EFFECT OF IRRADIATION OF ORGANIC PHOSPHORS ON THEIR PHOSPHORESCENCE DECAY KINETICS

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Tripaflavin-gelatin gels were submitted to intense white light and ionizing radiation and successive α-phosphorescence decay curves were recorded. Each decay curve was obtained after a single exciting flash by means of a specially designed phosphoroscope. It was found that after intense irradiation with white light the mean decay time of the afterglow is prolonged considerably, then slowly drops until it reaches, after several minutes, the value pertinent to the unirradiated phosphor. This effect is strong in gelatin solutions activated with tripaflavin, and much weaker when agar-agar and polyvinyl alcohol are the solvents. The time-dependence of the phosphorescence quantum yield after irradiation was measured. Experimental results are compared with the theoretical ralationship between relative quantum yield and quencher concentration found on the basis of the shell-model theory of the luminescence center. It is presumed that the changes in the mean decay time and phosphorescence yield are a result of quenching of excited centers by molecular oxygen dissolved in the solution.

1. Introduction

The phenomenon of α-phosphorescence[1] of rigid solutions (gels) of some organic dyes is associated with the occurence of a metastable state in the luminescent molecule [1]. This is a triplet state (T) [2] and, because of the intercombination forbiddenness [1], the mean life-time of the luminophor molecule in this state is longer by several orders of magnitude than in the lowest excited singlet state (S_1). Thanks to this, α-phosphorescence is a long-lived luminescence.

Interest in the triplet state of organic molecules has been aroused by the fact that this state participates in many physical and photochemical processes [3, 4].

A frequently used method of examining the electronic states of luminescent molecules immobilized in gels is that of investigating the luminescence decay kinetics [5–11].

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[1] This is a transition of the phosphor molecule from the triplet state T to the singlet state S_1 at the cost of the medium's thermal energy, and then to the ground state S_0 with emission of a quantum of light.

Among other things, α-phosphorescence is affected by such factors as strong irradiation with visible and ultraviolet light, the kind of atmosphere surrounding the sample, temperature, humidity, and so on.

The irradiation effect of luminophors on α- phosphorescence has been investigated by many authors [9–12]. Iwaki [10] found that for gelatin phosphors activated by tripaflavin and acridine orange the value of the decay constant drops as the exciting intensity increases. Other authors have stated that irradiation of a phosphor leads to an increased decay constant [9]. The results of Ref. [11] are similar to those of Ref. [10].

This work was undertaken in order to resolve the existing controversy, especially of that between Refs [9] and [10], and to find an interpretation of the change in α-phosphorescence decay kinetics of organic phosphors due to intense irradiation and the action of other physical and chemical factors.

2. *Experimental*

A special phosphoroscope was designed and built (Fig. 1), which enables phosphorescence decay curves to be recorded after a single excitation. Heretofore, phosphorescence observations were accomplished by means of phosphoroscopes conceived by Becquerel [13]

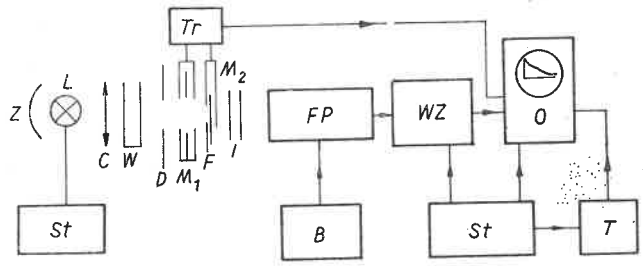


Fig. 1. Design of phosphoroscope: *Z*—reflector, *L*—light source, 500 W, *C*—condenser, *W*—water filter, *D*—diaphragm, M_1—photographic shutter, M_2—slit shutter, *F*—sample tested, *I*—optical filter, *FP*—photomultiplier, W_z—amplifier, *O*—double beam oscilloscope, *B*—battery, *St*—stabilizer, *T*—RC generator, *Tr*—relay circuit

and others [10, 14] with which decay curves do not originate from a single excitation but are average curves for multiple excitations. In the latter case it is impossible to scrutinize the processes which take place prior to the achievement of the steady-state conditions.

The principal part of the new phosphoroscope is the slit shutter M_2. Together with the camera shutter M_1 it permits long-duration irradiation of the phosphor and, after a short pause, flash (milliseconds) excitation. The time base of an oscillograph is coupled — *via* a relay system — with the shutter M_2. The decay curve is photographed on the oscillograph screen.

