Studies on the Organic Phosphorescence. IV. Quenching by Inorganic Salts

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(Received August 18, 1956)

Introduction

As a continuation of the preceding investigation, the present paper will chiefly deal with the effects of some inorganic salts upon the phosphorescence of trypaflavine-silica gel phosphor. Although the effects of some gases upon the trypaflavine-filter paper phosphor have also been investigated, they will be reported rather briefly since they are generally very small and cannot be discussed quantitatively.

Experimental

Sample.—*Trypaflavine-silica gel phosphor*—The phosphor prepared by the same method as described in part II was soaked in the aqueous solution of a salt (usually chloride) in vacuum and after standing for many hours (sometimes the sample was kept in a bath of 100°C to make the state of adsorption as uniform as possible), water was distilled off in vacuum. The sample then was once more evacuated at 200°C under as similar condition as that for a reference sample.

Salts employed are chloride of Fe^{3+}, Co^{3+}, Fe^{2+}, Cr^{3+}, Cu^{2+}, Cu^{+}, Ag^{+}, Ni^{2+}, Mn^{2+}, Co^{2+}, Pb^{2+} and Cd^{2+}.

Among these, cobaltic- and chromic- chloride were used in the form of ammine complex and silver- and cuprous-chloride were dissolved in the ammoniacal solution; in these cases ammonia could be expelled from the sample by the above treatment. The dye concentration was usually 0.4 μmol./g. and that of a salt was chosen in most cases to be more than several times larger.

Trypaflavine-filter paper phosphor. — Filter paper was dyed by immersing it in the aqueous solution of trypaflavine and was evacuated at 100°C. The concentration of dye was 0.8 μ mol./g. (filter paper, ca. 0.5 g.).

Procedures.—The quantities measured were

1) decay curves of the phosphorescence
2) the intensity of the steady state luminescence

$$I_L = I_F + I_{P0}$$

3) absorption spectra (only for the silica gel phosphor).

The methods for measuring (1) and (2) are essentially similar to those reported in the preceding papers.

The absorption spectra were likewise taken by the same method described in Part II. Short path cells (0.1 or 0.2 cm.) for Beckman DU were used and the solvent was a mixture of benzene and *n*-hexane 1 : 0.3 in volume ratio.

Experimental Results and Discussion

(a) Decay Curves.—Decay curves are little or scarcely affected by the adsorption of all the salts tested, except cupric ion, the results of which will be discussed separately. The following data show the upper limit of concentration of each salt examined in the present investigation (expressed in μmol./g.)

Fe^{3+}(2), Co^{3+}(4), Fe^{2+}(4), Cr^{3+}(6),
Cu^{+}(8), Ag^{+}(5), Ni^{2+}(7), Mn^{2+}(11),
Co^{2+}(3), Pb^{2+}(9), Cd^{2+}(12).

Decay curves can be analyzed by the scheme proposed in part II, and the chief results of analysis are shown in Table I. For other salts not included in this table, the decay curve was practically the same as that of the reference.

(b) The Intensity of the Steady State Luminescence I_L.—From I_L, the intensity of pure flurorescence I_F can easily be calculated from the formula $I_F = I_L - I_{P0}$.

As to the relation between I_F and the concentration of a salt, it has been established that Stern-Volmer's equation holds approximately

$$I_F^0 / I_F^q = 1 + K_Q C,$$

where I_F^0 is the fluorescence intensity of a reference sample while I_F^q is that of the sample containing a salt adsorbed on silica gel*. The concentration of a salt "C" is expressed in μmol./g. silica gel. The results are shown in Fig. 1 (a) and (b) (which includes the one of cupric ion) where $I_F^0 / I_{F'}^q$ are plotted against C.

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* π_1 in the preceding paper is replaced by $\pi' = \pi_1 + n_u n'_u/\pi = n_u' + n_1 + n'_e + n'_q + n'_t$, because the latter is more expedient when the value of $n_u n_u'/\pi$ changes.

π'' is the same as π_2.

n_q, n_q' and n_q'' in the preceding two papers correspond to $n_t + n_q$ etc. in this paper, n_i being the constant for inner quenching.

