

## Molecules with a Xe–O type interfragmentary bond. Diazonium salts and azides

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*Received October 25, 2002*

Molecules containing a Xe–O type bond between their fragments have been studied (diazoquinones, diazonium salts, azides, etc.) that are highly active in lower excited states or when an additional electron is transferred thereto. The sensitized photolysis of diazonium salts in liquid and solid solutions has been studied theoretically and in experiment. Quantum yield values have been found for sensitized photolysis of diazonium salts depending on the solvent nature, the dye (sensitizer) used, and the substituent in para position at the phenyldiazonium cation. The sensitization effect has been shown to be present in liquid solutions and in plasticized polymer layers but not in solid polymeric solutions. Quantum-chemical calculations have been performed that made it possible to describe the experimental results on condition that the dissociation of reduced diazonium cation proceeds from non-thermalized state. Thermalization of the reduced cation occurs in solid solutions that predetermine the full braking of the dissociation process.

Исследованы молекулы со связью типа Xe–O (диазохиноны, соли диазония, азиды и т.п.), которые характеризуются значительной активностью в нижних возбужденных состояниях или при перенесении на них дополнительного электрона. Проведены экспериментальные и теоретические исследования сенсibilизированного фотолиза солей диазония в жидких и твердых растворах. Найдены величины квантовых выходов сенсibilизированного фотолиза солей диазония в зависимости от природы растворителя, красителя (сенсibilизатора) и заместителя в пара-положении катиона фенилдиазония. Показано, что эффект сенсibilизации присутствует в жидких растворах и пластифицированных полимерных слоях и отсутствует в твердых полимерных растворах. Проведены квантово-химические расчеты, позволившие описать экспериментальные результаты при условии, что диссоциация восстановленного катиона диазония осуществляется из нетермализованного состояния. Термализация восстановленного катиона происходит в твердых растворах, которые определяют полное торможение процесса диссоциации.

Diazonium salts and azides are well-known photosensitive components of silver-free photographic materials [1]. Although those compounds are known as long ago as in the last decades of 19th century, their photochemical properties are insufficiently presented in literature.

In this work, the properties of excited states of those compounds are considered within the frame of a novel class of compounds. This may contribute to a better un-

derstanding of photochemical properties of a wide class of compounds and to use them more widely as light sensitive components in photography and phototechnology. The novel class mentioned above includes compounds with the Xe–O type bond between molecular fragments.

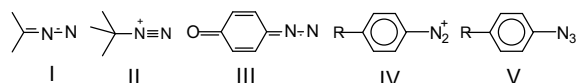
The classification of chemical bonds in molecules (covalent, ionic, donor-acceptor, hydrogen) is elaborated well enough. In this classification, chemical bond between an

atom with fully occupied atomic orbitals (AO), e.g., an inert gas atom (xenon, krypton) or a halogen anion ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ), and an oxygen atom is considered as a specific bond type. The formation of chemical (donor-acceptor) bond should be preceded by excitation of the oxygen atom from the state with  $(2p_z)^2(2p_x)^1(2p_y)^1$  electron configuration to that with  $(2p_z)^2(2p_x)^2(2p_y)^0$  one. Formation of such a bond results in molecules of  $\text{ClO}_n^-$  or  $\text{IO}_n^-$  ( $n = 1-4$ ) type and, as a consequence, in  $\text{XeO}_n$  molecule. It is known [2] that molecules of  $\text{ClO}_n^-$  or  $\text{IO}_n^-$  type act as electron acceptors in aqueous solutions in spite of interelectron repulsion. The neutral molecule  $\text{XeO}_n$  is naturally a considerably stronger oxidant causing an explosion in contact with even weak donors (e.g., with paper) [2].

In this work, the possibilities of molecule formation including bonds of the above type are widened. Instead of Xe and O atoms, we have selected molecules having the same features as those atoms, that is, one molecule should contain a fully occupied molecular orbital (MO) (including  $n$ -MO) while another, to be in triplet state.

The first type of molecule includes molecular nitrogen, molecules (including cyclic) with a heteroatom where the  $n$ -MO is localized ( $\text{R}_1\text{-O-R}_2$ ,  $\text{R}_1\text{-S-R}_2$ ,  $\text{R}_1\text{-N=R}_2$ ,  $\text{R}_1\text{-NH-R}_2$ ,  $\text{R}_1\text{-CO-R}_2$ , etc., where  $\text{R}_1$ ,  $\text{R}_2$  are arbitrary molecular fragments) and the like. The second type is represented by molecular structures such as carbenes ( $\text{R}_1\text{R}_2\text{C}$ ), nitrenes (RN), aryl cations (R), etc. Moreover, a halogen anion or oxygen atom may be one of the fragments mentioned.

