THE ROLE OF THE H-BOND IN THE PROCESSES OF DEACTIVATION OF EXCITED ELECTRONIC STATES OF MOLECULES LEADING TO THE FORMATION OF RADICALS

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Abstract

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THE ROLE OF THE H-BOND IN THE PROCESSES OF DEACTIVATION OF EXCITED ELECTRONIC STATES OF MOLECULES LEADING TO THE FORMATION OF RADICALS

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We have studied the processes of deactivation of excited molecules containing the chromophoric groups C=O and > N, which bear the principal responsibility for long-wavelength absorption ($n \to \pi^*$ electronic transition) and luminescence. These groups are also capable of forming complexes with molecules of certain solvents (for example, those containing the groups O–H, CO–OH, etc.).

The luminescence and e.p.r. spectra of anthraquinone and its derivatives, acridone derivatives, and various aromatic amines (triphenylamine, acridine, carbazole, etc.) were studied in different media (R–OH, Ar–OH, R–COOH, hydrocarbons) at molar ratios of 1 : 1 and others (in crystals) and at $C = 10^{-2}$, $5 \cdot 10^{-4}$, $5 \cdot 10^{-5}$ mole/l in solutions at 77°C. The experimental results are given in Figs. 1, 2, 3. In photoirradiated evacuated powders of the luminophores anthraquinone, 2-isopropylanthraquinone, N-ethylacridone, acridone, benzophenone, acridine, triphenylamine, carbazole, etc., at $T = 77$°K, no e.p.r. signals are detected. All the indicated powders (with the exception of acridine) phosphoresce. In samples crystallized from ethanol (mole ratio 1 : 1), and also in luminophore–X ... H–O–systems (1 : 1), singlet e.p.r. lines are observed, $\Delta H = 20$ G, $g = 2$, whose intensity increases proportionally to the intensity of the radiation source. The existence of the complex C=O ... H–O–R in the initial systems was confirmed by measurements of the i.r. spectra.

The occurrence of radicals in these systems can be explained by the interaction of the triplet C=O group with the O–H group of another molecule, which leads to transfer of a hydrogen atom from one group to the other. The process of hydrogen transfer takes place in a bridge with an H-bond, which lowers the activation energy of the transition (see Scheme 1).

Scheme 1

In a quantum-mechanical treatment of the H-bond in such a complex, it is necessary to take into account not only the interaction of three electrons (the electrons of the oxygen atom and the electron of hydrogen), but also the delocalization

Scheme 1: schematic representation of hydrogen transfer in an H-bonded complex, showing transitions $S \to S^* \to T$, irradiation $h\nu$, and radical formation involving $> \mathrm{C{=}O} \ldots \mathrm{H{-}O{-}Ar}$ and related species.

Figure 1: Scheme 1: schematic representation of hydrogen transfer in an H-bonded complex, showing transitions $S \to S^* \to T$, irradiation $h\nu$, and radical formation involving $> \mathrm{C{=}O} \ldots \mathrm{H{-}O{-}Ar}$ and related species.

of the unpaired electron occupying the excited molecular orbital.

We first observed the process of radical formation in systems with an H-bond (according to Scheme 1) while studying the luminescence of 1,4-anthraquinonedicarboxylic acid ([1]). In this case, as radicals accumulated, a gradual quenching of the luminescence was observed. The presence of radicals was confirmed by the e.p.r. method. The appearance of the singlet e.p.r. line may be explained by the formation of a radical complex.

The study of the luminescence and e.p.r. spectra of solutions of 2-isopropylanthraquinone, N-ethylacridone, triphenylamine, and acridine in ethanol, benzyl alcohol, and isobutyric acid also provides grounds for asserting that

[Figure labels: **Solvent**; **Luminophore**—triphenylamine, *N*-ethylacridone, 2-isopropylanthraquinone, anthraquinone; **isopentane**; **ethanol**; 50 sec.]

Fig. 1. EPR spectra of photobleached luminophore + solvent systems

that radical formation is due to the transfer of a hydrogen atom from the hydroxyl group of the solvent to the chromophoric group of the luminophore (Fig. 1).

In these systems, singlet EPR lines are observed, belonging to the complex (Scheme I), as well as EPR signals of solvent (matrix) radicals. The role of the hydrogen bond is important not only in the primary act of the reaction, but also in its continuation in the solvent medium. The presence of chains of solvent molecules formed by means of H-bonds explains the occurrence of secondary processes. Replacement of a hydroxyl-containing solvent by the corresponding ether or hydrocarbon sharply decreases the yield of radicals. This can be explained by the fact that C—H bonds interact only weakly with chromophoric groups and are not capable of forming chains of molecules.

In work ([2]) it was shown that the primary act in the process of radical formation from the matrix is the detachment of a hydrogen atom from the OH group of ethyl alcohol. Additional confirmation of the participation of complexes in the processes of radical generation is provided by experiments carried out with deuterated silica gel.

For solutions of triphenylamine in isopentane in the presence of deuterated silica gel, both EPR signals of cation radicals and signals of deuterium were detected.

The yield of cation radicals and deuterium atoms depends linearly on the intensity of the exciting light. Upon photobleaching of solutions of triphenylamine in ethanol in the presence of deuterated silica gel, neither cation radicals nor deuterium atoms were detected.

