Tetrahedron. Vol 32, pp. 1705 to 1711 Pergamon Press 1976. Printed in Great Britain

MO-THEORETICAL CHARACTERIZATION OF ORGANIC REACTION MECHANISMS—VI[1]

OUTER 3d ORBITAL PARTICIPATION IN THE REACTIONS OF SULFUR-CONTAINING COMPOUNDS

K. TATSUMI, Y. YOSHIOKA, K. YAMAGUCHI and T. FUENO*
Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan

(*Received in Japan 4 December 1975; Received in the UK for publication 19 February 1976*)

Abstract—Participations of 3d orbitals in reactions of sulfur-containing compounds are studied in terms of the triplet stability-instability criterion for the restricted Hartree-Fock molecular orbitals. The criterion seems to permit infallible judgment as to whether or not the introduction of d orbitals would really possess any chemical significance for the reacting systems. It is shown that sulfur d orbitals should play an important role in the Hofmann elimination of sulfonium salts as well as the thermal decomposition of thiirane 1,1-dioxide. In the addition of sulfenyl cations to olefin and the thermal allylic rearrangement of allyl sulfides, however, the d orbital participation is found to be of little significance. The conclusions find support in the results of analytic studies of the sulfur bondings involved.

INTRODUCTION

Participation of outer 3d orbitals in chemical bonding and reaction seems to constitute one of the central problems in the chemistry of second row atoms. Thus, for the compounds containing an S atom, d orbitals have often been utilized[2-8] to account for unusual facts apparently otherwise inexplicable. It is feared, however, that these successes may lead one to invoke d orbitals merely as a sort of conceptional savior even when the d orbital populations calculated theoretically[8-10] are not sufficiently large to justify chemical intuitions. Coulson[11] has aptly stated that the inclusion of outer d orbitals in the basis set will of course variationally improve wave functions but that no sound chemical conclusions can properly be drawn from small d orbital populations.

Recently, a symmetry consideration of the problem has been given by Ratner and Sabin.[12] According to the orbital symmetry criterion, it is generally advisable to include d-type functions when there are occupied molecular orbitals of such symmetries that the irreducible representations of the point group of the nuclear configuration match with those of the d orbitals but do not have a basis in the s- and p-type functions. The symmetry criterion is really clear-cut and fundamental, but in the case of molecules which do not have a high degree of symmetry the effectiveness of the criterion is deprived.

In previous papers,[13] we proposed a theoretical method of characterizing the reaction mechanisms of molecular systems with respect to the spin and space symmetry conservations. The former criterion is reflected in a triplet stability index λ_0. That is to say, the restricted Hartree-Fock (RHF) singlet ground state of a certain reacting system is triplet-unstable whenever its λ_0 takes on a negative value, and the occurrence of such an instability can be taken as an indication of the singlet biradical character of the system.[14] Chemical characteristics of given molecular systems can thus be inferred from the values of λ_0.

In the present work, we have examined the d orbital participation for some compounds and reacting systems which involve an S atom. When a system whose RHF ground configuration is triplet-unstable in the usual s and p orbital basis set is rendered triplet-stable by including d orbitals, there will be a really significant chemical meaning in talking about the role of d orbitals. On the contrary, when no triplet unstable-stable conversion is brought about by the inclusion of d orbitals, such orbitals will be of no fundamental importance to the system. The molecular systems and reactions with which we will be concerned here include sulfur ylides, the Hofmann elimination of sulfonium salts, addition of sulfenyl cation to olefin, thioallylic rearrangement and the thermal decomposition of thiirane 1,1-dioxide. Our instability criterion seems to permit infallible judgment on the role of d orbitals in these reactions.

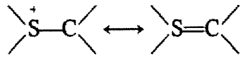
METHOD

By the triplet stability index λ_0 we specifically mean the lowest eigenvalue of the instability matrix.[14,15] The explicit expression for the matrix has been given elsewhere,[1,13,16] together with its applications to chemical processes.

The molecular orbital energies and wave functions of the entire systems were obtained by the original CNDO/2 method without modification. The triplet instability matrix elements were calculated using the wave functions, and the lowest eigenvalues obtained by diagonalizing the matrix. All computations were programmed in FORTRAN and performed on a FACOM 230-75 at the Kyoto University Computation Center.

RESULTS AND DISCUSSION

(A) *Structure of sulfur ylides.* Sulfur ylides are generally expressed as the following resonance hybrid:[17]


(1)

The hybrid structure implies that the stabilization of an ylide is due partly to resonance interaction and also partly to electrostatic interaction between the charged centers.

