INVESTIGATION OF ENERGY TRANSFER ALONG THE CHAIN $\sim\mathrm{CH}_2\sim$ BY THE METHOD OF LUMINESCENCE QUENCHING

1960

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

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INVESTIGATION OF ENERGY TRANSFER ALONG THE CHAIN $\sim \mathrm{CH}_2 \sim$ BY THE METHOD OF LUMINESCENCE QUENCHING

(Presented by Academician V. N. Kondrat' ev, 23 VI 1960)

The phenomena of luminescence of organic solutions of luminophores under γ- and ultraviolet excitation play an important role in the study of energy-transfer processes in matter. Using the luminescence method (in particular, luminescence quenching), one can find the values of cross sections (or quantities proportional to cross sections) of elementary reactions occurring with excited molecules in solutions: transfer of excitation energy from solvent molecules to molecules of the fluorescing substance (activator) or of the quencher, emission by activator molecules, etc.

Up to the present time, luminescence methods have usually been applied to the study of intermolecular transfer of excitation energy (see the corresponding literature in ([1], [2])). However, in principle, there is a possibility of studying by the luminescence method also intramolecular energy transfer along molecular chains of various types. For this purpose one may try to select substances in which the molecular chain of interest to us would be connected with a functional group capable either of emitting the energy absorbed by the molecule (or transferred to the molecule by a "neighbor"), or of exerting a quenching action. It is precisely this second variant of the method that was tested by the authors, using as an example the quenching of the luminescence of a solution of terphenyl in dioxane by alcohols with an aliphatic chain of different length.

Table 1

No.	Reaction	Description
1.	$S \rightarrow S^*$	Formation of excited solvent molecules under the action of γ-radiation.

No.	Reaction	Description
2.	$\mathrm{F} \to \mathrm{F}^*$	Formation of excited activator molecules under the action of γ-radiation.
3.	$\mathrm{Q} \to \mathrm{Q}$	Formation of excited molecules of the quenching substance under the action of γ-radiation.
4.	$\mathrm{S}^* \to \mathrm{S} + \text{photon}$	Emission by excited solvent molecules.
5.	$\mathrm{S}^* \to \mathrm{S}$	Spontaneous deactivation of excited solvent molecules (radiationless transitions).
6.	$\mathrm{S}^* + \mathrm{S} \to \mathrm{S} + \mathrm{S}$	Self-quenching of excited solvent molecules.
7.	$\mathrm{S}^* + \mathrm{F} \to \mathrm{S} + \mathrm{F}$	"Quenching" of excited solvent molecules by activator molecules.
8.	$\mathrm{S}^* + \mathrm{Q} \to \mathrm{S} + \mathrm{Q}$	Quenching of excited solvent molecules by molecules of the quenching substance.
9.	$\mathrm{S}^* + \mathrm{F} \to \mathrm{S} + \mathrm{F}^*$	Transfer of excitation energy from solvent molecules to activator molecules.
10.	$\mathrm{F}^* \to \mathrm{F} + \text{photon}$	Emission by excited activator molecules.
11.	$\mathrm{F}^* \to \mathrm{F}$	Spontaneous deactivation of excited activator molecules (radiationless transitions).
12.	$\mathrm{F}^* + \mathrm{S} \to \mathrm{F} + \mathrm{S}$	Quenching of excited activator molecules by solvent molecules.

No.	Reaction	Description
13.	$F^* + F \rightarrow F + F$	Self-quenching of excited activator molecules (concentration quenching).
14.	$F^* + Q \rightarrow F + Q$	Quenching of excited activator molecules by molecules of the quenching substance.

(methyl, ethyl, propyl, hexyl, and nonyl alcohols). Luminescence was induced by weak γ-radiation from an external source.

Let us consider formally the scheme of all processes which, in principle, can occur with excited molecules in such a solution, preliminarily freed from the oxygen dissolved in it (Table 1). In the table, S, F, and Q denote, respectively, molecules of the solvent, activator, and quencher; an asterisk denotes the excited state.

