A comprehensive investigation on the formation of organo-sulfur molecules in dark clouds via neutral-neutral reactions

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Received 11 June 2002 / Accepted 9 September 2002

Abstract. Fifteen reactions on the doublet HCN and singlet/triplet H2CS (n = 1, 2) potential energy surfaces have been investigated theoretically via electronic structure calculations to unravel the formation of hydrogen deficient, sulfur bearing molecules via bimolecular reactions of two neutral species in cold molecular clouds. Various barrierless reaction pathways to synthesize astronomically observed CnS and hitherto undetected HCnS (n = 1, 2) isomers are offered. These data present important guidance to search for rotational transitions of the elusive thioformyl HCS(X 2A′) and thietakenyl HCCS(X2Π) radicals in the interstellar medium.

Key words. astrochemistry – ISM: molecules – molecular processes – methods: miscellaneous

1. Introduction

Untangling the synthetic routes to form sulfur-carrying molecules in the interstellar medium is a significant instrument to understand the chemical evolution and physical conditions in star forming regions and in circumstellar envelopes (Minh & van Dishoeck 2000). The chemistry of sulfur carrying species can also be used as a clock to elucidate the history of cold molecular clouds. Compared to the cosmic carbon versus sulfur ratio of 15:1 (Bakes 1997), sulfur is severely depleted in carbon containing molecules. So far, only carbonmonosulfide (CS), carbonylsulfide (COS), thiocyanic acid (HNC), thiocyanic acid (H2S), two ions HCS+ and CS+, and the cumulenes C2S and C3S have been observed astronomically (Wootten 2002). Linear, sulfur terminated chains CnS (n = 1–3) present one of the most peculiar features in interstellar chemistry. Although these molecules are ubiquitous in cold molecular clouds OMC-1 and TMC-1 (Chernicharo et al. 1987; Petrie 1996; Yamamoto et al. 1990; Hirahara et al. 1992), in circumstellar envelopes of the protostellar object B335 (Velusamy et al. 1995), in the outflow of the carbon star IRC+10216 (Markwick et al. 2000; Chernicharo et al. 1987; Gordon et al. 2001), their hydrogen terminated counterparts HCnS and CnSH have not been detected in the interstellar medium yet. However, these molecules might represent the missing source of molecular-bound sulfur in the interstellar medium. Hydrogen deficient organosulfur molecules like HCS(X2A′) and HCCS(X2Π) resemble also important reaction intermediates which could lead to sulfur bearing polycyclic aromatic hydrocarbons (Kaiser et al. 1999; Kaiser et al. 2002).

Despite the importance of these sulfur carrying species in the interstellar medium, their formation mechanisms have not been well established. The very first chemical models simulating interstellar sulfur chemistry postulated the involvement of S+(2Pj) dominated ion-molecule reactions, for instance to synthesize C2S via the reaction sequence (1)–(3) (Scappini & Codella 1996) or via reactions (4) and (5) (Suzuki et al. 1992; Aschi & Largo 2001; Markwick 2000):

CCH + S+(2Pj) → C2S+ + H,
C2S+ + H2 → HC2S+ + H,
HC2S+ + e→ → C2S + H,
S+(2Pj) + C2H2 → HC2S+ + H,
HC2S+ + e→ → C2S + H.

Higher sulfur terminated carbon clusters were thought to be formed via encounters of sulfur ions with astronomically observed cyclopropenylidene (c-C3H2) and vinylidene carbene
(CCCH$_2$)$_n$ isomers (Redondo et al. 1999; Markwick et al. 2000). However, a detailed model of the circumstellar envelope surrounding IRC+10216 predicted number densities of C$_2$S and C$_3$S up to two orders of magnitude lower than actually observed (Millar & Herbst 1990). Therefore, solely ion–molecule reactions cannot account for the abundances of astronomically observed organo sulfur molecules quantitatively. Important reaction pathways to form these species are clearly lacking.

In the following years it emerged that rapid neutral–neutral reactions can also synthesize sulfur-carrying molecules in interstellar environments (Petrie 1996). Laboratory experiments augmented by electronic structure calculations of reactions of ground state carbon atoms C($^3P$) with hydrogen sulfide (H$_2$S) revealed explicitly the formation of the thioformyl radical HCS(X$^2A'$) (Kaiser et al. 1999; Ochsenfeld et al. 1999; Galland et al. 2001). Likewise, the reaction of the dicarbon molecule C$_2$(X$^1Σ_g^+$) with hydrogen sulfide yielded the thiotetylen radical HCCS(X$^2Π$) (Kaiser et al. 2002). The hydrogen sulfide reagent is also present in the interstellar medium and has been observed, for example, in molecular clouds TMC-1 and OMCH-1, toward the star forming region SgrB2, and around the circumstellar envelope of the carbon star IRC +10216 (Thaddeus et al. 1972). Likewise, atomic carbon has been detected in OB star forming regions, in circumstellar envelopes of evolved stars IRC+10216 and α Orionis (van der Keen et al. 1998), in molecular clouds like Orion A and TMC-1 (Tatematsu et al. 1999), and towards the protoplanetary nebulae CRL 618 and CRL 2688 (Young 1997). The dicarbon molecule is abundant in the circumstellar shell of IRC+10216 (Tatematsu et al. 1999; Combi & Fink 1997) and in translucent clouds (Gredel 1999; Gredel et al. 2001; van Dishoeck & Black 1989). Theory predicts further that C$_2$S and C$_3$S may be synthesized via barrier-less neutral-neutral reactions of S($^3P$) + C$_2$H and S($^3P$) + C$_3$H (Flores 2001a; Flores 2001b). Millar et al. (2001) extended previous reaction networks and incorporated both neutral-neutral reactions of atomic sulfur. However, although this refined model significantly increased the production of C$_2$S and C$_3$S, a quantitative agreement was not reached. This suggests that key production routes to sulfur carrying molecules involving reactions of two neutral particles are still missing.

