

## Molecules with bonds such as Xe–O between moieties and their application

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The molecules with the bond such as Xe–O (the bond is formed owing to the interaction of completely occupied atom orbital (AO) of xenon and partially occupied AO of triplet oxygen between moieties) are investigated. These investigations have shown that all such molecules (diazquinones, salt of diazonium, azides etc.) are characterized by considerable activity in lower excited states or upon the transfer of an additional electron into them. They allowed us to establish that the photodissociation of the diazonium cation or the molecule of azide is carried out owing to the predissociation into the dissociative  $\pi\sigma^*$  state, and the  $\sigma^*$  MO is located on the dissociative bond. The photodissociation of diazoquinones is carried out from the lower singlet  $\pi\pi^*$  state. The transfer of the electron into salt of benzenediazonium and phenylazides provides the necessary conditions for the dissociation of the molecule, nevertheless, it provides the opportunity of the sensitization of the dissociation process to the visible region of the spectra with dyes only of diazonium salts. The sensitization of the photolysis of azide is possible only with high-energy radiation that also allows us to use this substance, for example, for the registration of ionizing radiation.

Key words: *diazo; sensitization; photodissociation; registration*

### 1. Introduction

The salts of diazonium and azides are widely known as the photosensitive components of the photographic materials, which do not contain halogenides of silver [1]. And though these compounds have been known since the end of the XIX century, their photochemical properties have not been sufficiently examined.

We have analyzed the properties of the excited states of these compounds, within the frameworks of a new class of compounds that can promote more understanding of the

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photochemical properties of the large number of compounds and the expansion of opportunities of their use as the photosensitive components for the photographic and phototechnological processes. This new class of compounds are the compounds with the bonds such as Xe–O between molecule moieties.

The classification of the chemical bonds in molecules (valence, ionic, donor–acceptor, hydrogen) is sufficiently developed. A distinct type of the bond in this classification is the chemical bond between the atom with the completely occupied atom orbitals (AO), for example, of the inert gas atom (xenon, krypton) or the anion of halogen ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ) and the oxygen atom. In order to create the chemical (donor–acceptor) bond, preliminary excitation of the oxygen atom from the state with the electronic configuration  $(2p_z)^2(2p_x)^1(2p_y)^1$  into the state with the electronic configuration  $(2p_z)^2(2p_x)^2(2p_y)^0$  is necessary. The result of such a process is the formation of molecules such as  $\text{ClO}_n^-$  or  $\text{IO}_n^-$  ( $n = 1-4$ ) and the molecule  $\text{XeO}_n$ . It is known [2] that the molecules such as  $\text{ClO}_n^-$  or  $\text{IO}_n^-$  in water solutions act as the electron acceptors, despite the presence of interelectronic repulsion. It is clear that the neutral molecule  $\text{XeO}_n$  will be a considerably stronger oxidant that leads to the explosion of this substance at contact even with weak donors [2].

The opportunities of formation of molecules are extended at the expense of the above-mentioned type of bonds. Thus instead of the atoms Xe and O we investigated molecules, which would have the same properties as the specified atoms, namely, one of molecules should have the completely occupied molecular orbital (MO) (including n–MO), and another one – to be in the triplet state.

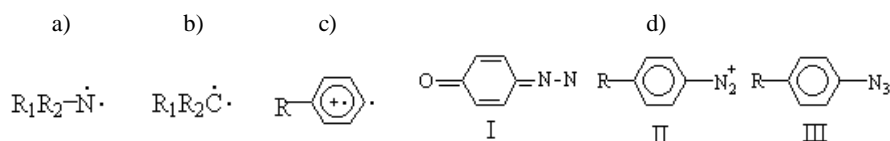


Fig. 1. Molecular structures of: a) carbenes, b) nitrenes, c) aryl cations, d) diazoquinone (I), salts of diazonium (II), azides (III)

To the first type of molecules there belong: molecular nitrogen ( $\text{N}_2$ ), molecules (including cyclic) with heteroatoms, on which n–MO is located ( $\text{R}_1-\text{O}-\text{R}_2$ ,  $\text{R}_1-\text{S}-\text{R}_2$ ,  $\text{R}_1-\text{N}=\text{R}_2$ ,  $\text{R}_1-\text{NH}-\text{R}_2$ ,  $\text{R}_1-\text{CO}-\text{R}_2$  etc., where  $\text{R}_1$ ,  $\text{R}_2$  are any molecule moieties) and others. The second type is represented by the molecular structures such as carbenes (Fig. 1a), nitrenes (Fig. 1b), aryl cations (Fig. 1c) and others. Besides the anion of halogen or the atom of oxygen can play a role of one of the moieties mentioned.

