Studies on the Organic Phosphorescence. I.

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(Received August 19, 1953)

Introduction

According to the current interpretation of the organic phosphorescence[1] which is emitted by many unsaturated compounds under suitable conditions, such as in solid solution or in adsorbed state, the whole process of phosphorescence concerns mainly the isolated molecule, and the phosphorescent state is a triplet state (T-state).

Now, the triplet state, which is considered to be of a biradical nature, deserves special attention from the photochemical standpoint[2] owing to its reactivity and especially to its extraordinary long life compared with the ordinary excited state (S′-state). But the role of the triplet state in connection with the photochemical reaction is not quite certain as yet, and the systematic studies are very much desirable.

The present authors have constructed an apparatus for the accurate measurement of decay of organic phosphorescence and are attacking the above problems by studying the quenching effects of many substances upon the phosphorescence, and especially are trying to determine whether quenchers affect on S′-state or T-state. The purpose of the present paper is to give some mathematical relations which may help to elucidate the mechanism of the quenching action, and to report some results as to the self-quenching (concentration quenching) of filter paper-Trypaflavine phosphor.

A. Kinetic Expressions for the Initial Intensity and the Life of Phosphorescence

From the standpoint of photochemistry, it may be essential to decide whether the quenching action operates selectively on the singlet S′-state or triplet T-state or alternatively on both states equally well. We considered about this problem on the basis of Lewis' scheme and arrived at the conclusion that the measurement of both the initial intensity and the life of phosphorescence in the absence and in the presence of quenching materials, may be much helpful for this decision. The mathematical procedure will be stated briefly below.

Lewis' scheme of phosphorescence is schematically represented as follows. (cf. Fig. 1)

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* Physicochemical Studies of Organic Dyestuffs in Relation to Photochemistry V.

[1] G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944); G. N. Lewis, M. Calvin and M. Kasha, *J. Chem. Phys.*, **17**, 804 (1949).

[2] M. Calvin and G. D. Dorough, *J. Am. Chem. Soc.*, **70**, 699; **71**, 4024 (1949).

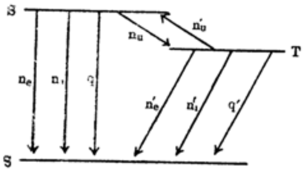

Fig. 1

1) S→S′: excitation by light absorption.

2) Fluorescence is the emission accompanied when the molecule excited by the process (1) directly falls down to S-state.

3) S′→T: transition to the triplet state.

4) β-phosphorerescence is the emission which is accompanied with the transition T→S.

5) α-phosphorescence is the emission accompanied with S′→S which succeeds the process T→S′.

Put the various transition probabilities as follows.

From S′

n_e: transition to the ground state accompanied with the emission

n_i: transition due to inner quenching effect (including the effect due to the interaction between adsorbent and dye molecule. The effect of inevitable impurity may also be included)

q: quenching effect of a substance

n_u: transition to the triplet state

From T

n_e': transition to the ground state accompanied with the emission

n_i': transition due to inner quenching effect (analogous to n_i)

q': quenching effect of a substance

n_u': transition to S′-state

Using these constants, the differential equations for the number of molecules in S′-state (N_S) and in T-state (N_T), after the interruption of illumination are given as follows:

$$\frac{dN_S}{dt}=-(n_e+n_i+n_u+q)\ N_S+n_u'\ N_T \qquad (1)$$

$$\frac{dN_T}{dt}=-(n_e'+n_i'+n_u'+q')\ N_T+n_u\ N_S \qquad (2)$$

If we take account of the fact that the life time of S′-state is $10^{-7}\sim10^{-8}$ sec, while that of triplet T-state is of the order of 0.1 sec, the exact solutions which consist of the exponential terms can be approximately expressed by a single exponential term. Thus N_T and N_S after the interruption of illumination are given as follows.

$$N_T=\frac{n_u\ Q}{\pi_s\,\pi_t-n_u\,n_u'}\cdot e^{-\left\{\pi_t-\frac{n_un_u'}{\pi_s}\right\}t} \qquad (3)$$

$$N_S=\frac{n_u\ Q}{\pi_s\,\pi_t-n_u\,n_i'}\cdot\frac{n_u'}{\pi_s}\,e^{-\left\{\pi_t-\frac{n_un_u'}{\pi_s}\right\}t} \qquad (4)$$

where Q is the number of molecules excited per second during illumination, and

$$\ _s=n_e+n_i+n_u+q$$
$$\pi_t=n_e'+n_i'+n_u'+q'$$

From (3) and (4) the intensity of phosphorescence at an arbitrary time (t) is given as follows.