Processes 1-3 are processes of primary excitation; owing to the low concentrations of activator and quencher used in our experiments, processes 2 and 3 exert only a weak influence on the light yield of the solution, and for the time being we neglect them. In the case of terphenyl, process 13 also need not be taken into account (^{3}).

Starting from the general scheme considered, one can obtain the kinetic equations

$$\frac{dn_s^*}{dt} = N - (p_4 + p_5 + p_6 + p_7 + p_8 + p_9)n_s^*,$$

$$\frac{dn_f^*}{dt} = p_9 n_s^* - (p_{10} + p_{11} + p_{12} + p_{14})n_f^*, \tag{1}$$

where n_s^*, n_f^* are the concentrations of excited molecules of the solvent and activator; N is the number of solvent molecules excited per 1 sec in a unit volume; p_4–p_{12}, p_{14} are the specific rates of the corresponding processes, with $p_7 = k_7 n_f$, $p_8 = k_8 n_q$, $p_9 = k_9 n_f$, $p_{14} = k_{14} n_q$; k_7, k_8, k_9, k_{14} are the rate constants of the corresponding elementary reactions; n_f, n_q are the concentrations of activator and quencher molecules.

The ratio of the light yields of solutions I and II, containing, respectively, concentrations n_{sI}, n_{fI}, n_{qI} and $n_{sII}, n_{fII}, n_{qII}$ of solvent, activator, and quencher, follows from (1), taking stationarity into account, and is equal to

Fig. 1. Dependence of the quenching cross section of the solvent, in arbitrary units, on the length of the chain $\sim \mathrm{CH}_2 \sim$.

Figure 1: Fig. 1. Dependence of the quenching cross section of the solvent, in arbitrary units, on the length of the chain $\sim \mathrm{CH}_2 \sim$.

$$\frac{I_{\mathrm{I}}}{I_{\mathrm{II}}} = \frac{n_{f\mathrm{I}}(1 + y n_{q\mathrm{II}} + z n_{f\mathrm{II}})(1 + x n_{q\mathrm{II}}) n_{s\mathrm{I}}}{n_{f\mathrm{II}}(1 + y n_{q\mathrm{I}} + z n_{f\mathrm{I}})(1 + x n_{q\mathrm{I}}) n_{s\mathrm{II}}}, \tag{2}$$

where

$$x = \frac{k_{14}}{p_{10} + p_{11} + p_{12}}, \qquad y = \frac{k_8}{p_4 + p_5 + p_6}, \qquad z = \frac{k_7 + k_9}{p_4 + p_5 + p_6}.$$

By measuring $I_{\mathrm{I}}/I_{\mathrm{II}}$ for different combinations of $n_{f\mathrm{I}}, n_{q\mathrm{I}}, n_{f\mathrm{II}}, n_{q\mathrm{II}}$, one can, using (2), determine successively the values of z, y, and x.

Experimental part and results

Into the photometric cuvette were introduced 5 ml of quencher solution and 10 ml of activator solution in dioxane of a specified concentration; the resulting mixture was purged with nitrogen for 5-7 min in order to remove oxygen. The detector of the light radiation was an FEU-19 photomultiplier, powered by a stabilized high-voltage rectifier at a voltage of 1400 V. The geometry of all measurements was strictly constant. The source of γ-radiation was the isotope Co^{60}. The dose rate in all experiments was ~ 5.4 r/hour. The measure of the relative light yield of the solution was the photomultiplier current, which was measured with a class 0.5 microammeter. The sensitivity of the photomultiplier was checked before each measurement against a standard (stilbene crystal), and the corresponding correction was introduced.

The experiments were carried out at room temperature. The relative light yield of the solutions in our experiments was measured for three concentrations of terphenyl ($2.89 \cdot 10^{-3}$, $7.23 \cdot 10^{-3}$, $2.89 \cdot 10^{-2}$ mole/l). The range of quencher concentrations was: methyl alcohol 0.21-1.03, ethyl alcohol 0.14-0.73; propyl alcohol 0.11-0.56; hexyl alcohol 0.07-0.34; nonyl alcohol 0.05-0.24 mole/l.