## 2. Experimental and calculations

The experimental and theoretical investigations of the compounds of the types mentioned above, such as diazoquinone (I), salts of diazonium (II) and azides (III) (Fig. 1d) were carried out.

Experimental investigations concerned spectroscopic and photochemical properties of those compounds, and the theoretical one – the quantum-chemical calculations (methods MNDO and AM1 [3]<sup>\*</sup>) of the excited states of molecules. For comparison the calculations of the molecules  $\text{ClO}_n^-$  and  $\text{IO}_n^-$  were carried out, which could help to understand the properties of the molecule  $\text{XeO}_n$ .

Luminescence of the solutions was excited using a mercury lamp DRSh-1000 equipped with colour filters. Spectra were recorded with the Specord M-40 spectrophotometer.

## 3. Results and discussion

### 3.1. Molecules $\text{ClO}_n^-$ and $\text{XeO}_n$

The results of calculations have shown that in the molecules under consideration all  $\pi$  MO are populated with electrons. The transfer of one electron from the  $\pi^*$  MO into the  $\sigma^*$  MO corresponds to the lower singlet state  $S_1$ , at that the  $\sigma^*$  MO is formed owing to the interaction of the  $p_z$ -AO of the interactive atoms. The quantum transition  $S_0 \rightarrow S_1$  or  $S_0 \rightarrow T_1$  does not result in the dissociation of the molecule. The dissociation is possible only at the  $\sigma \rightarrow \sigma^*$  excitation (the energy surfaces of the  $S(\sigma\sigma^*)$  and  $T(\sigma\sigma^*)$  states are clearly dissociative).

As the molecules  $\text{HalO}_n^-$  (Hal is the atom of halogen) act in solutions as acceptors of electrons, we have also calculated the energy surface  $\text{HalO}_n^{2-}$ . It turned out that it is exclusively dissociative that is, the transfer of an electron into  $\text{HalO}_n^-$  results in the separation of the anion of oxygen ( $\text{ClO}_n^- + e^- \rightarrow \text{Cl}^- + \text{O}^-$ ). In vacuum, the process of the transfer of the electron is impossible, as the reaction proceeds with increasing energy of the system owing to the inter-electronic repulsion. Nevertheless, in water solutions there will be the gain of energy at the expense of the interaction of  $\text{HalO}_n^{2-}$  with the molecules of the solvent (of the polarization of the solvent).

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<sup>\*</sup>We have established that the calculation by means of less exact methods, such as CNDO/2 or MINDO allows receiving similar data, with respect to the shapes of the potential surfaces of the excited states of molecules, and drawing the same conclusions concerning the mechanisms of the photodissociation of molecules.



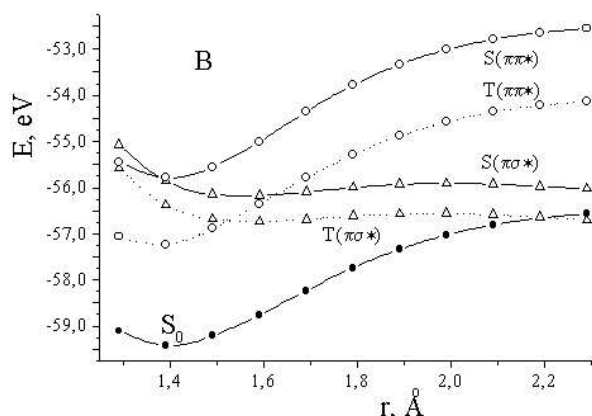


Fig. 2. The energy diagram of diazoquinone (A) ( $\Delta E(S_1(\pi\pi^*)) = 0.166$  eV) and *p*-hydroxyphenyldiazonium (B) ( $\Delta E(T(\pi\sigma^*)) = 0.166$  eV)

The protonation of molecule I with the formation of cation II entirely changes the properties of the molecule. Now the  $S(\pi\sigma^*)$  and  $T(\pi\sigma^*)$  states become dissociative, in which the cation will pass owing to the predissociation from the  $S(\pi\pi^*)$  state. Most likely the hydroxyphenylic cation in the excited singlet state will be the basic product of the dissociation, then its relaxation occurs into the basic triplet state. The energy barrier for the dissociation from the  $S(\pi\sigma^*)$  state does not exceed 0.2 eV, and from the  $T(\pi\sigma^*)$  state – 0.17 eV.

