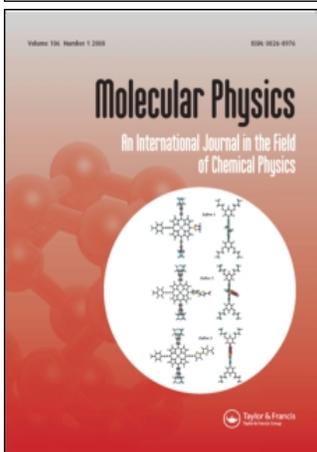


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The interaction of sulphur atoms with ethylene

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The interaction of sulphur atoms with ethylene

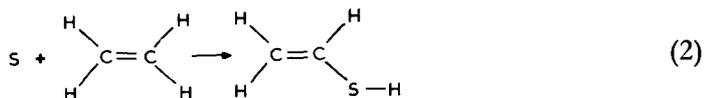
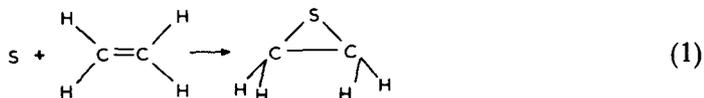
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A correlation diagram shows that 1D sulphur atoms may add to ethylene in a least-motion symmetry-allowed process. The computed potential surface for the interaction of a sulphur atom with an ethylene molecule reveals another local minimum in addition to the one leading to thiirane. This second minimum leads to the insertion product, vinyl thiol. We examine the potential surface in some detail to decide if both reactions branch from the same transition state or whether they are competing concerted processes. The latter view is favoured. Similar potential surfaces are calculated for a $S(^3P)$ configuration. A minimum leading to addition is found, but the one leading to insertion is lacking. The stereospecific addition of $S(^3P)$ is attributed to a correlation with an excited state of thiirane which retains CC bonding. A ring-opened thiirane intermediate is computed, with a planar geometry and a CSC angle of 114° . It closes by a conrotatory route with a calculated activation energy of 24 kcal/mole. We find no ground state intermediate in which a CS bond is broken. In the excited configuration of a thiirane we find two minima—one for a planar geometry with the CC bond cleaved, the other for a species with a CS bond broken, but retaining the original configuration of the CH_2CH_2 part.

1. INTRODUCTION

Through the elegant studies of Gunning, Strausz and their co-workers over the past several years we have learned much about the reactions of sulphur atoms, 1D and 3P , with simple molecules [1]. When the substrates are ethylenes, $S(^1D)$ engages in both addition (reaction (1)) and insertion (reaction (2)):

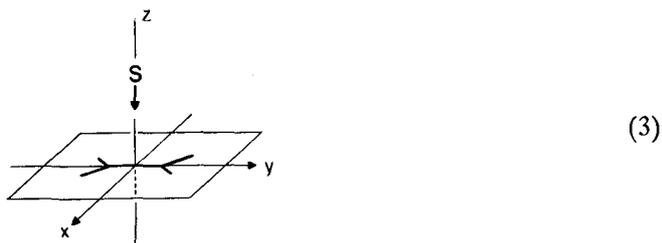


yielding thiiranes (episulphides) and vinyl thiols respectively [2]. $S(^3P)$ apparently yields only addition products [2]. The additions of $S(^1D)$ and, remarkably, $S(^3P)$ are both stereospecific, suprafacial processes [3]. The reverse reaction, the pyrolytic decomposition of thiirane, is similarly stereospecific [4].

In this work we report some preliminary calculations on a potential surface for the approach of sulphur atoms to ethylene, with emphasis on two points: the relationship of the reaction pathways leading to addition and insertion, and the differences noted between 1D and 3P reactivities.

2. ADDITION AND INSERTION OF S^(1D)

Consider (3), an ethylene symmetrically disposed in the xy plane, with the origin of a coordinate system at the mid-point of the C=C double bond. A sulphur atom approaches along the z axis. A level correlation diagram [5]



for this approach, one which leads to addition, is illustrated in figure 1. Levels are classified as symmetric or antisymmetric under reflection in the xz and yz mirror planes. The thirane levels are ordered according to an extended Hückel calculation