TABLE I

Dye conc., 0.4 μmol./g.; At 25°C. Time in sec.

Quencher		α	β	A/B	I_L/I_{P0}	π'*	π''*	n_1n_2	n_un_u'/π	I_F
Fe^{3+}	Reference	2.55	8.60	1.0	2.74	10.5	3.9	6.6	3.2	26
	0.4 μmol./g.	2.55	8.60	0.8	2.76	10.9	3.7	5.9	3.4	15
Cr^{3+}	Reference	2.61	8.49	1.1	2.81	10.0	4.1	6.5	3.0	36
	6.2 〃	2.91	10.0	1.2	2.91	11.3	4.8	9.8	3.2	18
Cu^{+}	Reference	2.58	9.11	1.2	2.78	10.7	4.2	8.0	3.2	58
	2.5 〃	2.72	9.52	0.9	2.77	11.7	4.1	7.3	3.6	35
Pb^{2+}	Reference	2.34	7.35	0.9	2.84	9.1	3.4	4.2	2.8	43
	9.1 〃	2.43	8.21	0.9	2.48	10.8	3.6	5.2	3.8	40

TABLE II

	Fe^{3+}	Co^{3+}	Cu^{2+}	Fe^{2+}	Cr^{3+}	Cu^{+}	Ag^{+}, Ni^{2+}, Mn^{2+}	Co^{2+}, Pb^{2+}, Cd^{2+}
K_Q	1.54	0.71	0.62	0.59	0.40	0.25	0.1∼0.05	0

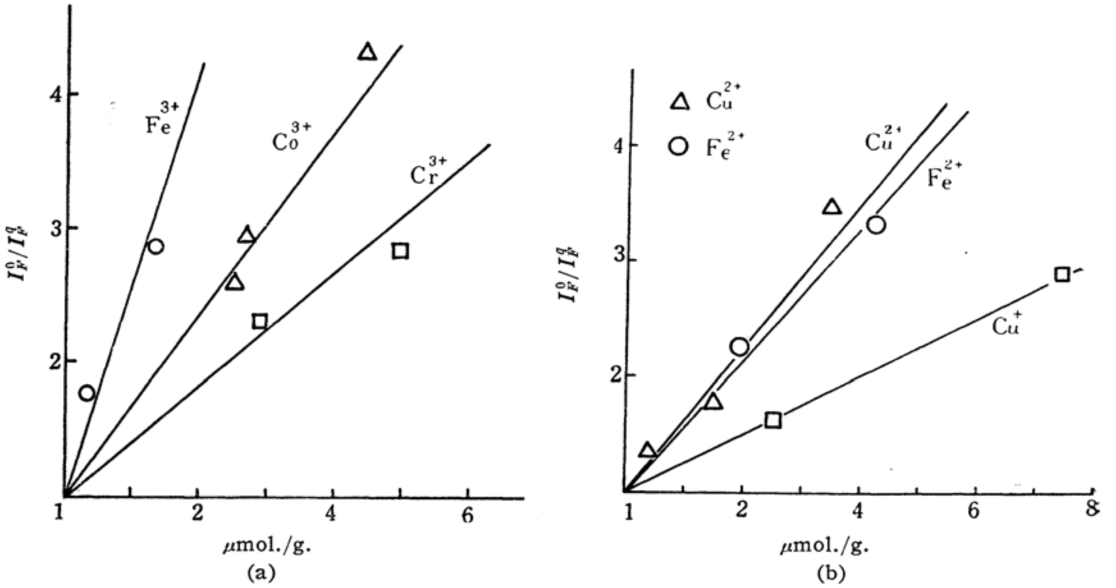

Fig. 1. Quenching of fluorescence.

Quenching constants are evaluated from the inclinations and are tabulated in Table II.

Cobaltous-, lead- and cadmium-ion show no noticeable effects up to concentration ca. 10 μmol./g..

