Table III. Comparison of Theoretical Data for Lattice and Gas-Phase Water Molecules

	θ	r_{OH}	Q_H[b]	Q_0[a]	a_0[c]	c_0[c]	Stabilization energy,[d] kcal/mol
Crystal	110.5	1.038	0.8279, 0.8208	6.3513	4.32	7.06	−4.5
Isolated	104.7[a]	1.029[a]	0.8584, 0.8584	6.2832			

[a] CNDO/2 theoretical values. [b] Calculated assuming $c_0 = 7.335$, $a_0 = 4.491752$ Å. [c] Experimental values[8] at −186°: $a_0 = 4.4968$, $c_0 = 7.3198$ Å. [d] Experimental value[18] = −11 kcal/mol.

molecules and the symmetrical centering of the molecules in the lattice, both serve to increase the (negative) binding energy.

Summary and Conclusions

In the foregoing sections, we have reported molecular orbital calculation, based on the CNDO/2 method, for the ice-1h crystal. The more interesting results from these calculations are collected in Table III. The agreement between theory and experiment is encouraging and suggests that the CNDO/2 method will prove useful for the theoretical study of hydrogen-bonded systems.

The present calculation also provides some interesting insight into the nature of the hydrogen-bonded interaction within large molecular aggregates. According to the present calculations, the change in the HOH bond angle of water that accompanies crystallization is not due to a nearest neighbor effect as generally supposed, but rather is the result of long-range interaction between the polarized charge densities of the lattice molecules.

The Reactions of Sulfur Atoms. XIV.

Ab Initio Molecular Orbital Calculations on the Ethylene Episulfide Molecule and the S + C_2H_4 Reaction Path

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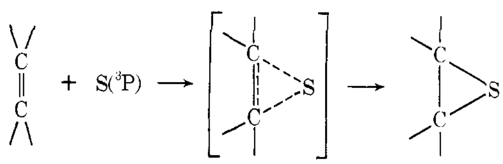
Contribution from the Departments of Chemistry, University of Alberta, Edmonton, Alberta, Canada, and the University of Toronto, Toronto, Ontario, Canada. *Received May 1, 1972*

Abstract: A nonempirical SCF molecular orbital study has been made on thiirane and the thiirane-forming addition of sulfur atoms to ethylene. All the lower lying triplet and singlet excited states of thiirane have a ring distorted equilibrium conformation in which the terminal methylene plane is orthogonal to the CCS plane and the considerable energy barrier with respect to rotation of the terminal methylene is responsible for the maintenance of the stereochemical information content of the addition reaction. Since all the vertical excited states lie at higher energies than the sum of the enthalpy change and activation energy of the reaction, a ring distorted triplet state activated complex is implicated which, in the $C_2H_4 + S(^3P)$ system, correlates with the third vertical triplet state of thiirane. The reaction product, the lowest nonvertical $^3\Sigma(12\sigma \rightarrow 13\sigma^*)$ excited state of thiirane, arises *via* the sequence: $C_2H_4(^1A_1) + S(^3P) \rightarrow C_2H_4S[^3B_2(4\pi \rightarrow 14\sigma^*)] \rightarrow C_2H_4S[^3A_2(4\pi \rightarrow 13\sigma^*)] \rightarrow C_2H_4S[^3\Sigma(12\sigma \rightarrow 13\sigma^*)]$. The ultimate fate of the triplet C_2H_4S is collision-induced intersystem crossing to the ground state. The $C_2H_4 + S(^1D_2)$ system correlates with the electronic ground state of thiirane; therefore the addition is a simple concerted process.

The experimental observation that the addition of ground triplet state sulfur atoms to olefins follows a unique stereospecific path[2] may be rationalized by assuming that the product thiirane is formed essentially in its final nuclear configuration *via* a symmetric transition state.[3]



To conserve spin and orbital symmetry the thiirane should be in one of its low lying triplet states. According to Hoffmann and coworkers' extended Hückel MO calculation,[3] this triplet (n,σ*) thiirane retains CC bonding but is unstable with respect to CS ring opening. The ring-opened intermediate has a computed CCS bond angle of 110° and the plane of the terminal meth-

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[1] (a) Department of Chemistry, University of Alberta; (b) Department of Chemistry, University of Toronto.

