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Activation Barrier for the α-Cleavage Process in Thiones

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The occurrence of the Norrish type I α-cleavage process in some thio compounds has been examined by using the MINDO/3 method and employing the configuration interaction. Results reveal that where the radiationless process is not efficient, thio compounds can undergo photodissociation into radicals in their lowest triplet and singlet excited states. The activation barriers in all these cases arise from an avoided crossing between two states of different symmetries. The calculations of activation barriers by the CNDO-CI and MINDO-CI procedures reveal that the MINDO-CI method leads to realistic values of the activation energies.

Introduction

Recently there has developed an increasing interest in the study of photochemistry of thio compounds. Thioformaldehyde is photostable and does not undergo the Norrish type I cleavage, unlike formaldehyde.[1] It has been suggested[2] that this may be due to the low excitation energy and short life time of thioformaldehyde. The energies of the lowest (nπ*) singlet and triplet states are 46 and 41 kcal M^{-1}, respectively, while the corresponding energies for formaldehyde are 81 and 72 kcal M^{-1}, respectively.[1] The Franck–Condon profile[2] of H_2CS suggests that the ground and lowest excited states have similar planar structures, while formaldehyde has an out-of-plane angle of about 40°[3] in its lowest triplet state. This would make the quenching of the triplet state by the ground-state thione more important. Thus, in H_2CS, photodissociation cannot be an important decay process. It would be of interest to examine photodissociation in those thio compounds which do not have very low excitation energies. In fact, recently, the occurrence of the Norrish type I α-cleavage has been established in substituted β-dithio lactones[4] and cyclopropenethiones[5] where the lowest singlet and triplet state energies are around 64 and 60 kcal M^{-1}, respectively.

The Norrish type I α-cleavage process is an unimolecular reaction. For an unimolecular reaction to compete in a singlet state with fluorescence the activation energy should be equal or below ~9 kcal M^{-1}. For a similar process to compete, in a triplet state, with phosphorescence these numbers become 18 kcal M^{-1}. For both unimolecular processes the preexponential factor is chosen to be 10^8 s^{-1}. Actual activation energies of the α-cleavage reactions have not been measured for any system. The reported experimental values for some ketones in the literature are of doubtful validity for reasons discussed by Mirbach et al.[6]

In this paper we shall deal with the theoretical potential energy surfaces (PES) for the α-cleavage process in some thio compounds. For this purpose we shall adopt the semiempirical molecular orbital (MO) theories which still occupy a unique position in organic chemistry. There are basically two approaches. One approach, exemplified by CNDO (or INDO),[7,8] argues that theory represents an approximation to the minimal Slater basis ab initio method, and therefore no expectation should be made to obtain experimental molecular properties. In the other approach, exemplified by MINDO family of methods,[9,10] the adjustable parameters are so chosen that theory directly reproduces experimental properties. This form of theory sometimes gives results that exceed the accuracy of the ab initio methods.[11] A review[12] on the application of MINDO/3 reveals that this method has not been applied to the study of the α-cleavage processes. Recently, an application of MINDO/3 with configuration interaction (CI) gives rise to very realistic activation barriers in PES of the α-cleavage processes in excited ketones.[13] On the other hand, the standard ab initio methods with CI give rise to very large activation barriers.[14,15] It is therefore argued that photocleavage of ketones into radicals may take place on the ground state reaction surface via the reactive intersystem crossing.[16]

Concepts and Computational Details

When the bond A–B in a homopolar or nearly homopolar diatomic molecule is elongated the bonding MO σ and the antibonding MO σ* are respectively destabilized and stabilized. The electronic states $^1(\sigma^2)$ and $^3(\sigma^1\sigma^{*1})$ are destabilized and stabilized, respectively, as the bond length A–B is increased. At the end of the cleavage these two states correlate with the diradical states $^{1,3}D_{\sigma\sigma}$ (Figure 1).[17] Normally the dissociative state $^3(\sigma^1\sigma^{*1})$ is of high energy and cannot easily be populated. If the molecule has a chromophore with a heteroatom, its (nπ*) state usually lies below the $(\sigma^1\sigma^{*1})$ state.

