

LUMINESCENCE IN THE SOLID STATE— BORIC ACID AS BASE

Part I. Phenolic and *o*-Hydroxy-Carbonyl Compounds as Activators

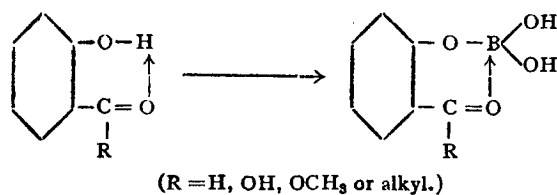
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LUMINESCENT bodies derived from boric acid as base and different organic compounds as activators (U. V. light excitation) have been prepared either by fusion or intensive drying of the mixture and studied by various workers, *viz.*, Tomaschek,^{1,2} Tiede *et al.*,³ Zhironov,⁴ Vinokurov and Levshin,⁵ Chause,⁶ and Tugarinov⁷. Their results and conclusions may be summarised thus:— (a) the phosphorescence of ordinary boric acid under U. V. excitation is due to traces of organic matter³; (b) phosphors could be prepared using boric acid itself, partially dehydrated boric acid as well as the fully dehydrated form, boron trioxide³; (c) the best results are obtained with partially dehydrated boric acid³; (d) the phosphors lose their ability to luminesce on prolonged exposure to air (hydration) as well as on intense dehydration, the luminescence of the boric acid and boron trioxide phosphors is generally weaker than that of the partially dehydrated form³; (e) the luminescence is greatly reduced by exposure to oxygen⁶; (f) a wide variety of organic compounds could serve as activators³; (g) compound formation between activator and base is not only possible but also probable in some cases³; (h) the organic molecule (activator) is the sole cause of the luminescence and is also the sole carrier of the light effect, the boric acid providing the necessary physical conditions³; (i) the phosphors are similar to solid solutions⁵; (j) some of these phosphors exhibit both fluorescence and phosphorescence⁵; (k) the properties of these phosphors differ in several respects from those of the impurity-activated metallic phosphors and the mechanisms of luminescence are also sharply distinguished^{1,5}; (l) the radiating centres of long and short duration are different⁷; (m) structurally the phosphorescent centres of boron trioxide phosphors differ from those of the boric acid phosphors and both from the sulphide phosphors⁴; (n) some correlation is possible between the constitutional features of the activators and the colour and intensity of the phosphorescence³; (o) no relationship seems to exist between the fluorescing capacity of a substance when pure and the after-glow with boric acid as base.³

Neelakantam *et al.*⁸ recently reported that boric acid activated the fluorescence of various types of *o*-hydroxy-carbonyl compounds dissolved in concentrated sulphuric acid. This activation consisted of a marked intensification of the fluorescence exhibited by them in daylight or under filtered U.V. light. In several cases fluorescence appeared only on the addition of boric acid, the solutions (H_2SO_4) of the compounds themselves being non-fluorescent. This effect was shown to be characteristic of *o*-hydroxy-carbonyl compounds, and no such intensification was observed with phenolic compounds. Some *o*-hydroxy-carbonyl compounds, however, gave negative results. No phosphorescence was noticed in any case under the experimental conditions adopted. Perhaps such effects could not be expected under these conditions since phosphorescence is generally confined to the solid state, although it may appear if the viscosity is very high.⁹ The mechanism of this "fluorescence effect" is not clear but Neelakantam *et al.*, assumed the formation of a chelate boron compound in the following manner:—



The function of the sulphuric acid is obviously that of a dehydrating agent and it has been shown that with resacetophenone, this acid could be replaced by phosphoric acid.⁸ Dehydration, could also be effected by fusion of the boric acid and the organic compound together and consequently it is of interest to determine if such fluorescence intensification (activation) occurred in the solid state also. This investigation, however, could not be undertaken for want of facilities at present for measurement of the relative intensities of fluorescence of the organic compound with and without the activating boric acid.

