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Theoretical Study on the Photochemical C-C Bond Cleavage Reaction via Acetophenone-type Excited Triplet State

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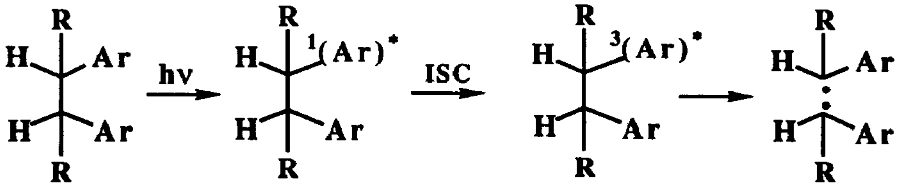
Summary: Electronic interaction between Cα-Cβ σ bonds of the alkyl groups and π-orbitals on the 4-acetylphenyl ring in the lowest triplet state of 4-acetylphenylpropane and 1,2-bis(4-acetylphenyl)ethane was studied as a function of Cα-Cβ bond length by means of semi-empirical MNDO MO calculations. The transition and final states of the title reaction were energetically estimated from potential curves of the lowest and σ,σ* triplet states to determine energy barriers and heats of reaction. The reactivity features of the photoreaction were discussed on the basis of these results.

The activation of a C-C σ bond in organic compounds by one-electron oxidation or reduction has received considerable attention in recent years from synthetic and mechanistic viewpoints.[1] A MO theoretical study on the electronic structure of ethylbenzene radical cation has indicateed that interaction between the singly occupied π-orbital of the phenyl ring and the σ- and σ*-orbitals of the ethyl group induces a dissociative reactivity in the C-C σ bond of the radical cation.[2] We have demonstrated experimentally that the photocleavage reaction of C-C σ bonds in 1,2-bis(4-acetylphenyl)cyclopropane,[3] 1,2-bis(4-acetylphenyl)cyclobutane,[4] and 2,3-bis(4-acetylphenyl)butane[5] occurs via their excited triplet states (Scheme 1). The reactivity in these photoreactions depended on molecular strain and also on conformation of the molecules. In fact, the highly strained cyclopropane and cyclobutane derivatives afforded efficiently 1,3- and 1,4-biradicals, respectively, from their excited triplet state without receiving pronounced quenching by any kind of triplet quenchers. In contrast, the less strained ethane derivative



R, R = CH_3, CH_3 ; $-(CH_2)_{n-2}-$ (n = 3 - 6)   Ar = $4\text{-}CH_3COC_6H_4$

Scheme 1.

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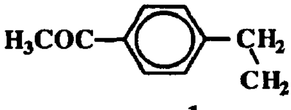
underwent the photocleavage reaction with less efficiency and its triplet state was efficiently quenched by triplet quenchers. In order to gain insight into the electronic and mechanistic features of these photoreactions, we have studied the electronic structure of 1-(4-acetylphenyl)propane (**1**) and 1,2-bis(4-acetylphenyl)ethane (**2**) that may serve as simplified model compounds for the above-mentioned photocleavage reaction. We now report the results of a MO theoretical study on the photocleavage reaction of these compounds. We focussed our attention on the $C\alpha$-$C\beta$ bond of propyl group or dimethylene group and π-electrons on the 4-acetylphenyl ring of these compounds in their excited triplet states. A considerable change in the electronic stuctutre of the $C\alpha$-$C\beta$ bond occurred during the reaction, particularly in the vicinity of the transition state.

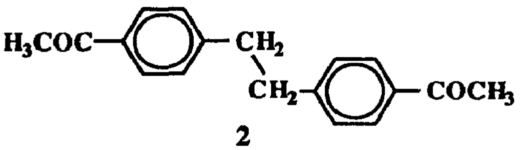
All calculations were carried out by the UHF method with the MNDO approximation,[6] except for the S_0 states. Variable geometrical parameters chosen for energy calculations of **1** and **2** were the dihedral angle φ and the $C\alpha$-$C\beta$ bond length r (see Figure 1). Ultimate products in the model photoreactions are (4-acetylphenyl)methyl radical and ethyl radical for **1** and two (4-acetylphenyl)methyl radicals for **2**. Geometries of the molecules were fully optimized by the energy gradient method with the Flecher-Powell algorithm.[7]