In this work, molecules of the above types, namely, diazomethane (I), methyl diazonium cation (II) diazoquinoline (III), diazonium salts (IV), and azides (V) have been investigated theoretically and in experiments.



In the experimental studies the spectroscopic and photochemical properties of the compounds were considered while in theoretical ones, the quantum-chemical calculations of excited molecular states (MNDO and AM1 methods [3]). For comparison, calculations were performed for  $\text{ClO}_n^-$  and  $\text{IO}_n^-$  molecules that could contribute to understanding of  $\text{XeO}_n$  molecule.

The experimental measurements were made on solutions using a Specord M-40 spectrophotometer and a mercury lamp, one emission line was isolated by light filters.

$\text{ClO}_n^-$  and  $\text{XeO}_n$  molecules. Calculation of energy diagram for  $\text{ClO}_n^-$  has shown that all  $\pi$ -MO in the molecule are occupied by electrons. The lower singlet state  $S_1$  corresponds to transfer of one electron from  $\pi^*$ -MO to  $\sigma^*$ -MO, the latter being formed as a linear combination of  $p_z$ -AO of interacting atoms. A potential well of about 0.5 eV depth with a minimum at  $r_{\text{Cl-O}} = 1.95 \text{ \AA}$  is clearly seen on surfaces of  $S_1$  and  $T_1$  states (in ground state,  $r_{\text{Cl-O}} = 1.70 \text{ \AA}$ ). This well is due to oxygen atom polarization in the chlorine anion field at long distances. The presence of the potential well results in that the photodissociation of excited  $\text{ClO}_n^-$  molecule is possible only from the hot  $S_1$  or  $T_1$  state. This process is possible in gas phase while being substantially hindered in a condensed one. An effective dissociation in condensed phase may occur only under  $\sigma \rightarrow \sigma^*$  excitation (energy surfaces of  $S(\sigma\sigma^*)$  and  $T(\sigma\sigma^*)$  states are purely dissociative).

Since  $\text{HalO}_n^-$  molecules (Hal = a halogen atom) in solutions are electron acceptors, the energy surface for  $\text{HalO}_n^{2-}$  was also calculated. It turned out to be a purely dissociative, that is, the electron transfer onto  $\text{HalO}_n^{2-}$  results in that an oxygen anion is splitted off ( $\text{ClO}_n^- + e^- \rightarrow \text{ClO}_{n-1}^- + \text{O}^-$ ). The electron transfer process is impossible in vacuum, since this reaction occurs with the system energy increase due to interelectron repulsion. Nevertheless, in aqueous solutions, an energy gain takes place due to interaction of  $\text{HalO}_n^{2-}$  with the solvent molecules (the solvent polarization).

In  $\text{XeO}_n$ , elimination of the interelectron repulsion effect results in a substantial increase of oxidative properties. That is why  $\text{XeO}_n$  in any aggregate state explodes in the presence of even trace amounts of an electron donor.

In what follows, in connection with such distinction in properties of  $\text{HalO}_n^-$  and  $\text{XeO}_n$ , we will compare the properties of two similar structures differing in the ground state charge as well as of one and the same structure in the ground and reduced (containing one electron more) states.

*Diazomethane molecule and methyl diazonium cation.* The diazomethane molecule (I) and its protonated form (II) are simplest systems. Calculations of energy surfaces for