The work of Tomaschek, Tiede *et al.*, and others (*loc. cit.*) showed that several kinds of organic molecules activated the phosphorescence of boric acid under U.V. excitation. In the comprehensive investigation of Tiede *et al.* the relative intensities (qualitatively) of phosphorescence with different activators are recorded but not the duration of after-glow in each case. These authors found that generally the after-glow period does not exceed two minutes, the greatest diminution in intensity being observed during the first thirty seconds. The data, however, are insufficient to enable a distinction to be drawn regarding the relative efficiencies of different types of com-

pounds as activators, efficiency being determined by both intensity and duration. As has already been stated these authors considered that in several cases it was not only possible but also probable that the activators reacted with the base (boric acid) to form compounds.³ Boric acid reacts with phenolic compounds forming simple esters and with *o*-hydroxy-carbonyl compounds chelate structures. Further, in the free state the latter compounds are generally chelated (intramolecular hydrogen bond) whereas with the former intermolecular hydrogen bond formation is the general rule. Since the organic molecule is regarded as the sole carrier of the light effect, the boric acid providing only the necessary physical conditions,³ it is of interest to enquire if any difference in luminiscence is exhibited by the two different structures. Such a study would throw light on the mechanism of the luminiscence. It may be pointed out here that in the "fluorescence effect" of Neelakantam *et al.* the simple phenolic compounds behaved differently from the *o*-hydroxy-carbonyl compounds, though chemical reaction with boric acid is possible in both cases. In view of the close relationship of fluorescence and phosphorescence both of which are probably phases of the same phenomenon, the present investigation has been undertaken with a view to compare the relative efficiencies of the phenols and phenolic compounds on the one hand and *o*-hydroxy-carbonyl compounds on the other as activators of phosphorescence of boric acid under U.V. excitation. The examination is purely qualitative. Further, Tomaschek² stated that generally no relationship seems to exist between fluorescing capacity of a substance and the after-glow of the phosphor prepared with boric acid as base, *i.e.*, its efficiency as an activator. In this investigation, therefore, the authors noted the fluorescence of the activator as well as that of the luminiscent product to verify this statement.

Tiede *et al.*³ reported the best results obtained in the several cases after a series of experiments with each activator under different conditions. In order that the results may be comparable, the present authors adopted the same procedure in all cases.

The present investigation has been carried out using various types of hydroxy-carbonyl compounds, those in which the two groups are ortho to each other as also those in which they are in other positions, and the simple phenols.

EXPERIMENTAL

U.V. Light.—A mercury arc enclosed in a cabinet provided with an U.V. filter which transmitted mostly in the U.V. and a little in the violet-blue region was employed for exciting luminiscence. A small box with

darkened walls placed near the cabinet was used for observations of phosphorescence. All the observations were made in a dark room.

Boric Acid.—A specially purified sample of boric acid which after fusion phosphoresced very feebly after excitation under U.V. was employed as only a qualitative comparison was aimed at in this investigation.

Solutions.—Solutions of the various compounds were prepared by dissolving weighed quantities in alcohol and making upto volume with the same solvent. If the substance gave a colourless solution, 25.0 mg., and if coloured, 5.0 mg., were weighed out for 25.0 c.c. of the solution. Aliquots ranging from 1.0 to 0.01 cc. were measured out by means of a graduated 1.0 c.c. pipette.

Procedure.—Boric acid (1.0 g.) was weighed out into a silica crucible and the solution of the activator pipetted into it. In the case of the smaller volumes, a little of the pure solvent was added to moisten the whole of the solid. The contents were dried and heated gradually in an electric furnace until fusion occurred (200°C.). As soon as the contents formed a clear melt, the crucible was taken out, rapidly cooled under an electric blower and placed in a desiccator. The melt was then powdered and placed in a previously dried glass tube which was immediately sealed. There was no visible decomposition of the organic molecule in any case.

