

# LUMINESCENCE IN THE SOLID STATE: BORIC ACID AS BASE

## Part III. Azo-Dyes from *o*-Hydroxy-Carbonyl Compounds as Activators

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OUT of nearly fifteen hundred dyes listed in the Colour Index only about eighty-five are classified as fluorescent in the dissolved state, the solvent being water, alcohol, xylene or tetralin. It is remarkable that not even a single azo-dye is to be found in the list. Recent work, however, has shown that many of the "non-fluorescent" dyes of the Index are quite as strongly fluorescent as the "fluorescent" dyes, when in a state of solid solution in solvents like gelatine, sugar, etc., or when adsorbed on wool. Under certain conditions they are even phosphorescent. Among azo-dyes also, there are several which fluoresce when dyed on silk, cotton or other textile fibres or when adsorbed on activated alumina.<sup>1</sup> It is well known that the phosphorescence of many compounds is specially strong when dissolved in solid anhydrous boric acid.<sup>2,3,4</sup> A variety of organic compounds have been utilised as activators of phosphorescence, with this base but among the dyes only those of the fluorescein series and a few others have been used so far and no systematic study of any group of dyes has been attempted by previous workers. The authors of the present paper have, therefore, taken up the study of the azo-dyes derived from *o*-hydroxy-carbonyl compounds<sup>5</sup> in this connection.

### EXPERIMENTAL

*Procedure.*—The procedure adopted for the preparation of activated boric acid mats and their examination under filtered U.V. light was identical with that already described in Part I.<sup>2</sup> Aqueous or alcoholic solutions of the dye-stuffs were employed. In all cases 1 gram of boric acid was used and with each dye, the amounts used were in the ratio of 100:10:1, the maximum amount of dye used being 1.0 mg. The results obtained with different concentrations of the activator in this ratio are reported in columns A, B and C respectively in the table. The figures in brackets indicate the period of after-glow in seconds. The intensities of phosphorescence in all cases were very weak.

| No. | Azo-dye                                | Luminescence (U.V. Excitation) |                    |                |                    |                     |                 |
|-----|--|--------------------------------|--------------------|----------------|--------------------|---------------------|-----------------|
|     |  | A                              |                    | B              |                    | C                   |                 |
|     |  | Fluorescence                   | Phosphorescence    | Fluorescence   | Phosphorescence    | Fluorescence        | Phosphorescence |
| 1   | Benzene-azo- <i>salicylic acid</i>     | Orange-red                     | Nil                | Yellow         | (5) Pale blue      | (10) Blue           |                 |
| 2   | <i>o</i> -Hydroxy-benzene-azo "        | Yellow                         | (6) Pale blue      | Pale yellow    | (8) Do             | (7) Pale blue       |                 |
| 3   | <i>p</i> -Hydroxy-benzene-azo "        | Blue violet                    | (8) Blue           | Pale blue      | (9) Do             | (8) Do              |                 |
| 4   | <i>p</i> -Sulpho-benzene-azo "         | Brownish yellow                | Nil                | Pale yellow    | (6) Light blue     | (6) Do              |                 |
| 5   | <i>p</i> -Chlor-benzene-azo "          | Bright orange-yellow           | Nil                | Yellow         | (4) Do             | (8) Blue            |                 |
| 6   | <i>p</i> -Nitro-benzene-azo "          | Yellowish brown                | Nil                | Yellow         | (6) Pale blue      | (8) Pale blue       |                 |
| 7   | <i>m</i> - do do "                     | Nil                            | Nil                | Pale yellow    | Nil                | (5) Do              |                 |
| 8   | <i>m</i> -Tolyl-azo-acid               | Orange-yellow                  | Nil                | Yellow         | (6) Pale blue      | (9) Do              |                 |
| 9   | $\alpha$ -Naphthyl-azo "               | Pale orange                    | (6) Light blue     | Pale yellow    | (10) Do            | (10) Do             |                 |
| 10  | $\beta$ - do do "                      | Orange red                     | (4) Pale blue      | Light orange   | (6) Light blue     | (7) Do              |                 |
| 11  | Benzene-azo-1-hydroxy-2-naphthoic acid | Orange-yellow                  | (6) Light blue     | Light yellow   | (9) Pale blue      | (10) Do             |                 |
| 12  | Benzene-azo-2-hydroxy-3-naphthoic acid | Dark red                       | Nil                | Rose red       | (6) Do             | (8) Do              |                 |
| 13  | Benzene-azo-resacetophenone (A)        | Brownish yellow                | Nil                | Pale yellow    | (6) Do             | (11) Do             |                 |
|     | (B)                                    | Yellow                         | Nil                | Do             | (8) Pale blue      | (8) Do              |                 |
| 14  | Chryssamine G                          | Pink                           | (4) Very pale pink | Pink           | (6) Very pale pink | (6) Do              |                 |
| 15  | Cotton yellow G. 1.                    | Bluish violet                  | (6) Very pale blue | Nil            | (9) Very pale blue | (10) Very pale blue |                 |
|     | Do R.                                  | Flesh colored                  | (10) Do            | Very pale pink | (14) Do            | (15) Do             |                 |
| 16  | Diamine brown M                        | Fiery red                      | (3) Do             | Flesh coloured | (7) Do             | (7) Do              |                 |
| 17  | Diamine Green B                        | Nil                            | (12) Green         | Nil            | (7) Green          | (7) Green           |                 |
| 18  | Diamond black F                        | Nil                            | (9) Greenish       | Nil            | (11) Greenish      | (16) Greenish       |                 |
| 19  | Diamond Green G                        | Orange                         | (4) Pale yellow    | Orange yellow  | (9) Pale blue      | (9) Pale blue       |                 |
| 20  |  |                                |                    |                |                    |                     |                 |

DISCUSSION

None of the dyes used in the above investigation fluoresce in aqueous or alcoholic solutions. As shown in a previous investigation<sup>3</sup> some of them fluoresce, though weakly, when dissolved in concentrated sulphuric acid and examined under U.V. light. On the addition of boric acid to this solution, intensification of fluorescence occurred in several cases. From the data presented in the table, it is clear that all the dyes fluoresce under U.V. excitation, when dissolved in anhydrous boric acid. The phosphorescence, however, is very weak in intensity in all cases. The period of after-glow is of the same order of magnitude as with the simple salicylic acid or resacetophenone molecule but the intensities are definitely weaker. It is well known that the azo group is markedly bathochromic although it does not destroy the ability to fluoresce completely. From the present study it is clear that the azo-dyes are poor activators of phosphorescence, although they fluoresce when dissolved in anhydrous boric acid. The azo-group is, therefore, on the whole a poor luminophore.

REFERENCES

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