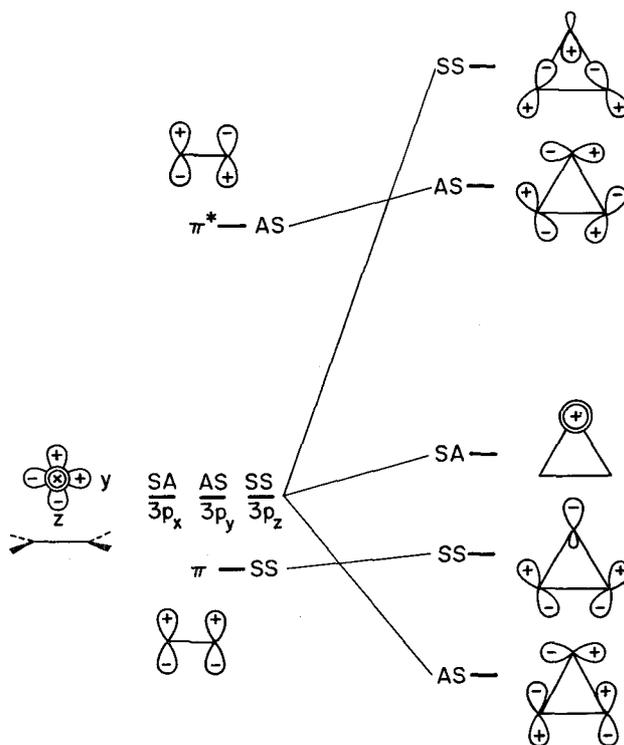


Figure 1. Level correlation diagram for the addition of S to C_2H_4 . The coordinate system is shown in the text. Level symmetries are specified with respect to reflection in the xz and yz mirror planes. At left are shown the π and π^* orbitals of ethylene and the three $3p$ orbitals of an isolated sulphur atom. At large separation the ethylene π level and the S $3p$ are accidentally located at essentially the same energy. They are offset in the diagram for greater clarity. The thirane orbitals on the right are ordered according to an extended Hückel calculation. The SA level is primarily a sulphur lone pair along the x direction.

[6]† with the observed geometry [8]. The lower SS and the two AS levels are derived from the familiar peripheral Walsh level set. One component of the sulphur 1D state is characterized by the configuration $(3p_x)^2(3p_y)^2 \equiv (SA)^2(AS)^2$ and correlates with the ground state of thiirane. The least-motion addition of $S(^1D)$ to ground state ethylene is thus a symmetry-allowed process [2]‡.

We have computed an extended Hückel potential surface for the approach of an S atom to ethylene. The olefin was initially frozen in an idealized planar geometry§. Two distinct minima were located. The first (A) corresponds to the least-motion approach of (3). Minimum A has the sulphur atom at cartesian coordinates (0, 0, 2.1), i.e. 2.1 Å above the centre of the double bond. The energy at this point is 2.3 eV below separated S and C_2H_4 , and the energy decreases monotonically from infinite separation to minimum A. If we allowed the potential surface two further degrees of freedom: lengthening the CC distance, and changing hybridization geometry at carbons from trigonal to tetrahedral, there is little doubt that the sulphur atom would move still further in to the correct thiirane geometry. Thus to the extent that the $(SS)^2(AS)^2(SA)^2$ configuration energy represents the energy of 1D sulphur and ground state ethylene we calculate a concerted 1D sulphur addition proceeding through the highly symmetrical least-motion reaction path, and entailing no activation energy.

We also discovered a second distinct minimum. This minimum, (B), positions the sulphur in the xy plane, the plane of the ethylene, at (1.9, 1.9, 0), i.e. approximately on an extension of the C–H bond line. B is some 1.5 eV below separated S and C_2H_4 , i.e. 0.8 eV above A. Figure 2 shows the interesting shape of the potential surface for S constrained to move in the xy plane. Clearly B is to be interpreted as leading to an incipient insertion process. A simple in-plane pivoting motion around the centre of the H–S line terminates in an acceptable vinyl thiol geometry. This pivoting is calculated to be energetically downhill all the way.

As we mentioned briefly in the introduction, both thiirane and vinyl thiol are produced in the reaction of ethylene with $S(^1D)$. Accepting a concerted formation of the thiirane, one is faced with the difficult task of distinguishing between two possible mechanisms for the formation of the insertion product, the thiol. First, this product could be formed by a concerted process competing with the addition. Secondly, the thiol could be formed by isomerization of a hot thiirane molecule, i.e. the insertion reaction could be a branch from the same transition state which would lead to addition. There is no direct experimental evidence at hand enabling us to decide between these possibilities, but the workers in the field favour a common intermediate [1, 2].