Generally with each activator the luminiscent bodies were prepared with a series of three different concentrations, namely, 1.0, 0.1 and 0.01 mg. or 0.2, 0.02 and 0.002 mg. per 1.0 g. of boric acid according to the depth of colour of the solution.

The sealed tube was placed in the filtered U.V. light for one minute and immediately transferred to the box and the colour, intensity and period of after-glow determined by visual observation and with the aid of a stopwatch. Observations of relative intensities are only qualitative. The fluorescence of the activator in the solid state was examined either by exposing the solid placed on the lid of a silica crucible or in the sample tube itself to filtered U.V. light.

RESULTS

The results obtained are given in the tables at the end of the paper. The figures given in brackets under phosphorescence indicate the period of after-glow.

Fluorescence Reaction in Sulphuric Acid.—The method of testing adopted was as already described.⁸

1-Hydroxy-2-naphthoic acid.—Dissolved in concentrated sulphuric acid, it gave a pale yellow solution which was non-fluorescent in daylight

but gave a bright blue fluorescence under filtered U.V. light. On the addition of boric acid it gave a pale violet fluorescence, visible in daylight itself and an intense violet fluorescence under U.V.

2-Hydroxy-3-naphthoic acid.—In concentrated sulphuric acid it gave a pale yellow solution with no fluorescence in daylight and a yellow fluorescence under filtered U.V. On the addition of boric acid, there was no fluorescence in daylight but under U.V. a deeper yellow fluorescence was obtained. The intensification was quite marked.

DISCUSSION

(1) The results now obtained show that generally the colour of fluorescence of the activator in the solid state and that of the luminiscent body prepared with it are different, *i e.*, the fluorescence occurs in different parts of the spectrum. Further an activator need not itself be fluorescent and several compounds which are themselves non-fluorescent under U.V. light do activate phosphorescence. The best phosphors are, however, obtained with some of the compounds which are markedly fluorescent, for example, the umbelliferone derivatives which fluoresce in alcoholic solution even in daylight. Even among these compounds 4:8-dimethyl-umbelliferone which is non-fluorescent both in the solid state under U.V. and in alcoholic solution in daylight gives as good results as 4-methyl-umbelliferone which possesses a deep violet fluorescence both in the solid state under U.V. and in alcoholic solution in daylight. Thus there seems to be no relationship between the fluorescing capacity of the activator and its ability to activate phosphorescence. This conclusion is in agreement with the statement of Tomaschek.²

(2) There seems to be no marked distinction as activators between the *o*-hydroxy-carbonyl compounds on the one hand and the simple phenols, and hydroxy-carbonyl compounds in which the two groups are not in ortho positions on the other. Umbelliferone and its derivatives which do not contain the *o*-hydroxy-carbonyl group yield the best phosphors both as regards intensity of phosphorescence as well as duration of after-glow. Of the compounds containing this group only 1-hydroxy-2-naphthoic acid yields similar results and the rest behave as do the simple phenols. It may be recalled that a marked distinction exists as regards intensification of fluorescence in sulphuric acid solution brought about by the addition of boric acid between the two classes, the phenols and *o*-hydroxy-carbonyl compounds. Thus there is no parallelism between phosphorescence activation and the intensification of fluorescence with boric acid.