(c) Absorption Spectra.—Except cupric ion, all the salts scarcely affect the features of the original spectra of trypaflavine adsorbed on silica gel. In all cases the extinction declines more or less, but the decrease is not so large, except in the case of cobaltic- and ferrous-ion, that it may be neglected as a first approximation. Some typical examples are shown in Fig. 2. Somewhat large decreases in the cases of cobaltic- and ferrous- ion, however, are most certainly to be attributed to the partial decomposition of dye during the evacuation at elevated temperature. As for cobaltic ion, it is almost certain that it really decomposes, since it is well known that cobaltic chloride is unstable in the solid state and a part of chlorine is eliminated during the above treatment.

In view of the above results, it is true that the quenching constants shown in Table II must be corrected since they have been derived from the total decrease of fluorescence intensity which is due to a genuine quenching action on one hand and to the decomposition of dye on the other. For semiquantitative discussion, however, they may be taken as a measure of a genuine quenching action exclusive of the case of cobaltic- and ferrous-ion.

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* Analogous notation will be used in general, when it is necessary to distinguish the quantity referring to the quenching experiment from that of the reference one.

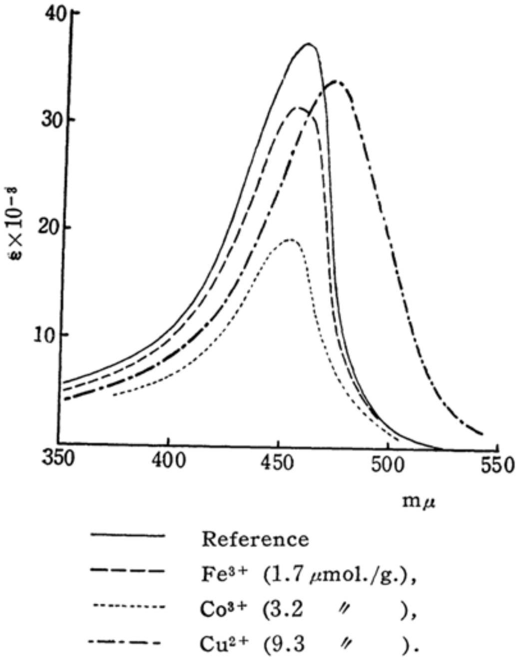

Fig. 2. Absorption spectra.

Even in the most extreme case of cobaltic ion the following data show that the fall of fluorescence intensity cannot be accounted for only by the decomposition of dye.

TABLE III

	$\varepsilon_{max.}$	I_F
Reference	37×10^3	33
with Co^{3+} (3.2 μmol./g.)	20×10^3	10

(d) Discussion. — It can be concluded from the above results that except cupric chloride, the addition of a salt to the phosphor scarcely affects the absorption spectra and yet it reduces remarkably the intensity of pure fluorescence. Values of I_F^0/I_F^q in Fig. 1 are considered to give the ratio π^q/π^0 which changes from ca. 2 to 4 in the case of ferric-, ferrous- and chromic-ion and yet the values of π'^q, π''^q, $n_1{}^q n_2{}^q$ and $n_u^q n'^q_u/\pi^q$ do not differ much from the corresponding values of a reference phosphor.

Taking the data relating to ferric ion 0.4 μmol./g., for example, the following estimation will be helpful to make the situation clear. From the 9th column of Table I,

$$n_u^0 n_u'^0/\pi^0=3.2/3.4\times n_u^q n_u'^q/\pi^q$$

If one assumes, as is probable, that $n_u'^q\simeq n_u'^0$

then, $\quad n_u^0/\pi^0=3.2/3.4\times n_u^q/\pi^q$

From the data of fluorescence, on the other hand,

$$\pi^q/\pi^0=1.7 \qquad (1)$$

Hence $\quad n_u^q=1.8\times n_u^0 \qquad (2)$

Combining (1) and (2) with the relations $\pi^0=n_\iota+n_e+n_u^0,\ \pi^q=n_\iota+n_e+n_u^q+n_q$,

one gets $\quad n_q=0.7(n_\iota+n_e)-0.1\times n_u^0$

Thus it can safely be concluded that the addition of a salt quenches S′-state not only in a genuine sense, but it also promotes S′→T transition to some extent.

