Studies on the Organic Phosphorescence. II. A Revision of Lewis' Mechanism for the Phosphorescence

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Introduction

In the previous paper¹⁾ the decay curves (i. e. the plots of the logarithms of the phosphorescence intensities against time) of the phosphorescence of trypaflavine-filter paper were measured and found to be approximately of the first order. The concentration effect of dye was particularly studied and the conclusion was reached, on the basis of Lewis' triplet theory, that the neighbouring dye molecules chiefly affect S' state and not T state.

Since then the apparatus has been much improved and it has now become possible to catch the features of the decay curves in the initial stage of the phosphorescence as well as to prolong the observation towards a much later stage. With this apparatus, similar experiments as reported in the previous paper were repeated, and the decay curves were found to deviate a little from a straight line, although the deviations were not so great in magnitude and moreover, only limited at the initial stage. The deviation from linearity was also observed when polyvinyl alcohol, cellophane and other substances were used as carriers, in agreement with the results reported in the literature²⁾, of the subject but it was most prominent in the case of trypaflavine-silica gel phosphor.

The object of the present paper is to report some experiments undertaken to

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1) S. Kato and M. Koizumi, This Bulletin, **27**, 189 (1954).

2) G. N. Lewis, D. Lipkin and T. T. Magel, *J. Am. Chem. Soc.*, **63**, 3005 (1941).

elucidate the cause for this deviation, chiefly using trypaflavine-silica gel phosphor, and the conclusion obtained therefrom.

It will be found that the results obtained are interpreted by an introduction of another metastable state coupled directly with T state, the emission taking place only in S′→S transition. Furthermore, the decay curves will successfully be analysed quantitatively on the ground of the above mechanism.

Experimental Procedures

Materials.—Silica gel was boiled in concentrated hydrochloric acid and was washed by hot water repeatedly until no chloride ion was detected by silver nitrate. Then the purified gel was dyed in the aqueous solution of trypaflavine in vacuum, and after decantation it was evacuated at 200°C.

To remove any trace of oxygen as completely as possible, the sample was further treated twice with water vapor, adsorption and desorption being done at room temperature and at 200°C respectively.

Apparatus.—The block diagram is shown in Fig. 1. At the beginning, the intensity of the luminescence under steady excitation (fluorescence plus phosphorescence) is recorded with switch S_1 and S_2 being closed. At the instant when the lamp is turned off, the switch S_1 is opened automatically, increasing the gain of the amplifier to some extent. When the photocurrent decreases under a certain value, the switch S_2 is opened also by an automatic device and the gain is once more increased so much that the later stage of a decay curve is accurately recorded.

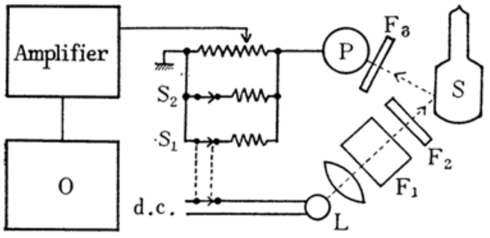

Fig. 1. Block diagram of the apparatus.
S: sample;
F_1: $CuSO_4$ solution;
F_2: Mazda V-VI filter which transmits 330–450 mμ;
F_3: a yellow filter which cuts off shorter than 450 mμ;
L: high pressure d. c. mercury lamp;
P: photomultiplier RCA 1P21;
O: electromagnetic oscillograph (Yokogawa, N-3).

In flash experiments, photoflash valves (the duration time is about 6 millisec.) are used as an exciting light. A shutter is inserted close to the window of a photomultiplier, which is opened immediately after the flashing of a valve.

Experimental Results and Discussion

In this paper the following notations are employed.

I_L: The intensity of luminescence during excitation.
I_P: The intensity of phosphorescence.
I_{P0}: The intensity of phosphorescence extrapolated to $t=0$.
$I_F=I_L-I_{P0}$: The intensity of pure fluorescence.

a) The Main Features of the Decay Curves.—All the decay curves were found to be practically linear in the later stage but they markedly deviate upwards in the initial stage. When measurements were extended as long as ca. five minutes*, however, the later stage was also found not to be exactly linear. An example is shown in Fig. 2. The latter deviation, which may plausibly be due to non-uniformity in the state of adsorbed dye or to reabsorption of phosphorescence, is so small in magnitude compared with the initial deviation, that the main points in the phosphorescence phenomenon will surely be elucidated by analysing the decay curves on the assumtion of the linearity in a later stage.

