

PHYSICAL PROCESSES OF IMAGE FORMING IN LUMINESCENT MATERIALS ON THE BASIS OF ANTHRACENE

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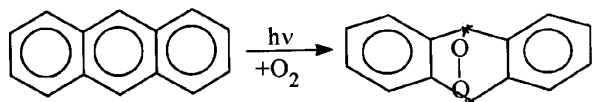
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The work is devoted to the investigation of the physical processes of the relaxation of excitation in the molecules of peroxide and, in particular, of mechanisms of the dissociation of a molecule from the basic and excited states. The theoretical and experimental investigations of the processes proceeding in the luminescent materials on the basis of anthracene (the solid polymeric solutions and the polycrystalline layers of anthracene) show that the primary process of recording of the information is the process of oxidation with the formation of anthracene peroxide. Then, in solid solutions, the dissociation of peroxide on the initial products occurs, while the further transformation of peroxide into anthraquinone is carried out in polycrystalline layers. The study of the properties of peroxide in the basic and excited states has shown that its thermal dissociation results in the detachment of the oxygen molecule overcoming the barrier ~ 1.2 eV. Lengthening the C—O-bond above 0.25 nm is accompanied by the crossing of the basic singlet state with the triplet one located on the same bond. As a result of the dissociation, an anthracene molecule in the singlet state and a molecule of oxygen in the triplet state are formed. The excitation of a peroxide molecule by capture of an exciton with the subsequent relaxation of excitation results in its localization in the triplet dissociative state located on the O—O-bond. At lengthening the bond up to 0.2 nm, the triplet state becomes the basic state of the molecule, of which anthraquinone is formed after the detachment of two atoms of hydrogen. The last, interacting with the excited molecules of anthracene, forms the charge-transfer complexes that efficiently extinguish the exciton fluorescence.

The study of the anthracene photooxidation processes in the crystalline state [1] and in a solid polymeric matrix [2–4] has shown that, in the presence of oxygen, the excitation of an anthracene molecule is accompanied by the intermolecular interaction which leads to the formation of anthracene photooxide (peroxide compound).



The investigations have shown that the formed peroxide compound in the solid polymeric matrix is

unstable at room temperature [2–4] and dissociates into the initial components within several hours (or days). At the same time, in the polycrystalline anthracene, the transformation of peroxide into anthraquinone actively quenching the exciton luminescence [5] occurs.

The presence of such a process promotes the creation of luminescent materials for the recording of information [2] and materials for the registration of phase holograms [5].

In the present work, the results of the experimental (the literary and original results) and theoretical researches on the physics of the excited states of molecules, explaining the mechanisms of specified processes, are stated. The theoretical results are obtained with the use of quantum-chemical calculations (the analytical calculations and calculations within the computing methods AM1 [6] and PM3 [7, 8] with the configuration interaction). Experimental researches included the study of the luminescent spectra and the absorption ones of the solid solutions and polycrystalline layers of anthracene (An).

In the calculations of the peroxide molecule and products of its dissociation, we took into account 78 electrons occupying 39 energy levels. For the correct determination of the energy of quantum transitions and the oscillator forces of appropriate transitions, the configuration interaction between 8 upper occupied and 8 bottom free states was taken into account. From the occupied states, 4 upper ones are represented by π -levels and the following 4 states — by σ -levels. Seven bottom free states (from N40 to N46) are represented by π -levels, and vacant level N44 is a hybrid one and consists of the molecular π -orbital (π -MO) located on phenyl rings and σ -MO located on the group COOC. We especially mark this MO, inasmuch as the localization of an electron on it will lead to the break of O—O-bond and give opportunities for the formation of anthraquinone.

The investigation of the mechanisms of formation of peroxide has shown that the binding energy of atoms in a peroxide molecule (-128.7 eV) is much less than the sum of binding energies of atoms in the molecules of anthracene and oxygen (-129.9 eV), which causes the instability of the peroxide molecule. On the other hand, it is necessary for the formation of peroxide (AnO_2) that the energy state of the excited pair of molecules anthracene + oxygen lie above the basic state of peroxide.