The examined phosphors were rigid solutions (gels) of dyes (tripaflavin, acridine yellow and eosine) in gelatin, polyvinyl alcohol and agar-agar. The dyes, for the sake of purification, were recrystallized from an ethanol solution. The solvents were not purified — they were commercially pure. The thin layers of phosphors on glass plates or celluloid

films were about 20 μm thick. The dye concentration in the dry phosphors ranged between 10^{-6} to 10^{-7} kg/m^3.

Each prepared portion of phosphor had three samples taken for examination. The first sample was sealed in a glass phial under 10^{-2} torr air pressure, the next was sealed in a phial filled with argon or dried air, whereas the last was left under ambient conditions.

Phosphor excitation time was 0.5 millisecond. Irradiation (with the same light source) lasted from 3 to 12 seconds. Phosphor illumination was about 7000 luxes.

The phosphors were also submitted to the ionizing X, α and β radiations. The respective doses were 10^3, 10^5 and 10^5 rads. No changes in the decay kinetics of the luminescence were observed, however.

Investigations also included the effect of temperature and humidity on the phosphorescence decay kinetics.

3. Results and conclusions

The α-phosphorescence decay curves of the phosphor in its normal state and after irradiation are shown by the oscillograms in Fig. 2, whereas their plots in the semi-logarithmic scale are seen in Fig. 3. Irradiation gives rise to an increase in intensity and a decrease in the decay constant of luminescence.

After the phosphor was irradiated the first time, it was submitted to a succession of excitations which gave single decay curves differing by their values of initial emission intensity and decay constant. Immediately after irradiation the intensity is high, whereas the decay constant is small. After several tens of seconds both quantities gradually return to their values prior to irradiation. The series of decay curves, plotted in the $\ln I/I_0 = f(t)$ reference system, obtained respectively after 4 (1), 20 (2), 35 (3) and 80 (4) seconds after the five-seconds irradiation with white light is concluded, is shown in Fig. 4. The initial intensity, I_0, is different for each curve. In order to make the decay constant changes more evident, all curves are led down to the initial point of curve *5* obtained for the unirradiated phosphor. The curve recorded 8 minutes after irradiation overlap curve *5*, obtained before irradiation.

A repeated irradiation of the phosphor gave the same series of curves again.

The time change of the decay constant $\Gamma(t)$ of the phosphorescence was describable by the equation

$$\Gamma(t) = A[1-\exp(-\alpha t)]+B \tag{1}$$

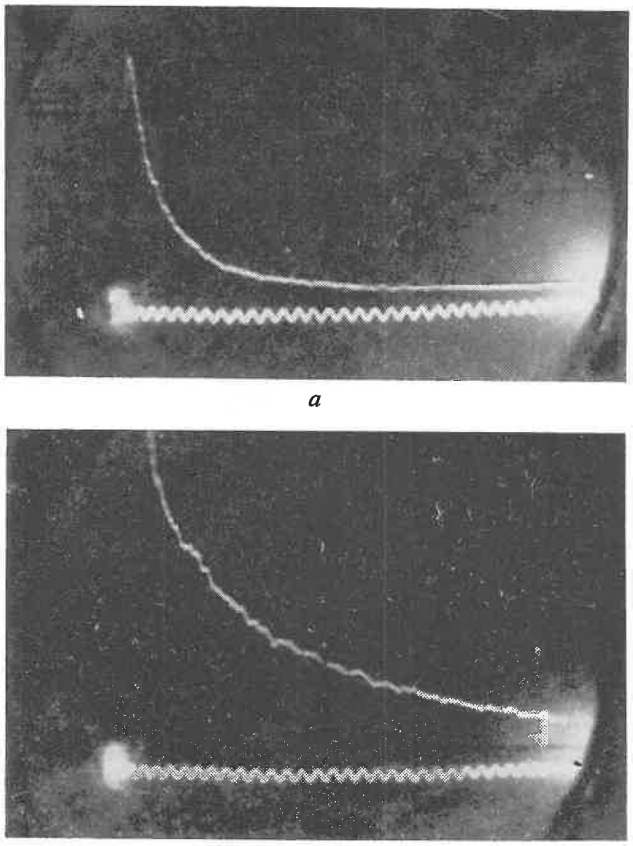
where A, B and α are constants, but of different values for different phosphors. Their values are found graphically, with consideration of the relationship

$$A+B = \Gamma_{\max}. \tag{2}$$

Phosphor irradiation did not bring about any changes in its emission and absorption spectra. It is concluded thus that associates are not formed in the phosphor, nor is there any chemical change in the luminescence centers.

In order to ascertain whether local heating of the phosphor is responsible for the irradiation effect, tests were made which showed that increased sample temperature gives an outcome quite opposite to that of irradiation.

