distances $r_1 = C_\alpha O_1$ and $r_2 = C_\beta H_2$ or OH_2, the asynchronization of the reaction as previously defined[20] can be estimated to be 23% and 62%, respectively, for reactions A and B. However the situation is more complicated because of the participation of other evolving bonds. These reactions belong to the concerted (without intermediates) but asynchronous addition type.[20]

Concluding Remarks. Although there is clear evidence from the calculations presented that the preferred mode of addition of water dimer is across the C=O (rather than the C=C) bond of ketene, the implied intermediate (the diol B) has not yet been observed experimentally. Since the technique used to follow the rapid hydration of ketene in one case was ionic conductivity,[7,33] the conversion of the diol, if formed first, to acetic acid (as acetate ion) must be rapid (since the diol would not be detected by using this technique in the pH range studied).
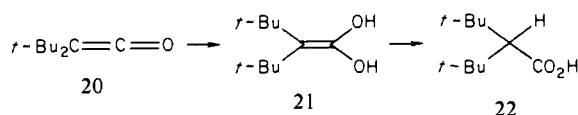
The problem of the reported[34,35] slow reaction of di-*tert*-butylketene

(20) with water remains. It has been pointed out[34] that proton transfer from H_3O^+ to carbon of the analogous di-*tert*-butyl enol ether is not subject to steric hindrance by the bulky *tert*-butyl groups. A steric effect in proton transfer to oxygen (the preferred transition state as shown by the present work) is even less likely (although the *tert*-butyl group could hinder the approach of the dimer). Hydration across the C=O bond would however give diol **21**, which could be slow to ketonize (to the acid **22**). Thus Hart[36] has pointed out that many enols are relatively stable; the key factor that slows ketonization is steric hindrance, which resists the reduction of the *t*-Bu–C–*t*-Bu bond angle (as in the conversion of **21** to **22**). Thus the slow step with highly sterically hindered ketenes (such as **20**) may be ketonization (**21** → **22**) rather than initial reaction of the ketene (to give diol **21**).

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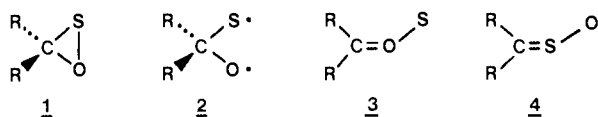(36) Hart, H., *Chem. Rev.* **1979**, *79*, 515.

An ab Initio CASSCF Study of the Photolytical Formation and Decomposition of Oxathiirane[1]

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Abstract: Ab initio calculations on the H_2CSO system have been carried out by the CASSCF method. It appears that photolysis of thioformaldehyde *S*-oxide most probably affords rearrangement into the three-membered ring oxathiirane via an excited singlet state. Further photolysis of oxathiirane apparently leads to a weakened S–O bond, the product being best described as a biradiacal, whereas no evidence for a possible ring opening to the corresponding formaldehyde *O*-sulfide was obtained. The wave function of the latter compound seems to be best described as a complex between a distorted sulfur atom and a formaldehyde molecule. On the basis of the calculations the previously reported photolyses of diarylthione *S*-oxides and the corresponding diaryloxathiiranes are discussed.

The appearance of diaryloxathiiranes (**1**, R = Ar) as inter-

mediates in the photolytic conversion of diaryl thioketone *S*-oxides (**4**, R = Ar) has recently been established by low-temperature electronic absorption spectroscopy.[2] Oxathiiranes appeared, not unexpectedly, to be thermally as well as photolytically highly labile compounds, which in both cases produced the corresponding ketones in high yield as reaction products. However, in the photolytic decomposition of diaryloxathiiranes a thermally highly labile intermediate was detected, apparently generated in approximately 10% yield.[2,3] A priori, several compounds could be

considered as reasonable candidates, the actual number, however, being reduced to two, the singlet biradial (**2**) and the zwitterionic structure (**3**), partly on the basis of low-temperature ESR spectroscopy and magnetic susceptibility measurements.[3]