Here it is to be noted, however, that there is another possibility which must be taken into account. This is related to the state of adsorption of a salt. Since in general, inorganic salts are not capable of adsorbing very easily on silica gel and in view of the method of preparation of samples, it is rather likely that the state of adsorption is not uniform. There may exist on silica gel surface such a situation as that instead of a uniform distribution of positive and negative ions, a group of many ions coalesces into a tiny crystalline grain, which is located at random from place to place. If it be the case, it may occur that the dye molecule which happens to lie close to this tiny grain of a salt cannot make any contribution to the emission phenomenon and only an isolated dye molecule participates in fluorescence and phosphorescence. It is evident that in such a situation fluorescence intensity remarkably decreases and yet the decay curve remains almost unaltered. The real situation may perhaps be a superposition of the above two cases. At any rate, there is no doubt that these quenchers chiefly affect S′-state but scarcely affect T- and M-state.

(e) Anomalous Behaviours of Cupric Ion.—The results obtained when cupric ion was employed as a quencher are very interesting from various viewpoints. The absorption spectra of trypaflavine in this case are shown in Fig. 2. As seen from it, the maximum displaces about 15 mμ towards a longer wavelength (which corresponds to about 1.7 kcal./mol.) showing that a cupric ion affects the electronic state of dye.

From the fact that pure fluorescence is markedly quenched by cupric ion (the

TABLE IV

Quencher	α	β	A/B	I_L/I_{P0}	π'	π''	n_1n_2	n_un_u'/π	I_F
Reference	2.53	8.47	1.1	2.66	10	4.0	6.5	3.3	28
1.5 μmol./g.	2.69	10.0	0.8	2.61	13	4.0	7.9	4.2	17
3.6 〃	3.92	20.0	0.4	1.94	35	5.1	18	16	8

quenching constant is 0.6 as listed in Table II), it is evident that S′-state is remarkably affected. But, in contrast to other salts, the change in the decay curve is rather large. The analysis is possible, at least approximately, on the basis of our scheme, and the results obtained from the analysis of the decay curves at 25°C are shown in Table IV.

A notable result in Table IV is that the value of n_un_u'/π is increased by the addition of cupric ion. In all the other cases so far investigated including gaseous molecules, this quantity is almost constant. π'' remains practically unaltered, while π', n_1n_2 and n_un_u'/π increase remarkably. Hence it can be said that M-state is not affected and the increase of n_1n_2 can be attributed mainly to n_1.

If one assumes that the adsorption of cupric chloride is uniform, the reduction of pure fluorescence must be attributed to the increase of π. For example in the case of 3.6 μmol./g. cupric chloride,

$$\pi^q=3.5\times\pi^0$$

from the data in Fig. 1.

Combining with the data in Table IV, $n_u^q n_u'^q=18\times n_u^0 n_u'^0$. Thus it is certain that the transitions between S′- and T-state are enormously promoted. If one assumes, as it seems probable, that the main part of the increase in $n_u^q n_u'^q$ is due to that of n_u^q, then the great value of π'^q must partially be attributed to the participation of a genuine quenching process.

Thus it is plausible that the cupric ion not only influences S'-state but also T-state pretty markedly while it scarcely affects M-state.

The temperature effect on various constants in the range from 0°C to 50°C, throughout which β-phosphorescence is practically negligible, is shown in Table V.

In this table, apparent activation energy obtained from the Arrhenius' plot for π', π'', n_un_u'/π and n_1n_2 respectively, is also included.

The activation energy for π', π'' and n_un_u'/π does not change beyond probable error but it seems quite definite that the activation energy for $n_1^qn_2^q$ is about half that for $n_1^0n_2^0$. Since n_2 is approximately independent of the existence of cupric ion and moreover π'' has practically the same temperature dependence, the above result is mainly due to the difference in the temperature dependence of n_1^0 and n_1^q.

Thus it seems plausible to consider that T→M transition is a process accompanied with an activation energy the magnitude of which, however, is much less than that for T→S′ transition; the promotion of the transition T→M by the cupric ion at least partially, is attributed to the decrease of this activation energy.

Finally the decrease of I_L/I_{P0} by the addition of a cupric ion and its temperature dependence will be discussed briefly.