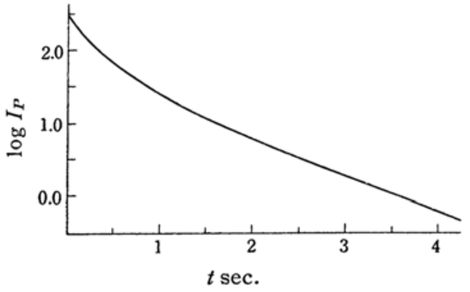

Fig. 2. An example of the decay curve.

Now in order to interpret the above result, it is evidently necessary to modify more or less the scheme proposed by Lewis2), according to which the decay is to be expressed by

$$I_P=A\exp(-\alpha t).$$

A formal amendment which occurs at once is to express I_P as the sum of several exponential terms. In practice, however, it was found that the introduction of another exponential term (equation (1)) is enough to represent the experimental results satisfactorily.

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* The measurements were not usually extended so long.

3) D. Yamamoto, *J. Chem. Soc. Japan*, **74**, 173 (1953).

$$I_P=A\exp(-\alpha t)+B\exp(-\beta t) \qquad (1)$$

Two other mathematical formulas were also tested in view of the mechanism proposed by Yamamoto[3] (for the phosphorescence in solid solution), who assumed the existence of a conduction band and took into consideration a bimolecular process between electrons in the conduction band and dye ions, simultaneously occurring with a main unimolecular process.

One formula here attempted corresponds to the scheme in which the phosphorescent state declines as a simultaneous process consisting of unimolecular and bimolecular emitting processes, and the other refers to the case in which the unimolecular emitting process and the radiationless bimolecular process take place. Putting N_T as a number of dye molecules in the phosphorescent state, the above two schemes are expressed analytically as follows:

for the former

$$I_P\propto -\mathrm{d}N_T/\mathrm{d}t=\alpha N_T+\beta N_T^2 \qquad (2)$$

while for the latter

$$I\propto{}_P\alpha N_T, \quad -\mathrm{d}N_T/\mathrm{d}t=\alpha N_T+\beta N_T^2 \qquad (3)$$

and the integrated forms for (2) and (3) are respectively

$$I_P=\frac{\alpha^2 C\exp(-\alpha t)}{\{1+\beta C\exp(-\alpha t)\}^2} \qquad (4)$$

$$I_P=\frac{\alpha^2 C\exp(-\alpha t)}{1-\beta C\exp(-\alpha t)}\,; \qquad (5)$$

(4) and (5) can represent the experimental results equally well and as satisfactorily as (1), hence it is not possible to decide which of (1), (4) and (5) is suitable from the analysis of decay curves.

b) Effect of Exciting Light Intensity.—The superiority of (1) against (4) and (5) was established by the examination of the effect of exciting light intensity, the results of which will be described below.

The intensity was varied with neutral filters and several decay curves were taken at various intensities down to 6 per cent of the full intensity. The result was that the shape of decay curves do not change; in other words, the curves under different intensities can be put upon one another by parallel displacement along the intensity axis, and the values of I_L and I_{P0} are proportional to the intensity of exciting light (Fig. 3).

The above result requires that the inclination of the curve or $\mathrm{d}/\mathrm{d}t\log I_P$ is a function only depending upon t and is not affected by the intensity of exciting light. This requirement is consistent with (1), since according to (1)

$$\frac{\mathrm{d}\ln I_P}{\mathrm{d}t}=-\frac{A\alpha\exp(-\alpha t)+B\beta\exp(-\beta t)}{A\exp(-\alpha t)+B\exp(-\beta t)}$$

which is a function of only t, if both A and B are proportional to the exciting light intensity.

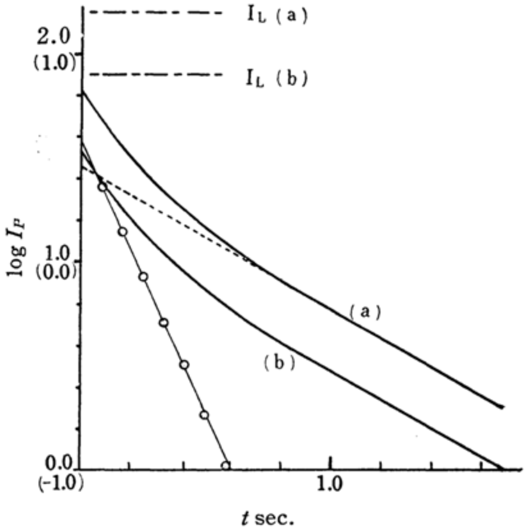

Fig. 3. Effect of exciting light intensity on the decay curve. (a) : 100, (b) : 6.0. In (b), the intensity scale takes the values in brackets.