To ascertain ultimately the role of neutral-neutral reactions to form small sulfur bearing molecules in molecular clouds and to unravel the most important reactions, it is crucial to explore the underlying potential energy surfaces extensively. In this paper, we present the very first comprehensive theoretical study of the synthesis of C$_2$S and HC$_n$S($^1$) (n = 1–2) species in cold molecular clouds via binary reactions of two neutral species. Fifteen reactions (6)–(20) are explored in depth via electronic structure calculations:

\[
\begin{align*}
\text{CH}(X^2Π) + S(^3P), \\
\text{C}(^3P) + \text{H}_2\text{S}(X^2Σ^+), \\
\text{CH}(X^2Π) + \text{SH}(X^2Π), \\
\text{CH}(X^2Π) + \text{H}_2\text{S}(X^2Σ^+), \\
\text{CS}(X^1Σ^+) + \text{H}_2(X^1Σ^+), \\
\end{align*}
\]

Due to the low number densities in molecular clouds of about $10^5$–$10^8$ cm$^{-3}$, we restrict this investigation to bimolecular collisions; ternary encounters occur only once in a few $10^9$ years and can be neglected considering mean interstellar cloud lifetimes of $10^9$ years. Likewise, the translational temperature of the reactant species ($\approx 10$ K) dictates that only exoergic processes without entrance barriers are open. Finally, only reagents in their electronic and vibrational ground states are considered.

2. Theoretical model

The potential energy surfaces (PESs) were examined in terms of ab initio molecular orbital methods. We have employed the hybrid density functional B3LYP method, i.e. Becke’s three-parameter non-local exchange functional (Becke 1992) with the non-local correlation functional of Lee et al. (Lee et al. 1988) and the 6-311G(d,p) basis set (Krishnan et al. 1988). The structures of the intermediates and transition states have been confirmed with the vibrational analysis; all relative energies are the corrected values of the zero-point vibrational energies with the B3LYP/6-311G(d,p) level of calculation. The coupled cluster CCSD(T) calculations with the aug-cc-pVTZ basis set (Dunning 1989) have also been performed at the optimized structures obtained with the B3LYP method in order to refine the energetics. All computations have been carried out using the GAUSSIAN 98 program package (Frisch et al. 1998). The relative energies stated in the text are the values obtained with the CCSD(T) method.

3. Results

3.1. The doublet HCS potential energy surface

Both the CH(X$^2Π$) + S($^3P$) and C($^3P$) + SH(X$^2Π$) reactions (6) and (7) present barrierless pathways to access the HCS potential energy surface (PES) (Figs. 1 and 2) yielding the thioformyl, HCS(X$^2A'$) (Int1), and isothioformyl, HSC(X$^2A'$) (Int2), radical intermediates, respectively. Both isomers are stabilized by 404 kJmol$^{-1}$ and 563 kJmol$^{-1}$ with respect to the separated CH(X$^2Π$)/S($^3P$) reactants. The energy difference of 159 kJmol$^{-1}$ is in excellent agreement with previous data of 161 kJmol$^{-1}$ (Galland et al. 2001) and 166 kJmol$^{-1}$ (Ochsenfeld et al. 1999) obtained at the CCSD(T)/cc-pVTZ//QCISD/cc-pVDZ and CCSD(T)/QZ3P levels of theory.
Fig. 1. Schematic representation of the doublet HCS potential energy surface. “Int” indicates an intermediate, “TS” a transition state, and “p” the products.

Fig. 2. Structures of reactants, intermediates, transition states, and products of the doublet HCS potential energy surface. Bond angles are given in degrees, bond distances in Ångström.

HCS(X^2A') and HSC(X^2A') can isomerize through a barrier of 77 kJmol^{-1} with respect to Int2 via TS1,2 and decompose via an atomic hydrogen loss to form the CS(X^1Σ^+) + H(2S1/2) products. These processes are either barrierless (from Int1) or involve an exit barrier of 15 kJmol^{-1} via TS2,p with respect to the final products. Note that an earlier study located a barrier of 5 kJmol^{-1} for TS1,p (Galland et al. 2001). The overall reactions to form CS(X^1Σ^+) + H(2S1/2) from CH(X^2Π)/S(3P) and C(3P)/SH(X^2Π) were found to be strongly exoergic by 362 kJmol^{-1} and 337 kJmol^{-1}, respectively.