In thiocarbonyl compounds, the lone pair orbital "n" or the highest occupied σ-MO is not just the atomic orbital localized on the sulfur atom. It has been found that this n orbital is delocalized over the σ-bonds adjacent to the thiocarbonyl group. Since the π-orbitals are hardly affected when a σ-bond adjacent to the π-system is elongated the energy of the so-called (nπ*) state increases as the α-bond is elongated and crosses the dissociative $^3(\sigma^1\sigma^{*1})$

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[1] Mayo, P. D. *Acc. Chem. Res.* **1976**, *9*, 52.

[2] Clouthier, D. J.; Kerr, C. M. L.; Ramsay, D. A. *Chem. Phys.* **1981**, *56*, 73.

[3] Clouthier, D. J.; Ramsay, D. A. *Annu. Rev. Phys. Chem.* **1983**, *34*, 31.

[4] Muthuramu, K.; Sundari, B.; Ramamurthy, V. *Tetrahedron* **1983**, *39*, 2719.

[5] Singh, S.; Bhadbhade, M. M.; Venkatesan, K.; Ramamurthy, V. *J. Org. Chem.* **1982**, *47*, 3550.

[6] Mirbach, M. F.; Mirbach, M. J.; Liu, K. C.; Turro, N. J. *J. Photochem.* **1978**, *8*, 299.

[7] Pople, J. A.; Segal, G. A. *J. Chem. Phys.* **1966**, *44*, 3289.

[8] Pople, J. A.; Beveridge, D. L.; Dobosh, P. A. *J. Chem. Phys.* **1967**, *47*, 2026.

[9] Dewar, M. J. S.; Haselbach, E. *J. Am. Chem. Soc.* **1970**, *92*, 590.

[10] Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285.

[11] Flanigan, M. C.; Komornicki, A.; McIver, J. W., Jr. In *Modern Theoretical Chemistry*; Segal, G. A.; Ed.; Plenum: New York, 1977; Sect. B, Vol. 8, Chapter 1.

[12] Lewis, D. F. V. *Chem. Rev.* **1986**, *86*, 1111.

[13] Sumathi, K.; Chandra, A. K. *J. Photochem. Photobiol., A* **1937**, *40*, 265.

[14] Jaffe, R. L.; Hayes, D. M.; Morokuma, K. *J. Chem. Phys.* **1974**, *60*, 5108.

[15] Grimbert, D.; Salem, L. *Chem. Phys. Lett.* **1976**, *43*, 435.

[16] Halevi, E. A.; Trindle, C. *Isr. J. Chem.* **1977**, *16*, 283.

[17] Sevin, A.; Bigot, B.; Devaquet, A. *Tetrahedron* **1978**, *34*, 3275.

0022-3263/88/1953-1239$01.50/0

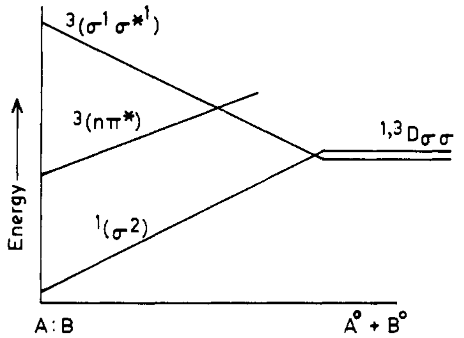

Figure 1. Stabilization and destabilization of electronic states of a σ-chemical bond in AB when the bond is elongated.

Table I. Activation Barriers in the α-Cleavage Processes

			activation barrier, kcal M^{-1}		
entry	molecules	α-bond	MINDO/ CI	CNDO/ CI	ab initio
1	formaldehyde	C–H	6.9	75.0	64.0[a]
2	Thioformaldehyde	C–H	18.0	164.0	50.4[b]
3	cyclopropenethione	C–C	12.5	86.0	
4	3-mercapto-2,2,4-trimethyldithio-3-pentenoic acid	C–S	4.6	83.4	
	β-thiolactone	C–C	7.8		

[a] Reference 15; STO-3G + CI. [b] Reference 26; 3-21G + CI + geometry optimization.

state (Figure 1). This crossing is usually avoided either through the vibronic coupling or through the spin–orbit coupling as these two states are of different symmetries. Thus, the molecule in its (nπ*) state is linked to the stable $^3D_{\sigma\sigma}$ diradical state. The barrier observed in such reaction profiles reflects the difficulty for energy to flow from the π- to the σ-plane.