From the relation

$$I_F/I_{P0}=I_L/I_{P0}-1=\frac{\pi_1-(n_1n_2/\pi_2)}{n_uu_u'/\pi}$$

it is evident that I_F/I_{P0} decreases when n_un_u'/π and n_1n_2/π_2 increases while it increases when π_1 increases. In the present case π_2 and n_2 are scarcely affected by a cupric ion and the increase of π_1 and n_1 partially cancels, so that the variation of the numerator on the right side becomes much less than that of n_un_u'/π. Thus the main factor which reduces I_F/I_{P0} is n_un_u'/π, which in the present case is remarkably increased by the addition of cupric ion.

The result that the value of I_F/I_{P0} decreases with rise of temperature, irrespective of the addition of cupric ion, is due to the fact that the temperature coefficient of n_un_u'/π is larger than that of π_1, π_2 and n_1n_2 (see Table V).

(f) Trypaflavine-filter Paper Phosphor.—As already reported in part II, deviation from linearity in decay curves is much smaller than that of silica gel phosphor. Moreover the effect of addition of a third substance is also much smaller than that in the case of silica gel, so that the analysis on the basis of the scheme involving M-state cannot be done very accurately. Here only a few examples will be shown and the results will be discussed only qualitatively.

The Table VI shows the results of analysis of the decay curve when oxygen or water vapor is added to the phosphor.

In the case of oxygen π' and π'' remain constant while n_1n_2 seems to be somewhat

TABLE V

Dye conc., 0.4 μmol./g.; $CuCl_2$, 3.6 μmol./g.; Time in sec.

$1/T$	α	β	A/B	I_L/I_{P0}	π'	π''	n_1n_2	n_un_u'/π
3.65×10^{-3}	2.08	15.4	0.48	2.53	22	2.9	10	7.2
3.51	2.65	16.6	0.48	2.38	24	3.7	12	8.7
3.36	3.92	20.0	0.40	1.94	35	5.1	17	16
3.24	4.58	23.6	0.29	1.87	44	5.6	19	22
3.12	6.5	27.1	0.24	1.73	58	7.6	22	32
Apparent activation energy (kcal./mol.)					1.7	1.6	1.2	2.6
Reference Sample								
3.65	1.43	4.58	1.4	3.73	4.59	2.4	2.2	0.99
3.53	1.84	6.28	1.3	3.12	6.9	3.0	3·9	1.8
3.36	2.53	8.47	1.1	2.66	10.3	4.0	3.3	6.3
3.24	3.04	10.35	0.77	2.53	13.7	4.4	7.8	4.7
3.12	4.51	14.85	0.75	2.42	21.7	5.8	12	8.1
Apparent activation energy (kcal./mol.)					2.3	1.3	3.2	2.4

TABLE VI

Dye conc., 0.8 μmol./g. (filter paper, ca. 0.5 g). At 25°C. Time in sec.

	α	β	A/B	I_L/I_{P0}	π'	π''	n_1n_2	n_un_u'/π	I_F
Reference	2.15	6.43	1.5	4.59	6.0	3.6	4.2	1.1	76
O_2, 2.4 *m*.mol. (190 mmHg)	2.08	5.79	0.7	5.95	6.0	2.8	2.2	0.9	65
O_2, 3.6 *m*.mol. (290 mmHg)	2.32	6.30	0.5	8.31	6.3	3.0	2.2	0.7	60
Reference	2.28	7.11	1.4	4.74	6.7	3.8	5.0	1.1	80
H_2O, 40 μmol. (1/4 mmHg)	2.35	6.85	1.4	5.04	6.3	3.9	4.3	1.0	55
H_2O, 320 μmol. (2 mmHg)	2.52	6.52	1.9	7.69	5.4	4.2	3.7	0.6	21

diminished. But since the results are not so certain and moreover data are rather few, it will not be suitable to discuss further about this point. There is however no doubt that the decrease of I_F is closely connected with that of n_un_u'/π. Hence broadly speeking, it can be said that only S'-state is affected and only fluorescence is quenched.

