

Mechanism of β -Cleavage in the Excited States of Keto Sulfides

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The β -cleavage process in photoexcited ketones of structure RCOCH_2X ($\text{X} = \text{CH}_2\text{CH}_3, \text{OCH}_3, \text{SCH}_3$; $\text{R} = \text{CH}_3, \text{Ph}$) has been studied using the configuration interaction procedure within the framework of MINDO/3. The results explain qualitatively why the β -cleavage process is faster than the α -cleavage process in keto sulfides while in keto ethers the reverse is true.

There are several reports of phenacyl sulfide being cleaved by radicals in a photochemical β -cleavage process.¹⁻⁶ This is in striking contrast to the photolytic behaviour of the analogous β -keto ether systems.⁷ The different behaviour is attributed to the relative weakness of the C-S bond (60 kcal mol⁻¹)* as compared to the C-O bond (85 kcal mol⁻¹) in their ground states. A more recent investigation⁸ on triplet phenacyl sulfides reveals that the β -cleavage process is very fast and competes with other triplet state reactions of phenacyl sulfides such as charge-transfer and γ -hydrogen abstraction processes.

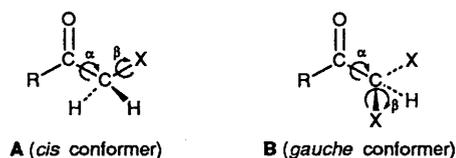
The object of this investigation is to understand the mechanism of the β -cleavage process in the excited states of β -keto sulfides. Recently, we reported⁹⁻¹¹ our systematic investigations on the photochemical α -cleavage process (Norrish type-I) in ketones and thioketones where rates of the cleavage process do not always depend on the bond strength of the cleaved bonds in the ground state. In order to understand the mechanism of β -cleavage processes a similar study has been made in which cleavage of both α - and β -bonds relative to the keto group are considered in the same molecule. We have employed the MINDO/3-CI method. Our experience⁹⁻¹¹ shows that a MINDO/3-CI treatment of organic molecules gives a qualitatively meaningful description of the various low-lying excited-state surfaces. The calculated excitation energies are almost in agreement with the observed values. On the other hand, MNDO-CI leads to large deviations from the observed excitation energies. Similar results of MNDO-CI calculations have been observed by others.¹² Although semiempirical methods are not reliable for obtaining accurate results, a trend in the results is obtained when a series of similar molecules is considered. The present paper deals with this trend, on which a concept can be developed which may be of use to organic chemists.

We have chosen a series of molecules RCOCH_2X ($\text{X} = \text{CH}_2\text{CH}_3, \text{OCH}_3, \text{SCH}_3$; $\text{R} = \text{CH}_3, \text{Ph}$). These molecules are conformationally flexible, especially in the ground state.¹³ Molecular mechanics calculations, dipole moment measurements and spectroscopic studies¹³⁻¹⁴ reveal that these molecules can exist in a number of conformations with small barriers to conformational change. In their lowest triplet states, MINDO/3 and MNDO calculations with geometry optimisations reveal that conformers **A** and **B** are important. The

detailed conformational studies, according to semiempirical methods, of these molecules will be published elsewhere.¹⁵ The main points to emerge are that in both acetyl and phenacyl sulfides, in the ground and lowest triplet states, the gauche conformer **B** is the most stable conformer. There is experimental evidence that keto sulfides exist in the *gauche* conformation in the excited state.⁸ The corresponding oxy compound and ketone have the *cis* conformer (**A**) as the most stable conformer. There is hardly any conformational change on excitation to the lowest triplet state.¹⁵ Evidence confirming that the oxy compound exists in the *cis* conformation in the lowest triplet state is also available.¹⁶

Scheme for Computation of Potential Energy Surfaces.—In this paper we deal with the theoretical potential energy surfaces (PES) for the α - and β -cleavage processes. For calculations of the PES for the various electronic states we have employed the extensive configuration interaction (CI) procedure in the singlet and triplet manifolds of the same molecule within the framework of the MINDO/3 method.¹⁷ We have considered all possible configurations arising from the top six occupied (MO) and the lowest six unoccupied molecular orbitals (MO). First, in a single configuration calculation, the geometry optimisations are carried out in the ground states as a function of elongation of the σ -bond length (α or β) adjacent to the chromophore. The MOs of the optimised geometry are then used to build singly- and doubly-excited configurations which are mixed by CI. The energy of the ground state is re-determined after mixing with the doubly-excited singlet configurations. The vertical excitation energies are then calculated at each value of the elongated bond length and are then added to the corresponding ground-state energies to obtain the PES for the excited states. This approach of determining the PES is particularly suited to those cases in which there is hardly any conformational change on excitation to the excited state. The wavefunctions of the excited states are a linear combination of several starting configurations having the same symmetry and spin multiplicity. We have ensured that any added configuration not present in the above CI program does not lead to any significant change in energy of the low-lying excited states. We have already seen¹⁰ that this method gives a qualitatively meaningful description of the low-lying excited-state surfaces of large organic molecules containing a heavy atom such as sulfur.

