LUMINESCENCE IN THE SOLID STATE— BORIC ACID AS BASE

Part II. Coumarin and its Derivatives as Activators

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THOUGH a considerable amount of work has been done on the preparation and properties of the boric acid phosphors,[1] there are several aspects which require further investigation and some of these which have a bearing on the present work may be stated as follows:—

(1) Of the large number of organic compounds available only a few have been so far employed as activators, and it is of considerable interest to investigate the use of other organic molecules especially with a view to prepare phosphors of long after-glow periods.

(2) According to Tiede *et al.*[1] the function of the boric acid is to supply the necessary physical conditions for the luminescence process; pure boric acid subjected to the same treatment does not luminesce and the electronic transitions, both in absorption and emission, take place in the molecule of the organic substance the nucleus of which remains unchanged. In a few cases, however, according to these authors it is not only regarded as possible but also probable that chemical reaction may occur between boric acid and the organic molecule but no suggestions have been put forward by them regarding the effect of such chemical reaction on the duration and intensity of phosphorescence. Neelakantam and Sitaraman[1] attempted to throw light on these questions by investigating the behaviour of phenolic and *o*-hydroxy-carbonyl compounds as activators but it was found that their results could be interpreted in different ways and more data was necessary before definite conclusions could be drawn.

(3) The results reported by the authors in Part I show that in several cases the fluorescence of the activator in the pure state under ultra-violet light was different from that of the luminescent body prepared with it. If the molecule of the activator remained unchanged these observations have to be explained on purely physical grounds such as the dielectric constant

and viscosity of the medium while in those cases in which chemical reaction may occur, new molecules may be the cause of the change.

(4) As phosphorescence depends firstly on the ability of the activator to absorb light quanta and re-emit them and secondly on the physical conditions being suitable for delaying emission of part or whole of the absorbed energy it would be of interest to investigate if an organic molecule which is strongly fluorescent in the solid state would also yield intense and long duration phosphorescence given suitable physical conditions. At the outset it may be stated that Tomaschek[1] found that no such relationship existed and that an activator which was strongly fluorescent in the pure state does not necessarily give rise to a strong phosphor. Our results reported in Part I are also in general agreement with this view but it was noted that some of the best phosphors obtained by us were prepared using activators which were themselves strongly fluorescent under ultra-violet. Tomaschek (*loc. cit.*) cites the case of anthracene which fluoresces strongly in the solid state but yields a weak phosphor. Bowen[2] has pointed out that while in the solid state the fluorescence efficiency of anthracene approaches unity, in the dissolved state it is actually one-fifth of this value; cases are known in which the efficiency in the dissolved state is much greater than in the solid state. It is well known that in the case of solutions the intensity as well as spectral distribution of fluorescence depends on various factors such as (*a*) nature of solvent, its viscosity and dielectric constant, (*b*) temperature, and (*c*) pH. It has also been pointed out by Pringsheim,[3] Seshadri[4] and others that one may expect as a rule an unequal power of fluorescence of a molecule in the ionised and non-ionised states. It is obvious, therefore, that in attempting any correlation between the fluorescence of the activators in the pure state and their activating abilities, it is necessary to prescribe suitable and definite conditions for the observations of the fluorescence. Very little work has been done along these lines. However, Levshin and Vinokurov[5] deduced that the luminescence efficiencies of preparations using dyes of the fluorescein series vary in the same sequence as in the case of liquid solutions of the respective dyes. Considering the facts that the boric acid phosphors are similar to solid solutions in behaviour and the activators are employed at very high dilutions (1 : 1,000 or more) it appears to the present authors that the fluorescence efficiencies in dilute solutions under U.V. light are perhaps best chosen for such comparisons. In the present investigation, however, it has not been possible to determine the fluorescence efficiencies. An attempt has, therefore, been made to correlate the fluorescence in dilute, neutral or weakly alkaline alcoholic solutions with the activating ability.

It is well known that the α-pyrone ring possesses marked luminescent properties, and the results reported by the present authors in Part I showed that the umbelliferones gave very good phosphors. Further with these activators both the intensity of the emitted light as well as the period of after-glow diminished with decreasing concentration of the activator. This is contrary to the behaviour of the sulphide phosphors[6] and also to the results obtained with organic molecules of other classes. It is, therefore, of interest to investigate whether diminution of both intensity and after-glow period with decreasing concentration of the activator is characteristic of all α-pyrones and an increase above the 1:1,000 limit, used previously, increases both.

