

## Sensitization processes in materials based on compounds containing a Xe–O bond

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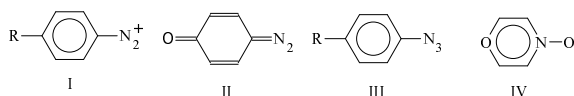
The work contains the results of experimental and theoretical studies of the sensitization processes in compounds with the Xe–O type bond between the molecule fragments. Such a bond is formed between a molecule containing completely occupied molecular orbitals and another one being in the triplet ground state. Such molecules include diazonium salts, azides, as well as molecules comprising a heteroatom with localized  $n$ -orbital to which an oxygen atom is connected. The studies have shown that all such compounds inherit a series of XeO molecule features, namely, exhibit a photochemical activity and might be photosensitized. The sensitization possibilities according to the electron transfer and energy transfer mechanisms as well as the chemical sensitization have been considered. All three sensitization types have been shown to be possible in diazonium salts. This is due to the fact that the dissociative state of diazonium cation is the lower excited state and, moreover, the an additional electron is localized on that state. For azides and molecules comprising an N–O bond, the sensitization according to the energy transfer mechanism is only possible except for the sensitization to hard radiation, when the electron capture becomes possible on the dissociative state of the photo-active molecule being a high-excited state.

Работа содержит результаты экспериментальных и теоретических исследований процессов сенсбилизации фотолиза соединений со связью типа Xe–O между фрагментами молекулы. Такая связь возникает между молекулами, одна из которых имеет полностью занятые молекулярные орбитали, а вторая находится в основном триплетном состоянии. К числу таких молекул относятся соли диазония, азиды, а также молекулы с гетероатомом, на котором локализована  $n$ -орбиталь, по которой присоединен атом кислорода. Исследования показали, что все эти соединения обладают фотохимической активностью и допускают сенсбилизацию светочувствительности. Рассмотрены возможности сенсбилизации по механизму переноса электрона, переноса энергии, а также химической сенсбилизации. Показано, что для солей диазония можно осуществить сенсбилизацию всех трех типов. Это обусловлено тем, что диссоциативное состояние катиона диазония является нижним возбужденным состоянием и, кроме того, на этом состоянии локализуется дополнительный электрон. Для азидов и молекул со связью N–O возможна сенсбилизация только по механизму переноса энергии, за исключением случая сенсбилизации к жесткому излучению, когда появляется возможность захвата электрона на диссоциативное состояние фотоактивной молекулы, которое является высоковозбужденным состоянием.

This work is aimed at the study of photosensitization processes in compounds with a Xe–O type bond between the fragments [1]. Instead of Xe and O atoms, molecules were considered having the same properties as

the above atoms. Namely, one molecule ( $N_2$ , azobenzene, resorufine, methylene blue, etc.) should comprise a completely occupied molecular orbital (MO) (including  $n$ -MO) while another one (oxygen atom, aryl cat-

ion, nitrene, carbene, etc.) should be in the triplet ground state. Those compounds include diazonium salts (DS) (I), diazoquinones (II), azides (III), molecules containing an N→O bond (IV), etc.



The compounds containing a Xe–O type bond between the fragments exhibit some features similar to those of XeO<sub>3</sub> (dissociate into the initial fragments under excitation or reduction [1–4]), that is why they are often used as the primary components in functional materials. For example, diazonium salts and azides are used as the photosensitive components in media for information optical storage; the compounds containing an N→O bond (resazurine, azoxybenzene, etc.) can be used as working substances in lasers based on dyes as well in development and production of data storage media.

In this work, we have intended to elucidate the main regularities in the photosensitization of the compounds under study. To that end, we have considered the following processes: (i) sensitization according to the photoinduced electron transfer mechanism; (ii) sensitization according to the energy transfer mechanism; (iii) chemical sensitization.

