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Abstract

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SPHERES OF ACTION OF QUENCHING IN THE CASE OF ENERGY TRANSFER VIA TRIPLET LEVELS

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The present work is devoted to determining the spheres of action of quenching for nonradiative transfer of the energy of electronic excitation between triplet levels in the phenomenon of sensitized phosphorescence of organic compounds in solid solutions, discovered by A. N. Terenin and the author in 1952 ([1,2]). In recent works by the author and A. N. Terenin ([3–5]) it was shown that the phenomenon of sensitized phosphorescence of organic compounds is due to exchange-resonance interactions of a triplet and an unexcited molecule. Exchange-resonance interactions develop when there is weak overlap of the peripheral parts of the electron shells of the excited molecule, the energy donor, with the unexcited molecule, the acceptor, and lead to nonradiative transfer of electronic energy from the former to the latter ([6]). In contrast to inductive-resonance interaction ([7–9]), in the case of which effective energy transfer is observed only for allowed transitions in the energy acceptor, exchange-resonance interactions can also induce forbidden transitions in the energy acceptor, including intercombination-forbidden singlet-triplet transitions ([6]). In works ([3–5]) it was also noted that, in the case of sensitized phosphorescence, the dependence of the magnitude of quenching of the donor phosphorescence I_0/I on the concentration of acceptor in a solid solution is well described by F. Perrin' s formula ([10,9])

$$I_0/I = \exp(vN'C),$$

where I_0 and I are the intensities of donor phosphorescence, respectively without acceptor and with acceptor; $N' = 6.02 \cdot 10^{20}$ is the number of molecules of dissolved substance in 1 cm^3 of solution at a concentration of 1 mol/l; C is the concentration in moles per liter; v is the sphere of action of quenching in cubic centimeters, independent of the concentration of the components for a given pair of energy donor and acceptor.* In the present work we have tested the applicability of F. Perrin' s formula over a broader range of variation in the magnitude of quenching and have used it to determine the spheres of action of quenching v for a large number of combinations of energy donor and acceptor.

The relative yields of sensitized phosphorescence were also measured, i.e. the ratio of the number of quanta emitted as acceptor phosphorescence to the quantum intensity of the quenched part of the donor emission $(\eta_A/(\eta_{0D} - \eta_D))$.

Measurements of the intensity and spectra of luminescence were carried out on a light-sensitive spectrometric setup described earlier ([4,11]). The solutions being measured were poured into flat, identical quartz cuvettes, immersed in a plane-parallel quartz Dewar vessel with liquid air or nitrogen. Excitation was carried out with mercury lines at 3650 or 3340 Å through a monochromator with a diffraction grating. Measurements of quenching and spectra were carried out under continuous excitation (for a short phosphorescence decay time, $\tau \leqslant 10^{-2}$ sec) or with a two-disk phosphoroscope ($\tau \geqslant 10^{-1}$ sec). An alcohol-ether mixture (2 : 1 by volume), which freezes at 77°K as a glass, was used as the solvent. The purification of the substances and solvents has been described earlier ([12,4,11]).

Figure 1 gives examples of the dependence of the quenching of the fluorescence of the energy donor on the concentration of the acceptor. It is evident from the figure that F. Perrin' s formula is obeyed quite well over the entire concentration range of the acceptor investigated.

Fig. 1. Dependence of the logarithm of the phosphorescence quenching of the energy donor ($\ln(I_0/I)$) on the acceptor concentration C for various donor-acceptor combinations. 1 –benzophenone + 1-bromonaphthalene; 2 –carbazole + naphthalene; 3 –phenanthrene + naphthalene. All in an alcohol-ether mixture, 93°K. Excitation was in the spectral region where only the energy-donor molecules absorb, λ3650 Å for benzophenone (1) and λ3340 Å for carbazole and phenanthrene (2 and 3).

From the slopes of the straight lines one can determine the sphere of action for quenching of the donor by the acceptor from the formula:

$$v = (\ln I_0/I)(N'C)^{-1} \text{ cm}^3.$$

The spheres of action for quenching determined in this way are given in Table 1. The sizes of the spheres of action indicate that, for the development of exchange-resonance interactions ending in nonradiative transfer of the energy of electronic excitation, a very small overlap of the peripheral parts of the electron shells of the interacting molecules is sufficient. If it is assumed that both interacting molecules have the shape of spheres, then the distances R between the centers of the molecules at which nonradiative energy transfer over triplet levels occurs are those given in Table 1.

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* In deriving F. Perrin' s formula it is assumed that around the excited donor molecule there is a sharply delimited sphere of action of quenching, into which, when a quencher molecule enters, "instantaneous" quenching occurs.