The present investigation has been carried out using several coumarin derivatives, some of which exhibit fluorescence in the solid state itself in daylight, which were available to us as a result of the work of Seshadri *et al.* Reference to the literature shows that of the wide variety of coumarins which have been synthesised only the naturally occurring æsculin (the glucoside of æsculetin, 6:7-dihydroxy-coumarin) has so far received attention in this connection.

Seshadri *et al.* deduced that the essential requirement for the production of fluorescence by the coumarins in alkaline and strongly acid solutions is the existence of a hydroxyl group in the 7-position; the effect of this group is either enhanced or diminished by the presence of other groups in the molecule according to their nature and position. On alkylation of the 7-hydroxyl, the fluorescence in alkaline solution disappears but the compound still retains its ability to fluoresce in strongly acid solutions. When the hydroxyl is free chemical reaction is possible with boric acid but not when it is alkylated or acylated. Thus by examining closely related compounds of both types as activators it may be possible to throw some light on the question of compound formation and its effect on the intensity and after-glow of the phosphorescence.

Experimental

The procedures adopted for the preparation of the solutions as well as the phosphors are identical with those already described.[1] For the sake of uniformity with the previous investigation, at first the activators at three different concentrations, *viz.*, 1·0, 0·1 and 0·01 mg. per 1·0 g. of boric acid were employed. To determine the effect of increasing concentration of activator 2·0 and 5·0 mg. of activator per 1·0 g. of boric acid were also used. The latter experiments were also carried out with the five umbelliferones which were included in the previous investigation.

Since evaporation with alcohol causes some loss of boric acid, in the case of experiments with 5·0 mg. of activator the usual procedure was modified as follows:—5·0 c.c. of the alcoholic solution of the activator was pipetted into the empty crucible and then evaporated to small bulk on a hot plate. The boric acid was then added and after mixing, the contents were dried and then heated as before. In this way losses of boric acid were cut down and uniformity maintained.

Four compounds (1 to 4 in Table I) which fluoresce in the solid state in daylight are also included in this investigation.

The aqueous alcoholic solutions of the activators which were employed in this investigation were examined for fluorescence both in daylight as well as under filtered U.V. light. In the course of the examination in daylight it was found that the fluorescence was best observed in a thin column of liquid drawn up in a graduated 1·0 c.c. pipette. Examined in this way several solutions which appeared weakly or non-fluorescent when examined in bulk appeared relatively more fluorescent. Hence this method was used and the results thus obtained reported in Table II. Examination under U.V. light was carried out using quartz test-tubes. Rectified spirit was employed in all cases for preparing the solutions but it is possible that on long standing in glass bottles they become slightly alkaline. The results obtained should therefore be interpreted bearing this in mind.

The fluorescence of the activator in the solid state under U.V. light was examined as already described.[1] The phosphorescence was excited in all cases by means of filtered U.V. light.

Results

The results obtained are recorded in the tables below. The figures given in brackets under phosphorescence in Table I are the periods of afterglow in seconds. For purposes of comparison with the results already reported the intensity of phosphorescence with 5·0, 2·0 and 1·0 mg. of activator in each case was determined qualitatively with reference to preparations obtained in the previous investigation. These intensities have been classified qualitatively by visual observation as very strong (V.S.), strong (S), moderately strong (M.S.), weak (W), and very weak (V.W.). The abbreviations under phosphorescence have this significance. To enable ready reference some of the data relating to the umbelliferones previously reported upon has been included in the table.

In Table II the fluorescence of the activator in the solid state under U.V. light and that of the alcoholic solution, both in daylight and under