In our continuing study of the potential surfaces for simple reactions [10], the present surface is the first encountered in which potential minima leading to two separate reactions are clearly exhibited. We thus devoted some time to study the paths in the many-dimensional potential surface which connect minima A and B.

Preliminary investigation indicated that in moving from A to B in an optimum manner the sulphur atom would not depart significantly from the plane defined by

† Coulomb integrals were those used previously, plus S $2s$ -20.00 eV, S $2p$ -13.20 eV. The H $1s$ exponent was taken as 1.3 and the C and S Slater exponents were the optimized set of [7].

‡ This conclusion and the corresponding level diagram have been also derived in [9]. Our level scheme for thiirane differs from that proposed in [9], but we support their analysis of the specificity of triplet sulphur additions.

§ C=C 1.34 Å, C-H 1.09 Å, all angles 120° . The parameters are noted in [6].

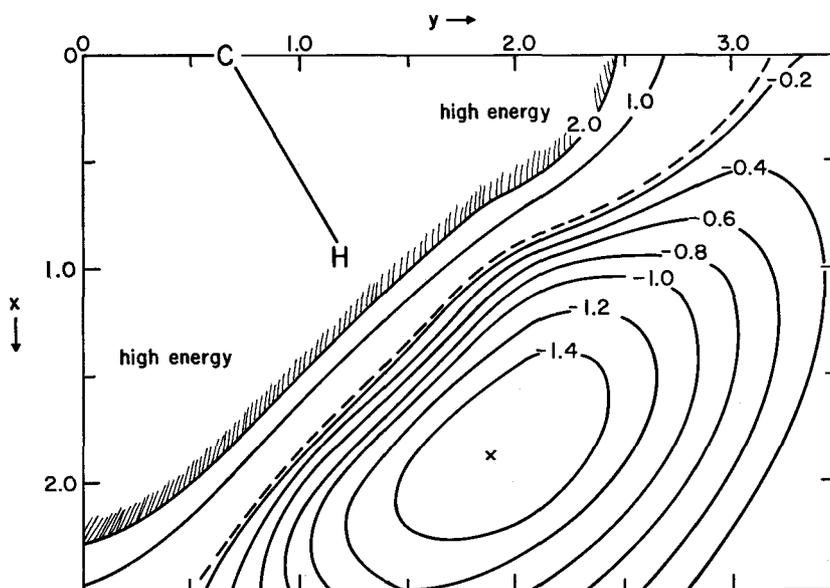


Figure 2. Potential energy surface for the motion of a sulphur atom in the xy plane. The coordinate scales are in ångströms. A C-H fragment of ethylene shows up in the illustrated quadrant. The contour values are energies in electron volts relative to infinite separation. The dashed line is a zero contour.

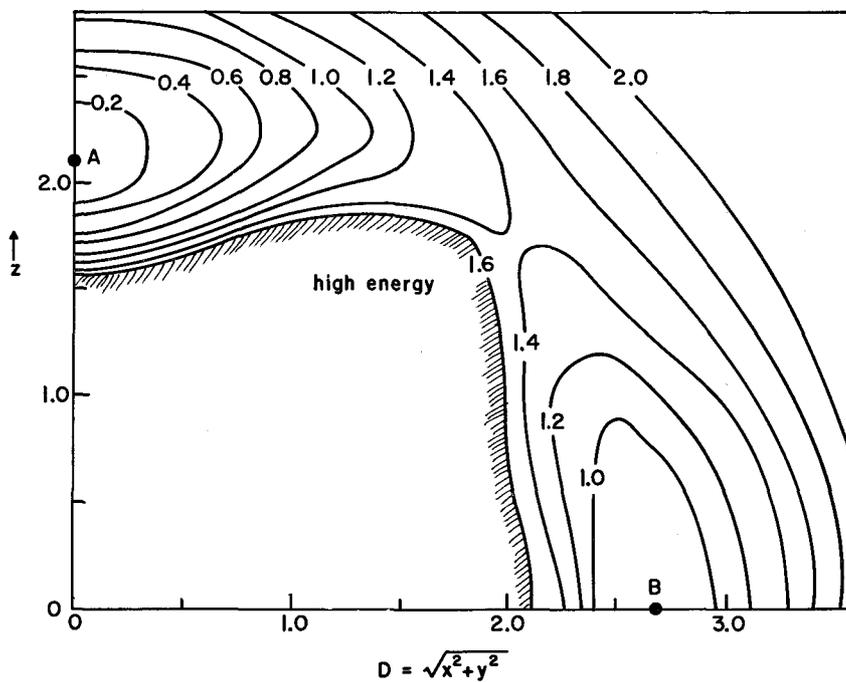


Figure 3. Potential energy surface for the motion of a sulphur atom in the plane $x=y$. The contour values are energies in electron volts relative to an arbitrary zero at minimum A. The horizontal scale is the distance D along the line $x=y$. $D = (x^2 + y^2)^{1/2} = \sqrt{2} x = \sqrt{2} y$.