3.2. The H_2CS potential energy surface

3.2.1. The singlet H_2CS potential energy surface

Both the CH(X^2Π) + SH(X^2Π) and S(3P) + CH_2(X^3B_1) reactions (8) and (9) have no entrance barrier. The methylidene radical either adds to the terminal sulfur atom or inserts into the S-H bond of the SH(X^2Π) radical to form thiohydroxycarbene (Int3, HSCH, ^1A') or thioformaldehyde (Int4, H_2CS, X^1A1), respectively (Figs. 3–5). The thiohydroxycarbene molecule can exist in the trans (Int3) or cis (Int3') form. The latter is energetically less favored by 6 kJmol^{-1}; both isomers are connected through transition states via configuration inversion of the carbon atom and rotation around the carbon-sulfur bond. The calculations show further that Int3 and Int4 reside in deep potential energy wells of 407 kJ mol^{-1} and 592 kJmol^{-1} with respect to the separated CH(X^2Π) + SH(X^2Π) reactants; the trans structure can undergo a hydrogen shift to Int4 via TS3,4 located at 132 kJmol^{-1} above the thiohydroxy molecule. Additionally, Int3 can isomerize through hydrogen migration forming Int5 (X^1A1) via TS3,5 located 89 kJmol^{-1} above Int5. The latter is the least stable H_2CS isomer on the singlet surface and only stabilized by 98 kJmol^{-1} with respect to CH(X^2Π)/SH(X^2Π). The S(^3P) + CH_2(X^3B_1) reaction (8) proceeds via addition of atomic sulfur to the carbon atom of the methylidene radical to form Int4; no reaction pathways via an insertion of atomic sulfur into a C-H-bond to Int3 was found. The reaction of CS(X^1Σ^+) with H_2(X^1Σ^+) (10) is closed in cold molecular clouds as an entrance barrier of 195 kJmol^{-1} inhibits formation of Int4 via TS_3,4.

The intermediates involved can emit a hydrogen atom to form the thioformyl radical HCS(X^2A') (from Int3, Int4) or HSC(X^2A') (from Int3, Int5). Each atomic hydrogen elimination has no exit barrier. The pathways to form HCS and HSC from the CH(X^2Π) + SH(X^2Π) reactants were found to be exoergic by 211 kJmol^{-1} and 51 kJmol^{-1}. Therefore, the thiohydroxy isomer is expected to be the major product via an H atom loss. Considering the S(^3P) + CH_2(X^3B_1) reactants, the synthesis of HSC is endoergic by 21 kJmol^{-1} and hence not feasible in cold molecular clouds; however, the formation of...
the HCS isomer is open as this pathway was calculated to be exoergic by 139 kJmol$^{-1}$. Note, however, that Int4 can also fragment via a molecular hydrogen loss to form carbonmonosulfide CS(X$^1\Sigma^+$). Here, the exit transition state is tight, and the overall reactions were found to be exoergic by 437 kJmol$^{-1}$ (CH(X$^2\Pi$)/SH(X$^2\Pi$)) and 365 kJmol$^{-1}$ (S(3P)/CH$_2$(X$^3\Pi$)).

3.2.2. The triplet H$_2$CS potential energy surface

The reaction of CH(X$^2\Pi$) with SH(X$^2\Pi$) (8) presents also a barrier-less route to enter the triplet H$_2$CS potential energy surface forming a thiohydroxycarbene intermediate (Int6, HSCH, $^3A$) via a radical – radical recombination (Figs. 6 and 7). The latter is stabilized by 330 kJmol$^{-1}$ with respect to the separated reactants. An insertion of the methylidene reactant into the S-H bond of SH(X$^2\Pi$) can also form to triplet thioformaldehyde (Int7, H$_2$CS, $^3A''$). This isomer resides in a potential well of 423 kJmol$^{-1}$ compared to the reactants and is connected to Int6 via transition state TS$_6$ located 88 kJmol$^{-1}$ above HSCH. The reaction of C(3P) with H$_2$S(X$^1A_1$) leads to the triplet surface as well giving Int8 (H$_2$SC, $^3A''$) without entrance barrier. This intermediate is only slightly more stable by 70 kJmol$^{-1}$ with respect to atomic carbon and hydrogen sulfide and can rearrange via hydrogen shift to Int6. The reaction of C(3P) with H$_2$S(X$^1A_1$) leads to the triplet surface as well giving Int8 (H$_2$SC, $^3A''$) without entrance barrier. This intermediate is only slightly more stable by 70 kJmol$^{-1}$ with respect to atomic carbon and hydrogen sulfide and can rearrange via hydrogen shift to Int6. The barrier of this process via TS$_8$ was determined to be 43 kJmol$^{-1}$ with respect to Int8.