On the contrary, for the case (2)

$$-\mathrm{d}\ln I_P/\mathrm{d}\,t=\alpha+2\beta N_T \qquad (6)$$

and for the case (3)

$$-\mathrm{d}\ln I_P/\mathrm{d}t=\alpha+\beta N_T \qquad (7)$$

and according to these relations, $-\mathrm{d}\ln I_P/\mathrm{d}t$ must depend on N_T, the number of dyes in the phosphorescent state, which depends on the intensity of light source. Thus the schemes (2) and (3) which involve the bimolecular process can be discarded definitely.

Constants α, β, A and B in (1) can easily be obtained in the following way. If β is larger than α, then the second term will vanish at larger t values and the straight part of the decay curve corresponds to the first term. Extrapolating this straight part to the ordinate, α and A can be decided from the inclination and the intersection respectively. Then the second term is obtained by substracting $A\exp(-\alpha t)$ from I_P and putting logarithms of these values against t, a straight line results from which B and β can be determined. In Fig. 3, the values of

TABLE I

AT 25°C; THE TIME UNIT IS ONE SECOND

Dye Concentration 10^{-6} mol./g. silica gel	α	β	A/B	I_L/I_{P0}	π_1	π_2	n_1n_2	n_un_u'/π
0.039	1.98	6.7	0.83	3.13	5.5	3.1	3.9	2.0
0.077	1.95	6.3	0.82	2.94	5.4	2.8	3.1	2.2
0.21	1.89	6.3	0.99	2.90	5.3	2.9	3.5	2.2
0.44	1.83	5.8	0.98	2.87	4.9	2.8	2.9	2.1

$\log\{I_P - A\exp(-\alpha t)\}$ are plotted against t as small circles, which lie satisfactorily on a single straight line.

Some examples of the analysis are shown in Table I, which contains the results for samples of different dye concentrations. It is seen from this table that A, B, α and β are almost constant, the concentration quenching being negligible in the region of dye concentration lower than 0.5 μmol./g. A slight decrease in α and β with the increase of dye concentration may perhaps be due to the reabsorption of phosphorescence[4]. The last four columns will be refered to later.

From the fact that formula (1) fits the experimental results there is no doubt that another metastable state other than Lewis' T state participates in the phenomenon of phosphorescence, the life of the former being of the same order as that of the latter.

This metastable state will be denoted conventionally as " M " state in distinction from Lewis' T state.

Thus it has now become another interesting problem to characterize this M state and further to elucidate the interrelation between M and T states.

The remainder of this paper will chiefly be devoted to this problem.

c) Absorption and Emission Spectra. —Supposedly if M and T state were completely independent, it might happen that the emission of two different types would be observed. Hence the spectra of phosphorescence (corresponding to I_P) and fluorescence (plus phosphorescence in a rigorous sense—corresponding to I_L) were at first examined and were compared with the absorption spectra.

Absorption spectra of trypaflavine adsorbed on silica gel were measured by use of the following technique. First, the sample was ground into powder and was mixed with silica gel powder to make its optical density suitable for measurement. Then the mixture of benzene and petroleum benzine with the same refractive index as that of the sample was poured into the cell. The sample now became transparent and the absorption spectra could easily be measured by a Beckman D. U. spectrophotometer. The result was that the maximum of the extinction displaced about 10 mμ to longer wave length compared with that in an aqueous solution.

The fluorescence and phosphorescence spectra were taken by a spectrograph at 25°C using a high pressure mercury lamp as a light source. A phosphoroscope with a rotatory disc was employed for taking the phosphorescence spectrum. Both spectra were almost identical and were approximately a mirror image of the absorption spectrum as shown in Fig. 4.

