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THE INFLUENCE OF HEAVY ATOMS ON INTERCOMBINATION TRANSITIONS IN PORPHYRIN MOLECULES

The probabilities of intercombination transitions in organic molecules—phosphorescence $T_1 \to S_0$, singlet-triplet absorption $S_0 \to T_1$, intercombination conversion $S_1 \rightsquigarrow T_1$, and intercombination degradation $T_1 \rightsquigarrow S_0$ (see Fig. 1)—are determined by the magnitude of the spin-orbit interaction. This interaction is enhanced when heavy* or paramagnetic atoms are introduced into a molecule, which leads to enhancement of phosphorescence and $S-T$ absorption ([1,2]).

In 1952 Kasha discovered that the influence of heavy atoms on an intercombination transition ($S-T$ absorption) can also be manifested in the case when the heavy atom is not chemically bound to the skeleton of the molecule under study, but is part of the solvent molecule ([3]). This effect was investigated by McGlynn and co-workers ([4–8]) and was called the external heavy-atom effect, in contrast to the internal effect, which occurs when the heavy atom is incorporated into the molecule. It should be noted that KI, containing the heavy iodine atom, has long been known as an effective fluorescence quencher; moreover, work by Zelinskii' s group showed that the action of this quencher is connected with the transfer of excited molecules into the triplet state ([9]).

The properties of triplet states and the probabilities of intercombination transitions in porphyrin and metalloporphyrin molecules attract the attention of researchers primarily in connection with the possible participation of triplet states of chlorophyll molecules in the process of photosynthesis. From phosphorescence data it has been established that, for metalloporphyrins, an internal heavy-atom (metal) effect occurs ([10–16]). The present communication sets forth the results of an experimental study of the external heavy-atom effect for porphyrins and metalloporphyrins.

Etioporphyrin I and its metal complexes were chosen as the objects of study, as well as, in some experiments, porphin, chlorin, chlorophyll, and a number of metalloporphyrins. Alkyl iodides (CH_3I, C_2H_5I, etc.) were used as solvents containing heavy atoms. For some low-temperature experiments, glass-forming

Fig. 1. Diagram of the levels of an organic molecule

Figure 1: Fig. 1. Diagram of the levels of an organic molecule

mixtures based on ethyl iodide were prepared.

The very first experiments showed that the introduction of iodine atoms into the solvent molecules leads to a sharp decrease in the fluorescence yield. Fluorometric measurements showed that the decrease in the fluorescence yield ρ** is proportional to the shortening of the fluorescence lifetime τ, i.e., quenching occurs in the excited state (quenching of the second kind according to S. I. Vavilov).

* The term *heavy atom* is customarily used to characterize an atom with a large nuclear charge Z. It is known from atomic spectroscopy that the spin–orbit interaction is proportional to Z_{eff}^4, where the subscript eff takes into account the screening of the nucleus by electrons of the inner shells.

** Since recently the letter γ has often been used to denote the yield of intercombination conversion (transition to the triplet state), and its use to denote the quantum yield of fluorescence is inconvenient, we prefer the classical notation ρ, used by the school of S. I. Vavilov.

Investigation of the dependence of ρ_{rel} on the concentration of alkyl iodide in benzene solution showed that it agrees well with the Stern–Volmer–Vavilov formula $\rho_0/\rho = 1 + k\tau_0 C$. The results of the measurements are presented in Fig. 2, the caption to which also gives the corresponding values of k. If such a dependence is regarded as evidence for the bimolecular character of the quenching, then it must be assumed that the constant k is determined by the efficiency of a single collision and by the diffusion rate. Comparison of the largest value of k (10^9 l/mole · sec) with the diffusion constant in benzene shows that the collision efficiency estimated in this way does not exceed 0.1.