The intermediate **2/3** appeared as a strongly colored compound (R = C_6H_5: λ_{max} 550 nm ($\epsilon \approx 11\ 000$)).[2,3] Due to the highly labile nature, it was not possible to obtain, e.g., cycloaddition products with dipolarophiles. The structural assignment of the intermediate was, with this background, left for theoretical considerations. Results from earlier semiempirical MNDO and CNDO/S-CI calculations together with the experimental data

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were consistent with the existence of closed-shelled carbonyl sulfides (**3**) as observable, though labile, intermediates from photolysis of oxathiiranes.[3]

In the present study a mechanism for the photolytical formation and decomposition of the parent oxathiirane (**1**, R = H) is reported, on the basis of ab initio quantum chemical calculations using the complete active space SCF (CASSCF) method.[4,5] The results obtained are used for a discussion of the experimental data available for diaryloxathiiranes.

Computational Details

Theoretical calculations of the geometries and energies for different forms and different electronic states of the CH_2SO system have been performed, using the CASSCF method.[4,5] The CASSCF method is a special form of the multiconfigurational SCF (MCSCF) method where the configuration selection problem is avoided simply by including in the CI expansion of the wave function all possible configurations generated by a set of active orbitals. The method has been described in detail elsewhere,[4-6] and only a brief review of the main features is therefore given here. The molecular orbital space is divided into three subspaces: inactive, active, and secondary orbitals. The inactive orbitals are assumed to be doubly occupied in all configurations of the CASSCF wave function. The remaining electrons occupy the active orbitals; however, this occupancy is made completely flexible by including in the wave function all possible configurations and spin-couplings consistent with the given overall spin and spatial symmetry of the wave function. In order to account for all possible near-degeneracy effects the active space was constructed to include two orbitals from the CH_2 group, corresponding to the singly occupied orbitals in the methylene radical, and three orbitals each from the S and O atoms, corresponding to their valence p orbitals. A CASSCF wave function constructed from 8 active orbitals and 10 electrons consists of 1176 spin adapted configurations for a singlet state and 1512 for a triplet. These figures are reduced roughly by a factor of 2 when the spatial symmetry of the studied forms of the CH_2 SO is taken into account.

The orbital optimization was performed by using the approximate super-CI method based on the MCSCF Fock operator as described elsewhere.[5] Since this method has first-order convergence properties only, it is of interest to discuss briefly the convergence behavior. The first calculations on each form of the CH_2SO system were made with closed-shell SCF orbitals as a starting guess. The super-CI process then converged in around 15 iterations (convergence thresholds were 10^{-5} au in energy and 10^{-3} au in energy derivative, respectively). Subsequent calculations for a similar geometry required 7–10 iterations to reach the same thresholds.

In a first set of surveying calculations a basis set of double-ζ (DZ) quality was used, consisting of 9s, 5p contracted to 4s, 2p for C and O,[7a] 12s,9p contracted to 6s,4p for S,[7b] and 4s contracted to 2s for hydrogen.[7a] A basis set of this quality is not capable of accurately reproducing molecular geometries and energy differences. From a previous study of the O_3 system[8] it is known that bond lengths obtained with a similar basis set may be up to 0.06 Å too long, reflecting the fact that the basis set used is optimized for atoms and consequently favors atomlike structures. With this basis set all bond lengths and angles connecting the C, S, and O atoms were optimized. The CH bond length was assumed to be 1.087 Å and the HCH angle was set equal to 118.4°. The value of the angle can be expected to favor structures **1**, **3**, and **4** relative to **2**[8] Coupling between the optimized variables was allowed.