For calculations of the PES for the various electronic states we have employed the CI procedure in the singlet and triplet manifolds and within the framework of the CNDO/2 and MINDO/3 methods. First, in a single configuration calculation the geometry optimizations are carried out in the corresponding residues in the ground states as a function of elongation of the σ-bond length adjacent to the chromophore. These MO's are then used to build singly and doubly excited configurations which are mixed by CI. The energy of the ground state is redetermined after mixing with the doubly excited singlet configurations. The vertical excitation energies are then calculated at each value of the elongated bond length and then added to the corresponding ground-state energies to obtain the PES for the excited states. The wave functions of the excited states are a linear combination of the various starting configurations having the same symmetry and spin multiplicity.

Results

Our results show that the lowest singlet and triplet states for all molecules in Table I are primarily the (nπ*) states. They are nearly of the same energies in each molecule and are hardly affected by CI. The activation barriers for the α-cleavage processes obtained by the CNDO-CI and MINDO-CI procedures from their respective PES are reported in Table I. For comparison the result for formaldehyde is given, and the results obtained by the ab initio method for H_2CO and H_2CS are also reported in the last column of Table I. Our results reveal that both the CNDO-CI and ab initio CI procedures lead to overestimation of the heights of the activation barrier while the MINDO-CI procedure gives realistic values for unimolecular reactions from the excited states. In Figures 2, 4, and 6 are shown the reaction surfaces of the various electronic states of thioformaldehyde, cyclopropenethione, and β-dithio lactone obtained by the MINDO-CI method. The various electronic states in the above figures are indicated by the most dominant configuration in the CI wave functions.

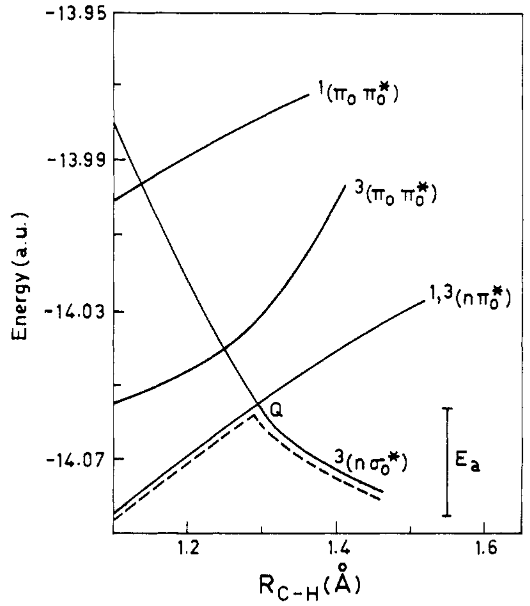

Figure 2. Reaction profiles of some electronic states of thioformaldehyde for the α-cleavage process.

Discussion

Thioformaldehyde. Figure 2 shows the PES for the α-cleavage process in thioformaldehyde in its various electronic states. The process from the ground state (not shown in Figure 2) is an usual homolytic bond rupture which is energetically costlier than the molecular fragmentation from the excited states. The process from the lowest^{1,3} (nπ*) state surfaces is of practical importance. These surfaces cross the $^3(n\sigma^*)$ state surface at the point Q (Figure 2). Since the height of the activation barrier is ~18 kcal M^{-1} which is the upper limit for a unimolecular reaction to compete with phosphorescence if the life time is 1 μs, the reaction from the lowest singlet state is ruled out. At the same level of calculations formaldehyde requires an activation barrier of 6.9 kcal M^{-1} for its α-cleavage from its lowest triplet state.

When an α-bond is elongated in H_2CS its symmetry is reduced from C_{2v} to C_s. In the C_s symmetry the $^3(n\pi^*)$ state is A'' and the $^3(n\sigma^*)$ state is A'. So the crossing at the point Q (in Figure 2) can be avoided by an out-of-plane nuclear distortion of the A'' symmetry. The reactive $^3(n\pi^*)$ state is, thus linked to the dissociative $^3(n\sigma^*)$ state at the point Q through the vibronic coupling matrix element $\langle n\sigma^*|dV/dQ|n\pi^*\rangle Q$, where V is the one-electron nuclear-electron potential operator and Q the nuclear coordinate of the A'' symmetry. Since the value of $\langle\sigma^*|dV/dQ|\pi^*\rangle Q$ is approximately 500 cm^{-1} for $Q \approx 1.0$ (au) the actual activation energy[18] from the lowest $^3(n\pi^*)$ state should be slightly less than 18 kcal M^{-1}. Although this value of the barrier height is within the upper limit, the nonobservation

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[18] Bigot, B.; Devaquet, A.; Turro, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 6.

