INVESTIGATION OF AN ORGANOPHOSPHOR IN THE PREEXICITED STATE

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The phosphorescence decay curve of acridine yellow in gelatin after long preexcitation in linearly polarized light has been investigated. It was found that the decay constant of the luminescent group of centres increases exponentially with the preexcitation time. An increase in the decay constants conditions the decreases in the total light of phosphorescence in the deformed (preexcited) state. These changes are caused by the appearance, during strong preexcitation, of unstable isomers of the dye.

1. Introduction

The object of this paper is to investigate the influence of preexcitation on the phosphorescence decay curve of acridine yellow in gelatin.

As a result of long illumination in intense light a number of organophosphors change their properties. Such a state of the phosphor will be called the deformed state and will be denoted by P. The state of the same phosphor not subjected to preexcitation will be called the undeformed state and denoted by P^0.

Frölich and Szalay (1948) distinguished two characteristics of the deformed state according to the ratio of the intensity of the emitted phosphorescence in the deformed state to the intensity of the phosphorescence in the undeformed state for the same conditions of excitation. If the intensity of phosphorescence of the state P is greater than the undeformed state P^0, then we speak of a positive P^+ deformed state and in the opposite case, of an negative P^- deformed state.

It turns out that the character of the deformed state of the phosphor can be changed from P^+ to P^- by a change in the temperature. A measure of the deformed state (according to the phosphorescence intensity) is the ratio $I(P)/I(P^0) = A$ where $I(P)$ denotes the intensity of phosphorescence in the deformed state P and $I(P^0)$ is the intensity in the undeformed state. The experiments of Frölich and Gyalai (1936) showed that the state P and A change with the time ellapsed from the moment the preexcitation is interrupted. The deformed state P tends to the undeformed state

$$P^0 \text{ and } A \to 1.$$

The numerical value of A depends on the time and intensity of preexcitation, and on the direction of polarization of the preexciting and exciting light. For some dyes the value of A is greater if the electric vectors of the preexciting and exciting light are parallel than if they are perpendicular to each other. For other dyes, the opposite is the case. The value of A depends also on the dye concentration.

The investigations of Lewis and his coworkers (1941, 1942, 1943) showed that there exist molecules:

a) whose absorption optical axes in the deformed state (preexcitation is obtained by excitation of the phosphor in linearly polarized light at the maximum of the absorption band are parallel to the electric vector of the preexciting light, and such molecules

b) whose absorption optical axes in the state P (with the same preexcitation as before) are parallel to the electric vector of the linearly polarized preexciting light.

In case (a) we obtain maximum absorption of linearly polarized light if the electric vectors of the preexciting and absorbed light are parallel. In case (b) the absorption maximum is obtained if these vectors are perpendicular to each other. The above described properties induced Lewis to divide the molecules into two groups. In the first group he included molecules whose properties are described under point (a) and he considered the orientation of their axes to be normal; in the second group he included molecules with properties described under point (b) and he considered the orientation of their axes to be anomolous.

On the basis of the division introduced by Lewis, we can distinguish the deformed state P with normal or anomolous orientations of the absorption axis of the molecules.

The deformed state is maintained for a longer time after interruption of the preexcitation. In gelatin, for example, for Rhodulin-Orange-N the deformed state disappears after 1 to 3 hours depending on the dye concentration. In rigid solutian, for some dyes the orientation of the molecules is stable and can be destroyed only by dissolving.

Fröhlich and Szalay (1948) attempted to give a full explanation for the deformed states P^+ and P^- by assuming that during preexcitation the molecules become oriented parallelly or perpendicularly to the direction of the electric vector of the linearly polarized preexcitation light. This assumption leads to some conclusions which the authors have not yet been able to establish experimentally. This is the reason for undertaking investigations of the deformed state.

2. Experimental Procedure

The investigation of the deformed state was made on acridine yellow in gelatin. The phosphor was prepared in the following way: An unexposed film strip (Ultra-Rapid) 1.80 m in length was fixed and dried. It was then placed in a bath of an aqueous solution of acridine yellow, rinsed in running water and dried in a dark room. The concentration of the dye in gelatin was determined by means of a Pulfrich colorimeter.

