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Experimental and theoretical studies on possible formation routes of organosulfur compounds in extraterrestrial environments

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Abstract. The reactions of atomic sulfur in the first excited metastable ^{1}D state with C_2H_2, C_2H_4, and CH_4 have been investigated at the most detailed level by means of the crossed molecular beam technique with mass spectrometric detection and *ab initio* calculations of the relevant potential energy surfaces. The nature of the primary products and their yield have been established and complemented with statistical estimates of product branching ratios. In the case of the reactions between S(^{1}D) and C_2H_2/C_2H_4, we have observed the formation of molecular species containing a novel C−S bond, namely HCS, HCCS, CH_2CS and CH_2CHS. Therefore, these reactions are feasible routes of formation of organosulfur compounds in extraterrestrial environments where both S(^{1}D) molecular precursors and simple hydrocarbons are present. In the S(^{1}D)+C_2H_4 reaction the channel leading to HS+C_2H_3 is also important, while the HS+CH_3 formation channel is the only one open for the reaction with methane. The two reactions are therefore a source of HS and hydrocarbon radicals. The observed reaction schemes can be generalized and extended to other reactions involving larger alkynes, alkenes and alkanes. Finally, the ionization energy of the HCCS radical has been determined to be 8.9±0.3 eV. The present results can help to unravel the complex impact-induced chemistry that occurred during the collision of Shoemaker-Levy 9 with Jupiter, to account for the inventory of sulfur compounds in comets and to understand sulfur chemistry during the Solar System formation.

Key words. astrochemistry - methods: laboratory - molecular processes - comets: general - ISM: molecules

1. Introduction

Simple organosulfur (*i.e.* containing a C−S bond) compounds have been observed in interstellar clouds (ISCs) (see (Yamada et al. 2002) and references therein), nearby galaxies (Bayet et al. 2009), cometary comae (Smith et al. 1980; A'Hearn et al. 1983; Meier & A'Hearn 1997; Bockelee-Morvan et al. 1991; Woodney

Send offprint requests to: N. Balucani et al. 1997a,b; Irvine et al. 2000; Bockelee-Morvan et al. 2000; Wallis & Krishna Swamy 1987; Jackson et al. 2004) and also in planetary atmospheres (Noll et al. 1995), raising the question of how they are formed under such different conditions (Yamada et al. 2002). Amongst those observations, probably the most striking one is the detection of CS, CS_2 and S_2 for several days after the impact of the comet Shoemaker-Levy 9 on Jupiter (Noll et al. 1995).

Various routes of formation of organosulfur compounds have been indicated and tested in the modelling of the above mentioned extraterrestrial environments (Millar & Herbst 1990; Millar et al. 2001; Yamada et al. 2002; Meier & A'Hearn 1997; Saxena et al. 2003; Jackson et al. 1982; Borunov et al. 1997; Atreya et al. 1995). In the modelling of ISCs chemistry, for instance, a series of ion-molecule reactions have been suggested to be responsible for the formation of the observed neutral interstellar species (namely CS, COS, HNCS, CH_3SH, H_2CS, C_2S, and C_3S, see Woon 2010). Nevertheless, models including only ion-molecule reactions largely underestimate the observed number densities of those species (see, for instance, Millar & Herbst 1990). A number of neutral-neutral reactions have, therefore, been considered (Millar et al. 2001; Yamada et al. 2002), including reactions between two open-shell species, such as $S(^3P)+C_2H$ and $S(^3P)+C_3H$ (Flores et al. 2001; Flores & Gomez 2001), thus improving the model predictions. Remarkably, reactions of atomic carbon and dicarbon with hydrogen sulfide proved to be easy and efficient pathways towards the formation of C−S containing molecules (Kaiser et al. 1998, 2002) and have also been invoked to explain the formation of CS/CS_2 during the impact of the comet Shoemaker-Levy 9 on Jupiter (Kaiser et al. 1998). Other suggestions have been put forward (Borunov et al. 1997; Atreya et al. 1995), including the reactions of atomic sulfur − generated during the impact by some molecular precursor originally present in the comet or Jovian atmosphere − and simple hydrocarbons − also present either in the comet or in the Jovian atmospheres (Atreya et al. 1995).

