J. Am. Chem. Soc. **1986**, *108*, 5059–5064

A Theoretical Study of Atomic Sulfur Reactions with Alkanes, Alkenes, and Alkynes

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Received January 15, 1986

Abstract: The results of an MNDO study of the potential energy surface for reaction of sulfur in its ground S(^{3}P) and first excited state S(^{1}D) with alkanes, alkenes, and alkynes are reported. In agreement with experiments, S(^{1}D) inserts into CH bonds of alkanes (CH_4 and C_2H_6) but S(^{3}P) does not. MNDO provides a reasonable explanation for the observed differences in S(^{1}D) and S(^{3}P) addition to ethylene. The stereoselectivity of S(^{3}P) addition is postulated to result from rapid intersystem crossing rather than from a high methylene rotational barrier in the triplet biradical. Ethenethiol is predicted to result from isomerization of hot thiirane rather than from sulfur insertion into the CH bond. In the addition of sulfur to acetylene, S(^{3}P) is predicted to yield thioketocarbene while thiirene, thioketene, and ethynethiol are predicted from S(^{1}D) addition.

It is well-known[1-9] that sulfur atoms are highly reactive and that their reactivity is dependent on the electronic state. Rigid selection rules permit the excited atoms to undergo bimolecular reations before decay occurs to the ground state. Photolysis of COS is the standard source of S(^{1}D) sulfur atoms which are initially formed along with the ground state S(^{3}P) in a greater than 2:1 ratio. In addition, electronically pure triplet ground state can be achieved by mercury sensitization.

In the excited state S(^{1}D) sulfur atoms react with alkanes, alkenes, and alkynes either by adding to the unsaturated bond (for alkenes and alkynes) or by inserting into a CH bond to form a thiol. Ground-state sulfur atoms S(^{3}P), on the other hand, react with nonaromatic unsaturated compounds but are unreactive at room temperature with saturated molecules. They react with alkanes[2] only at elevated temperature (140–150 °C), initially with the formation of H_2S and at higher temperatures with formation of a variety of other products.

The reaction of singlet or triplet sulfur atoms with 2-butene is found to be stereoselective.[3] Short reaction times result in less isomerization of the product and the trans isomer leads to a greater selectivity than the cis isomer. The reaction of sulfur atoms with ethylene yields a ratio of ethenethiol to thiirane that depends on contact time, total pressure, and ratio of ethylene to COS. The ratio decreases with an increase of the total pressure or a reduction of the ethylene to COS ratio, while the ratio increases with shorter contact time. The dependence on total pressure was interpreted as evidence for unimolecular isomerization of an initially formed hot thiirane molecule.

The addition of S(^{3}P,^{1}D) to acetylene is known to occur, but elucidation of the mechanism has been difficult.[4,8,9] It is known, however, that thiirene thermally converts only to thioketene but not ethynethiol,[10,11] while the photolysis of 1,2,3-thiadiazoles forms primarily ethynethiol as well as thioketene in smaller yields. Several mechanisms on the SC_2H_2 surface have been proposed involving intermediacy[12,13] of thioformylmethylene, $\dot{S}CH\dot{C}H$, in one of its closely spaced electronic states. For example, it is known[14] that the thioketocarbene, thiobenzoylphenylmethylene, isomerizes to the thioketene structure in a first-order process with an activation energy of 5.4 kcal/mol which was assigned to the singlet–triplet separation.

Procedure

All calculations were made with UMNDO, a spin-unrestricted version of MNDO[15] or MNDO/HE/CI,[16] a version which involves 3 × 3 CI with orbitals calculated by the half-electron (HE)[16] formalism. As the UMNDO method provides a variationally optimized wave function, gradients can be calculated by using the assumption that the bond order remains constant with respect to small distortions of the geometry. Thus, rapid optimization of geometries can be carried out, and a single energy calculation can be done with 3 × 3 CI (for singlets) with the MNDO/CI/HE formalism. A second advantage of UMNDO is that singlet biradical-like species can be calculated[17] without using configuration interaction. If the restricted solution is avoided,[18] a lower energy UHF solution is obtained for the singlet biradical species which yields two different MOs for the "unpaired" electrons (better known as the doublet instability phenomenon).[19] Previous testing of MNDO has shown that UHF energies of triplets and biradical-like species can be too negative by 15–25 kcal/mol.[20] For this reason the MNDO/CI/HE energies are perhaps more reliable.