We deal with the simplest and idealized sulfur ylide SH_2CH_2 as a model for existing ylides. Since our primary interest is in the bonding between the S and C atoms, geometries of the SH_2 and CH_2 terminuses have been fixed simply as follows: the S–H and C–H bond distances are 1.33 and 1.08 Å, respectively, and both the H–S–H and H–C–H angles are 120°. Since the S–C bond has a partial double bond character, we have adopted an S–C distance of 1.65 Å, intermediate between the single (1.77–1.84 Å) and double (1.53–1.59 Å) bond lengths.[18] Calculations were carried out by varying the dihedral angle θ between the CH_2 and SH_2 planes as well as the bending angles α and β of the terminuses as shown in Fig. 1.

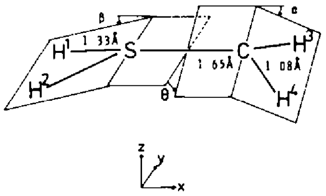


Fig. 1. Geometry and coordinate system assumed for the sulfur ylide.

Table 1. λ_0-values for a sulfur ylide (H_2S^+-CH_2^-) with and without sulfur d orbitals

Angles (degree)			λ_0(eV)	
θ	α	β	sp	spd
0	0	0	−0.628	−0.109
	30	0	−2.074	−0.282
	0	30	−2.054	1.176
	30	30	−1.195	1.496
90	0	0	−0.856	1.355
	30	0	−0.501	1.401
	0	30	−0.395	2.312
	30	30	−0.191	2.288

Calculated λ_0-values are listed in Table 1 for both the cases with and without sulfur 3d orbitals. Without the d orbitals in the basis set, the λ_0-values are negative for all the conformations under consideration. When the orbitals are included, the λ_0 increases considerably and attains a value positive in sign except for the case in which $\theta = \beta = 0°$. Particularly interesting here is that the planar conformation still has a slight singlet biradical character. Because the equilibrium conformation of sulfur ylides has not yet been established, we cannot assess this indication in any decisive term. However, aside from the case $\theta = \beta = 0°$, our criterion can attach a chemical significance to the inclusion of d orbitals. Even for the case $\theta = \beta = 0°$, the d orbital participation seems to be important; the λ_0 values have noticeably increased by the inclusion of d orbitals.

The role of the d orbitals is clearly manifested in the properties of the highest occupied molecular orbital (HOMO) of the ylide. In an attempt to examine the nature of the S–C bondings in detail, we have taken up two extreme geometries with $\theta = 0$ and 90° for both of which the bending angles α and β have been fixed at 0 and 30°, respectively. For the sake of convenience, the former geometry will be expressed by a symbol (‖) while the latter, by (⊥). In the absence of 3d orbitals, the HOMO for each geometry is mainly the lone-pair orbital p_z of carbon:

$$\begin{aligned}\psi^{HO}(\|) = {} & 0.320(Ss) + 0.165(Sp_z) - 0.136(Cs) + 0.189(Cp_x) \\ & - 0.726(Cp_z) - 0.379(H^1 + H^2) + 0.036(H^3 + H^4)\end{aligned}$$

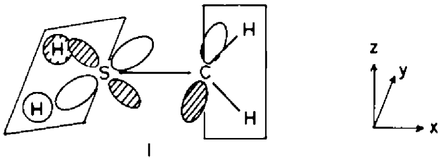
$$\psi^{HO}(\perp) = 0.006(Sp_y) - 0.918(Cp_y) + 0.280(H^1 - H^2).$$

The orbital energies are −9.03 and −9.28 eV, respectively, and both orbitals have a node between sulfur and carbon. Upon inclusion of 3d orbitals in the basis set, their compositions change to

$$\begin{aligned}\psi^{HO}(\|) = {} & 0.303(Ss) + 0.287(Sp_z) + 0.241(Sd_{z^2}) \\ & - 0.432(Sd_{xz}) - 0.565(Cp_z) - 0.321(H^1 + H^2)\end{aligned}$$

$$\begin{aligned}\psi^{HO}(\perp) = {} & 0.116(Sp_y) + 0.520(Sd_{xy}) + 0.783(Cp_y) \\ & - 0.221(H^1 - H^2).\end{aligned}$$

The former HOMO is stabilized as a result of the π bonding between the sulfur $3d_{xz}$ and the carbon $2p_z$ orbitals, the orbital level being at −11.20 eV. A similar stabilization of the latter HOMO is effected by the π overlapping between the sulfur $3d_{xy}$ and the carbon $2p_y$ orbitals; the orbital energy being −12.55 eV. This is due to a hyperconjugative interaction in the xy plane between the carbon $2p_y$ orbital and the SH_2 bonding orbital of the same symmetry (1).