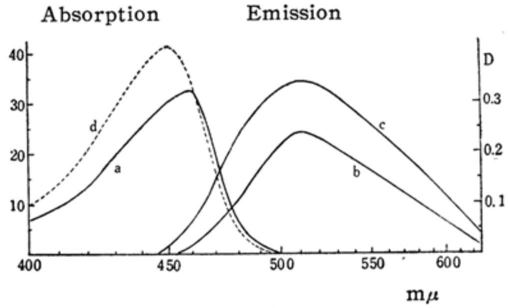

Fig. 4

a) Trypaflavine-silica gel 0.25 μmol./g.;
b) Fluorescence spectrum of the same sample;
c) Phosphorescence spectrum;
d) Trypaflavine in aqueous solution 12 μmol./l.;
ε: Extinction coefficient 1000 cm^2/mol.;
D: Density of plate darkening.

Next, the decay curve for the limited wave-length region of phosphorescence was taken and compared with the result in (a); thus an orange filter cutting off shorter than 540 mμ was used in place of a yellow one, but the decay curve was exactly the same in shape.

Lastly, it was cheked by the following experiments that Lewis' β phosphorescence is negligible for such an adsorbed phosphor at room temperature. When a film of polyvinyl alcohol dyed with trypaflavine

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[4] J. B. Birks and W. A. Little, Proc. Phys. Soc. (London), **66A**, 921 (1953).

(4.88×10^{-7} mol./g. P. V. A.) was stretched, it showed a distinct dichroism. The extinction was about seven times larger when the electric vector of the light was perpendicular to the stretched direction than parallel. (The decay curve showed a slight deviation from linearity at the initial stage, though the order of magnitude was much smaller than in the case of trypaflavine-silica gel phosphor.) Now it was found that the green phosphorescence (and fluorescence) at room temperature had a polarization perpendicular to the stretched direction, while at liquid air temperature, the yellow phosphorescence that is Lewis' β phosphorescence, was polarized parallel, and at dry ice temperature, the phosphorescence consisted of α- and β-components, the former being observed only in a perpendicular direction, while the latter in a parallel direction.

At room temperature there was no β phosphorescence observed in a parallel direction, hence β phosphorescence can be ignored in the case of polyvinyl alcohol trypaflavine phosphor at room temperature. The situation may be the same for the case of silica gel phosphor.

From the results mentioned in this section, it is almost certain that there is only one type of emission and that it corresponds to Lewis' α phosphorescence.

A Plausible Scheme for the Phosphorescence

In order to make the quantitative investigation about the decay curve, it may be desirable to put forward, at this stage, a plausible scheme which will enable us to carry out the mathematical analysis.

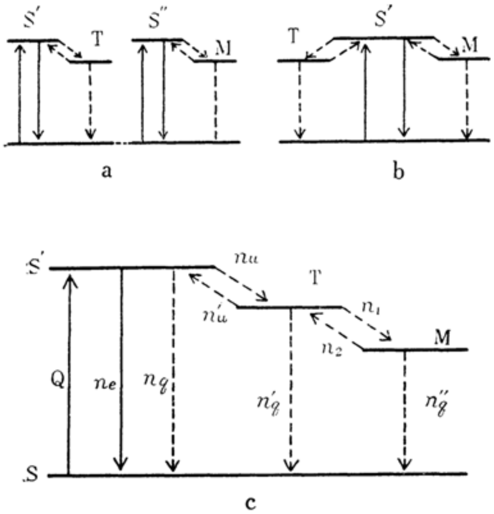

Fig. 5. Possible schemes for the phosphorescence.

Now, for the interrelation between T and M states, there are three possible schemes conceivable, which are shown in Fig. 5. In this figure, the full lines are transitions connected with radiation, while the dotted ones are radiationless transitions. The most suitable scheme will be selected by examining which of these three will fit best the following experimental results.

1) The variation of dye concentration does not affect the decay curve (at least in the small concentration range). (Table I)

2) Deviations from linearity in decay curves depend upon the nature of a carrier (the fact mentioned in introduction).

3) There is only one emitting state at ordinary temperature (the result demonstrated in (c)).

4) Even at liquid air temperature, deviations from linearity are still observed, though the magnitude becomes much smaller (preliminary observation).

Now the scheme (a) which consists of two independent processes is not compatible with the result (3), unless one supposes that the two processes are not the ones in isolated molecules but are closely related with the state of adsorption. But even if one adopts the view that there are statistically two different states of adsorption (which cause different lifetimes but do not affect the spectral behaviors), this scheme is not compatible with the result (1), since the participation of M and T states should vary in magnitude with the dye concentration.