As the result, the capture of the electron by cation II was expected. Its affinity to the electron in the equilibrium geometrical configuration is 5.9 eV and grows up to 8.25 eV at lengthening of the C–N bond up to 0.2 nm. The energy surface of the restored cation II has no barrier at the lengthening of the C–N bond. Hence, the phototransfer of the electron into cation II will cause its dissociation into the aryl radical and the molecule of nitrogen.

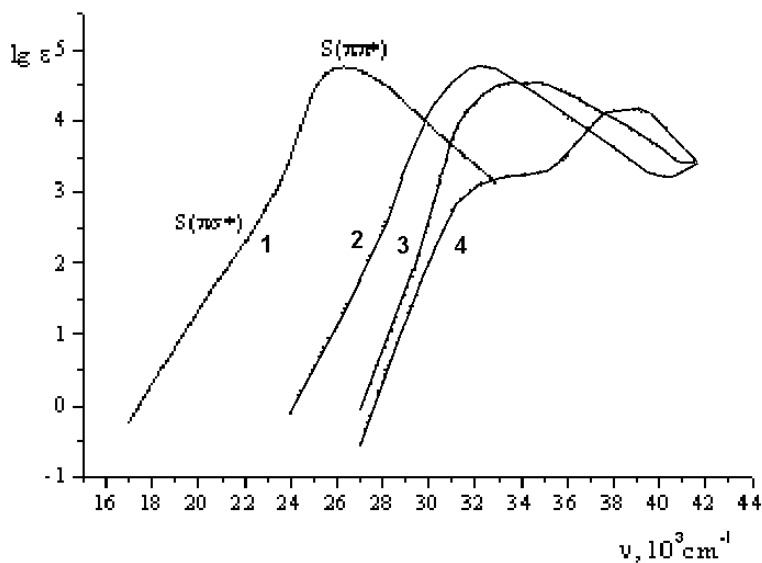


Fig. 3. The spectra of absorption of water solutions of *para*-substituted salts of benzenediazonium. The substituents: 1 –  $\text{N}(\text{C}_2\text{H}_5)_2$ , 2 –  $\text{OCH}_3$ , 3 –  $\text{Br}$ , 4 –  $\text{H}$

The replacement of the substituent in cation II does not change the mechanisms of the dissociation – from the dissociative singlet and triplet  $\pi\sigma^*$  states, in which the cation will pass owing to the predissociation from the  $S(\pi\pi^*)$  state.

Experimental investigation and theoretical calculations show that energy of the excitation into the  $S(\pi\pi^*)$  state naturally grows with increasing of electron-acceptor properties of the substituent (from  $\text{NH}_2$  to  $\text{NO}_2$ ). Both the  $\pi \rightarrow \pi^*$  and  $\pi \rightarrow \sigma^*$  quantum transitions can be experimentally observed (Fig. 3), as the weak  $\pi \rightarrow \sigma^*$  quantum transitions (they are seen only as the long-wave break on the band of absorption at the room temperature and as the band in the frozen solutions [4, 5]) are in the region of smaller energy than the long-wave  $\pi \rightarrow \pi^*$  transition. It is seen from Fig. 3 that the extinction coefficient for the  $\pi \rightarrow \sigma^*$  quantum transition is some orders smaller than for the  $\pi \rightarrow \pi^*$  transition. As the  $\pi\sigma^*$  state is dissociative, the direct excitation into the weak band will cause the dissociation of the diazonium cation with the same quantum efficiency as at the excitation into the  $S(\pi\pi^*)$  state [5]. Hence, on account of the electronic configuration of the diazonium cation, the relaxation of the excitation energy proceeds entirely through the  $\pi\sigma^*$  state.