[2] H. E. Gunning and O. P. Strausz, in *Advan. Photochem.*, 4, 143 (1966); E. M. Lown, H. S. Sandhu, H. E. Gunning, and O. P. Strausz, *J. Amer. Chem. Soc.*, 90, 7164 (1968).

[3] (a) E. Leppin and K. Gollnick, *Tetrahedron Lett.*, 3819 (1969); (b) R. Hoffmann, C. C. Wan, and V. Neagu, *Mol. Phys.*, 19, 113 (1970).

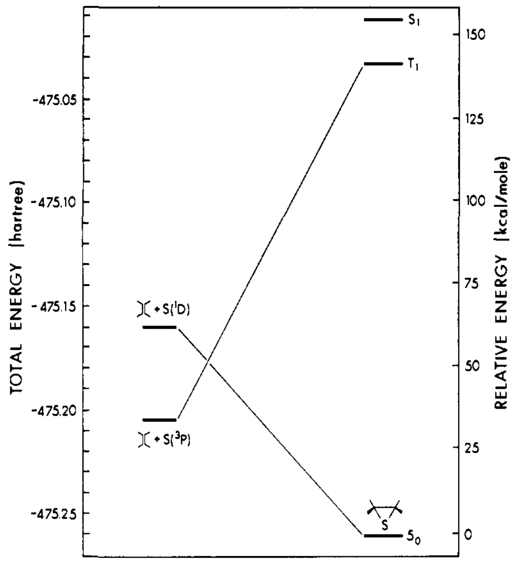

Figure 1. Comparison of some low-lying electronic configuration energies for the initial and final states of the reaction $C_2H_4 + S \rightarrow C_2H_4S$ as computed with the 32 sp basis set.

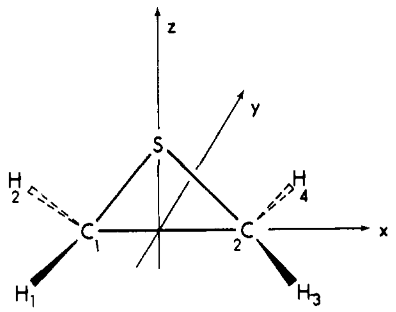

Figure 2. Cartesian right-handed coordinate system for C_2H_4S.

ylene group is perpendicular to the CCS plane. The calculated energy barrier for rotation of the methylene is 5 kcal/mol.

We now wish to report the results of a recent nonempirical SCF–MO calculation which sheds light on the details of the reaction path and reflects the nature of the primary reaction product.

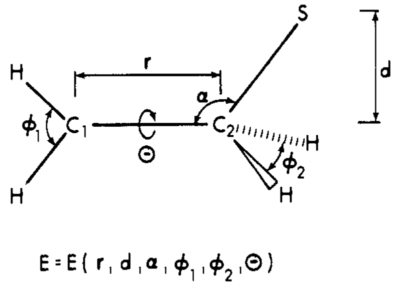

Figure 3. Internal geometrical parameters of C_2H_4S varied.

Method

The individual atomic orbitals used were built up by contraction from primitive Gaussian-type functions, and the molecular orbitals were obtained from a 32 contracted s,p basis set by linear transformations.[4] A previous study on thiirane and its isomers indicated[5] that such a basis set (32 sp) gives sufficiently reliable numerical results. The computations were carried out on an IBM 360/65 computer using IBMOL-IV.[6,7] The sulfur basis set used was that of Veillard[8] $((12^s, 9^p)$ contracted to $[6^s, 4^p])$ while the basis orbitals associated with the carbon $((8^s, 3^p)$ contracted to $[2^s, 1^p])$ and hydrogen atoms $((3^s)$ contracted to $[1^s])$ were originally suggested by Klessinger.[9] Total energy values associated with the lowest singlet and triplet excited configurations of thiirane were computed by the virtual orbital technique.[10]

Results and Discussion

As pointed out earlier,[5] the addition of $S(^3P)$ atoms to ethylene is energetically an unfavorable process if the spin momentum is to be conserved. The energetics of this process are recomputed with the present basis set and summarized in Table I and Figure 1. For this calculation the same molecular geometry,[11] Figure 2, was used as before.[5]

Table I. Computed Energy Values for Some Low-Lying States of Thiirane and Its Fragments[a] $C_2H_4 + S$

Ethylene + sulfur[b]		Thiirane	
State	Energy	State	Energy
$^1A_1 + {}^3P$	−475.20548	$^1A_1$ (S_0)	−475.26221
$^1A_1 + {}^1D$	−475.16024	$^3A_2$ (T_1)	−475.03492
		$^1A_2$ (S_1)	−475.01379

[a] All energy values were computed using a 32 sp basis.[5] [b] Individual values were reported in ref 5.

