At least some of the difference in behavior arises because absorbance is a linear function of [Co^{III}] while potential is a logarithmic function. It may also be that the potential of the platinum electrode is particularly sensitive to [Br_2]. If that hypothesis is correct, we might be able to follow [Co^{III}] and [Br_2] simultaneously and thus test the predictions of our mechanism more quantitatively.

We also believe the characterization of Co^{III} solutions could be improved. However, the amount of information already accumulated about this system is so great that we believe publication at this time is warranted. A detailed molecular mechanism has been generated, and computations to test it are under way. We believe that after those computations have been carried out will be an appropriate time for further experimental study.

Acknowledgment. This research was supported in part by Grants No. CHE8405518 and 8717791 from the National Science Foundation to the University of Oregon. A.J.C. was on leave from the Department of Chemistry, University of Mar del Plata and CONICET, Argentina. E.G. was on leave from the Department of Chemistry, University of Mar del Plata and CIC, Argentina. We are particularly indebted to Drs. James Jensen, Mark Roelofs, and Edel Wasserman of the du Pont Company who encouraged us to undertake an independent study of the reaction that they had discovered and who provided us with results of their own further investigations. Dr. John Guslander of the University of Oregon provided much assistance during efforts (not reported here) to model various hypothetical mechanisms. He has also developed a skeleton mechanism with only three independent variables that reproduces some (but not all) of the features of this system and that is of mathematical interest in its own right. That work will be reported elsewhere.

Note Added in Proof. Only after this paper was being set in type did we discover the study by Reimus, Massie, and Hudson.[16] These authors studied the same reaction with the chemicals continuously introduced in a flow reactor. They simulated oscillations with a mechanism very similar to that of Roelofs, Wasserman, and Jensen[4] but with somewhat fewer steps.

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Stereospecificity of the S(^3P_J) + Butene-2 Reaction and the NMR Spectra of the 1,2-Dimethylthiiranes: An Experimental and Theoretical Study

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Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2. *Received March 14, 1990*

Abstract: The gas-phase addition of S(^3P_J) atoms to *cis*- and *trans*-butene-2 has been investigated and both reactions have been shown to be 100% stereospecific, yielding the lowest excited triplet state of the 2,3-dimethylthiirane end product. The triplet thiirane has a long collisional lifetime and is capable of undergoing facile, reversible addition to the butenes causing their geometrical isomerization, while retaining its own original geometry. The cause of the gradual loss of stereospecificity in the 2,3-dimethylthiirane product with increasing conversion has been identified as this geometrical isomerization of the butene-2 substrate by the primary triplet thiirane and those produced in the secondary photolysis of the thiirane product. Ab initio SCF-MO with 6-31G* basis set and limited CI calculations predict the lowest triplet ring opened A″ state of thiirane to lie 54 kcal mol^{-1} above the ground state with a rotational energy barrier for the terminal methylene of 5.4 kcal mol^{-1}. The total computed reaction energy for the model reaction S(^{3}P) + C_2H_4 is thus approximately the same as the change in internal energy of the reaction, 58.0 kcal mol^{-1}, estimated from thermochemical data, and therefore isomerization will be slow relative to collisional deactivation. This gives a plausible account of the origin of the complete stereospecificity of triplet sulfur addition to olefins. The reaction initially proceeds in a concerted least-motion path on the lowest $^3B_1$ (C_{2v}) repulsive surface which intersects the lowest attractive $^3A''$ surface 1.9 kcal mol^{-1} above the reactant state. This intersection is identified as the transition state of the reaction for which the reported experimental activation energy is 1.6 kcal mol^{-1}. Both the $^3A''$ and the next higher lying $^3A'$ surfaces feature a significant intrinsic activation energy barrier and therefore they are effectively eliminated as adiabatic reaction surfaces. The NMR spectra of the isomerically pure *cis*- and *trans*-2,3 dimethylthiiranes have been obtained and assigned by computer simulation.

The chemistry of sulfur atoms has been systematically explored since the early 1960s, and it was soon established that both ground triplet and lowest excited singlet state sulfur atoms readily add to olefinic double bonds to give the cycloadducts, thiiranes.[1] The reactivity of $^1D_2$ sulfur atoms conforms to the general reactivity of singlet state divalent reagents in that their addition follows a stereospecific path and they are capable of insertive attack at the carbon–hydrogen bond to yield thiols. On the other hand, ^3P_J sulfur atoms do not appear to follow the pattern of reactivity established for triplet state divalent reagents since their addition to olefins is a nearly stereospecific process.[2] With *cis*-butene-2 the retention of configuration in the 2,3-dimethylthiirane product (DMT) is about 90% and with *trans*-butene-2 over 98%.

The adducts from triplet reagent additions are assumed to be initially formed in their lowest excited triplet state. This can be envisioned as a 1,3-biradical in which rotation about the C–C bond

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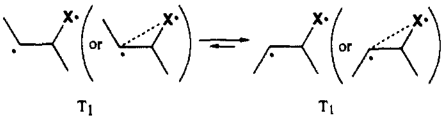
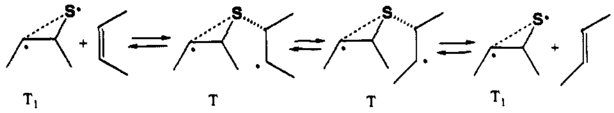
may or may not occur depending on the presence or absence of a significant rotational energy barrier or residual bonding between the terminal atoms.



The ultimate fate of the excited adduct is rearrangement, decomposition, or collision-induced intersystem crossing to the ground state. With sulfur atoms only the latter process is operative and the thiirane end product can be obtained in nearly quantitative yields.[1]

During the addition of $S(^3P_J)$ atoms to *cis*- or *trans*-butene-2 the unreacted olefin undergoes extensive geometrical isomerization.[3,4] The agent responsible for this isomerization has been shown to be the thiirane (T_1) molecule, the initial product of the addition of $S(^3P_J)$ to the butene, which is capable of reversibly adding to the butene[5]



causing its isomerization. The quantum yield of isomerization is large (it can exceed 100), meaning that one triplet thiirane molecule can induce the isomerization of more than a hundred butene-2 molecules before being deactivated to the ground state. It follows that not only the radiative lifetime but also the collisional lifetime of the T_1 state thiirane is long and that, in the adduct, the thiirane moiety preserves its cyclic structure and thus retains its original steric conformation.

The sulfur atom + olefin reaction and the cause of the high degree of stereospecificity of the addition of $S(^3P_J)$ to olefins have been investigated theoretically with molecular orbital computational methods on the model system $S(^3P_J,{}^1D_2) + C_2H_4$. From early semiempirical EHMO studies, Leppin and Gollnick[6] and Hoffmann and co-workers[7] predicted a concerted, least-motion, symmetry-allowed reaction path without any activation energy for the addition of $S(^1D_2)$ to C_2H_4. In the $S(^3P_J)$ addition, in order to conserve spin and orbital symmetry, the thiirane is required to form in one of its low-lying triplet states. Hoffmann and co-workers[7] predicted a ring-opened triplet intermediate with an energy barrier of 5 kcal mol^{-1} for rotation of the terminal methylene. From ab initio SCF calculations with the primitive virtual orbital techniques,[8] Strausz et al.[9] obtained a rotational energy barrier of 23 kcal mol^{-1} in the T_1 excited state with $\Delta E_{exc} \approx 46$ kcal mol^{-1}. From this they concluded that the stereospecificity of the reaction is due to the insufficient energy release in the reaction, $\Delta E_{rxn}(\text{exp}) = -58.0$ kcal mol^{-1}, to drive the system through the energy barrier for isomerization, calculated to be 69 kcal mol^{-1}. More recently, semiempirical and ab initio studies by McKee[10] suggested that the energy barrier in the triplet state is small, 2–3 kcal mol^{-1}, and that $\Delta E_{exc} + E_{rot} \approx 31$–$33$ kcal mol^{-1}. The latter is considerably less than ΔE_{rxn} and therefore the stereospecificity was attributed by McKee to a rapid intersystem crossing to the ground state rather than to the existence of a substantial rotational energy barrier in the T_1 state. This postulate, however, is contrary to experimental observations relating to the efficient geometrical isomerization of the unreacted butene-2[3-5] and therefore cannot be correct.