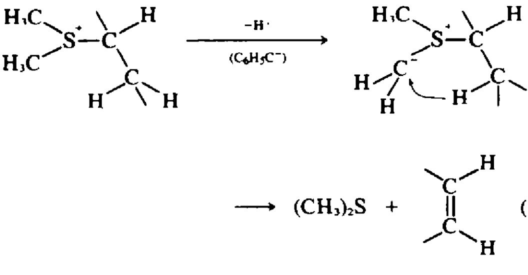


I

Although the HOMO is not the only orbital that is responsible for the triplet stability of the system, the above-mentioned variation in the HOMO level height is in accord with that in the value of λ_0; the more stable the HOMO, the greater is the λ_0-value.

The charge distributions in the compound also reflect the effect of d orbital participation. Figure 2 shows the net atomic charges (signed numbers) for the two extreme geometries with and without d orbitals. When the d orbitals are included, the charge separation is greatly reduced for both geometries, while the ylide C atom remains to be highly negative in net charge. A similar charge leveling was noted for a phosphonium ylide by Hoffmann.[19] The extent of the charge reduction through the Sd_π–Cp_π interaction is greater at $\theta = 90°$ than at $\theta = 0°$, and the Sd_π–Cp_π bond order (unsigned numbers) for the former conformation is greater than that for the latter.

(B) *Hofmann elimination of sulfonium salt.* Franzen and Mertz have provided concrete evidence for the intermediacy of an ylide in the Hofmann elimination reactions of sulfonium salts effected by the presence of triphenylmethide anion.[20] The ylide produces an olefin stereospecifically via a cyclic intermediate which is to be collapsed by the subsequent α',β-elimination.



(2)

We will here examine only the latter part of reaction (2), i.e. the α',β-elimination of a ylide. To economize on computation time we have replaced the intact Me group

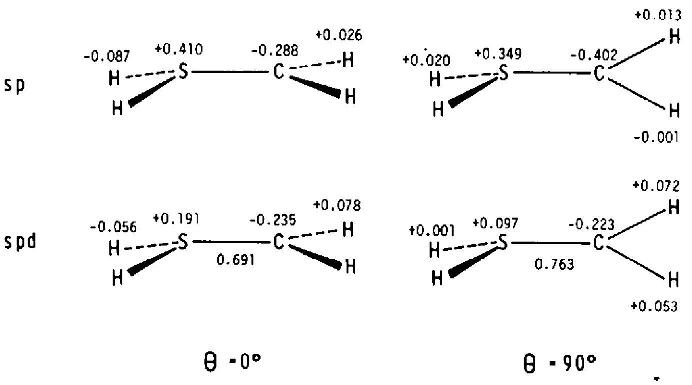


Fig. 2. The net atomic charges (signed numbers) and the Sd_π–Cp_π bond orders (unsigned numbers) for $H_2S{=}CH_2$. Angles α and β are fixed at 0° and 30°, respectively.

by an H atom, thus assuming $CH_2\ SH^+C_2H_5$ as a model species. Figure 3 shows geometry of the reacting system assumed for calculation where the S atom and the three C atoms are all placed on the xy plane. Description of the progress of reaction would necessitate simultaneous variations of three parameters, i.e. the S–C^2 distance R_1, the C^1–C^3 distance R_2, and the position R_3 of the migrating hydrogen. To avoid complication, we have first chosen only the former two distances, R_1 and R_2, as parameters, maintaining the bridging hydrogen at the middle point of the line connecting two points A and B (Model I).

Figure 4 illustrates how the lowest eigenvalue λ_0 for Model I varies with the changes in R_1 and R_2 when we include sulfur 3d orbitals in the basis set. The λ_0-value is positive in sign over a wide range; the reacting system should have no biradical character at intermediary stage of the reaction.

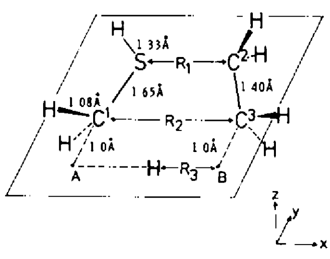


Fig. 3. Geometry and coordinate system assumed for the Hofmann elimination reaction of $CH_2^-SH^+C_2H_5$.

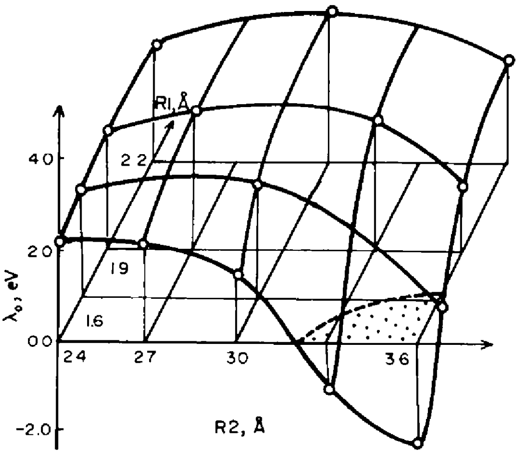
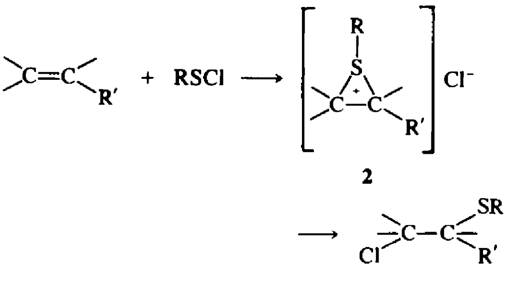