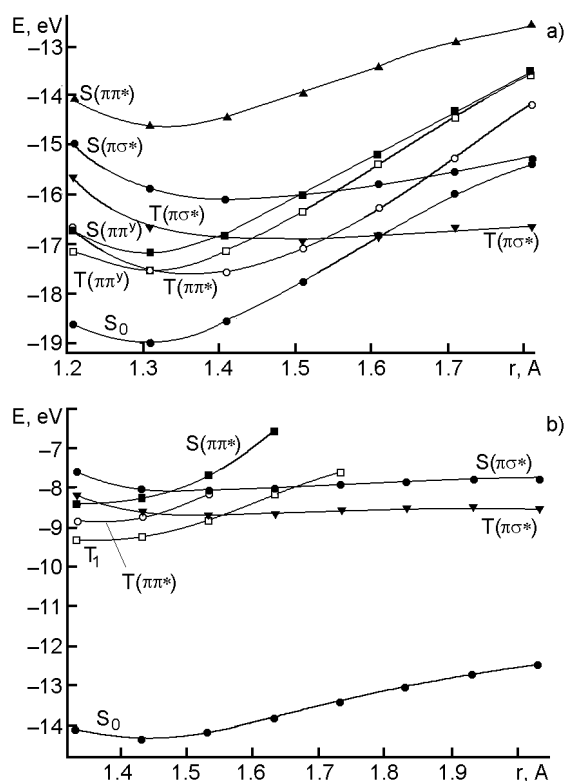


Fig. 1. Energy diagrams for H<sub>2</sub>CN<sub>2</sub> (A) and H<sub>3</sub>CN<sub>2</sub><sup>+</sup> (B).

Under varying C–N bond length show that such a molecule has an absorption band in UV spectral region related to  $\pi \rightarrow \pi^*$  quantum transition as well as weak absorption bands at the boundary between visible and UV regions related to  $\pi \rightarrow \sigma^*$  and  $\pi \rightarrow \pi^\nu$  quantum transitions (Fig. 1). The mentioned  $\sigma^*$  MO is localized on the C–N bond while the  $\pi^\nu$ , on the diazo group. It is seen from the energy diagram that the molecule dissociation is possible both from the hot  $S(\pi\sigma^*)$  state (the molecule excitation at small C–N bond length) and from  $T(\pi\sigma^*)$  one. The latter is formed most likely due to energy transfer from  $S(\pi\pi^\nu)$  state to  $T(\pi\sigma^*)$  one (pre-dissociation) and causes the molecule dissociation even from thermalized state (low potential well depth) resulting in formation of carbene in triplet state and N<sub>2</sub> molecule.

The calculation has shown that capturing of one electron by the molecule almost does not change the molecular energy in the ground state (the affinity energy is close to zero). Thus, reduction of molecule I does not result in its dissociation.

The diazomethane protonation with methyl diazonium (II) formation changes

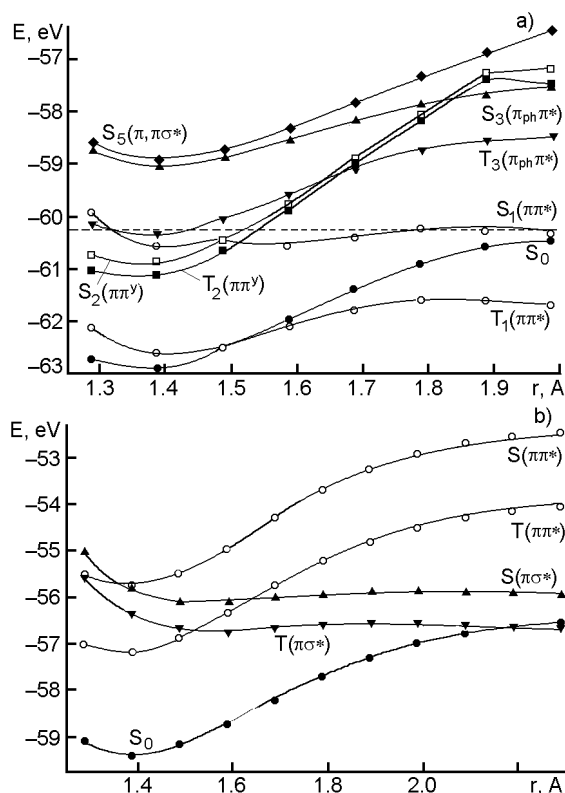


Fig. 2. Energy diagram of diazoquinone (A) ( $\Delta E[S_1(\pi\pi^*)] = 0.166$  eV) and *p*-hydroxyphenyl diazonium (B) ( $\Delta E[T(\pi\sigma^*)] = 0.166$  eV).

substantially the energy surface structure for the ground and excited states. Such molecule dissociates easily from  $S(\pi\sigma^*)$  and  $T(\pi\sigma^*)$  states that are formed by pre-dissociation from the  $S(\pi\pi^*)$  state. This process, however, requires a higher exciting quantum energy than in the case of molecule I.