In all the cases there is the a small energy barrier for the dissociation of the cation from the  $S(\pi\sigma^*)$  state. In rigid solvents, particularly in frozen matrices, the process of the dissociation can be hindered owing to the steric factors. It will result in the  $S(\pi\sigma^*) \rightarrow T(\pi\sigma^*)$  conversion and dissociation of the cations only from the  $T(\pi\sigma^*)$  state. The process of the photodissociation has high efficiency even in a frozen solution up to 4.2 K.

### 3.3. Azides

Azides (III) belong to the group of compounds with the bonds between molecular moieties (such as Xe–O). These molecules consist of the linear group  $N_3$  and the moiety R. The atom of hydrogen or alkaline element, any multi-atom moiety (radical) can play the role of the last one. The substituted phenylazides (PA) have the most widespread application.

Azides, as well as the salts of diazonium, similarly as  $XeO_n$  tend to explode. The transfer of the electron into  $XeO_n$  and CD causes the dissociation of the molecule, which may initiate the process of the explosion. Let us now consider similar processes in azides.

The results of the calculations of energy levels of phenylazide have shown that in this case the efficiency of the photodissociation will be high both from the  $S(\pi, \sigma^*)$  and the  $T(\pi, \sigma^*)$  states. The energy barrier at the  $T(\pi, \sigma^*)$  state makes only 0.06 eV that enables proceeding the photodissociation practically at any temperature. We have shown experimentally that the photodissociation of phenylazide in frozen alcohol solutions (4.2 K) or in polymeric layers really took place. It also appeared that the molecular nitrogen crystallizes in certain sites of the solvent (of the polymeric layer). When heating the sample, the nitrogen passes through the gas phase and creates vesicles in the polymeric matrix owing to high pressure of gas. Thus the theoretical calculations of the energy structure and mechanisms of the photodissociation of azides are entirely confirmed experimentally.

The transfer of the electron into the phenylazide molecule results in increasing the energy of the electronic system by 1 eV at the equilibrium geometry of the molecule. The energy surface of phenylazide with the superfluous electron corresponds to the dissociative surface. Hence, during the transfer of the electron into phenylazide its dissociation will take place. Nevertheless, as it results from the calculation and from our experiments, the sensitization of this process by dye molecules is not possible. Most likely, the transfer of the electron may proceed from the matrix or dye molecule only at high-energy excitation.

## Conclusions

The theoretical and experimental investigation of the molecules with the bond such as Xe–O between molecular moieties are carried out. The mechanisms of the photodissociation of the specified compounds and their acceptor properties capable to provide the opportunity of the sensitization of photolysis of the specified compounds by dyes were established. Comparison of properties of the compounds under investigation with their prototypes ( $ClO_n^-$ ,  $IO_n^-$  and  $XeO_n$ ) enabled understanding the essential differences in the properties of diazoquinones and of diazonium salts, which differ only by presence of the positive charge on the cation of diazonium. The analysis of the research results has allowed to show that:

- there exist whole classes of molecules (diazonium salt, azides and etc.) capable to the photodissociation at the excitation to the long-wave band of absorption due to the predissociation into the  $\pi\sigma^*$  state, at that the  $\sigma^*$  MO is located on the dissociative bond; these molecules do not fluoresce or phosphoresce owing to the effective relaxation of the excitation through the  $\pi\sigma^*$  state;
- the results of calculations concerning the excitation of the diazocations and molecules of azides into the  $\pi\pi^*$  and  $\pi\sigma^*$  states, are matched with the experimental data concerning the spectra of absorption, according to which there is the weak band of  $\pi \rightarrow \sigma^*$  absorption at the long-wave side from the band of  $\pi \rightarrow \pi^*$  absorption;
- the transfer of the electron to the salt of benzenediazonium and phenylazides provides necessary conditions for the dissociation of the molecule, nevertheless, it provides the opportunity of the sensitization to the visible region of the spectra by dyes only of diazonium salts that is **the basis for creation of the sensitized diazo materials**; the sensitization of the photolysis of azide is possible only to high-energy radiation;
- the experimental investigation of photolysis of diazonium salts and azides at low temperature (4.2 K) confirm the results of the calculation concerning the dissociative character of the  $\pi\sigma^*$  state.

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