Two ways of the formation of AnO_2 through the interaction of An and O_2 are possible. At that, both molecules should be in the singlet or triplet state, inasmuch as the basic state of AnO_2 is a singlet. It turned out that the excitation of the oxygen molecule into the singlet ($^1\Delta_g$) or the $^1\Sigma_g^+$ -state yields the energy of the specified pair of molecules which is equal to, respectively, -129.1 or -128.7 eV. Hence, the peroxide molecule practically is not formed from these states of the excited pair. For its formation, it is necessary that the anthracene molecule be excited into the T_1 -state (from the experiment at $\lambda=670$ nm, the energy of the pair is -128.0 eV). The transfer of the triplet excitation on the oxygen molecule will be a competing process proceeding, as a rule, with high efficiency. This fact also yields a low quantum yield of the formation of peroxide. A very large rate of formation of peroxide is possible in the case where the anthracene molecule is in the excited S_1 -state, and the oxygen molecule is not excited or excited into the singlet $^1\Sigma_g^+$ -state. Only the small life-time of the anthracene molecule in the S_1 -state can be the obstacle for such a reaction.

Under the irradiation of a solid solution of anthracene ($\lambda = 365$ nm, 250 W-mercury lamp), the absorption spectrum of anthracene disappears and is replaced by other spectrum (Fig. 1). In all transformations (photochemical ones and in dark), two points are kept invariable (isobestical) in the spectrum: at 31600 cm^{-1} (316 nm) and 38290 cm^{-1} (261 nm). This testifies to that there are only two compounds in the solid solution, one of which is the product of transformation of the second one.

There are the quantum transitions into the triplet and singlet states in the excitation spectrum of the peroxide molecule (Table). There are the ($S_0 \rightarrow S_1$)-absorption band in the range of 395 nm and the quantum transitions into the upper triplet states (425 and 400 nm) in the excitation spectrum of the anthracene molecule. We mark just these triplet states, inasmuch as they lie

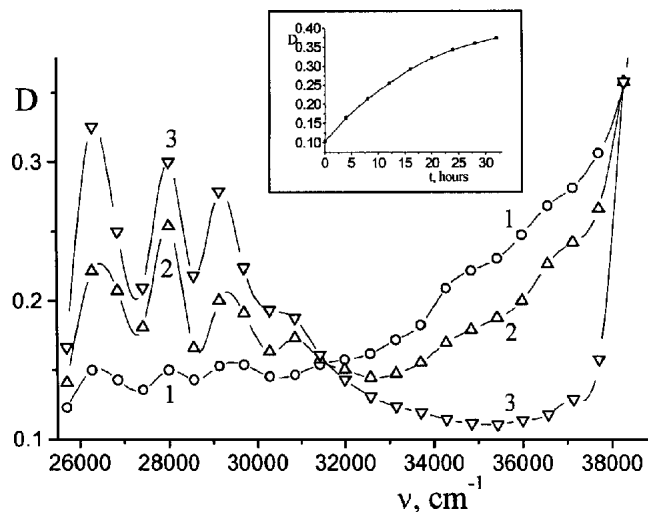


Fig. 1. Absorption spectra of anthracene in polyethylene after irradiation (1), in 6 hours (2), and in 18 hours after irradiation (3). On the insert: the kinetics of restoration of the optical density of anthracene at 295 K

between the singlet and the triplet excitation of peroxide.

It follows from Table that the absorption spectrum of peroxide develops since 315 nm and reaches the maximum in the range of 222 nm, which corresponds mainly to the quantum transitions in phenyl rings. The quantum transition in the range of 315 nm corresponds to the electron transition from hybrid MO N35 containing the delocated σ -MO and the π -MO located on group COOC onto MO N44. The oscillator force of such quantum transition is lower by 5 times, than that of the ($S_0 \rightarrow S_1$)-absorption of the anthracene molecule.

Using the calculation procedure MOPAC [9], we succeeded to optimize the geometry of the peroxide molecule during its dissociation at all intermediate lengths of the dissociating bond and to find channels of the thermal dissociation of peroxide into the initial products and the photochemical one with the formation of anthraquinone.