A linear phosphoroscope was used to investigate the phosphorescence decay curves. A detailed description of the method of measurement of the decay curves and of the linear phosphoroscope is given the paper of Frąckowiak (1957a). In order to increase the intensity of preexcitation an additiônal light source and optical arrangement was connected to the phosphoroscope. A diagram of the set-up is shown in Fig. 1.
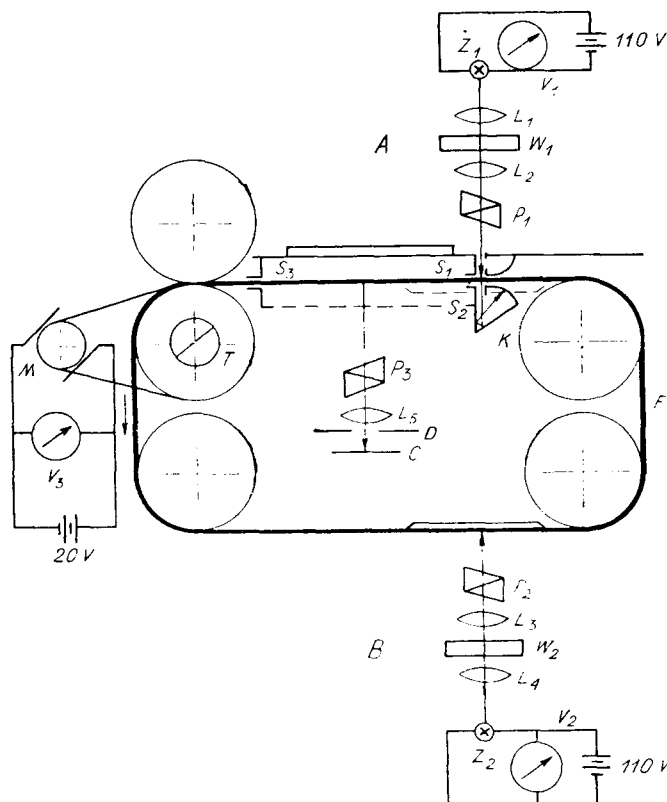

Fig. 1. Diagram of phosphoroscope. Z — light source, L — lenses, W — water filters, P — polaroids, K — trap, V — voltmeter, D — diaphragm, C — photographic plate, M — motor, T — tachometer, F — phosphor.

The phosphor is preexcited by both light sources A and B (Fig. 1). The measurements of the decay curves are made by means of arrangement A. The phosphoroscope speed during preexcitation is considerably smaller than during the measurements of the decay curves. In such an arrangement oneobtains interrupted preexcitation. Since, however, the duration of the deformed state is of the order of hours, and the modulation frequency of the light is of the order of sec^{-1}, it can be assumed that the deformed state during the time between two successive illuminations of the phosphor does not effectively change. This permits the use of the preexcitation time τ just as in the case of continuous preexcitation.

τ can be calculated from the phosphor speed and geometry of the arrangement. Henceforth in this paper we shall use only the time τ calculated in this way.

After a given time of preexcitation, the preexcitation is interrupted and the speed of the phosphor is increased. Thirty seconds after the interruption of the preexcitation source A is switched on and the decay is measured. The measurements were made under the following conditions:

1. Room temperature 20°C.
2. The phosphoroscope speed during preexcitation was (382 ± 60) cm/sec.
3. The phosphoroscope speed during excitation was (1150 ± 60) cm/sec.
4. The time of exposure was 60 sec.
5. The time between the interruption of the excitation and the moment of observation of the decay curve was 5×10^{-4} sec.
6. The preexcitation times were $\tau = 0, 1, 3$, and 6 min.
7. The preexcitation and excitation light was white, linearly polarized (with parallelly oriented electric vectors).
8. The intensity of the preexcitation light was twice as large as the excitation intensity.
9. The measurements of the decay curves for different times of preexcitation were made for one and the same phosphor.
10. Three hours passed between two successive preexcitations, the time of the decay curve measurements being included.
11. The time of the decay curve measurements for each preexcitation time τ did not exceed 5 min.
12. The excitation time was $t_0 = 10^{-4}$ sec.

3. Experimental results

The components of the decay curve of phosphorescence parallel $I_{||}(t)$ and perpendicular $I_\perp(t)$ to the electric vector of the linearly polarized excitation light was expanded by a well-known method (e. g. Frąckowiak 1957a) into a series of exponential functions. The components of the decay curves and their exponential functions are given in Figs. 2, 3, 4, and 5.