The methyl diazonium turned out to have a higher affinity energy to electron (exceeding 7 eV), this energy increasing with the C–N bond length. As a result, the C–N binding energy decreases from 2.15 eV (in methyl diazonium) to 0.53 eV (in its reduced form). This effect is sufficient for dissociation of the reduced molecule at room temperature, that is, the methyl diazonium dissociation can be sensitized by the photoinduced electron transfer.

**Diazoquinone and diazonium cation.** Now let the structures III and IV be considered. The calculation results show that the diazoquinone dissociation is possible only from its  $S(\pi\pi^*)$  state that is the  $S_1$  state of the molecule (Fig. 2). The energy barrier height for dissociation from that state is as low as 0.17 eV, thus providing a high dissociation efficiency. All other states have been found

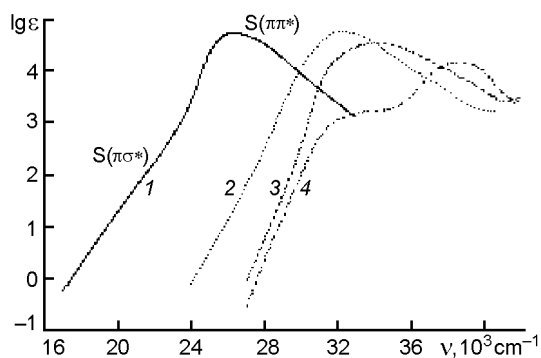


Fig. 3. Absorption spectra of aqueous solutions of *p*-substituted diazonium salts. Substituents:  $\text{N}(\text{C}_2\text{H}_5)_2$  (1),  $\text{OCH}_3$  (2), Br (3), H (4).

to be inactive for the dissociation process. Molecule II exhibits a high electron affinity energy (about 3 eV) that is almost independent of the C–N bond length, since the  $\sigma^*$  MO is not involved, therefore, the C–N binding energy remains almost unchanged. That is why the molecule cannot dissociate after the electron capturing.

Protonation of III under formation of cation IV changes dramatically the molecule properties. Now it is just  $S(\pi\sigma^*)$  and  $T(\pi\sigma^*)$  states that become dissociative; the cation transits to those states due to pre-dissociation from the  $S(\pi\pi^*)$  one. The main dissociation product is most likely hydroxy phenyl cation in excited singlet state that is relaxed then into the ground triplet one. The energy barrier for dissociation from  $S(\pi\sigma^*)$  state is as low as 0.2 eV and from the  $T(\pi\sigma^*)$  one, 0.17 eV.

The result of electron capturing by cation IV is to be expected. The cation IV electron affinity energy in the equilibrium geometry turns out to amount 5.9 eV and to increase up to 8.25 eV as the C–N bond length increases up to 0.2 nm. The energy surface of reduced cation IV has no barrier as the C–N bond length increases. Thus, the photoinduced transfer of electron to cation IV provides its dissociation into aryl radical and nitrogen molecule.

Variation of substituent in cation IV does not change the dissociation mechanism from dissociative singlet and triplet  $\pi\sigma^*$  states, the cation transiting into those states due to pre-dissociation from the  $S(\pi\pi^*)$  one.

Experimental studies and theoretical calculations show that the energy of excitation into  $S(\pi\pi^*)$  state increases regularly as the electron-accepting properties of the substi-

tuent become stronger (from  $\text{NH}_2$  to  $\text{NO}_2$ ). Both  $\pi \rightarrow \pi^*$  quantum transitions and  $\pi \rightarrow \sigma^*$  ones are observable in experiment (Fig. 3) because weak  $\pi \rightarrow \sigma^*$  quantum transitions (visible only as long-wavelength knee in the  $\pi \rightarrow \pi^*$  absorption band at room temperature and as a weak band in frozen solutions [4, 5]) are within the region of lower energy than the long-wavelength  $\pi \rightarrow \pi^*$  transition. It is seen from Fig. 3 that the extinction coefficient for  $\pi \rightarrow \sigma^*$  transition is several orders lower than that for  $\pi \rightarrow \pi^*$  one. Since the  $\pi\sigma^*$  state is dissociative, a direct excitation to the weak band results in the diazonium cation dissociation with the same quantum yield as that at excitation into  $S(\pi\pi^*)$  state [5]. Thus, the energy structure of diazonium cation provides the cation excitation relaxation only via  $\pi\sigma^*$  state.