This result is in sharp contrast with that obtained for the case of trypaflavine-silica gel phosphor. It is to be noted, however, that in the present case the quantity of oxygen is very large compared with that in the case of silica gel.

The situation is quite similar for the quenching caused by water vapor; thus only S'-state is affected and the intensity of pure fluorescence decreases without any noticeable effect on the decay curve.

The influence of the addition of some organic vapors such as acrylonitrile (the quantity is 1700 times that of dye), styrene (about equal to that of dye), etc. was also tested but none of them showed any effects beyond experimental error.

General Features of the Quenching Phenomena as Revealed from the Results so far Obtained

The main features of the quenching phenomena so far established can be summarized in Table VII.

TABLE VII

Carrier	Quencher	S'		T		M
Silica gel	Gases	×	$\overset{\times}{\leftarrow}$	○	$\overset{\circ}{\rightarrow}$	∘
	SO_2	×	$\overset{\times}{\leftarrow}$	○	$\overset{\circ}{\rightarrow}$	○
	Salts	○		×		×
	$CuCl_2$	○		○	$\overset{\circ}{\rightarrow}$	×
Filter-paper	O_2, H_2O	○		×		×
	Self-quenching	○		×		×

In this Table ○ and × under S'-, T- and M-state represent respectively that the state in question is affected or not by a quencher. A small circle means that the action is somewhat small. Very little can be said whether each transition is influenced or not by a quencher, but the results written in this Table are reliable.

The informations summarized in the above Table are still very scanty, yet some suggestive arguments will be based upon them.

From the survey of the above Table it seems permissible to classify the quenching effects into two groups; collisional quenching which attacks chiefly T- and M-state, and a static one attacking S′-state. Let us consider the results from this point of view.

That the quenching action of oxygen toward silica gel phosphor is of collisional nature has been argued already in part III. Hence it is considered that oxygen on silica gel phosphor is so weakly adsorbed that it is quite free to move.

On the contrary, filter paper is less porous than silica gel and oxygen adsorbed on it is supposed to be fixed at a definite position. The adsorbed oxygen in this case is thus remote from the adsorbed dye molecule and this is perhaps the reason why it falls into the class of a static type. There may be no question that salts act as static quenchers since they are adsorbed on fixed positions. Self quenching in the case of filter paper is also undoubtedly of static type. Thus all the results conform well with the above classification.

Now, this classification becomes more plausible and more instructive if one assumes the following molecular model of adsorbed dye. From the observations made when polyvinyl alcohol was used as a carrier (Part II), it seems probable that molecules of trypaflavine are fixed on a carrier at the positions of two amino-groups. It is very natural then, to suppose that if the two amino-groups attached on a carrier are subject to some perturbation, then T- or M-state will be affected appreciably. Such a reasoning conforms well with the general view that molecular rigidity is one of the essential conditions for the phosphorescence to be observed. Thus it is comprehended that only when a quencher molecule approaches closely to an amino-group can it affect T- or M-state. This may be the reason why only collisional quenching affects T- and M-state. In the case of a cupric ion which is a sole exception in static quenching, the field may be so intense that it is able to affect amino-groups to some extent.

To sum up, the behavior of T- and M-state probably depends on the interaction of amino and polar group of a carrier and is supposed to be perturbed only by extremely short range force.

The physical or chemical property of M-state is not yet known, but the fact that cupric chloride only affects T-state while oxygen and other gases attack both T- and M-state seems to be due to a specific nature of this state.

In order to reveal the nature of M-state, it will be most helpful to study about various combinations of dye and carrier.

Summary

The effects of the addition of inorganic salts upon trypaflavine-silica gel phosphor were studied, and it was found that decay curves are not affected much by any of the metallic ions except cupric ion. On the contrary, the intensity of pure fluorescence (I_L-I_{P0}) was reduced more or less by many metallic ions. From these results, it was concluded that many metallic ions chiefly affect S′-state but not T- and M-state.

The result for cupric chloride was somewhat anomalous on the point that a cupric ion affects both S′- and T-state.

A general survey on the quenching action of various substances upon adsorbed trypaflavine phosphor was given.

The cost of the present research has been partly defrayed from the Scientific Research Grant from the Ministry of Education.

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