XXI.—*Anticathodic Luminescence of some Organic Substances.*

By JOSEPH KENNETH MARSH.

WHEN organic substances are cooled and bombarded with cathode rays there is very frequently an emission of light of greater or less intensity. This phenomenon was first extensively studied by Goldstein (*Verh. deut. physikal. Ges.*, 1904, **6**, 156). Later a study was made by O. Fischer (*Z. wiss. Phot.*, 1908, **6**, 305) of a number of substances which gave discontinuous spectra. From his work, it is evident that there is usually some degree of regularity in the position of the bands given by each substance, and Baly (*Phil. Mag.*, 1915, **29**, 223) and Henri (" Etudes de Photochimie," 1919) have both found support for their theories with regard to the relationship of infra-red and ultra-violet spectra from the positions of the anticathodic luminescence bands.*

The present work was undertaken in the hope that some further information might be gained as to the origin and significance of the anticathodic glow. Visual observations were made of a large number of organic substances, but in the great majority of cases the glow was too feeble to admit of photography, and also it was often continuous in character. Goldstein distinguished three different spectra which it was possible for one substance to exhibit, *viz.*, an initial spectrum, the chief spectrum, and a solution spectrum. The present investigation has been confined to pure substances, so that it is not concerned with solution spectra. All the substances examined showed a partial loss of luminescent power after a few minutes or even seconds of bombardment. This was due in part to the fading of the initial spectrum. Partial recovery sometimes occurred after an interval of rest, but some of the loss of luminescent power was due to a surface decomposition of the material. The initial spectrum was usually of greatest interest, as it sometimes consisted of distinct, bright bands; these gradually diffused them-

---

* These spectra have usually been termed cathodo-luminescence, but are produced when the materials act as anticathodes in a discharge tube, and so the term anticathodic luminescence would seem to be more fitting,

selves into a continuous spectrum—the chief spectrum of Goldstein. A phosphorescence lasting often for a minute or more was frequently seen on stopping the bombardment. This sometimes gave a spectrum which consisted of the same bands as were observable during the bombardment and, like the initial spectrum, decreased after a period of excitation.

A discharge tube similar in type to that used by Fischer was employed, and liquid air was used for cooling. In some cases, the glow, and likewise the phosphorescence, was stronger at temperatures higher than that of liquid air. There was also the disadvantage that the liquid exhibited several absorption bands across the usual range of the anticathodic luminescence spectrum, but, on the other hand, it enabled rather volatile substances to be examined. A small silica vacuum cup with an unsilvered patch held the liquid air into which the end of the discharge tube dipped. The spectrograph was a two-prism glass instrument giving a bright visible spectrum about 5 cm. long.

The materials examined fall into four classes, giving, respectively, (1) little or no glow, (2) a continuous spectrum only, although often of a distinctive hue, (3) a glow identifiable with the fluorescence spectrum, and (4) a distinctive banded spectrum.

(1) Those giving little or no spectrum include fully saturated compounds, nitro-compounds, strongly coloured substances, aldehydes, etc.; the following substances were found to belong to this class : hexane, paraffin wax, oleic acid, dipentene, bisdiphenylene-ethylene, carbon tetrachloride, hexachloroethane, nitrobenzene, *m*-nitroanisole, *o*-nitrophenol, benzaldehyde, cinnamaldehyde, quinone, quinol, 1 : 2-naphthaquinone, diphenyl ether, acridone, azobenzene, rosaniline, *p*-anisidine, benzaldoxime, and quinoline.

(2) A continuous spectrum was furnished by the following substances. The glow was most often blue or violet to the naked eye. Other colours are recorded in brackets after the substance. Stilbene, tolane, phthalic acid, terephthalic acid, *p*-hydroxybenzoic acid, phenol (green), *p*-cresol (green), fluorenone (green), coumarin, benzonitrile, *p*-chloroaniline, *p*-chlorobenzaldehyde, ethyl *p*-aminobenzoate (white), acridine (green), phenazone, sodium naphthionate, methyl propyl ketone, *s*- and *as*-diphenylurea, acenaphthenequinone (orange), 9 : 10-dinitroanthracene (yellow), benzanilide.