In all cases, there is a low energy barrier for the cation dissociation from the  $S(\pi\sigma^*)$  state. In rigid solvents, especially in the frozen ones, the dissociation process may be slowed due to steric hindrances. This results in the  $S(\pi\sigma^*) \rightarrow T(\pi\sigma^*)$  conversion and the cation dissociation from the  $T(\pi\sigma^*)$  state. We have proven that the photodissociation process efficiency is high even in solutions frozen at 4.2 K.

Independent of the substituent nature in cation IV, it has a high electron affinity energy (from 4.5 eV for amino substituted phenyl diazonium (PhD) to 6.5 eV for nitro substituted one). The electron capturing at room temperature results in dissociation into nitrogen molecule and aryl radical. Thus, photolysis of any diazo cation (DC) can be sensitized by dyes. Since the DC electron affinity depends on the substituent nature, any dye may act as photolysis sensitized only for a DC with a certain set of substituents providing an energy gain at the electron transfer from the excited dye molecule to the DC. For example, experiments [6] have shown that xanthene dyes sensitize efficiently DC with substituents ranging from  $\text{OCH}_3$  to  $\text{NO}_2$ , while in the case of  $p\text{-N}(\text{C}_2\text{H}_5)_2\text{-PhD}$ , the quantum yield of electron photoinduced transfer is 2 decimal order lower.

*Azides.* Azides (V) form another group of substances with a Xe–O type bond between molecular fragments. Those molecules consist of a linear  $\text{N}_3$  group and a fragment *R*. The latter can be a hydrogen or alkali metal atom as well as any polyatomic fragment

(radical). It is just substituted phenyl azides (PhA) that are used most widely.

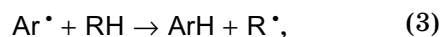
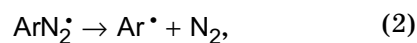
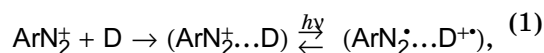
As well as diazonium salts, azides are similar to  $\text{XeO}_n$  in that those are explosive. It was shown above that the electron transfer to  $\text{XeO}_n$  and DC causes the molecule dissociation that can give rise to explosion. Now let similar processes in azides be considered. Investigation of  $\text{HN}_3$  and  $\text{LiN}_3$  as model systems has shown that in both cases the molecule electron affinity energy is low (0 to 0.5 eV in  $\text{HN}_3$  and 0 to 0.3 eV in  $\text{LiN}_3$ , depending on the dissociating bond length). Calculation of the excited state energy diagram for those molecules has shown that  $\text{HN}_3$  can dissociate from the triplet  $T(\pi, \pi^y + \sigma^*)$  state or from hot  $S(\pi, \pi^y + \sigma^*)$  one at arbitrary temperature. For both those states, it is just an MO being a hybrid between  $\pi^y$  and  $\sigma^*$  ones that is active. A similar calculation for  $\text{LiN}_3$  has shown that it can dissociate only from the hot  $T(\pi, \sigma^*)$  state, because the energy barrier is as high as 1 eV. The polar solvent effect is the only factor favoring the  $\text{LiN}_3$  dissociation. It is seen that the electron transfer or photodissociation cannot explain the explosive properties of  $\text{LiN}_3$  without account for other factors.

Energy diagram for phenyl azide are similar to that for  $\text{HN}_3$ . In this case, the photodissociation efficiency is high both from  $S(\pi, \sigma^*)$  and  $T(\pi, \sigma^*)$  states. The energy barrier in the  $T(\pi, \sigma^*)$  state is as low as 0.06 eV, thus making the photodissociation possible at substantially any temperature. Experimental investigations of phenyl azide in frozen (4.2 K) alcoholic solutions or in polymer layers have shown that the photodissociation really occurs. The molecular nitrogen has been found to crystallize in certain areas of the solvent (or polymer layer). As the sample is heated, nitrogen forms high-pressure gas bubbles (vesicles) in the polymer matrix. Thus, theoretical calculations of energy structure and photodissociation mechanisms in azides have been well confirmed in experiment.

The electron transfer onto phenyl azide molecule results in an increase of the electron system energy by 1 eV at the equilibrium molecular geometry. The phenyl azide energy surface with one excess electron answers to the dissociative one. Thus, phenyl azide dissociates under electron transfer. Nevertheless, it follows both from calculated and experimental data that the dye sensitization of that process is impossible.

The electron transfer from the matrix or dye is possible most likely only under a high-energy excitation.

