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Quantum Chemical Evaluation of the Astrochemical Significance of Reactions between S Atom and Acetylene or Ethylene†

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Addition−elimination reactions of S atom in its ^3P ground state with acetylene (C_2H_2) and ethylene (C_2H_4) were characterized with both molecular orbital and density functional theory calculations employing correlation consistent basis sets in order to assess the likelihood that either reaction might play a general role in astrochemistry or a specific role in the formation of S_2 ($X^3\Sigma_g^-$) via a mechanism proposed by Saxena, P. P.; Misra, A. *Mon. Not. R. Astron. Soc.* **1995**, *272*, 89. The acetylene and ethylene reactions proceed through C_2H_2S ($^3A''$) and C_2H_4S ($^3A''$) intermediates, respectively, to yield HCCS ($^2\Pi$) and C_2H_3S ($^2A'$). Substantial barriers were found in the exit channels for every combination of method and basis set considered in this work, which effectively precludes hydrogen elimination pathways for both S + C_2H_2 and S + C_2H_4 in the ultracold interstellar medium where only very modest barriers can be surmounted and processes without barriers tend to predominate. However, if one or both intermediates are formed and stabilized efficiently under cometary or dense interstellar cloud conditions, they could serve as temporary reservoirs for the S atom and participate in reactions such as $S + C_2H_2S \rightarrow S_2 + C_2H_2$ or $S + C_2H_4S \rightarrow S_2 + C_2H_4$. For formation and stabilization to be efficient, the reaction must possess a barrier height small enough to be surmountable at low temperatures yet large enough to prevent redissociation to reactants. Barrier heights computed with B3LYP and large basis sets are very low, but more rigorous QCISD(T) and RCCSD(T) results indicate that the barrier heights are closer to 3−4 kcal/mol. The calculations therefore indicate that S + C_2H_2 or S + C_2H_4 could contribute to the formation of S_2 in comets and may serve as a means to gauge coma temperature. The energetics of the ethylene reaction are more favorable.

1. Introduction

Due to the very low temperatures (10 K) and densities (10^4 cm^{-3}) that characterize dense interstellar clouds,[1] gas-phase chemistry in these objects is necessarily dominated by processes with little or no activation energy. Behavior in cometary comae is likewise restricted, though the temperature may rise to 200 K or higher near perihelion.[2,3] While many ion−molecule reactions do not have barriers and can thus make contributions under the coldest conditions, some reactions between open-shell atoms or molecules and unsaturated hydrocarbons can also be efficient enough to be competitive. In addition to possessing little or no impeding barriers anywhere along the pathway, reactions must also be at least minimally exothermic to be relevant to gas-phase chemistry in the interstellar medium. A number of addition reactions involving radicals such as C_2H, CN, and C and various hydrocarbons possessing double or triple bonds have been shown both experimentally and theoretically to meet these criteria.[4−29] Examples of both cyclic and noncyclic hydrocarbon reactants are known.

Dimeric sulfur, S_2, was initially identified by A’Hearn et al.[30] in 1983 in comet IRAS-Aracki-Alcock (1983d). It has not been definitively identified in the interstellar medium to date. In 1995, Saxena and Misra[31] considered a possible pathway to S_2 in comet Halley that begins with the addition of S to C_2H_4, both in their ground electronic states:

$$S + C_2H_4 \rightarrow C_2H_4S \tag{1}$$

$$S + C_2H_4S \rightarrow S_2 + C_2H_4 \tag{2}$$

They cited work of Philips and Slater[32] that reported a rate for eq 1, the limiting step, of $1.2 \pm 0.15 \times 10^{-12}$ cm^{-3} s^{-1}. The second step, between two radicals, is assumed to have no barrier; its rate should be close to the simple collision rate. Saxena and Misra also noted that a similar process involving C_2H_2,

$$S + C_2H_2 \rightarrow C_2H_2S \tag{3}$$

$$S + C_2H_2S \rightarrow S_2 + C_2H_2 \tag{4}$$

could be a competitive or alternative pathway, assuming the rate of C_2H_2S production in eq 3 is comparable to that of reaction shown in eq 1. In this and subsequent work modeling chemistry in comet Hyakutake,[33] Saxena and co-workers concluded that the proposed mechanism is sufficient to account for the observed S_2. A’Hearn et al.[34] later proposed an alternative mechanism, the direct reaction between ^1D excited-state S and OCS. Rodgers and Charnley[35] subsequently evaluated both mechanisms and found that neither could account for the observed quantity of S_2. While they used the most favorable parameters that were realistically possible, they carried over

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some of the assumptions of Saxena and Misra, including the published rate for the reaction shown in eq 1.