The decay constants determined from these curves for the individual liminescent groups of centres and their limiting degree of polarization are collected in Table I.

Knowing the components $I_{||}(t)$ and $I_\perp(t)$ one may determine the decay curve of phosphorescence $I(t)$ emitted in all directions from the relation

$$I(t) = I_{||}(t) + 2I_\perp(t) \qquad (1)$$

The decay curve $I(t)$ found in this way can be compared with the theoretical curve for isotropic rigid solutions (Jabłoński 1954, 1955, 1957) for the simplified model of the centre

$$I(t) = B \sum_k \frac{\gamma_k^2}{\Gamma_k} (1 - e^{-\Gamma_k t_0}) \frac{v^{k-1}}{(k-1)!} e^{-\Gamma_k t} \qquad (2)$$

Table I

Acridine yellow in gelatin. Dependence of the decay constants of groups of centres and their limiting degrees of polarization on the preexcitation time

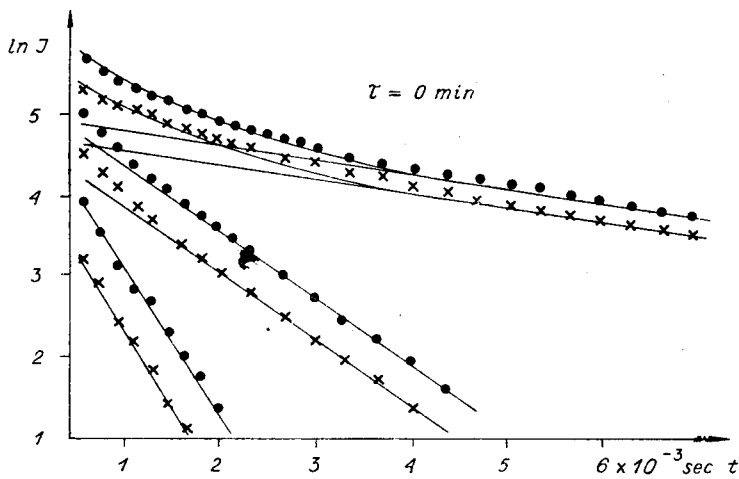| Preexcita-tion time	k	Decay constants	ln decay constants	Limiting degree of polarization
τ min		$\Gamma_k \sec^{-1}$	$\ln \Gamma_k$	p_k %
0	1	5.86×10^3	8.67	36.9
	2	6.50×10^2	6.48	25.7
	3	1.60×10^2	5.07	12.4
1	1	7.60×10^3	8.93	21.2
	2	1.05×10^3	6.96	31.7
	3	1.80×10^2	5.19	10.5
3^1	1	6.95×10^3	8.85	26.9
	2	1.10×10^3	7.00	12.7
	3	1.90×10^2	5.25	8.5
6	1	7.78×10^3	8.96	31.8
	2	1.42×10^3	7.26	28.3
	3	2.50×10^2	5.52	8.9

Fig. 2. Acridine yellow in gelatin. Logarithm of phosphorescence intensity illumination time $\tau = 0$ min
—o— parallel componenet and its exponential functions,
—×— perpendicular component and its exponential functions.

[1] Measurement made under somewhat varied conditions.
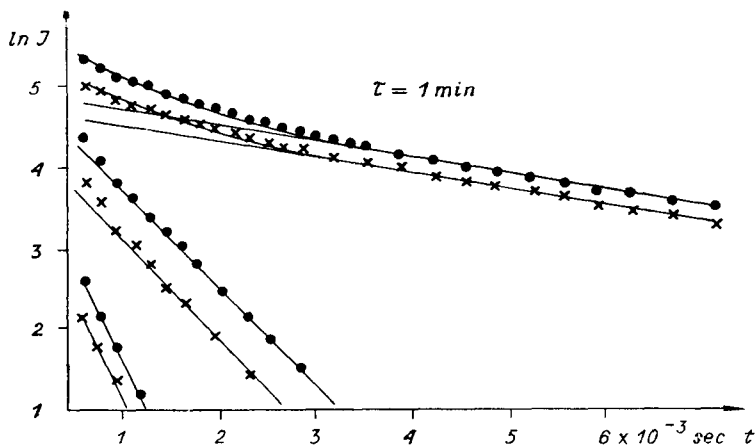
Fig. 3 type same as above, but 1min.