In the last column of the table are given the relative yields of sensitized phosphorescence. The quantity $\eta_A/(\eta_{0D} - \eta_D)$ is constant for all investigated concentrations of donor and energy acceptor, but strongly depends on the type of donor and energy-acceptor molecules. For the donor–acceptor combinations listed in the table, the relative yield of sensitized phosphorescence varies from 0.07 to 1.0. The reasons determining the magnitude of the relative yield of sensitized phosphorescence are not yet clear. However, the phenomenon of sensitized phosphorescence makes it possible to excite the acceptor molecule directly into the triplet state, bypassing the fluorescent state, which, naturally, is of interest from the standpoint of the possibility of separating the quenching processes that occur in the fluorescent and phosphorescent states of organic molecules.

The values of the spheres of action for quenching measured by us are of special interest in connection with the recently performed experiments of Backström and Sandros (^{13}) on observing the phenomenon of energy transfer over triplet levels in liquid solutions. In their calculations, Backström and Sandros assumed the sphere of action for quenching of the triplet state to be equal to the kinetic one. Our data indicate that in fact the spheres of action somewhat exceed the kinetic ones. The high efficiency of energy transfer over triplet lev—

Table 1

Quenching action spheres and quantum yields in the phenomenon of sensitized phosphorescence *

No.	Donor	Acceptor	$v \cdot 10^{21}$ in cm^3	R in Å	$\eta_A(\eta_0 D - \eta_D)$
1	Benzaldehyde	Naphthalene	6.8 **	12	0.13 **
2	Benzaldehyde	1-Chloronaphthalene	7.0	12	0.22
3	Benzaldehyde	1-Bromonaphthalene	7.2	12	0.27
4	Benzophenone	Naphthalene	8.6	13	0.07
5	Benzophenone	1-Methylnaphthalene	9.5	13	0.07
6	Benzophenone	1-Chloronaphthalene	9.5	13	0.12
7	Benzophenone	1-Bromonaphthalene	8.6	13	0.20
8	Benzophenone	1-Iodonaphthalene	8.6	13	0.35
9	Benzophenone	Quinoline	7.2	12	0.14
10	Acetophenone	Naphthalene	6.0	11	0.10
11	*p*-Chlorobenzaldehyde	Naphthalene	6.7	12	0.14
12	*p*-Chlorobenzaldehyde	1-Bromonaphthalene	6.2	11	0.49

No.	Donor	Acceptor	$v \cdot 10^{21}$ in cm^3	R in Å	$\eta_A(\eta_0 D - \eta_D)$
13	*o*-Chlorobenzaldehyde	Naphthalene	5.4	11	0.11
14	*m*-Iodobenzaldehyde	Naphthalene	5.8	11	0.11
15	*m*-Iodobenzaldehyde	1-Bromonaphthalene	5.7	11	0.30
16	Xanthone	Naphthalene	9.2	13	0.11
17	Anthraquinone	Naphthalene	5.9	11	0.10
18	Anthraquinone	1-Bromonaphthalene	~ 7.6	~ 12	~ 0.27
19	Triphenylamine	Naphthalene	9.3	13	0.07
20	Carbazole	Naphthalene	14	15	0.08
21	Phenanthrene	Naphthalene	10	13	0.30
22	Phenanthrene	1-Chloronaphthalene	11	14	0.73
23	Phenanthrene	1-Bromonaphthalene	~ 11	~ 14	~ 0.99

* All measurements were carried out in an alcohol–ether mixture at 93 or 77° K. For Nos. 1-16 excitation was produced by the mercury line λ 3650 Å, and for Nos. 17-23 by 3340 Å.
** The accuracy in determining the quantities v and $\eta_A(\eta_0 D - \eta_D)$ is 10–15%.

phenomena in liquid solutions indicates the necessity of taking such processes into account in photochemical reactions in liquid solutions and vapors, which, as was first shown by A. N. Terenin (^{14}), often proceed with the active participation of the triplet state of the reacting molecules. On the other hand, this circumstance also suggests the possibility of altering the course of a photochemical reaction by using energy transfer along triplet levels. By adding to the solution a suitable substance—an energy acceptor—it is possible to deactivate the triplet state of the reacting molecule while leaving the fluorescent state. For this it is necessary to choose a quencher whose triplet level would be lower, and whose fluorescent level would be higher, than the corresponding levels of the photochemically active substance.

In conclusion I consider it my pleasant duty to express my deep gratitude to my teacher A. N. Terenin for his attention to this work.

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