We have not carried out the geometry optimisation on the excited-state surfaces and, therefore, the exact location of the saddle point cannot be determined. For large molecules this is extremely tedious at the CI level at which the number of configurations is large. However, one can locate the transition state approximately at the crossing point of the two electronic states of different symmetries while their conformations are identical.¹⁸ Thus, calculations are performed with care to ensure that the results are qualitatively correct and that the height of the barriers reported here are called the diabatic barriers.



* 1 cal = 4.184 J.

Results and Discussion

The lowest triplet states in both acetylonyl and phenacyl sulfides lie at *ca.* 2.4 eV above the ground state. Non observation of the phosphorescence band in this region (516 nm) may be attributed to the rapid rate of various competing photo-reactions. The two peaks in the observed phosphorescence spectra of butyl phenacyl sulfide (see Fig. 3 of ref. 8) correspond to valerophenone (3.20 eV) and acetophenone (2.8 eV)¹⁹ which could be present as impurity and major photo-product, respectively, in the system. This state of phenacyl sulfide corresponds primarily to the transition from the HOMO orbital on sulfur to the π^*_{CO} level. These MOs are, however, delocalised. In fact, due to hyperconjugative effects in conformer **B**, the π^*_{CO} level shows considerable mixing with the $\sigma^*_{\text{C-S}}$ (β -bond). This should lead to a large decrease in the bond order of the C-S bond (β to the carbonyl) and a small increase in the bond order of the α -C-C bond in this $n_s\pi^*_{\text{CO}}$ configuration. The bond order index B_{a-b} of an a-b bond is calculated according to the definition of Meyer²⁰ as eqn. (1), where S is the overlap

$$B_{a-b} = \sum_{\mu} \sum_{\tau} (PS)_{\mu\tau}(PS)_{\tau\mu} \quad (1)$$

matrix and P the density matrix. In the semiempirical treatment S is the unit matrix. For molecules in the ground state, the bond-order indices of the α - and β -bonds are calculated for the equilibrium geometry using the most dominant configuration, where the doubly-excited configurations are ignored in the calculation of bond order. For acetylonyl sulfide, methoxyacetone and methyl propyl ketone in their lowest triplet states, the bond order index is calculated for the most dominant configuration in the CI expansion, their coefficients being in the range 0.95–0.98. However, the wavefunction of the lowest triplet state of phenacyl sulfide is given in the CI expansion, in which the different singly-excited states [eqn. (2)] make almost compar-

$${}^3\Psi = 0.57\Psi_{n_s \rightarrow \pi^*_{\text{CO}}} - 0.43\Psi_{\sigma_{\text{C-S}} \rightarrow \pi^*_{\text{CO}}} - 0.46\Psi_{n_{\text{CO}} \rightarrow \pi^*_{\text{C}}} + 0.33\Psi_{n_s \rightarrow \pi^*_{\text{CHCO}}} + \dots \quad (2)$$

able contributions to the total wavefunction. So allowance is made for all the major configurations in order to obtain the final bond-order index for the α - and β -bonds.

Table 1 shows the magnitude of the bond order of the α - and β -bonds in the ground and lowest triplet states. The results in Table 1 reveal that in acetylonyl and phenacyl sulfides the β -C-S bonds show considerable weakening in their lowest triplet states. The large decrease of the bond-order index on the β -C-S bonds is due to depopulation of the HOMO which has some amplitude on the C-S bonds and population of the π^*_{CO} orbital which has some antibonding β -C-S character.

Figs. 1 and 2 and Figs. 3 and 4 show the PESs of the various electronic states as functions of elongations of the α - and β -bonds in phenacyl sulfides and methoxyacetone, respectively. The energies of the appropriate radical limits are shown on the right hand side of those Figures. The energies of the separated radicals are obtained by the MINDO/3 + CI method with geometry optimisation in the ground states. Our results indicate that the energies of the ground and the lowest triplet states may converge to that of radical limits. The height of the ground state curves at the separated radical limits give an estimate of the bond strength. Our MINDO/3 calculations reveal that bond strengths of the β -bonds relative to the carbonyl group in acetylonyl sulfide (or phenacyl sulfide), methyl propyl ketone (diagram not shown) and methoxyacetone increase in the order C-S < C-C < C-O in their ground states. This is in qualitative agreement with the available bond energy data.²¹

Table 1 The bond-order indices of the α - and β -bonds in the ground and lowest triplet states