The experimental studies (absorption spectra in visible and UV regions, the photochemical process kinetics) were carried out using solutions of the photo-active compounds and sensitizers in ethanol or in a polymer matrix (polyvinyl acetate). To obtain the solid polymeric solutions, all the components were dissolved in ethanol and the solution was poured onto a horizontal glass plate and dried, then the polymer layer was detached from the glass. The photochemical experiments were carried out using a mercury arc lamp and light filters. To record the absorption spectra, Specord UV/VIS and Specord M40 spectrophotometers were used. The X-ray examinations were carried out using the a URS-55 instrument with iron anticathode (the maximum emission at  $\lambda = 0.1753$  nm;  $\lambda_{min} = 0.4$  ) and a DRON-2M one with copper anticathode (the maximum emission at  $\lambda = 0.15393$  nm). As the photosensitizers of the compounds containing a Xe→O bond to the long-wavelength spectral region, dyes of various classes were used, namely, derivatives of xanthene (eosin, Eoz), oxazine (resazurine), thiazine (methylene blue, MB)

Table 1. Ionization potentials and affinity energies of photo-active compounds with a Xe–O type bond

Molecule	Ionization potential, eV	Affinity energy, eV
H <sub>2</sub> CN <sub>2</sub>	8.32	0.18
H <sub>3</sub> CN <sub>2</sub> <sup>+</sup>	8.44	7.12
DEAPhN <sub>2</sub> <sup>+</sup>	12.04	6.25
H <sub>3</sub> COPhN <sub>2</sub> <sup>+</sup>	12.97	6.63
HOPhN <sub>2</sub> <sup>+</sup>	13.27	6.23
PhN <sub>2</sub> <sup>+</sup>	13.84	6.91
O <sub>2</sub> NPhN <sub>2</sub> <sup>+</sup>	14.24	7.53
Diazoquinone	8.31	2.74
HN <sub>3</sub>	9.79	0.35
DEAPhN <sub>3</sub>	7.93	0.91
H <sub>3</sub> COPhN <sub>3</sub>	7.85	0.88
HOPhN <sub>3</sub>	7.76	2.30
PhN <sub>3</sub>	8.18	0.88
O <sub>2</sub> NPhN <sub>3</sub>	9.02	1.96

and others [1, 5]. To sensitize the compounds to the short-wavelength spectral region, heavy metal salts were used (HgCl<sub>2</sub>, CdCl<sub>2</sub>, ZnCl<sub>2</sub>). The quantum-chemical studies of the photo-active component were carried out using the semi-empirical MNDO/d method [6].

Sensitization according to the photoinduced electron transfer mechanism. Depending on the problem setting, a photosensitive compound can be sensitized to the long-wavelength (visible) or short-wavelength (UV and X-ray range) spectral region as well as to the region corresponding to the absorption spectrum of the active compound.

The photolysis of diazonium salts and azides occurs due to the direct excitation into the dissociative S( $\pi\sigma^*$ ) state [1] or due to the excitation into the lower S( $\pi\pi^*$ ) state followed by pre-dissociation into the singlet or triplet  $\pi\sigma^*$  state [1, 3, 4]. We have shown before [1] that the photosensitivity sensitization of diazonium salts occurs according to the photoinduced electron transfer mechanism. This is possible due to a high electron affinity energy of the diazonium cations, Table 1 [7]. Moreover, after the electron photoinduced transfer (without any subsequent thermalization), there is no potential barrier for the C–N bond breaking with a nitrogen molecule release. The quan-

tum-chemical calculation results agree perfectly with the experimental data.

The direct photolysis of diazonium salts and azides has been stated to occur even in solutions chilled down to 4.2 K. Therefore, the energy surface of the  $\pi\sigma^*$  state is a purely dissociative one. The attempts to sensitize azides using dyes have been found to be unsuccessful. The quantum-chemical calculations have shown that the absence of the sensitizing effect is caused by a low electron affinity energy of azides (Table 1) as well as the presence of potential barrier hindering the N–N bond breaking in the reduced azide molecule. The barrier height exceeds 1 eV for non-optimized geometry of the anion-radical and is about 1.8 eV for the optimized one. This, however, does not exclude the possible dissociation from the excited dissociative state of the anion-radical that is formed due to capture of free electrons (the sensitization to a high-energy radiation).

It has been found in experiment that the X-ray sensitivity of diazonium salts and azides is sensitized a little by heavy metal salts (the optical density decrease rate of diazonium salts and azides increases somewhat when  $\text{HgCl}_2$ ,  $\text{CdCl}_2$ , of  $\text{ZnCl}_2$  are introduced into the layer).

The compounds containing an N–O bond (e.g., resazurine) form a separate class of compounds including the Xe–O type bond. Since the dissociative surface of resazurine corresponds to a highly excited state [2], the photoinduced electron transfer to the dye molecule does not provide the N–O bond dissociation. Moreover, the photoinduced electron transfer from the dye is found to be impossible due to the low electron affinity energy of the dye (Table 2). The experimental attempts to sensitize the resazurine photolysis by eosin were unsuccessful.