At the time when Sidhu et al.[2] reported the original study of the $S(^3P_J)$ + butene-2 reaction, the occurrence of the isomerization of the butene, complicating the evaluation of the extent of stereospecificity of the sulfur addition reaction, was not recognized. For this reason and because of the controversial results of the molecular orbital computations with regard to the interpretation of the origin of the stereospecificity of triplet sulfur atom additions, a reexamination of the $S(^3P_J)$ + *cis*- and *trans*-butene-2 reaction was undertaken. These experimental studies were complemented with detailed ab initio SCF molecular orbital and CI computational studies to map out the reaction path for the model system $S(^3P_J) + C_2H_4$. The NMR spectra of the *cis*- and *trans*-dimethylthiirane (DMT) products have not been previously reported, and for this reason we have recorded the high-field NMR spectra of these compounds and analyzed them by computer simulation.

Experimental Section

The gas-phase reactions of $S(^3P_J)$ atoms with *cis*- and *trans*-butene-2 were studied in a cylindrical quartz cell (10 cm × 5 cm) attached to a mercury-free high-vacuum rack. $S(^3P_J)$ atoms were generated by the 225–260-nm photolysis (Hanovia-3062 medium-pressure Hg arc with 4-mm Vycor 791 filter) of COS in the presence of the butene substrate and a large excess of CO_2, as described previously.[2] The gas pressures were measured with either a Speedivac-C.G.3. or a Wallace & Tiernan-FA160-MM1 3270 gauge.

At the conclusion of each irradiation the reaction products were analyzed as follows: CO was distilled at −196 °C and collected in a gas buret for volumetric measurement with a Toepler pump and subsequently transferred into an on-line GC inlet for analysis on an 8-ft molecular sieve 5-Å column. The GC assembly consisted of a GowMac Model 9999 D1 power supply connected to a homemade two-chamber thermistor detector housed in a GowMac Model 24-500 temperature controller. The excess COS, butene, and CO_2 were removed by distillation at −123 °C, and the residue was analyzed by GC on a 16-ft 10% tricresyl phosphate on chromosorb WAW DMCS column at 30 °C. The absolute amounts of the thiirane products were determined from the corrected calibration curve of *n*-butanethiol. In order to determine the isomeric composition of the residual butene-2, an aliquot of the −123 °C distillable fraction was passed through the gas chromatograph on a 20-ft 30% glutaronitrile–propylene carbonate column at 0 °C.

Materials. For the NMR spectroscopic study of the thiirane products, high-purity samples of the cis and trans isomers were prepared by trapping them separately from the GC effluent.

The COS (Matheson) used was purified as described previously.[11] The *cis*- and *trans*-butenes (Aldrich) were degassed at −130 °C and distilled at −78 °C. CO_2 (Airco Assayed Reagent with stated purity >99.99%) was used without further purification.

NMR Spectroscopic Studies of *cis*- and *trans*-DMT. The NMR samples were prepared in 5-mm NMR tubes by dissolving 0.399-mg of *trans*-DMT or 1.362-mg of *cis*-DMT in 0.5-mL of $CDCl_3$. The concentrations were 9.06 and 30.9 mM, respectively. The samples were sealed and stored at −20 °C.

The NMR measurements were performed on a Bruker AM400 NMR spectrometer at ambient temperature. Data collection and data processing were controlled by an Aspect 3000 computer equipped with an Array Processor using 1987 Bruker DISNMR software. Spin simulation and iteration were carried out on the same computing system by using a 1985 version of Bruker's PANIC (Parameter Adjustment in NMR by Iteration Calculation) program. The chemical shifts are referenced to internal TMS.

In order to obtain good digital resolution (0.06 Hz/point) without having to handle huge data files, only a 1000-Hz sweep width was recorded, thus deliberately folding the TMS and the signal of the undeuterated portion of the solvent. 16K (zero-filled to 32K) data points were acquired (acquisition time 8.2 s). A large number of scans (64 and 128, respectively) were accumulated to obtain an excellent signal-to-noise ratio allowing extensive resolution enhancement. We found that multiplying the FID with a slightly shifted ($\pi/32$) sine bell function provided excellent resolution without a severe distortion of the individual lines or the baseline. With regard to spectrum distortion the sine bell filter yielded a much better result than the more commonly used Gaussian multiplication and was therefore used for the spectra of both isomers.

Theoretical Methods. All molecular geometries were optimized at the SCF level by the energy gradient method with the 6-31G* basis set.[12-16]

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The RHF open-shell SCF method was used for the triplet state energy calculations. Configuration interaction (CI) calculations including all singly and doubly excited configurations (CISD) with respect to the SCF configuration were performed by using the direct CI method[17] at the SCF optimized geometry. Quadruple excitation correction was calculated by Davidson's formula[18] and added to the CI result (CISDQ). For CI calculations of ground and excited states of thiirane, only the lowest 40 orbitals have been used with the lowest seven occupied orbitals corresponding to C, 1s and S, 1s, 2s, 2p core orbitals kept doubly occupied and frozen. To calculate the relative energies of the separated entities, total CI energies were calculated at 100-Å separation between the center of the C–C bond and the sulfur atom. Also, for comparative purposes, S(^{3}P and ^{1}D) energies at the CI level were calculated with all electrons and orbitals and also keeping the lowest five occupied orbitals corresponding to 1s, 2s, 2p core orbitals, doubly occupied and frozen, and the topmost single virtual orbital frozen. For the ground state (^1A_g) ethylene, only the lower 22 molecular orbitals were used in the CI calculations, with the lowest two occupied orbitals corresponding to C 1s, core orbital, doubly occupied, and frozen. All computations were performed with the modified version of the Gaussian 82 program,[19] the MONSTERGAUSS program.[20]

The neglect of zero-point energy corrections[21] and doing the geometrical optimization at the SCF rather than the CI level introduce some small errors in the computed values; however, these are considered to have a negligible effect on the relative numerical values of the computed quantities.[22-24] Thus, Tanaka and Yoshimine[22] showed, for the analogous oxygen system (oxirene, ketene and hydroxy acetylene), that the relative energies calculated at the SCF and CI level optimized geometries agree within 0.2–0.4 kcal/mol.

Results and Discussion

Experimental Studies. Sulfur atoms were generated by the photolytic step[25]

$$\mathrm{COS} \xrightarrow[225\text{–}260\ \mathrm{nm}]{h\nu} \mathrm{CO} + \mathrm{S}(^1D_2)\ (\sim 98\%) + \mathrm{S}(^3P_J)\ (\sim 2\%) \quad (1)$$

and the excited singlet atoms rapidly deactivated to the ground triplet state with quenching reaction

$$\mathrm{S}(^1D_2) + \mathrm{CO}_2 \rightarrow \mathrm{S}(^3P_J) + \mathrm{CO}_2^{\dagger} \quad (2)$$

with $k_2 = 1.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.[26] From the available rate constants it can be estimated that under the reaction conditions employed, 80 Torr of COS and 1200 Torr of CO$_2$, about 97% of the sulfur atoms will react as triplets. The residual singlet reacts rapidly with COS

$$\mathrm{S}(^1D_2) + \mathrm{COS} \rightarrow \mathrm{CO} + \mathrm{S}_2 \quad (3)$$

with $k_3 = 8.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.[26]

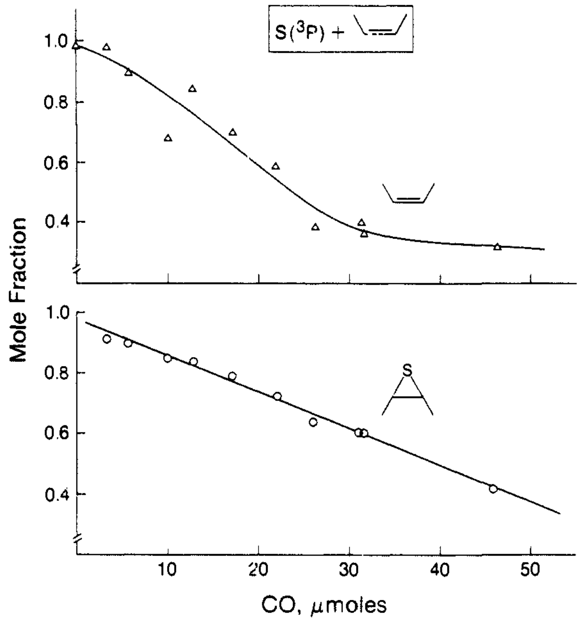

Figure 1. Addition of S(^{3}P) atoms to *cis*-butene-2. Plot of the mole fraction of *cis*-DMT and *cis*-butene as a function of CO.