Theoretical studies of chemical processes may commence from the forward or the reverse direction owing to the principle of microscopic reversibility. In the present case it is more convenient to proceed by considering the product episulfide and to examine the dissociation or distortion of the three-membered ring leading to dissociation.

A complete study of the problem would require the generation of a hypersurface: $E(r,d,\alpha,\phi_1,\phi_2,\theta)$ as illustrated in Figure 3. However, in the present initial study, only a limited number of two- and three-dimensional cross sections could be investigated.

Three modes of motion were examined: (i) symmetric ring distortion $E(r,d)$, (ii) asymmetric ring distortion $E(\alpha)$, and (iii) methylene torsion $E(\theta)$, as illustrated in Figure 4.

In the case of symmetric ring distortion (C–S stretch) eight points were chosen to form a path, Figure 5, which might be assumed to be reasonably close to that reaction coordinate which passes through the equilibrium geometry.

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(4) I. G. Csizmadia, M. C. Harrison, J. W. Moskowitz, and B. T. Sutcliffe, *Theor. Chim. Acta*, **6**, 191 (1966); **7**, 156 (1967); R. E. Kari and I. G. Csizmadia, *J. Chem. Phys.*, **50**, 1443 (1969).

(5) O. P. Strausz, R. K. Gosavi, A. S. Denes, and I. G. Csizmadia, *Theor. Chim. Acta*, **26**, 367 (1972).

(6) A. Veillard, "IBMOL: Computation of Wave Function for Molecules of General Geometry, Version 4," IBM Research Laboratory, San Jose, Calif.

(7) The program was modified for multiprogramming environment by Drs. M. A. Robb and L. M. Tel. The authors are indebted to Dr. E. Clementi for making the program available prior to distribution through the Quantum Chemistry Program Exchange.

(8) A. Veillard, *Theor. Chim. Acta*, **12**, 405 (1968).

(9) M. Klessinger, *ibid.*, **15**, 353 (1969).

(10) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

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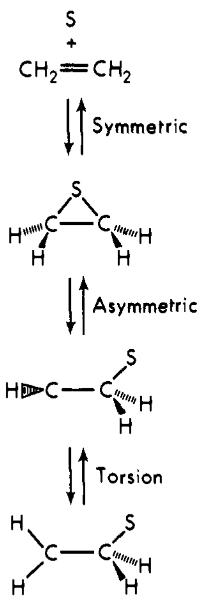

Figure 4. Internal geometrical distortions of C_2H_4S investigated.

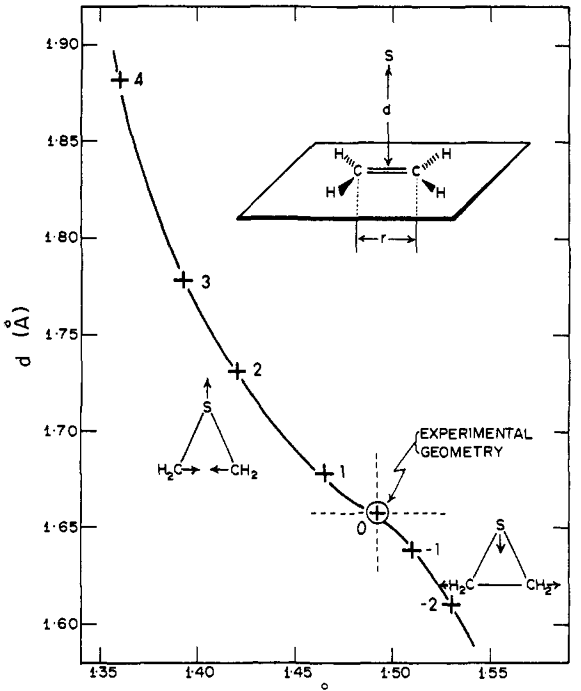

Figure 5. Points along the assumed reaction coordinates of symmetric ring distortion for C_2H_4S.

The orbital energies obtained from the first seven SCF calculations are shown graphically in Figure 6. It is to be noted that some of the orbital energy levels cross over as d is varied. The crossing of the two lowest virtual orbitals (originating from the π and π^* orbitals of ethylene) occurs at a relatively large separation while the crossing of the occupied orbitals and the higher lying virtual orbitals occur in the neighborhood of the equilibrium geometry. A detailed description of the nature of the orbitals involved is given in Table 3 of ref 5.