Fig. 4. The λ_0-surface for the transition state of hydrogen migration in the Hofmann elimination reaction of $CH_2^-SH^+C_2H_5$. Sulfur 3d orbitals are included in the basis set. The dotted area indicates the triplet-instability region.

Further calculations were carried out by varying R_3 with R_1 and R_2 being fixed at 1.9 and 3.3 Å, respectively (Model II). Calculated λ_0-values were 1.220, 2.492, and 2.922 eV at $R_3 = 1.15$, 1.65 and 2.15 Å, respectively. Since these λ_0-values are all positive in sign, it is confirmed that the α′,β-elimination should proceed by a nonradical mechanism. When sulfur 3d orbitals are left out of the basis set, negative λ_0-values have resulted: $\lambda_0 = -2.138$ and -2.475 eV at $R_3 = 1.65$ and 2.15 Å, respectively. Thus, the effects of the participation of sulfur 3d orbitals is of fundamental importance to the description of the mechanism of α′,β-eliminations.

Schematically shown in Fig. 5 is the variation in composition of the HOMO with the progress of reaction. The node which initially existed between C^2 and C^3 atoms moves until it is displaced to a region intermediate between C^3 and the migrating H atom. The variation in the nodal property of the HOMO adequately depicts the progress of the reaction; the C^3–H bond is cloven while the C^2–C^3 π bond is formed, leading thus to the formation of two products, ethylene and a sulfide. Throughout the reaction, sulfur 3d orbitals play an important role to maintain the S–C^1 bonding.

(C) *Addition of sulfenyl cation to olefin.* The addition of sulfenyl halides to olefins gives rise exclusively to trans adducts of the anti-Markovnikov orientation.[21,22] A mechanism involving an episulfonium ion intermediate (2) has been postulated to account for the stereochemistry.[22]



(3)

In this section, we will consider an initial attack of the sulfenyl cation on ethylene which leads to the formation of an episulfonium ion intermediate. We have calculated the λ_0-value for the addition, by varying the distance R and the bending angle θ as defined in Fig. 6. For the sake

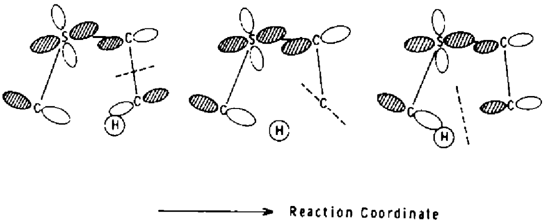


Fig. 5. Variation in the nodal property of the HOMO for $CH_2^-SH^+C_2H_5$ undergoing the Hofmann elimination.

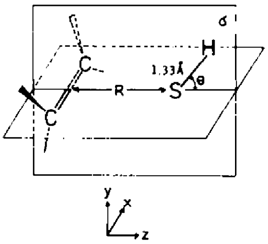


Fig. 6. Geometry and coordinate system assumed for the addition of a sulfenyl cation to olefin.

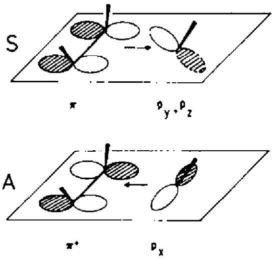
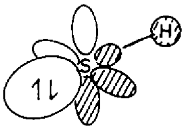


Fig. 8. Two bonding-type interactions between olefin and SH^+. The symbols S and A respectively denote the orbitals symmetric and antisymmetric with respect to the plane σ defined in Fig. 6.

of convenience, the substituent group R on the sulfenyl cation was replaced by an H atom. The resulting λ_0-surfaces are shown in Fig. 7.