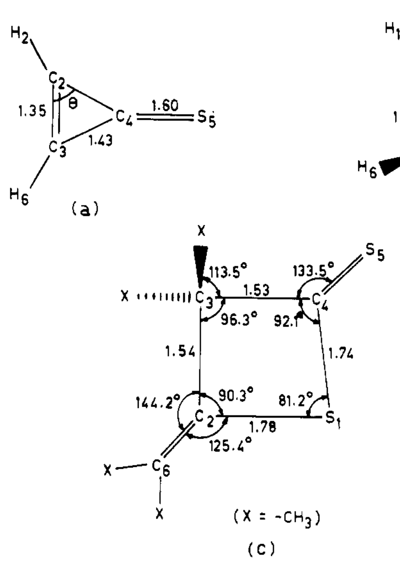

Figure 3. MINDO/3 results for the singlet ground (a) and the lowest triplet ($n\pi^*$) state (b) of cyclopropenethione and the singlet ground state (c) of 3-mercapto-2,2,4-trimethyldithio-3-pentenoic acid β-thiolactone. (a) C_{2v} symmetry, $\theta \approx 61.5°$. (b) C_1 symmetry, $\phi(H_6)$; the out-of-plane bending angle corresponds to the angle between the C_3–H_6 bond, and the plane of the ring is 30.6°; $\phi(H_1)$ = 2.6°. (c) C_s symmetry, all dihedral angles are close to 0°. All bond lengths are given in Å and bond angles in degrees.

of photodissociation in H_2CS might be due to its very effective quenching of the lowest triplet state by the ground-state thione.

Cyclopropenethione. We then consider cyclopropenethione where the optimized geometries of the ground and the lowest triplet states are different and shown in Figure 3a,b. The lowest excitation energies[19] in some substituted cyclopropenethiones are also higher than that observed in H_2CS. The geometries in Figure 3 are arrived at by the single configuration MINDO/3 calculations. Single-configuration STO-3G calculations with geometry optimizations also lead to similar geometries of the lowest triplet state.[20] It is rather obvious that this structure of the lowest triplet tends toward the geometry of the α-cleavage intermediate with the longest C_3–C_4 bond in the ring corresponding to the α-bond being broken and the pyramidal C_3 atom becoming the ultimate carbene center.[21]

Figure 4 shows the PES vs θ of the various electronic states including the ground state (GS), where θ is the angle at the C_2 corner of the triangle (Figure 3a). Our CI calculations of cyclopropenethione give two low-lying ($n\pi^*$) states which differ in energies by 4.8 kcal M^{-1} only, when $\theta \approx 61.5°$. For each ($n\pi^*$) state the singlet–triplet separation is negligibly small for all values of θ. It is seen that the lowest state, i.e., $^{1,3}(n\pi_1^*)$, surface increases in energy when θ is increased from the equilibrium value of 61.5°. On the other hand, the next higher energy state, i.e., $^{1,3}(n\pi_0^*)$, decreases in energy with the increase of θ and becomes almost constant in energies at larger values of θ.

It will be useful at this stage to examine how the various MO's of cyclopropenethione behave as the three-membered ring gradually opens up. In Figure 5 are shown how some high-lying occupied and low-lying unoccupied MO's change their positions when θ is increased to 90°. In the equilibrium structure of the ground-state π_0^* and π_1^* MO's differ in energies by 4.4 kcal. When the symmetry of the molecule is reduced from C_{2v} to C_s the π_0^* and π_1^* MO's interchange their positions. The subscript 0, 1, etc. determines the sequence of energies of the various MO's of each type in Figure 5. In the C_{2v} symmetry π_0^* is primarily the MO localized on the C_2 and C_3 atoms with a slightly bonding character between C_3 and C_4 atoms, while π_1^* is primarily localized on the C_4 and S atoms with an anti-