Fig. 1. Diagram of the levels of an organic molecule

Fig. 2. Dependence of the relative quantum yield of fluorescence of porphyrins in benzene on the concentration of alkyl iodides, 293°K.
a—etioporphyrin I (CH_3J, $k = 5.0 \cdot 10^8$ l/mole · sec);
b—Mg-etioporphyrin I (CH_3J, $k = 10^9$ l/mole · sec);
v—Zn-etioporphyrin I (CH_3J, $k = 1.6 \cdot 10^9$ l/mole · sec);
g—Al-etioporphyrin I (C_2H_5J, $k = 2 \cdot 10^8$ l/mole · sec)

However, we believe that the quenching has another mechanism. Experiments showed that a 50-fold decrease in the diffusion constant due to the viscosity of the solvent decreases k by only a factor of 3. Moreover, on freezing glass-forming mixtures the viscosity increases by many orders of magnitude, while the constant k decreases by only one order of magnitude. This means that diffusion processes are of secondary importance, contributing to a more effective approach of the porphyrin molecule and the quencher. Apparently, the main

mechanism is the migration of electrons of the luminescing molecule in a certain static field of the solvent containing heavy atoms. Interaction with the solvent may be either purely physical (of the exchange type) or quasi-chemical (charge-transfer complexes, as asserted by McGlynn ([4])). The available experimental material does not make it possible to decide this question reliably; however, it should be noted that the absorption spectra of the porphyrins studied in CH_3J do not differ from the spectra in other organic solvents, i.e., charge-transfer complexes either do not exist or are very weak. Incidentally, experiments with KJ established that this quencher is considerably less effective than CH_3J, and this may be connected with the weak electron-acceptor ability of the J^- ion.

Assuming that the probability of internal conversion d, whose existence in organic molecules is in general disputed with considerable justification (see ([17,18]), and also below), does not depend on the presence of heavy atoms, since it is not determined by spin-orbit interaction, and taking $f = \text{const}$ on the basis of the invariance of the absorption spectra, we obtain the expression

$$\Delta r = r - r_0 = 1/\tau - 1/\tau_0 = [(\tau_0/\tau) - 1]/\tau_0 = [(\rho_0/\rho) - 1]/\tau_0.$$

Thus, from the quenching data one can determine the dependence of the probability of intercombination conversion r on C. Such a dependence

for Al-etioporphyrin is shown in Fig. 3. In connection with the fulfillment of the Stern–Volmer–Vavilov formula, it is represented by a straight line.

We determined the change in r by another method–by measuring the quantum yield of intercombination conversion (γ) using pulse spectroscopy (by the method of Porter and Bowers ([19])). The results of determining r by the two methods agree with one another, which confirms the reliability of both types of measurements and the correctness of the assumption $d = \text{const}$.

The following circumstance is noteworthy. For Al-etioporphyrin studied by the pulse method at 77°K, $\gamma_0 = 0.8$, whereas $\rho_0 = 0.2$; i.e., $\gamma_0 + \rho_0 = 1$. This means that nonradiative transitions $S_1 \rightsquigarrow S_0$ are practically absent. An analogous result was obtained ([19]) for chlorophylls a and b. The question of the existence of intramolecular internal conversion in organic molecules is currently debatable, but an increasing number of experimental facts (see ([18])), including our data, show that the probability d, at least, is very small, if not equal to 0.

Quenching of the fluorescence of porphyrins by heavy atoms is accompanied (at low temperatures) by an increase in the quantum yield of phosphorescence φ. Naturally, φ/ρ increases still more sharply. If in ordinary organic solvents the phosphorescence of Mg- and Al-etioporphyrin is very weak ($\varphi/\rho < 0.01$), then in CH_3J $\varphi/\rho \sim 10$. The spectra of this phosphorescence are analogous to the spectra of complexes with heavier metals. This effect makes it possible to measure also the phosphorescence spectrum of metal-free porphyrins, the yield of which is considerably smaller than that of complexes with light metals. Figure 4 presents the spectra

Fig. 3 and Fig. 4

Figure 2: Fig. 3 and Fig. 4

Fig. 3. Dependence of Δr (1) and $\Delta q(1/\tau_{\text{phosph}})$ (2) for Al-etioporphyrin I on the concentration of C_2H_5J (Δr at 293°K, Δq at 77°K).