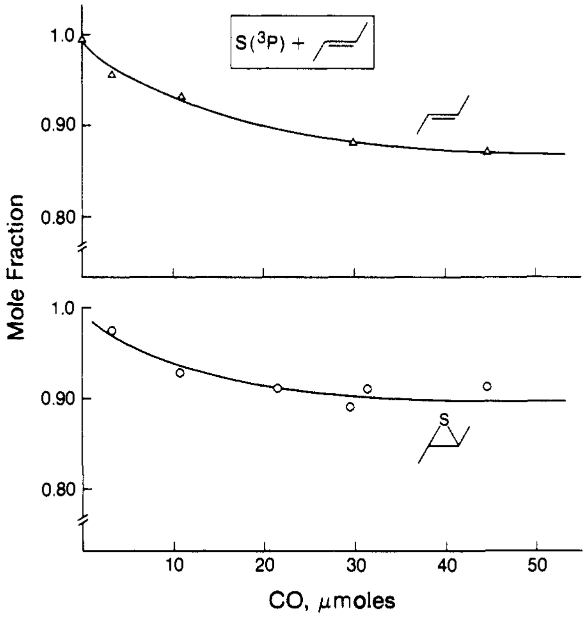

Figure 2. Addition of S(^{3}P) atoms to *trans*-butene-2. Plot of the mole fraction of *trans*-DMT and *trans*-2-butene as a function of CO.

When 30–40 Torr of butene-2 is added to this system, essentially all the triplet atoms are scavenged by the butene as DMT

$$\mathrm{S}(^3P_J) + \text{butene-2} \rightarrow \mathrm{DMT}$$

and about 2% of the residual singlet atoms react with butene-2 to yield DMT and small quantities of butene-2 thiols.

A series of experiments were performed with 80 Torr of COS + 1200 Torr of CO$_2$ + 38.5 Torr of *cis*- or *trans*-butene-2, and the geometrical isomeric composition of the DMT product and of the residual butene were determined as a function of the amount of sulfur atoms produced, as measured by the CO yield. The results are plotted in Figures 1 and 2. As seen from the plots, the isotopic purities of the product thiiranes and residual butene decrease with increasing conversion. Extrapolation of the DMT mole fraction from the *trans*-butene reaction to zero conversion gives an initial value of 0.99 for *trans*-DMT, which is about the same as the mole fraction of *trans*-butene in the initial reactant. The results of the *cis*-butene system are analogous, and the zero-conversion extrapolated value for the mole fraction of *cis*-

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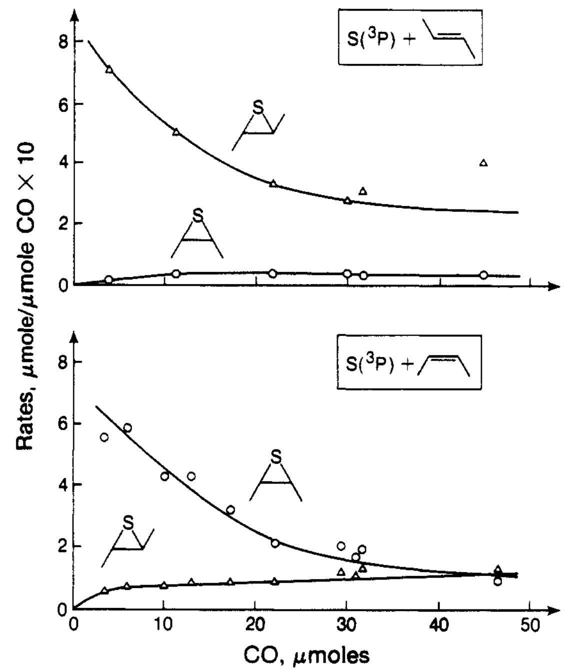

Figure 3. Plot of the rates of formation of DMT from the addition of S(^{3}P) atoms to *cis*- and *trans*-2-butene.

DMT in the product is about 0.98, which again is equal to the *cis*-butene mole fraction in the initial reactant. From these results, it is concluded that within experimental error, the addition of triplet sulfur atoms to both *cis*- and *trans*-butene-2 is 100% stereospecific:

$$S(^3P_J) + \textit{cis}\text{-butene-2} \rightarrow \textit{cis}\text{-DMT} \qquad (4)$$

$$S(^3P_J) + \textit{trans}\text{-butene-2} \rightarrow \textit{trans}\text{-DMT} \qquad (5)$$

The declining trend in isomeric purity with increasing conversion is then due to secondary reactions involving the triplet DMT-sensitized geometrical isomerization of the butene, and participation of the isomeric butene in the scavenging of S atoms, the photopolymerization and decomposition of the DMT products, and the destruction of DMT by attack of S atoms:

$$\textit{cis}\text{-DMT}(T_1) + \textit{cis}\text{-}(\textit{trans}\text{-})\text{butene-2} \rightarrow \textit{cis}\text{-DMT}(T_1) + \textit{trans}\text{-}(\textit{cis}\text{-})\text{butene-2} \qquad (6)$$

$$S(^3P_J) + \textit{trans}\text{-}(\textit{cis}\text{-})\text{butene-2} \rightarrow \textit{trans}\text{-}(\textit{cis}\text{-})\text{DMT} \qquad (5a)$$

$$\textit{cis}\text{-}(\textit{trans}\text{-})\text{DMT} + h\nu \rightarrow \textit{cis}\text{-}(\textit{trans}\text{-})\text{DMT}(S_n) \rightarrow \textit{cis}\text{-}(\textit{trans}\text{-})\text{DMT}(T_1) \qquad (7)$$

$$\text{DMT}(T_1) \xrightarrow{\text{butene}} \text{polymerization/decomposition} \qquad (8)$$

$$\textit{cis}\text{-}(\textit{trans}\text{-})\text{DMT} + S(^3P_J) \rightarrow \textit{cis}\text{-}(\textit{trans}\text{-})\text{butene-2} + S_2,\ \text{etc.} \qquad (9)$$

From the data plotted in Figure 3, the major cause can be identified as the photopolymerization–decomposition of the major isomeric DMT, accentuated by the isomerization of the butene substrate (reactions 5 and 6). The minor isomer of DMT is affected less by photopolymerization, and this is overcompensated by the increasing importance of the butene substrate isomerization (reactions 5 and 6) with increasing conversion. All these effects, the photopolymerization–decomposition of DMT, the isomerization of butene, and the formation of the minor DMT isomer, are clearly more important in the cis than in the trans system showing that the trans isomers of butene and DMT are the more thermodynamically stable ones.

Table I. Calculated Total and (^{1}D–^{3}P) Separation Energy of the S Atom with the 6-31G* Basis Set

	total energy, au		$\Delta E(^1D{-}^3P)$, kcal mol^{-1}
	^{3}P	^{1}D	
SCF	−397.472 260	−397.392 667	49.95
CISD[a]	−397.570 886	−397.508 999	38.83
	(−397.580 954)	(−397.518 375)	(39.27)
CISDQ	−397.575 584	−397.523 860	32.46
	(−397.586 131)	(−397.532 954)	(33.37)
expt[b]			26.40

[a] CI energies were calculated with lowest S core orbitals corresponding to 1s, 2s, 2p kept doubly occupied and frozen. The topmost virtual orbital was also kept frozen. Values in parentheses are CI energies calculated with all electrons and all orbitals. [b] Reference 1.