The S(^{1}D) state is composed of five microstates corresponding to closed-shell (103.8 kcal/mol) and open-shell (79.1 kcal/mol)

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Table I. Comparison of ab Initio and MNDO Energies (kcal/mol) on the SC_2H_2 Potential Energy Surface Relative to Thioketene

molecule	MNDO/ HE/CI	STO3G/[a] CISDQ	6-31G*/[a] CISDQ	SCI-(DZ+P)[b]
thioketene (**19**)	0.0	0.0	0.0	0.0
thiirene (**23**)	28.0	35.0	35.1	37.5
Ethynethiol (**21**)	9.8	7.4	7.8	17.4
thioformylmethylene ($^3A''$) (**18**)	39.6	49.2[c]	47.7[c]	52.0
thioformylmethylene ($^1A'$) (**N**)	52.0			59.8
$H2\overline{C{-}C{-}S}$ ($^1A'$) (**25**)	62.1	44.8	55.5	45.2
$H2\overline{C{-}C{-}S}$ ($^3A''$) (**26**)	84.2			76.6
TS **O 23** → **19**	76.4	68.6		
TS **P 23** → **21**	70.4	73.4		

[a] Reference 30. [b] Reference 31. [c] $^3A''$ state in trans conformation.

solutions of sulfur. If the average of these two calculated heats of formation (91.4 kcal/mol) is used as the approximate energy of $S(^1D)$ and the experimental heat of formation of $S(^3P)$ (66.4 kcal/mol) which appears in MNDO as a parameter is used as the energy of $S(^3P)$, a triplet–singlet splitting of 25.0 kcal/mol is obtained. The experimental triplet–singlet splitting was determined to be 26.4 kcal/mol.[1]

When singlet sulfur atoms react along a pathway which maintains a plane of symmetry, two electronic surfaces will be important. One microstate of sulfur $S(^1D)$ will correlate with closed-shell products while another will correlate with open-shell products. In the former pathway, orbitals are doubly occupied while the state symmetry is $^1A'$ (in C_s point group). In the latter pathway, the two unpaired electrons are in orbitals of different symmetry resulting in a state symmetry of $^1A''$ (in C_s point group). In the present study all transition states resulting from the reaction of $S(^1D)$ were calculated with the UHF method. In each case the resulting solution corresponded to the closed-shell solution; however, large deviations from the expected spin-squared values, indicating significant spin polarization, were observed.

Despite the tendency for the UMNDO method to give too negative heats of formation for biradicals due to inclusion of "extra" correlation, it is likely that reactions do take place with $S(^1D)$ on the closed-shell surface with little activation energy since more accurate calculations of the addition of $C(^1D)$ to CH_4,[21a] NH_3,[21b] and H_2O[21c] also predict small barriers. For stable products of reaction, the UHF solution was identical with the RHF solution which indicates that no stable biradical solution exists.

Calculations were carried out with use of the published parameters.[22] Geometries were optimized by the standard Davidson–Fletcher–Powell[23] method with use of internal coordinates, and reactions were followed by the dual reaction-coordinate method.[24] The transition states were refined by minimizing the scalar gradient of the energy and identified as saddle points by diagonalizing the Hessian (force constant) matrix as suggested by McIver and Komornicki.[25] A detailed discussion of the validity of MNDO in studying reaction paths has been published.[26] In a recent comparison of MNDO and experimental data for sulfur-containing compounds,[27] the method has been shown to be very successful in predicting molecular properties.

Several computational studies have been reported for various species on the SC_2H_2 surface.[28-31] The most thorough study is an ab initio study[30] in which some stationary points were evaluated at the double-ζ plus polarization and correlation level. Comparisons of relative energies of species with MNDO and ab initio are generally very good (Table I) except for the two barrier heights (**O** and **P**) which are predicted to be in the opposite order by MNDO (vide infra for notation definitions).

A tabulation of results is given in Table II for stable species and in Table III for transition states. Energies are reported at the optimized geometries by using the UMNDO formalism. When a lower energy spin polarized solution is obtained for a singlet ($\langle S^2 \rangle \neq 0.0$), the MNDO closed-shell energy is also given at the MNDO optimized geometry. The MNDO/HE/CI energies are evaluated at the UMNDO geometries. For singlets the energies correspond to a 3 × 3 CI starting with HE reference orbitals while triplets and doublets are HE energies without CI. The $^1A''$ electronic state of **17** corresponds to an open-shell electronic state and not to a broken symmetry solution.

The geometries of species on various potential energy surfaces are given in Figure 1. A notation for stable species (**1**–**26**) and transition states (**A**–**Q**) is included in Tables I–III and Figure 1 and is used consistently throughout. Unless stated otherwise, energies are at the MNDO/HE/CI level with use of UMNDO geometries. The Minimum Energy Reaction Profile (MERP) is given for $S(^3P)$ and $S(^1D)$ addition to ethylene in Figures 2 and 3 and to acetylene in Figures 4 and 5.

