Reports of the Academy of Sciences of the USSR

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1965

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Abstract

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Reports of the Academy of Sciences of the USSR

1965. Volume 160, No. 1

PHYSICAL CHEMISTRY

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THE ROLE OF $n \to \pi^*$ PROMOTION IN PROCESSES OF RADICAL GENERATION

(Presented by Academician S. S. Medvedev on 18 VIII 1964)

In works ($^{1-4,6}$) it was shown that excited molecules containing chromophoric groups $C = O^\times$, $-N^\times$, etc., responsible for long-wavelength absorption (the $n \to \pi^*$ electronic transition) and luminescence, can be deactivated through interaction with molecules of the medium (alcohol, etc.) with formation of the corresponding radicals. In such processes the yield of matrix (ethanol) radicals is proportional to the light intensity I^m, where $m \approx 2$. On this basis, in some works (^{5,7}) the conclusion was drawn that the process of matrix-radical generation occurs at a triplet excited level.

However, in works ($^{2-4}$) it was shown that the process of radical generation is a two-stage process proceeding without participation of the triplet excited level. In investigations ($^{1-4}$) it was shown that the process of radical generation proceeds through a complex (luminophore + matrix) formed by means of an H bond. It was assumed that, at the triplet level (scheme 1), transfer of a hydrogen atom from the matrix molecule to the luminophore molecule occurs, with formation of a radical complex. 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. In such processes the radical yield must also be proportional to the light intensity I^m, where $m \approx 2$.

In the present communication a quantum-mechanical substantiation is given for the possibility of addition of a hydrogen atom, detached from a matrix molecule, to a luminophore molecule in the ($n\pi^*$) state, and the question of the relevance of the $S_{n\pi^*}$ and $T_{n\pi^*}$ states in the processes under consideration is resolved.

It is known that in the ground state, in a complex with an H bond, there exists a four-electron system
$> C = O \downarrow\uparrow \ldots H \downarrow\uparrow O - R$, in which a weak donor-acceptor interaction is

effected by the n electrons of the $= O$ atom, partially using the s orbital of the hydrogen atom of the $H - O-$ group.

Upon excitation of the complex as a result of realization of the $(n\pi^*)$ state of the luminophore molecule, the donor-acceptor interaction is disrupted, and in the H-bond bridge there arises a three-electron system
$> C = O \uparrow \ldots H \downarrow\uparrow O - R$. In this case the $= O \uparrow$ atom has an unpaired n electron on an atomic orbital and a relatively reduced electron density.

Thus, in systems with $(n\pi^*)$ states a new type of promotion is realized, consisting in the fact that the promoted electron occupies a molecular π^* orbital, which is considerably more favorable than promotion from a $2p$ to a $2s$ orbital of the oxygen atom. This leads to the appearance of an additional valence of the oxygen atom at a relatively smaller expenditure of energy. Two electronic states are possible: singlet ex-

excited state $(S^*_{n\pi^*})$: $> \mathrm{C} \overset{\downarrow}{=} \mathrm{O} \uparrow \ldots \mathrm{H} \downarrow\uparrow \mathrm{O} - \mathrm{R}$ and the triplet state $(T^*_{n\pi})$: $> \mathrm{C} \overset{\uparrow}{=} \mathrm{O} \uparrow \ldots \mathrm{H} \downarrow\uparrow \mathrm{O} - \mathrm{R}$, which lead to the formation of the corresponding radicals according to the following schemes:

Schemes 1

$$> \mathrm{C} \overset{\downarrow}{=} \mathrm{O} \uparrow \ldots \mathrm{H} \downarrow\uparrow \mathrm{O} - \mathrm{R} \to> \mathrm{C} \overset{\downarrow}{=} \mathrm{O} - \mathrm{H} \ldots \mathrm{O} \uparrow -\mathrm{R} \to> \mathrm{C} \downarrow -\mathrm{O} - \mathrm{H} \ldots \mathrm{O} \uparrow -\mathrm{R}$$

$$> \mathrm{C} \overset{\uparrow}{=} \mathrm{O} \uparrow \ldots \mathrm{H} \downarrow\uparrow \mathrm{O} - \mathrm{R} \to> \mathrm{C} \overset{\uparrow}{=} \mathrm{O} - \mathrm{H} \ldots \mathrm{O} \uparrow -\mathrm{R} \to> \mathrm{C} \uparrow -\mathrm{O} - \mathrm{H} \ldots \mathrm{O} \uparrow -\mathrm{R}.$$