*Sensitization of diazonium salt (DS) photosensitivity.* During three last decades, several tens of works were published dealing with sensitization of DS photolysis [6–10] where light sensitivity of sensitized diazotypic materials was considered. It was shown that the DS photolysis sensitization is due to electron transfer from the sensitizer to DS, both molecules being bound into an association due to electrostatic forces, according to the following scheme:



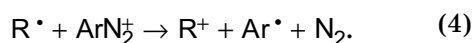
where Ar is the aryl fragment of DC; D, the electron donor (sensitizer); RH, the solvent.

The DC association with the sensitizer molecule is confirmed by the charge transfer absorption bands [8], by the sensitization efficiency dependence on the solvent dielectric constant [11] as well as by the optical density dependence in the dye absorption spectrum on the DS concentration [10]. Those results allowed to find the electron affinity energy for DC bearing various substituents at the phenyl fragment [12]. The electron affinity energy turned out to increase regularly as the Gamet  $\sigma^+$  constant increases (from 4.5 eV for p- $\text{N}(\text{CH}_3)_2$ - to 6.5 eV for p- $\text{NO}_2$ -phenyl diazonium). It is clear that for the electron photoinduced transfer from the sensitizer molecule to DC was possible, the ionization potential of the excited molecule ( $I_G^* = I_G - h\nu$ ) should be lower than the DC electron affinity energy ( $E_A$ ) while the potential  $I_G$  should exceed  $E_A$  so that the electron transfer would be impossible in dark conditions. Such interrelations restrict the sensitizer selection.

Our studies have shown that efficient sensitization of DS photolysis (para substituted phenyl diazonium boron fluorides were investigated) can be realized using dyes, in particular, xanthene, thiazine, oxazine, polymethine ones, etc. In contrast, aromatic compounds (polyacenes) are unsuitable for DS sensitization.

Since the DC electron affinity energy depends on the substituent nature, the sensitization efficiency increases regularly with the the Gamet  $\sigma^+$  constant [13] (see Table).

As a rule, the optical density in the dye absorption region decreases in the course of sensitized DS photolysis according to reaction (1). This effect is observed not only in aqueous solutions but also in ethanol or acetone. No dye concentration decrease occurs only in formamide ( $\text{H}_2\text{NCHO}$ ) due to formation of the solvent active radical ( $\text{R}^\bullet = \text{H}_2\text{NC}^\bullet\text{O}$ ). Moreover, the activity of that radical has found to be sufficient to reduce all DC except for  $p\text{-(C}_2\text{H}_5)_2\text{N-PhD}$ , thus making it possible to realize the chain dissociation reaction of those DC:



In other solvents, the activity of the  $\text{R}^\bullet$  radical was low.

Judging from the data presented, the sensitization would be expected to take place both in liquid and solid solvent and to be temperature-independent. Nevertheless, UV absorption spectra and EPR ones of irradiated solutions measured by us have shown that there is no electron photoinduced transfer from the sensitizer molecule to DC in frozen solutions.

On the other hand, investigation of sensitized DC photolysis in polymer layers has shown that at room temperature in the solid polymer solution the electron photoinduced transfer reaction does not occur and thus there is no DS sensitization effect. Introduction of a plasticizer (polyethylene glycol, PEG) into the polymer layer provides the sensitized DS photolysis, the reaction rate increasing with the plasticizer concentration in the layer. The dependence of sensitized DS photolysis rate on the polymer matrix nature is explained by that PEG plasticizes different matrices in different ways. The best plasticization is attained in polyvinyl acetate (PVA) and polyvinyl pyrrolidone (PVP), it is somewhat worse in methyl metacrylate-metacrylic acid copolymer (MMC) and in polyvinyl ethylal (PVE). The plasticized polymer is similar to a gel substantially in all cases. Thus, the efficiency

Table. Quantum yields of photodissociation sensitization for aqueous solutions (pH = 6) of diazonium salts

Dye	DS	$p\text{-(C}_2\text{H}_5)_2\text{N-PhD}$	$p\text{-CH}_3\text{O-PhD}$
Fluoresceine	$3.2 \cdot 10^{-3}$	0.25	0.34
Eosine	$1.6 \cdot 10^{-2}$	1.18	1.37
Bengalia pink	$4.6 \cdot 10^{-2}$	0.29	0.27