In a second set of calculations all bond lengths for the C, S, and O atoms were optimized with the DZ basis set augmented
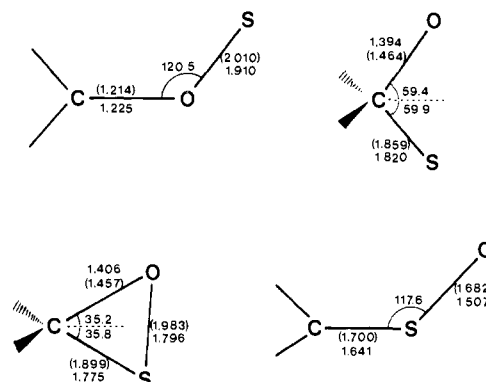

Figure 1. Optimized geometries. Bond lengths in Å, and angles in deg. Angles from DZ calculations. Bond lengths in parentheses are from DZ calculations. Other bond lengths are from DZP calculations.

with a d orbital (exp = 0.8 for C and O and 0.5 for S). This basis set will be labeled DZP. All other parameters were kept at the best values in the previous optimization.

An estimate of remaining correlation effects (within the smaller basis set) was also included in the calculation, based on second-order perturbation theory.[9] Apart from giving an estimate of dynamical correlation effects, these results could also be used to check if enough orbitals were included in the active subspace in the CASSCF calculations (i.e., if all near-degeneracy effects were included in the wave function). The energies obtained by this technique will be referenced as PT-CI energies (vide infra).

Results

By use of the computational procedure outlined above, the geometries of four isomers of the H_2COS system have been determined for the ground electronic state $^1A'$ (C_S symmetry). The optimized geometries are visualized in Figure 1. Calculations have also been performed for the lowest states of $^1A''$, $^3A'$, and $^3A''$ symmetries as well as for the first excited state of $^1A'$ symmetry, using ground-state equilibrium geometries. The results are summarized in Table I. In the following the results for each of the H_2CSO isomers will be discussed separately.

1. Thioformaldehyde S-Oxide. As illustrated in Figure 1, the CASSCF calculations (DZP basis) predict the C–S and S–O bonds in thioformaldehyde S-oxide (**4**, R = H) to be 1.64 and 1.47 Å, respectively, in agreement with the experimentally determined structure recently reported by Block and co-workers[10] (R_{CS} = 1.610 Å, R_{SO} = 1.469 Å). However, it appears that the potential curve for stretching one of the C–S and S–O bonds and simultaneously shortening the other is extremely flat. A similar result has previously been reported for the biradical minimum for methylene peroxide,[8,11] where the C–O and O–O distances were found to be approximately equally long.

The wave function for thioformaldehyde S-oxide appears to exhibit only a weak biradical nature, the occupation numbers for the third and fourth natural orbitals in the π-system being 1.92 and 0.10, respectively. Consequently, one finds that the lowest triplet state is found to have a high energy (E = 2.65 eV; cf. Table I); that is, no unpaired electrons are present, in agreement with the lack of ESR signals from sulfines.[3]

The first excited singlet state is $^1A''$, according to the results of the calculations, corresponding to an n,π^* excitation where n is the oxygen lone-pair orbital. The calculated vertical excitation energy corresponds to a wavelength of 280 nm. A second excited singlet state (of A' symmetry) at 208 nm corresponds to an excitation from the π orbital with the occupation number 1.92 to the same π^* orbital. According to a Mulliken population analysis the charge on the CH_2 group is changed from –0.07 to –0.01 as