Table II. SCF-Optimized Molecular Parameters and Total Energies of Ethylene with the 6-31G* Basis Set

	$\tilde{X}^1A_g$
R(C–C), Å	1.317 (1.330)[a]
R(C–H), Å	1.076 (1.076)
∠HCH, deg	116.38 (116.60)
E(SCF)	−78.031718
E(CISD)[b]	−78.168642
E(CISDQ)	−78.178678

[a] Experimental value, from ref 27. [b] CI calculations were carried out with only the lowest 22 orbitals. The lowest two occupied orbitals corresponding to carbon 1s core orbitals were kept doubly occupied and frozen.

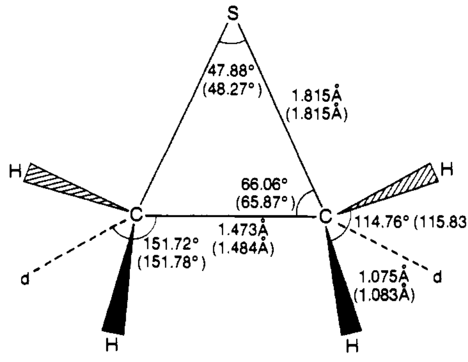

Figure 4. Optimized molecular geometry of thiirane. Values in brackets are experimental values.[31]

The number of *cis*-butene molecules isomerized per DMT(T$_1$) initially produced from the addition of S(^{3}P$_J$) to *cis*-butene varies during the reactions. For the 30 µmol of S(^{3}P$_J$) produced, the number can be estimated (from Figure 2) to be 10. The real value would be lower because of the secondary photolytic production of additional DMT(T$_1$) from the product DMT. This can be compared with the number of *cis*-butene molecules isomerized per triplet thiirane molecules, 50, in the photolysis of thiirane in the presence of 43 Torr of *cis*-butene.[5] This difference in efficiency can be reasonably attributed to the presence of 1200 Torr of CO$_2$ in the present system, which acts as a quencher of DMT(T$_1$).

The maximum yields of DMT obtained at the lowest conversions involved were somewhat over 80%, in terms of sulfur atoms produced in the primary step.

Molecular Orbital Studies. The ground state (^{3}P) and the lowest excited state (^{1}D) energies of the sulfur atom were calculated at the SCF as well as CI level with 6-31G* basis set (with $\alpha_d = 0.58$ for S), and the results with singlet–triplet state energies are summarized in Table I. As seen, CI calculations are necessary for a better approximation of the experimental values. Optimized molecular parameters of ground state ethylene (^{1}A$_g$) along with the total energy, reported in Table II, are in good agreement with the experimental values.[27] The SCF-optimized molecular parameters of ground state (^{1}A$_1$) thiirane shown in Figure 4 are similar to earlier reported[28,29] optimized values and are in good agreement with the experimental values obtained by microwave

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Table III. Total and Relative Energies of C_2H_4S

		total energy (au)			rel energy, kcal mol^{-1}	
	state	SCF	CISD	CISDQ	SCF	CISDQ
thiirane (I)	$^1A_1$	−475.546 804	−475.815 697	−475.844 614	0.00	0.00
biradical (IIa)	$^3A''$	−475.498 288	−475.734 349	−475.758 020	30.44	54.34
			(−475.734 687)^a	(−475.758 477)		(54.05)
biradical (IIb)	$^3A'$	−475.495 447	−475.730 740	−475.754 273	32.23	56.69
			(−475.731 133)	(−475.754 778)		(56.37)
rotational transition state (IIIa)	$^3A'$	−475.495 632	−475.727 206	−475.749 906	32.11	59.43
rotational transition state (IIIb)	$^3A''$	−475.493 702	−475.724 920	−475.747 579	33.32	60.89
$S(^1D) + C_2H_4(^1A_g)^b$	$^1A_1$	−475.424 385	−475.659 311	−475.687 639	76.82	98.50
$S(^3P) + C_2H_4(^1A_g)^b$	$^3B_1 = {}^3A''$	−475.503 978	−475.727 291	−475.750 049	26.87	59.34^c

^{a} Values in parentheses are with the CISDQ-level optimized angle between the terminal methylene ($C_2H_6H_7$) plane and the C_1–C_2 axis (IIa 190° and IIb 185°). ^{b} At 100 Å separation between the S atom and the center of the C–C bond. ^{c} Experimental value, $\Delta E = -58.0$ kcal mol^{-1} from thermochemical data.

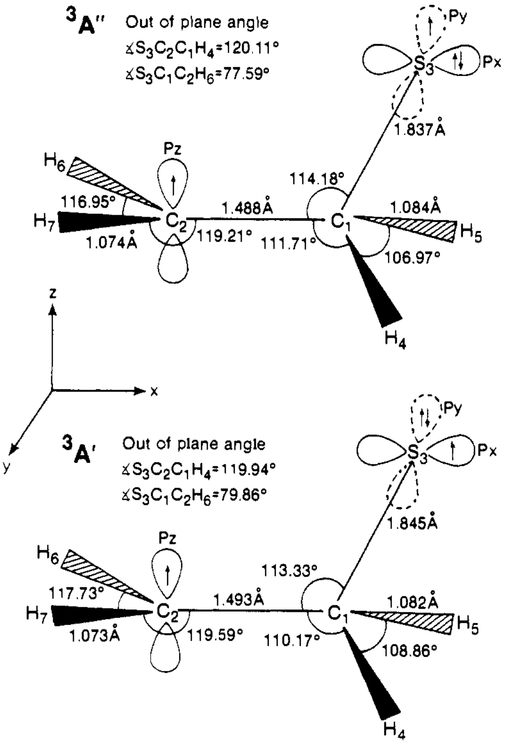

Figure 5. $^3A''$ and $^3A'$ biradical optimized geometries.

Table IV. Calculated Rotational Barrier Energies (kcal mol^{-1})

	SCF	CISDQ
$^3A''$ biradical (IIa) →	1.67	5.09
$^3A'$ rotational transitional state (IIIa)		(5.38)^a
$^3A'$ biradical (IIb) →	1.10	4.20
$^3A''$ rational transition state (IIIb)		(4.52)

^{a} Values in parentheses are with the optimized angle between the terminal methylene ($C_2H_6H_7$) plane and the C_1–C_2 axis at the CISDQ level.