These findings indicate that correlation of *configuration* energy levels are complex, and qualitative arguments[2] used in their derivation may not necessarily be applicable.

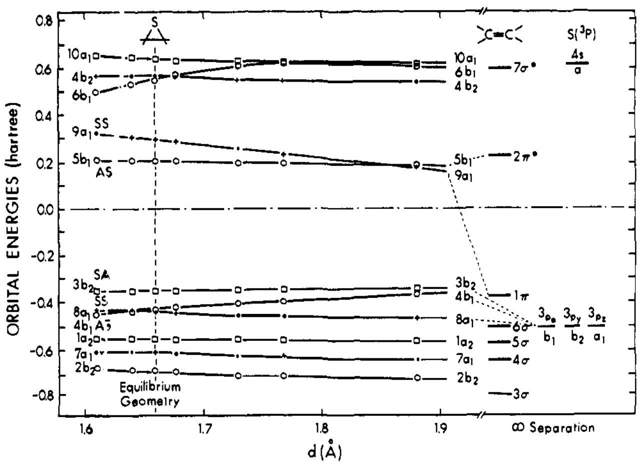

Figure 6. A Hoffmann-Walsh type orbital energy correlation diagram.

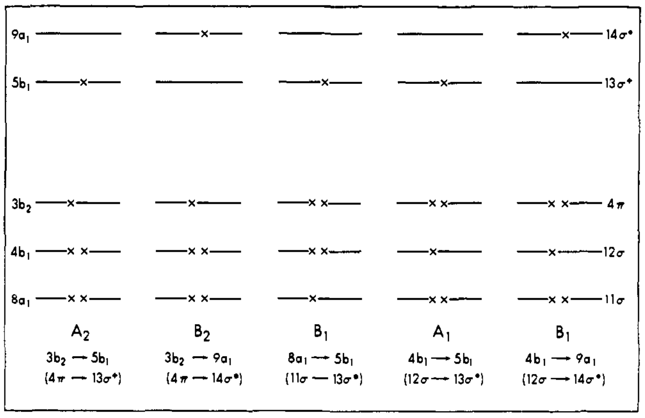

Figure 7. Five low-lying excited electronic configurations studied, having singlet and triplet multiplicity.

From the ground electronic configuration obtained by the SCF procedure, a number of excited electronic configurations were generated using the virtual orbital technique. The five lowest energy configurations are illustrated in Figure 7. The variation of total energy with distance and the accompanying geometrical changes are plotted in Figure 8.

Using the coordinate system as defined in Figure 2, the $3p_x$, $3p_y$, and $3p_z$ atomic orbitals of sulfur may be characterized as belonging to the b_1, b_2, and a_1 irreducible representation, respectively. Applying the direct products rule[12] for the C_{2v} species of C_2H_4S one can see that the $(b_1)^1(b_2)^1(a_1)^2$ configuration (*i.e.*, $3p_x^1$, $3p_y^1$, $3p_z^2$) represents an A_2 excited configuration. In Hoffmann's description which is based on orbital symmetry alone, this corresponds to the lowest mode of excitation ($3b_2 \rightarrow 5b_1$; *cf.* Figures 6 and 7). However, the energy of this particular triplet state, $^3A_2$ ($3b_2 \rightarrow 5b_1$), is the lowest only at the equilibrium geometry, and it becomes the third triplet excited electron configuration at large ethylene–sulfur separation ($d \approx$ 1.9 Å). On the other hand the triplet configuration $^3B_2$ ($3b_2 \rightarrow 9a_1$) which is energetically the closest to the separated ethylene–sulfur system (at large d values) correlates with a $(b_1)^2(b_2)^1(a_1)^1$ (*i.e.*, $3p_x^2$, $3p_y^1$, $3p_z^1$) configuration. Nevertheless, this $^3B_2$ configuration is

[12] K. J. Laidler, "The Chemical Kinetics of Excited States," Clarendon Press, Oxford, 1955, p 173.

