The Reactions of Sulfur Atoms. XI. The Intermediacy of a Hybrid π-Thiacyclopropane in the Addition Reactions to Olefins and in the Thermal Decomposition of Episulfides

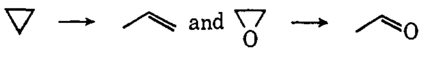
Sir:

The stereochemical aspect of the addition reactions of excited-, ^1D, and ground-state, ^3P, sulfur atoms has been explored. With three isomeric pairs of olefins, *cis*- and *trans*-but-2-enes, *cis*- and *trans*-1,2-difluoroethylenes, and *cis*- and *trans*-1,2-dichloroethylenes, both species have been found to add in an equally highly stereospecific manner.[1] To our knowledge this reaction provided the only known example for a stereospecific triplet addition, and there appeared to be no plausible explanation at hand to rationalize this behavior. The role of spin multiplicity in the addition reactions of polyvalent radicals has experimentally been derived largely from carbene chemistry. The majority of singlet carbene additions are stereospecific (to various degrees), while triplets add nonspecifically. There have been two theories advanced which for methylene itself correctly predict the experimental result, but for entirely different reasons. According to Skell,[2] stereochemistry is governed by the spin-conservation principle and thus the spin state of the reagents, while Hoffmann's[3] recent extended Hückel MO calculation attributes stereochemical differences not to differences in spin but to the spatial part of the wave function.

In order to shed light on the details of the reaction path and to elucidate the nature of the possible intermediates involved in sulfur atom addition reactions, we have investigated the reverse reaction, the thermal decomposition of ethylene episulfide.

Below 250° the gas-phase thermolysis gives rise to ethylene and sulfur. The amount of ethylene is equal to the amount of episulfide consumed. Above 250° isomerization to vinyl mercaptan and another mode of decomposition, probably a molecular split into acetylene and hydrogen sulfide, become operative, which, however, in the present context have no relevance.

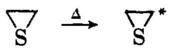
This behavior represents a significant departure from that of the analogous ring structures, cyclopropane or ethylene oxide, which upon low-temperature thermolysis undergo isomerization to the acyclic structures, by a 1,2 hydrogen shift. The reluctance of episulfides

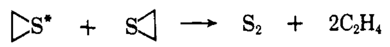


to undergo this type of transformation was also noted in the addition reactions of sulfur atoms to olefins[1] and acetylenes[4] and has been explained by the relatively small difference in bond energy between the C–S single and double bonds.

The main kinetic features of the decomposition may be summarized as follows. (a) It is a homogeneous first-order reaction (above 150 torr). (b) E_a (high pressure) = 40.2 kcal, whereas from thermochemical data $\Delta H(\text{episulfide} \rightarrow C_2H_4 + S(^3P)) = 58$ kcal and we estimate $D(\text{episulfide} \rightarrow \cdot C\text{–}C\text{–}S\cdot) = 52$ kcal. Consequently neither of these reactions can occur in the primary step. (c) $\Delta S^{\neq} = -2.5$ eu, indicating that the cyclic structure is preserved in the activated complex. (d) Scavenging experiments with pent-1-ene indicate that atomic sulfur is not implicated in the reaction. The only effect of pent-1-ene is a suppression of the rate of ethylene formation (approximately equal to that of CO_2) without the appearance of additional products. (f) The low-temperature thermolysis of *cis*- and *trans*-but-2-ene episulfides is stereospecific; the *cis* isomer affords >90% *cis*- and <10% *trans*-but-2-enes, and the *trans* ~99% *trans*-but-2-ene as products.

This information forces us to conclude that the reaction is pseudounimolecular (eq 1 and 2, where the rate-determining step (above 150 torr) is (*1*).