Results and Discussion

Alkanes. The addition of atomic sulfur to methane and ethane was first studied. It was not possible to locate precisely the transition state for addition of $S(^3P)$ to methane. This process, however, is very unfavorable, proceeding with an activation barrier of about 60 kcal/mol.

Two pathways were studied for addition of $S(^1D)$ to methane resulting in two stationary points (**6a** and **6b**) (Figure 6a,b). When the force constant matrix of **6a** was calculated and diagonalized, two negative eigenvalues resulted. One eigenvector indicated a distortion toward thiomethanol and the other toward **6b** which was 3 kcal/mol lower in energy than **6a**. Diagonalizing the force constant matrix of **6b** resulted in one negative eigenvalue proving it to be a true transition state.

A very similar result was reported[21a] for the reaction of $C(^1D)$ with CH_4 where transition state **6b** ($C(^1D)$ in place of $S(^1D)$) was 2.7 kcal/mol more stable than stationary point **6a** at the MP3/6-31G** + ZPC level (double-ζ plus polarization with correlation and zero point correction).

The activation barrier of 5.4 kcal/mol for addition of $S(^1D)$ to methane was very similar to that calculated for addition to ethane (5.5 kcal/mol; Table III). A variety of products is predicted by MNDO as thiomethanol (**7**) is formed with enough energy (82.1 kcal/mol) to homolytically cleave the SC bond (BDE, 65 kcal/mol)[32] to form methyl and HS radicals. The transition state for $S(^1D)$ addition to methane (Figure 1, **A**) is very early as seen from the long forming SC and SH bonds (2.370 and 1.557 Å) and the short breaking CH bond (1.189 Å).

Alkenes. Singlet sulfur $S(^1D)$ has an activation barrier (**F**) of 10.6 kcal/mol for addition to ehtylene to form thiirane (**15**) while $S(^3P)$ has an activation barrier (**C**) of 17.6 kcal/mol to form a biradical species (**10**). Both barriers are overestimated since the $S(^3P)$ addition barrier is observed[33] to be 1.6 kcal/mol while the $S(^1D)$ barrier is expected to be similar. The values of the

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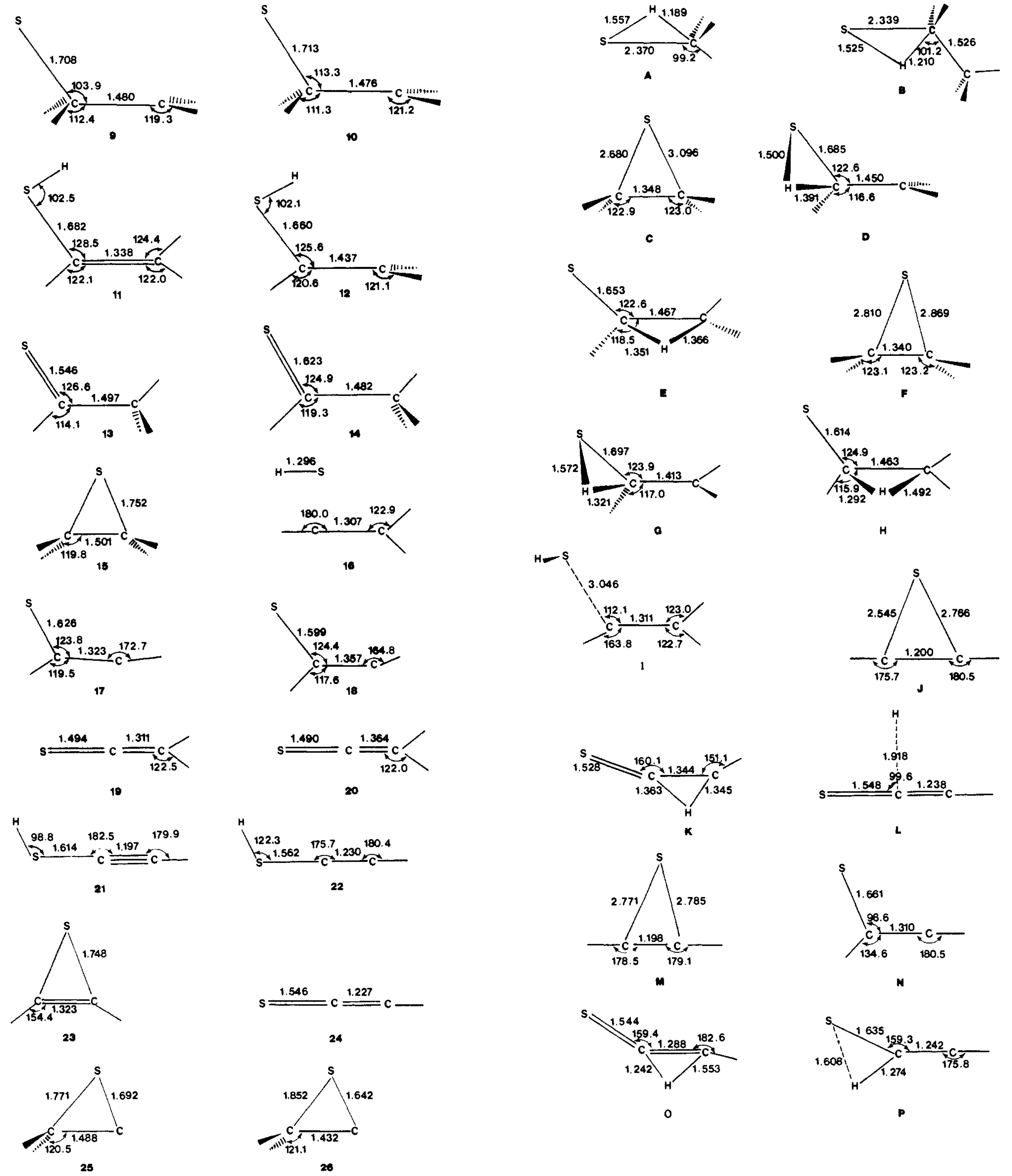