(3) Tiede and others have shown that phosphorescence can also be activated by hydrocarbons which can form no compounds with boric acid. Tiede *et al.*, however postulated that with certain other types of activators chemical reaction with boric acid is not only possible but also probable. The results reported now, however, can be interpreted in three different ways, *viz.*, (a) assuming chemical reaction to occur, the type of compound formed, chelate or ester, does not have much effect on the luminiscence, (b) no chelate boron compounds are formed by the *o*-hydroxy-carbonyl compounds with boric acid in the molten state so that both phenols and these compounds yield ester-like compounds and hence behave similarly, and (c) compound formation is not an important factor in activation. The evidence for the postulate of Tiede is based on analogy with the formation of pyroboracetate complexes in acetic anhydride solutions suggested by Dimroth *et al.*, and the mixed anhydrides of boric acid with organic acids reported by Pictet.¹² To explain the colour changes which occur when many α -hydroxy-anthraquinones dissolved in sulphuric acid are treated with boric acid, Feigl and Krumholz¹³ assumed the formation of inner-complex (chelate) compounds. Neelakantam *et al.*⁸ have also assumed the formation of the chelate structures to explain the "fluorescence effect". The available evidence, however, is scanty and hence no definite conclusion could be drawn regarding the relationship between the type of compound formed and its effect on activation of luminiscence.

(4) Generally the intensity of phosphorescence diminishes with decreasing concentration of activator but the period of after-glow increases. With umbelliferone and its derivatives as well as 1-hydroxy-2-naphthoic acid both intensity and after-glow period diminish with decreasing concentration of activator. It is remarkable that all these compounds are also strong activators. When the phosphorescent preparations with these activators were exposed to filtered U.V., both fluorescence and phosphorescence were found to occur simultaneously; while the exposed part fluoresced, phosphorescence occurred from the portions not directly exposed to the light.

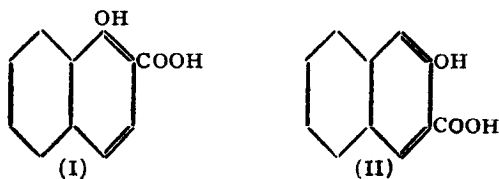
(5) As has been stated already the umbelliferone derivatives gave the best phosphors. In this connection it is of interest to note that some of the best known examples of organic compounds which fluoresce in daylight in the solid state itself are coumarin derivatives (Seshadri *et al.*¹⁰). Thus it appears that the α -pyrone structure possesses marked luminescence capacity.

(6) An interesting observation is the difference in behaviour of 1-hydroxy-2-naphthoic acid and 2-hydroxy-3-naphthoic acid as activators

of phosphorescence of boric acid. While the former is a powerful activator the latter is weak in this respect. Tiede also reported similar results with these two compounds. Since both of them contain a hydroxyl ortho to the carbonyl group and are closely related, they may be expected to behave similarly. Both compounds in fact behave similarly in the fluorescence reaction and resemble other *o*-hydroxy-carbonyl compounds in this respect but they differ markedly as activators of phosphorescence. An examination of their constitutions, however, indicates that an explanation may be offered on the following lines:—According to current ideas the double bonds of naphthalene are not free to migrate and at least in one part of the molecule they are fixed, as shown below:—



1-hydroxy-2-naphthoic acid and 2-hydroxy-3-naphthoic acid then have the respective structures I and II shown below:—



It is well known that molecules which readily form chelate rings with hydrogen or metals contain the group: $-\text{C}(\text{OH})=\overset{\text{I}}{\text{C}}-\text{CO}-$.¹⁴ Structure (I) contains this group but not (II) and this explains the difference. Should this be the sole cause of the difference in activating ability then it indicates some connection between ability to form an intra-molecular hydrogen bond and activation. There is evidence for the existence of both inter- and intra-molecular hydrogen bonds in the solid state.¹⁵ Further it is known that even when the molecule contains the $-\text{C}(\text{OH})=\overset{\text{I}}{\text{C}}-\text{CO}-$ group, hydrogen bond (chelate) formation may be impossible for steric reasons.¹⁴ Perhaps this explains the differences among themselves of *o*-hydroxy-carbonyl compounds as activators. It may be pointed out in this connection that even in the “fluorescence test” some of these compounds give a negative reaction. However, the evidence available at present is not sufficient to arrive at any definite conclusion.