Similar to the singlet surface, these intermediates can fragment via various atomic hydrogen loss pathways yielding the thioformyl radical HCS(X$^2A'$) (from Int6, Int7) or HSC(X$^2A'$) (from Int6, Int8). The decomposition of Int8 via TS$_8$ involves a barrier of 10 kJmol$^{-1}$ above the final products. Previous calculations overestimated the barrier slightly by 5 kJmol$^{-1}$ (Galland et al. 2001). The existence of an exit barrier has important consequences: TS$_8$ is located below the energy of the separated CH(X$^2\Pi$)/SH(X$^2\Pi$) reactants, but above the C(3P)/H$_2$S(X$^1A_1$) reagents. Therefore, HSC isomers cannot be formed via reaction (11) in cold molecular clouds. A fragmentation of Int7 to the thioformyl isomer involves an exit barrier of 5 kJmol$^{-1}$ with respect to the products. Since this barrier is well below the CH(X$^2\Pi$)/SH(X$^2\Pi$) and C(3P)/H$_2$S(X$^1A_1$) reactants, the synthesis of the HCS radical is feasible even in cold molecular clouds. The H atom ejection from Int6 to form HSC proceeds barrier-less; the formation of HCS, however, goes via a loose transition state TS$_6$ which is situated only 2 kJmol$^{-1}$ above the final products. Note that an earlier study suggests that this process is barrier-less.
Fig. 5. Structures of intermediates and transition states of the singlet \( \text{H}_2\text{CS} \) potential energy surface. Bond angles are given in degrees, bond distances in Angström. The structures of the products \( p_1 \) and \( p_2 \) are shown as \( \text{Int}_1 \) and \( \text{Int}_2 \) in Fig. 2.

(Galland et al. 2001). The overall reaction energies to form the thioformyl radical in reactions (11) and (8) is calculated to be \(-169 \text{ kJ mol}^{-1} \) and \(-211 \text{ kJ mol}^{-1} \), respectively; the formation of the HSC isomer is less exoergic by 160 \text{ kJ mol}^{-1}. Intrinsic reaction coordinate (IRC) calculations show that no triplet \( \text{H}_2\text{CS} \) intermediate connects to molecular hydrogen and a triplet carbon monosulfide product, \( \text{CS}(a^3\Sigma) \).

3.3. The doublet \( \text{HC}_2\text{S} \) potential energy surface

This section investigates four barrierless entrance channels to the doublet \( \text{HC}_2\text{S} \) potential energy surface via reactions (12)–(15) (Figs. 8 and 9). Binary collisions of atomic sulfur with an ethynyl radical (reaction (12)) yield the linear thioetyl radical \( \text{HSCCS}(X^2\Sigma^\pm) \) (\( \text{Int}_9 \)) which is stabilized by 458 \text{ kJ mol}^{-1} compared to the separated reactant; an insertion of \( \text{S}(3P) \) into the acetylenic \( \text{C-H} \) bond is not open. Reaction (13) also has no entrance barrier and proceeds via addition of \( \text{CH}(X^2\Pi) \) either to the terminal carbon atom forming \( \text{HCCS}(X^2\Sigma^\pm) \) (\( \text{Int}_9 \)) or to the carbon-sulfur triple bond giving the cyclic isomer \( \text{c-CH}_2\text{S}(X^2\Sigma^\pm) \) (\( \text{Int}_{10} \)). The latter is less stable by 115 \text{ kJ mol}^{-1} with respect to \( \text{Int}_9 \). Note that an addition of \( \text{CH}(X^2\Pi) \) to the sulfur atom can be excluded; the hypothetical \( \text{CSCH} \) structure presents no local minimum on the \( \text{HC}_2\text{S} \) potential energy surface. An addition of \( \text{SH}(X^2\Pi) \) to the terminal carbon atom is also important in the \( \text{C}_3\text{H}(X^2\Sigma^\pm)/\text{SH}(X^2\Pi) \) system (reaction (14)); this pathway forms the bent \( \text{HSCCS}(X^2\Sigma^\pm) \) isomer (\( \text{Int}_{11} \)); compared to \( \text{Int}_9 \), this structure is less stable by 193 \text{ kJ mol}^{-1}. The decreasing stability from \( \text{Int}_9 \) via \( \text{Int}_{10} \) to \( \text{Int}_{11} \) is in excellent agreement with a previous study (Flores et al. 2001) depicting relative energies of 0 \text{ kJ mol}^{-1} (\( \text{Int}_9 \)), 117 \text{ kJ mol}^{-1} (\( \text{Int}_{10} \)), and 192 \text{ kJ mol}^{-1} (\( \text{Int}_{11} \)). Last but not least, reaction (15) leads to \( \text{c-CH}_2\text{S}(X^2\Sigma^\pm) \) (\( \text{Int}_{10} \)) via addition of the carbon atom to the sulfur-carbon double bond; neither an insertion into the \( \text{C-H} \) bond nor an addition to the terminal sulfur atom of the HCS radical are viable. These intermediates can undergo various isomerization processes. \( \text{Int}_9 \) shows a ring closure via \( \text{TS}9_{10} \) (+224 \text{ kJ mol}^{-1}) to form \( \text{Int}_{10} \); the latter can ring open to the \( \text{Int}_{11} \) isomer via either \( \text{TS}10_{11} \) or \( \text{TS}11_{12} \) (+201 or +207 \text{ kJ mol}^{-1}). There is no pathway connecting \( \text{Int}_9 \) via a single hydrogen shift to \( \text{Int}_{11} \). A hydrogen migration occurs only from \( \text{Int}_9 \) to yield \( \text{Int}_{12} \) (\( \text{SCHC}(X^2\Lambda^\pm) \)) via \( \text{TS}9_{12} \); this intermediate \( \text{Int}_{12} \) is less stable by 235 \text{ kJ mol}^{-1} compared to \( \text{Int}_9 \).