Figure 7 shows that, whether the d orbitals are included or not, there exists no biradical region so far as θ is greater than 30°. Conspicuous difference in results between the sp and spd treatments appears only in a small region where θ is nearly 0°. However, the sulfenyl cation should have a filled orbital of the lone pair type projecting in the direction opposite to the S-H bond (3). Further, it has been shown that θ should be greater than 50° for the equilibrium conformation of an episulfonium ion.[23] Thus, the highly symmetrical approach (C_{2v}, $\theta = 0°$) of the cation to olefin seems to be quite unlikely to occur. On all these grounds, it may be concluded that the d orbital participation would be of little importance to this particular type of reaction. The conclusion is in harmony with the results that the contribution of d orbitals to the total energy of episulfonium ions is negligibly small.[23]



3

We have then attempted to look into the nature of the C-S bondings in the episulfonium ion for which θ is taken to be 60°. The interaction between olefin and sulfenyl cation could well be depicted by the two bonding molecular orbitals (Fig. 8). One is the symmetric (S) orbital composed of the ethylene π orbital and a mixture of the sulfur p_y and p_z orbitals while the other is the antisymmetric (A) combination of the ethylene π^* orbital with the sulfur p_x orbital. The bonding picture is similar to the donation (S) and back-donation (A) scheme proposed by Dewar[24] and by Chatt and Duncanson.[25] To clarify the bonding properties, charge densities for the two carbon p_z orbitals of ethylene have been decomposed into contributions from the S and A symmetry types of molecular orbitals:

$$q(\pi) = 4\sum_{S}^{occ} C_{p_z}^2 \tag{4}$$

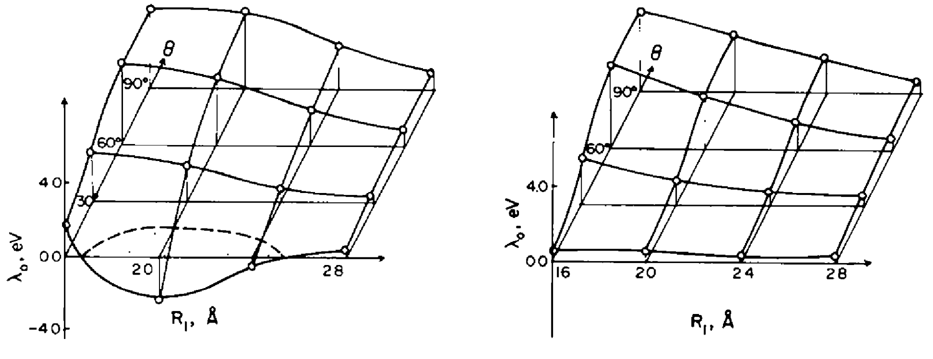
$$q(\pi^*) = 4\sum_{A}^{occ} C_{p_z}^2 \tag{5}$$

The results are given in Table 2 for the varying distance R.

Table 2. q values and sulfur d orbital populations for the ethylene-SH^+ system[a]

R(Å)	q(π)	q(π*)	$d_{z^2}+d_{x^2-y^2}$(S)	d_{xz}(A)
2.8	1.7649	0.0018	0.0780	0.0023
2.4	1.6224	0.0130	0.1069	0.0083
2.0	1.5187	0.0734	0.1282	0.0280
1.6	1.4918	0.3058	0.1608	0.0781

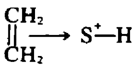
[a] $\theta = 0°$.



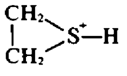
sp spd

Fig. 7. The λ_0-surfaces for the addition of the sulfenyl cation SH^+ to ethylene.

Table 2 shows a monotonous increase of q(π^*) and a steady decrease of q(π) with the decreasing R, a result which indicates smooth developments of both donation and back-donation with the progress of reaction. It is noteworthy here that the q(π^*) is relatively small even at R = 1.6 Å. The corresponding value for Zeise's salt[26] is as large as 0.520, and yet the olefin moiety in the complex is reported to be capable of rotation at room temperature.[27,28] Thus, the sulfonium ion formed on the sulfenyl cation addition to olefin would better be formulated as a π-complex[29] (4) rather than a classical episulfonium ion (5).



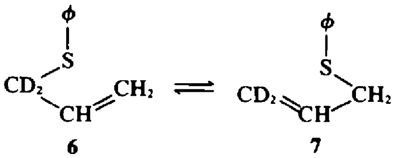
4



5

In Table 2, we have also listed the electron populations on sulfur d orbitals. The populations do not seem to be so large as to mar our conclusion that the d orbital participation will not be of essential importance to the sulfenyl complexation.

(D) *Thioallylic rearrangement.* Kwart and Cohen[30] first suggested the occurrence of thermal allylic rearrangement of allyl aryl sulfides, in order to explain the anomaly of the thio-Claisen rearrangement. The suggestion was later justified by the observation that the appropriate deuterated allyl phenyl sulfide (6) isomerizes unimolecularly to give an isotopic equilibrium mixture with 7.[31]



(6)

Since the reaction is just a 1,3-sigmatropic rearrangement, we will be here concerned only with the transition state where the S atom is equidistant from the allyl terminuses.

We have calculated the λ_0-values for the transition state by varying the distance R as defined in Fig. 9, where the sulfur atom is situated on the line which is perpendicular to the allyl plane and passes through the midpoint of the C^1 and C^3 atoms. The phenyl substituent on sulfur has been replaced by a hydrogen atom for the sake of computational economy.