Figure 1. Optimized geometries of relevant species at the UMNDO level. The structure of transition state Q is not given since it is very similar to I.

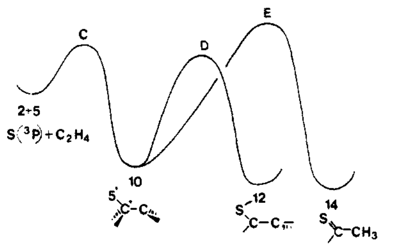

Figure 2. Minimum energy reaction profile (MERP) for the addition of S(^{3}P) to ethylene. All structures are triplets.

UMNDO level for the addition of S(^{1}D) and S(^{3}P) seem, in this instance, to be more reasonable (3.1 kcal/mol, **F**; 3.9 kcal/mol, **C**; Table III).

While only marginally stable toward collapse to thiirane, the singlet biradical (**9**) is calculated to have nearly the same energy as the triplet biradical (**10**). In both spin states, the biradical is predicted to have a barrier on the order of 1 kcal/mol to rotation of the methylene group (MNDO/HE/CI and UMNDO predict an opposite ordering of the two structures).

The configuration obtained for the two singlet biradicals is given in Figure 7. In Figure 7a the broken symmetry solution involves

Table II. Molecular Properties Calculated by MNDO for Various Species on the Singlet and Triplet Surfaces

notation	molecule (multiplicity)	mol sym	elect sym	$\Delta H_f{}^a$ MNDO/HE/CI	$\Delta H_f{}^{a,b}$ UMNDO(MNDO)	$\langle S^2 \rangle$
1	$S(^1D)$	K	^1D	91.4	79.1 (103.8)	1.00
2	$S(^3P)$	K	^3P	66.4	66.4	2.00
3	CH_4	T_d	$^1A_1$	-16.6	-11.9	0.00
4	C_2H_2	$D_{\infty h}$	$^1\Sigma_g{}^+$	57.8	57.3	0.00
5	C_2H_4	D_{2h}	$^1A_1$	6.8	15.3	0.00
6	C_2H_6	D_{3d}	$^1A_{1g}$	-19.4	-19.7	0.00
7	$HSCH_3$	C_s	$^1A'$	-7.3	-8.2	0.00
8	$HSCH_2CH_3$	C_s	$^1A'$	-14.3	-14.2	0.00
9	SCH_2CH_2 (1)	C_s	$^1A'$	55.0, 51.4^d	44.7, 45.2^d	0.94, 1.01^d
10	SCH_2CH_2 (3)	C_s	$^3A''$	50.0, 50.3^d	44.3, 45.4^d	2.02, 2.01^d
11	$HSCH{=}CH_2$ (1)	C_s	$^1A'$	10.2	16.2	0.00
12	$HSCHCH_2$ (3)	C_s	$^3A''$	44.3	38.9	2.01
13	$S{=}CHCH_3$ (1)	C_s	$^1A'$	18.6	12.7	0.00
14	$S{=}CHCH_3$ (3)	C_s	$^3A''$	40.4	35.7	2.01
15	$H_2C{-}CH_2{-}S$	C_{2v}	$^1A_1$	17.3	14.2	0.00
16	$HS + HCCH_2$	$C_{\infty v}$, C_s	$^2\Sigma^-$, $^2A'$	100.4	95.3	0.75, 0.94
17	$SCH{=}CH$ (1)	C_s	$^1A''$	100.2	88.6	1.05
18	$SCH{=}CH$ (3)	C_s	$^3A''$	89.9	77.5	2.20
19	$S{=}C{=}CH_2$ (1)	C_{2v}	$^1A_1$	50.3	46.6	0.00
20	$S{=}C{=}CH_2$ (3)	C_{2v}	$^3B_2$	71.2	65.5	2.05
21	$HSC{\equiv}CH$ (1)	C_s	$^1A'$	58.4	56.4	0.00
22	$HSC{\equiv}CH$ (3)	C_s	$^3A''$	130.1	119.4	2.16
23	$HC{=}CH{-}S$	C_{2v}	$^1A_1$	76.0	74.6 (74.9)	0.25
24	$H + S{=}C{=}CH$	K, C_s	^2S, $^2\Pi$	132.7	128.2	0.75, 0.87
25	$H_2C{-}C{-}S$	C_s	$^1A'$	112.4	113.5 (113.7)	0.15
26	$H_2C{-}C{-}S$	C_s	$^3A''$	134.5	123.8	2.02