where B — is a proportionality coefficient

$$\Gamma_k = \gamma_k + W_f + W_k$$

γ_k — is the probability of an electron transition accompanied with emission of photoluminescence in the k-th group of centres

W_f — is the probability of internal decay and decay by molecules of the solvent

W_k — is the probability of decay the unexcited luminescent molecules in a centre of the k-th group

$$v = n \cdot v$$

n — is the number of luminescent molecules in 1 cm³ of solution

v — is the volume of the active sphere of the centre

t — is the time

k — is the index of the kind of group to which the given centre belongs.
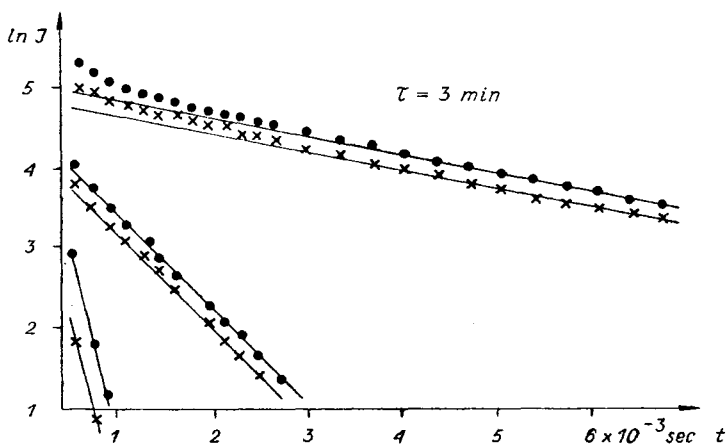

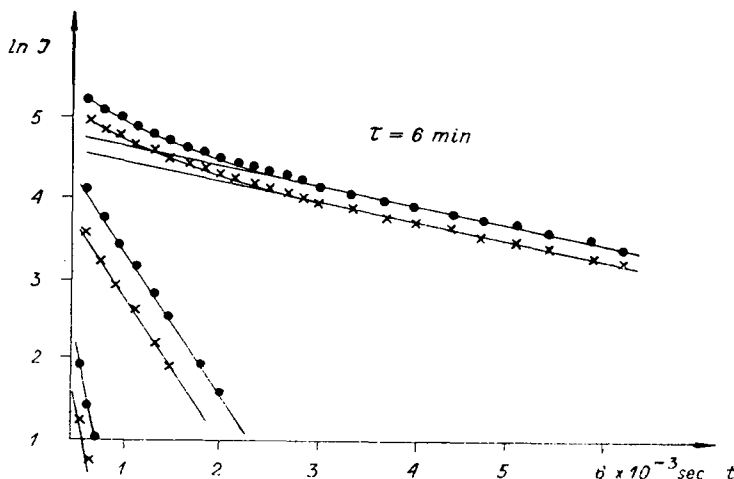Fig. 4 type same as above, but 3 min.

Fig. 5 type same as above, but 6 min.

If it is assumed that there is no decay in the solution under investigation, then, $\Gamma_k = \gamma_k$ Eq. (2) passes over into (3)

$$ I(t) = B \sum_k \gamma_k (1 - e^{-\gamma_k t_0}) \frac{\nu^{k-1}}{(k-1)!} e^{-\gamma_k t} \qquad (3) $$

All the constants in the theoretical formular (3) except for ν can be determined from the analysis of the experimental decay curves. The value of ν can be found by a trial method.

A value *of* ν is chosen so that the theoretical curve best coincides with the experimental curve.

Fig. 6 shows the experimental and theoretical (3) decay curves of phosphorescence of acridine yellow in gelatin for different preexcitation times τ.

The values of ν found in the above-described manner and the radius of the active sphere calculated from the relation $\nu = nv$ are given in Table II. It is worth noting that the mean value of the radius of the active sphere is in agreement with the value obtained in the previous investigations of the decay curves (Frąckowiak 1957b).