The S + C_2H_2 reaction has evidently not been the focus of a previous dedicated theoretical study, although Yamada et al.[36] state that it "has a barrier of 8−15 kJ mol^{-1}" (1.9−3.6 kcal mol^{-1}) in their extensive investigation of plausible formation pathways to organo-sulfur species in the interstellar medium. There is an older study[37] of S + C_2H_4, but the reaction has apparently not been treated with correlated molecular orbital (MO) methods. In the present work, we have investigated both the S + C_2H_2 and S + C_2H_4 reactions. As well as its value to astrochemistry, this study presented an opportunity to compare and contrast the behavior of representative MO methods and density functional theory (DFT) used in conjunction with the correlation consistent basis sets of Dunning and co-workers.

This work focused solely on triplet surface reactions. Its conclusions may be affected if intersystem crossings to the singlet surfaces should prove to be efficient, as has been demonstrated to be the case by Schmoltner et al.[38] in the analogous reaction between O (^{3}P) and C_2H_4. In that reaction, one of the principal reaction channels involved the triplet intermediate species crossing to the singlet surface, followed by an internal rearrangement and scission of the C−C bond to form CH_3 and HCO.

2. Methodology

The development of the correlation consistent basis sets[39−48] provided an approach to systematically converge upon the complete basis set limit of the 1-electron expansion of molecular orbitals. In conjunction with high-level correlation treatments such as singles and doubles coupled cluster theory with perturbative treatment of triple excitations [RCCSD(T)], the correlation consistent sets make accurate predictions possible for systems of modest size. Many applications have followed in the ensuing years. During the same period of time, gradient-corrected density functional theory methods have come to dominate much of quantum chemistry, after Pople and co-workers incorporated them into *Gaussian*[49] and found that DFT could generate competent predictions for systems well beyond the reach of accurate correlated molecular orbital methods. With scaling much more favorable than MO methods, DFT has allowed practitioners to routinely treat systems of significantly pragmatic value. It is important, however, to continue to benchmark the two approaches side-by-side and identify their successes and shortcomings.

The calculations in this work were performed with the *Gaussian 03*[50] and *Molpro*[51] suites of codes. The former was used for DFT calculations with the popular B3LYP functional,[52,53] unrestricted (UMP2), spin-projected (PMP2), and restricted open-shell (ROMP) Møller-Plesset perturbation theory,[54] and quadratic configuration interaction [QCISD and QCISD(T)].[55] Optimization and analytical frequency calculations were performed, as available. *Molpro* was used for RCCSD(T)[56,57] optimizations and single-point energy calculations. For sulfur, both the original[41] aug-cc-pVXZ and the expanded[47] aug-cc-pV(X+d)Z sets were employed in limited cases in order to study the extent to which it is advisable to use the latter for ascertaining barrier heights in this application. Zero-point energy (ZPE) corrections were included, though sometimes these were transferred from a method for which analytical second derivatives were available (as noted in the tables). The transition states (TS) at the RCCSD(T)/aug-cc-pV(D+d)Z level were approximated with constrained optimizations at fixed points of the C−S or relevant C−H separation. Optimizations at the RCCSD(T)/aug-cc-pV(T+d)Z level were prohibitive; single-point calculations were performed at the RCCSD(T)/aug-cc-pV(D+d)Z structures. Optimizations were also not performed for PMP2, ROMP2, or QCISD(T) due to the absence of analytical gradients for these methods in *Gaussian 03*. No corrections were made for basis set superposition error for the weakly bound S−C_2H_2 or S−C_2H_4 structures (or elsewhere). The barrier heights at the best level of theory are expected to be accurate to within 1−2 kcal mol^{-1}.