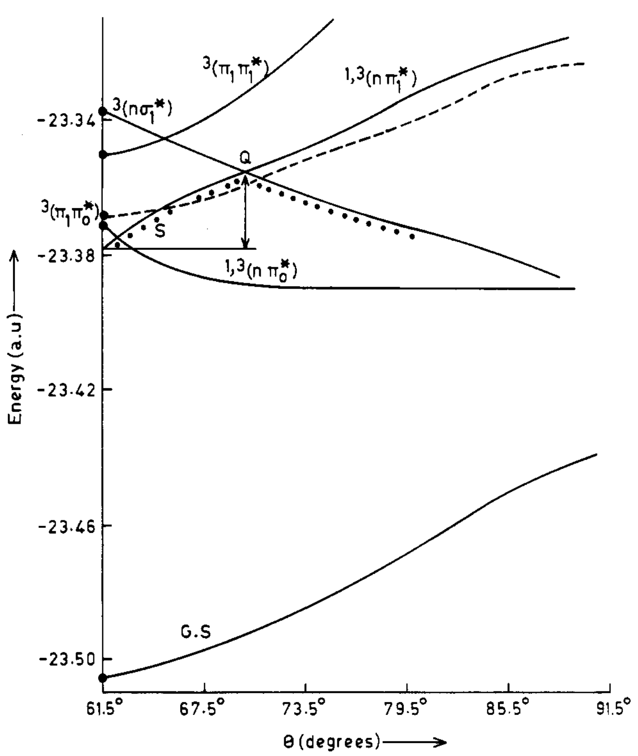

Figure 4. Reaction profiles of the ground state and some low-lying excited states of cyclopropenethione as a function of θ.

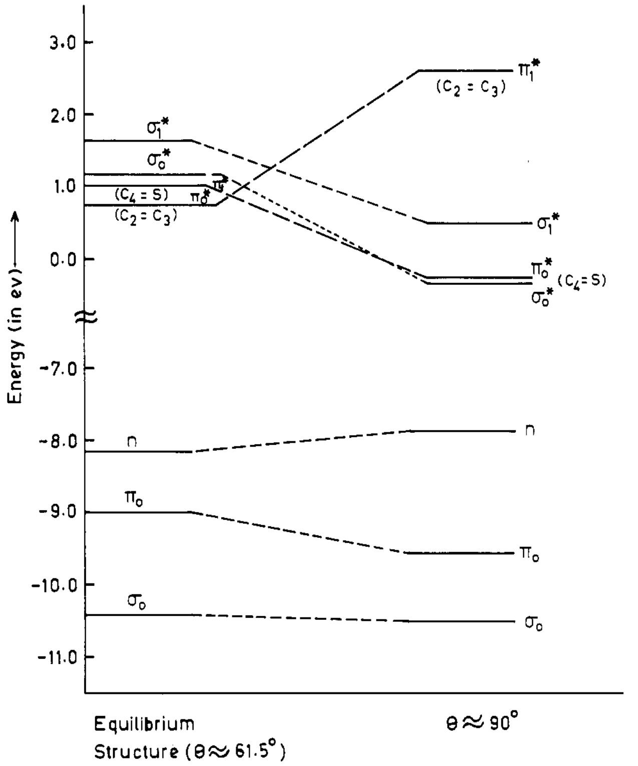

Figure 5. Changes in positions of the molecular orbitals of cyclopropenethione when θ is increased from 61.5° to 90°.

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[19] Singh, S. Ph.D. Thesis, Indian Institute of Science, Bangalore, India, 1985.

[20] Chandrasekhar, J. Indian Institute of Science, Bangalore, India, unpublished results.

[21] Usha, G.; Nageswar Rao, B.; Chandrasekhar, J.; Ramamurthy, V. *J. Org. Chem.* **1986**, *51*, 3630.

bonding character between C_3 and C_4. When θ is increased one expects π_1^* to decrease and π_0^* to increase in energies. Thus, as the ring opens up the densities on C_4 and S increase at the expense of densities on C_2 and C_3 in the $^{1,3}(n\pi_0^*)$ state. This would mean that the spin–orbit coupling between the singlet ground state and the $^3(n\pi_0^*)$ state could be significant at higher values of θ. Therefore, molecules moving along the $^3(n\pi_0^*)$ state surface can decay by a radiationless process to the ground-state surface, giving back the reactant molecule in the ground state. The extra energy can be effectively dissipated in the environment of the solvent in which the reaction is carried out.[5] Besides the favorable spin–orbit coupling for radiationless decay, the rapid internal conversion to GS is also expected through a "funnel"-type of mechanism in a region of geometries where the energy gap is small and the difference in slopes of the two surfaces is large.[22,23]