Geometry optimizations were performed for the S_0 and T_1 states of **1** and **2**; for the S_0 state, the RHF method was used. Electronic excitation to the T_1 state caused structural deformations to some extent for both the compounds; shortening of the C-C bond between the acetyl and phenyl groups due to incorporation of a bonding character in π^*-orbital, and lengthening of the C=O double bond due to incorporation of a n,π^* character. Potential energy curves (PEC's) for rotation of the 4-acetylphenyl ring of **1** in the S_0 and T_1 states were estimated as a function of the dihedral angle φ. They were quite similar and the barrier height was 22.2 kJ mol^{-1}in both the states. The energy minima and maxima appeared at $\varphi = 90°$ and 0°, respectively, also in both the states.

PEC's for the $C\alpha$-$C\beta$ bond cleavage processes of **1** and **2** are shown in Figures 2a and 2b, respectively. In these cases, the $C\alpha$-$C\beta$ bond length r, which was supposed to be dissociated in the T_1 states, was chosen as a variable parameter, while the dihedral angle φ was fixed at 90° that corresponded to



1



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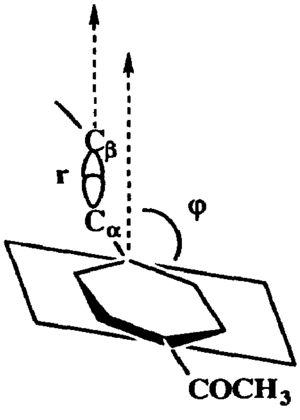

Figure 1. Definition of the dihedral angle φ between $C\alpha$-$C\beta$ σ bond and plane of of the ring

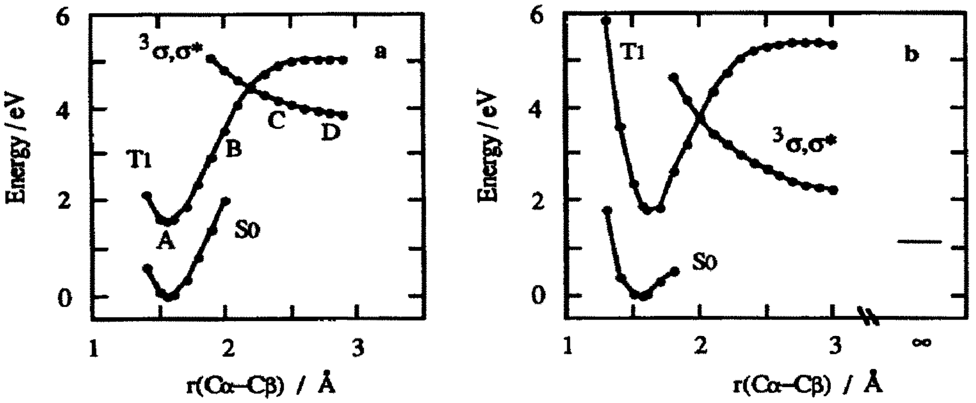

Figure 2. Potential energy curves for the C-C cleavage reaction for **1** (a) and **2** (b) as a function of the bond length r(Cα-Cβ)

the energy minimum at the reactant S_0 state. Three electronic states (S_0, T_1, and triplet σ,σ* state, ($^3\sigma,\sigma^*$)) were taken into consideration for construction of PEC's.

The energy minimum in the S_0 state of **1** was found at r = 1.55 Å and the location of this energy minimum remained unchanged by excitaion to the T_1 state. The PEC for the T_1 state was crossed with that for a higher dissociative $^3\sigma,\sigma^*$ state at r = 2.2 Å.[8] This crossing point corresponds to the transition state of the photocleavage reaction. The barrier height to the transition state was estimated to be 2.91 eV (280 kJ mol^{-1}). The C_α-C_β bond dissociates at r = 2.8 Å, and the heat of cleavage reaction was calculated to be 1.7 eV (164.0 kJ mol^{-1}). The high endothermicity of this reaction can be attributed to the unstability of the resulting ethyl radical.