[a] kcal/mol. [b] The heats of formation reported in the present work may vary slightly from values reported earlier (ref 27) due to the fact that one-center integrals which were given as data rounded to two decimal places are now computed from the symmetry relations between the appropriate Coulomb integrals.[c] The present value for molecules containing sulfur is about 0.2–0.3 kcal/mol higher in energy. [c] Thiel, W. *J. Am. Chem. Soc.* **1981**, *103*, 1413–1420. [d] The first value is for a staggered methylene group while the second value is for an eclipsed methylene group.

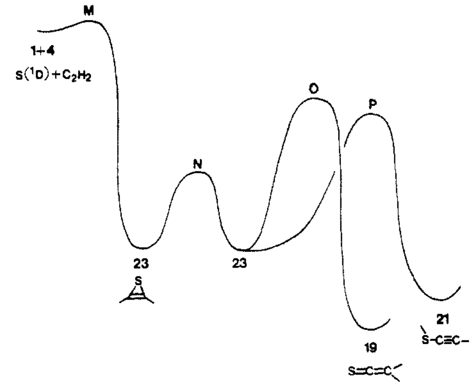

Figure 3. MERP for the addition of $S(^1D)$ to ethylene.

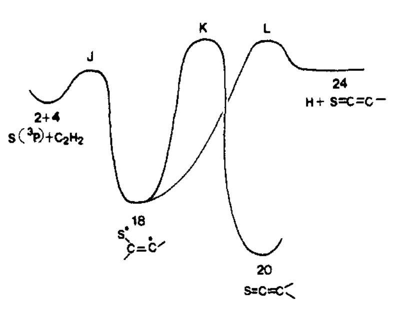

Figure 4. MERP for the addition of $S(^3P)$ to acetylene.

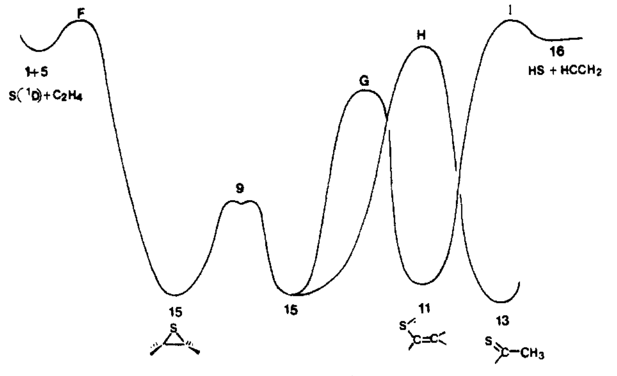

Figure 5. MERP for the addition of $S(^1D)$ to acetylene.

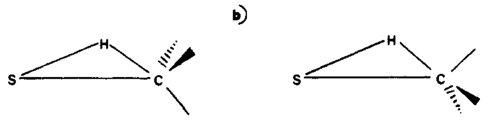

Figure 6. Two possible orientations (**6a** and **6b**) for the addition of $S(^1D)$ to methane. Only **6b** represents a true transition state.