To cause the sensitization effect to the visible spectral region according to the photoinduced electron transfer mechanism, conditions are to be provided where the intermolecular photoinduced electron transfer between the A and B molecules will be energy favorable. In that case, the reactions



will occur. In the first case (diazonium cation and dye anion) the energy required is

$$\Delta Q = E_A^A - h\nu - I_B - E_C$$

while in the other one (electrically neutral molecules with a Xe–O type bond)

Table 2. Ionization potentials and affinity energies of molecular compounds

Molecule	Ionization potential, eV	Affinity energy
MB <sup>+</sup>	10.82	6.10
MB <sup>+</sup> ·Cl <sup>-</sup>	7.22	2.51
MBO <sup>+</sup> ·Cl <sup>-</sup>	8.02	3.39
ResH	7.76	2.85
Res <sup>-</sup>	4.15	-0.89
ResH <sub>2</sub> <sup>+</sup>	12.55	7.07
RfH	8.02	2.46
Rf <sup>-</sup>	3.67	-1.51
RfH <sub>2</sub> <sup>+</sup>	12.02	6.83
AB	8.24	1.62
ABO	7.64	2.01
EozH	8.31	3.14
Eoz <sup>-</sup>	4.49	-0.25
EozH <sub>2</sub> <sup>+</sup>	11.55	6.91

$$\Delta Q = I_A - h\nu - E_B^A - E_C,$$

where  $I_{A,B}$  is the ionization potential of the electrically neutral molecules (radicals) A and B;  $E_{A,B}^A$ , the electron affinity energy of the same molecules;  $E_C$ , the Coulomb interaction energy between the  $A^{-+}$  and  $B^{\pm}$  ions. The photochemical process is realized at  $\Delta Q \leq 0$ .

The quantum-chemical examination results are presented in Tables 1 and 2. The experimental determination results of the electron affinity energy are described in [7]. Both calculated and experimental data [8] evidence that the photoinduced electron transfer from the dye molecules (Table 2) to p-methoxybenzene diazonium chloride ( $\text{H}_3\text{COPhN}_2^+$  in Table 1) occurs at a high efficiency, while the process is significantly hindered in p-diethylaminophenyl diazonium ( $\text{DEAPhN}_2^+$ ) boron fluoride and  $\text{HOPhN}_2^+$  due to presence of the energy barrier (Table 1).

It is to note that the sensitized (dye) cations show also a high electron affinity energy. Therefore, those compounds can act as electron acceptors with subsequent chemical reactions. The further studies have shown that there is only a restricted group of molecules containing a Xe–O type bond that can dissociate into two or more fragments after photoinduced electron transfer due to a significant energy decrease of the

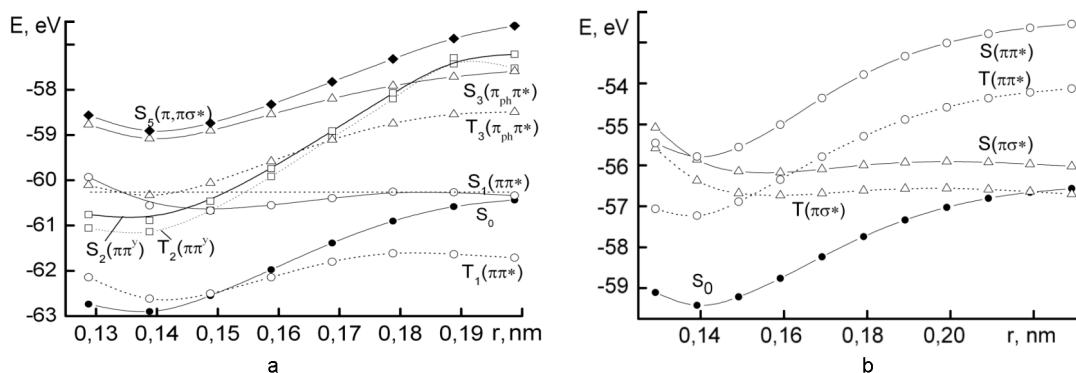


Fig. 1. Energy diagrams of diazoquinone (A) and p-hydroxyphenyl diazonium (B) depending on the length of the C–N bond being dissociated. The C–N bond energy in the  $S_1(\pi\pi^*)$  state of diazoquinone is 0.166 eV and in the  $T(\pi\sigma^*)$  state of diazonium cation, 0.16 eV.

bond being dissociated [1]. However, the reduced molecule dissociates from a non-equilibrium state even in those cases.