From these schemes it is evident that the process of deactivation of the $(n\pi^*)$-excited states of luminophore molecules can be divided into five stages that determine the energetics of the entire process, namely: formation of a complex through an H-bond in the ground state, excitation of the $(n\pi^*)$-state, the reaction of hydrogen-atom transfer, formation of a ketyl radical, and formation of a radical complex by means of an H-bond. For a complete description of the entire process, in order to determine the reaction rate and the radical yield, an analysis of all its stages is necessary. However, for ascertaining the fundamental possibility of the process occurring with the participation of $(n\pi^*)$-states of luminophore molecules, the decisive importance belongs to the stage connected with attachment of the hydrogen atom to the excited luminophore molecule. In order to simplify the problem considered, this stage of the process is modeled in the present work by the reaction of interaction of a luminophore molecule $\mathrm{R_2C = O}$, in $(n\pi^*)$-states, with a hydrogen atom. It is assumed that rupture of the $\mathrm{H - O}$ bond participating in the formation of the complex can occur if the energy released upon interaction of the hydrogen atom with the luminophore molecule in the $(n\pi^*)$-state is of the same order of magnitude as the energy of the O − H bond in the matrix molecule. To calculate the interaction energy of the excited molecule $R_2C = O$ with a hydrogen atom, the Heitler–London method was applied.

The wave function of the system $R_2C = O + H$ has the form

$$\Psi = \sqrt{N}\,\hat{P}(-1)^{d(\sigma_i+\sigma_k)} \prod_{i}^{n} \varphi_i, \tag{1}$$

where $\sqrt{N}$ is the normalization factor, determined from

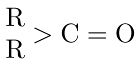
$$N = \frac{1}{\int \Psi^{\times}\Psi\, d\tau}; \tag{2}$$

$\hat{P}$ is the operator of permutation of electron coordinates; $d(\sigma_i + \sigma_k)$ is a function defined by the relation

$$d(\sigma_i + \sigma_k) = \begin{cases} 0, & \text{if } |\sigma_i + \sigma_k| = 0, \\ 1, & \text{if } |\sigma_i + \sigma_k| = 1, \end{cases} \tag{3}$$

where σ_i and σ_k are the spins of the permuted i- and k-electrons.

As φ_i were used the atomic orbital $1s$ of the hydrogen atom, the π-electron molecular orbitals



$$\begin{matrix} \mathrm{R} \\ \mathrm{R} \end{matrix} > \mathrm{C} = \mathrm{O}$$

and the n-orbital of the oxygen atoms.

The bond energy of the system $R_2C = O + H$, in accordance with (8), has the form

$$E_{\text{bond}} = \sum_{\substack{i,k \\ i<k}} K_{ik}\lambda + \sum_{\substack{i,k \\ i<k}} A_{ik}\lambda - (-1)^{d(\sigma_i+\sigma_k)} + \sum_{g,g'} \frac{Z_g Z_{g'}}{R_{gg'}} + \sideset{}{'}\sum_{i,g} C_{ig}\lambda, \tag{4}$$

where K_{ik} is the energy of the Coulomb interaction of the i- and k-electrons; A_{ik} is the energy of the exchange interaction of the i- and k-electrons; $\frac{Z_g Z_{g'}}{R_{gg'}}$ is the energy of the Coulomb interaction of nuclei g and g'; C_{ig} is the energy of the Coulomb interaction of the i-electron with the g-nucleus (the prime means that the interaction of the electron only with foreign nuclei is taken into account); λ is a coefficient arising from the nonorthogonality of φ_i and defined by the expression

Fig. 1. Dependence of the interaction energy of a hydrogen atom with a molecule $(CH_3)_2C = O$ in the $(n\pi^*)$-state. 1—triplet $E_{\text{min}} = -4.16$ eV; 2—singlet $E_{\text{min}} = -4.46$ eV

Figure 1: Fig. 1. Dependence of the interaction energy of a hydrogen atom with a molecule $(CH_3)_2C = O$ in the $(n\pi^*)$-state. 1—triplet $E_{\text{min}} = -4.16$ eV; 2—singlet $E_{\text{min}} = -4.46$ eV

$$\lambda = \frac{n!}{N}, \tag{5}$$

where n is the order of the product (1).

The binding energy of a hydrogen atom with an excited $C = O$ group is obtained from (4) if, in the summation, we fix the sign corresponding to the $1s$-electron of the hydrogen atom and its nucleus.