$x=y$. Accordingly, figure 3 shows the energy contours in that plane. The well-defined transition state is at approximately (1.5, 1.5, 1.7) and some 1.35 eV above minimum A.

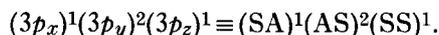
The above transition state for the motion from A to B was calculated with the constraint of a frozen ethylene geometry. We wanted to examine if the activation energy could be reduced by allowing the hydrogen involved in the insertion reaction to move while the sulphur atom was coming down. Independent motions of S and H would necessitate six degrees of freedom, and there was no obvious reaction coordinate for moving from A to the thiol. We resorted to the following stratagem.

Fixing S somewhere along the reaction path of figure 3 we optimized the position of H, allowing it the full three degrees of freedom in its motion. We then kept the hydrogen atom at the optimum location and varied the position of S in three dimensions. This procedure was repeated several times. When the starting positions were on the A side of the reaction, the hydrogen moved below the ethylene plane, as it would be expected to do for an addition reaction. The final S position was back at A. On the B side of the reaction path the initial hydrogen motion was to positive z . Eventually S and H returned to the xy plane, converging to a *cis*-H-vinyl thiol with C-S 1.89 Å, S-H 0.79 Å, angle CCS 124°, angle CSH 114°. The CSH angle is too large, and the S-H distance much too short compared to observed sulphide structures [11]. The discrepancies are of the magnitude we have learned to expect in extended Hückel calculations.

The transition state for the A→thiol interconversion moves to somewhat lower z (compared to figure 3) and is slightly stabilized. A substantial activation energy remains. Figures 2 and 3 imply that any impact geometry in which the sulphur atoms impinge in the region $-1.5 < z < 1.5$, a sizeable region of coordinate space, would lead to insertion. We thus tend to favour the view that insertion is a competing concerted process.

3. TRIPLET SULPHUR REACTIONS

One component of the S(³P) state is derived from the configuration



The corresponding SA→SS excitation in the product thiirane (figure 1) promotes an electron from a sulphur lone pair to one component of the 'central' antibonding Walsh pair. The SS orbital is bonding between the carbons, and thus this particular excited state of thiirane should show no tendency to open up the C-C bond. If anything it should have a stronger C-C (and a weaker C-S) bond than the ground state molecule. This situation must be contrasted with the addition of triplet methylene [10 (*a*)], where the cyclopropane excited state formed does open up the bond opposite to form a trimethylene diradical. Thus S(³P) adds stereospecifically, while CH₂(³B₁) does not.

Our explanation for the specificity of S(³P) reaction is essentially identical to that given by Leppin and Gollnick [9]. A minor difference is that our extended Hückel calculations do not place the second SS level as low, and thus do not indicate that the lowest triplet of thiirane should be SA→SS, i.e. ³B₁.

The question remains how a process shown to proceed through an excited triplet state could be concerted. There are two possible cases: either the excited

triplet of product is attained or it is not reached. In the former case there is no difficulty providing that relaxation to the equilibrium geometry of the excited triplet does not lose the stereochemical information content. In the thiirane case we have argued that the ethylene geometry is maintained, in the cyclopropane case it is lost. Once the metastable product excited state is reached a radiative or radiationless transition will return the molecule to the product ground state. The second case, where the excited product is energetically unattainable, does not, in our mind, present any special difficulties. We believe that orbital symmetry considerations dictate to excited reactants a certain set of motions which are facile. These symmetry-allowed motions are initiated in the excited reactants. There is no need to reach the excited state of products. The allowed motions are accompanied by a radiationless transition to the ground state of the product. The occurrence of such a process presents no more conceptual difficulty than any radiationless transition within a single molecule†.

Our qualitative arguments on the (SA)¹(AS)²(SS)¹ configuration of an approaching sulphur atom are confirmed by the calculations. A single minimum is located for that configuration, with the sulphur atom at approximately (0, 0, 3.1). This minimum, bound by only 0.3 eV relative to separated atoms, is much shallower than minimum A of the previous section. In sharp contrast to the S(¹D) addition there is in this case no other minimum, the potential surface in the *xy* plane being entirely repulsive. This is in accord with the experimental absence of insertion products in S(³P) reactions [1].