TABLE I

Sl. No.	Activator	Phosphorescene (U. V. Excitation)				
		5·0 mg.	2·0 mg.	1·0 mg.	0·1 mg.	0·01 mg.
1	5 Methoxy-4:7-dimethyl-coumarin-3-acetic acid	Yellowish green (16; S.)	Yellowish green (15; S.)	Yellowish green (19; S.)	Yellowish green (16)	Yellowish green (10)
2	Do ethyl ester	Do (10; S.)	Do (17; S.)	Do (17; S.)	Do (11)	Do (10)
3	5:7-Dimethoxy-4-methyl-coumarin-3-acetic-acid	Do (16; S.)	Do (18; S.)	Do (16; S.)	Do (15)	Do (14)
4	Do ethyl ester	Do (16; S.)	Do (20; S.)	Do (17; S.)	Do (11)	Do (10)
5	4-Methyl-7-methoxy-coumarin ..	Bluish green (26; V. S.)	Bluish green (29; V. S.)	Bluish green (29; V. S.)	Bluish green (23)	Bluish green (21)
6	4-Methyl-5:7-dimethoxy-coumarin ..	..	..	Blue (16; S.)	Greenish blue (15)	..
7	3-Phenyl-umbelliferone ..	..	? (9; V. W.)	? (10; V. W.)	? (6)	? (6)
8	4:8-Dimethyl-umbelliferone acetate ..	Yellowish green (25; V. S.)	Yellowish green (24; V. S.)	Yellowish green (26; V. S.)	Green (24)	Green (23)
9	7-Methyl-coumarin ..	Bluish green (20; M. S.)	Bluish green (19; M. S.)	Green (19; M. S.)	Do (18)	? (13)
10	4:7-Dimethyl-coumarin ..	Do (26; S.)	Do (26; S.)	Bluish green (24; S.)	Pale blue (17)	Pale blue (15)
11	5-Hydroxy-4:7-dimethyl-coumarin ..	Do (15; S.)	Do (21; S.)	Do (17: S.)	Greenish blue (15)	Do (14)
12	Do methyl ether	Do (23; S.)	Do (19; S.)	Do (15; S.)	Do (13)	Do (11)
13	5:7-Dihydroxy-4-methyl-coumarin-3-acetic acid	Do (16; M. S.)	Do (15; M. S.)	Do (20; M.S.)	Pale blue (15)	Do (14)
14	7:8-Dihydroxy-4-methyl-coumarin-3-acetic ester	Pale blue (10; W.)	Pale blue (12; W.)	Do (13; W.)	Green (14)	? (12)
15	Coumarin ..	..	Do (15; V. W.)	Do (7; V. W.)	Pale blue (5)	..
16	Umbrelliferone ..	Bluish green (18; V. S.)	Bluish green (20; V. S.)	(22; V. S.)	(20)	(18)
17	4-Methylumbelliferone ..	Do (24; V. S.)	Do (26; V. S.)	(30; V. S.)	(25)	(20)
18	4:8-Dimethyl-umbelliferone ..	Green (22; V. S.)	Green (26; V. S.)	(30; V. S.)	(27)	(24)
19	8-Allyl-umbelliferone ..	Greenish yellow (15; S.)	Greenish yellow (16; V. S.)	(18; V. S.)	(16)	(14)
20	5-Methyl-3-carboxy-ethyl-umbelliferone ..	Do (21; V. S.)	Do (20; V. S.)	Do (22; V. S.)	(16)	(16)

TABLE II

Sl. No.	Activator	Fluorescence of Solid Activator (U. V. Excitation)	Fluorescence of preparation (U. V. Excitation)	Fluorescenee of Activator (Alcoholic Solution)	
				Daylight	U. V. Light
1	5-Methoxy-4:7-dimethyl-coumarin-3-acetic acid	Violet	Bluish green	Pale violet-blue	Violel-blue
2	Do ethyl ester ..	Do	Do	Do	Do
3	5:7-Dimethoxy-4-methyl coumarin-3-acetic acid	Deep violet	Blue	Violet	Deep violet-blue
4	Do ethyl ester ..	Do	Do	Do	Do
5	4-Methyl-7-methoxy-coumarin ..	Violet	Violet	Nil	Violet
6	4-Methyl-5:7-dimethoxy-coumarin ..	Pale blue	Deep blue	Violet	Do
7	3-Phenyl-umbelliferone ..	Blue	Do	Deep blue	Deep blue
8	4:8-Dimethyl-umbelliferone acetate ..	Nil	Violet-blue	Pale green	Light blue
9	7-Methyl-coumarin ..	Pale violet	Pale green	Nil	Do
10	4:7-Dimethyl-coumarin ..	Deep violet	Pale blue	Nil	Deep violet-blue
11	5-Hydroxy-4:7-dimethyl-coumarin ..	Deep blue.	Bluish green	Nil	Yel.ow
12	Do methyl ether ..	Pale violet	Do	Pale violet-blue	Deep violet-blue
13	5:7-Dihydroxy-4-methyl-coumarin-3-acetic acid	Nil	Deep blue	Pale violet	Deep violet
14	7:8-Dihydroxy-4-methyl-coumarin-3-acetic ester	Nil	Pale blue	Nil	Nil
15	Coumarin ..	Deep violet	Do	Nil	Light blue
16	Umbelliferone ..	Light violet-blue	Deep violet	Deep blue	Deep blue
17	4-Methyl-umbelliferone ..	Deep vio.et	Do	Deep violet-blue	Do
18	4:8-Dimethyl-umbelliferone ..	Nil	Do	Pale green-ish blue	Light blue
19	8-Allyl-umbelliferone ..	Blue	Deep violet blue	Do	Do
20	5-Methyl-3-carboxy-ethyl-umbelliferone	Green	Do	Deep violet-blue	Deep violet-blue

U.V. is reported. The fluorescence of the luminescent body under U.V. light is also reported in this table.