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Table I

molecule	state symmetry	state no.	energy, +511 (au) CASSCF DZ-P	CASSCF DZ	PT-CI DZ
thioformaldehyde *S*-oxide	$^1A'$	1	-0.3508	-0.2309	-0.3951
	-''-	2	-0.1320	-0.0866	-0.2569
	$^1A''$	1	-0.1884	-0.1321	-0.3019
	$^3A'$	1	-0.2536	-0.1683	-0.3453
	$^3A''$	1	-0.2024	-0.1248	-0.3150
oxathirane, ring form	$^1A'$	1	-0.3183	-0.2604	-0.4269
	-''-	2		-0.0905	
	$^1A''$	1	-0.1893	-0.1679	-0.3406
	-''-	2		-0.1238	
	$^3A'$	1	-0.1199	-0.1359	-0.3101
	$^3A''$	1	-0.2147	-0.1901	-0.3617
oxathirane, open form	$^1A'$ $(\pi_1{}^2)^a$	1	-0.2986	-0.2350	-0.4020
	-''- $(\pi_1{}^2\pi_2{}^2)$	2	-0.2591		
	$^1A''$ $(\pi_O{}^1\pi_S{}^2)$	1	-0.2874	-0.2273	-0.3992
	-''- $(\pi_O{}^2\pi_S{}^1)$	2	-0.2668		
	$^3A'$ $(\pi_1{}^2)$	1	-0.2961	-0.2330	-0.4006
	-''- $(\pi_1{}^2\pi_2{}^2)$	2	-0.2616		
	$^3A''$ $(\pi_O{}^1\pi_S{}^2)$	1	-0.2885	-0.2321	-0.4031
	-''- $(\pi_O{}^2\pi_S{}^1)$	2	-0.2696		
formaldehyde *O*-sulfide	$^1A'$	1	-0.3368	-0.2720	-0.4279
	-''-	2	-0.2095	-0.1628	-0.3271
	$^1A''$	1	-0.2183	-0.1771	-0.3451
	$^3A'$	1	-0.2306	-0.1641	-0.3272
	$^3A''$	1	-0.2659	-0.2341	-0.4031
formaldehyde	S(D)		-0.2956	-0.2287	-0.3914
	S(^{3}P)		-0.3419	-0.2825	-0.4428
thioformaldehyde	O(^{1}D)		-0.1828	-0.1413	
	O(^{3}P)		-0.2650	-0.2134	

^{a} The occupancies of the π-system are indicated by specifying the number of electrons in each π orbital: π_1 is the bonding combination of the sulfur 3p and the oxygen 2p orbitals; π_2 is the corresponding antibonding orbital; π_S is the sulfur 3p orbital; π_O is the oxygen 2p orbital.

a result of the weakening of the π-bond in this state. Hence, it seems most likely that this state will rearrange to oxathiirane (**1**, R = H). The two studied triplet states (cf. Table I) have relatively high energies and they are probably of less chemical importance for the problems investigated here, which agrees with the experimental fact that the photolytical conversion of sulfines proceeds via excited singlet states.[12,13]

It is of supplementary interest to note that thioformaldehyde *S*-oxide is found to have the lowest energy of the four CH$_2$SO isomers studied, in agreement with experiment,[10] and is predicted to be relatively stable, since the dissociation products, thioformaldehyde and O(^{3}P), have a higher energy (the computed dissociation energy is 225 kJ/mol (CASSCF-DZP basis)). A methodically interesting observation is that the inclusion of d orbitals in the basis set lowers the energy for the ground state of thioformaldehyde *S*-oxide with roughly 0.12 au, whereas the corresponding lowering for the other studied forms are considerably lower, ≈0.06 au. This reflects the fact that the sulfur d orbitals are of large importance in thioformaldehyde *S*-oxide due to the complicated binding situation.

2. Oxathiirane. The electronic structure of the ring form of oxathiirane (**1**, R = H) is similar to that of the ring form of ozone or dioxirane.[8,14] These systems have all valence π-orbitals double occupied, and the lowest excited states are obtained by exciting one of the π electrons to an antibonding σ-orbital. The two lowest excited singlet states are, according to the CASSCF calculations, both of A'' symmetry. Both of them correspond to excitation into the antibonding S–O σ orbital. The first $^1A''$ state has the highest π orbital singly occupied. This orbital is antibonding in the S–O region. The second $^1A''$ state corresponds on the other hand to