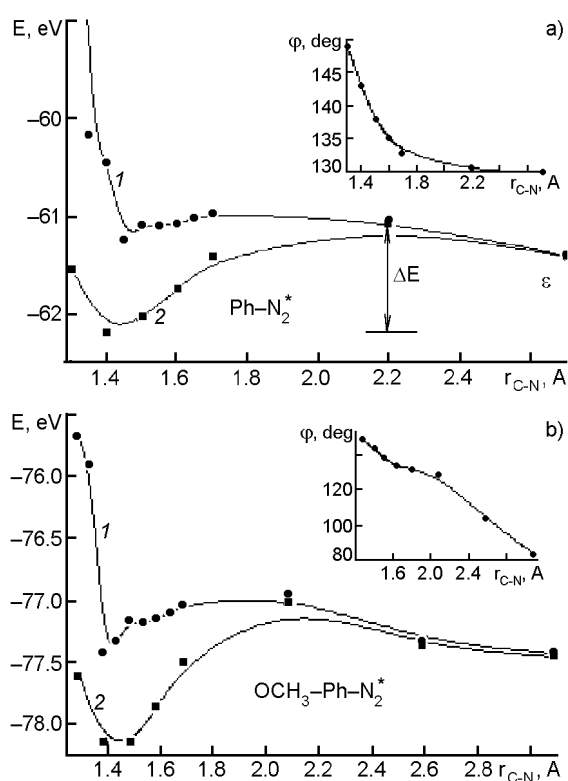


Fig. 4. Potential surface curves for reduced  $p$ -substituted phenyl diazonium cations of linear (1) and optimized (2) geometry. Insets: C-N-N angle value as a function of C-N bond length at optimized radical geometry.

of sensitized DS photolysis increases as the polymer solution rigidity drops.

To elucidate this effect of the polymer solvent on the sensitized DS photolysis rate, quantum-chemical calculations of electron system energy surface have been performed for DC and its reduced form ( $\text{ArN}_2^\bullet$ ) as function of the dissociating bond length  $r_{\text{C-N}}$ . To that end, MNDO and AM1 methods [14] were used. The calculations were done for optimized DC geometry, then, an additional electron was introduced and the dissociating C-N bond length was specified. The calculated results are presented in Fig. 4. It is seen that when an electron is transferred to DC, its geometry becomes non-



spectral range by dyes while azides can be sensitized to high-energy radiation only. The photoinduced reaction of electron transfer from the excited dye molecule to DC provides the sensitized DS photolysis in liquid solutions but not in polymer layers. In plasticized polymer layers, the sensitized DS photolysis occurs, the reaction rate increasing in parallel with the plasticizer content. Quantum-chemical calculations of reduced DC have shown that the photoinduced electron transfer results in formation of  $\text{ArN}_2^*$  in hot state. It is just the geometry with broken C–N–N group that answers to the thermalized  $\text{ArN}_2^*$  state. The  $\text{ArN}_2^*$  thermalization results in stopping of  $\text{ArN}_2^*$  dissociation, at the same time, the reaction of the reciprocal electron transfer to the oxidized dye molecule takes place. The sensitized DS photolysis is possible only if the ionization energy of excited dye molecules ( $I_G^* = I_G - h\nu$ ) is lower than the DC electron affinity energy, the latter being within limits of 4.5 eV for p– $\text{N}(\text{C}_2\text{H}_5)_2$ –PhD to 6.5 eV for p– $\text{NO}_2$ –PhD.

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## Молекули зі зв'язком типу Хе–О між фрагментами. Солі діазонію та азидиї

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Досліджені молекули зі зв'язком типу Хе–О (діазохінони, солі діазонію, азиди тощо), як характеризуються значною активністю в нижніх збуджених станах або при перенесенні на них додаткового електрона. Проведено експериментальні і теоретичні дослідження сенсibilізованого фотолізу солей діазонію в рідких і твердих розчинах. Знайдено величини квантових виходів сенсibilізованого фотолізу солей діазонію в залежності від природи розчинника, барвника (сенсibilізатора) і замісника в пара-положенні катіона фенілдіазонію. Показано, що ефект сенсibilізації присутній в рідких розчинах і пластифікованих полімерних шарах і відсутній в твердих полімерних розчинах. Проведено квантово-хімічні розрахунки, які дозволили описати експериментальні результати за умови, що дисоціація відновленого катіона діазонію здійснюється з нетермалізованого стану. Термалізація відновленого катіона відбувається в твердих розчинах, що визначають повне гальмування процесу дисоціації.