Despite their potential role, a substantial lack of experimental data has so far prevented to establish the role of the reactions of atomic sulfur with hydrocarbons or hydrocarbon radicals in all of the above environments. In the light of the general interest of sulfur atom reactions and the paucity of information on sulfur reactivity, we have started a systematic investigation of sulfur atom reactions by means of the crossed molecular beam (CMB) technique with mass−spectrometric (MS) detection. For a general description of the experimental method see Casavecchia et al. 2009, Balucani et al. 2006 and Kaiser & Balucani 2001. The investigation of atomic sulfur reactions was made possible by the development of a beam source for the production of atomic sulfur (Alagia et al. 1997; Leonori et al. 2009a,b). The sulfur atoms are produced in both the ground, ^3P, and first electronically excited, metastable ^1D, states. The first reactive systems we have investigated are those involving $S(^1D)$ and simple hydrocarbons, namely C_2H_2, C_2H_4 and CH_4 (Leonori et al. 2009a,b,c; Berteloite et al. 2010) which are widely spread in extraterrestrial environments. The analogous reactions involving atomic sulfur in the ground ^3P state are indeed very slow (Tsuchiya et al. 1996) and do not produce species containing a novel C−S bond Woon (2007). The CMB results have been complemented by kinetic investigations at very low temperature (Leonori et al. 2009b,c; Berteloite et al. 2010), theoretical calculations on the relevant singlet and triplet potential energy surfaces (PESs) (Leonori et al. 2009a,b,c; Berteloite et al. 2010) and statistical estimates of the product branching ratio via the Rice-Ramsperger-Kassel-Marcus (RRKM) theory (Leonori et al. 2009a,c). Remarkably, while the reactions of $S(^1D)$ can only play a minor role in the low-density environments typical of ISCs, because ^1D is a metastable state with a radiative litefime of 28 s, they might be of interest in several, relatively dense extraterrestrial environments, such as planetary atmospheres and cometary comae (Meier & A'Hearn 1997; A'Hearn et al. 2000). As a matter of fact, $S(^1D)$ can be produced in planetary atmospheres and cometary comae by UV photodissociation or electron-impact induced dissociation of several precursor molecules relatively abundant in those environments, namely OCS and CS_2 (Meier & A'Hearn 1997). Even the photodissociation of H_2S at the Lyman-α wavelength can occur via a three body dissociation with S(^{1}D) formation Cook et al. (2001) and the UV photodissociation of radicals, such as SH, leads to the formation of atomic sulfur in the first electronically excited state Janssen et al. (2007). Since the lifetime of the metastable ^{1}D excited state is long enough to allow collisions to take place both in cometary comae and in dense planetary atmospheres, sulfur atoms in the excited ^{1}D state may well react with other gaseous species. Therefore, in the light of the low reactivity of atomic sulfur in its ground electronic ^{3}P state with closed shell species, S(^{1}D) reactive collisions can play an important role in the formation of organosulfur or other sulfur-containing compounds in various environments. It is to be noted that the UV photodissociation of H_2S in the primeval terrestrial atmosphere has been suggested as a possible initiating step of gas-phase prebiotic synthesis on Earth (Miller 1986).

In this contribution, after a brief description of the experimental technique and theoretical methods employed, we will summarize the main results on the reactions S(^{1}D)+C_2H_2, C_2H_4 and CH_4. The implications for the S(^{1}D) chemistry in extraterrestrial environments will also be addressed.

2. The experimental technique

The CMB technique with MS detection is a powerful technique for the study of elementary reactions (Casavecchia et al. 2009; Balucani et al. 2006) and has recently been applied to the study of reactions of relevance in astrochemistry Kaiser & Balucani (2001); Kaiser (2002); Costes et al. (2006); Balucani et al. (2009); Balucani (2009); Balucani et al. (2007). The peculiarity of the CMB technique is that the reactants are confined into separate beams which cross each other at a specific angle; the species of each beam are produced with a well defined velocity and collide only with the molecules of the other beam, allowing us to observe the consequences of well defined molecular collisions. The products are formed at the collision center and reach undisturbed the detector, since we operate at a very low pressure (10^{-6} hPa). The use of electron ionization (EI) MS detection makes it possible to determine the nature of any primary product (including transient species, because secondary and wall collisions are avoided) and is particularly advantageous compared to spectroscopic techniques when the optical properties of the products and/or their nature itself are unknown. When more than one reaction channels are open, it is also possible to determine the product branching ratio (see, for instance, Casavecchia et al. 2009 and Balucani et al. 2006). In general, the CMB technique with EI-MS detection allows determining (a) the nature of the primary reaction products, (b) the branching ratios of competing reaction channels, (c) the microscopic reaction mechanisms, and (d) the product energy partitioning among translational and internal degrees of freedom.

