EFFECT OF SUBSTITUENTS AND PROTONATION ON PHOTOLYSIS OF THE 2,5-DIPHENYL-OXAZOLE MOLECULE

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Based on quantum chemical calculations, we consider the effect of substitution by groups with different donor–acceptor properties and protonation on the probability of opening of the oxazole ring of the 2,5-diphenyloxazole molecule (PPO). We show the determining role of the hydrogen-containing medium in this photoconversion. We have established that a substituent introduced into the para position of the 5-phenyl radical, depending on its donor–acceptor properties, can either enhance the efficiency of photolysis (donor substituent) or weaken it (acceptor substituent). We have found the photodissociative states and have determined their multiplicity for the considered substituted PPOs.

Laser-active media based on 2,5-diphenyloxazole (PPO) have found practical application in dye lasers in the blue region of the spectrum, but their low photostability is a weak point in their practical use. In order to create active media with a long useful operating life, we need a detailed and deep understanding of their physicochemical properties and the mechanisms of the primary photoconversions, and their relation to the structure of the molecule and intermolecular interactions. This is not always possible to do by means of only experimental methods. Fruitful approaches to solving this problem prove to be quantum chemistry methods which allow us to detail the mechanisms of photochemical and photophysical processes and to establish the dependences of the properties on their structure and intermolecular interactions.

The goal of this work was to investigate the effect of substituents with different donor–acceptor properties and protonation as an extreme case of a hydrogen bond, in the considered case leading to formation of C–H bonds, on the experimentally established mechanism for opening of the oxazole ring in the PPO molecule [1]. In order to solve the problem posed, we used a previously developed and rather simple approach based on application of standard quantum chemical calculations in an investigation of the reaction of photodissociation of polyatomic molecules [2-4]. The structural formulas for the investigated substituted derivatives and their protonated forms are presented in Fig. 1.

We have experimentally established that in excitation of a PPO molecule to an intense long-wavelength absorption band in a hydrogen-containing medium, opening of the oxazole ring occurs with formation of new NH, CO, and CH bonds according to the scheme

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\text{HC-NH} \rightarrow \text{HC} = \text{NH} + \text{CO} + \text{CH}
\]

In studying the photoreaction, we used the semiempirical INDO method with spectroscopic parametrization [5]. Explanation of the formation of new chemical bonds requires investigation of the pathways for addition of hydrogen atoms from the solvent. Assuming that the first step in this case is protonation, the pathway for approach of the proton to the molecule was determined with the help of the electrostatic potential method, allowing us to calculate the interaction energy between the proton

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and the molecule and to find the most probable sites for its addition. In order to study the effect on the considered reaction of a proton-donor medium, in addition to the calculation for the PPO molecule and its substituted derivatives, we did the calculation for their forms protonated at the nitrogen atom (Fig. 1). With the goal of isolating the bonds whose strength decreases in the excited states, we calculated the populations of these bonds \( P_{AB} \) according to [2] in the ground state and excited states (Table 1).

As follows from Table 1, in the ground state the populations of both C=O bonds of the oxazole ring have close values, i.e., the \( O_1-C_2 \) and \( O_1-C_3 \) bonds have identical strength. Introducing an OH group into the ortho position of the 5-phenyl radical (Fig. 1) does not affect the values of \( P_{AB} \). Substitution by \( SO_2F \) and \( N(CH_3)_2 \) groups in the para position of the same radical (Fig. 1) increases the population of both bonds; in this case, in the ground state the donor substituent makes the \( O_1-C_3 \) bond stronger; an acceptor substituent makes the \( O_1-C_2 \) bond stronger. In the singlet and triplet \( \pi \sigma^* \) states, localized either on the \( O_1-C_2 \) bond or on the \( O_1-C_3 \) bond, the strength of the CO bonds proves to be smaller than other bonds of this ring.

According to the data in Table 1, we can arrange the substituents in the series \( N(CH_3)_2 > SO_2F > OH \) according to their effect on the strength of the C-O bonds in the ground state. We should note that in the absence of an effect from the proton-donor solvent, the \( O_1-C_5 \) bond is the most weakened on excitation rather than the \( O_1-C_2 \) bond, as was found in the experiment in [1]. From the data in Table 1 it follows that the interaction of the PPO molecule with protons of the medium occurs most efficiently at the nitrogen atom, which is connected with the presence of an unshared electron pair there. Calculations by the electrostatic potential method suggest that in the ground state, the acceptor substituent \( SO_2F \) reduces this interaction while a donor substituent enhances this interaction. In the excited state \( S_1(\pi\pi^*) \), the interaction between PPO and the solvent decreases, while introducing an acceptor group \( SO_2F \) enhances this tendency. Substitution of a donor group \( N(CH_3)_2 \) increases the interaction with the medium not only in the \( S_0 \) state but also on excitation to the state \( S_1(\pi\pi^*) \).

Addition of a proton to the nitrogen atom of the PPO molecule fundamentally changes the pattern for populating the CO bonds in the heterocycle. In the \( \pi \sigma^* \) excited state of the \( O_1-C_2 \) and \( O_1-C_3 \) bond, the PPO molecules become different in strength, and specifically protonation strengthens the \( O_1-C_2 \) bond more than the \( O_1-C_3 \) bond (Table 1), which corresponds to experiment [1]. Protonation of substituted molecules in \( \pi \sigma^* \) states weakens both C=O bonds compared with their unprotonated analog, but substitution by groups with different donor-acceptor properties gives a different effect. Thus in \( \pi \sigma^* \) states on protonation of the PPOSO_2F molecule, the \( O_1-C_2 \) bond remains stronger than the \( O_1-C_3 \) bond, while in the protonated PPON(CH_3)_2 molecule, the \( O_1-C_2 \) bond proves to be the most weakened on excitation. Its population is markedly reduced compared with the PPO molecule. As far as the PPOH...O system is concerned, with a proton transferred to the nitrogen atom, both C=O bonds prove to be the strongest compared with protonated structures in excited \( \pi \sigma^* \) states (Table 1).

In order to establish the shape of the potential curves of the investigated molecular structures in the electronically excited states, we performed quantum chemical calculations of the energy of these states using the change in the \( O_1-C_2 \) or \( O_1-C_3 \) bond length as the reaction coordinate; in this case, the potential curve of the ground state is modeled by a Morse...