Fig. 1. Dependence of the interaction energy of a hydrogen atom with the molecule $(CH_3)_2C = O$ in the $(n\pi^*)$-state.
1—triplet $E_{\text{min}} = -4.16$ eV; 2—singlet $E_{\text{min}} = -4.46$ eV

It follows from formula (4) that in the ground state the $C = O$ group cannot, in the main, form a bond with a hydrogen atom, since its ground state is singlet and the exchange integrals vanish. Only the ordinary H-bond is realized. Each state $R_2 > C = O$ is occupied by two electrons; therefore the exchange integral of the $1s$-electron of the hydrogen atom with one of these electrons will be positive, and with the other negative and equal in absolute value. The situation changes sharply upon excitation. Now, even if the excited state is singlet, the exchange energy is not equal to zero, since the wave function in the excited state may differ sharply from the wave function in the ground state. Apparently, this effect is especially noticeable for $n \to \pi^*$ excitation, since in this case the difference in the exchange integrals of the $1s$-orbital of the hydrogen atom with the $|n\rangle$-orbital and the $|\pi^*\rangle$-orbital $(R_2C = O)^*$ is especially large.

Concrete calculations were carried out for the reaction of an acetone molecule in the excited $S_{n\pi^*}$-state and $T_{n\pi^*}$-state with a hydrogen atom. A preliminary calculation of the acetone molecule was carried out by the MOLCAO method in the π-electron approximation. The following parameters were chosen ([9]): $\beta_{C=O} = 0.9\beta_{C=C}$, $\delta\alpha_0 = +1.2\beta_{C=C}$. The molecular orbitals of $(CH_3)_2C = O$ in the ground and excited states were calculated. As the orbital of the n-electron of the oxygen atom, its sp^2-hybrid orbital was taken ([10]). The integrals entering into (4) were calculated according to ([11]). The results of the calculations are presented in Fig. 1. From Fig. 1 it follows that the bond in the singlet $(n\pi^*)$-state is somewhat greater than in the triplet one (under the assumption of the same spatial function of $C = O$ in the $S_{n\pi^*}$- and $T_{n\pi^*}$-states). This circumstance is connected with the fact that the exchange integrals of the n- and π^*-orbitals with the $1s$-orbital have different signs owing to the fact that the overlap integral

$$\int \pi^* 1s \, d\tau = 0.$$

Indeed, the two-center exchange integral has the form

$$A_{ik} = S_{ik} \int \left(-\frac{Z_i}{r_i} - \frac{Z_k}{r_k} \right) \varphi_i^* \varphi_k \, d\tau + \int \frac{\varphi_i^*(1)\varphi_i(2)\varphi_k(1)\varphi_k^*(2)}{r_{12}},$$

and when $S_{ik} > 0$, then $A_{ik} < 0$ (in the case of the n-electron); when $S_{ik} = 0$, then $A_{ik} > 0$ (in the case of the π^*-electron).

The difference in bond energy in the triplet $(n\pi^*)$ and singlet $(n\pi^*)$ states, amounting to 0.3 eV, is, as the calculation shows, completely compensated by the S—T splitting in the acetone molecule, equal to ~ 0.7 eV (12). The principal contribution to the bond energy is made, naturally, by the exchange interaction of the $1s$-electron with the n-electron of the oxygen atom, owing to the spatial arrangement of the n-electron, which ensures the formation of an ordinary σ-bond.

Calculation of the radical $> \mathrm{C} \uparrow \mathrm{O—H}$ in the excited $(n\pi^*)$ state gives, for the O—H bond energy, a value of 4.16 eV; whereas the O—H bond energy in ethanol, calculated in the same approximation, proves to be equal to 3.93 eV.

Thus, formation of the radical $> \mathrm{C}\uparrow\mathrm{O—H}$, arising upon addition of a hydrogen atom to an $(n\pi^*)$-excited luminophore molecule, must proceed with liberation of energy. The calculation showed that, from the energy standpoint, under the assumptions made, the triplet state is only slightly more favorable than the singlet state (by approximately 0.4 eV). However, from the kinetic standpoint the triplet state is more advantageous than the singlet state because of the considerably longer lifetime of the excited state, which is necessary for the reaction to proceed.

The mechanism considered for radical formation can be extended to hydrogen-abstraction reactions occurring with participation of an oxygen molecule in the triplet state (1). Thus, a quantum-mechanical treatment, in agreement with the experimental data, shows the possibility of abstraction of a hydrogen atom in a complex with an H-bond from a matrix molecule by a luminophore molecule in the $n\pi^*$-state, and the decisive role of $(n\pi^*)$-promotion in the processes of radical generation.

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Received17 VIII 1964

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