Because of the usually very low number density of products to be detected in these experiments, a high electron energy (70-200 eV) is used for product ionization. The peak of the ionization cross section, in fact, is roughly 70 eV for most neutral species. Unfortunately, the use of such a high electron energy is usually accompanied by the well-known phenomenon of dissociative ionization, which has represented a limit for MS detection in CMB experiments. In our laboratory, for the first time in CMB experiments we have implemented product ionization by *soft* EI, which is achieved by using a tunable electron impact ionizer (energy range: 7−100 eV) (Balucani et al. 2006; Casavecchia et al. 2009). In this way, by tuning the electron energy below the threshold for dissociative ionization of interfering species, it is possible to eliminate or reduce the background signal that might impede reactive scattering experiments.

Remarkably, the use of a tunable electron impact ionizer in our CMB instrument permits measuring the EI efficiency curves of the products as a function of electron energy down to their ionization thresholds and, from these, obtaining a direct estimate of the ionization energy of the product radicals. In other words, we have developed the capability of measuring the ionization energy of radical species by synthesizing them in CMB reactive scattering experiments (Balucani et al. 2006; Casavecchia et al. 2009). This approach has also been applied to determine the previously unknown ionization energy of the HCCS radical (see below).

3. Theoretical methods

The potential energy surfaces of the SC_2H_2, SC_2H_4 and SCH_4 systems have been investigated by localizing the lowest stationary points at the B3LYP level of theory in conjunction with the correlation consistent valence polarized set aug-cc-pVTZ, augmented with a tight d function with exponent 2.457 for the sulfur atoms to correct for the core polarization effects (we denote this basis set as aug-cc-pV(T+d)Z). At the same level of theory we have computed the harmonic vibrational frequencies. The energy of all the stationary points was computed at the higher level of calculation CCSD(T) using the same basis set aug-cc-pV(T+d)Z. Both the B3LYP and the CCSD(T) energies were corrected to 0 K by adding the zero point energy correction computed using the scaled harmonic vibrational frequencies evaluated at B3LYP/aug-cc-pV(T+d)Z level. Selected calculations were performed also at the W1 level of theory. All calculations were performed using Gaussian 03 Frisch et al. (2004) while the analysis of the vibrational frequencies was performed using Molekel Portmann & Lüthi (2000). Bond angles and distances for all the involved intermediates and transition states can be found in Leonori et al. 2009a, Leonori et al. 2009c and Berteloite et al. 2010.

We have also performed RRKM calculations to estimate the statistical product branching ratio for the $S(^1D)+C_2H_2$ and $S(^1D)+C_2H_4$ reactions, using a code developed for this purpose Leonori et al. (2009a,c). In accordance with the RRKM scheme, the microcanonical rate constant for a specific reaction at a specific total energy (hereby denoted by $k(E)$) is given by the expression

$$k(E) = \frac{N(E)}{h\rho(E)} \qquad (1)$$

where $N(E)$ stands for the number of states (orthogonal to the reaction coordinate) open at the transition state at an energy, and $\rho(E)$ denotes the reactant density of states at the same energy. The rotational densities of states, both for the reactants and for the transition states, were calculated using an inverse Laplace transform of the corresponding partition functions. Subsequently, the rotational densities of states were convoluted with the corresponding vibrational ones using a direct count algorithm. Tunnelling was found, in all cases, to make no important contribution to the rate constants. In the cases of loose transition states (monotonic dissociation channels), we performed ab initio and RRKM calculations at various points along the dissociation coordinate, choosing as a transition state the point yielding the minimum value of the rate constant in accordance with the variational (VTST) approach. The vibrational frequencies and rotational constants derived from the constrained optimization at the intermediate points were used as inputs in the RRKM calculations Leonori et al. (2009a,c).