Scheme (b) in which M and T states are separately coupled with S′ state does not fit the fact (4). Because if one assumes scheme (b) the result (4) must be interpreted to be due to the fact that M state as well as T state must emit phosphorescence at low temperature and this seems very improbable from the general view about the emission phenomena. Moreover, it seems quite strange that T and M states which have a long life don't interrelate with each other and yet they are separately coupled with an extremely short-lived S′ state.

The remaining scheme (c) in which T and M are directly coupled, is not only plausible from the general view point, but also fits the above facts well, if one assumes that M state is closely connected with the state of adsorption. Thus the result (1) can be comprehended as due to the fact that the state of adsorption is uniform at least approximately.

There is no question about the results (2) and (3) on the basis of this scheme.

The result (4) can be comprehended if the transition between T and M takes place partially by virtue of tunneling effect.

Thus although the above discussions are not quite conclusive, the scheme (c) seems to be most suitable; hence the quantitative treatment will be given below on the basis of this scheme. One may expect that the plausibility of this scheme will be further supported by the results obtained from such an analysis. (See the following two papers)

Quantitative Interpretation of the Decay Curve

The mathematical treatment will be given on the basis of scheme c) as shown schematically in Fig. 5c.

In this figure, S, S′ and T are ground state, excited singlet state and triplet state respectively; M is a metastable state with a life time of the same order as that of T state.

Since the spectra of phosphorescence are identical with those of fluorescence and the yellow phosphorescence is never observed at room temperature, the direct emitting transition from T or M to S can be ignored.

Furthermore

n_e: The rate constant of S′→S emitting transition.

n_q, n_q', n_q'': The rate constant of S′→S, T→S, M→T transition respectively (without emission).

Q: The number of molecules excited per second by irradiation.

From the above scheme, the phosphorescence intensity I_P (in number of photons), the rate of the decrease in the number of the molecules in T state and that in M state are represented respectively by the following equations

$$I_P=n_e n_u' N_T/\pi \tag{8}$$

$$-\mathrm{d}N_I/\mathrm{d}t=\pi_1 N_T-n_2 N_M \tag{9}$$

$$-\mathrm{d}N_M/\mathrm{d}t=\pi_2 N_M-n_1 N_T \tag{10}$$

where

$$\pi_1=n_u'(1-n_u/\pi)+n_q'+n_1{}^*$$

$$\pi_2=n_2+n_q''$$

$$\pi=n_e+n_q+n_u.$$

Integrating (9) and (10) one gets

$$N_T=a_1\exp(-\alpha t)+b_1\exp(-\beta t) \tag{11}$$

$$N_M=a_2\exp(-\alpha t)+b_2\exp(-\beta t) \tag{12}$$

where

$$\alpha,\beta=\frac{1}{2}\{\pi_1+\pi_2\mp\sqrt{(\pi_1-\pi_2)^2+4n_1n_2}\} \tag{13}$$

and from (9), (11) and (12)

$$a_2/a_1=(\pi_1-\alpha)/n_2,\quad b_2/b_1=(\pi_1-\beta)/n_2. \tag{14}$$

The values of a_1, a_2, b_1 and b_2 are determined by the initial condition, which corresponds to a stationary state (during the illumination) established between the exciting light and all the states involved.

The stationary state in question can be represented by the following equations,

$$-\mathrm{d}N_S/\mathrm{d}t=\pi N_{S0}-Q-n_u' N_{T0}=0 \tag{15}$$

$$-\mathrm{d}N_T/\mathrm{d}t=(\pi_1+n_u n_u'/\pi)N_{T0}-n_u N_{S0}-n_2 N_{M0}=0 \tag{16}$$

$$-\mathrm{d}N_M/\mathrm{d}t=\pi_2 N_{M0}-n_1 N_{T0}=0 \tag{17}$$

where N_{S0}, N_{T0} and N_{M0} are the values of N_S, N_T and N_M in the stationary state. From (11) and (12) on the other hand

$$N_{T0}=a_1+b_1,\quad N_{M0}=a_2+b_2 \tag{18}$$

From (14), (15), (16), (17) and (18) one gets

$$a_1=\frac{\pi_2-\alpha}{\alpha(\beta-\alpha)}\frac{n_u Q}{\pi},\quad b_1=\frac{\beta-\pi_2}{\beta(\beta-\alpha)}\frac{n_u Q}{\pi} \tag{19}$$