spectral studies.[30,31] The calculated dipole moment of 2.34 D is similar to the value of 2.32 D calculated[28] by the 6-31G** basis set and is 27% higher than the experimental value[30] of 1.84 D. The calculated total energies at the SCF and CI levels are tabulated in Table III, from which the energy difference between the ground state thiirane ($^1A_1$) and the sum of the total energies of the $S(^3P)$ and ethylene (^1A_g) ground states, at the SCF level (26.87 kcal mol^{-1}), is much smaller than the experimental value of 58.0 kcal mol^{-1} calculated from the heats of formation. Inclusion of the CI-calculated correlation energy, however, increases the calculated energy difference to 59.34 kcal mol^{-1}, very close to the experimental value. The lowest triplet excited states of thiirane have an open-ring biradical structure with one of the C–S bonds broken. The molecular geometries of these low-lywing A″ and A′ triplet states of biradicals IIa and IIb were optimized at the RHF open-shell SCF level (Figure 5), and the total energies calculated at the SCF and CI levels with relative energies compared to ground state ($^1A_1$) thiirane are summarized in Table III. Both the C–C and C–S bond lengths in the triplet biradical structures IIa and IIb are slightly longer than those in the ground state, and both CH_2 groups are in the plane perpendicular to the CCS molecular plane. The terminal methylene $C_2H_6H_7$ is bent toward the sulfur atom. The potential energy surface, studied at the CISDQ level with fixed SCF-optimized geometry and varying only the angle between the C_1–C_2 axis and the $C_2H_6H_7$ plane, resulted in a shallow potential energy surface between 175° and 200° in both the $^3A''$ and $^3A'$ states with minima at 190° in $^3A''$ and 185° in $^3A'$. The single electron on the terminal methylene carbon in both states is in the p_z orbital (Figure 5). In the $^3A''$ state, the lone-pair electrons on the sulfur are in the p_x orbital in the molecular plane (xz) and the single electron is in the p_y orbital perpendicular to the molecular plane. The $^3A''$ is the lowest lying triplet state, closely followed by the $^3A'$ state with 2.32 kcal mol^{-1} above it. In the $^3A'$ state the lone pair electrons of sulfur are in the p_y orbital, which is perpendicular to the molecular plane (xz), and the single electron is in the p_x orbital. Previous theoretical studies with unoptimized geometries have also predicted an open-ring biradical structure for the low-lying triplet state with CCS angles of 110°,[7] 100°,[9] and, from the recent UMNDO geometry optimization by McKee,[10] 113.3°. At the SCF-level complete optimized geometry, the CCS angles for $^3A''$ and $^3A'$ are 114.18° and 113.33°, respectively. The lower lying $^3A''$ state is 54.05 kcal mol^{-1} above the ground state thiirane, and only 5.29 kcal mol^{-1} below the separated entities $S(^3P)$ and ethylene (^1A_g) at 100-Å separation at the CISDQ level. As before, the calculated relative energies at the SCF level are different and show not as good agreement with the experimental values in general as the CI level values. Consequently, from here on, only the CI values will be considered.

To calculate the rotational barrier around the C–C bond in the $^3A''$ and $^3A'$ biradicals, the terminal methylene group, $C_2H_6H_7$, was rotated 90° around the C–C bond so that the hydrogen atoms H_6 and H_7 are in the CCS plane, above and below the C–C bond. As a result of this rotation the single electron in the p_z orbital of C_2, which lies in the CCS plane in the ring-opened biradical structure, moves to the p_y orbital which is in the plane perpendicular to the molecular CCS plane. The SCF-optimized geometries of the corresponding triplet rotational transitional states IIIa and IIIb, $^3A'$ and $^3A''$ structures, are given in Figure 6. As a result of the rotation, the $^3A''$ state biradical goes through the $^3A'$ rotational transition state IIIa and $^3A'$ state biradical, through the $^3A''$ rotational transition state IIIb. The C–C bond lengths in both transition states are slightly longer than in the corresponding equilibrium states, whereas the C–S bond length is slightly smaller. The CCS angle remains practically the same

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(30) Cunningham, G. L.; Boyd, A. W.; Myers, R. J.; Gwinn, W. D.; LeVan, W. I. *J. Chem. Phys.* **1951**, *19*, 676.

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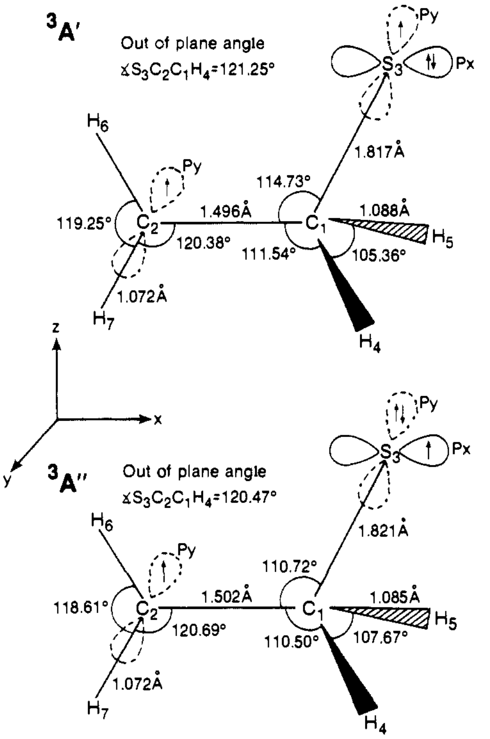

Figure 6. $^3A''$ and $^3A'$ biradical optimized geometries for the rotational transition state.

on going from the $^3A''$ biradical IIa to the rotational transition state $^3A'$ (IIIa). On the other hand the CCS angle is decreased from 113.33° in the $^3A'$ biradical (IIb) to 110.72° in the $^3A''$ rotational transition state (IIIb). The total energies of the rotational transition states IIIa and IIIb calculated at the SCF and CI level are summarized in Table III and the rotational energy barriers in Table IV. The values of the latter, calculated at the CI level, are 5.38 and 4.52 kcal mol^{-1} in the $^3A''$ and $^3A'$ states, respectively. At the SCF level the values are significantly smaller.

The potential energy surface for the addition reaction of $S(^3P)$ and $S(^1D)$ to ground-state ethylene was studied as a function of distance R between the center of the C–C bond in ethylene and the incoming sulfur atom. In this reaction path the S atom approaches in the plane perpendicular to the ethylene plane. Total energies were calculated at the CI level with the SCF-level optimized geometry. For $S(^1D)$ addition to ground-state ethylene a symmetric approach was assumed, in which the S atom approached along the C_{2v} rotational axis throughout the entire reaction path. Closed-shell $^1A_1$ state energies were calculated as a function of distance R, with all other molecular parameters optimized at the SCF level, and total energies at the CI level were calculated with this optimized geometry. From the resulting potential energy curve, plotted in Figure 7, it is seen that there is no activation energy for the reaction. Localized molecular orbital (LMO) analysis shows that at $R \geq 2.5$ Å the sulfur atom and ethylene remain as separate entities. Bond formation between both carbon and sulfur atoms takes place at shorter distances. Molecular orbital correlations in the C_{2v} symmetry for the addition of $S(^1D)$ to ground-state ethylene forming ground-state ($^1A_1$) thiirane are shown in Figure 8. From the results it is seen that the addition reaction is a symmetry-allowed, least-motion process featuring no activation energy. Leppin and Gollnick[6] and Hoffmann and co-workers[7] had also predicted similar results from simple EHMO calculations. Moreover, the present calculation of the potential energy surface at the CI level confirms the absence of any activation energy barrier for the reaction. The value for the activation energy barrier recently obtained by McKee[10] with the MNDO/HE/CI method was 10.6 kcal mol^{-1}, which decreased to 3.1 kcal mol^{-1} with use of UMNDO calculations. The experimental value that can be estimated from the reported[26] rate constant of the reaction, 4.0×10^{-10} cm^3 molecule^{-1} s^{-1}, is near zero. From the present molecular orbital studies it is concluded that the addition reaction of $S(^1D)$ atoms to ground-state ethylene (^1A_g) proceeds along a suprafacial, concerted, least-motion symmetry- and spin-allowed reaction path giving vibrationally excited ground state thiirane ($^1A_1$). The geometrical configuration of the reacting olefin is maintained during the reaction due to the concertedness of the process. All these conclusions are in agreement with earlier experimental observations on this system.[2,32]

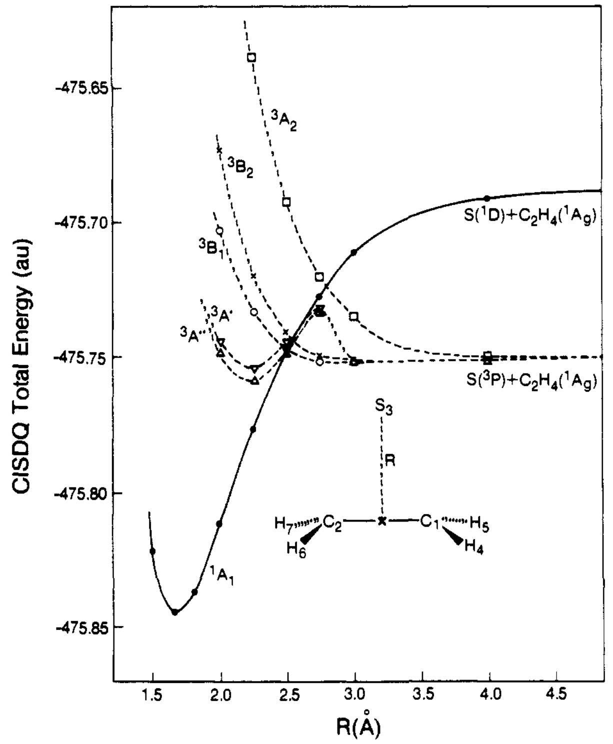

Figure 7. Reaction surface for $S(^3P)$ and $S(^1D)$ addition to $C_2H_4(^1A_g)$.