4. The reaction $S(^1D)+C_2H_2$ and the ionization energy of the HCCS radical

The reaction of $S(^1D)$ with acetylene has been investigated in kinetic experiments and found to be fast with a room temperature rate constant of ca. 5.0×10^{-11} cm^3 $molec^{-1}$ s^{-1} (Little & Donovan 1972). No information was available on the nature of the primary products before our work. According to our *ab initio* calculations, the possible reaction channels are:

$$
\begin{aligned}
S(^1D)+C_2H_2 &\rightarrow HCCS+H \quad \Delta H_0^o=-36.0\ \text{kJ/mol}\\
&\rightarrow CCS(^1\Delta)+H_2 \quad \Delta H_0^o=+27.3\ \text{kJ/mol}\\
&\rightarrow CCS(^3\Sigma^-)+H_2 \quad \Delta H_0^o=-30.2\ \text{kJ/mol}
\end{aligned}
$$

All other channels are strongly endothermic (see Leonori et al. 2009a for a complete list). Molecular hydrogen elimination can form either CCS in a singlet state through a quite endothermic channel or CCS in its ground $^3\Sigma^-$ electronic state. In the latter case, however, an inter-system crossing (ISC) to the triplet C_2H_2S PES is necessary.

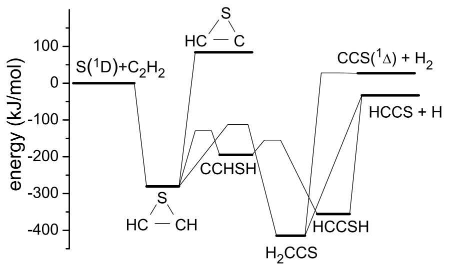

Fig. 1. Simplified schematic representation of the S(^{1}D)+C_2H_2 potential energy surface. See Leonori et al. 2009a for the complete scheme and further details.

We have performed reactive scattering experiments at a collision energy, E_c, of 35.6 kJ/mol and explored the possibility of both H-displacement and H_2-elimination occurrence. The H_2 elimination channel has not been observed to occur to an appreciable extent under the conditions of our experiments, while the

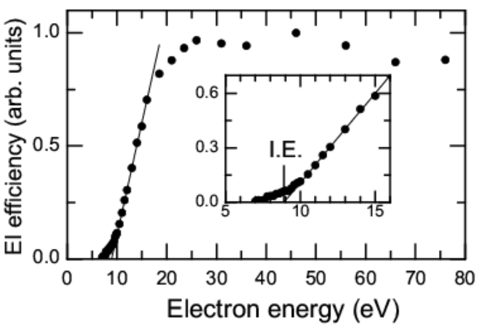

Fig. 2. Electron ionization efficiency as a function of electron energy of the HCCS radical product (m/z=57) from the S(^{1}D)+C_2H_2 reaction at E_c=35.6 kJ/mol, measured at the center-of-mass angle. The estimated ionization threshold of the HCCS reaction product is 8.9±0.3 eV (see text). For more details see Leonori et al. 2009a.

dynamics of the H-displacement channel has been characterized. According to our experimental findings, the reaction proceeds through the formation of a bound intermediate, the lifetime of which is comparable to its rotational period. The experimental results gain full support from the *ab initio* calculations of the SC_2H_2 PES, according to which there are two possible pathways leading to the only exothermic H-displacement channel (see Fig. 1). Both pathways are affected by the formation of bound intermediates and initiate with the electrophilic addition of S(^{1}D) to the π system of acetylene, leading to a first addition cyclic intermediate (thiirene, HC(S)CH). Because of its high internal energy content, thiirene can either dissociate to cyclic-HC(S)C+H in a quite endothermic channel (not open in the conditions of our experiment and in low temperature environments) or rearrange by ring opening and H migration to H_2CCS (thioketene, the most stable isomer along the singlet C_2H_2S PES) through a barrier of 156.7 kJ/mol. Once formed, thioketene can dissociate directly to HCCS+H or CCS($^1\Delta$)+H_2. The latter channel is endothermic and barely accessible at the collision energy of the present experiment. In the alternative pathway, the PES minimum configuration of thioketene is never reached and the succession of rearrangements after thiirene formation is isomerization to CCHSH (through a barrier of 151.3 kJ/mol) followed by isomerization to HCCSH (through a barrier of 40.2 kJ/mol), which, in turn, can undergo an S-H bond fission to HCCS+H. There are no simple arguments to infer which of the two pathways leading to HCCS+H is the dominant one: the isomerization from thiirene to thioketene is characterized by a larger isomerization barrier, but in the second pathway it is necessary to undergo two isomerizations before reaching the configuration of an intermediate, HCCSH, which can dissociate into HCCS+H products. RRKM estimates help to elucidate which of the two pathways is the dominant one. Preliminary estimates Leonori et al. (2009a) indicate that the rate constant associated to isomerization from thiirene to thioketene, 8×10^9 s^{-1}, is smaller than the one associated to the isomerization to CCHSH,

$2{\times}10^{10}$ s^{-1}. The conversion from CCHSH to HCCSH is also very fast with a rate of $7{\times}10^{10}$ s^{-1}. Therefore, the second pathway appears to be slightly favored.