These intermediates fragment via atomic hydrogen loss to form numerous \( \text{C}_2\text{S} \) isomers without exit barrier in strongly exoergic reactions. Our calculations suggest that the linear CCS structure \( \text{C}_2\text{S}(X^2\Sigma^\pm) \) (\( p_3 \)) is the most stable \( \text{C}_2\text{S} \) isomer; the \( a^3\Delta \) state is 57 \text{ kJ mol}^{-1} higher in energy (\( p_4 \)). The investigations suggest also the existence of a cyclic \( \text{c-C}_2\text{S} \) isomer (\( X^1\Lambda^\pm \)) (\( p_5 \)) ranging 80 \text{ kJ mol}^{-1} above \( p_3 \). As pointed out previously (Flores et al. 2001), the Renner-Teller effect splits the \( X^2\Sigma^\pm \) state of the HCCS radical (\( \text{Int}_9 \)) into a \( 2^2\Sigma^\pm \) and \( 3^2\Sigma^\pm \) state; the latter correlates with the \( \text{C}_2\text{S}(X^2\Sigma^\pm) + \text{H}(2S_{1/2}) \) products. The \( \text{HC}_2\text{S} \) intermediate (\( \text{Int}_{10} \)) decomposes without exit barrier to form \( \text{c-CH}_2\text{S}(X^1\Lambda^\pm) + \text{H}(2S_{1/2}) \), whereas \( \text{HSCCS}(X^2\Sigma^\pm) \) (\( \text{Int}_{11} \)) fragments to the \( \text{C}_2\text{S}(X^2\Sigma^\pm) + \text{H}(2S_{1/2}) \). Finally, \( \text{SCHC}(X^2\Lambda^\pm) \) (\( \text{Int}_{12} \)) can lose a hydrogen atom forming \( \text{C}_2\text{S}(a^3\Delta) \). Note, however, that a non-planar geometry of \( \text{Int}_{12} \) correlates with the \( \text{C}_2\text{S}(X^2\Sigma^\pm) + \text{H}(2S_{1/2}) \) products.

The reaction exoergicity to form the \( \text{C}_2\text{S}(X^2\Sigma^\pm) + \text{H}(2S_{1/2}) \) via reaction (12) was calculated to be \(-31 \text{ kJ mol}^{-1} \). Therefore, only \( \text{C}_2\text{S}(X^2\Sigma^\pm) \) can be formed in cold molecular clouds, whereas the formation of \( \text{c-CH}_2\text{S}(X^1\Lambda^\pm) \) and \( \text{C}_2\text{S}(a^3\Delta) \) is closed. However, since the enthalpies of formations of the reagents (reactions (13)–(15)) are larger by 28 \text{ kJ mol}^{-1}, 119 \text{ kJ mol}^{-1}, and 154 \text{ kJ mol}^{-1} with respect to the \( ^3P/\text{C}_3\text{H}(X^2\Sigma^\pm) \) system, \( \text{C}_2\text{S}(X^2\Sigma^\pm) \), \( \text{C}_2\text{S}(a^3\Delta) \), and \( \text{c-CH}_2\text{S}(X^1\Lambda^\pm) \) might be formed in these systems via exoergic pathways. The calculations of the branching ratios is currently under investigation; but based on the energetics, we expect \( \text{C}_2\text{S}(X^2\Sigma^\pm) \) to be the dominant product, whereas the cyclic structure should be less prominent. Once \( \text{c-CH}_2\text{S}(X^1\Lambda^\pm) \) is formed, this structure is stable in cold molecular clouds towards ring opening; we determined the inherent barrier to the \( \text{C}_2\text{S}(a^3\Delta) \) isomer to be 81 \text{ kJ mol}^{-1} – well above the averaged translational temperature in these environments (Fig. 10).