In the case of **2**, the energy minima were found at r = 1.56 Å in both the S_0 and T_1 states. The PEC for the T_1 state was crossed with that for a dissociative $^3\sigma,\sigma^*$ state at r = 2.0 Å. The barrier height to the transition state was estimated to be 1.95 eV (180 kJ mol^{-1}). The heat of cleavage reaction was calculated to be -0.7 eV (-69.6 kJ mol^{-1}), indicating that the reaction was exothermic. These results show that the photochemical C-C bond cleavage reaction of **2** is much more favorable than that of **1**. This is apparently attributable to the stability of the resulting benzyl-type radical. The heat of photocleavage reaction can also be estimated from the reported values for the C-C bond energy (344 kJ mol^{-1}), the energiy of phophorescence for acetophenone-type triplet (302 kJ mol^{-1}), and the stabilization energy of two benzyl-type radicals (50 x 2 = 100 kJ mol^{-1}). The estimated value (344 - 302 - 100 = -58 kJ mol^{-1}) for the heat of photocleavage reaction from these values also supports the exothermicity of the process.[5] A strain energy within the molecule further enhances the exothermicity and also lowers the barrier height to the transition state.[3] The estimated values for the heat of reaction are in good agreement with each other, although the calculated triplet energy (174 kJ mol^{-1}) does not agree with the experimental value, probably by a poor estimation for an electron-electron correlation energy in the MNDO method.

The analysis of the variation of MO's along the reaction coordinate for **1** disclosed the electronic feature of the photocleavage reaction. A key orbital that governed a dissociative reactivity in the photocleavage reaction was the lower singly occupied MO (SOMO). To clarify a MO picture for the photocleavage reaction, four points A, B, C, and D along the reaction coordinate were chosen as representative points: A, B, C, and D corresponds to the C_α-C_β bond lengths r = 1.55, 2.00, 2.40, and 2.80 Å, respectively (Figure 2a). Schematic representation of the SOMOs at these points are shown in Figure 3. The $2p_z$-$2p_z$ orbital interaction between C_α and C_β atoms changes drastically from a bonding σ state to an anti-bonding σ^* state around the transition state. Whereas, the $2p\pi$-$2p_z$ orbital interaction between C_1 and C_α atoms does not change appreciably, retaining an anti-bonding character. At the point A, the unpaired electron density is localized mainly on the C_1 atom. As the C_α-C_β bond is lengthened toward the transition state, the phase of $2p_z$ orbital on the C_β atom is reversed (see points B and C). Afterwards, the unpaired electron became localized largely on the C_β atom (point D).

It is important to note that the photochemical C_α-C_β bond cleavage reaction occurs with the appearance of an unpaired electron on the C_β atom in the transition state. This requires that the compound undergoing the photocleavage reaction should have a π,π^* character in the T_1 state, because an n,π^* state is symmetrically forbidden. This is in contrast to the Type I reaction of aryl alkyl ketones in which an n,π^* state becomes a reactive state and a π,π^* state is rather unreactive.[9] The present MNDO calculations provided a new aspect about the electronic feature of the photochemical C-C bond cleavage reaction of arylalkanes via their triplet states; in this reaction, the π^*-σ^* orbital interaction in the triplet state plays an important role in determining the photoreactivity.

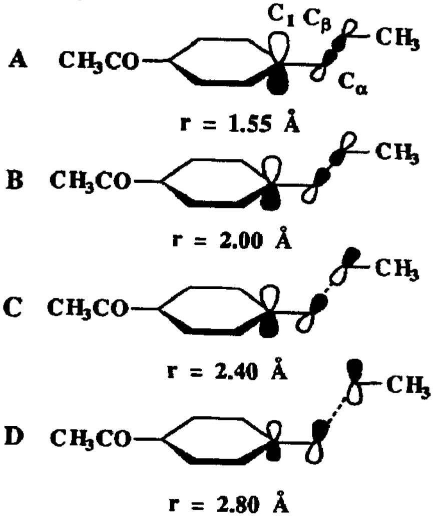

Figure 3. Schematic illustration of the SOMOs along the reaction coordinate of **1** (A, B, C, and D) as shown in Figure 2a.

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