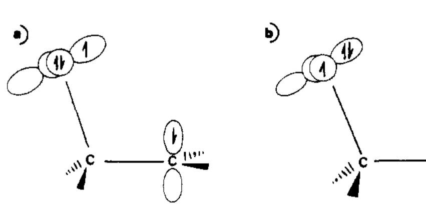

Figure 7. Schematic representation of the orbitals in singlet SCH_2CH_2 (**7a** and **7b**) which change occupation as the methylene group is rotated.

a localized lone pair on sulfur perpendicular to the molecular plane while an α and β spin electron have delocalized into an orbital in the molecular plane on sulfur and carbon. When the methylene group is rotated (Figure 7b), the broken symmetry solution now corresponds to a lone pair localized on sulfur in the molecular plane, while the α and β are delocalized in π-type orbitals on sulfur and carbon. The two solutions in the triplet biradical for both orientations of the methylene group are analogous, with the singly and doubly occupied p orbitals on sulfur interchanged.

A C–S bond energy of 37.7 kcal/mol (MNDO/HE/CI) is calculated from the difference in energy of $^1A'$ state (**9**) and thiirane (**15**) which compares to an experimental value of about 40 kcal/mol.[34] In addition, the overall exothermisity of the

Table III. Calculated Properties of Transition States and Barrier Heights (kcal/mol) by MNDO

notation	transition state reactant → product	mol sym	elect sym	$\Delta H_f{}^a$ MNDO/HE/CI	$\Delta H_f{}^a$ UMNDO (MNDO)	barrier height MNDO/HE/CI (UMNDO)	$\langle S^2 \rangle$
A	**1** + **3** → **7**	C_s	$^1A'$	80.2	78.5 (83.7)	5.4 (11.3)	0.48
B	**1** + **6** → **8**	C_s	$^1A'$	77.5	71.5 (75.9)	5.5 (12.1)	0.39
C	**2** + **5** → **10**	C_s	$^3A''$	90.8	85.6	17.6 (3.9)	2.10
D	**10** → **12**	C_1	^3A	87.4	81.5	34.4 (35.7)	2.03
E	**10** → **14**	C_1	^3A	98.0	92.1	48.0 (46.3)	2.05
F	**1** + **5** → **15**	C_{2v}	$^1A_1$	108.8	97.5 (119.8)	10.6 (3.1)	0.98
G	**15** → **11**	C_1	^1A	67.3	69.9 (84.4)	50.1 (55.7)	0.73
H	**15** → **13**	C_1	^1A	81.8	76.9 (85.8)	64.5 (62.7)	0.60
I	**11** → **16**	C_1	^1A	106.6	96.5	96.4 (80.3)	1.17
J	**2** + **4** → **18**	C_s	$^3A''$	133.4	128.0	9.2 (4.3)	2.01
K	**18** → **20**	C_s	$^3A''$	144.3	133.8	54.4 (56.3)	2.14
L	**18** → **24**	C_s	$^3A''$	143.0	132.5	53.1 (55.0)	2.19
M	**1** + **4** → **23**	C_s	$^1A'$	151.6	139.7 (161.6)	2.4 (3.3)	0.99
N	**23** → **23**	C_s	$^1A'$	102.3	93.0 (104.2)	26.3 (18.4)	0.90
O	**23** → **19**	C_s	$^1A'$	126.7	115.1	50.7 (40.5)	0.00
P	**23** → **21**	C_s	$^1A'$	120.7	113.1 (120.0)	44.7 (38.5)	0.61
Q	**2** + **5** → **16**	C_1	^3A	101.0	95.6	22.4 (13.9)	2.20

[a] The calculated heats of formation are in kcal/mol.

reaction S(^{1}D) plus ethylene to give thiirane is predicted to be in good agreement with experiment (80.9 kcal/mol, MNDO/HE/CI; 85.9 kcal/mol, experimental[35,36]).

Barriers of 50.1 and 64.5 kcal/mol are calculated for formation of ethenethiol (**11**) and thioacetaldehyde (**13**), respectively. From preliminary studies[4] on the thermal rearrangement of thiirane to ethenethiol, this barrier has been estimated to be 55–65 kcal/mol in reasonable agreement with MNDO. When formed, thiirane has 91.5 kcal/mol of excess energy and could pass over the second and third barriers (Figure 4, **G**, **H**). Although ethenethiol is observed, thioacetaldehyde is not, probably[3] because it trimerizes and is deposited on the walls.

Also studied was the ease of starting a polymerization reaction by formation of the SH and $HCCH_2$ radicals (**16**). It is seen from Table III that this process (I) is unfavorable as the heat of formation for the cleavage transition state is only 2.2 kcal/mol less than the heat of formation of the addition transition state (Figure 4). The same products could be formed by direct abstraction of hydrogen from ethylene by triplet sulfur S(^{3}P) which is predicted to be 27.2 kcal/mol endothermic (experimental 24.1 kcal/mol). In order for this pathway to compete efficiently, the barrier for hydrogen abstraction should not be much larger than the barrier for addition (17.6 kcal/mol, **C**). The MNDO/HE/CI value for the addition barrier is much too high since the observed barrier is only 1.6 kcal/mol.[33] Therefore, since the calculated hydrogen abstraction barrier for **2** + **5** → **16** is calculated to be 22.4 kcal/mol (Table III, **Q**), abstraction should not be competitive with addition.