In all cases, HCCS was the sole observed reaction product.

As for the molecular hydrogen elimination channel, the lack of $CCS(^1\Delta)$ observation is not surprising, because at the collision energy of the present experiment, that reaction channel has just become open on energetic grounds, but the rise of the reactive excitation function (*i.e.*, reaction cross section as a function of E_c) to appreciable values can be quite displaced from its onset. The failure to observe the $CCS(^3\Sigma^-)$ product implies that ISC from the singlet to the triplet PES with subsequent reaction along it is not occurring to an appreciable extent under the conditions of our experiment.

Finally, the experimental electron ionization efficiency curve (*i.e.*, the ionization cross section as a function of electron energy) of the HCCS product was measured by detecting the mass-to-charge ratio (m/z) 57 signal intensity at the center-of-mass angle as a function of electron energy, from threshold up to 80 eV. The efficiency curve is shown in Fig. 2. The ionization threshold of HCCS was determined to be 8.9±0.3 eV Leonori et al. (2009a) from the simple straight-line extrapolation method (the absolute energy scale was calibrated by using several stable species for which the ionization cross section is known with great accuracy, see Casavecchia et al. 2009 and Leonori et al. 2009a). The experimental value compare swell with the calculated one, which is 9.15 eV Leonori et al. (2009a).

5. The reaction $S(^1D)+C_2H_4$

The reaction of $S(^1D)$ with ethylene has been investigated in kinetic experiments in the 23-298 K temperature range. The rate coefficient is as large as $4{\times}10^{-10}$ cm^3 $molec^{-1}$ s^{-1} down to the lowest T investigated, thus indicating the absence of a reaction barrier (Leonori et al. 2009b,c). No information was available on the nature of the primary products before our work. According to our *ab initio* calculations, the possible reaction channels are:

$S(^1D)+C_2H_4 \rightarrow$

$$
\begin{array}{ll}
CH_2CHS+H & \Delta H_0^o{=}-26.2\ \text{kJ/mol} \\
CH_2CS+H_2 & \Delta H_0^o{=}-244.6\ \text{kJ/mol} \\
HCS+CH_3 & \Delta H_0^o{=}-9.1\ \text{kJ/mol} \\
HS+C_2H_3 & \Delta H_0^o{=}-5.2\ \text{kJ/mol} \\
CS+CH_4 & \Delta H_0^o{=}-233.7\ \text{kJ/mol} \\
CH_3CS+H & \Delta H_0^o{=}+12.4\ \text{kJ/mol}
\end{array}
$$

All the other conceivable channels are endothermic. The reactive scattering experiments were performed at the two E_c of 37.0 kJ/mol and 45.0 kJ/mol. Product laboratory angular distributions were recorded at m/z=59 (corresponding to the ion $C_2H_3S^+$), 58 ($C_2H_2S^+$) and 45 (HCS^+). In Fig. 3 are shown the m/z=59, m/z=58 and m/z=45 laboratory angular distributions together with the velocity vector (Newton) diagram displaying the kinematics of the experiment at E_c= 37.0 kJ/mol. The three distributions appear quite different as they reflect the different kinematics of the three channels contributing to the global reaction. During the data analysis it has been possible to disentangle the contributions of the channels leading to C_2H_3S, CH_2CS and HCS and to estimate their relative yield (see Leonori et al. 2009c for the details). Even though we had some signature of a contribution from the channel leading to $HS+C_2H_3$, we were not able to record reactive scattering distributions for this channel because of some contamination from the elastic scattering of the ^{33}S isotope present in the beam of atomic sulfur. In the range of masses that we have been able to explore, the dominant contribution is the one leading to HCS, followed by C_2H_3S, with a minor contribution from C_2H_2S (Leonori et al. 2009b, Leonori et al. 2009c). For this system as well, the experimental results were corroborated by the *ab initio* calculations of the relevant PES. According to them, the electrophilic $S(^1D)$ atom adds, without any barrier, to the double bond of ethylene, forming an internally excited cyclic intermediate, thiirane ($H_2C(S)CH_2$). Thiirane is a stable molecule, but it is formed with a very high internal energy content so that