an excitation from the S–O bonding π orbital to the same antibonding σ orbital. The third excited singlet state (which is of A' symmetry) can be seen as an excitation from the bonding S–O σ orbital to the corresponding antibonding σ orbital. The results of the CASSCF calculations predict the corresponding wave lengths to be 490, 332, and 267 nm, respectively, at the DZ level. The excitation energies increased when d orbitals were added to the basis set and the lowest excitation occurs at 351 nm. Similar results have previously been obtained from an CNDO/S-CI study of the electronic absorbtion spectrum of oxathiirane.[15] The second of these absorptions (at 332 nm) can be assumed to exhibit only a low intensity, as it corresponds to an almost symmetry-forbidden transition in the pseudo-C_{2v} symmetry of the molecule. A typical example is the diphenyloxathiirane (**1**, R = Ph) absorption at 390 nm $\epsilon \approx 200$) found by low-temperature electronic absorption spectroscopy.[2] An important feature of all the three excited states is the weakening of the S–O bond whereas no weakening of the C–S bond has been obtained.

The electronic structure of the open form of oxathiirane (oxythiomethane; **2**, R = H) can best be understood from the fact that the π– and σ-lone-pair orbitals on O and S are almost degenerate; that is, the total energy of the system is a almost independent of their occupancies as long as three electrons are distributed among the oxygen orbitals and three electrons among sulfur orbitals. Consequently there will be four A' and four A'' states with almost the same energy for each total spin. The energies for the two lowest states of each spin and space symmetry have been computed and are given in Table I. The largest energy difference between the ground state of each symmetry is computed to be 0.3 eV (between $^1A'$ and $^1A''$). This situation is similar to that found for dioxymethane,[14,16] where the singlet–triplet separation was found to be less than 0.1 eV. The electronic structure

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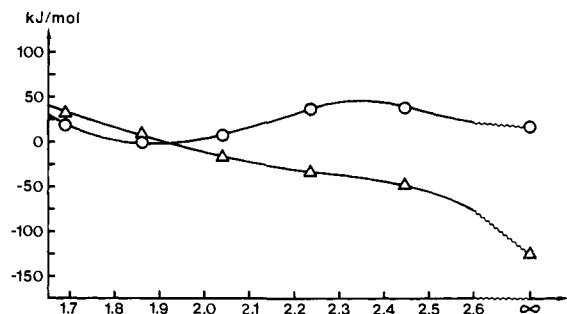(16) Siegbahn, P. E. M. *J. Chem. Phys.* **1979**, 70, 5391.

Figure 2. Potential curve for the dissociation of the singlet and the triplet state of oxythiomethane (DZ basis).

of each state is indicated in Table I by specifying the occupancies of the π system.

3. Formaldehyde O-Sulfide. The wave function for formaldehyde O-sulfide (**3**, R = H) is, according to the results of the present calculations, best described as a complex between a distorted sulfur atom and a formaldehyde molecule. The first excited singlet state, $^1A''$, corresponds to an excitation from a sulfur σ lone pair to the empty π^*-orbital. The energy of this state corresponds to an excitation line at 376 nm. The second line at 351 nm ($^1A'$) corresponds to an excitation from the highest occupied π orbital (on the sulfur atom) to the same π^* orbital.

4. Potential Energy Surfaces. Finally, a series of calculations were preformed with the DZ basis set on the possible fragmentations of **2** and **3** (R = H) into formaldehyde and $S(^3P)$ or $S(^1D)$. In the search for the reaction path the geometry of the CH_2 group was held fixed whereas all other geometry parameters were varied, restricting the molecules to be C_s symmetric. The saddle point found in the energy surface for the dissociation of **2** into H_2CO and $S('D)$ was detected as a geometry with one negative eigenvalue of its hessian matrix. The $^3A''$ state of oxythiomethane (**2**, R = H) was found to be purely repulsive, while the $^1A'$ state dissociated into H_2CO and $S(^1D)$ via an activation barrier of 45 kJ/mol, along the planar reaction path studied. The computed barrier is 16 kJ/mol with the DZ basis and 8 kJ/mol with the DZ+P basis (Figure 2). A change of spin symmetry does, however, seem quite likely due to the near-degeneracy of the two states, $^1A'$ and $^3A''$, for oxythiomethane.