4. Discussion

All decay curves, as may be seen from Figs. 2, 3, 4, and 5, can be decomposed into three exponential functions irregardless of the preexcitation time. The theoretical curves shown in Fig. 6 have (within the limits of error) the same values ν and the same values of k ($k = 1, 2, 3$). These curves, for different preexcitation times, differ only in the proportionality coefficients and decay constants. It thus follows that:

1. both in the deformed and undeformed states the same groups of centres (groups of centres of the same population and the same active sphere radius) take part in the process of phosphorescence;

Table II

Acridine yellow in gelatin. Variation of ν, radius of active sphere, and totel light of phosphorescence with preexcitation time

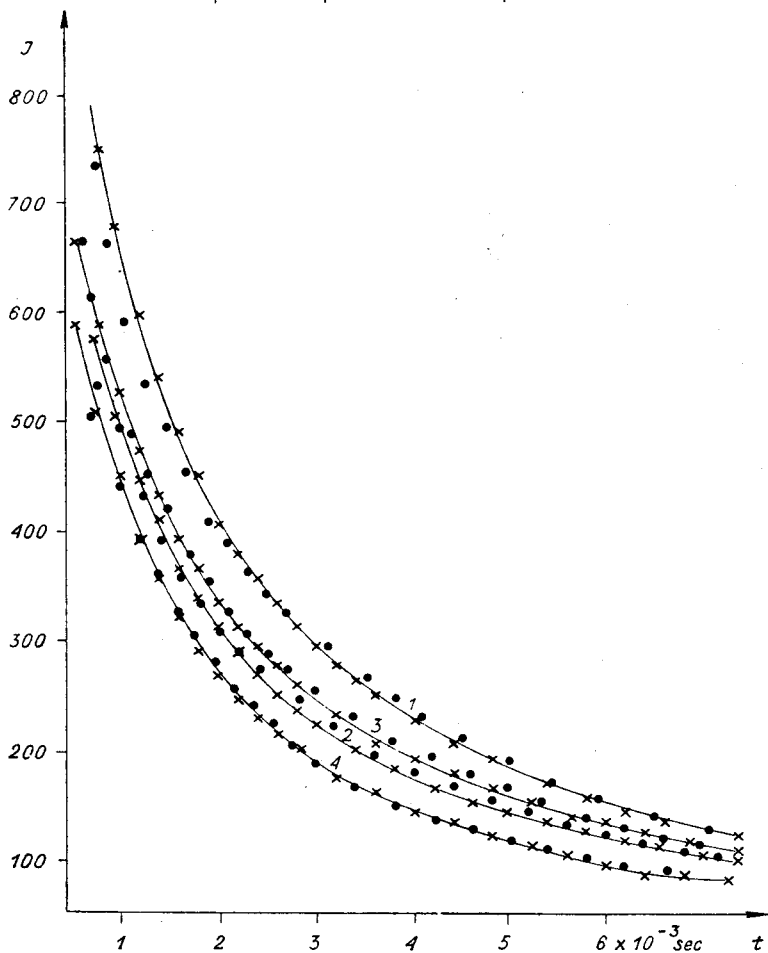| Preexcitation time τ min	ν	Radius of active sphere $r(\text{Å})$	Light sum $\sum\limits_{k} \dfrac{I_k^{(0)}}{\Gamma_k}$
0	7.9	22.1	3.02
1	7.9	22.1	2.47
3	10.0	23.5	2.84
6	8.0	22.3	1.75
Mean value	8.45	22.5	

Fig. 6 Acridine yellow in gelatin. Phophorescence intensity vs illumination time and preexcitation time.
1 — $\tau = 0$ min.   2 — $\tau = 1$ min.   3 — $\tau = 3$ min.   4 — $\tau = 6$ min.
o   experimental points   — x — theoretical curves

2. the decay of phosphorescence in the deformed and undeformed states is described by Eq. (3), differing only in the proportionality coefficient and decay constants.