We now concern ourselves with the relative ease of formation of thiirane (**15**) vs. ethenethiol (**11**). Studies have shown[37] that the ethenethiol to thiirane ratio markedly decreases in the condensed phase relative to the gas phase, suggesting that isomerization in the condensed phase is effectively suppressed by collisional stabilization of the hot thiirane molecule. In the work of Strausz and co-workers[4] it was demonstrated that increasing the partial pressure of an efficient singlet quencher such as COS while keeping the total pressure constant causes a decrease in the ratio of ethenethiol to thiirane. This is evidence that ethenethiol does not arise from hydrogen abstraction by S(^{3}P) since efficient quenching would increase the ratio but rather a consequence of the fact that ethenethiol arises only from the singlet manifold and withdrawing S(^{1}D) from the system reduces its formation. Increasing the total pressure also has the effect of decreasing the ethenethiol to thiirane ratio because the hot thiirane is being stabilized before isomerization. Also, if SH radicals were involved, other products would arise which have not been reported.[38]

At low pressures and high $[C_2H_4]/[COS]$ ratios the ethenethiol to thiirane ratio is greater than 1 ($\sim$1.6).[4] As MNDO predicts thiirane to be 7.1 kcal/mol less stable than ethenethiol, this result may be rationalized if the reaction is under thermodynamic control, or alternatively there may be little deactivation of thiirane before the second transition state (**G**) is reached since ethenethiol should be deactivated more efficiently than thiirane.

There is some question whether the formation of ethenethiol (**11**) is due to S(^{1}D) insertion into the vinylic CH bond or due rather to the isomerization of thiirane (**15** → **11**). Extensive studies[37] on the sulfur atom–olefin system have shown that ethenethiol forms only when the olefin contains at least one unsubstituted carbon. In the case of propylene[37] small quantities of propene-2-thiol have been detected, but the absence of alkene-2-thiols among the reaction products from more highly substituted olefins argues against a nondiscriminant CH insertion mechanism. More likely the thiirane–ethenethiol rearrangement (**15** → **11**) is taking place. A search was made for a direct transition state involving insertion of a sulfur atom into the CH bond of ethylene, but the hydrogen shift occurred only when the SC bond was short (1.697 Å, **G**). Propylene may be a reasonable exception as the isomerization may go through a transition state stabilized by the formation of the allylic–HS biradical system.

Intersystem Crossing in SC_2H_4. The triplet biradical requires 34.4 kcal/mol and 48.0 kcal/mol to form triplet ethenethiol (**12**) and thioacetaldehyde (**14**), respectively. As one can see from Table III and Figure 2, the lower barrier (**D**) is only 4.1 kcal/mol lower than the transition state to the biradical (**C**). It is unlikely that a molecule could retain enough vibrational energy to go over the second barrier before stabilizing to the biradical. This very nicely accounts for the absence of ethenethiol for S(^{3}P) addition to ethylene. More difficult to rationalize is the observed[3] stereoselective addition to *cis*- and *trans*-2-butene. This could be explained if the barrier to rotation of the triplet biradical is sufficiently high; however, MNDO predicts this barrier to be only 0.3 kcal/mol. This barrier was predicted to be 5 kcal/mol by Hoffmann and co-workers[39] using extended Hückel MO calculations. An ab initio calculations[40] found a larger barrier of 23.0 kcal/mol though the total energy values of the triplet were computed by the dubious virtual orbital technique[41] and geometries were not optimized.

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In order to investigate whether a significant rotational barrier might be present in higher level calculations, ab initio calculations including correlation were carried out for the triplet biradical (Figure 7). The GAUSSIAN 82 system[42] was used to optimize geometries at the 6-31G* level, and single-point calculations were made at the MP2/6-31G* level. The rotation barrier at the 6-31G* level is 2.7 kcal/mol which increases to 3.3 kcal/mol at the MP2/6-31G* level. Similar to MNDO, the configuration of Figure 7a contains an α electron on sulfur perpendicular to the molecular plane, while in the rotational transition state (Figure 7b) this orbital is doubly occupied. It is believed that this is a system in which intersystem crossing[19c] is fast even when compared to a relatively low calculated barrier. The two relevant orbitals are on sulfur, and it is known that rates of intersystem crossing increase when a heavy nucleus is present.[19c] The singlet and triplet biradicals are almost isoenergetic and isogeometric at the MNDO level which should also increase the rate of crossing. If the triplet crosses to the singlet, there is no appreciable barrier to ring closure on the singlet surface to thiirane.