$$I_p=n_e'\ N_T+n_e\ N_S=\frac{Q\ n_u}{\pi_s\,\pi_t-n_u\,n_u'}\left[n_e'+\frac{n_u'n_e}{\ _s}\right]e^{-\left\{\pi_t-\frac{n_un_u'}{\pi_s}\right\}t} \qquad (5)$$

The formula (5) gives the decay constant α (reciprocal of the average life τ, $\alpha=\frac{1}{\tau}$) and the initial intensity of phosphorescence as follows.

$$\alpha=\pi_t-\frac{n_un_u'}{\pi_s}=(n_e'+n_i'+q')+\frac{n_u'(n_e+n_i+q)}{\pi_s} \qquad (6)$$

$$I_{po}=\frac{n_u\ Q}{\pi_s\,\pi_t-n_u\,n_u'}\left(n_e'+\frac{n_u'n_e}{\pi_s}\right)=\frac{n_u\ Q}{\alpha}\cdot\frac{n_e'\pi_s+n_u'n_e}{(\pi_s)^2} \qquad (7)$$

(6) and (7) are the general expressions when the quencher acts both on S'-and T-states.

(6) and (7) are completely correct in the practical sense so long as the natural life of T-state is extraordinary long compared with that of S′-state which is $10^{-7}\sim10^{-8}$ sec.

When the quenching substance is absent, α and I_{po} in (6) and (7) are put as $\alpha^{(0)}$ and $I_{po}{}^{(0)}$ respectively, then the formulas for $\alpha^{(0)}$ and $I_p{}^{(0)}$ are given as follows.

$$\alpha^{(0)}=\pi_t{}^{(0)}-\frac{n_un_e'}{\pi_s{}^{(0)}}=n_e'+n_i'+\frac{n_u'(n_e+n_i)}{\pi_s{}^{(0)}} \qquad (8)$$

$$I_{po}{}^{(0)}=\frac{Q}{\alpha^{(0)}}\ \frac{n_u(n_e'\pi_s{}^{(0)}+n_en_u')}{(\pi_s{}^0)^2}=\frac{Q}{\alpha^{(0)}}\ \frac{n_u\{n_e'(n_e+n_i+n_u)+n_en_u'\}}{(n_e+n_i+n_u)^2} \qquad (9)$$

where

$$\pi_s{}^{(0)}=n_e+n_i+n_u$$
$$\pi_t{}^{(0)}=n_e'+n_i'+n_u'$$

Now when the quenching substance affects only T-state, a remarkably simple relation holds as described below. Putting α and I_{po} in this case as $\alpha^{(q')}$ and $I_{po}{}^{(q')}$, these are easily derived from (6) and (7). $\alpha^{(q')}$ and $I_p{}^{(q')}$ thus obtained, when compared with $\alpha^{(0)}$ and $I_p{}^{(0)}$ (eq. (8) and (9)), lead to the following relation.

$$\alpha^{(q')}=\alpha^{(0)}+q'$$

$$I_{po}{}^{(q')}=\frac{Q}{\alpha^{(q')}}\ \frac{n_u\{n_e'\pi_s{}^{(0)}+n_en_u'\}}{(\ _s{}^{(0)})^2}=\frac{Q}{\alpha^{(q')}}\ \frac{n_u\{n_e'(n_e+n_i+n_u)+n_en_u'\}}{(n_e+n_i+n_u)^2}=I_{po}{}^{(0)}\frac{\alpha^{(0)}}{\alpha^{(q')}}$$

therefore

$$\frac{I_{po}{}^{(q')}}{I_{po}{}^{(0)}}=\frac{\alpha^{(0)}}{\alpha^{(q')}} \qquad (10)$$

Thus in this case, the inital intensity of phosphorescence and the average life is proportional to each other.