DISCUSSION

(1) The results obtained (Table II) show that generally the colour of the fluorescence of the activator in the solid state and that of the luminescent body prepared with it are different. Molecules containing one or more free hydroxyls may enter into chemical reaction with the boric acid and this may be suggested as the explanation of the change but it can be clearly seen that such an explanation is untenable as the change occurs even when no hydroxyl, free or alkylated, is present as in the case of coumarin. The explanation must, therefore, be found in the altered physical conditions of the activator. It is well known that quenching of fluorescence in the solid state may occur as a result of association and close-packing of the molecules but dilution

producing an increase in the number of simpler molecules can account for an increase in intensity of the fluorescence but not for a change in the spectral region of emission. Among physical causes changes in viscosity and dielectric constant of the solvent (medium) are known to produce such a change in the region of emission and an explanation should therefore be sought for on these lines.

(2) The activating abilities of the coumarins now examined (Table I) are of the same order as those of the umbelliferones previously reported upon. The intensities of the phosphorescence are in some cases very strong but the after-glow period in no case exceeds 30 seconds (visual observations).

(3) The first four compounds in Table I are marked by their ability to fluoresce in daylight in the solid state itself and in solution also these compounds are prominently fluorescent under U.V. light. Even these compounds, however are not characterised by any special activating ability. Actually they are weaker in this respect than some compounds which do not fluoresce in the solid state in daylight or even under U.V. light, *e.g.*, 4 : 8-dimethyl-umbelliferone and its acetate.

(4) With a few exceptions, all the compounds now examined fluoresce more or less strongly in alcoholic solution as well as in the solid state under U.V. light (Table II). As activators of phosphorescence, 3-phenyl-umbelliferone, 7 : 8-dihydroxy-4-methyl-coumarin-3-acetic acid and coumarin are weak especially as regards intensity of phosphorescence. The other activators yield moderately strong to very strong phosphorescence and afterglow period also is appreciable reaching a maximum of thirty seconds. From the available data it is clear that no correlation could be established between fluorescence of the activator either in the solid state or in solution with the activating ability in phosphorescence.

(5) The presence of a free hydroxyl group does not appear to be necessary for activation. 4 : 8-Dimethyl-umbelliferone and its acetate give similar results and so also 5-hydroxy-4 : 7-dimethyl-coumarin and its ether, and 4-methyl-umbelliferone and its ether. This evidence indicates that chemical reaction with the base (boric acid) is not a factor at all in activation, at any rate, in this group of organic molecules.

(6) At activator concentration of 1 in 100,000 the intensity of phosphorescence is very poor but with increasing concentration of activator it increases until it reaches a maximum at about 1 in 1,000. At higher concentrations of activator there is neither an appreciable increase nor diminution of intensity as far as could be judged by visual estimations. A peculiar

feature of these phosphors is that at lower concentrations the after-glow period also increases with increasing concentration of the activator until a maximum is reached and at still higher concentrations it shows a tendency to fall. A maximum is reached with each activator though at different concentrations. With the Lenard phosphors decreasing concentration of activator below the optimum at which phosphorescence is maximum reduces the intensity but increases the after-glow period while at higher concentrations it is shortened.[6] All the coumarin derivatives examined behaved in this manner and in this respect they are distinguished from the phenolic and *o*-hydroxy-carbonyl compounds examined previously.[1] However, the case of 1-hydroxy-2-naphthoic acid which belongs to the latter class, is exceptional in that it also behaves like the coumarins as regards fall in intensity and duration with diminishing concentration of activator. It is remarkable that the closely related 2-hydroxy-3-naphthoic acid behaves unlike the former and similarly to the other molecules. Attention has already been drawn to the marked distinction between these two molecules as activators; the former yields a good phosphor with intense emission of 25 seconds duration while the latter phosphoresces very weakly and for 6 seconds only at the same concentration.

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