3.4. The \( \text{H}_2\text{C}_2\text{S} \) potential energy surface

3.4.1. The singlet \( \text{H}_2\text{C}_2\text{S} \) potential energy surface

The singlet \( \text{H}_2\text{C}_2\text{S} \) potential energy surface is shown in Fig. 11. All reactions (16)–(18) present barrier-less pathways to form
strongly bound H$_2$C$_2$S intermediates. The dicarbon molecule reacts with hydrogen sulfide via addition to the sulfur atom of H$_2$S(X$^1A_1$) giving H$_2$SC(S$^1A_1$) (Int13) which is stabilized by 194 kJmol$^{-1}$ with respect to the separated reactants (Fig. 12). The radical-radical recombination of C$_2$H(X$^2\Sigma^+$) and SH(X$^2\Pi$) leads to thiohydroxyacetylene HSCCH(X$^1A'$) (Int14); this isomer is more stable by 330 kJmol$^{-1}$ compared to Int13. Finally, the reaction of HCS(X$^2A'$) with CH(X$^2\Pi$) can follow an insertion and addition pathway to thioketene H$_2$CCS(X$^1A_1$) (Int15) and cyclothiopropene c-C$_2$H$_2$S(X$^1A_1$) (Int16), respectively. Thio ketene represents the global minimum of the singlet H$_2$C$_2$S surface and resides in a deep potential energy well of 585 kJmol$^{-1}$ with respect to C$_2$(X$^1\Sigma^+$) plus H$_2$S(X$^1A_1$); compared to this isomer, the cyclic structure Int16 is less stable by 136 kJmol$^{-1}$ and can isomerize via hydrogen shift through TS$_{16\_17}$ to c-H$_2$CCS(X$^1A'$) (Int17). Note that Int17 can be formally synthesized, for instance in cometary comae, via an addition of electronically excited carbon atoms (C$^1D$) to thioformaldehyde (H$_2$CS). HSCCH(X$^1A'$) (Int18) presents also a stable minimum and is energetically favorable by 173 kJmol$^{-1}$ compared to Int13; Int18 connects Int13 and Int14 via TS$_{13\_18}$ and TS$_{14\_18}$ via two hydrogen shifts. All intermediates involved can isomerize through various transition states via hydrogen migration (TS$_{14\_15}$) and ring openings/closures (TS$_{16\_17}$, TS$_{15\_16}$, TS$_{15\_17}$).

The singlet H$_2$C$_2$S intermediates can fragment via atomic hydrogen loss to form various HC$_2$S isomers. These are HCCS(X$^2\Pi$) (from Int14 and Int15), c-C$_2$S(X$^2\Sigma^+$) (from Int16, Int17 and Int18), HSCCC(X$^2A''$) (from Int13 and Int14), and SCHC(X$^2A'$) (from Int17). The energetics depend strongly on the nature of the reagent molecules (reactions (16)–(18)); considering the C$_2$(X$^1\Sigma^+$/H$_2$S(X$^1A_1$) system, the formation of HCCS(X$^2\Pi$) + H$_2$(S$_2$1$^2S$) is exergic by 208 kJmol$^{-1}$, of c-C$_2$S(X$^2\Sigma$) by 93 kJmol$^{-1}$, and of HSCCC(X$^2A''$) by only 15 kJmol$^{-1}$. Reaction (16) cannot synthesize SCHC(X$^2A'$) in molecular clouds as this pathway is endoergic by 27 kJmol$^{-1}$. However, due to the larger enthalpies of formation of the reactants in (17) (+77 kJmol$^{-1}$), even the synthesis of SCHC(X$^2A'$) is energetically feasible in this system. In strong contrast, the energy of the C$_2$H(X$^2\Sigma^+$)/SH(X$^2\Pi$) reactants is much lower.
(by 88 kJmol\(^{-1}\)) compared to the \(\text{C}_2(\text{X}^1\Sigma^+_g)/\text{H}_2\text{S(}X^1\Lambda_1)\) system. Note that in all systems studied, the reversed reactions of the \(\text{HC}_2\text{S}\) isomers with the hydrogen atom were found to have no entrance barriers. Our studies located also three transition states of a molecular hydrogen loss (Fig. 13). All transition states involved are well-below the energies of the separated \(\text{C}_2(\text{X}^1\Sigma^+_g) + \text{H}_2\text{S}(X^1\Lambda_1)\) reactants and hence open. However, the \(\text{H}_2\) loss channels are closed in reaction (18) as they are endoergic. Therefore, only reactions (16) and (17) can form interstellar \(\text{C}_2\text{S}\) isomers in cold molecular clouds.
Fig. 11. Schematic representation of the singlet H₂C₂S potential energy surface. “Int” indicates an intermediate, “TS” a transition state, and “p” the products.

Fig. 12. Structures of reactants, intermediates, and transition states of the singlet H₂C₂S potential energy surface. Bond angles are given in degrees, bond distances in Angström. The structures of the products p6–p9 are shown as Int9-Int12 in Fig. 9.
Fig. 13. Schematic representation of the molecular hydrogen elimination to form singlet C2S isomers on the singlet H2C2S potential energy surface.