Next, when the quenching substance affects only S′-state, the result is not so simple as in the former case. The formulas for I_{po} and α in this case are as follows.

$$\alpha^{(q)}=n_e'+n_t'+\frac{n_u'(n_e+n_t+q)}{\pi_s} \qquad (11)$$

$$I_{po}^{(q)}\frac{Q}{\alpha^{(q)}}\quad\frac{n_u(n_e'\pi_s+n_en_u')}{(\pi_s)^2} \qquad (12)$$

Comparing with (8) and (9)

$$\frac{I_{po}^{(q)}}{I_{po}^{(0)}}=\frac{\alpha^{(0)}}{\alpha^{(q)}}\times\frac{(n_e+n_t+n_u)^2}{(n_e+n_t+n_u+q)^2}$$

$$\times\frac{n_e'(n_e+n_t+n_u+q)+n_en_u'}{n_e'(n_e+n_t+n_u)+n_en_u'} \qquad (13)$$

From (13) it may be anticipated that the intensity of phosphorescence decreases remarkably in contrast to a rather small change of life; because on the right side of equation (13), the quenching factor (q) exists in the denominator as a quadratic term in addition to the ratio $\alpha^{(0)}/\alpha^{(q)}$. It may be mentioned that there exists (q) term in the numerator of the third factor, but at ordinary temperature, when the condition $n'_e < n'_u$ holds in many cases, the effect is presumably rather small.

To sum up the above results, one can hope to judge whether quenchers affect on S′-state or T-state predominantly, if one measures the initial intensity and average life of the quenched phosphorescence and compares them with those of unquenched one.

B. Apparatus and Procedure

The life of filter paper-Trypaflavine phosphor being of the order of 0.1 sec, it can be measured accurately by the use of electromagnetic oscillograph. But, the intensity being so weak that it is necessary to use a photomultiplier and amplify the photocurrent further to some extent. We have designed our apparatus to control the amplificaction in a wide range and at the same time, made use of a relay circuit to record, on the same oscillograph paper, the initial and the final stage of the one decay curve with the same order of accuracy. Two kinds of vessels were used for the sample; A) one is an ampule of a simple type, which contains a piece of filter paper (immersed previously in the aqueous solution of Trypaflavine and evacuated) close to the inner surface of the vessel. B) The other is of a Dewar-flask type with a ground joint, of which the vacuum part contains several kinds of samples fitted close arround the inner brass wall. The latter vessel is convenient for measuring at various temperatures. The details of the apparatus for the measurement and of the vessels of samples will be reported elesewhere.

C. Some of the Experimental Results

a) Results obtained with the vessel A.

When the logarithm of the phosphorescence intensity is plotted against time, an almost straight line is obtained in most cases; some of the examples are shown in Fig. 2. It is certain that the decay curve is expressed by a single exponential form.

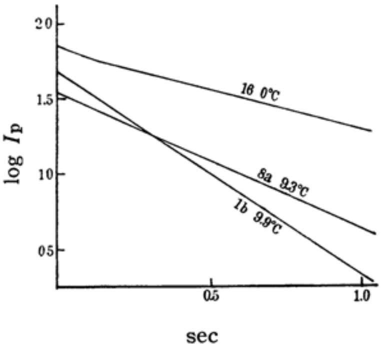

Fig. 2

$$I_p=I_{po}e^{-\alpha t} \qquad (1)$$

where I_{po} is the initial intensity and α is the reciprocal of the average life or the decay constant.

From the inclination of the line one can easily calculate α, and by exterpolating the line to $t=0$ one can get the value I_{po} (relative). Some reults are tabulated in Table I.

TABLE I

α AND I_{po} AT VARIOUS DYE CONCENTRATION

Sample	Conc. of adsorbed dye 10^{-6} mol/g.	(at 10°C) α*	(Vessel A) I_{po} (relative)
1a	15.3	3.23	44
1b		3.07	31
”		3.13	47
”		3.05	49
2a	9.02	2.75	80
”		2.74	98
2b		2.62	75
3b	2.84	2.43	146
”		2.41	133
4	1.11	2.00	110
		2.00	123
		2.13	136
5	0.602	2.01	99
		1.98	68
6	0.361	1.94	75
7	0.241	2.08	50
8a	0.120	2.08	34
”		2.02	36
8c		2.04	34
8d		2.02	43
W1**	5.81	2.11	109
W2	1.11	1.92	141
W3	0.182	1.76	53

The small temperature effect is corrected for the experimental value.

The filter paper was washed with distilled water for a long time.