3. S + C_2H_2 and S + C_2H_4

We characterized the following addition−elimination reactions:

$$S + C_2H_2 \rightarrow C_2H_2S \rightarrow HCCS + H \tag{5a}$$

$$\rightarrow c\text{-}C_2H_2S \tag{5b}$$

$$S + C_2H_4 \rightarrow C_2H_4S \rightarrow C_2H_3S + H \tag{6}$$

As noted in eq 5b, it is possible for intermediate C_2H_2S to cyclize on the triplet surface. Computed structure predictions for singlet or triplet states of thiirene go back at least to Siegbahn et al.[58] and Gosavi and Strausz.[59] While there is a stable minimum structure for *c*-C_2H_4S on the singlet surface (ethylene sulfide or thiirane), the structure on the triplet surface is a high-lying transition state for the uninteresting process of transferring sulfur from one carbon to the other. At the B3LYP/aug-cc-pV(T+d)Z level, it is 38.5 kcal mol^{-1} above the reactants.

Energy diagrams and the structures of minima, transition states, and products for the reactions shown in eqs 5a and 6 are depicted in Figures1 and 2, respectively. The cyclic minimum and associated TS for the isomerization of C_2H_2S (eq 5b) are shown in Figure 3. The energy differences with respect to the separated reactants for a number of combinations of methodology and basis set are given in Tables 1 and 2 for the two reactions. While there are shallow intermolecular minima in the reactant channels in some cases, they were not present at the RCCSD(T)/aug-cc-pV(D+d)Z level for either reaction.

In the previous addition−elimination reactions we have studied, CN + C_2H_2,[5] C_2H + C_2H_2,[12] and both CN and C_2H with benzene,[27] there were barriers in the exit channels, but they were well below the energy of the reactant asymptote. There was also at least one exothermic product channel. While there is a large amount of variation in the values, it is evident that very substantial barriers are present for eliminating H from the intermediate for both S + C_2H_2 and S + C_2H_4, and neither product is exothermic. Completion of either reaction is unlikely under typical interstellar or cometary conditions. The remainder of the discussion will therefore largely focus on the barriers in the entrance channels (labeled TS1 in both cases in the figures).

It is quite evident that the B3LYP barrier heights are significantly lower than those of the MO methods, regardless of basis set. The best ZPE-corrected values, at the B3LYP/aug-cc-pV(Q+d)Z level, are +0.5 and −0.5 kcal mol^{-1}, relative to the sum of the reactant energies for S + C_2H_2 and S + C_2H_4, respectively. There is less than 1 kcal mol^{-1} of variation between the different basis sets for both reactions and only minor differences between the aug-cc-pVXZ and corresponding aug-cc-pV(X+d)Z barrier heights even at the DZ level, where the tight d function lowers the value by −0.15 kcal mol^{-1} for both cases. The shift is just −0.10 kcal mol^{-1} at the TZ level. These results indicate that there is little to be gained in the present application by using the larger sets.