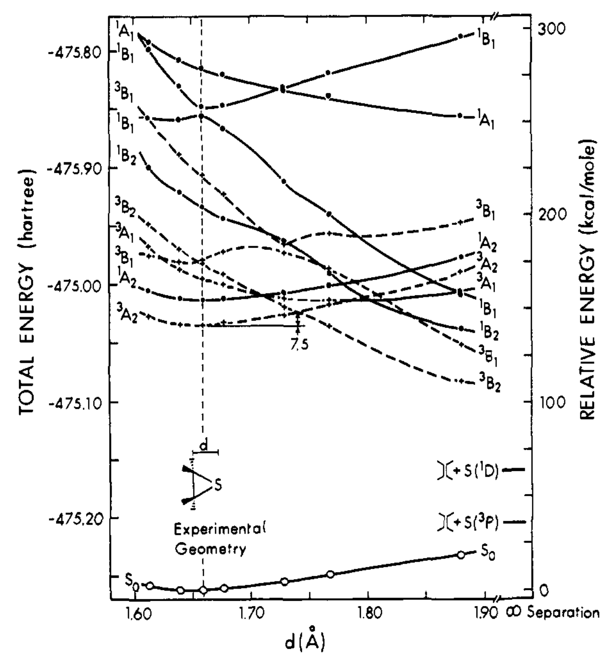

Figure 8. Variation of total energy with distance (d) for the ground and some low-lying electronic excited configurations of thiirane.

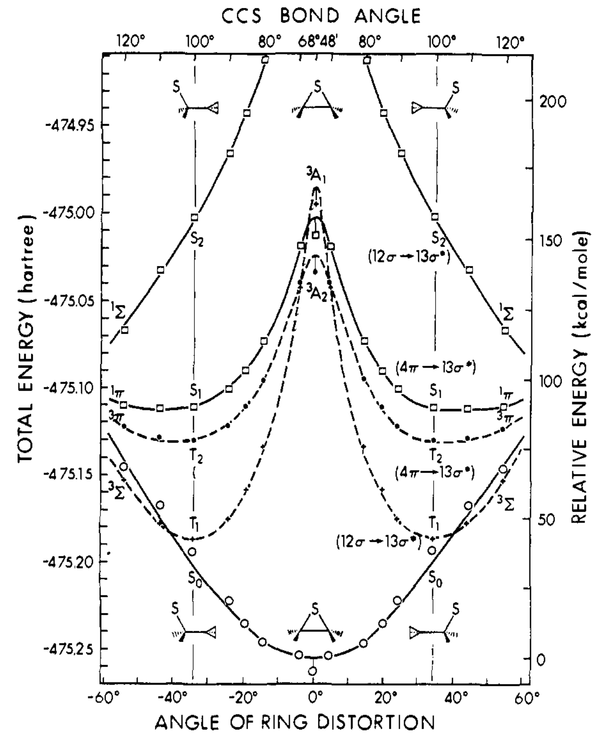

Figure 9. Calculated total energy variation as a function of angle of asymmetric ring distortion for the ground state (S_0), lowest vertical triplet (T_1), and lowest vertical singlet state (S_1) of the thiirane molecule.

not the lowest triplet when the equilibrium geometry is approached in the range of $1.78 \leqslant d \leqslant 1.83$ Å (with equilibrium value 1.819 Å) but oscillates between the second and third positions.

The crossing of the $^3B_2$ and the $^3A_2$ potentials occurs at about $d = 1.86$ Å with a barrier for symmetric dissociation (from the equilibrium geometry to this crossover) in the order of 7.5 kcal/mol. The occurrence of a barrier to potential curve crossing has been postulated before[13] on experimental grounds. A theoretical analysis of level crossings as a function of bond stretching has also been reported recently.[14]

The calculated variations in total energy as a function of angle of asymmetric ring distortion $E(\alpha)$ for the ground and lower lying excited singlet and triplet states of thiirane are plotted in Figure 9.

It should be mentioned that the terminal CH_2 group is kept planar here. Since this HCH bond angle was not varied in this study the ground state potential curve does not pass through the energy associated with the experimental geometry but it is shifted upward by ~5 kcal/mol.

The stable configuration for all low-lying excited states is the ring-distorted structure with CCS bond angles of 100° or larger.