Molecule	Bonds	Ground state	Triplet state
Phenacyl sulfide (α 90°, β 180°)	$\alpha_{\text{C-C}}$	0.92	0.91
	$\beta_{\text{C-S}}$	0.93	0.69
Acetylonyl sulfide (α 90°, β 180°)	$\alpha_{\text{C-C}}$	0.93	1.00
	$\beta_{\text{C-S}}$	0.93	0.61
Methyl propyl ketone (α 180°, β 180°)	$\alpha_{\text{C-C}}$	0.92	0.81
	$\beta_{\text{C-C}}$	0.97	0.95
Methoxy acetone (α 180°, β 180°)	$\alpha_{\text{C-C}}$	0.89	0.78
	$\beta_{\text{C-O}}$	0.96	0.98

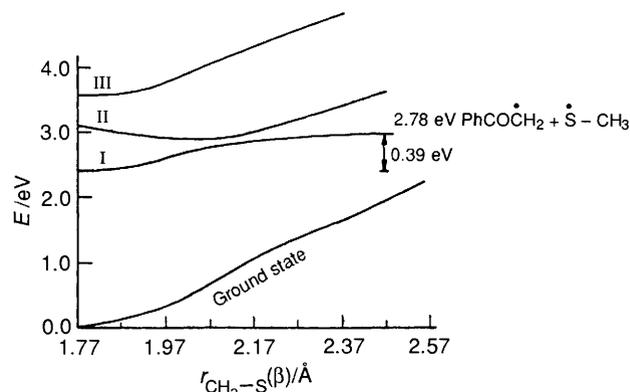


Fig. 1 Variation of energies of the various states for the α -cleavage process as a function of the $\alpha_{\text{C-C}}$ bond elongation in phenacyl sulfide. The appropriate radical limit is shown on the right of the Figure.

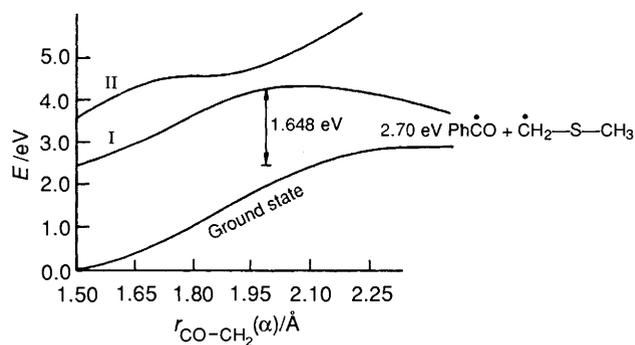


Fig. 2 Variation of energies of the various states for the β -cleavage process as a function of the $\beta_{\text{C-S}}$ bond elongation in phenacyl sulfide. The radical limit is shown on the right.

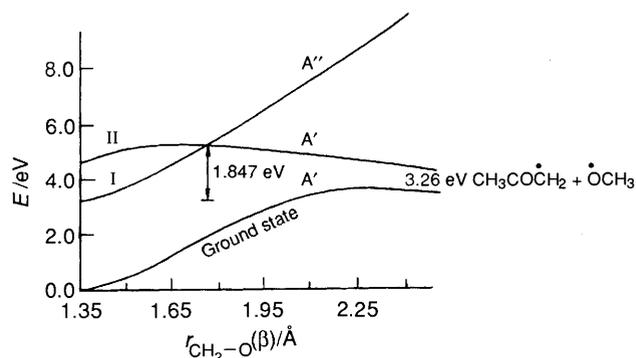


Fig. 3 Variation of energies of the various states for the β -cleavage process as a function of the $\beta_{\text{C-O}}$ bond elongation in methoxyacetone. The radical limit is shown on the right.

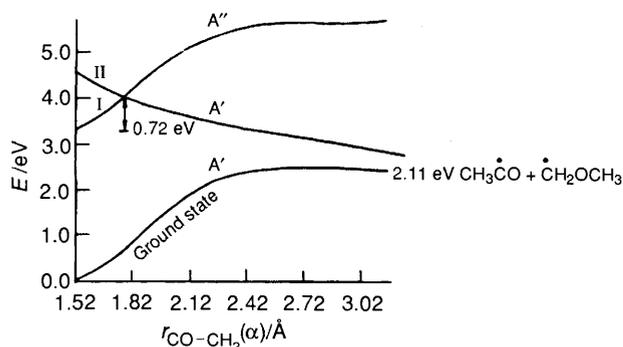


Fig. 4 Variation of energies of the various states for the α -cleavage process as a function of the α_{C-C} bond elongation in methoxyacetone. The radical limit is shown on the right.