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TABLE I

No.	Activator	Fluorescence of Activator (U.V. Excitation)	Luminescence (U.V. Excitation)						Intensity of Phosphorescence (Activator 1.0 mg.)
			1.0 mg.		0.1 mg.		0.01 mg.		
			Fluorescence	Phosphorescence	Fluorescence	Phosphorescence	Fluorescence	Phosphorescence	
	<i>O-Hydroxy-carbonyl compounds</i>								
1	Resacetophenone	Green	Blue	Blue (5)	Blue	Blue (7)	Blue (10)	Blue (10)	Strong
2	γ -Resacetophenone	Dull yellow	Green	Green (10)	Bluish green	Bluish green (10)	Bluish green (10)	Bluish green (10)	Moderately strong
3	α -Methoxy-	Greenish-yellow	Yellow	Yellow (7)	Light blue	Light blue (7)	Light blue (9)	Light blue (9)	Weak
4	Phloracetophenone	Dull yellow	Yellowish green	Yellowish green (5)	Yellowish green	Yellowish green (12)	Yellowish green (12)	..	Very weak
5	β -Resoreic aldehyde	Nil	Yellow	Yellow (5)	Light blue	Light blue (10)	Light blue (10)	? (10)	do.
6	3-methyl-	Yellow	do.	do. (7)	Light yellow	Light yellow (9)	Yellow (9)	Yellow (10)	do.
7	Benzoyl-phloroglucin-aldehyde	Dull yellow	Orange-yellow	Light yellow (7)	Light orange yellow	Light yellow (11)	Light yellow (11)	Light yellow (12)	do.
8	Methyl-2:4-dihydroxy-3-formyl benzoate	do.	Light greenish yellow	Light greenish yellow (6)	Very light greenish yellow	Very light greenish yellow (10)	Green (11)	? (11)	do.
9	7-Hydroxycoumarin-8-aldehyde	Deep yellow	Pale green	Green (10)	Green	Green (11)	Green (11)	? (11)	Weak
10	7-Hydroxy-3-methoxy-flavone-8-aldehyde	do.	Blue	Blue (7)	Blue	Blue (9)	Blue (9)	? (10)	Moderately strong
11	Salicylic acid	Deep blue	Violet	do. (10)	Violet	do. (12)	do. (12)	Blue (14)	do.
12	Sulphosalicylic acid	do.	do.	Greenish blue (12)	do.	Greenish blue (14)	Blue (8)	..	do.
13	β -Resoreic acid	Light blue	Blue	Blue (6)	Blue	Blue (8)	Blue (8)	Pale blue (10)	Weak
14	1-Hydroxy-2-naphthoic acid	Deep blue	Deep violet blue	Deep greenish yellow (25)	Violet blue	Greenish yellow (20)	Greenish yellow (20)	Greenish yellow (15)	Very strong
15	2-Hydroxy-3-naphthoic acid	Lemon yellow	Green	Yellow (6)	Green	Yellow (8)	Yellow (8)	Yellow (10)	Very weak
16	Ethyl orsellinate	Violet blue	Light blue	Light blue (8)	Light blue	Light blue (9)	Light blue (9)	Light blue (10)	do.