It turned out that the equilibrium geometry of the peroxide molecule is provided by the sp^3 -hybrid atom orbitals of the carbon atoms in positions 9 and 10 of the

Excited states of a peroxide molecule

Quantum transition	Wavelength λ , nm	Oscillator force f	Assignment
$S_0 \rightarrow T_1$	437	0	$\pi_4 \rightarrow \pi_5, \pi_1 \rightarrow \pi_7$
$S_0 \rightarrow T_3$	380	0	$\sigma_{\text{Ph}}\pi_{\text{CO}} \rightarrow \pi_{\text{Ph}}\sigma_{\text{COOC}}$
$S_0 \rightarrow S_1$	316	0.004	$\pi_4 \rightarrow \pi_6, \pi_3 \rightarrow \pi_5$
$S_0 \rightarrow S_2$	315	0.021	$\sigma_{\text{Ph}}\pi_{\text{CO}} \rightarrow \pi_{\text{Ph}}\sigma_{\text{COOC}}$
$S_0 \rightarrow S_n$	222	0.734	$\pi_4 + \sigma_{\text{Ph}}\pi_{\text{CO}} \rightarrow \pi_5$

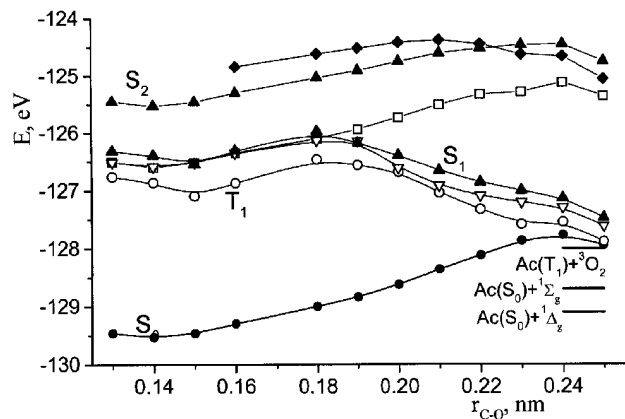


Fig. 2. Diagram of the energy states of peroxide depending on the C—O-bond length

anthracene main body. Such a hybridization causes the break of the anthracene main body onto the specified atoms of carbon, so that the angle equal to 118° is formed between planes, in which two halves of the molecule lie. Lengthening the dissociating bond results in a gradual increase in the angle. The angle 180° is reached at the lengthening of O—O-bond and C—O-bond up to 0.4 nm and 0.26 nm, respectively.

As follows from the diagram of energy states of peroxide depending on the length of C—O-bond (Fig. 2), the molecule of peroxide cannot dissociate from the equilibrium excited state though the photodissociation from the nonequilibrium state is not excluded. However, it turned out that the binding energy of the group of two atoms of oxygen with a deformed molecule of anthracene does not exceed $1.3 \div 1.5$ eV that provides the thermal instability of a molecule, as follows from experiment. At the lengthening of C—O-bond above 0.25 nm, the triplet state becomes the basic state of the intermediate product. It is necessary to note that, at such a lengthening, the dissociation rate considerably exceeds the interconversion rate, and the molecule dissociates with the formation of two molecules in the triplet state. And only then the relaxation of the anthracene molecule into the basic state occurs. Hence, at the specified lengthening of the bond, the peroxide molecule dissociates irreversibly.

The calculations show that the probability of the thermal formation of anthraquinone from peroxide is negligibly small, inasmuch as the interconversion into the triplet dissociative state should occur after the thermal excitation of the peroxide molecule (the same energy is required as that for the dissociation of peroxide with the

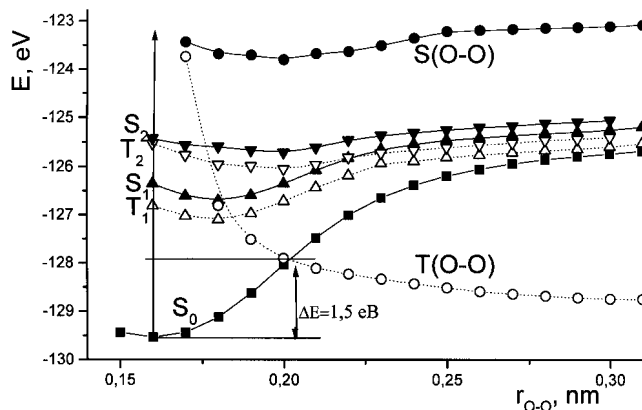


Fig. 3. Diagram of the energy states of peroxide depending on the O—O-bond length

detachment of oxygen). The necessity of such a process lowers the reaction rate approximately by 4 orders of magnitude.