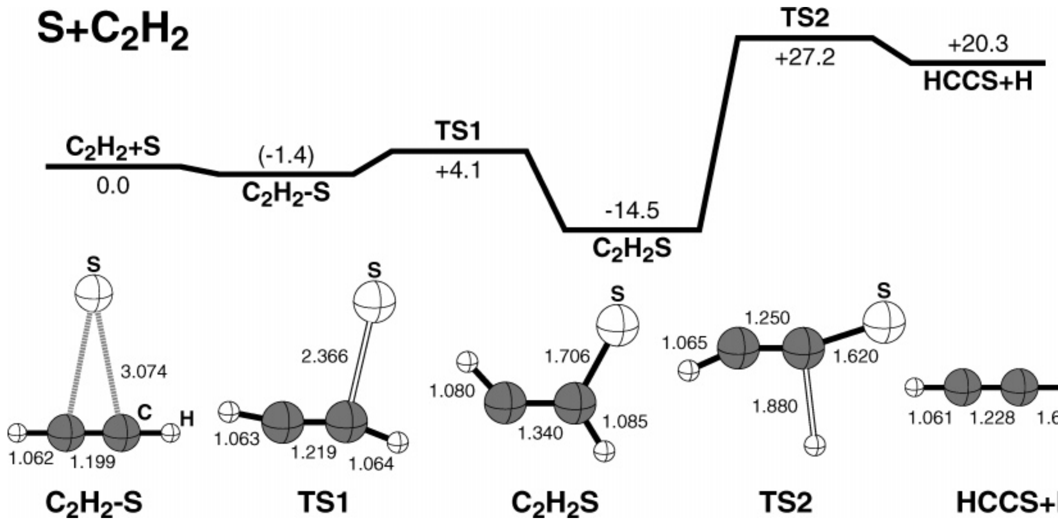

Figure 1. Energy diagram and structures for S + $C_2H_2 \rightarrow C_2H_2S \rightarrow$ HCCS + H. Energy differences in kcal mol^{-1} are relative to reactants at the RCCSD(T)/aug-cc-pV(T+d)Z//RCCSD(T)/aug-cc-pV(D+d)Z level; bond lengths in Å at the B3LYP/aug-cc-pV(Q+d)Z level.

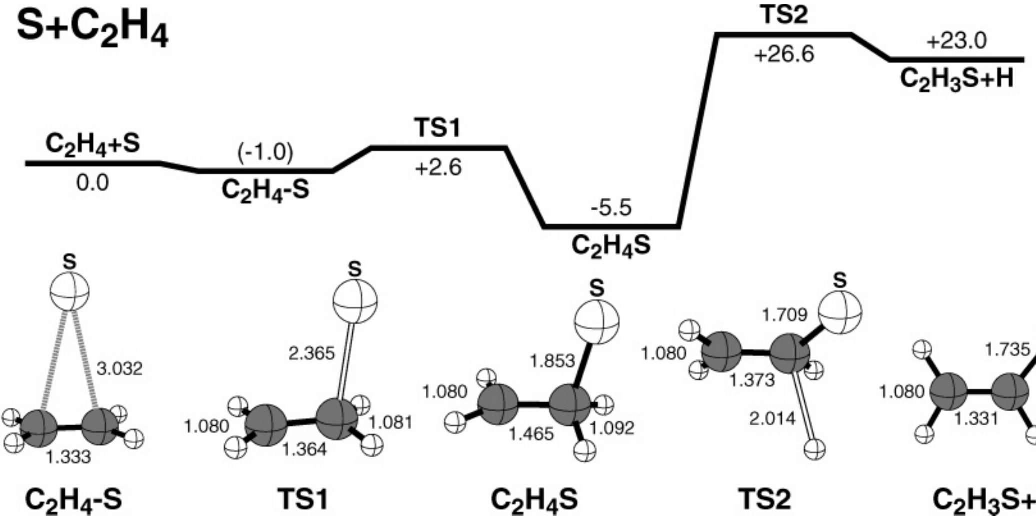

Figure 2. Energy diagram and structures for S + $C_2H_2 \rightarrow C_2H_2S \rightarrow$ HCCS + H. Energy differences in kcal mol^{-1} are relative to reactants at the RCCSD(T)/aug-cc-pV(T+d)Z//RCCSD(T)/aug-cc-pV(D+d)Z level; bond lengths in Å at the B3LYP/aug-cc-pV(Q+d)Z level.

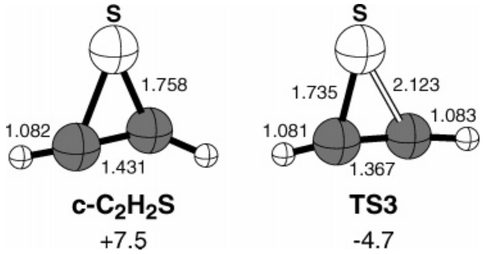

Figure 3. Energy differences in kcal mol^{-1} relative to reactants and structures for cyclic C_2H_2S isomer and TS at the B3LYP/aug-cc-pV(T+d)Z level.