17	<i>Phenols</i> Catechol ..	Nil	Nil	Pale blue (10)	do.
18	Resorcinol ..	Nil	do. (10)	do. (10)	do.
19	Hydroquinone ..	Violet blue	do. (10)	do. (10)	do.
20	Pyrogallol ..	Nil	do. (5)	do. (10)	do.
21	Phloroglucinol ..	Blue	do. (18)	do. (5)	do.
22	α -Naphthol ..	Nil	do. (18)	do. (18)	Weak
23	β -Naphthol ..	Nil	do. (18)	Cream coloured (9)	Very weak
	<i>Umbelliferone and derivatives</i>								
24	Umbelliferone ..	Light violet blue	Deep violet	Greenish yellow (22)	Violet	Greenish yellow (20)	Light violet	Greenish yellow (18)	Very strong
25	4-Methyl-umbelliferone ..	Deep violet	Deep violet	Bluish green (30)	Violet	Bluish green (25)	Light violet	Bluish green (20)	Very strong
26	4 : 8-Dimethyl-umbelliferone	Nil	do.	Deep green (30)	do.	Deep green (27)	Bluish violet	Deep green (24)	do.
27	8-Allyl-umbelliferone ..	Blue	Deep violet-blue	Greenish yellow (18)	Violet blue	Greenish yellow (16)	Light violet blue	Pale green (14)	do.
28	5-Methyl-3-carboxyethyl-umbelliferone	Green	do.	do. (22)	do.	do. (16)	do.	do. (16)	do.
	<i>Miscellaneous compounds</i>								
29	Vanillin ..	Nil	Greenish-yellow	Pale blue (6)	Very weak
30	Isovanillin ..	Nil	Blue	Blue (6)	do.
31	<i>m</i> -hydroxy-benzoic acid	Bluish pink	Greenish yellow	Greenish yellow (15)	Strong; greater than with salicylic acid
32	<i>p</i> -Hydroxy-benzoic acid ..	Blue	Pale violet	Blue (15)	Moderately strong; less than with salicylic acid
33	Mandelic acid ..	Nil	Nil	Pale blue (12)	Very weak
34	Benzoin ..	Orange-yellow	Nil	do. (10)	do.
35	2-Methyl-3-methoxy-7-hydroxy-chromone	Nil	Deep violet	Yellow (10)	Deep violet	Yellow (10)	Deep violet	Yellow (10)	Strong
36	3-Benzoyl-7-hydroxy-flavone	Nil	Greenish yellow	Pale blue (12)	Pale green	Pale blue (11)	Pale green	Pale blue (10)	do.
37	6 : 8-Diallyl-7-hydroxy-flavone	Yellow	do.	Greenish blue (11)	Greenish blue	Greenish blue (11)	Greenish blue	Greenish blue (12)	Moderately strong

TABLE II

No.	Activator	Fluorescence of Activator (U.V. Excitation)	Luminescence (U.V. Excitation)						Intensity of Phosphorescence (Activator 0.2 mg.)
			0.2 mg.		0.02 mg.		0.002 mg.		
			Fluorescence	Phosphorescence	Fluorescence	Phosphorescence	Fluorescence	Phosphorescence	
1	<i>Flavonols</i> Morin ..	Red	Greenish yellow	Greenish yellow (5) Pale blue (9)	Green	? (6)	? (9)	Very weak	
2	Quercetin ..	Orange	Yellowish green	Yellow (5) do. (9) Blue (8)	Yellowish green Light yellow Deep yellow Deep blue	Pale blue (10) Yellow (8) do. (10) Blue (8)	Pale blue (10) Yellow (11) do. (10) Blue (9)	do.	
3	Quercetagetin ..	Nil	Yellow	Yellow (5) do. (9) Blue (8)	Light yellow Deep yellow Deep blue	Light yellow do. (10) Blue (8)	Yellow (11) do. (10) Blue (9)	do.	
4	Cannabiscetin ..	Light red	Deep yellow	Yellow (5) do. (9) Blue (8)	Deep yellow Deep blue	do. (10) Blue (8)	do. (10)	Weak	
5	7-Methoxy-flavonol ..	Lemon yellow	Deep blue	Yellow (5) do. (9) Blue (8)	Deep yellow Deep blue	do. (10) Blue (8)	do. (10)	do.	
6	<i>α-Hydroxy-anthraquinones</i> Alizarin ..	Nil	Bright orange yellow	? (5)	Nil	do. (10)	? (10)	Weakest	
7	Quinizarin ..	Orange red	Orange yellow	Nil	Yellow	Yellow (7)	Yellow (7)	do.	
8	Anthrarufin ..	Deep orange	Orange red	Orange red (5)	Light greenish yellow	do. (7)	do. (8)	Very weak	

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