Analogous calculations on the formaldehyde O-sulfide system revealed that formation of this molecule from formaldehyde and $S(^1D)$ proceeds without any activation barrier, the binding energy being estimated to be 112 kJ/mol with DZ basis, and 108 kJ/mol with the DZ+P basis.

Parenthetically it might be worth mentioning that the calculated $^1D-^3P$ separations of the sulfur and oxygen atoms are (fortuitously) in reasonable agreement with experiment for the DZ basis, in spite of the limited basis sets used, and the lack of dynamical correlation: calculated values are 1.46 (S) and 1.96 eV (O), while the experimental values are 1.15 and 1.97 eV, respectively. A similar result is obtained with the DZ+P basis which yields 1.26 and 2.24 eV, respectively.

Discussion

The results presented in the previous section will be used below to discuss and interpret the experimental studies on the photolytic formation and decomposition of diaryloxathiiranes (**1**, R = Ar).[2,3] An important difference between the experiments and the calculations is the nature of the substitutents R; while all calculations have been performed with R = H, most experimental information is obtained with R = Ph. The phenyl groups are likely to stabilize the more diffuse excited states, thus leading to smaller energy differences.

The first observed electronic absorption bands for diaryl sulfines are found around 330 nm, the molar aborption coefficient being around 10 000, strongly indicative for the π,π^* nature of these absorptions.[2,3] However, the slightly green to yellow color of these compounds indicate the existence of weak n,π^* transitions at somewhat higher wavelengths. This suggestion is in full agreement with the two calculated transitions for thioformaldehyde S-oxide,
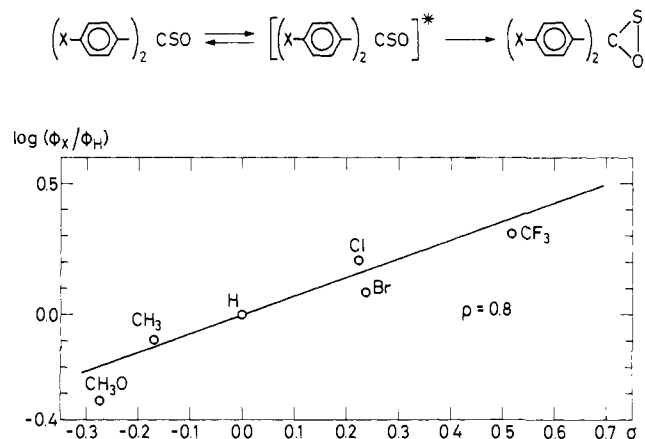

Figure 3. Photolysis (λ_{ex} 330 nm) of diarylsulfines (293 K): relative quantum yield (ϕ_x/ϕ_H) as a function of the Hammett σ constants.

corresponding to wavelengths of 280 and 208 nm, if the red shift of the phenyl groups are considered. Aliphatic sulfines are reported to exhibit their first observed absorption band around 270 nm, probalbly to be assigned to a π,π^* transition[17]. On this basis the 330 nm absorption in diaryl sulfines is assigned to the π,π^* transition leading to the $^1A'$ state. As mentioned above, this state most probably will rearrange to the diaryloxathiirane by a nucleophilic attack of the negatively charged oxygen on the neutral carbon atom. Experimental support for this mechanism is obtained from a study of the relative quantum yields for the photolysis of diary sulfines (λ_{ex} 330 nm), thiobenzophenone (**4**, R=C_6H_5) being chosen as reference (Figure 3). The slightly positive ρ value of 0.8 is in perfect agreement with the proposed mechanism. Furthermore, it is observed that the quantum yield for the photolysis of **4** (R = C_6H_5) is ca. five times higher in hexane than in ethanol.[18] This can be explained as a stabilizing effect of the polar solvent on the more polar structures, in **4**, the nucleophilic attack of the oxygen atom on the central carbon atom consequently being less probable.