The two $(n\pi^*)$ state surfaces, i.e., $^{1,3}(n\pi_0^*)$ and $^{1,3}(n\pi_1^*)$ (Figure 4) are of the same symmetry in the C_s group and cross at the point S. Since the barrier at this point of crossing is low, the reactant molecules can easily overcome this barrier and move along the $^{1,3}(n\pi_1^*)$-state surfaces. The dissociative $^3(n\sigma_1^*)$-state surface decreases in energy when θ is increased and crosses the $^{1,3}(n\pi_1^*)$-state surfaces near $\theta \sim 70°$. At the point of crossing Q as indicated in Figure 4, the crossing can be avoided either through the spin–orbit coupling given by the integral $\langle {}^1n\pi_1^*|H_{so}|{}^3n\sigma_1^*\rangle$ or through the nuclear distortion of the A'' symmetry given by the integral $\langle {}^3n\pi_1^*|(\mathrm{d}V/\mathrm{d}Q)Q|{}^3n\sigma_1^*\rangle$. Both these matrix elements depend on the magnitude of transition densities $\rho_{\sigma_1^*\pi_1^*}$ localized either on the heavy atom(s) for the spin–orbit coupling to become effective or on any atom which contributes to the out-of-plane nuclear distortion of the A'' symmetry. Near the point of crossing Q, the value of $\rho_{\sigma_1^*\pi_1^*}$ on sulfur is negligible and the spin–orbit coupling is expected to be ineffective. The vibronic matrix element can be reduced to one-electron integrals over $\rho_{\sigma_1^*\pi_1^*}$ as

$$\langle n\pi_1^*|\mathrm{d}V/\mathrm{d}Q|n\sigma_1^*\rangle = \langle \pi_1^*|\mathrm{d}V/\mathrm{d}Q|\sigma_1^*\rangle = \int \rho_{\sigma_1^*\pi_1^*}(\cos\theta/r^2)\mathrm{d}\tau \quad (1)$$

The integral on the right hand side of eq 1 is called transition force and is large when the transition density is localized in the region of nuclear motion.[24] We should therefore consider the one-center integrals in eq 1. The transition density $\rho_{\sigma_1^*\pi_1^*}$ on any atom is made up of S, p_x, p_y, and p_z orbitals. All one-center integrals except those which involve S and p_z orbitals on one center vanish. Both CNDO/2 and MINDO/3 calculations reveal that such density is largest on C_3 in cyclopropenethione near the point of crossing Q. We, therefore, expect large pyramidalization of the C_3 atom in the transition state. An early indication of pyramidalization of the C_3 atom is given in the optimized geometry of the lowest triplet state of cyclopropenethione (see Figure 3). This has been used to explain the observed regioselectivity in the α-cleavage process of substituted cyclopropenethiones.[21] The height of the activation barrier calculated from the point of crossing Q as indicated in Figure 4 is 12.5 kcal M^{-1}, which is within the upper limit required for an unimolecular process to compete with phosphorescence. But, with such a barrier, an unimolecular process cannot compete with fluorescence. We, therefore, conclude, both from the height of the barrier and from the ineffective spin–orbit coupling that the α-cleavage process in cyclopropenethione can take place in the lowest triplet state.

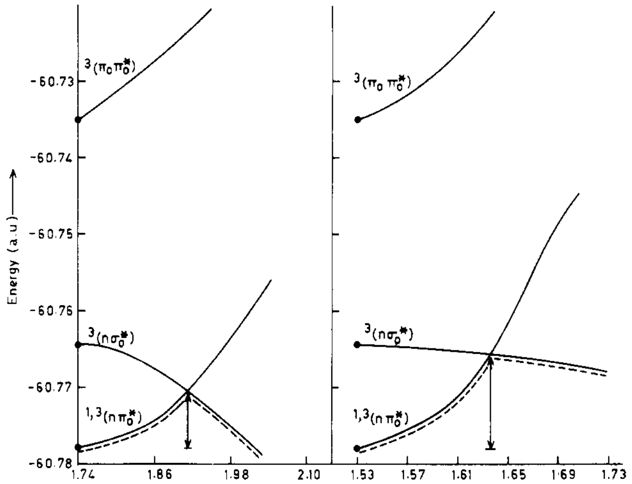

Figure 6. Reaction profiles of some electronic states of a β-dithio lactone for the α-cleavage process as a function of (a) the C–S bond elongation and (b) the C–C bond elongation.