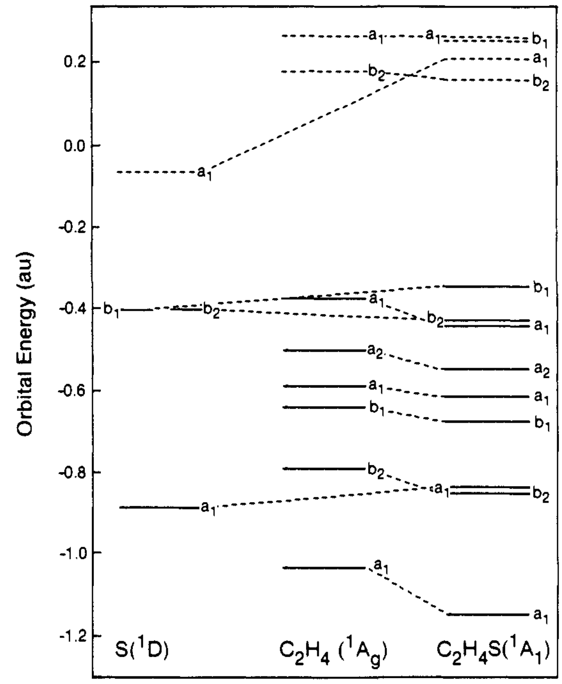

Figure 8. Orbital symmetry correlations of $S(^1D) + C_2H_g(^1Ag) \rightarrow C_2H_4S(^1A_1)$.

As noted above, the ground triplet state sulfur atom addition reaction to alkenes to yield thiirane represents the only known example of a stereospecific addition of a divalent triplet reagent. The formal reverse reaction, the low-temperature thermolysis of *cis*- and *trans*-DMT, also follows a stereospecific path.[33]

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(32) Lown, E. M.; Dedio, E. L.; Strausz, O. P.; Gunning, H. E. *J. Am. Chem. Soc.* **1967**, *89*, 1056.

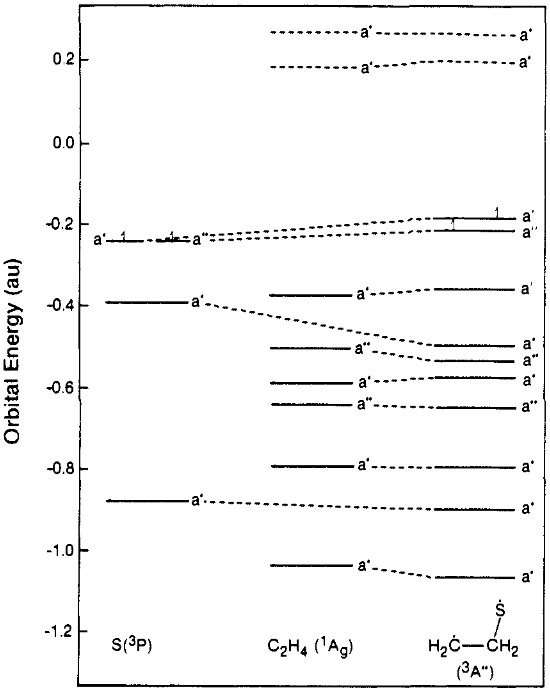

Figure 9. Orbital symmetry correlations of $S(^3P) + C_2H_4(^1A_g) \rightarrow C_2H_4S(^3A'')$.

Early EHMO studies of the model addition reaction of a ground-state S atom to ground-state ethylene forming the low-lying excited triplet thiirane as the initial product predicted a symmetry-allowed reaction with no activation energy. Our present ab initio MO calculations also predict that the ground (^3P) state S and ^1A_g state ethylene molecular orbitals correlate with the lowest $^3A''$ and $^3A'$ states of thiirane (Figure 9).

The potential energy surface for the addition of $S(^3P)$ to (^1A_g) ethylene has now been studied as a function of the distance R between the center of the C–C bond in ethylene and the incoming sulfur atom (Figure 7). Two reaction paths were explored, one along the C_{2v} rotational axis as in the case of $S(^1D)$ atoms and the other along an asymmetric path in which the C_1XS_3 angle was also allowed to vary. All points were fully optimized with respect to R at the RHF open-shell SCF level, and the total energies as a function of distance R were calculated at the CI level with the SCF-optimized geometry. The symmetric C_{2v} approach gives rise to the three fully repulsive surfaces, $^3B_1$, $^3B_2$, and $^3A_2$, of which $^3B_1$ is the lowest, followed by the $^3B_2$ and $^3A_2$ surfaces. In the asymmetric path with C_s symmetry, the C_1XS_3 angle was allowed to vary and was optimized with other molecular parameters. The asymmetric approach gives rise to the two surfaces, $^3A''$ and $^3A'$. For $R \geq 2.75$ Å, the S atom and ethylene remain as separate entities and the asymmetric potential energy curves merge with the symmetric ones at an optimized C_1XS_3 angle of 90°. Both the $^3A''$ and $^3A'$ surfaces are weakly bonding with minima corresponding to the open-ring biradical structures, as shown in Figure 5, and both feature significant intrinsic activation energies, making it unlikely that they would represent the true reaction surfaces. Of these two states, the $^3A''$ is the lowest triplet, lying 54.05 kcal mol^{-1} above the ground state and 5.29 kcal mol^{-1} below the separated reactants at the CISDQ level. The $^3B_1$ repulsive curve crosses the $^3A''$ state near $R = 2.52$ Å, 1.91 kcal mol^{-1} above the reactant state, as calculated at the CI level with respect to the separated reactants. The present calculations require the addition of $S(^3P)$ to ethylene to proceed initially on the $^3B_1$ surface with internal conversion to the $^3A''$ surface. The energy of the computed intersection of these surfaces, 1.91 kcal mol^{-1}, can then be identified with the activation energy for the reaction. This computed value compares more favorably, and is in better agreement, with the reported[34] experimental value of 1.58 kcal mol^{-1} than McKee's semiempirical values[10] of 17.6 kcal mol^{-1} (MNDO/HE/CI) and 3.9 kcal mol^{-1} (UMNDO). Similarly, the next higher symmetric $^3B_2$ curve crosses the $^3A'$ asymmetric curve near $R = 2.53$ Å at an energy of 4.42 kcal mol^{-1} relative to the separated reagents at $R = 100$ Å. This path represents another, higher energy, parallel reaction channel which would also become accessible at elevated temperatures. Thus, from the present calculations the addition of $S(^3P)$ atoms to ethylene initially follows a symmetric, least-motion path on the lowest, repulsive $^3B_1$ surface and then crosses over to the lowest attractive $^3A''$ surface with an activation energy of 1.9 kcal mol^{-1}, giving the excited thiirane (T_1) adduct as the initial product. Earlier EHMO studies[7] with unoptimized geometry have also predicted similar results. With regard to potential energy curve crossings, it should be noted that each of the four triplets discussed above crosses the ground $^1A_1$ state surface close to the point where the symmetrically coupled pairs $^3B_1$–$^3A''$ ($R = 2.52$ Å) and $^3B_2$–$^3A'$ ($R = 2.53$ Å) cross one another. These crossings may provide the path for the collisional relaxation of the excited triplet states.