Experimentally, diaryloxathiirane is found to exhibit electronic absorptions around 390 nm.[2,3] These weak absorptions, $\epsilon \approx 200$, are a priori assigned to n,π^* transitions. Photolysis of diaryloxathiiranes by excitation into these states results in decomposition of **1** (R = Ar) into the corresponding diaryl ketones and the strongly colored intermediate mentioned in the introduction, which tentatively has been assigned to **2** or **3**.[2,3] In the photolysis of diphenyloxathiirane, monothiobenzoic acid O-phenyl and S-phenyl esters (**5** and **6**) (vide infra) were also detected.

In order to rationalize the photolysis on the basis of the present calculations it should be emphasized that any of the three excited states, which reasonably can be associated with the 390-nm absorption band, exhibit a weakened S–O bond, and it seems most likely that the system will photolytically break this bond. It is in this connection of interest to note that all three excited states correlate with a set of almost degenerate states in the open form of oxathiirane (**2**, R = H). Also, when the open form of **2** is created, it is vibrationally excited. Hence, although the singlet states are bound, the vibrational energy is large enough to overcome the activation barrier to generate benzophenone and a singlet D sulfur atom (cf. Figure 2). Most probably the thiono/thiolo benzoic acid esters are formed by migration of the phenyl groups in a way similar to the way formic acid is formed from dioxymethane.[8] In addition, the possibility of a singlet–triplet transition should be noted. The molecules that manage to relax into their vibrational ground state will rapidly change spin state and subsequently dissociate into formaldehyde and a triplet P sulfur atom (cf. Figure 2). The calculations show clearly that the $^3A''$ state is dissociative, yielding an aldehyde and $S(^3P)$. The

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(18) Carlsen, L.; Holm, A.; Lohse, C. to be published.

same is probably true for the $^3A'$ state, but this process was not studied since the reaction path is completely unsymmetric and therefore more complicated to calculate. Thus one may conclude that, unless the $^1A'$ state is drastically favored with an increased accuracy of the calculation, this molecule is not stable but will dissociate into an ketone and a sulfur atom.

It seems on this basis reasonable to conclude that the strongly colored intermediates found in the photolyses of diaryl-oxathiiranes[2,3] at low temperature are not to be assigned to the biradical **2** (R = Ar), which leave the carbonyl *O*-sulfides as the most reasonable candidates for the experimentally observed 550-nm absorptions, as tentatively suggested previously.[3] As was the case in the CNDO/S study,[3] the agreement between the observed transition energy, 2.25 eV, and the calculated energy differences, 3.23 eV for $^1A''$ and 3.47 eV for $^1A'$, is, however, not satisfactory. The same errors as mentioned above in the thio-carbonyl *S*-oxide case are, of course, operating here, and it seems most likely that introduction of aryl groups will cause a red shift of the computed transitions, bringing the calculated and experimentally observed transitions in closer agreement.

Finally, the possible formation of the carbonyl sulfides as apparent intermediates in the photolysis will be discussed. from the previous discussion it appears that the photolysis of oxathiiranes most probably will give rise to the corresponding ketones and ^1D sulfur atoms. In the cases studied experimentally, these products are formed in a cold and rather rigid matrix (EPA or PVC); i.e., their possibility of moving apart is strongly reduced. Consequently, it is suggested that the carbonyl sulfides (**3**, R = Ar) are formed by a consecutive reaction between initially formed diaryl ketones and $S(^1D)$ atoms, a reaction which apparently proceeds without any reaction barrier (vide supra).