It is naturally to expect that the photoinduced electron transfer to the electrically neutral diazoquinone is possible, since the electron affinity energy of the molecule is high. That effect, however, does not provide any sensitization reaction due to the presence of a significant energy barrier in the ground state of the diazoquinone anion-radical. That molecule can be sensitized only under simultaneous excitation of the anion-radical into a dissociative state. On the other hand, the protonation of diazoquinone causes its transformation into diazonium cation with all the consequences ensuing therefrom. The experimental results confirm those conclusions entirely [8].

The energy transfer (the molecule excitation) results always in dissociation at the Xe–O type bond. Along with that bond, other bonds can of course be broken in some cases.

The intermolecular singlet-singlet energy transfer is in essence identical with the direct excitation of the molecule. Therefore, the results of that effect can be considered using the data shown in Figs. 1 and 2. Proceeding from those, it is clear that the diazonium salts and azides can be sensitized if the energy being transferred from the sensitizer exceeds the  $S_0 \rightarrow S_1$  energy of the photo-active compound. Such a sensitization has a sense if the extinction coefficient in the sensitizer long-wavelength band exceeds significantly the corresponding value for the azide or the diazonium salt to provide the complete absorption of the actinic light. As to the compounds containing an N $\rightarrow$ O bond, that energy should exceed that of the

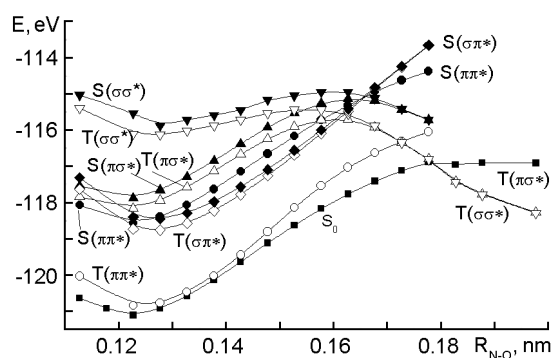


Fig. 2. Energy diagram of neutral resazuring molecule depending on the length of the N–O bond being dissociated.

excitation into a dissociative state if the latter results from a  $\pi \rightarrow \sigma^*$  transition or should be equal to the excitation energy in the case of a  $\sigma \rightarrow \sigma^*$  transition. This is due to the fact that the oscillator strength of the first mentioned transition is very low while it is high for the second one.

The sensitization to the long-wavelength spectral region is possible only in the case when the triplet excitation energy is transferred. For such a sensitization, the singlet-triplet split in the sensitizing molecule should be insignificant (e.g., as in benzophenone) but simultaneously the sensitizer triplet state in to be higher than the corresponding state of the azide or diazonium salt molecule. In principle, such molecules are available. However, those are difficult to be used due to a small radius of the triplet-triplet transfer of the excitation energy.

Chemical sensitization of photochemical processes is well known and used for a long time. For example, in [9], literature data have been mentioned on the chemical sensi-

tization of secondary alcohol photo-oxidation with benzophenone.

To provide chemical sensitization of light sensitivity in compounds containing a Xe–O type bond, first of all, a photosensitive compound should be available that absorbs the visible light where photochemical processes run with an active radical formation. Then, the active radical should have a low ionization potential, resulting in the diazonium cation reduction reaction running in the dark. In searching for such a photosensitive compound, we have paid attention to the fact that when one C–H bond in a  $C_nH_{2n+2}$  hydrocarbon becomes broken, the ionization potential is lowered by about 3 eV [10]. The electron donating substituents introduced into ethane cause a lowered ionization potential of the molecule. On the other hand, introduction of iodine atom results in a shift of the absorption spectrum towards the visible region. That is why we have studied the photochemical properties of diamino iodoethane  $H_3CC(NH_2)_2I$  having the ionization potential of 8.7 eV. Furthermore, its solution is colored yellow due to a weak absorption in the sky-blue spectral range. The quantum-chemical calculations have shown that the excitation of  $H_3CC(NH_2)_2I$  results in its dissociation with release of atomic iodine and formation of diamino ethyl radical with the ionization potential of 5.7 eV. This is quite enough to provide reduction of some diazonium salts in the dark. The photolysis of diamino iodoethane runs at a high quantum yield due to presence of two triplet states  $T_2$  and  $T_3$  arranged closely to one another between the lower triplet state ( $T_1$ ) and two singlet ones  $S_1$  and  $S_2$  close together (Fig. 3). Moreover, the effect of a heavy atom in the singlet-triplet conversion  $S_1 \rightarrow T_1$  is of a great importance.