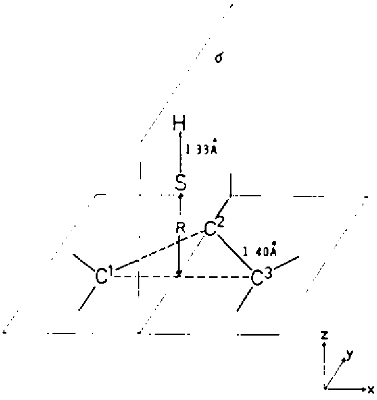
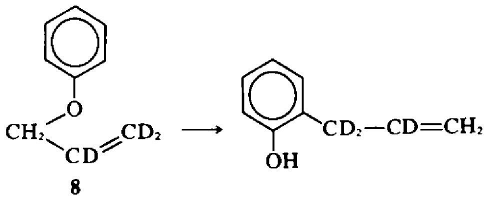


Fig. 9. Geometry and coordinate system assumed for the thioallylic rearrangement.

As can be seen in Fig. 10, no negative λ_0-value exists at the transition state both with and without sulfur d orbital inclusion. Sulfur d orbital participation in the reaction is, therefore, of little chemical significance.

Schematically depicted in Fig. 11 are the nodal structures of the HOMO and a lower orbital (A) at the transition state. The thioallylic rearrangement is a striking example of the symmetry allowed 1,3-sigmatropic rearrangements[32] where a p orbital (perhaps with a small d orbital participation) of the migrating group keeps the group bound to the allylic skeleton. This type of bonding is accomplished in the A symmetry orbital. In our criterion, however, characteristics of the reaction should be judged from the stability of the S symmetry orbital (HOMO). This is analogous to the suggestion made by Berson and Salem,[33] although their S symmetry orbital is subjacent.

Our viewpoint will become clearer when one examines an oxygen analog of 6. It was reported that deuterated phenyl allyl ether (8) can survive heating at 160° for more than 5 hr.[31] When the temperature was raised to 195°, the only reaction that took place was Claisen rearrangement (7), no sign of thermal oxyallylic rearrangement having been observed.[31]



(7)

Figure 12 shows a plot of λ_0 against R for the transition

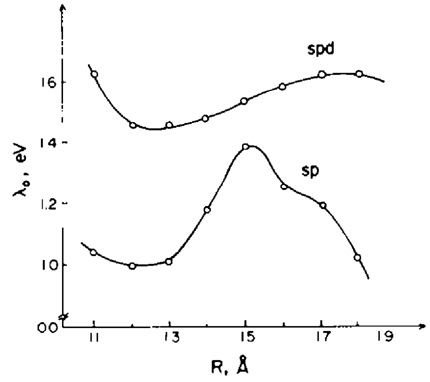


Fig. 10. The λ_0-curves for the transition state of the thioallylic rearrangement.

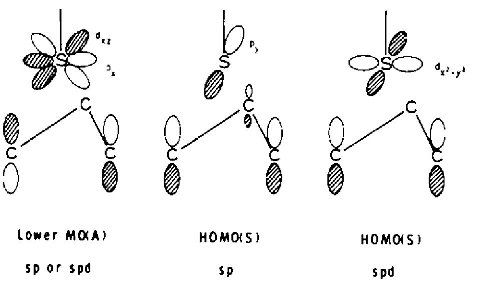


Fig. 11. Schematic representations of π molecular orbitals at the transition state of the thioallylic rearrangement. S and A respectively signify that the orbitals are symmetric and antisymmetric with respect to the plane σ defined in Fig. 9.

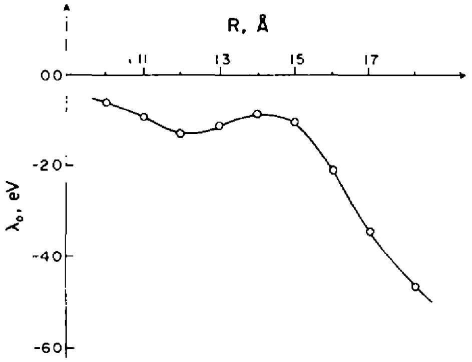
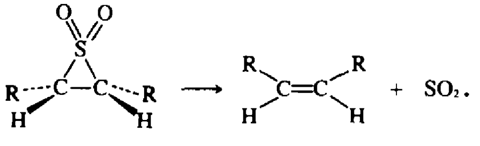


Fig. 12. The λ_0-curve for the transition state of the oxyallylic rearrangement.

state of the oxyallylic rearrangment. The phenyl substituent was also replaced by an H atom and the geometry was taken to be the same as in Fig. 9, except for the O–H bond length (0.97 Å). As is apparent from Fig. 12, the oxyallylic rearrangement must possess a biradical character at the transition state. The HOMO is also of S-symmetry, the A-symmetry orbital which consists of the oxygen p_x orbital and the allyl orbital of the same symmetry lying lower than the HOMO. The observed reluctance of the allylic ether against the symmetry-allowed oxyallylic rearrangement is compatible with the negative λ_0-value, i.e. the lack of sufficient bonding interaction between the migrating group and the carbon skeleton at the transition state. The different appearances for the allylic rearrangements between sulfur and oxygen should thus be attributed to the difference in size of the valence s and p orbitals but *not* to the role of sulfur 3d orbitals.