3.4.2. The triplet H2C2S potential energy surface

Figures 14–16 depict the simplified triplet H2C2S potential energy surface together with the structures of transition states, intermediates, and products involved. All reactions (17)–(20) were found to have no entrance barrier and form deeply bound triplet H2C2S intermediates. The recombination of the C2H(X2Σ+) and SH(X2Π) radicals (reaction (18)) yields triplet thiohydroxyacetene structures HCCSH (Int19). It is important to note that this isomer exists in a cis (Int19; 3A), trans-cis (Int19′; 3A′′), and trans-trans forms (Int19′′; 3A′′′) which are stabilized by 181 kJmol⁻¹, 170 kJmol⁻¹, and 171 kJmol⁻¹ with respect to the separated reactants. The isomerization involves barriers of 107 kJmol⁻¹ (TS19_19′) and 89 kJmol⁻¹ (TS19′_TS19′′), respectively. Reaction (17) of HCS(X2A′) with CH(X2Π) can proceed via insertion and an addition forming thioketene H2CCS(a3Σ+) (Int20) or cyclothiopropene (Int21). The two hydrogen atoms of this cyclic isomer are either located trans (3B; Int21) or cis (3A′; Int21′) with respect to the ring. These structures are more stable by 182 kJmol⁻¹ (Int20) and 79 kJmol⁻¹ (Int21; Int21′) compared to Int19. Binary collisions of carbon atoms (C(3P)) with thioformaldehyde H2CS(X1A′) give another cyclic isomer c-CSCH2(3A″; Int22) which resides in a potential energy well of 210 kJmol⁻¹ with respect to C2H(X2Σ+) plus SH(X2Π). Triplet thioketene (Int20) can be also accessed via reaction (20) of CS(X1Σ+) with CH2(X2B1). The remaining H2C2S structures HSCCH (Int23) and SCHCH (Int24) cannot be formed instantly from the reactants via reactions (17)–(20). Both isomers exist in a trans (3A″, Int23; 3A″, Int24) or cis (3A′, Int23′; 3A′, Int24′) form and are stabilized by 145 kJmol⁻¹, 137 kJmol⁻¹, 318 kJmol⁻¹, and 308 kJmol⁻¹ compared to the C2H(X2Σ+) and SH(X2Π) reactants. Note that the trans and cis forms are connected via transition states TS23_23′ and TS24_24′ located 125 kJmol⁻¹ and 93 kJmol⁻¹ above the trans structure; the trans structures can also isomerize through TS23_24. Int19-Int24 were found to rearrange via various transition state structures of hydrogen shifts and ring opening/closures. Note that the reaction of atomic sulfur with acetylene can also lead to triplet H2C2S intermediates. However, this reaction has an entrance barrier between 8–15 kJmol⁻¹. Our calculations show further that the reaction of H2(X1Σ+) with C2S(X3Σ+) to form HCCS(X2Π) and atomic hydrogen has also an entrance barrier (+67 kJmol⁻¹). Therefore, these pathways are closed in cold molecular clouds. It is important to stress that the reaction of electronically excited dicarbon, C2(a3Πu), which is present in cometary comae, does not form any triplet H2C2S intermediates. Instead, both reactants yield a cyclic van-der-Waals complex followed by an hydrogen abstraction to yield C2H(X2Σ+) and SH(X2Π) (Fig. 17).

The triplet intermediates decompose via atomic hydrogen loss. With respect to the separated C2H(X2Σ+) and SH(X2Π) reactants, the formation of HCCS(X2Π) p6 is exoergic by 170 kJmol⁻¹. The pathway to form p8–p9 are en-dorhetic and hence closed in molecular clouds. Note that the enthalpies of formation of the reagents in reaction (17) are larger by 115 kJmol⁻¹ compared to (18), and p7–p9 can be also formed. Considering reaction (19), the enhanced reagents enthalpies of formation of ≈62 kJmol⁻¹ suggests that the synthesis of p6–p8 is feasible. Finally, our calculations show that CS(X1Σ+)/CH2(X2B1) range 89 kJmol⁻¹ below the C2H(X2Σ+)/SH(X2Π) system. Therefore, no H2C2S isomer can be formed via reaction (20). Intrinsic reaction coordinate calculations depict that a molecular hydrogen elimination to form C2S isomers does not take place on the triplet surface.

4. Astrophysical implications

The electronic structure calculations revealed distinct pathways to form various CnS and HCnS isomers (n = 1–2) in cold molecular clouds via bimolecular reactions between two neutral particles. This comprehensive study suggests that thirteen reactions investigated have no entrance barrier and proceed via indirect reaction dynamics through the formation of polyatomic intermediates. These structures were found to decompose predominantly via atomic hydrogen loss to form HCS and HCCS isomers; singlet intermediates can lose also molecular hydrogen giving the sulfur bearing carbon molecules CS and C2S, respectively (Fig. 18). On the HCS potential energy surface, CS(X1Σ+) was found to be the sole reaction products. Incorporating a second hydrogen atom leads to the singlet and triplet H2CS surfaces. Here, the thioformyl radical HCS(X2A′) is the dominant reaction product on the triplet manifold, whereas CS(X1Σ+) can be formed on the singlet surface, too. Note that the thermodynamically less stable HSC(X2A′) isomer is expected to be only a minor byproduct at the most. A second carbon atom increases considerably the complexity of the potential energy surfaces involved. Four reactions can access the HC2S surface; the intermediates eject atomic hydrogen; the astronomically detected C2S(X2Σ+) molecule can
be formed in three systems; the calculations reveal also that
the hitherto unobserved cyclic isomer c-C_2S(X_1A_1) might be
also a significant product. Electronically excited C_2S(a^1Δ) –
if it is formed in molecular clouds – is expected to phospho-
rescence to the triplet surface; the a^1Δ → X^3Σ^– transition is
expected to occur around 2.097 μm (4768 cm⁻¹) in the in-
frared regime. Five systems have been tackled theoretically
to explore the triplet and singlet H_2C_2S surfaces; these inter-
mediates decompose via atomic hydrogen loss synthesizing
predominantly the hitherto unobserved thietkenyl isomer
HCCS(X^2Π); based on the energetics, the three remaining iso-
mers are expected to be of minor importance. Similar to H_2CS
intermediates, singlet H_2C_2S structures can also release mole-
cular hydrogen giving c-C_2S(X_1A_1) and/or C_2S(a^1Δ).