Phenacyl sulfide has C_1 symmetry, therefore all electronic states are of the same symmetry. At the point of intended crossing the crossing is avoided due to the CI procedure. The β -cleavage process from the lowest triplet state (state I) is endothermic. The state II (triplet) which initially decreases with elongation of the β -C-S bond arises from transition from a MO which is primarily a σ_{C-S} orbital to the σ^*_{C-S} . The state III corresponds primarily to the $n_{CO}\pi^*_{CO}$ state which has been thought to be the reactive excited state by Wagner and Lindstorm,⁸ who observed the corresponding absorption band at 340 nm. This band corresponds to our calculated value of 3.4 eV (360 nm) for the singlet state III. Our analysis reveals that β -cleavage does not take place from the corresponding triplet state III. The molecule excited to the singlet state III reverts rapidly (presumably without changing conformation) to the state I (triplet) by a radiationless process and intersystem crossing followed by cleavage. The results in Figs. 1 and 2 show that the β -bond in phenacyl sulfide breaks more readily than the α -bond. Similar results are obtained for acetonyl sulfide (see Table 2).

We then examined the cleavage processes in methyl propyl ketone and methoxyacetone. Figs. 3 and 4 show the PESs of the various electronic states as a function of elongation of the α - and β -bonds in methoxyacetone and the energies of the appropriate radical limits in their ground state. These molecules exist as the stable conformer A (symmetry C_s) in the triplet state. The various states are therefore of either A' or A'' symmetry. The PESs of the different symmetry cross and the crossing can be avoided by a vibronic coupling in the triplet manifold. In this molecule the lowest triplet state is $n_{CO}\pi^*_{CO}$ (I) because the lone-pair orbital of the ether oxygen lies below that of the carbonyl oxygen. This state crosses the ${}^3n_{CO}\sigma^*$ state (II) at which the σ^* orbital is a delocalised MO to begin with. When the β -C-O bond is stretched this σ^* MO becomes increasingly localised on the C-O bond and on large elongation the $n_{CO}\sigma^*$ state goes to the radical limit ($CH_3COCH_2\cdot + \cdot OCH_3$). On the other hand, when the α -C-C bond is stretched in the same molecule the same σ^* MO becomes increasingly localised on the stretched C-C bond and the $n_{CO}\sigma^*$ state then reaches the appropriate radical limit, as shown in Fig. 4. In methyl propyl ketone the lowest triplet state is $n_{CO}\pi^*_{CO}$ which crosses the ${}^3n_{CO}\sigma^*$ state. The latter goes to the appropriate radical limits on stretching the α -C-C and/or β -C-C bond. The results in Figs. 3 and 4 show that the α -bond cleaves more rapidly than the β -CO bond. Similar results are obtained for methyl propyl ketone in which the α -C-C bond cleaves more readily than the β -C-C bond. We have also examined the cleavage of the γ -C-C bond (relative to the carbonyl) in the lowest triplet state of methyl propyl ketone. Our results reveal that the relative activation barriers increase in the order α bond < β bond < γ bond. The height of the

Table 2 Activation barriers for the α - and β -cleavage processes from the lowest triplet states. Energies are in kcal mol⁻¹

Molecule	α bond	β bond
Phenacyl sulfide Conformer B	34.6	6.4
Acetonyl sulfide Conformer B	31.1	9.8
Methoxyacetone Conformer A	13.2	39.2
Methyl propyl ketone Conformer A	20.4	41.6

barriers are calculated from the points of crossing. Table 2 gives the relative activation barriers for the α - and β -cleavage processes in various molecules from their lowest triplet states, after taking into account the appropriate zero-point energy corrections. For example, for the cleavage of the C-S bond we consider the zero-point energy of the C-S stretching motion ($\tilde{\nu} \approx 700$ – 900 cm⁻¹), because it is this vibration which is lost in the transition state. Results reveal that in keto sulfides the β -bond cleaves readily in the lowest triplet state while in alkoxy ketones the α -bond cleaves more readily than the β -bond.

If we assume the pre-exponential factor for the unimolecular cleavage process to be 10^{13} s⁻¹, which is expected for zero entropy of activation, the rate constants for the triplet state β -cleavage process are ca. 10^8 s⁻¹ for phenacyl sulfide and 10^5 s⁻¹ for acetonyl sulfide at 25 °C. The observed rapid rate of the β -cleavage process in phenacyl sulfide⁸ is in agreement with this result.

Conclusions

It is now evident that there are two reasons for the different behaviour of keto sulfides and keto ethers on photoexcitation. Firstly, the reactive conformers are different in the two molecules. Secondly, the lone-pair ionisation potential of sulfur is lower whereas that of the ether oxygen is higher than that of the carbonyl oxygen. This leads to different reactive excited states in the two molecules.

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