The most reliable predictions in this work are expected to be the RCCSD(T) results in the larger basis set. The RCCSD(T)/aug-cc-pV(T+d)//RCCSD(T)/aug-cc-pV(D+d)Z barrier heights with B3LYP/aug-cc-pV(Q+d)Z ZPE corrections are 4.1 and 2.6 kcal mol^{-1} for S + C_2H_2 and S + C_2H_4, respectively. The B3LYP predictions are therefore low by about 3−4 kcal mol^{-1}. However, UMP2 decidedly overestimates the barrier heights—by over 10 kcal mol^{-1} for the S + C_2H_2 reaction. The PM2 and ROMP2 predictions are better, particularly for the ethylene reaction, where they are close to the RCCSD(T)/aug-cc-pV(D+d)Z values. For the acetylene case, the predicted PMP2 and ROMP2 barrier heights are 6.2 and 1.5 kcal mol^{-1} larger than the RCCSD(T) value, respectively. The single-point QCISD(T)/aug-cc-pVDZ barrier heights for both reactions (at the QCISD geometries) are comparable to the RCCSD(T) results with a similar basis set.

Even the lower of the best values for the two barrier heights is prohibitively high for the conditions in cold clouds. The barriers are low enough, however, to possibly allow one or both reactions to contribute to coma chemistry as a comet approaches and departs perihelion. The S + C_2H_4 reaction is clearly favored, with a barrier predicted to be 1.5 kcal mol^{-1} lower than that of S + C_2H_2. The small reaction energy for forming the C_2H_4S intermediate, just 5.5 kcal mol^{-1} below the reactant asymptote at the RCCSD(T)/aug-cc-pV(T+d)//RCCSD(T)/aug-cc-pV(D+d) level, should also improve its chances of being stabilized compared to reactions with more energetic intermediates. While the determination of an accurate rate for either reaction is beyond the scope of the present work, the S_2 concentration could possibly be used to gauge coma temperature as a function of distance from the sun.

The predicted barrier height for cyclizing C_2H_2S is 7.5 kcal mol^{-1} at the B3LYP/aug-cc-pV(T+d) level (Figure 3). While it is not as large as the barrier in the exit channel, it is still prohibitive under either interstellar or cometary gas-phase

TABLE 1: Energies Relative to the Reactant Asymptote for S + C_2H_2 Intermediates, Transition States, and Product (kcal mol^{-1})

	ΔE_e (ΔE_0)				
method/basis[a]	S−C_2H_2	TS1	C_2H_2S	TS2	HCCS + H
B3LYP/AVDZ	−1.98 (−1.77)	−0.35 (−0.19)	−22.32 (−20.91)	25.52 (20.61)	21.23 (15.81)
B3LYP/AVTZ	−1.62 (−1.41)	0.74 (0.55)	−19.74 (−18.74)	26.64 (21.39)	21.53 (16.00)
B3LYP/AV(D+d)Z	−2.01 (−1.81)	−0.50 (−0.34)	−24.02 (−22.60)	23.12 (18.25)	18.79 (13.34)
B3LYP/AV(T+d)Z	−1.64 (−1.43)	0.63 (0.45)	−20.66 (−19.65)	25.35 (20.13)	20.19 (14.66)
B3LYP/AV(Q+d)Z	−1.59 (−1.37)	0.70 (0.52)	−20.82 (−19.78)	25.21 (19.99)	20.04 (14.51)
QCISD/AVDZ[b]	−1.37 (−1.15)	5.70 (5.52)	−14.82 (−13.79)	36.88 (31.65)	30.85 (25.33)
QCISD(T)/AVDZ[b]	−1.67 (−1.45)	4.01 (3.83)	−15.79 (−14.75)		
UMP2/AVDZ	−1.90 (−1.35)	16.39 (18.32)	−6.70 (−4.13)	47.08 (43.05)	31.63 (28.09)
PMP2/AVDZ[c]	−1.94 (−1.39)	8.10 (10.03)	−13.68 (−11.11)	35.18 (31.15)	24.79 (21.25)
ROMP2/AVDZ[c]	−1.92 (−1.37)	3.41 (5.34)	−11.36 (−8.78)	34.91 (30.88)	25.61 (22.07)
RCCSD(T)/AV(D+d)Z[b]		3.99 (3.81)	−16.57 (−15.53)	32.23 (27.01)	26.56 (21.03)
RCCSD(T)/AV(T+d)Z[b,d]		4.25 (4.07)	−15.55 (−14.52)	32.44 (27.22)	25.79 (20.27)

[a] Notation: AVXZ is shorthand for aug-cc-pVXZ, AV(X+d) for aug-cc-pV(X+d)Z; ZPE-corrected results are in parentheses. [b] ZPE correction from B3LYP/AV(Q+d)Z calculation; QCISD(T) calculation at QCISD geometry. [c] Energy calculations using the UMP2/AVDZ structure (as well as its ZPE correction). [d] Energy calculation using the RCCSD(T)/AV(D+d)Z structure.