1. Reproducibility. As is seen from Table I, each measurement is quite reliable and the process of phosphorescence is quite reproducible so long as the treatment of the sample is the same, although a special pretreatment of the filter paper such as washing with distilled water for a long time gives a different α-value (cf. W in Table I).

2. Effect of Temperature. The result is that I_{po} scarecely depends upon the temperature, while α shows a conspicuous increase with the rise of temperature. The activation energy is calculated to be about several Kcal. by the use of Arrhenius equation. (Of course the calculation is approximate in nature and it was made merely for the purpose of correcting the experimental results in order to compare at the same temperature.

3. Effect of the Incident Light Intensity. Under the present experimental conditions, I_{po} is completely proportional to the intensity of incident light, while α does not depend upon it.

4. Effect of Concentration of Dye. When one plots the α-values and I_{po}-values against the dye concentration, curves as shown in Fig. 3 are obtained. In this figure a dotted curve is an adsorption isotherm plotted against the equilibrium concentration of the solution given along the right side ordinate.

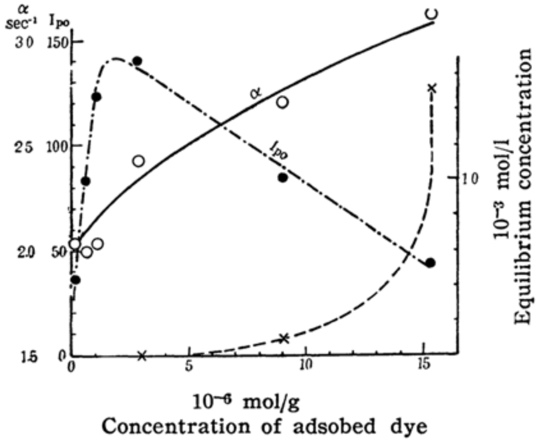

Fig. 3. I_{po} and α against the dye concentration (10°C) (Vessel A)

As is apparent from the figure, I_{po} increases quite rapidly in the range of small concentration, and after reaching a maximum, decreases almost linearly down to 1/3∼1/4 of the maximum value in the region of saturated adsorption. On the contrary, α-value is almost constant in the region where I_{po} curve rises but thereafter it increases monotonously until it reaches the value about 30% larger than the original one.

b) The Results Obtained with the Vessel B. In this case log $I_p \sim t$ curve shows a slight curvature at the initial stage and this curvature seems to increase with the concentration of dye (see Fig. 2). But the magnitude of this curvature being very small, α value was calculated from the linear part. The results at 0°C and 10°C are given in Table II and Fig. 4. I_{po} varies with the dye concentration in the same way as in the case of vessel A. α seems to show a different tendency from the former curve, the reason of which is not certain. But the magnitude of increase is quite the same as before.

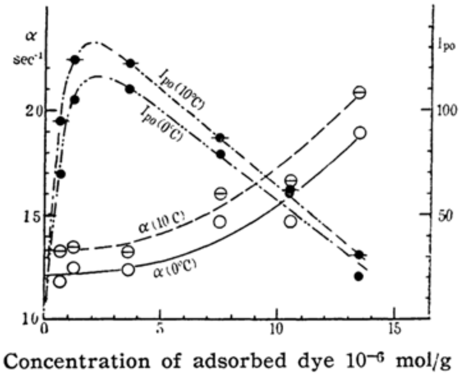

Fig. 4. I_{po} and α against the dye concentration (0°, 10°C) (Vessel B)

TABLE II

α AND I_{po} AT VARIOUS DYE CONCENTRATION

(at 10°C and 0°C) (vessel B)

Sample	Conc. of adsorbed dye 10^{-6} mole/g	α		I_{po}	
		0°C	10°C	0°C	10°C
11	13.5	1.89	2.08	21	31
12	10.5	1.47	1.66	62	60
13	7.5	1.47	1.60	79	87
14	3.6	1.24	1.33	110	122
15	1.22	1.25	1.35	105	124
16	0.64	1.18	1.33	69	95

D. Discussion

It still remains open to question that the mechanism of organic phosphorescence, especially in the case of adsorbed phosphor, is completely explained by Lewis' model. But our results show quite definitely that the process is expressed as a unimolecular reaction and there is no reason to reject Lewis' scheme.