As may be seen from Fig. 6, the intensity of phosphorescence decreases with an increase in the preexcitation time. An exception is the curve denoted by the number 3. The measurement of this curve was made under somewhat different conditions (24 hours after the measurements of the other curves). We thus ascribe less weight
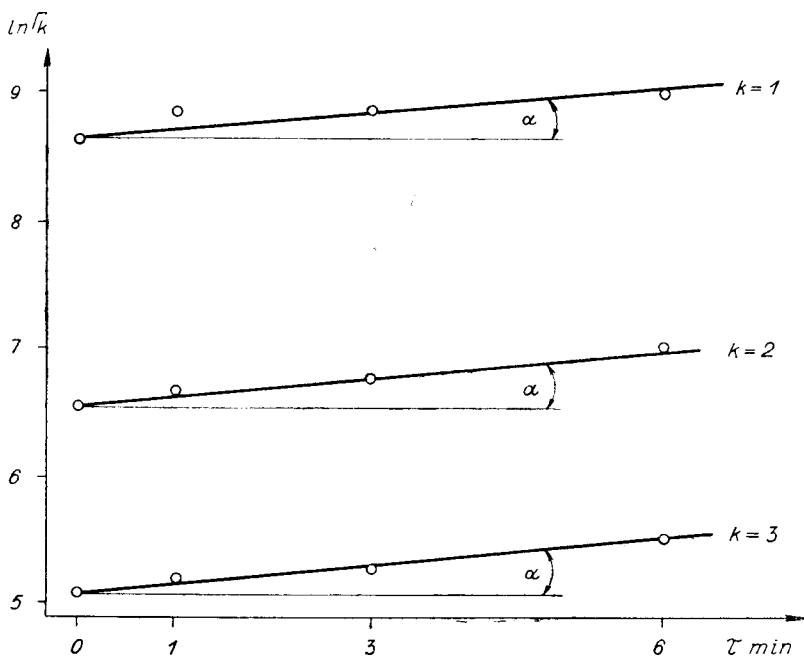
Fig. 7. Acridine yellow in gelatin. Logarithm of decay constants of groups of centres vs preexcitation time

to this curve. We may therefore state that, in the case of our experiments, acridine yellow in gelatin changes into the deformed state P^- as a result of preexcitation (in accordance with the definition of Frölich).

In analyzing Table I it may be noted that with a change in the preexcitation time limiting degree of polarization P_k of a given group of centres and their decay constants Γ_k also change.

The limiting degree of polarization changes irregularly so that it is difficult to draw conclusions from these changes. On the other hand the decay constants Γ_k change very regularly with the preexcitation time.

Fig. 7 show the changes of the natural logarithms of the decay constants Γ_k as a function of the time of preexcitation τ.

As seen from this figure, these changes are represented by a series of parallel straight lines. These lines can be described (in the limits of the preexcitation time investigated) by the formula

$$\Gamma_k = \gamma_k c^{\alpha\tau} \tag{4}$$

where Γ_k — is the probability of electron transition accompanied by the emission of phosphorescence in the deformed state,

γ_t — is the probability of electron transition accompanied by the emission of phosphorescence in the undeformed state,

α — is a constant which we shall interpret later,

τ — is the time of preexcitation.

The observed changes of the decay constants of a group of centres can be employed (analogously to the characteristic of the deformed state given by Fröhlich (1948) to characterize the deformed state.

If $\Gamma_k/\gamma_k > 1$ or $\Gamma_k/\gamma_k < 1$ we shall speak of a positive or negative deformed state with respect to the decay constants of a group of centres. We denote it therefore by ($+$ or $-$).

The observed process of the growth of the deformed state, as seen from Eq. (4), is exponential. Fröhlich and Gyulai (1936) observed the extinction of the deformed state P^+ with time after the interruption of the preexcitation. He also noted the exponential character of this decay.

The decay curves of phosphorescence of the undeformed state P^0 and the deformed state $P^{+,-}$ are described by Eq. (3) and differ, as already mentioned, only in the proportionality coefficient and in the decay constants. The increase of the decay constants Γ_k in the state $P^{-,+}$ with a simultaneous decrease in the intensity of the emitted phosphorescence indicates the existence (in this state) of a "quenching".

Because of this, let us ecamine the assumptions on which basis Jabłoński (1957) derived Eqs. (2) and (3). The most important assumptions from the point of view of our discussion are:

1. Eq. (3) is valid only in case there is no phosphorescence decay, that is, if $W_f = W_k = 0$. In this case the total light of phosphorescence should be constant if the absorption or the ratio of the fluorescence to phosphorescence efficiencies does not change.

2. The probability of transition from a fluorescent level F to a metastable level M is proportional to the transition from the level $M \rightarrow F$ and equal to $B\gamma_k$.

As may be seen from Fig. 6 (curve 1), the theoretical curve described by the formula fits very well to the experimental curve of phosphorescence decay in the underformed state P^0.

Thus if there exists a "quenching" then it appears only in the undeformed state $P^{-,+}$. It thus follows that the decay curve in the deformed state must be described by Eq. (2) where $\Gamma_k = \gamma_k + \varphi_k$, and where φ^k denotes the probability proportional to time of any process quenching the phosphorescence.