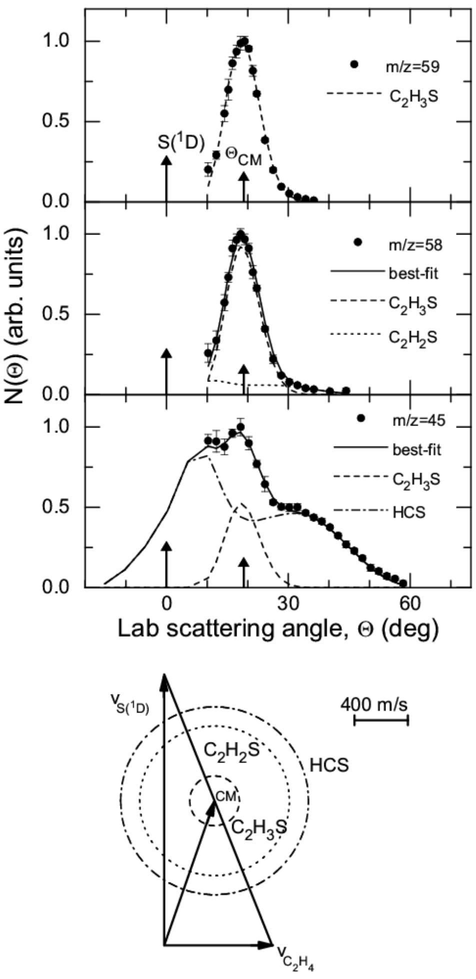

Fig. 3. LAB angular distributions of (top panel) m/z=59, (middle panel) m/z=58, and (bottom panel) m/z=45 products from the reactions $S(^1D)+C_2H_4$ at E_c=37.0 kJ/mol, together with the velocity vector diagram of the experiment. Error bars, when visible outside the dots, represent ±1 standard deviation from the mean. The circles in the Newton diagram delimit the maximum speed that the CH_2CHS, CH_2CS and HCS products can attain if all the available energy is channelled into product translational energy.

it undergoes either bond fission or isomerization. In particular, it can directly undergo ring-opening and three-center H_2 elimination forming thioketene (CH_2CS) or, more readily, isomerize to vinylthiol (CH_2CHSH) which, in turn, can undergo C-H bond rupture to thiovinoxy(CH_2CHS)+H or to $HS+C_2H_3$ (see Fig. 10 of Leonori et al. 2009c). Vinylthiol can also isomerize to the slightly more stable thio-acetaldehyde (CH_3CHS) intermediate, which can undergo C-C bond cleavage to CH_3 + HCS. In the case of this reaction, it is also possible that $S(^1D)$ inserts into one of the C–H bonds of ethylene, rather than adding to the π bond. Both approaches are barrierless and, even though we can imagine that long-range forces will favor the approach towards the electron-rich π orbital of ethylene, we cannot rule out that the insertion mechanism contributes substantially to the reaction. In this second case, vinylthiol (CH_2CHSH) is directly formed by insertion and from it the same kinds of rearrangements and bond-fissions seen before can take place. As a matter of fact, the RRKM branching ratio predictions are rather similar for both addition and insertion pathways, with the only important difference being related to the yield of the channel CH_2CS+H_2 which is the only one directly formed by the thiirane fission (see Table 1). The RRKM branching ratio can be directly compared to the experimental one for the channels investigated. To make the comparison easier, we have set the experimental yield of the HCS channel equal to the one predicted by RRKM calculations for the addition mechanism and scaled accordingly the yields of the other two channels investigated (we recall that in our experiments we can only derive the relative yield of the observed channels, see Leonori et al. 2009c). As visible in Table 1, while the experimental yield of the channel CH_2CHS+H is in line with both RRKM predictions for the insertion and addition mechanisms, the yield of CH_2CS+H_2 is more in line with the RRKM prediction for the insertion mechanism. Finally, according to RRKM predictions the channel leading to HS and C_2H_3 is the dominant one. Further effort is therefore necessary to characterize it also experimentally. It is to be noted that, even though we expect a statistical behaviour for this system - because it involves seven atoms and strongly bound long-lived intermediates - we

Table 1. Channel branching ratio for the $S(^1D)+C_2H_4$ reaction at E_c=37.0 kJ/mol. The uncertainty of the CMB values is about 25%.

channel	RRKM (addition)	RRKM (insertion)	CMB
CH_2CHS+H	0.036	0.038	0.044
CH_2CS+H_2	0.084	0.022	0.016
$HCS+CH_3$	0.136	0.145	0.136
$HS+C_2H_3$	0.741	0.791	n.a.
$CS+CH_4$	0.003	0.003	n.a.
CH_3CS+H	0.0001	0.0001	n.a.

cannot rule out non-statistical effects in the reaction dynamics.