In fact, we have found in experiment that the decomposition of diamino iodoethane sensitizes the photosensitivity of p-methoxy phenyldiazonium  $H_3COPhN_2^+$  with the long-wavelength absorption band maximum near 313 nm.

To conclude, consideration of literature data as well as comprehensive theoretical and experimental studies of the sensitization processes in compounds containing a Xe–O type bond have shown what follows. The sensitization to the visible or short-wavelength (UV, X-ray) spectral regions according to the photoinduced electron transfer mechanism is possible if the ionization potential of the sensitizer is low and the

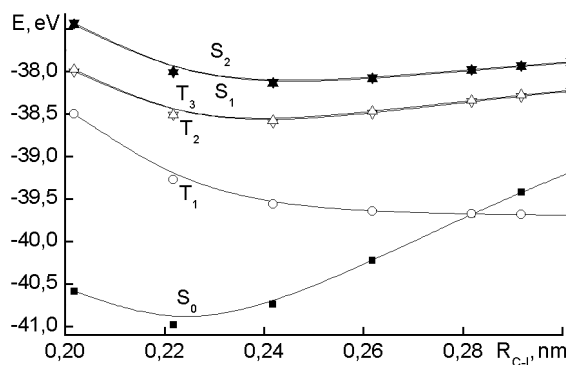


Fig. 3. Energy diagram of  $H_3C-C(NH_2)_2I$  depending on the length of the C–I bond.

electron affinity energy of the photo-active compound is high, thus, the reaction is energy-favorable. The energy of dissociating bond in the reduced photo-active molecule should not exceed a critical value, or the electron is transferred into a hot state with an energy exceeding that of the corresponding bond. The sensitization is possible if the electron is transferred to the excited dissociative state of the radical. That mechanism is more efficient when the sensitization is occurred to the short-wavelength spectral region. The sensitization to the long-wavelength spectral region according to the energy transfer mechanism is only possible in the case when the lower triplet state of the photo-active compound is active. The photosensitivity increase of a recording material to the self-absorption region of the photo-active compound having a low extinction is possible due to inductive-resonance energy transfer from the sensitizer with a long lifetime in the lower excited singlet state. There is a sensitization possibility of interest in the short-wavelength spectral region, since in this case, the processes can be sensitized that run only in a highly excited state of the photo-active compound (in N→O bond containing compounds among the Xe–O type ones). Chemical sensitization of Xe–O type bond containing compounds to the long-wavelength spectral region supposes the electron transfer from an intermediate radical (the sensitized photolysis product) to the ground state of the photo-active compound radical.

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## Процеси сенсibilізації матеріалів на основі сполук зі зв'язком типу Хе–О

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Робота містить результати експериментальних і теоретичних досліджень процесів сенсibilізації фотолізу сполук зі зв'язком типу Хе–О між фрагментами молекули. Такий зв'язок виникає між молекулами, одна з яких має повністю зайняті молекулярні орбіталі, а друга знаходиться в основному триплетному стані. До таких молекул належать солі діазонію, азиди, а також молекули з гетероатомом, на якому локалізована *n*-орбіталь, по якій приєднаний атом кисню. Дослідження показали, що всі ці сполуки мають фотохімічну активність і допускають сенсibilізацію світлочутливості. Розглянуті можливості сенсibilізації за механізмами перенесення електрона, перенесення енергії, а також хімічної сенсibilізації. Показано, що для солей діазонію можна здійснити сенсibilізацію всіх трьох типів. Це обумовлено тим, що дисоціативний стан катіона діазонію є нижнім збудженим станом і, крім того, на цьому стані локалізується додатковий електрон. Для азидів і молекул із зв'язком N–O можлива сенсibilізація тільки за механізмом перенесення енергії, за винятком випадку сенсibilізації до жорсткого випромінювання, коли з'являється можливість захоплення електрона на дисоціативний стан фотоактивної молекули, який є високозбудженим станом.