(1)


(2)

We have also investigated the fall-off region of the unimolecular rate constant (below 150 torr), where the reaction becomes higher order. Numerical evaluation of the Kassel integral permitted to make comparison with the experimental fall-off curve. Using the limiting high-pressure rate constant value of 3.70×10^{-5} sec^{-1} at 225°, best agreement was obtained for a reactant diameter of 5.0×10^{-8} cm and an effective number of oscillators of 5 (out of a total of 15). These results are close to those expected for a truly unimolecular reaction, and therefore it appears that step II is not the rate-controlling factor of the reaction even at pressure considerably lower than 150 torr (though it may partly be responsible for the negative value of $\Delta S^{\neq}$).

Our main concern now is the nature of the excited molecule. The observation that the reaction is first order and has an activation energy lower than the endothermicity required for split-off of the sulfur atom implicates an electronically excited species. This conclusion is further substantiated by the effect of inert gas: were the reaction an adiabatic process, inert gases could enhance the rate or not affect it, but could not suppress it. There are two distinctly different types of electronic excitation possible:[5] promotion of one of the nonbonding p electrons of sulfur to one of the low-lying d orbitals, or promotion of one of the C–S bonding electrons into an antibonding orbital. From the fact that neither in the photochemical nor in the thermal decompositions of acyclic monosulfides has any evidence been found for the intervention of a deactivable intermediate, but on the other hand in both photochemical[6] and thermal decompositions of episulfides there have been such intermediates found, we conclude that the former type of transition has no significant role in these reactions. The latter alternative in the present instance would be equivalent to a π-thiacyclopropane structure, analogous to the one postulated for the lowest excited singlet state of cyclopropane and invoked as an intermediate in the thermolysis of cyclopropane, the addition of methylene to ethylene, and the thermolysis of pyrazolines.[3,7] This

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[1] K. S. Sidhu, E. M. Lown, P. O. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **88**, 254 (1966); E. M. Lown, E. L. Dedio, O. P. Strausz, and H. E. Gunning, *ibid.*, **89**, 1056 (1967); H. A. Wiebe, H. E. Gunning, and O. P. Strausz, to be published.

[2] P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956).

[3] R. Hoffmann, *ibid.*, **90**, 1475 (1968).

[4] O. P. Strausz, J. Font, E. L. Dedio, P. Kebarle, and H. E. Gunning, *ibid.*, **89**, 4805 (1967).

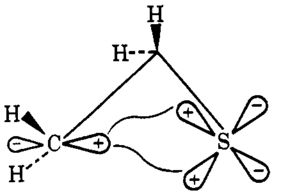
[5] R. E. Davis, *J. Org. Chem.*, **23**, 216 (1958).

[6] O. P. Strausz, K. S. Sidhu, and H. E. Gunning, to be published.

[7] R. J. Crawford, R. J. Dummel, and A. Mishra, *J. Am. Chem.*

trimethylene species has a planar structure and lies ~64 kcal above the ground state.[3,7] The energy barrier for rotation of the terminal methylenes has been estimated as ~12 kcal.

Our extensive kinetic data on both the addition reactions of sulfur atoms to olefins and the thermolysis of episulfides suggest a similar excited π-thiacyclopropane structure intermediate. This state should then lie not more than 40.2 kcal above the ground state and, in order to maintain the geometrical configuration of the starting material in the product, the terminal methylene should be nonplanar, distorted out of the plane of the two carbon and sulfur atoms, one hydrogen being above and the other below the plane. This is not an unreasonable conformation for this species. In the episulfide molecule the presence of the nonbonding 3p orbital (and the possible participation of d orbitals) may be expected to alter the bonding situation considerably. (π-Cyclopropane belongs to the C_{2v} symmetry while π-thiacyclopropane to the C_s symmetry group.) If the two nonbonding p orbitals of the sulfur become degenerate one may envisage a σ–π hybrid bond between the terminal methylene carbon and the sulfur which would be fully capable of accounting for all of our kinetic and stereochemical observations. We also believe that in the addition of S(^{3}P) atoms to olefins the π-thiacyclopropane is in a triplet state which, in contrast to trimethylene, still possesses a relatively high energy barrier to rotation of the terminal methylene.



