π_{CO} bonding states; and secondly, apart from the destabilising effect of the $\sigma_{Si}{}^n$ lone-pair MO on the $\sigma_{CO}{}^n$ lone-pair MO, the bonding in the CO ligand remains largely unperturbed in $^2\Pi$ SiOC$^+$. The distinguishing feature of the $^2\Pi$ SiCO$^+$ MO scheme is the introduction of a σ_{SiC} MO, which is a mixture of the $\sigma_C{}^n$ orbital and an empty 3p orbital of Si. π_{SiC} bonding in either isomer is negligible, and probably non-existent, as the single 3p Si electron resides in localised non-bonding orbitals.[36] We conclude that the bonding in the ground state of SiOC$^+$ is exclusively electrostatic; in the case of $^2\Pi$ SiCO$^+$, the electrostatic contribution is also important. However, in addition to the electrostatic component, stabilisation is also gained through the formation of the previously described donor–acceptor bond. An interesting question now arises: on the basis of the B3LYP wavefunctions, is it suitable to classify the ground state of SiCO$^+$ as a silicon carbonyl, as we have arbitrarily chosen, or does the bonding situation more closely resemble what could be expected in a silaketene? The evidence from the NBO analysis, outlined below, suggests the Si$^+$–CO interaction in the ground state of this isomer is a mixture of 'electrostatic + carbonyl-like', and that formation of silaketene-like species appears to be energetically unfavourable.

First, Si possesses a large, polarisable core, in contrast to C, for which the core is small and tight (1s^2 electrons). This has several implications for the formation of multiple bonds involving Si. For efficient *n*p orbital overlap (in a π-MO sense) between bonding partners, a short Si–X bond (X = heteroatom) is necessary. As a first step towards π-bond formation between ^{2}P Si$^+$ and a ligand, reduction of the core repulsions from the closed 3s shell is required. This can be achieved by either promotion of one of these electrons into an empty 3p orbital, or alternatively, addition of strong electron-withdrawing groups, such as halogens, to the silicon centre. The former approach can be formally considered as ^{2}P Si$^+$ →^{4}P Si$^+$, for which the energy requirement at the all-electron CCSD(T) level is 5.05 eV. If we now compare the Si$^+$–C bond lengths in the various SiCO$^+$ minima that were located, it is apparent that formation of higher order Si–C bonds is energy demanding (the lowest energy isomer with a Si$^+$–C bond of higher order is 2.37 eV less stable than the ground state). Furthermore, reduction of the C–bond order accompanies formation of higher order Si$^+$–C bonds, so that donation into the π_{CO}* orbital increases as the Si$^+$–C bond length decreases. For comparison, the bond length in free ^{1}CO is 1.128 Å.

As an additional indicator of the character of the bonding in $^2\Pi$ SiCO$^+$, we have analysed the B3LYP/TZDP C-O stretching frequencies of this ion and the ground states of the neutrals ^{1}CO, ^{3}CCO,[37] and ^{3}SiCO. The value for ^{1}CO is 2212 cm^{-1}, which can be used as a reference to gauge the weakening of the CO bond in XCO, X = C, Si$^{0/+}$, attributable to the carbonyl-like back donation into π_{CO}*. Indeed, the value for the C–O stretch in SiCO$^+$ (2194 cm^{-1}) suggests CO bond weakening is insignificant, or that there is little back-donation. Inspection of the π_{CO}* orbital population reveals 0.22 e$^-$ are back-donated into this orbital from the singly occupied $\pi_{Si}{}^n$ MO. The second-order resonance stabilisation energy of these MOs (23 kcal mol^{-1} = resonance alpha energy)[27–29] is suggestive of this interaction. Further evidence of a weak carbonyl-like bonding interaction in ground state SiCO$^+$ is donation from the $\sigma_C{}^n$ orbital of CO to form the σ_{SiC}

bond. The degree of sigma donation can be quantified using the atomic charge of the Si centre (+0.96 e$^-$), and from this a CO-donation population of 0.26 e$^-$ is determined. Together with the CO bond weakening, the Si$^+$–CO interaction is entirely consistent with our proposal of 'electrostatic + carbonyl-like'. We now turn to the case of $^3\Sigma^-$ SiCO and $^3\Sigma^-$ CCO, both of which have been previously studied by Schaefer and co-workers.[8] If we begin by simply comparing the C–O bond lengths (^{3}SiCO, $r_{CO} = 1.160$ Å; ^{3}CCO, $r_{CO} = 1.163$ Å), the stretching in these particular bonds already suggests significant weakening with respect to free CO. This is also supported by much lower calculated C–O stretching frequencies (ω_{CO}, ^{3}SiCO = 1955 cm^{-1}; $\omega_{CO} = 2038$ cm^{-1}, ^{3}CCO). Although these values adhere to at least some notion of carbonyl-like bonding, other features of the natural bond order analysis seem to contradict this. For instance, the π_{CO}* orbitals in ^{3}CCO and ^{3}SiCO are completely empty. In contrast, the orbitals π_{SiC}*, π_{CC}* both have significant populations (ca. 0.15 e$^-$) due to favourable interactions with oxygen-centred non-bonding MOs. This hints at a fundamentally different type of bonding interaction for these neutrals, somewhere between a ketene and a carbonyl (see Scheme 2). Considering the limitations of the single configuration MO approach we have adopted to study these neutrals, as well as the inadequacies of a localised description of π-bonding, we leave further studies for the valence bond experts. Nevertheless, the bonding in the cation is much closer to a carbonyl, rather than a ketene, model.



I II III

Scheme 2.

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[31] Ionisation of the dissociation product CO (arising from cation or neutral processes) in the second collision event of NR cannot be ruled out.

[32] The SCF energies obtained (in Ha) at the CCSD(T)/cc-pVQZ//B3LYP/TZDP are: $^2\Pi$ SiOC$^+ = -401.94624280$; $^2\Pi$ SiCO$^+ = -401.97244919$; ^{2}P Si$^+ = -288.68242616$; $^1\Sigma$ CO $= -113.24617510$ Ha.

[33] The divalent state (s^{2}p^2) is, in nearly all cases, more energetically favourable than the tetravalent state (s^{1}p^3) for unsaturated systems containing heavy group IV elements. A representative example is XH$_2$, where X = Si-Pb. For C, the ground state is $^3B_1$ CH$_2$, whereas the $^1A_1$ XH$_2$, X = Si-Pb, are the ground states of the heavier congeners by as much as 20–25 kcal mol^{-1}: See a) L. A. Curtiss, J. A. Pople, *Chem. Phys. Lett.* **1988**, *88*, 1775 ; b) R. C. Binning, L. A. Curtiss, *J. Chem. Phys.* **1990**, *92*, 3688. For a general discussion of the inert pair effect, see: c) P. Pyykkö, *Chem. Rev.* **1988**, *88*, 563.

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[36] These arguments assume that a single configuration wavefunction, even though correlated by the B3LYP potentials, is suitable for describing the bonding in these ions.

[37] At the B3LYP/TZDP level of theory for $^3\Sigma^-$ CCO, $r_{CC} = 1.357$ Å, $r_{CO} = 1.163$ Å, $E_{SCF} = -151.3047715$ Ha, ZPE = 5.6 kcal mol^{-1}.

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