There is a certain optimal value of dose rate of irradiation of the phosphor at which the observed effect is the strongest. Hence, the time factor plays a certain role. This implies



a

b

Fig. 2. Oscillogramme of the decay of α-phosphorescence of phosphor, unexposed (a) and after exposure (b)

that relatively slow reversible processes take place in the phosphor which lead to a rise in α-phosphorescence intensity and a drop in the value of the decay constant, or, in other words, to an increase in quantum yield.

The relative quantum yield of α-phosphorescence and its variation with time were found from the decay curves. Quantum yield is proportional to the sum of emitted light during luminescence decay. The light sum for the various decay curves (Fig. 4) can be presented as

$$L = \sum_{k=1}^{n} \int_{0}^{\infty} I_k dt = \sum_{k=1}^{n} \int_{0}^{\infty} I_{0k} e^{-\Gamma_k t} dt \qquad (3)$$

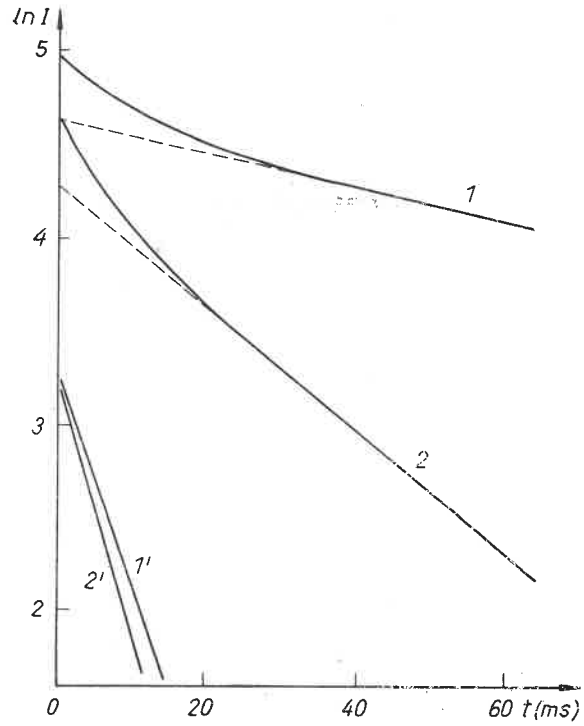


Fig. 3. Phosphorescence decay curves copied from the oscillogramme (Fig. 2) presented in linear-logarithmic coordinates: *1* — after irradiation of phosphor, *2* — before irradiation, *1'* and *2'* — short life components of α-phosphorescence, following from the graphical distribution of curves *1* and *2*, respectively

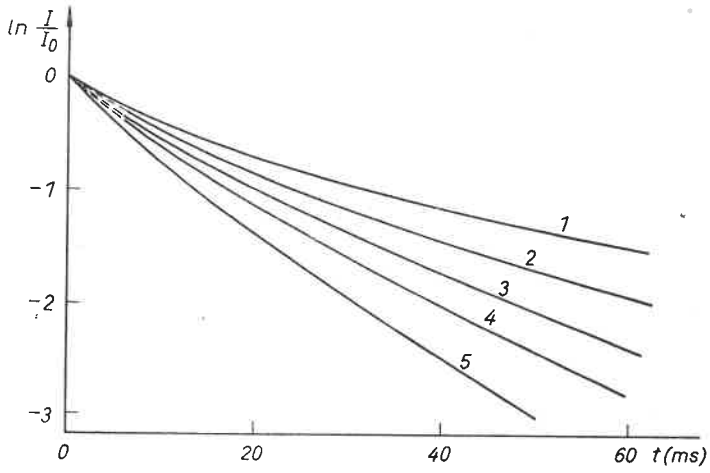


Fig. 4. Series of decay curves of α-phosphorescence for tripaflavine in gelatine (concentration $4 \cdot 10^{-7}$ kg/m^3), exposed to white light during 5 seconds; *1* — after 4 seconds after irradiation, *2* — after 20 s, *3* — after 35 s, *4* — after 80 s, *5* — before irradiation and also after 6 min. after irradiation

where I_k is the intensity of the α-phosphorescence of the centers of group k giving a purely exponential decay.

Denoting by L_0 the light sum for the unirradiated phosphor and by L that of the irradiated phosphor, enables us to write the relative quantum yield in the form

$$W = \frac{\eta}{\eta_0} = \frac{L}{L_0}, \tag{4}$$

where η_0 and η are the quantum yields proportional to the light sums emitted under identical conditions of phosphor excitation in the unirradiated and irradiated states.