The suggestion that intersystem crossing may be fast with respect to other processes was put forth by DeMore and Benson.[43] Considering methylene addition to olefins, these authors felt that both singlet and triplet additions proceed via a short-lived biradical intermediate, and the degree of stereospecificity will be determined largely by the relative rates of rotation vs. ring closure rather than by the spin state of the reagent. Also, it may be expected that the excess energy may be slow in partitioning into torsional modes. At any rate, that the reaction shows stereoselectivity rather than stereospecificity indicates that intersystem crossing need only be competitive with methylene rotation.

Alkynes. We next used MNDO to study the addition of sulfur atoms to acetylene, a well-studied system whose mechanism, however, is little understood. With use of MNDO an activation barrier of 9.2 kcal/mol was calculated (Table III, **J**) for the addition of triplet sulfur to acetylene compared to an observed barrier[7] of 3.0 kcal/mol. The product formed is predicted to be triplet thioketocarbene (**18**) which may intersystem cross to the singlet manifold (**17**). However, in this case the triplet is more stable than the singlet biradical by 10.3 kcal/mol and with the proper low-temperature trapping experiment it might be trapped. The other avenues of escape are over very high energy transition states (Figure 4). The transition state for formation of triplet thioketene (**K**) is 10.9 kcal/mol higher than the addition barrier (**J**) while there is no transition state to ethynethiol but rather the CH bond is homolytically cleaved (**L**, 9.6 kcal/mol higher than addition barrier). Triplet sulfur plus acetylene is 6.8 kcal/mol less stable than H + S=C=C—H (**24**).

Sulfur $S(^1D)$ is predicted to add even more readily than $S(^3P)$ with an activation barrier of 2.4 kcal/mol (Figure 5, **M**). The transition state leads directly to thiirene (**23**)[44] which is predicted to have 72.7 kcal/mol of excess energy. From thiirene there are two transition states (**O**, **P**) leading to thioketene (**19**) and ethynethiol (**21**). In contrast to the addition of $S(^3P)$ these barriers are not excessive, being 50.7 and 44.7 kcal/mol above thiirene, respectively. By bombarding acetylene in an argon matrix with sulfur atoms one might expect to see all three products: thiirene, thioketene, and ethynethiol. The observation that thioketene is observed under pyrolytic conditions and ethynethiol is not[10,11] may be due to the greater thermodynamic stability of thioketene. The reverse barriers from thioketene and ethynethiol to thiirene are 76.4 and 62.3 kcal/mol, respectively.

The S–C bond strength in thiirene is calculated to be 26.3 kcal/mol which is the difference in energy between the $^1A'$ biradical (**N**) and thiirene (**23**). For comparison ab initio calculations predict the C–S bond strength to be 15[30] or 22.3 kcal/mol.[31]

The primary adducts formed in the addition of sulfur atoms to acetylenes are inherently unstable,[5] making mechanistic interpretation difficult. Excited $S(^1D)$ atoms have been postulated to form thiirene[1] while $S(^3P)$ atoms probably form the vibrationally excited ground state thioketocarbene by analogy with ground state $O(^3P)$ which is believed[6] to give triplet ketocarbene as a primary product. Rate studies have been based[7] on disappearance of sulfur in its triplet state revealing nothing about possible product ratios, while trapping experiments[1] for $S(^1D)$ suggest an initially formed thiirene which forms a thiophene on reacting with excess acetylene.

Acknowledgment. Professor M. J. S. Dewar is acknowledged for support during the early statges of this work as well as the University of Texas Computer Center. I thank Auburn University Computation Center for a generous allotment of computer time. Drs. Peter D. Livant and Philip B. Shevlin are acknowledged for helpful conversations.

Registry No. **3**, 74-82-8; **4**, 74-86-2; **5**, 74-85-1; 6, 74-84-0; **7**, 74-93-1; **8**, 75-08-1; **9**, 103069-72-3; **11**, 917-59-9; **12**, 103069-73-4; **13**, 6851-93-0; **15**, 420-12-2; **16**, 2669-89-8; **17**, 85181-66-4; **19**, 18282-77-4; **21**, 53750-02-0; **23**, 157-20-0; **24**, 81566-82-7; **25**, 50983-86-3; HS$^\bullet$, 13940-21-1; H$^\bullet$, 12385-13-6.

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