Finally a brief comment on the apparent long lifetime of the π-thiacyclopropane intermediate would be appropriate. Benson[8] estimated the activation energy of the ring-closure reaction of the trimethylene intermediate in the thermolysis of cyclopropane as 8.2 kcal. This value is now meaningless since it is based on a double doublet trimethylene, while the actual intermediate is more likely a singlet excited trimethylene.[3,7] The only estimate of E_a (ring closure) presently available is that of Hoffmann's computed value[3] of 1 kcal. In the excited thiacyclopropane the σ–π hybrid bond may be considerably stronger than the π bond in trimethylene, and consequently E_a (ring closure) could be higher as well. It should also be noted that the temperature of the thiacyclopropane reaction was about 200° lower than that of the cyclopropane thermolysis studies.

Acknowledgments. We thank the National Research Council of Canada and Imperial Oil Enterprises Ltd. for financial support and Mr. A. Jodhan for helpful experimental assistance.

Soc., **87**, 3023 (1965); R. J. Crawford and A. Mishra, *ibid.*, **87**, 3768 (1965); **88**, 3963 (1966).

[8] S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961).

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Received July 16, 1968

Electron Spin Resonance Evidence for Bromide Ion Exchange with the Tetrabromomanganese(II) Complex in Acetonitrile

Sir:

Recently, the electron paramagnetic resonance spectrum of the tetrahedral $[MnBr_4]^{2-}$ complex in acetonitrile was reported.[1] The widths of the ^{55}Mn nuclear hyperfine components were found to be unusually broad, and it was noted that the line broadening became more pronounced with increasing bromide concentration. It was suggested that the bromide-dependent line broadening might be due to ligand exchange. In this communication, we set forth evidence to confirm this interpretation.

The resonance widths of the esr spectrum of the $[MnBr_4]^{2-}$ complex were studied as a function of both temperature and excess bromide concentration. All solutions were prepared by dissolving tetra-*n*-butylammonium bromide and $MnBr_2$ in acetonitrile. Bromide concentrations in excess of the stoichiometric 4:1 ratio were taken to be the excess concentration. Intensity measurements indicated that in solutions containing the stoichiometric concentration of bromide, the Mn(II) had been converted almost completely to the complex.[1] Resonance widths were extracted by comparing experimental and computer-synthesized spectra.

The possibility of resonance broadening due to superexchange *via* the diamagnetic solvent molecules and halide ions was eliminated by studying the resonance widths as a function of Mn(II) concentration. The resonance widths were found to change insignificantly over the Mn(II) concentration range of 0.005–0.05 *m*, provided the excess bromide concentration was constant. The effect of the tetraalkylammonium counterion was also considered, and, although it influences the over-all resonance width, it does not contribute to the observed bromide-dependent width. Details of the counterion effect will be treated in a subsequent paper.

Garrett and Morgan[2] have established that electron spin relaxation of the unpaired electrons in solvated Mn(II) complexes arises principally from modulation of the dynamical axial zero-field splitting resulting from transient distortions of the complex by solvent fluctuations in the immediate surroundings of the paramagnetic ion. If this mechanism were the only one operative here, the resonance widths would vary linearly with the correlation time characteristic of the solvent fluctuations and would not be strongly dependent upon the bromide concentration. It has been suggested[2,3] that this correlation time is proportional to $\eta M/\rho T$, where η is the viscosity of the solution, M is the molecular weight of the solvent, and ρ is the density of the solvent at temperature T. In Figure 1, we have plotted the variation of the esr resonance widths *vs.* $\eta M/\rho T$ for three solutions, each containing a different excess bromide concentration (0, 0.084, 0.304 *m*). It is interesting that, whereas the resonance widths for each of these solutions do vary linearly with $\eta M/\rho T$ as the solvent structural correlation

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[1] S. I. Chan, B. M. Fung, and H. Lütje, *J. Chem. Phys.*, **47**, 2121 (1967).

[2] B. B. Garrett and L. O. Morgan, *ibid.*, **44**, 890 (1966).

[3] J. Frenkel, "Kinetic Theory of Liquids," Oxford University Press, London, 1946, pp 188–208.