QUANTUM CHEMICAL STUDY OF MECHANISM OF THE PHOTODISSOCIATION REACTION IN POLYATOMIC MOLECULES

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The study of the photodissociation reaction of disulfide molecules based on the quantum chemistry methods is presented. A reaction mechanism is proposed as a result of analysis of photophysical processes and the dependences of quantum yield of photodissociation are explained on the exciting light frequency and on the electronic structure of the species under study.

The question on the mechanism of photochemical dissociation of polyatomic molecules is of primary importance in the current molecular photochemistry. Recently, we have developed an approach which allows one to find the electron excited states from which photodissociation can occur on the basis of quantum chemical calculations.¹ The proposed approach was tested on molecules whose photodissociation was well studied experimentally, i.e., diphenyldisulfide, bis–(π –aminophenyl) disulfide, π –aminothiol, and phenol.^{2–5}

Let us remind the basic features of the proposed approach. At the initial stage the scheme of electron excited states, matrix elements of the spin—orbital coupling (SOC) operator and the rate constants of internal conversion are calculated that enables one to draw conclusions regarding the physical processes in a molecule and formation of its spectral and luminescent properties. Investigation of the origin of the electron excited states and the degree of localization of the excitation on some bonds together with the calculation of the bond populations in the ground and electron excited states allows one to reveal those of them which are essentially weakened at the electron excitation. Such states of the molecules under study turned out to be the states of $\pi\sigma$ type, where the σ -orbital is mostly localized on the bond to be broken.

At the next stage the potential curves of the electron excited states are constructed based on the quantum chemical calculations with variation of the length of the bond to be broken and using the Morse potential for the ground state.⁶ The potential curves of electron excited states of a diphenylsulfide molecule are shown in Fig. 1, where the lengths of bonds with populations sharply reducing at excitation are taken as the reaction coordinate. It follows from Fig. 1 that only the potential curves of singlet and triplet $\pi\sigma_{ss}$ states are the repulsion curves while all other potential curves have their minima.

The proposed approach allows one not only to relate the photochemical processes to the origin of the electron excited states but also to describe in detail the primary mechanisms of the photodissociation reactions.

Let us consider the photodissociation mechanism in disulfides in more detail. It was found experimentally for these compounds^{3–5} that the photoexcitation is followed by the break of the S-S bond (the structures of molecules under study are presented in Figs. 2 *a* and *b*) and by the formation of phenyl-tiil radicals S-RX (where X = H, NH₂) whose formation is detected in the absorption spectra.

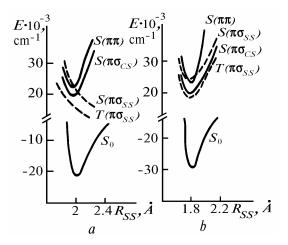


FIG. 1. Potential curves of the electron excited states of a diphenyldisulfide molecule: a) the length of S-S bond is changed and b) the length of the C-S bond is changed.

The energy schemes of electron excited states of disulfides and the values of matrix elements of the SOC operator calculated using the PIDO/s method^{8–10} are shown in Fig. 2.

To calculate the constant of the internal conversion process we have employed a formula which enables us to take into account explicitly the orbital origin of wave functions of interacting electron states, keeping the dependence of the rate constant of the internal conversion on the energy gap (E_{pq})

$$K_{pq} = G_{pq} N_{X-H} \cdot K_{pq}(E_{pq}), \tag{1}$$

where $K_{pq}(E_{pq})$ is the value of the rate constant evaluated according to the Plotnikov–Dolgikh formula,⁷ N_{X-H} is the number of the X-H bonds and X is the heavy atom.

$$G_{pq} = \sum_{\alpha}^{N_{X-H}} |\Omega_{pq}^{\alpha}|^2, \tag{2}$$

where the sum over α denotes the summing over oscillators corresponding to the *X*-*H* bonds in the molecule. Within the framework of the MO–LCAO method,

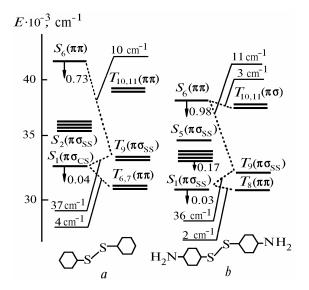


FIG. 2. The energy diagrams of the electron excited states and spin-orbital interaction for molecules of diphenylsulfide (a) and bis- $(\pi$ -aminophenyl) disulfide (b).

$$\Omega_{pq}^{a} = \sum_{i\kappa} A_{i\kappa}^{p} A_{i\kappa}^{q} \sum_{\mu \in \alpha} (C_{\kappa\mu}^{2} - C_{i\mu}^{2}) - \sum_{i\kappa \neq j\kappa} A_{i\kappa}^{p} A_{j\kappa}^{q} \sum_{\mu \in \alpha} C_{i\mu} C_{l\mu} + \sum_{i\kappa \neq l} A_{i\kappa}^{p} A_{i\kappa}^{q} \sum_{\mu \in \alpha} C_{\kappa l} C_{l\mu} , \qquad (3)$$

$$|\Psi_p| = \sum_{i\kappa} A^p_{i\kappa} |\Phi_{i\kappa}\rangle, \tag{4}$$

where $|\Phi_{i\kappa}\rangle$ are the deterministic functions of singly excited states constructed from the molecular orbitals $|\phi_i\rangle$ which are the linear combinations of atomic orbitals $|\chi_{u}\rangle$