Let us consider, therefore, the concentra-

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1) Filter paper used for this series was washed thoroughly with distilled water.

tion effect according to the results derived in (A) on the ground of Lewis' model. As seen from Fig. 3 and Fig. 4, $I_{po}\sim c$ and $\alpha\sim c$ curves show the same features for both cases at least qualitatively, and so the main characters of the phosphorescent process may be discussed upon the data of the present report, though the detailed discussion such as about the various transition probabilities may require more exact measurements.

In the present case, there is no special quencher added, but if the self-quenching due to the interaction of the adsorbed dye molecules exists, it may conventionally be represented by q and q'. Other transition constants n_e, n_i, n_u, n_e', n_i', n_u' might be affected by the dye concentration, but are approximated to be constant tentatively in the following discussion.

Let us consider at first how the rise of I_{po} in the low concentration region can be explained. In this region α is almost constant and therefore, the self-quenching can be neglected completely, and it may also be certain that all other transition probabilities keep the same value. Then, from (7) I_{po} must be proportional to Q, the number of molecules excited to S′-state per second during illumination (or the number of photons absorbed per sec.), which can be put as $(1-e^{-\varepsilon cd})$, where ε is the molecular extinction coefficient and cd is the number of moles of dye (in the ground state) in 1000 cm^2 of the cross section of the light path.

Now, as was stated in the previous section the intensity of phosphorescence is completely proportional to that of the incident light. Therefore, the state of affairs is far below the photosaturation and the number of molecules in the ground state can be put equal as an analytical quantity.

Now, it turned out that up to the region of max. I_{po}-value (about 1.11×10^{-6} mol/g), the experimental relation between I_{po} and c(analytical) could be expressed successfully by the equation

$$I_{po}=\text{const}\ (1-k^{-\varepsilon cd})$$

where ε is put as 7×10^4. With regard to the above value of ε, we could demonstrate that its order was very plausible by measuring the absorption coefficient for a cellophane Trypaflavine phosphor.

Thus it can safely be concluded that the increase of I_{po} in the region of small dye concentration is due to the increase of absorption of light.

Next, let us consider the high concentration region. Using the above ε value, it can be confirmed that beyond 2.2×10^{-6} mol/g, the absorption of light is more than 95% and so Q can be put as constant. Therefore, the decrease of I_{po} must be attributed to the selfquenching in the broad sense of the word.

The following three possible phenomena may be considered as the cause for the self quenching.

1) Accompanied with the increase of concentration, the dye molecules aggregate into such polymers (including dimers) that can not emit fluorescence nor phosphorescence at all.

2) The interaction between excited dye molecule and the neighbouring normal molecule causes the excess energy of the former to be dissipated into thermal energy.

In such a case, two possibilities must be discriminated.

a) The state affected is S′-state.

b) The state affected is T-state.

Of course it may be possible that the above three phenomena superpose. Among these three phenomena, the first is quite plausible in view of the fact that the absorption spectrum of Trypaflavine adsorbed on cellophane, changes conspiquously with the increase of dye concentration. Evidently, the electronic states in question (ground and excited states), in this case, are not concerned with a monomeric dye molecule but concerned, so to speak, a different molecular species. But there is no doubt that they are singlet states.

If 2b) is the case, then I_{po} must be reciprocally proportional to α, which contradicts the experimental results; thus I_{po} at 15×10^{-6} mol/g. of the dye concentration is only about one third of that at 1.5×10^{-6} mol/g., while the increase of α-value is about 30%.

Therefore the possibility that 2b) is the main and principal process of quenching is definitely denied. On the other hand 2a) does not contradict with the experimental results, since in this case I_{po} ought to decrease conspicuously in contrast to a rather small increase of α.

The conclusion is that the states related with the quenching process are chiefly singlet states, irrespective whether the mechanism be 1) or 2a).

Summary

Assuming Lewis' scheme, mathematical formulation was given for the decay of organic phosphorescence, which would help us to judge whether the quenching action of the added substance affects on singlet or triplet state. The decay curves of Trypa-

flavine-filter paper phosphor in various concentrations, were accurately measured by and oscillograph, and from the results obtained, it was tentatively concluded that the triplet state is not affected much in the concentration quenching.

Full accounts of the experiment and more detailed discussions will be published in Journ. Polytech. Osake City University.

The cost of this research has been partly defrayed from the Scientific Research Grant from the Ministry of Education, to which the present authors wish to express their gratitude.

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