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RELATION OF THE RATIOS OF THE QUANTUM YIELDS OF PHOSPHORESCENCE AND FLUORESCENCE TO THE POSITION OF THE FLUORESCENCE SPECTRUM

(Presented by Academician A. N. Terenin on 23 XI 1957)

In works ([1],[2]) the supposition was advanced that the probability of transition to the metastable state depends on the position of the fluorescence spectrum. It would seem that this supposition could readily be tested by measuring the change in the phosphorescence yields at low temperatures for substances whose fluorescence-spectrum position and fluorescence yield change sufficiently on passing from one solvent to another. In reality, however, this simple program proves impracticable. First of all, at low temperature, when temperature quenching of phosphorescence is absent and when a change in the phosphorescence yield truly characterizes a change in the probability of transition to the metastable state, most solutions crystallize, forming an opaque mass. Consequently, measurement of phosphorescence yields at low temperature is excluded in most media.

Furthermore, the data of the above-mentioned works, which made it possible to assume the existence of a dependence of the probability of transition to the metastable state on the position of the fluorescence spectrum, were obtained using aminoderivatives of phthalimide as the objects of investigation. It would have been natural to use these compounds also for studying the relation of the phosphorescence yield to the position of the fluorescence spectrum. However, the dependence of the position of the fluorescence spectrum on the solvent, observed for this group of substances at 20° ([3]), proves to be completely disturbed at −196° ([4]). First of all, in all media that, upon lowering the temperature, solidify as a transparent glassy mass and are therefore suitable for determining phosphorescence yields, the fluorescence spectra of many aminophthalimide derivatives occupy almost the same position. Thus the question of the dependence of the yield on the position of the spectrum is removed precisely in those media in which measurements of the phosphorescence yield would be possible.

Fig. 1

Figure 1: Fig. 1

Consequently, as objects of investigation there remain, in the main, snow-like media. In snow-like media one cannot determine phosphorescence yields, but one can, with a certain approximation, determine the ratios of the phosphorescence and fluorescence yields: $q_{\mathrm{phos}}/q_{\mathrm{fl}}$; their change in the absence of deactivation at the metastable level characterizes the change in the probability of transition to the metastable state (^{5}, ^{6}). The reduction in the change of the spectra as a function of the solvent does not make it possible to obtain data on $q_{\mathrm{phos}}/q_{\mathrm{fl}}$ for 3- and 4-amino-N-methylphthalimides, for which a relation between the fluorescence yield and the position of the fluorescence spectrum had been shown. Only a limited number of objects proved suitable for studying the dependence of $q_{\mathrm{phos}}/q_{\mathrm{fl}}$ on the position of the fluorescence spectrum.

$q_{\mathrm{phos}}/q_{\mathrm{fl}}$ was investigated for certain phthalimide derivatives. $q_{\mathrm{phos}}/q_{\mathrm{fl}}$ was determined by the method described in work (^{7}), with the exception that the phosphorescence intensity was related not to the fluorescence intensity ···

of a reference solution with known absolute yield, and to the intensity of the total emission of the phosphorescing solution itself. The fluorescence spectrum was obtained from the normalized spectrum of the total emission by subtracting from it the normalized phosphorescence spectrum, reduced by a factor of q_c and $1/q_{\mathrm{phos}}$.

Fig. 1. Numbering of solvents (st.—media that form a glassy mass at −196°): 1 —crystalline state, 2 —water, 3 —benzene, 4 —carbon tetrachloride, 5 —menthol, 6 —α-chloronaphthalene, 7 —acetic acid, 8 —anisole, 9 —nitromethane, 10 —dioxane, 11 —triethylamine (st.), 12 —formamide, 13 —propyl acetate (st.), 14 —ethyl acetate, 15 —ethyl formate, 16 —acetone, 17 —tert-butyl alcohol (st.), 18 —acetic anhydride (st.), 19 —methyl alcohol, 20 —glycerol (st.), 21 —chloroform, 22 —ethyl alcohol (st.), 23 —diisopropyl ether, 24 —diisobutyl ether, 25 —diisoamyl ether (st.), 26 —toluene (st.), 27 —isooctane, 28 —pseudocumene, 29 —*m*-xylene, 30 —pyridine, 31 —butyl alcohol (st.), 32 —*n*-hexane, 33 —*o*-xylene, 34 —isobutyl alcohol (st.), 35 —isopropyl alcohol (st.), 36 —glue No. 235 (st.), 37 —diethyl ether.