TABLE 2: Energies Relative to the Reactant Asymptote for S + C_2H_4 Intermediates, Transition States, and Product (kcal mol^{-1})

	ΔE_e (ΔE_0)				
method/basis[a]	S−C_2H_4	TS1	C_2H_4S	TS2	C_2H_3S + H
B3LYP/AVDZ	−2.45 (−1.95)	−1.14 (−0.99)	−6.79 (−7.31)	28.16 (23.28)	34.27 (28.56)
B3LYP/AVTZ	−2.02 (−1.54)	−0.62 (−0.44)	−6.32 (−6.77)	28.74 (23.91)	34.35 (28.64)
B3LYP/AV (D+d)Z	−2.49 (−1.99)	−1.31 (−1.14)	−7.78 (−8.36)	26.46 (21.58)	32.70 (26.98)
B3LYP/AV (T+d)Z	−2.04 (−1.57)	−0.73 (−0.54)	−6.88 (−7.36)	27.82 (22.99)	33.48 (27.77)
B3LYP/AV (Q+d)Z	−1.98 (−1.51)	−0.65 (−0.46)	−7.00 (−7.49)	27.71 (22.87)	33.35 (27.63)
QCISD/AVDZ[b]	−1.45 (−0.98)	4.53 (4.72)	−1.94 (−2.42)		
QCISD(T)/AVDZ[b]	−1.85 (−1.37)	3.11 (3.30)	−2.48 (−2.97)		
UMP2/AVDZ		8.31 (8.97)	−2.66 (−2.82)	46.80 (42.89)	33.55 (32.55)
PMP2/AVDZ[c]		2.62 (3.29)	−4.04 (−4.20)	40.08 (36.17)	32.94 (31.94)
ROMP2/AVDZ[c]		2.66 (3.33)	−2.74 (−2.89)	41.15 (37.24)	33.46 (32.46)
RCCSD (T)/AV(D+d)Z[b]		3.32 (3.51)	−3.01 (−3.49)	32.58 (27.74)	29.64 (23.93)
RCCSD (T)/AV(T+d)Z[b,d]		2.41 (2.60)	−5.05 (−5.53)	31.47 (26.63)	28.69 (22.97)

[a] Notation: AVXZ is shorthand for aug-cc-pVXZ, AV(X+d) for aug-cc-pV(X+d)Z; ZPE-corrected results are in parentheses. [b] ZPE correction from B3LYP/AV(Q+d)Z calculation; QCISD(T) calculation at QCISD geometry. [c] Energy calculations using the UMP2/AVDZ structure (as well as its ZPE correction). [d] Energy calculation using the RCCSD(T)/AV(D+d)Z structure.

conditions. The prediction may also be underestimating the correct barrier height, if it parallels the behavior of the barrier in the entrance channel.

4. Conclusions

The S + C_2H_2 and S + C_2H_4 reactions were characterized on their triplet surfaces with various combinations of density functional or molecular orbital theory and correlation consistent basis sets as large as aug-cc-pV(Q+d)Z. Both reactions possess high barriers in their exit channels, precluding the elimination of H in either the interstellar medium or in comet comae. The barrier for cyclizing C_2H_2S is smaller, but still too large to be efficient at low temperature. The best predictions for the barrier heights that impede the formation of the C_2H_2S and C_2H_4S intermediates are 4.1 and 2.6 kcal mol^{-1}, respectively, for the acetylene and ethylene reactions with S at the RCCSD(T)/aug-cc-pV(T+d)Z level. Other methods either underestimate or overestimate the barrier heights by various amounts. The energetics for the formation of C_2H_4S, with best predictions of the barrier height and reaction energy of 2.6 and −5.5 kcal mol^{-1}, respectively, indicate that it is the best candidate for serving in the S_2 formation mechanism proposed by Saxena and Misra.[31] As noted in the Introduction, this work did not explore the possibility that intersystem crossings may be efficient enough that alternative pathways may be accessible, particularly in cold interstellar clouds.

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