4. THE RING-OPENED THIIRANE

In a previous analysis of cyclopropane [10 (a)] we located a second minimum in the ground state potential energy surface for a ring-opened structure with angle CCC around 125°, terminal methylene groups coplanar with the carbon skeleton. This weakly bound minimum preferred a conrotatory closure back to the cyclopropane. A more strongly bound minimum and a greater preference for a conrotatory closure was anticipated for a ring-opened oxirane—a carbonyl ylid. We have now examined a model thiirane‡, and assuming trigonal hybridization at the methylene groups have allowed it three degrees of freedom: CSC angle opening, and independent rotation of both terminal methylene groups.

We locate a well-defined secondary potential minimum for a ring-opened intermediate, (4), with CSC angle approximately 114°, terminal methylene groups



coplanar with the CSC skeleton. As anticipated, its π -electronic structure resembles that of allyl anion. We verified the consequent preference for a conrotatory closure. The activation energy for the reclosure is calculated as 24 kcal/mole.

In all of the calculations previously reported in this paper *3d* orbital on sulphur were omitted. In the case at hand we repeated all calculations including S *3d*

† Further cases where concerted triplet reactions may occur are discussed in [5, (b)].

‡ Geometry taken from [8], except for configuration of methylene groups.

orbitals with a Coulomb integral of -4.0 eV and a Slater exponent of 0.8 . There is essentially no effect on the occupied level ordering, the preference for conrotatory motion and the stability of the ring-opened structure. There is a small and predictable effect on the geometry of (4)—when d orbitals are included the equilibrium CSC angle increases by approximately 2° . This is the result of an energy-lowering mixing of the antisymmetric highest occupied MO of (4) with a $3d_{xz}$ orbital, as in (5).



Thiiranes fragment pyrolytically in a stereospecific manner and with an unusually low activation energy [4]. Thermal population of an excited state was implicated. This excited state was suggested to have one C-S bond partially broken, with partial bonding maintaining stereochemistry [4]. We have investigated a two-dimensional potential surface of a $\text{CH}_2\text{CH}_2\text{S}$ species (6), varying independently the CCS angle



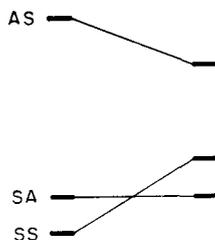
and the rotation of the terminal methylene group, assumed trigonal. To give the $3d$ orbitals maximum opportunity to interact we included them with a $3d$ Slater exponent of 1.5 and a valence state ionization potential of -8.0 eV. The potential surface contains but a single minimum—a geometry with small CCS angle, which if we allowed a pyramidal CH_2 group would become thiirane. There is thus no indication of another minimum in the ground state potential energy surface.

The excited configuration potential surface contains two non-equivalent energy minima. The first is an intermediate with a CC bond broken, of geometry essentially identical to (4). It is a somewhat 'stiffer' molecule than the corresponding excited configuration in the trimethylene-cyclopropane case [10 (a)], but still has lower barriers to rotation of CH_2 groups and opening of CSC angle than the ground state intermediate.

The second minimum is for an intermediate with a CS bond broken, with SCC angle approximately 110° and the terminal methylene group plane perpendicular to the CCS plane. This intermediate, in which the local ethylene fragment geometry is maintained, is close in structure to that suggested by Gunning, Strausz and co-workers [4]. Its calculated barrier to twisting a methylene group by 90° is, however, a low 5 kcal/mole.

There is an interesting aspect of this second intermediate in that it appears to be derived from a second excited state of the thiirane. If one examines the thiirane orbitals of figure 1 one notices that the bonding SS level is bonding between carbon and sulphur, the SA level is non-bonding and the unoccupied AS level is antibonding. Accordingly these levels should move as shown below as the

carbon-sulphur bond is broken:



This is confirmed by the computations. At a CCS angle of approximately 95° the SS and SA levels cross. The two lower configurations of an excited thiirane, $(SS)^2(SA)^1(AS)^1$ and $(SS)^1(SA)^2(AS)^1$, both prefer to open up a carbon-sulphur bond. Though our calculations put the $(SS)^1(SA)^2(AS)^1$ minimum at lower energy, the actual state ordering remains uncertain.

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