On the basis of the present results and the above discussions, the photolytical formation and decomposition of oxathiiranes are rationalized as visualized in the following scheme.
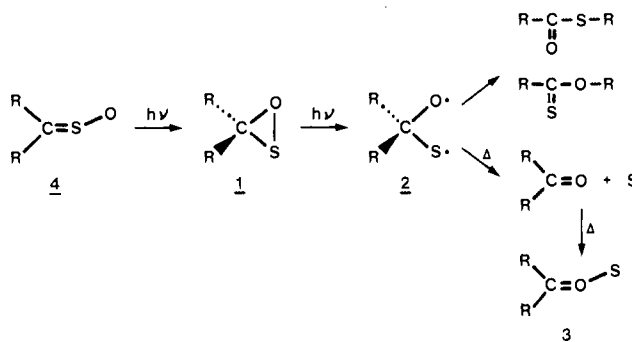
Conclusion

Oxathiiranes are generated photolytically from thioketone *S*-oxides via an excited[1] A' state. Further photolysis of the oxathiirane leads a priori to the singlet biradical **2**, which by vibrational relaxation may eliminate a singlet D sulfur atom and form the corresponding ketone and/or rearrange into the thioesters **5** and/or **6**. The experimentally observed ketone *O*-sulfides are most likely formed in the cold matrix by addition of the D sulfur atom to the ketone.

Activation of Single-Bond Cleavage Processes on Metal Surfaces: A Comparison of Dissociative Hydrogen Adsorption with Simple Gas-Phase Exchange Reactions

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Abstract: Certain simple dissociative chemisorption processes on metal surfaces may be viewed as analogues of gas-phase bimolecular exchange reactions: AB + MM → AM + BM. We compare in detail the process of HH (or HD) dissociation on a model Ni(100) surface with both the low-barrier collinear exchange H_2 + D → HD + H reaction and the HH + DD → 2HD reaction which has a much higher barrier. We show that the state evolution which occurs during the surface reaction is entirely comparable to that in the molecular processes, and in all cases the barrier height is determined purely by the ease with which the reactants are able to meet the requirements of the Pauli principle. By analyzing the reaction on this fundamental level, we are able to avoid arguments that are based on molecule or surface orbital symmetries. The results confirm the common conjecture that low activation energies in surface reactions are in part the result of the high metal density of states and, further, demonstrate in detail how this density of states is employed to produce low barriers. We point out that, although d orbitals possess local symmetry properties that naturally satisfy certain of the Pauli principle constraints, s- and p-band metal electrons are no less capable of doing so when the density of surface states (projected onto the reaction site) is high.

I. Introduction

The concept of "reaction selection rules" is a well-known one in organic chemistry, having been the subject of a variety of theoretical studies. Efforts have ranged from the molecular-orbital-based efforts of Woodward and Hoffmann[1] and others,[2–4]

to the valence-bond arguments presented originally by Goddard.[5] Each of these approaches has enjoyed considerable success, providing an understanding of a wide range of reaction phenomena in organic chemistry via relatively simple electronic structure

(1) See, for example, R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim, Germany, 1970, and references within.

(2) K. Fukui in "Modern Quantum Chemistry", O. Sinanoglŭ, Ed., Academic Press, New York, 1965 and references within; K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jpn.*, **41**, 1989 (1968); K. Fukui, *ibid.*, **39**, 498 (1966).

(3) H. Longuet-Higgins and E. W. Abrahamson, *J. Am. Chem. Soc.*, **87**, 2045 (1965).

(4) R. Pearson, *J. Am. Chem. Soc.*, **91**, 1252, 4957 (1969); *Acc. Chem. Res.*, **4**, 152 (1971); *Theor. Chim. Acta*, **16**, 107 (1970).

(5) (a) W. Goddard III, *J. Am. Chem. Soc.*, **92**, 7520 (1970); (b) W. Goddard III and R. C. Ladner, *ibid.*, **93**, 6750 (1971); (c) W. Goddard III, *ibid.*, **94**, 793 (1972).