The described procedure can be used in the case where the fluorescence spectra of quenched and unquenched solutions do not differ appreciably from one another. It is known (^{4}) that, for the emission spectrum of a terphenyl solution in toluene, no appreciable change is observed upon addition of methyl alcohol (up to 30 vol. %). It may be assumed that this condition remains valid also for the other alcohols investigated by us.

Fig. 1. Dependence of the quenching cross section of the solvent, in arbitrary units, on the length of the chain $\sim \mathrm{CH}_2 \sim$.

Table 2 gives the values of the quantities x, y, and z for five alcohols and for a solution of terphenyl in dioxane. Each value is the mean of the results of several determinations by formulas obtained from expression (2).

Consideration of the tabulated data for y and x shows that: 1) quenching is due chiefly to the interaction of excited solvent molecules with alcohol molecules; 2) the quenching cross section increases linearly (within the limits of experimental error) with the length of the $\sim CH_2 \sim$ chain (the number of carbon atoms) in the alcohol molecule. For clarity this dependence is shown graphically (see Fig. 1).

The increase in the quenching cross section with increasing length of the $\sim CH_2 \sim$ chain might be attributed to the ability of the chain itself to exert a quenching action. Special experiments were carried out in which, instead of an alcohol, an equivalent number of moles of the corresponding hydrocarbon was added to the solution. It was found that in this case quenching is practically not observed.

Thus, in the present case, the scheme of the energy-transfer process is apparently justified, in which the $\sim CH_2 \sim$ chain serves as an "antenna," receiving and transmitting energy to the $-OH$ group, which, in a way as yet generally unknown, causes the dissipation of this energy. It is interesting that up to the longest

Table 2*

Quencher	Luminescing solution	z, l/mol	y, l/mol	x, l/mol
Methyl alcohol CH_3OH	Terphenyl in dioxane	115 ± 12	$0,66 \pm 0,09$	$0,04 \pm 0,02$
Ethyl alcohol C_2H_5OH	Terphenyl in dioxane	115 ± 12	$0,93 \pm 0,15$	$0,07 \pm 0,02$
Propyl alcohol C_3H_7OH	Terphenyl in dioxane	115 ± 12	$1,18 \pm 0,16$	–
Hexyl alcohol $C_6H_{13}OH$	Terphenyl in dioxane	115 ± 12	$1,82 \pm 0,55$	–
Nonyl alcohol $C_9H_{19}OH$	Terphenyl in dioxane	115 ± 12	$2,88 \pm 0,42$	$0,17 \pm 0,05$
Water	Terphenyl in dioxane	115 ± 12	$0,23 \pm 0,03$	–

Quencher	Luminescing solution	z, l/mol	y, l/mol	x, l/mol
Carbon tetrachloride	Terphenyl in xylene	62	28	18
Carbon tetrachloride	Terphenyl in xylene	415	217	10

* For comparison, quantities are given that characterize the quenching by water and carbon tetrachloride of the luminescence of a terphenyl solution in dioxane (our own measurements) and xylene (results taken from work ([3])).

chain consisting of 9 carbon atoms, the cross section increases linearly with the length of the chain. This indicates that the probability of energy transfer along such a chain is much greater than the probability of its transfer from the chain —the "neighbor."

Naturally, a scheme in which, so to speak, the property of the chain to transmit energy and the property of the OH group to scatter it are added together is an approximate one. In reality, of course, one cannot assume that the system of excitation levels of ROH is divided into independent systems R and OH. However, as the chain lengthens, such an approximation should apparently become more and more accurate.

The results obtained on energy transfer along the $\sim CH_2 \sim$ chain can naturally, as always in kinetic studies of this kind, be interpreted from the standpoint of charge transfer.

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Received
18. VI 1960

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Note: Figure translations are in progress. See original paper for figures.