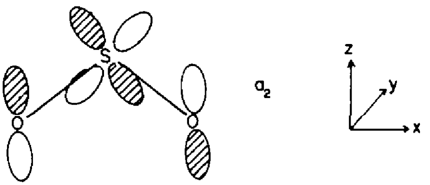
(E) *Decomposition of thiirane* 1,1-*dioxide. cis*- and *trans*-Dimethylthiirane 1,1-dioxides and *cis*-2,3-diphenylthiirane 1,1-dioxide decompose stereospecifically with retention of the alkane configuration:[34,35]



(8)

The non-linear cheletropic extraction path of the reaction is theoretically characterized as a symmetry-allowed $({}_{\sigma}2_s + {}_{\sigma}2_a)$ process.[32]

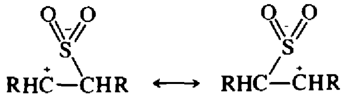
Before dealing with the decomposition, we have examined the d orbital participation in sulfur dioxide. The λ_0-values calculated with and without sulfur d orbitals are 4.46 and −2.12 eV, respectively, indicative of an important contribution of the d orbitals to the S–O bondings. The primary role of the d orbitals lies in the stabilization of the antisymmetric combination of oxygen $2p_z$ orbitals (**9**) (a_2 symmetry with respect to C_{2v} point group). Only one d orbital, d_{xz}, can overlap with the A combination; no p orbital has the a_2 symmetry. By interaction, the energy level of this orbital, which should otherwise be the HOMO, is lowered below an a_1 orbital which is essentially a lone pair orbital on the sulfur atom. It is because of this stabilization of the a_2 orbital that the RHF solution for SO_2 is rendered triplet-stable by the inclusion of d orbitals.



9

We now return to the decomposition of thiirane 1,1-dioxide. Because the S–O π bonding should be maintained throughout the reaction, we have decided to retain the sulfur 3d orbitals. Calculations of λ_0 were performed by varying two parameters R and θ as defined in Fig. 13. The resulting λ_0-surface is shown in Fig. 14, where it can be seen that there exists no biradical region at all throughout the reaction. The $({}_{\sigma}2_s + {}_{\sigma}2_a)$ reaction should thus be characterized as a symmetry-allowed nonradical (AN), i.e. concerted, reaction.[13,16]

There is one important point to make at this point, however. The λ_0-value is slightly positive even in the reaction path of the least-motion type ($\theta = 0°$), which must be a typical symmetry-forbidden process in the sense of the Woodward-Hoffmann rule. If the reaction is found to proceed along the least-motion path, it will have to be regarded as what we call a symmetry-forbidden nonradical (FN) reaction.[13,16] The reaction should then be deemed as involving a dipolar intermediate of the form:



(9)

The observation that the decomposition takes place

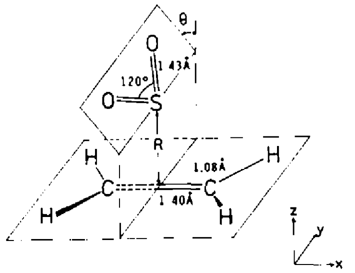


Fig. 13. Geometry and coordinate system assumed for the decomposition of thiirane 1,1-dioxide.

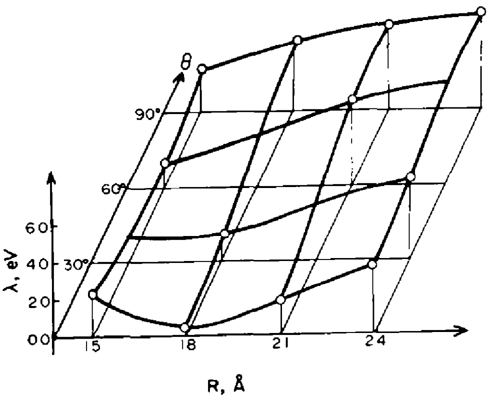


Fig. 14. The λ_0-surface for the decomposition of thiirane 1,1-dioxide with sulfur 3d orbitals included in the basis set.

with ease cannot in itself be accepted as evidence for the occurrence of the concerted reaction. Rather, the observed acceleration of decomposition in polar solvents is in favor of the alternative mechanism which involves the intermediacy of a dipolar species.