Fig. 4. Phosphorescence spectra in CH_3J at 77°K. 1—etioporphyrin I, 2—Mg-etioporphyrin I

of phosphorescence of etioporphyrin and Mg-etioporphyrin in CH_3J. We note that the phosphorescence spectrum of metal-free porphyrin obtained by us does not at all correspond to the phosphorescence spectrum described by Allison and Becker ([11]) for mesoporphyrin in EPA, either in the shape of the spectrum (the spectrum in ([11]) lacks the structure characteristic of porphyrins) or in the position of the maxima. The magnitude of the singlet-triplet interval is practically the same for etioporphyrin and its magnesium complex (3200 and 3300 cm^{-1}, respectively).

Simultaneously with the enhancement of phosphorescence, a shortening of its duration is observed, and within several τ_{phosph} no de-

marked deviations from the exponential character of the decay law. Table 1 gives the results of measurements of τ_{phosph} in EPA and in CH_3J. It is evident from the table that the shortening effect on the lifetime is not observed only for nonfluorescing palladium and copper complexes, where, apparently, the relative contribution of the external heavy-atom effect to the values of the probabilities p and q is small, since they are determined by a stronger internal effect.

Table 1

Substance*	$\tau_{\text{phosph}} \cdot 10^2$ sec in EPA	$\tau_{\text{phosph}} \cdot 10^2$ sec in CH_3J	$\frac{\tau_{\text{EPA}}}{\tau_{CH_3J}}$
Etioporphyrin I	2.4	0.085	28
Al-ETIO	11.5	0.31	37
Mg-ETIO	13	0.32	40.5
Zn-ETIO	4.5	0.4	11.2
Pd-ETIO	0.18	0.18	1
Cu-ETIO	0.012	0.012	1
Mg-TBP	12	0.3	40
Zn-TBP	4.2	0.34	12.3
Cd-TBP	0.75	0.13	5.7
Zn-TPP	2	0.6	3.3

* ETIO—etioporphyrin I, TBP—tetrabenzoporphyrin, TPP—tetraphenylpor-

phyrin.

The dependence of τ_{phosph} on the concentration of C_2H_5J was investigated (see Fig. 3). The experimental points fit well onto a straight line in the coordinates $1/\tau_{\text{phosph}}$ and C. Since the probability p is small (φ remains small in pure alkyl iodide), this means that the probability q, equal to $(1/\tau_{\text{phosph}}) - p$, increases linearly with the quencher concentration, similarly to the probability r: $q = q_0 + k'C$ ($r = r_0 + kC$). At the same time, the probability p increases nonlinearly with the quencher concentration (otherwise the yield $\varphi = \gamma p/(p+q) \simeq \Delta p/(\Delta p + \Delta q)$ would not increase).

There are disagreements in the literature as to which of the probabilities p, q, or r is more sensitive to the heavy-atom effect (see [20]). In our opinion, the answer to this question depends on how it is posed. One may judge the degree of influence of the heavy atom from the magnitudes Δp, Δq, and Δr; then, evidently, for the compounds we studied $\Delta r \gg \Delta q > \Delta p$. Let us give specific data for Al-etioporphyrin at 77°K and a concentration of C_2H_5J of 2 mol/liter: $\Delta r = 4 \cdot 10^8$ sec^{-1}, $\Delta q = 37$ sec^{-1}, $\Delta p \simeq p$, $\varphi/rp\tau_{\text{phosph}} = 0.1$ sec^{-1}. One can also judge by the relative quantities $\Delta p/p_0$, $\Delta q/q_0$, and $\Delta r/r_0$; then $\Delta r/r_0 = 0.55$; $\Delta q/q_0 = 4.1$; $\Delta p/p_0$ is large (difficult to estimate because of the smallness of p_0). Finally, one may say that p is more sensitive to the influence of heavy atoms, since it increases with the quencher concentration more rapidly (nonlinearly) than q and r.

It follows from the material presented that we are dealing with an interesting physical phenomenon, which undoubtedly deserves further careful study.

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