The theory of luminescence quenching by impurities based on the shell model of a luminescence center gives the relationship between the mean relative quantum yield and the mean number v of quenching molecules in a center [15, 16] in the form

$$\frac{\bar{\eta}}{\eta_0} = e^{-zv} \sum_{k_1=0}^{\infty} \cdots \sum_{k_z=0}^{\infty} \prod_{l=1}^{z} \frac{v^{k_l}}{k_l!} \frac{1}{1+\sum_{l=1}^{z} \frac{k_l}{l^2}} \tag{5}$$

where z is the number of shells and k_l is the number of quenchers in the l-th shell. For $z = 3$ the $\bar{\eta}/\eta_0 = f(v)$ dependence is shown as the continuous curve in Fig. 5 [16]. Experimental points for three different samples are drawn in this graph, for which purpose

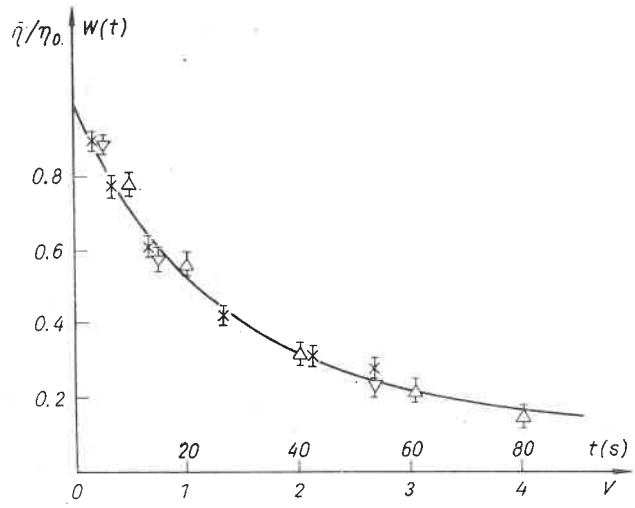


Fig. 5. Dependence of relative quantum yield of α-phosphorescence on the average number v of quenchers in the centre of luminescence (theoretical curve), and on the time t after irradiation of phosphors (experimental curves) for three samples: Δ — concentration: $4 \cdot 10^{-7}$ kg/m^3 tripaflavine in gelatine, measured in ambient conditions, ∇ — concentration: $1 \cdot 10^{-7}$ kg/m^3 tripaflavine in gelatine, sample encased in a vacuum glass vessel, $\times$ — concentration: $1 \cdot 10^{-7}$ kg/m^3 tripaflavine in gelatine, sample tested in humid air

a time scale is added to the v-axis. A comparison of the v and t scales shows that the $\bar{\eta}/\eta_0$ *vs* t relation is almost the same as $\bar{\eta}/\eta_0$ *vs* v, that is, against the number of quenchers in the center. This means that since phosphor irradiation is terminated the increase of quencher population in the center is approximately proportional to time. Phosphor irradiation causes a drop in the number of quenchers. The reversibility of the process implies that light does not give rise to any chemical conversions of the luminescent molecules in the phosphor. Chemical changes (a bleaching of the phosphor) are due to ultraviolet radiation.

Examination of samples in oxygen, air, argon and vacuum made it possible to ascertain that molecular oxygen is responsible for quenching the luminescence; molecular oxygen is known as an effective quencher of the triplet state [17]. The rate of decay of phosphor molecules in the triplet state (T) is conditioned by the concentration of oxygen in the ground state $^3\Sigma_g^-$ [18, 21]. The transfer of electronic excitation energy from the phosphor molecule in the T state to the oxygen causes the oxygen to transit from the triplet ground state (a state of high activity) to the singlet excited state $^1\Delta_g$ [18–20]. The quenching of tripaflavin in gelatin by oxygen probably takes place according to the scheme

$$^3D + {}^3O_2 \rightarrow D + {}^1O_2,$$

where ^3D and D are the lowest triplet and ground states of the phosphor, respectively, and $^3O_2$ and $^1O_2$ are the triplet ground state and singlet excited state of oxygen.

In the dark the $^1O_2$ state transits back to the $^3O_2$ state. The mean transition time is determined by the constant k in Eq. (5), the value of which for two phosphors of 1×10^{-7} and 4×10^{-7} kg/m^3 of tripaflavin in gelatin, was respectively 1.62×10^{-2} sec^{-1} and 1.75×10^{-2} sec^{-1}.

It is evident that at higher dye concentrations the process of the re-transition of the quencher from the less active to the more active form occurs faster, while the decay constant achieves a higher value. It is highly probable that apart from quenching by impurities an important role is played by concentrational quenching. To get an exact explanation of this phenomenon it would be necessary to establish experimentally the exact dependences between the irradiation effect and the concentration of oxygen and dye in the phosphor. It is particularly difficult to get an exact determination of the oxygen concentration in the phosphor and to change its concentration.

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