The results of measurements of $q_{\mathrm{phos}}/q_{\mathrm{fl}}$ for phthalimide derivatives are presented in Figs. 1-3 in comparison with the frequencies of the maxima of the corresponding fluorescence spectra. The accuracy in determining the positions of the points that characterize the relation between $q_{\mathrm{phos}}/q_{\mathrm{fl}}$ and $\nu_{\mathrm{fl}}^{\mathrm{max}}$ varies greatly depending on the magnitude of $q_{\mathrm{phos}}/q_{\mathrm{fl}}$. The highest accuracy is achieved when $q_{\mathrm{phos}}/q_{\mathrm{fl}}$ is of the order of 0.2-1. In the case of very small $q_{\mathrm{phos}}/q_{\mathrm{fl}}$, the reliability of determining the phosphorescence intensity decreases. When $q_{\mathrm{phos}}/q_{\mathrm{fl}}$ is too large, the accuracy of determining the positions of the points decreases because of the reduced accuracy in determining $\nu_{\mathrm{fl}}^{\mathrm{max}}$ and the

Fig. 2

Figure 2: Fig. 2

shapes of the fluorescence spectra. In general, the values of $q_{\text{phos}}/q_{\text{fl}}$ reported in the present work are more accurate than in works (^{5,8}), where, as indicated in article (^{5}), some of the values of $q_{\text{phos}}/q_{\text{fl}}$ were determined from the ratio of the readings of the recording instrument for spectrally unresolved fluxes of phosphorescence and total emission.

Figure 1 shows $q_{\text{phos}}/q_{\text{fl}}$ as a function of $\nu_{\text{fl}}^{\text{max}}$ at -196° for 3-methylacetylamino-6-acetylamino-N-methylphthalimide in 26 media differing in chemical nature (I). As can be seen, for this substance $\nu_{\text{fl}}^{\text{max}}$ differs very strongly in different media: $\nu_{\text{fl}}^{\text{max}}$ in ethyl alcohol at -196° is equal to 23500 cm^{-1}, while in the crystalline form it is 19900 cm^{-1}. The values of $q_{\text{phos}}/q_{\text{fl}}$ also vary over wide limits—from 0.04 in the crystalline state—

state, from 0.12 in water to 1.75 in ethyl alcohol. All points obtained for a given substance are grouped along one curve, with most of them fitting this curve well. The points deviating more strongly are those in simple ethers and toluene (underestimated values of $q_{\text{phos}}/q_{\text{fl}}$) and in anisole, where $q_{\text{phos}}/q_{\text{fl}}$ is somewhat higher than would follow from the curve. However, even these points that deviate from the curve do not violate the general regularity, occupying an intermediate position both in $\nu_{\text{fl}}^{\text{max}}$ and in the magnitude of $q_{\text{phos}}/q_{\text{fl}}$. The course of the curve shows that, with increasing $\nu_{\text{fl}}^{\text{max}}$, the value of $q_{\text{phos}}/q_{\text{fl}}$ increases.

Fig. 2. The numbering of the solvents is the same as in Fig. 1

In the same Fig. 1 the dependence of $q_{\text{phos}}/q_{\text{fl}}$ on $\nu_{\text{fl}}^{\text{max}}$ at -196° is shown for 3-acetylamino-N-methylphthalimide in 23 solvents (II). Curves I and II have the same character and almost repeat one another.

Figure 2 presents the dependences of $q_{\text{phos}}/q_{\text{fl}}$ on $\nu_{\text{fl}}^{\text{max}}$ at -196° for 3,6-diacetylamino-N-methylphthalimide (I) and 4-hydroxy-N-methylphthalimide (II). For these compounds the maximum $q_{\text{phos}}/q_{\text{fl}}$ values are small (0.4 and 0.10, respectively).