These results suggest a reaction path comprised of the following sequence: $C_2H_4(^1A_1) + S(^3P) \rightarrow C_2H_4S(^3B_2(4\pi \rightarrow 14\sigma^*)) \rightarrow C_2H_4S(^3A_2(4\pi \rightarrow 13\sigma^*)) \rightarrow C_2H_4S(^3\Sigma(12\sigma \rightarrow 13\sigma^*))$.[15] A detailed theoretical description of the first two of these three steps requires the variation of the sulfur–ethylene distance (d) along the symmetrical stretch (Figure 8), and the third step requires the variation of the CCS bond angle (α) (Figure 9). In fact, the above processes are probably concerted and the reaction coordinate represents the simultaneous variation of both internal coordinates α and d. Elucidation of additional details in the microscopic mechanism, however, requires the generation of a complete reaction surface of the type $E(d,\alpha)$ which will be the object of a future study.

The ring distorted nonvertical excited $^3\Sigma$ thiirane can be viewed as the primary product of the $C_2H_4 + S(^3P)$ reaction. It contains approximately 20 kcal/mol of excess vibrational energy. In order to maintain the stereospecific course of the reaction, torsional rotation of the terminal methylene in the $^3\Sigma$ intermediate must be slow and possess an energy barrier ≥ 20 kcal/mol. From calculated total energy variations with respect to angle of CC rotation at a distorted CCS angle of 100°, Figure 10, the energy barriers for rotation in the S_0, T_1, and S_1 states of thiirane are 54.9, 23.0, and 7.4 kcal/mol, respectively. Total energies and rotational barriers for the five lowest lying excited states are listed in Table II. The 23 kcal value for the T_1 state indicates a considerable binding interaction between sulfur and the terminal methylene and is more than necessary to account for the experimental results. Thus, we attribute the stereospecificity of triplet sulfur atom addition to the relatively strong binding interaction between sulfur and the terminal methylene carbon. In contrast, the interaction between the terminal carbons in the lowest triplet state of trimethylene is negligibly small and nearly free rotation exists.[16] The CH_2CH_2O intermediate of the $O(^3P) + C_2H_4$ reaction should present an intermediate case, and correspondingly the isomeric dis-

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[13] O. P. Strausz, *Pure Appl. Chem.*, **4**, 165 (1971); O. P. Strausz, W. B. O'Callaghan, E. M. Lown, and H. E. Gunning, *J. Amer. Chem. Soc.*, **93**, 559 (1971); J. Connor, A. van Roodselaar, R. W. Fair, and O. P. Strausz, *ibid.*, **93**, 560 (1971).

[14] W. D. Stohrer and R. Hoffmann, *ibid.*, **94**, 1661 (1972).

[15] The $^3\Sigma$ state corresponds to the $^3A_1$ vertical state which is the third lowest lying level of the vertical manifold, Figure 8.

[16] R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968); P. J. Hay, W. J. Hunt, and W. A. Goddard, III, *ibid.*, **94**, 638 (1972); A. K. Q. Siu, W. M. St. John, 3rd, and E. F. Hayes, *ibid.*, **92**, 7249 (1970); J. A. Horsley, Y. Jean, C. Moser, L. Salem, R. M. Stevens, and J. S. Wright, *ibid.*, **94**, 279 (1972).

Table II. Variation of Total Energy of the Ground and Low-Lying Excited States of Open Thiirane[a] with θ (C–C Rotational Angle)

State	Total energy, hartrees $\theta = 0°$ [b]	 $\theta = 90°$ [c]	Rotational barrier, kcal/mol
S_0	−475.19455	−475.10711	54.9
T_1	−475.18772	−475.15105	23.0
S_1	−475.11198	−475.10024	7.4
T_2	−475.13020	−475.10923	13.2
S_2	−475.00231	−475.05565	−33.5
T_3	−475.01585	−474.99052	15.9
S_3	−474.93127	−474.98262	−32.2
T_4	−474.92066	−474.87805	26.7
S_4	−474.88433	−474.83998	27.8
T_5	−474.90403	−474.87623	17.5
S_5	−474.88249	−474.83472	30.0

[a] The CCS bond angle is 100°. [b] Nuclear repulsion = +91.86389. [c] Nuclear repulsion = +92.12807.

tribution of products is temperature dependent[17,18] indicating restricted rotation around the CC bond.

The $C_2H_4 + S(^1D_2)$ system correlates with the $^1A_1$ ground state of thiirane and the reaction proceeds along a suprafacial, concerted least motion path as has been described in the literature.[2,3] The enthalpy change of the reaction is 85 kcal/mol, while the calculated CC rotational energy barrier is 54.9 kcal/mol. From this, the rotational rate constant can be estimated to be $\sim 10^8$ l. mol^{-1} sec^{-1}, and geometrical isomerization is predicted to be effectively suppressed at atmospheric pressures, in agreement with experiment.