Our investigations have shown that the sensitization of peroxide by anthracene (transport of energy into the triplet state of peroxide) promotes the break of O—O-bond (Fig. 3). At the lengthening of O—O-bond by more than 0.2 nm, the triplet state is the basic state of the molecule. The relaxation from the triplet intermediate state to a flat structure should be carried out during the half-period of vibrations of the anthracene main body, that is, for the time $t \sim 10 \div 12$ s. Therefore, it would be improbable that, during such a relaxation of the molecule, it interacts with the oxygen molecule, whose final result would be the formation of the anthracene molecule.

It turned out that the creation of anthraquinone from the triplet intermediate state is connected to some difficulties. It is caused by that the singlet state is the basic state of a molecule of anthraquinone. Besides that in order to receive a molecule of anthraquinone from a transient state, it is necessary to provide the separation of atoms of hydrogen which remain strongly removed from each other at all geometric changes of the transient state. At the lengthening of O—O-bond on a distance about 0.4 nm, the molecule appeared unstable concerning the localization of atoms of hydrogen. It is more favorable to remove them on the next atoms of carbon in the molecule. We have found the single opportunity for the separation of both atoms of hydrogen simultaneously with the help of a free molecule of oxygen. It turned out that the transport of atoms of hydrogen onto an oxygen molecule is energetically favorable. At that, the molecule of anthraquinone and

the molecule of hydrogen peroxide are formed. For both molecules, the singlet state is basic.

Thus, the experimental and theoretical researches of the processes of interaction of an excited anthracene molecule with a molecular oxygen and of the processes of relaxation of the excited state in the peroxide molecule have shown that

— interaction of the anthracene molecule excited into the triplet or singlet state and the oxygen molecule causes the formation of the stable product — peroxide;

— in the polycrystalline anthracene layers, the transfer of the exciton excitation on peroxide promotes the formation of an anthraquinone molecule in the presence of an oxygen molecule and of a number of other products in its absence;

— anthraquinone with an anthracene molecule forms a charge-transfer complex [5] effectively quenching the exciton luminescence; the last provides the creation of a luminescent image;

— the processes of formation of peroxide and anthraquinone in polycrystalline anthracene layers occur in parallel. The efficiency of the formation of anthraquinone rises owing to the capture of the exciton excitation from a rather large volume of anthracene determined by the length of a diffusive displacement of singlet excitons [10];

— at room temperature in the absence of excitation, peroxide slowly dissociates into the initial products (anthracene and oxygen molecule). The dissociation of peroxide from a nonequilibrium excited state is also probable. In this case, the process of dissociation into the initial products will compete to the process of formation of anthraquinone.

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ФІЗИЧНІ ПРОЦЕСИ ФОРМУВАННЯ ЗОБРАЖЕННЯ В ЛЮМІНЕСЦЕНТНИХ МАТЕРІАЛАХ НА ОСНОВІ АНТРАЦЕНУ

П.О. Кондратенко, Ю.М. Лопаткін

Резюме

Робота присвячена дослідженню фізичних процесів релаксації збудження в молекулах пероксиду і, зокрема, механізмів дисоціації молекули з основного і збудженого станів. Теоретичні й експериментальні дослідження процесів, що протікають у люмінесцентних матеріалах на основі антрацену (тверді полімерні розчини і полікристалічні шари антрацену) показують, що первинним процесом запису інформації є процес окислювання з утворенням перекису антрацену (пероксиду). Потім у твердих розчинах здійснюється дисоціація пероксиду на вихідні продукти, у той час як у полікристалічних шарах відбувається подальше перетворення пероксиду в антрахінон. Вивчення властивостей пероксиду в основному і збудженому стані показало, що його термічна дисоціація приводить до відщеплення молекули кисню, яка при цьому долає бар'єр близько 1,2 еВ. В результаті подовження С—О-зв'язку понад 0,25 нм виникає перетин основного синглетного стану з триплетним, локалізованим на цьому ж зв'язку. У результаті дисоціації утворюється молекула антрацену в синглетному стані і молекула кисню у триплетному стані. Збудження молекули пероксиду шляхом захоплення екситона з наступною релаксацією збудження приводить до його локалізації в триплетному дисоціативному стані, локалізованому на О—О-зв'язку. При подовженні цього зв'язку до 0,2 нм триплетний стан стає основним станом молекули, з якого після відщеплення двох атомів водню й утворюється антрахінон. Останній, взаємодіючи зі збудженими молекулами антрацену, утворює комплекси з переносом заряду, що ефективно гасять екситонну флуоресценцію.