β-Dithio Lactone. We then consider 3-mercapto-2,2,4 trimethyldithio-3-pentenoic acid β-thiolactone. The four-membered ring in this β-dithio lactone is planar in its ground state and nearly planar in the lowest triplet state. The optimized geometry of the ground state is shown in Figure 3c. Figure 6 shows the PES of its various low-lying excited electronic states as functions of the α C–S bond and α C–C bond lengths. The cleavage processes from the ground state (not shown in Figure 6) are the usual homolytic bond ruptures where the C–S bond breaks more readily than the C–C bond. But these are energetically higher than the molecular fragmentation from the excited states. The processes from the lowest $^{1,3}(n\pi^*)$-state surfaces are of practical importance in photochemistry. It is seen that these surfaces increase in energy when either the α C–S bond or the α C–C bond is elongated, while the $^3(n\sigma_0^*)$-state decreases in energy and crosses the $^{1,3}(n\pi_0^*)$-state surfaces. At the point of crossing, Q in Figure 6 the crossing can be avoided either through the spin–orbit coupling given by the integral $\langle {}^1n\pi_0^*|H_{so}|{}^3n\sigma_0^*\rangle$ or through an out-of-plane nuclear distortion given by the integral $\langle {}^3n\pi_0^*|\mathrm{d}V/\mathrm{d}Q|{}^3n\sigma_0^*\rangle Q$. These integrals depend on the magnitude of transition densities $\rho_{\sigma_0^*\pi_0^*}$ on different atoms of β-dithio lactone near the point of crossing, Q. On the the basis of these densities, the spin–orbit coupling is found to be nearly as important as the vibronic coupling with pyramidalization of the C_4 atom. The height of the activation barrier calculated from the point of crossing Q in Figure 6 is 4.6 kcal M^{-1} for the cleavage of the α C–S bond and 7.8 kcal M^{-1} for the cleavage of the α C–C bond adjacent to the thiocarbonyl group. Our calculations predict the preferential photocleavage of the C–S bond rather than the C–C bond in β-dithio lactones. This has been established in a series of experiments with the various substituted β-dithio lactones.[4] Similar calculations using the CNDO-CI procedure predict cleavage of the α C–S bond in the lowest $^{1,3}(n\pi^*)$ state with the activation energy of 83.4 kcal M^{-1}. On the other hand when the α C–C bond is elongated, no singly excited state decreases in energy.

Since neither triplet sensitizer sensitizes nor a triplet quencher quenches the α-cleavage process in β-dithio lactones, it was concluded that the reactive state was most likely to be the $^1(n\pi_0^*)$ state.[4] Since our calculated activation barrier by the MINDO-CI method for the α-cleavage process is less than 9 kcal M^{-1}, it is quite possible that

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(22) Michl, J. *Top. Curr. Chem.* **1974**, *46*, 1.

(23) Salem, L.; Leforestier, C.; Segal, G.; Wetmore, R. *J. Am. Chem. Soc.* **1975**, *97*, 479.

(24) Salem, L. *Chem. Phys. Lett.* **1969**, *3*, 99.

reaction takes place in the lowest excited singlet state. It is also to be noted that the α C–C cleavage process does not require very much higher activation barrier. The reported observation[25] of the α-cleavage process in cyclobutane dithione in its lowest excited singlet state is not surprising.

Results in Table I reveal that the calculated activation barriers for photodissociation into radicals on the lowest singlet or triplet ($n\pi^*$) surfaces obtained by the CNDO-CI procedure are approximately an order of magnitude higher than that obtained by the MINDO-CI procedure. But, both methods lead to approximately similar trend. It should be noted that ab initio calculations with geometry optimization in the lowest excited state also leads to very high activation barrier in most compounds. From the present results and our previous observations,[13] we tend to believe that the present MINDO-CI procedure leads to more realistic values of activation energies for the photochemical α-cleavage processes.

Conclusions

Although the activation barrier for the α-cleavage process in H_2CS is within the upper limit required for an unimolecular process to compete with phosphorescence, the nonobservation of photocleavage is due to the effective quenching of its triplet state by the ground state. In cyclopropenethiones the α-cleavage process can take place in its lowest triplet state with an activation barrier of about 12.5 kcal M^{-1}. In β-dithio lactones the similar process can take place in its lowest excited singlet state as its activation barrier is even lower.

Registry No. Formaldehyde, 50-00-0; thioformaldehyde, 865-36-1; cyclopropenethione, 69903-36-2; 3-mercapto-2,2,4-trimethyldithio-3-pentenoic acid β-thiolactone, 10181-61-0.