6. The reaction $S(^1D)+CH_4$

The reaction with methane has also been investigated by means of the CMB technique, very low temperature kinetic experiments and *ab initio* calculations Berteloite et al. (2010). The reaction is very fast, with rate coefficients in the gas kinetic range also at very low temperature, and is dominated by an insertion mechanism leading to the formation of a strongly bound intermediate, CH_3SH (methanethiol). CH_3SH undergoes bond fission with the formation of $HS+CH_3$ products exclusively. A manuscript reporting on CMB and kinetic experiments, complemented by *ab initio* calculations of the relevant triplet and singlet PESs is under preparation (Berteloite et al. 2010).

7. Implications for astrochemistry and conclusions

The present studies have allowed us to characterize the primary products of reactions which might take place in relatively dense gaseous environments where both $S(^1D)$ molecular precursors and simple hydrocarbons are present. In the case of the reactions between $S(^1D)$ and C_2H_2/C_2H_4, we have observed the formation of molecular species containing a novel C−S bond. Therefore, they are feasible routes of formation of organosulfur compounds. In the $S(^1D)+C_2H_4$ reaction the channel leading to $HS+C_2H_3$ is also important, while the $HS+CH_3$ formation channel is the only one open for the reaction with methane. The two reactions are therefore a source of HS and hydrocarbon radicals. The observed reaction schemes can be generalized and extended to other reactions involving larger alkynes, alkenes and alkanes. As a consequence, the formation of products containing a novel C−S bond is possible for the reactions of $S(^1D)$ with alkynes and alkenes, while HS is formed in the case of the reactions with alkanes and alkenes.

As pointed out in the Introduction, we expect that these reaction routes might be at work in planetary atmospheres or cometary comae. Regarding planetary atmospheres, the planets where sulfur species are abundant are poor in hydrocarbons (*e.g.* Venus or Io), so that the contributions from the reactions investigated will not be significant at present. A notable exception is related to the impact of the comet Shoemaker-Levy 9 on Jupiter after which CS and CS_2 species were observed (Noll et al. 1995). The organosulfur species identified in this study (HCS, HCCS, CH_2CS and CH_2CHS) can all be precursors of CS and CS_2 via secondary collisions with other molecular species or dissociation, as already suggested by Kaiser et al. (1998). Our results can therefore help to unravel the complex impact-induced chemistry that occurred during the collision of Shoemaker-Levy 9 with Jupiter.

As for the importance in the chemistry of cometary comae, $S(^1D)$ produced in the innermost coma from fast dissociation of CS_2 has been already invoked as a precursor of S_2 by its fast reaction with OCS A'Hearn et al. (2000). Similarly, in hydrocarbon-rich comets the $S(^1D)$ reactions with hydrocarbons might be responsible for some sulfur chemistry and lead to observed species like H_2CS Woodney et al. (1997b), thus enlarging the chemical inventory of the comae.

Finally, a more complete set of reactions of sulfur atoms can help to establish the diminat processes involving sulfur during the Solar System formation Pasek et al. (1995).

A more general conclusion is that, in a combined effort, detailed laboratory experiments and theoretical calculations can provide an unprecedented knowledge of elementary reactions, that are fundamental to setting up realistic chemical models of extraterrestrial environments Kaiser & Balucani (2001); Kaiser (2002); Balucani et al. (2007); Balucani (2009). We are now planning to investigate other reactive systems involving atomic sulfur both in the ground ^{3}P and excited ^{1}D states. Since we have recently succeeded in investigating reactions between two open-shell species − namely O+CH_3 and O+C_3H_5 (Leonori et al. 2007) − in CMB experiments, we plan to investigate reactions involving S(^{3}P) and hydrocarbon radicals, such as S(^{3}P)+CH_3. Furthermore, since it might be of interest for the chemistry of cometary comae, we plan to investigate the reaction of S(^{1}D) with abundant cometary species, such as H_2O.

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