Making use of Eq. (4) and (2), we find the formula for the phosphorescence decay curve in the undeformed state $P^{-,+}$ as a function of the preexcitation time τ:

$$I(t) = Be^{-2\alpha\tau} \sum_k \Gamma_k (1 - e^{-\Gamma_k t_0}) \frac{\nu^{k-1}}{(k-1)!} e^{-\Gamma_k t} \qquad (5)$$

As may be seen from Eq. (5), for a fixed preexcitation time τ the phosphorescence decay curve in the deformed state $P^{-,+}$ is described by a formula of the same as (3) but differing from it only in the proportionality coefficient and the decay constants. Other decay curves shown in Fig. 6 (curves denoted by the numbers 2, 3, and 4) are compared with the theoretical curve (5).

In order to interpret the constant α occuring in the formula we shall investigate the total light of phosphorescence $L(\tau)$ in the state $P^{-,+}$ as a function of the preexcitation time τ From (5) we obtain

$$L(\tau) = \int_0^{\infty} I(t)\, dt = Be^{-2\alpha\tau} \sum_k (1 - e^{-\Gamma_k t_0}) \frac{\nu^{k-1}}{(k-1)!} = \sum_k \frac{I_k(0)}{\Gamma_k} \qquad (6)$$

where $I_k(0)$ is the intensity of the phosphorescence emitted by the k-th group of centres at the time the excitation was interrupted. From the experimentally obtained decay curves we may determine $I_k(0)$ and Γ_k or γ_k. The numerical values $\sum_k \frac{I_k(0)}{\Gamma_k}$ are given in the last column of Table II.

In Fig. 8 are given the natural logarithms of the total light of phosphorescence as a function of the preexcitation time. As seen from Fig. 8, the function $L(\tau)$ decreases exponentially with an increase in τ. From the slope of the straight line shown in Fig. 8 we can determine the decay constant β of the function $L(\tau)$. The absolute value of this constant is $\beta = 16.0 \times 10^{-4} \text{ sec}^{-1}$.

It follows from Eq. (6) that the function $L(\tau)$ is not a simple exponential function because of the dependence of Γ_k on τ defined by Eq. (4). In our experiments, however,
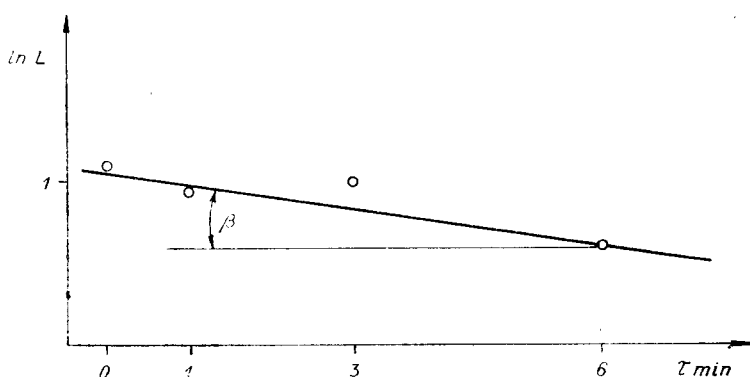

Fig. 8. Acridine yellow in gelatin. Logarithm of light sum of phosphorescence vs preexcitation time.

the value of the expression $e^{-\Gamma_k t_0}$ appearing in Eq. (6) is contained, as has been calculated, in the numerical interval $0.4 < e^{-\Gamma_k t_0} < 0.5$ for all times τ and decay constants Γ_k. This factor thus has such slight effect on the function $L(\tau)$ that in the interval of preexcitation time we are investigating, it can be treated as an exponential function. In a similar way the constant α occurring in Eq. (4) can be determined from the slope of the lines shown in Fig. 7. The value of this constant is $\alpha = 8.3 \times 10^{-4} \text{ sec}^{-1}$.

Comparison of the values of both constants (α and β) gives

$$\beta \approx 2\alpha \tag{7}$$

which proves the correctness of Eq. (5) and (6).

It thus follows that we can interpret the constant α as a quantity proportional to the transition from the undeformed state P^0 to the deformed state P^{-+}. Let us consider at present the energetic scheme of the measurements of phosphorescent molecules given by Jabłoński (1935). Let N, M, F denote the normal, metastable, and fluorescent levels in state P^0 and N', M', F' the corresponding levels in state P^{-+}.