Substituting (11) and (19) into (8), an ultimate expression for the phosphorescence intensities is obtained as follows:

$$I_P=A\exp(-\alpha t)+B\exp(-\beta t) \tag{20}$$

where

$$A=\frac{n_e n_u n_u'(\pi_2-\alpha)Q}{\pi^2\alpha(\beta-\alpha)}$$

$$B=\frac{n_e n_u n_u'(\beta-\pi_2)Q}{\pi^2\beta(\beta-\alpha)}$$

(20) is identical with (1) and the following relations hold, as are easily verified.

$$\left.\begin{aligned} &A/B=(\pi_2-\alpha)/(\beta-\pi_2)\times\beta/\alpha && \text{(i)}\\ &\alpha+\beta=\pi_1+\pi_2,\quad \alpha\beta=\pi_1\pi_2-n_1n_2 && \text{(ii)}\\ &I_L/I_{P0}=\pi\alpha\beta/n_u n_u'\pi_2+1 && \text{(iii)}\end{aligned}\right\} \tag{21}$$

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* Since the life time of S′ is $10^7\sim10^8$ times shorter than that of T and M, it is possible to apply a stationary state method to S′ state. Hence it is easily proved that, the fraction n_u/π of the molecules transferred from T to S′ returns to T state, leading the net decrease of the molecules in T via S′ as $n_u'(1-n_u/\pi)$.

Since A/B, α, β and I_l/I_{P0} are determined experimentally, π_1, π_2, n_1n_2 and n_un_u'/π can be calculated from (21). Some of the results are shown in Table I.

Flash Excitation.—Now it will be interesting to examine how the decay curve will change in shape when a sample is excited by a flash lamp. In this case, since the duration of a flash (several milliseconds) is much shorter than the life time of T and M state, the stationary state cannot be established except for S′. Thus the initial condition for the decay curve will approximately be such that there are no molecules in M state.

Assuming such an initial condition, (16) and (17) must be replaced by the following relations.

$$N_{M0}=0 \quad \text{hence} \quad a_2+b_2=0 \tag{22}$$

$N_{T0}=Qn_u/\pi$ (Q is a total number of photons absorbed)

From (22) and (14) one gets

$$A/B=(\pi_2-\alpha)/(\beta-\pi_2) \tag{23}$$

Comparing (21 i) and (23) it can be expected that the values of A/B in flash experiments are smaller than those in steady excitation by a factor near α/β, while the values of α and β must not change, since the rate constants n_e, n_u, n_q' etc. are only dependent on the sample.

Now, the decay curves were taken for the same sample, using a mercury lamp on one hand and replacing it by a photoflash valve on the other. The result was that the two decay curves markedly differ with each other. Three parameters, A/B, α and β for the same sample are shown in Table II for flash and mercury lamps. In both excitations, α and β have the same or approximately the same values (within experimental accuracy) while A/B differs about two or three times.

TABLE II

0.5 μmol./g. AT 25°C

Sample	Exciting Light	α	β	A/B	$A/B\times\alpha/\beta$
a	Hg-lamp	1.74	5.67	0.78	0.24
	Flash	1.74	6.25	0.31	—
b	Hg-lamp	2.18	7.45	0.91	0.27
	Flash	2.18	7.08	0.24	—

The values in column 3 and 4 conform with the above requirements quite well. The agreement between A/B in flash excitation and $A/B\times\alpha/\beta$ in steady excitation is better than expected*.

Thus it can be concluded that the present mechanism not only explains the experimental results of various kinds qualitatively, but it is quite satisfactory from a quantitative standpoint.

Summary

Decay curves of the trypaflavine-silica gel phosphor were measured accurately by means of an oscillograph and a marked deviation from linearity was found at the initial stage. From the spectroscopic studies of fluorescence and phosphorescence, and the effect of light intensity on the shape of the decay curve, it was concluded that Lewis' scheme must be modified in such a way that another state with a life time of the same order as that of T state directly couples with T state.

The quantitative analysis was performed successfully and some of the transition constants between the states involved were partially evaluated.

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* It is to be noted, however, that scheme (a) and (b) can interpret the result of a flash experiment equally well. Hence the above success cannot be considered as a strong support for the scheme(c).