The present calculations are also consistent with the available spectroscopic data on thiirane. The uv spectra display two broad, overlapping long wavelength bands with maxima around 39,000 and 41,000 cm^{-1}. The first of these weak bands may be assigned to the nonvertical $S_0 \rightarrow S_1$ transition with a calculated excitation energy of 32,970 cm^{-1}.

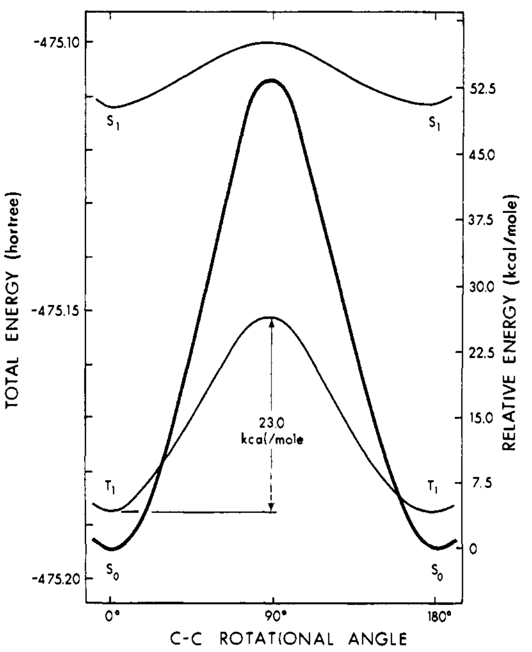

Figure 10. Calculated total energy variation as a function of CC rotational angle for the ground state (S_0), lowest triplet (T_1), and lowest singlet state (S_1) of the thiirane molecule at a CCS angle of 100°.

Further studies on the ethylene plus sulfur and ethylene plus oxygen systems are in progress and will be reported at a later date.

Acknowledgments. We thank the National Research Council of Canada and the Province of Ontario for support of this research.

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(17) M. D. Scheer and R. Klein, *J. Phys. Chem.*, 73, 597 (1969).
(18) R. J. Cvetanovič, *Advan. Photochem.*, 1, 115 (1963).

An Example of Mechanistic Similarity between Oxidative Addition and Classical Donor Coordination

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Abstract: A kinetic study of the reactions $H(CO)(Ph_3P)_2Ir + Ph_3P \rightleftharpoons H(CO)(Ph_3P)_3Ir$ (k_{+P}, k_{-P}) and $H(CO)(Ph_3P)_2Ir + (CH_3)_n(C_2H_5O)_{3-n}SiH \rightleftharpoons H_2(CO)[(CH_3)_n(C_2H_5O)_{3-n}Si](Ph_3P)_2Ir$ (k_{+Si}, k_{-Si}) is reported. For the case where $n = 3$, the kinetic parameters for the phosphine and silane reactions were almost identical: $\Delta H^{\ddagger}_{-P} = \Delta H^{\ddagger}_{-Si} \approx 23$ kcal/mol, $\Delta S^{\ddagger}_{-P} = \Delta S^{\ddagger}_{-Si} \approx 16$ eu, $\Delta H^{\ddagger}_{P} - \Delta H^{\ddagger}_{Si} = 0$ kcal/mol, $\Delta S^{\ddagger}_{P} - \Delta S^{\ddagger}_{Si} = 13$ eu. For the case where $n = 1$ and $n = 0$, the activation enthalpies for addition were again 23 kcal/mol, but for the elimination reactions substantially larger values of $\Delta H^{\ddagger}_{Si}$ were observed (for $n = 1$, $\Delta H^{\ddagger}_{-Si} = 28$ kcal/mol), in agreement with results reported previously. The results are interpreted to mean that phosphine addition and silane addition are mechanistically similar processes and that the observed activation enthalpies are largely due to a prerequisite deformation of the square-planar iridium complex.

The class of reactions, known as "oxidative addition" reactions, has attracted a great deal of attention in the recent past. In addition to providing useful insight into the functioning of a variety of coordination catalysts, oxidative additions are of considerable interest because some of them at least seem to represent a major new mechanistic class of reaction.[1,2]

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(1) L. Vaska, *Accounts Chem. Res.*, 1, 335 (1968).
(2) J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, 7, 53 (1968).