The stereospecificity of the $S(^3P)$ addition reaction to alkenes was originally explained on the basis of a relatively strong binding interaction between the sulfur atom and the terminal methylene carbon.[33] EHMO calculations by Hoffmann et al.[7] with unoptimized geometry predicted a rotational barrier energy of 5 kcal mol^{-1} for the excited triplet thiirane intermediate. Our earlier ab initio molecular orbital calculations with unoptimized geometry, using the crude virtual orbital technique[9] to calculate the excited state energies, predicted a large rotational barrier, 23 kcal mol^{-1}, in the lowest triplet state. Recent MNDO calculations with geometry optimization by McKee[10] yielded a rotational energy barrier of only 0.3 kcal mol^{-1}. He also calculated the rotational barrier with geometry optimization by ab initio MO methods using the 6-31G* basis set and reported 2.7 kcal mol^{-1} at the SCF level and 3.3 kcal mol^{-1} at the MP2/6-31G* level. The configuration chosen in these calculations was the higher lying $^3A'$ state of the biradical structure rather than the lowest $^3A''$ state. The present calculations, including correlation energy at the SCF-optimized geometry, predict 5.4 kcal mol^{-1} for the rotational barrier in the $^3A''$ state and 4.5 kcal mol^{-1} in the next highest $^3A'$ state. These rotational barriers may increase with the substituents. McKee explains the stereospecificity of this reaction on the basis that intersystem crossing of a triplet biradical to the singlet state is much faster than methylene rotation when a heavy nucleus is present. Our calculations show very shallow potential energy surfaces for the $^3A''$ and $^3A'$ states of the C_2H_4S biradical, lying only 5.29 and 2.97 kcal mol^{-1}, respectively, lower in energy than the separated ethylene and $S(^3P)$ atom, maintaining the ethylene configuration. These energies are lower than the rotational barriers of 5.4 and 4.5 kcal mol^{-1}, respectively, in the $^3A''$ and $^3A'$ state biradical intermediates. The sterospecific nature of the $S(^3P)$ addition to alkenes can then be accounted for in terms of the insufficient energy (58.0 kcal mol^{-1}) provided by the change in internal energy of the reaction to drive the system over the rotational energy barrier in the lowest triplet state thiiranes (54.05 + 5.38 = 59.43 kcal mol^{-1}) produced in the reaction. Hence, geometrical isomerization will be slow and collisional removal of the excess vibrational energy will effectively compete, resulting in the retention of the original geometry of the reacting alkene in the thiirane end product.

Reactivity of DMT(T_1). The chemical properties of triplet state thiiranes deserve some comments. As was discussed above, both thiirane(T_1) and DMT(T_1) are capable of undergoing reversible addition to olefins many times before being deactivated, causing geometrical isomerization (in *cis*- and *trans*-butenes). Atomic spin density calculations (Table V) show that the spins are localized on the terminal carbon and the sulfur atom with near

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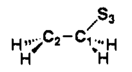
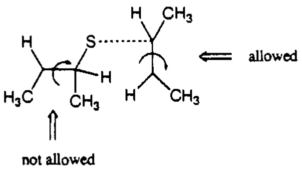
Table V. Net Atomic Charges and Spin Densities of $^3A''$ and $^3A'$ Thiirane



	net atomic charge			atomic spin density		
	C_1	C_2	S_3	C_1	C_2	S_3
$^3A''$ (IIa)	−0.482	−0.318	0.006	0.006	0.950	1.022
$^3A'$ (IIb)	−0.467	−0.336	0.006	0.003	0.964	1.019
rotated						
$^3A'$ (IIIa)	−0.474	−0.352	0.013	0.004	0.974	0.978
$^3A''$ (IIIb)	−0.451	−0.363	0.009	0.003	0.986	0.979

unit values on each. Thus, addition can take place on either the carbon or the sulfur end of the molecule. The addition of thiyl radicals to simple olefins, however, is more facile than the addition of alkyl radicals, and addition from the sulfur end, therefore, would be kinetically favored. It has been known for some time that the addition of thiyl radicals to olefins can be reversible, resulting in the geometrical isomerization of the olefin.[35] Thus, triplet thiirane behaves like a thiyl radical. What makes the thiirane (T_1) case so unique is that, while in the complex, the stereochemical information content of the olefin is lost whereas that of the thiirane is maintained:



This would seem to suggest that the two carbon–sulfur bonds in the complex are not equivalent, i.e. the S–C (olefin) bond is not a full covalent bond, which in turn would explain the apparent inefficiency of the collisional deactivation of the complex to give thiolane.

The results obtained clearly indicate that the rate of the unimolecular geometrical isomerization of DMT(T_1) is slow compared to the addition–decomposition sequence

$$\mathrm{DMT(T_1) + butene \xrightarrow{k\ addition} [DMT\cdots C_4H_8](T_1) \xrightarrow{k\ decomp} DMT(T_1) + butene}$$

A rough estimate of the rate of rotation of the terminal methyl methylene can be made by using the Rice–Rampsberger–Kassel relation $k_r = A[(E - E_a)/E]^{s-1}$ with the following values for the input parameters: $A = 10^{11}\ s^{-1}$; s is the number of active vibrational modes $\sim n/2 \sim 17$ where $n = 3N - 6 = 33$, $E = sRT = 10.1$ kcal/mol, and E_a, the rotational barrier about 3 kcal/mol higher than the computed value of 5.4 kcal/mol for thiirane, is 8.4 kcal/mol. These give $k_r = 10^{11}[(10.1 - 8.4)/10.1]^{16} \sim 4 \times 10^{-2}\ s^{-1}$. The rate of decomposition of the complex can be estimated in a similar manner. Thus, taking the following values for the input parameters, $A = 10^{13}\ s^{-1}$, $N = 25$, $n = 69$, $s = 35$, $E = sRT = 21$ kcal/mol, and $\Delta E_{addition} \approx -10$ kcal/mol, we obtain $k_{decomp} \sim 10^{13}[((21 + 10) - 10)/31]^{34} \sim 1.8 \times 10^7\ s^{-1}$.

For the rate constant of the addition step we can assume the same value as was reported[35] for the addition of the methylthiyl radical to *cis*-butene, 2×10^7 L mol^{-1} s^{-1}. The rate at 38.5 Torr of butene then becomes $2 \times 10^7 \times 38.5/(22.4 \times 760) = 4.5 \times 10^4\ s^{-1}$, which is about 400 times slower than the rate of decomposition of the complex. Since on the average about four butene molecules are isomerized by the triplet DMT before it suffers deactivation, the rate of deactivation can be estimated as being about $1 \times 10^4\ s^{-1}$. Thus, the rate of deactivation of DMT(T_1) is $1 \times 10^4/(4 \times 10^{-2}) = 2.5 \times 10^5$ times faster than its rate of geometrical isomerization, and consequently isomerization cannot occur.

Table VI. Total and Relative Energies of C_2H_4O

		total energy, au		rel energy, kcal mol^{-1}	
	state	SCF	CISDQ	SCF	CISDQ
oxirane	$^1A_1$	−152.867 354	−152.933 740	0	0
biradical A[a]	$^3A''$	−152.818 985	−152.872 318	30.35	38.54
	$^3A'$	−152.815 557	−152.868 692	32.50	40.82
biradical B[b]	$^3A'$	−152.818 547	−152.871 536	30.63	39.03
	$^3A''$	−152.816 541	−152.868 895	31.89	40.69

[a] Terminal CH_2 is perpendicular to the CCO plane. [b] Terminal CH_2 is in the same plane as CCO.