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(25) Muthuramu, K.; Ramamurthy, V. *J. Org. Chem.* **1980**, *45*, 4532.

(26) Pope, S. A.; Miller, I.; Guest, M. F. *J. Am. Chem. Soc.* **1985**, *107*, 3789.

Ruthenium Carbonyl Catalyzed Reductive Carbonylation of Aromatic Nitro Compounds. A Selective Route to Carbamates

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$Ru_3(CO)_{12}$ (1) and $Ru(CO)_3(PPh_3)_2$ (2) catalyze the reductive carbonylation of nitrobenzene and of substituted aromatic mononitro compounds to give the corresponding methylcarbamates, in toluene–methanol, at 160–170 °C and 60 atm, with high selectivity, in the presence of $NEt_4{}^+Cl^-$ as cocatalyst. Compound 1 also catalyzes the conversion of 2,4-dinitrotoluene into the corresponding dicarbamate although less efficiently. The effects of CO pressure, reaction temperature, and amount and nature of the added alcohol and cocatalyst have been studied. The mechanism of the reaction catalyzed by 1 has been investigated by studying the reactivity and catalytic activity of possible intermediates.

Introduction

The catalytic carbonylation of aromatic nitro compounds is an area of current interest, both from an academic and an industrial viewpoint.[1,2] Many important nitrogen-containing organic compounds such as isocyanates, carbamates, ureas, azo compounds, Schiff bases, amines, and heterocyclic derivatives can now be selectively obtained in this way. However, the potential utility of these reactions has not yet been fully explored and, for example, only very recently we reported that the carbonylation of 2-nitrostyrenes catalyzed by $Fe(CO)_5$, $Ru_3(CO)_{12}$, and $Rh_6(CO)_{16}$ gives indoles in good yields.[3] We also recently briefly reported that $Ru_3(CO)_{12}$ (1) and $Ru(CO)_3(PPh_3)_2$ (2) catalyze the reductive carbonylation of aromatic nitro compounds to the corresponding carbamates with high selectivity in the presence of $NEt_4{}^+Cl^-$ as cocatalyst (eq 1).[4]

$$ArNO_2 + 3CO + MeOH \xrightarrow[\substack{NEt_4{}^+Cl^- \\ toluene}]{Ru\ cat.} ArNHCO_2Me + 2CO_2 \quad (1)$$

We report here a full account of this work. Carbamates are important pesticides and, moreover, they can be transformed into isocyanates by thermal cracking (eq 2).[2]

$$ArNHCO_2R \xrightarrow{T} ArNCO + ROH \quad (2)$$

They are usually obtained by reaction with alcohols of the corresponding isocyanates which, on the other hand, are obtained by reaction of phosgene with amines (eq 3).[5]

$$ArNH_2 + COCl_2 \rightarrow ArNCO + 2HCl \quad (3)$$

Thus the discovery of alternative syntheses of carbamates is of interest not only in view of the importance of these chemical products but would also give a phosgene-free route to isocyanates, which are of practical interest in the manufacture of polyurethanes. In the patent literature there are many reports on the synthesis of carbamates by reductive carbonylation of aromatic nitro compounds in the presence of alcohols catalyzed by heterogeneous, usually complex, catalytic systems.[2] One of these based on metallic palladium with iron(III) chloride and pyridine as cocatalysts has been considered of industrial interest.[6]

Homogeneous catalysts are also known for this reaction.[2] The catalytic system discovered by us works in relatively mild conditions, and it is one of the most selective reported

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(1) Iqbal, A. F. *Chemtech* **1974**, 566.

(2) Cenini, S.; Pizzotti, M.; Crotti, C. *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; Reidel: Dordrecht, 1988; Vol. VI.

(3) Crotti, C.; Cenini, S.; Rindone, B.; Tollari, S.; Demartin, F. *J. Chem. Soc., Chem. Commun.* **1986**, 784.

(4) Cenini, S.; Pizzotti, M.; Crotti, C.; Porta, F.; La Monica, G. *J. Chem. Soc., Chem. Commun.* **1984**, 1286; Italian Patent 21591 A/83, June 7, 1983.

(5) Ozaki, S. *Chem. Rev.* **1972**, *72*, 457.

(6) Mitsui Toatsu, *Chem. Week* **1977**, *March 9*, 43.

0022-3263/88/1953-1243$01.50/0