In the undeformed state, at room temperature, the probability of an electron transition accompanied by the emission of phosphorescence is practically equal to the transition $M \to F$ and equal in our case to γ. (It is sufficient to discuss one luminescent centre of any group and we omit the index k). Similarly, in the deformed state the probability of transition accompanied by the emission of phosphorescence is equal to the transition $M' \to F'$ and, by Eq. (5), equal to Γ.

In the undeformed state P^0 the probability of the $F \to M$ transition is, as already meantioned, equal to $B\gamma$. On the other hand, in state P^{-+}, by (5) and (4) the probability of the transition $F' \to M'$ is equal to $Be^{-2\alpha\tau} \Gamma = Be^{-\alpha\tau} \gamma$. Comparing the last relation with Eq. (4) we see that in state P^{-+} the probability of the transition $M' \to F'$ decreases with the increase in the probability of the transitions $F' \to M'$ (according to the inverse of the law (4)). Owing to these changes in the state P^{-+} the phosphorescence efficiency decreases and the fluorescence efficiency increases simultaneously and, as a result, there is observed a decrease in the total light of phosphorescence of state P^{-+} with respect to P^0.

The phenomenon appears to proceed as if in state P^{-+} there exists a „quenching", which, as shown above, really does not exist.

It may be noted that this phenomena does not depend on whether the absorption in the deformed state changes in relation to the undeformed state, or whether it remains the same. It thus follows that the changes in absorption which can take place in the deformed state are a characteristic feature independent of changes in the intensity of the emitted phosphorescence.

Comparing Eq. (4) and (6), we note that in the case of the decay constants of a group of centres in the deformed state decreasing according to the inverse law in relation to (4) we obtain an increase in the total light of phosphorescence. In accordance with the nomenclature adopted by us we would obtain in this case the deformed state P^{+-}. It thus follows that the second sign describing the character of the deformed

state, owing to changes of the probability of the transition $M' \rightarrow F'$, defines the first sign. It may therefore be assumed that the deciding factor conditioning changes of the inensity of phosphorescence in the deformed state are changes in the probabilities of the transitions $M' \rightarrow F'$ and $F' \rightarrow M'$.

In order to explain the occurrence of the deformed state it may be assumed, as one of many possibilities, that during strong and long preexcitation there take place certain reversible structural changes (unstable isomers) in the luminescent molecules. The centres formed from undeformed molecules as well as from deformed molecules (isomers) therefore take part in the process of phosphorescence in the deformed state.

If the deformed molecules (isomers) differ in certain characteristics from the undeformed molecules, then the deformed state should also differ from the undeformed state.

Since, as already mentioned, after preexcitation both types of centres (deformed and undeformed) take part in the phosphorescence, then the properties of the deformed state are the result of the superpostion of effects, and may more or less differ from the properties of the undefomed state according to the number of deformed centres.

As a result, for a given intensity of preexcitation and preexcitation time it should be expected that the effect of the deformed state depends on the concentration of the luminescent molecules. The investigations of Frölich and Gyulai (1957) showed the existence of such a dependence.

It seems necessary to discuss in detail the system composed of the undeformed and deformed molecules and to make further investigations of the various properties of the deformed state.

6. Summary

The decay curves of acridine yellow in gelatin have been investigated as a function of the preexcitation time. From the analysis of the decay curves the decay constants of the individual groups of centres and their limiting degree of polarization has to be determined. Changes in the decay constants of groups of centres the preexcitation time has been expressed in a formula as a function of time. By means of this formula and the formula of Jabłoński for the decay of phosphorescence in the undeformed state a formula for the change of the total light phosphorescence in the deformed state has been given as a function of the preexcitation time. It has been shown by comparison there is agreement between the theoretical and experimental decay curves of phospho- rescence in the deformed and undeformed states. The radius of the active sphere of centres in both states has been calculated. The radii of the active spheres in both states prove to be the same. A new characteristic of the deformed state dependent on the changes of the decay constants and total light of phosphorescence has been introduced. It is shown that the reduction of the total light of phosphorescence in the deformed state is connected with the increase in the ratio of fluorescence to phospho-

rescence efficiencies. This increase arises as a result of the increase in the probability of transition from the metastable to the fluorescent state with a simultaneous reduction in the probability of transition from the fluorescent to the metastable state.

The occurrence of the deformed state is explained by the appearance in the phosphor, as a result of preexcitation, of unstable luminescent isomers of the dye under investigation.

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