REFERENCES

[1] Part V: K. Tatsumi, K. Yamaguchi and T. Fueno, *Tetrahedron* **31**, 2899 (1975).

[2] H. C. Longuet-Higgins, *Trans. Faraday Soc.* **45**, 173 (1949).

[3] L. Pauling, *J. Phys. Chem.* **56**, 361 (1952).

[4] D. P. Craig and C. Zauli, *J. Chem. Phys.* **37**, 609 (1962).

[5] T. Jordan, H. W. Smith, L. L. Lohr and W. N. Lipscomb, *J. Am. Chem. Soc.* **85**, 846 (1963).

[6] S. Wolfe, A. Rauk and I. G. Csizmadia, *Ibid.* **91**, 1567 (1969); A. Rauk, S. Wolfe and I. G. Csizmadia, *Can. J. Chem.* **47**, 113 (1969).

[7] R. Hoffmann, H. Fujimoto, J. R. Swenson and C. C. Wan, *J. Am. Chem. Soc.* **95**, 7644 (1973).

[8] V. B. Koutecký and J. I. Musher, *Theoret. Chim. Acta Berl.* **33**, 227 (1974).

[9] P. C. Van Der Voorn and R. S. Drago, *Ibid.* **88**, 3255 (1966).

[10] A. Rauk, L. C. Allen and K. Mislow, *Ibid.* **94**, 3035 (1972).

[11] C. A. Coulson, *Nature* **221**, 1106 (1969).

[12] M. A. Ratner and J. R. Sabin, *J. Am. Chem. Soc.* **93**, 3542 (1971).

[13] K. Yamaguchi, T. Fueno and H. Fukutome, *Chem. Phys. Lett.* **22**, 461, 466 (1973); K. Yamaguchi and T. Fueno, *Ibid.* **22**, 471 (1973).

[14] H. Fukutome, *Progr. Theoret. Phys.* **47**, 1156 (1972).

[15] J. Čížek and J. Paldus, *J. Chem. Phys.* **47**, 4976 (1967); J. Paldus and J. Čížek, *Ibid.* **52**, 2919 (1970).

[16] T. Okada, K. Yamaguchi and T. Fueno, *Tetrahedron* **30**, 2293 (1974).

[17] A. W. Johnson, *Ylid Chemistry*. Academic Press, New York (1966).

[18] A. D. Mitchell (Editor), *Table of Interatomic Distances and Configuration in Molecules and Ions*. The Chemical Society, London (1958).

[19] R. Hoffmann, D. B. Boyd and S. Z. Goldberg, *J. Am. Chem. Soc.* **92**, 3929 (1970).

[20] V. Franzen and C. Mertz, *Chem. Ber.* **93**, 2819 (1960); V. Franzen and H. J. Schmidt, *Ibid.* **94**, 2937 (1961).

[21] N. Kharasch and C. M. Buess, *J. Am. Chem. Soc.* **71**, 2724 (1949).

[22] W. H. Mueller and P. E. Butler, *Ibid.* **88**, 2866 (1966).

[23] Y. Kikuzono, T. Yamabe, S. Nagata, H. Kato and K. Fukui, *Tetrahedron* **30**, 2197 (1974).

[24] M. J. S. Dewar, *Bull. Soc. Chim. Fr.* **18**, C79 (1951).

[25] J. Chatt and L. A. Duncanson, *J. Chem. Soc.* 2939 (1953).

[26] H. Kato, *Bull. Chem. Soc. Japan* **44**, 348 (1971).

[27] S. Maricic, C. R. Redpath and J. A. S. Smith, *J. Chem. Soc.* 4905 (1963).

[28] H. P. Fritz, K. E. Schwarzhans and D. Sellman, *J. Organometal. Chem.* **6**, 551 (1966).

[29] M. J. S. Dewar, *Bull. Soc. Chim. Fr.* **18**, C71 (1951).

[30] H. Kwart and M. H. Cohen, *Chem. Commun.* 319 (1968).

[31] H. Kwart and N. Johnson, *J. Am. Chem. Soc.* **92**, 6064 (1970).

[32] R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*. Academic Press, New York (1970).

[33] J. A. Berson and L. Salem, *J. Am. Chem. Soc.* **94**, 8917 (1972).

[34] N. P. Neureiter and F. G. Bordwell, *Ibid.* **85**, 1209 (1963); N. P. Neureiter, *Ibid.* **88**, 558 (1966).

[35] N. Tokura, T. Nagai and S. Matsumura, *J. Org. Chem.* **31**, 349 (1966).

[36] F. G. Bordwell, J. M. Williams, Jr., E. B. Hoyt, Jr. and B. B. Jarvis, *J. Am. Chem. Soc.* **90**, 429 (1968).