These considerations help us to “design” future searches for
hitherto unobserved HCS(X^2A') and HCCS(X^2Π) molecules in
dark clouds. Since each isomer has a significant dipole moment
of 1.23 Debye and 1.29 Debye, respectively, a search for their
Fig. 16. Structures of intermediates and transition states of the triplet H$_2$C$_2$S potential energy surface. Bond angles are given in degrees, bond distances in Angström.
microwave transitions is advisable. The thioketenyl isomer is linear, and hence only B-type transitions can occur; this suggests that this isomer can be detected relatively easily. Table 1 compiles dipole moments, rotational constants, and infrared frequencies to assist an identification of important, but hitherto unobserved sulfur-bearing molecules. Preliminary studies of the crossed beam reaction of dicarbon with hydrogen sulfide suggest further the existence of two reaction channels, i.e. HCCS(X^2Π) + H and C2S + H2 (Kaiser et al. 2002); therefore, both molecules are expected to be present in OMC-1 and TMC-1 where C2S is known to exist (Suzuki et al. 1992). We presented further compelling evidence that up to thirteen reactions can synthesize C_nS and C_3S isomers (n = 1–2) in cold molecular clouds. To extract representative information on the chemical evolution of these extraterrestrial environments, it is important to include all, but not only selected reactions into future chemical models which investigate the sulfur chemistry in the interstellar medium. Obviously, this requires also the knowledge of temperature dependent rate constants together with branching ratios if multiple pathways are open. These studies are currently in progress.

Finally, we like to address briefly possible routes to form C_3S and HC_3S isomers via neutral – neutral reactions in cold molecular clouds. Previous crossed beam experiments showed...
that bimolecular reactions of atomic carbon C(1P) and dicarbon molecules C2(X1Σ+g) with hydrogen sulfide can indeed form HCS(X1Σ+) + H2S1/2 and HCCS(X3Πg) + H2S1/2 (Kaiser et al. 1999; Kaiser et al. 2002) via a C2(SCCH2) reaction scheme which is stabilized by 2 kJmol−1 with respect to the reactants. Therefore, we must conclude that bimolecular encounters between tricarbon and hydrogen sulfide do not form C3S or H2CS isomers in cold molecular clouds. However, the reaction of the dicarbon molecule C2(X1Σ+) with ubiquitous interstellar thioformaldehyde (HC2S) might form these elusive isomers in strongly exoergic reactions:

$$\text{C}_3 \left( X^1 \Sigma^+ \right) + \text{H}_2 \text{S} \rightarrow \text{HCCS} + \text{H} \left( 3 \Sigma^+_{1/2} \right)$$

Based on this versatile reaction scheme, we investigated also the reaction of tricarbon C3(X1Σ+) with hydrogen sulfide in a crossed beam setup (Kaiser 2002). Although two of three reaction pathways (22)–(24) are exoergic and hence energetically open, no reactive scattering signal for the CCCS molecule was observed.

$$\text{C}_3 \left( X^1 \Sigma^+ \right) + \text{H}_2 \text{S} \rightarrow \text{HCCS} + \text{H} \left( 3 \Sigma^+_{1/2} \right)$$

Our electronic structure calculations reveal that the potential between the two closed shell species tricarbon and hydrogen sulfide is repulsive; an H2SCCC structure in analogy to Int13 is not bound. Preliminary calculations suggest that the reaction of C3(X1Σ+) with H2S follows rather an endoergic hydrogen abstraction (+43 kJmol−1) and might involve a van-der-Waals complex which is stabilized by 2 kJmol−1 with respect to the reactants.
Previous studies of reactions of dicarbon with unsaturated hydrocarbons acetylene, ethylene, and methylacetylene (Kaiser et al. 2002; Kaiser 2002) depict no entrance barrier; if this concept of a barrier less reaction pathway of dicarbon with thioformaldehyde can be also verified, reactions (25) and (26) present compelling candidates to form C$_3$S or HC$_3$S isomers in the interstellar medium. These pathways are currently under investigation.

Acknowledgements. This research was supported by the Grants-in-Aid for Scientific Research on Priority Areas from the ministry of Education, Science, and Culture, Japan (Y.O.). Most of the ab initio calculations were carried out at the computer center of the Institute for Molecular Science, Japan. RIK acknowledges support from The University of York, UK. This work was performed within the International Astrophysics Network (http://www.chem.hawaii.edu/Bil301/welcome.html/).

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