Especially interesting objects for investigation proved to be 3-hydroxy-N-methylphthalimide (see Fig. 3, I) and 3-hydroxyphthalimide (II), for which at -196° ν_{fl} varies from 17000 cm^{-1} in water to 26300 cm^{-1} in chloroform, and $q_{\text{phos}}/q_{\text{fl}}$ from 0.00 in water to 10 in chloroform. In this case, for convenience, $q_{\text{phos}}/q_{\text{s.i.}}$ is plotted on the ordinate axis. Most of the points are well encompassed by a curve common to both analogs.

It would seem that the data presented convincingly support the assumption that the probability of transition to the metastable state increases as the fluorescence spectrum shifts to the short-wavelength side*. However, objections of a purely experimental character may be raised against the material proposed above.

Fig. 3. Numbering of solvents is the same as in Fig. 1

Figure 3: Fig. 3. Numbering of solvents is the same as in Fig. 1

As was indicated in work (4), for many amino derivatives of phthalimide at −196° in glassy media the maxima of the fluorescence spectra occupy one and the same position—at the highest frequencies for the given substance. On the other hand, the maxima of the spectra in the crystalline state occupy positions at the lowest frequencies compared with their position in most other media. Since many media crystallize on freezing, the natural assumption may arise that the observed effect of a relation between $q_{\text{phos}}/q_{\text{fl}}$ and $\nu_{\text{fl}}^{\max}$ is explained by the fact that a greater or smaller part of the dissolved fluorescent substance also crystallizes when the solvent crystallizes. Then, by superposing the spectra of the precipitated substance and of the partially remaining glassy solution, one could obtain, depending on the relative amount of one or the other component, various intermediate positions of the spectra. On the other hand, the ratio—

···that the ratio $q_{\text{phos}}/q_{\text{fl}}$ would depend on the relative amount of the fluorescing substance that had precipitated in crystalline form and that remaining in solution. Such decomposition of the solution would simulate a dependence of $q_{\text{phos}}/q_{\text{fl}}$ on $\nu_{\text{fl}}^{\max}$. However, in the authors' work (4) it is shown that the shift of spectra in certain snow-like media toward lower frequencies, apparently, cannot be attributed to precipitation of the fluorescing substance in crystalline form. First of all, this is indicated by cases in which, in a snow-like medium, the spectrum is shifted toward the long-wavelength side more than for the substance in crystalline form. Further, in the case of intermediate positions of the spectra, the spectra would have had to broaden, or even become double-humped, since the spectra in crystalline form and in glass-like media sometimes differ very strongly. In fact this is not observed. Finally, if this supposition were correct, the spectra in snow-like media would depend very strongly on the method of cooling and on the concentration of the substance. In most cases, however, $q_{\text{phos}}/q_{\text{fl}}$ and the fluorescence spectra were determined at two concentrations differing by a factor of 10-100 (within 10^{-5}–10^{-7} g/cm^3). The spectra would also depend on whether an N-methylphthalimide derivative or its unmethylated analogue was used, since their solubilities differ greatly, while the fluorescence spectra of analogous methyl and unmethylated phthalimide derivatives in crystalline form are strongly shifted relative to one another. Despite the fact that the proposed material was obtained to a considerable extent on crystallized systems, the same results as with snow-like systems were obtained also in the case of glass-like systems, regarding which no objections of this sort can be raised; moreover, all of them fall into a single regularity.

Fig. 3. Numbering of solvents is the same as in Fig. 1

* The scope of the article does not allow us to consider analogous dependences of $q_{\text{phos}}/q_{\text{fl}}$ on $\nu_{\text{fl}}^{\max}$ observed for compounds from other chemical classes.

Thus, the data presented show that in most media the ratios $q_{\text{phos}}/q_{\text{fl}}$ do not depend at all on the nature of the medium or on its state, but are determined entirely by the position of the emission spectrum. Apparently, it should be considered that a connection between $q_{\text{phos}}/q_{\text{fl}}$ and the position of the fluorescence spectrum really exists, which indicates a corresponding change in the probability of transition to the metastable state with a change in the position of the fluorescence band.

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