Table VII. ^1H Chemical Shifts (±0.01 ppm, Relative to Internal TMS) and Coupling Constants (±0.02 Hz) of DMT in $CDCl_3$ at 294 °C

	trans isomer	cis isomer
δ_H	2.65	3.04
δ_{CH_3}	1.50	1.49
$^3J_{H\text{-}H'}$	+5.32	+7.04
$^3J_{H\text{-}CH_3}$	+5.80	+6.07
$^4J_{H\text{-}CH_3'}$	−0.36	−0.26
$J_{CH_3\text{-}CH_3'}$	0	+0.05

In contrast to S(^{3}P), the addition reaction of O(^{3}P) atoms to butene-2 is known to be nonstereospecific.[36] In order to see whether a calculation similar to the one described above for sulfur would correctly predict this feature of the oxygen addition reaction, an RHF SCF-MO CI calculation was carried out with use of the 6-31G* basis set. The CI calculation was done at the SCF-optimized geometry with three core orbitals frozen and only the lowest 20 orbitals used. From the results, summarized in Table VI, it is seen that the same type of biradical species may form as with S(^{3}P) atoms and that indeed the rotational energy barriers in the triplet states are low, less than 0.5 kcal mol^{-1}, and the energy of the lowest triplet (38.54 kcal mol^{-1}) lies considerably below the experimental change in internal energy of the reaction (−84.02 kcal mol^{-1}). An earlier calculation by the spin projection APUMP2 method[37] yielded an excitation energy for the triplet $\sigma\pi$ biradical of 66.4 kcal/mol, but the rotational energy barrier in the triplet state was not calculated. Even with this higher triplet energy, rotation of the terminal methylene would be quite facile, and thus all available calculations predict the formation of highly vibrationally excited triplet C_2H_4O biradicals which should be capable of isomerization, in agreement with experimental observations.

NMR Studies. In order to assign the geometries of the DMT products on an absolute basis, detailed NMR studies were undertaken. The experimental spectra of both isomers of DMT are shown in Figure 10. The complexity of the spectra clearly demonstrates the anticipated higher order effects due to the magnetic nonequivalence of the single protons as well as the methyl groups. C_2 symmetry for the trans isomer and C_s symmetry for the cis isomer lead to the $AA'X_3X_3'$ eight-spin systems in both cases.[38] Due to the fast rotation of the methyl groups on the NMR time scale, they can be simulated as two groups of three equivalent $^1/_2$-spin nuclei each. On the basis of previous experience with spin simulation,[39,40] the starting values for the coupling constants were estimated taking into account literature data[38] for the cis and trans $^3J_{H\text{-}H'}$ of unsubstituted thiirane. In general, individual coupling constants (or pairs of coupling constants, because of the symmetry relationship) were altered until a good fit was found. Only then was an iteration routine applied in order

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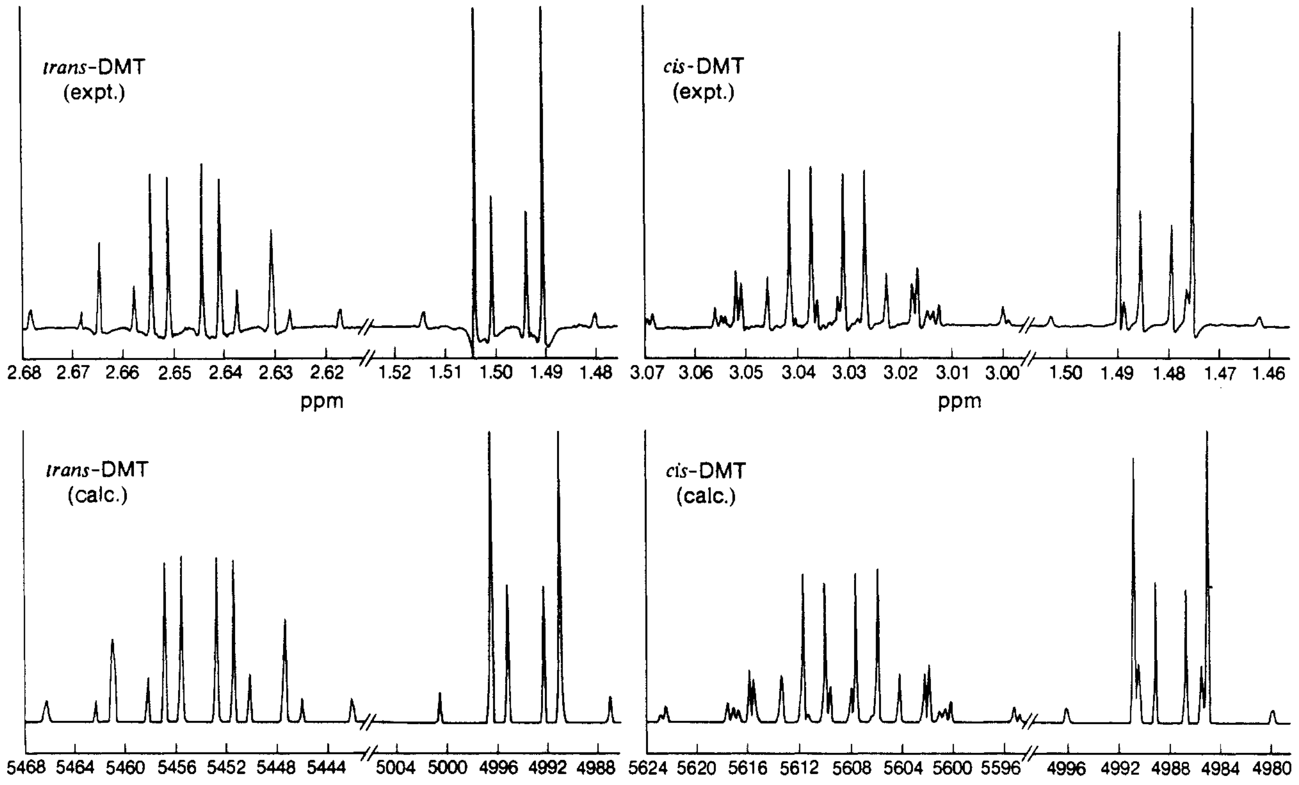

Figure 10. Low-field part of the 400-MHz proton NMR spectra of *cis*- and *trans*-DMT in $CDCl_3$ (upper traces). The spectra simulated with use of the parameters listed in Table VII and a Gaussian line shape (line width 0.15 Hz) are shown in the lower traces.

to further optimize the parameters. With more than 95% of the theoretical transitions assigned, the RMS value reduced very sharply to a final value of <0.05. The spectra plotted with the refined parameter sets as a line width of 0.15 Hz (Gaussian line shape) are shown in Figure 10, and the parameters are summarized in Table VII. A comparison between the experimental and calculated traces demonstrates a very good fit, and the values obtained for ${}^3J^{trans}_{H-H'}$ and ${}^3J^{cis}_{H-H'}$ are similar to literature data for the unsubstituted three-membered ring.[38] In particular, the trans coupling is considerably smaller than the cis counterpart. The ${}^4J$ coupling constants are of negative sign. The overall appearance of the calculated spectrum is very sensitive to the sign of ${}^4J_{H-CH_3'}$ in both isomers, and therefore the decision whether ${}^4J > 0$ or ${}^4J < 0$ can be made easily. Such considerations are unnecessary for ${}^3J$ coupling constants since they are positive in general. A special remark concerning the coupling constant between the two methyl groups should be made. For the trans isomer the simulation/iteration shows clearly that it is zero, as expected for a completely saturated system. The cis isomer, however, can only be simulated correctly with $J_{CH_3-CH_3'} > 0$. Although the value of this coupling constant cannot be measured in the spectrum in terms of distances between individual lines, the relative intensities of the lines of the methyl resonance are clearly inadequate if the interaction is set to zero. On the other hand, a value of 0.10 Hz increases the number of observed lines and should thus be considered too large. By simulating the spectrum with a few different values between 0.01 and 0.10 Hz, we estimate 0.05 Hz as the best value, subsequently resulting in a good fit. This result is at first somewhat surprising, but it is well-known[41] that couplings can be observed between nuclei that are many bonds apart but physically very close in space. This effect, often referred to as "through-space" coupling, is especially distinct for fluorine nuclei, but it has also been noticeable for ${}^1H-{}^1H$ interactions. The fact that in the trans isomer, where the two methyl groups are much further apart than in the cis isomer, no such effect is found clearly corroborates the assumption of a "through-space" coupling interaction.

Thus, it has been established that as expected the DMT from the *cis*-butene reaction had the cis geometry and that from the *trans*-butene reaction the trans geometry.

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(41) Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; Pitman: London, U.K., 1983; p 226.