In the case where the nitrogen atom is not the chromophoric group, generation of radicals from the matrix molecules occurs very weakly. Thus, for example, upon photobleaching of acridine solutions in ethanol, radical generation was not observed. It is known that in the acridine molecule the luminescence is deter-

···determines the $\pi \rightarrow \pi^*$ electronic transition of the aromatic system, and not the $n \rightarrow \pi^*$ electronic transition of the nitrogen atom. Thus, for the generation of radicals from the matrix it is necessary that a complex be formed with the direct participation of the chromophoric group that absorbs the energy of the light quantum and localizes it to a considerable extent.

The ratio of the intensities of the singlet line (characterizing the radical complex) and of the EPR lines of the matrix radicals depends on the structure of the luminophore (τ-phosph. coplanarity, etc.) and of the matrix. The more stable the radical complex (which is determined mainly by the magnitude of the delocalization energy of the unpaired electrons), the greater the relative intensity of the singlet line (Fig. 1).

Fig. 2. Dependence of the yield of matrix radicals and of the radical complex on the concentration of H—O—R.
1 —alcohol radical, 2 —isobutyric acid radical, 3 —singlet line in alcohol, 4 —singlet line in isobutyric acid.

Fig. 3. EPR spectra of photoirradiated TPA in ethanol ($C = 10^{-3}$ mol $\cdot$ l^{-1}), obtained upon successive irradiation with light of λ 313 and 365 mμ.

Upon dilution of solutions of luminophore + ethanol with an inert solvent (for example, isopentane), the yield of matrix radicals drops sharply when a certain concentration of it in the solution is reached. In the case of the triphenylamine + ethanol system, the yield of ethanol radicals ceases at an ethanol concentration of 0.8-1%. For solutions of *N*-ethylacridone in isopentane, even at very low concentrations (0.01%) of isobutyric acid, its radicals are generated (Fig. 2). These facts point to the important role of complexes formed by means of H-bonds in the processes of radical generation.

It is known that in dilute solutions of ethanol in inert solvents the distances between alcohol molecules increase and the complexes decompose. In contrast to alcohol, molecules of isobutyric acid remain associated in the form of dimers even upon strong dilution. This can explain the different behavior of weak solutions of ethanol and isobutyric acid in isopentane.

Upon prolonged storage of photoirradiated solutions, or upon their gradual thawing, the singlet EPR line disappears last, indicating the high stability of the radical complex.

Photoirradiation of the radical complex in some systems (for example, triphenylamine + alcohol, Fig. 3) leads to disappearance of the singlet line and to the appearance of matrix radicals. Figure 3 gives the EPR spectra of photoirradiated TPA in ethanol, obtained upon successive excitation at λ 313, 365, and 405 mμ. Upon excitation at λ 313 mμ (which corresponds to absorption by TPA), an EPR spectrum is observed with a relatively intense singlet line and weak EPR lines of matrix radicals. If this system is then acted upon with light of λ 365 or 405 mμ (which does not excite TPA), a sharp decrease in the intensity···

···of the singlet line and the corresponding increase in the intensity of the EPR lines of the matrix radicals. The yield of radicals from the matrix increases linearly with the light intensity. Thus, the experiments showed that the process of formation of radicals from the matrix with the participation of luminophore molecules can proceed in two stages (Scheme II).

Scheme II

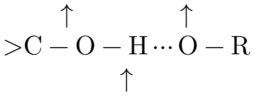
[[chemical scheme showing excitation of the luminophore–matrix complex, hydrogen-bonded solvent chains, formation of a triplet radical complex, and subsequent radical formation]]

At the triplet level in the luminophore + matrix complex, transfer of a hydrogen atom from the matrix molecule to the luminophore molecule occurs, with formation of the corresponding radicals. The radical complex corresponds to a singlet EPR line. The second stage of the process is the decomposition of the radical complex (in the presence of chains with H-bonds) upon absorption of a light quantum corresponding to the transition $S_R \to S_R^*$, with formation of matrix radicals and hydrogen atoms. Such a process may be called a consecutive two-quantum process. Thus, in such processes the yield of radicals should be proportional to the light intensity I^n, where $n \leq 2$. The yield of matrix radicals is determined by the magnitude of the potential barrier (ε) for transfer of hydrogen from a solvent molecule to a luminophore molecule and by the stability of the radical complex.

In the course of the process of formation of radicals from the matrix (Scheme III), the triplet excited level does not participate.

The relevance of the excited electronic level of luminophore molecules for this process is determined exclusively by the amount of energy required for its occurrence.

An approximate calculation shows that the radical complex



$$\begin{array}{ccccccccc} & & \uparrow & & & & \uparrow & & \\ >\mathrm{C} & - & & \mathrm{O} & - & \mathrm{H}\cdots & \mathrm{O} & - & \mathrm{R} \\ & & & & \uparrow & & & & \end{array}$$

is energetically more favorable than the triplet

$$C = O\uparrow \cdots H - O - R.$$

This explains the deactivation of excited molecules at the T-level.

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named after L. Ya. Karpov

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CITED LITERATURE

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