$$|\varphi_i\rangle = \sum_{\mu} C_{i\mu} |\chi_{\mu}\rangle.$$

Analysis of calculational results has shown the following. An intense long-wave absorption band in the absorption spectrum of diphenylsulfide is mainly formed by the $S_0 \rightarrow S_6(\pi\pi)$ transitions. The long-wave wing of this band originates due to weak transitions of different origin $(S_1 - S_5$ states). The $\pi\sigma$ states giving rise to the electron transitions in this spectral region differ from each other by the origin of σ -orbital, i.e., one of them is characterized by the localization of the σ -orbital on the C-S bond ($\pi\sigma_{cs}$ state) and the other has the σ -orbital on the S-S bond ($\pi\sigma_{ss}$ state). The substitution by NH₂ groups initiates the long-wave shift of all the electron transitions and the noticeable increase in the oscillator strength of the $S_0 \rightarrow S_3(\pi\pi)$ -transition (Fig. 2 b) what is related to an increase of the value of the density of electrons transferred to phenyl rings due to the donor properties of the NH₂ group. Really, in the experimentally observed absorption spectrum the long–wave shift of the absorption band and a distinct inflection in the long-wave wing of this band are observed.³

Analysis of the values of matrix elements of the SOC operator shows that the low singlet state of molecules under study is coupled via noticeable spin—orbital interaction with the lower triplet states (2–6 cm⁻¹, see Fig. 2). At such values of the spin—orbital coupling the rate constant of the $S \sim \rightarrow T$ conversion can reach $10^{11} \, \text{s}^{-1}$, see Refs. 11 and 12. Evaluation of the efficiency of the internal $S_1 \sim \rightarrow S_0$ conversion according to Eq. (1) gives the value less than $10^6 \, \text{s}^{-1}$. Along with the small value of the rate constant of the radiative dissociation of the $S_1 \, (\pi\sigma)$ state ($\sim 2 \cdot 10^6 \, \text{s}^{-1}$) this fact explains the absence of a detectable fluorescence of molecules under study.³ Low efficiency of the process of the $S_1 \sim \rightarrow S_0$ conversion confirms the impossibility of the dissociation difenylsulfide molecules from the vibrationally excited ground state.

Let us consider in more detail the principle peculiarities in the schemes of the electron excited states of the disulfides under study. First, the substitution by aminogroups only slightly changes the energies of the photodissociating $\pi\sigma_{ss}$ states (Fig. 2). Second, the dissociating triplet states are located between the singlet states giving rise to the long-wave and short-wave absorption and are related to them via effective spin-orbital coupling. In this case the excitation of the bis- $(\pi$ aminophenyl) disulfide in the long-wave region of the absorption band ($\lambda_{\rm b} = 337$ nm) leads to the dissociation of the molecule through the predissociation mechanism. However, the efficiency of this process will be low because of the energy barrier between the S_1 state and the higher dissociative $T(\pi\sigma_{ss})$ state. Just this fact explains a small value of the quantum yield of the photodisociation ($\eta = 0.05$) at $\lambda_b = 337$ nm. In the case of excitation in the short-wave region of the absorption band of the aminosubstituted disulfide $(\lambda_{\rm b} = 264 \text{ nm})$ the photodisociation mechanism can be represented by the scheme (see Fig. 3).

In the case of the short-wave absorption the competition of the processes of the internal conversion in the system of singlet states and the intercombination conversion $S_6(\pi\pi) \sim \to T_{10}(\pi\sigma), S_6(\pi\pi) \sim \to T_9(\pi\sigma_{ss})$ takes place what leads to the population of the dissociative triplet state. Nevertheless, the process of intercombination conversion is more efficient than at the excitation in the long-wave region of the absorption band because of the absence of the energy barrier. This fact explains the increase of the quantum yield of the dissociation with increasing energy of the exciting quantum. For better understanding of this mechanism it is of interest to compare the data on the values of the quantum yield of the dissociation in the case of excitation in the short-wave region of the substituted and nonsubstituted molecules. The results of calculations that the change in the molecular structure show (introduction of two aminogroups) leads to the appearance of the triplet state in the substituted molecule (just the presence of the aminogroup causes the origin of this state) located near the $S_6(\pi\pi)$ state and coupled with it by a strong spin-orbital interaction. This means that in the bis-(π -aminophenyl) disulfide molecule in the case of excitation in the short-wave region of the absorption band the processes of the intercombination conversion is more efficient than in the diphenylsulfide molecule because along with the $S_6(\pi\pi) \sim \rightarrow T_9(\pi\sigma_{ss})$ channel an effective channel of the $S_6(\pi\pi) \sim \rightarrow T_{10}(\pi\sigma)$ conversion appears in the substituted molecule followed by the internal conversion to the dissociative state.

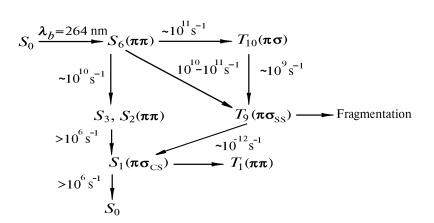


FIG. 3. Scheme of photodissociation mechanism of disulfide molecules.

The above results allow one to understand qualitatively and to explain noticeable difference in quantum yields of photodissociation of the diphenyldisulfide molecule ($\eta = 0.18$) and of its aminosubstituted molecule ($\eta = 0.57$) in the case of excitation in the short—wave region of the absorption band.

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