(3) In the following instances the glow was similar to the usual fluorescence spectrum : Anthracene, 1 : 2-benzanthracene, 9-phenylanthracene, 9 : 10-dichloro- and -dibromo-anthracenes, carbazole, aniline, α- and β-naphthylamines, diphenylamine, *p*-phenylenediamine. Probably also the blue glow given by a number of substances in the previous list is a continuation of the ultra-violet

fluorescence reaching up into the visible region under strong stimulation.

(4) Of those substances which gave banded spectra, only a minority have been completely investigated by photography. In other instances, the spectrum was too weak. Characteristic of all the stronger spectra was a well-marked head making an abrupt termination to the end of shorter wave-length. This head was often in the green region and never below the greenish-blue, but was sometimes in the red. The bands appeared on a bright continuous background, and to the blue side of the first head there was often a continuous spectrum also, although distinctly weaker.

The substances which have been photographed were chiefly aromatic hydrocarbons and naphthalene derivatives. Some of these have already been fully examined by Fischer, but others are now dealt with.

Toluene gave a continuous spectrum throughout the visible, but strongest between 4200 and 4800 Å. There was a strong band at 1/λ 2090, and others at 2193, 2151, and 1816.

p-*Cymene* glowed green and showed two distinct bands at 1/λ 2153 and 2083, and faint ones at 2222 and 1942, thus giving a series having an interval of about 70.

m-*Xylene* gave a spectrum less intense and much more diffuse than those of its isomerides (Fischer, *loc. cit.*). The same is true also of the absorption and fluorescence spectra. It showed, however, one very definite head at about 1/λ 2105 and signs of a second at 2224.

Mesitylene had five or six bands beginning in the bluish-green region, but fading quickly; it was not successfully photographed.

Naphthalene. The spectrum was in substantial agreement with Fischer's figures, but the first band on commencing excitation showed a doubling, which, however, was lost after a short time. The two heads were at 1/λ 1854 and 1850.

Tetrahydronaphthalene possessed a remarkably strong luminescence. Edge of spectrum, 1/λ 2123. Very strong double band, 2096 and 2075; also bands at about 2018, 1976, 1925, 1862, 1805, and 1715. The band 1925 is strong; the others are rather diffuse.

Octahydroanthracene also gave an intense spectrum starting at 2044 and having a strong double band at 1/λ 2043 and 2027. There were diffuse bands at about 1907, 1862, 1740, and a continuous region to the limit of the visible red.

Acenaphthene glowed orange-red and gave a number of bands which were fairly sharp on the blue edge in the case of the stronger ones. Positions, 1/λ 1767, 1748, 1717, 1691, 1629—1605, 1558. The fourth and the last are the strongest.

Triphenylmethane had a head at 1/λ 1930—1912 at the beginning of a continuous region extending to the limit of the red, with another diffuse maximum about 1750.

Diphenylmethane gave a yellowish-green glow which, however, was difficult to photograph. A change appeared to take place, the material giving a white solid of higher melting point.

α-*Methylnaphthalene* gave three strong bands, 1/λ 1825, 1690, 1556, and a faint one about 1640. There was also a strong continuous emission from the violet to 5000 Å.

β-*Methylnaphthalene* showed two strong heads, 1/λ 1657 and 1521, the former being particularly intense. There appeared to be a number of lesser maxima about 1815, 1780, 1604, and 1568, as well as a continuous region from the violet to 5000 Å.

α-*Naphthol* glowed red but soon fatigued, and showed only very indefinite maxima at about 1/λ 1664 and 1567.

β-*Naphthol* glowed less strongly than the last and more yellow in colour. The methyl ether showed bands at 1/λ 1757 and 1658.

Other substances which gave banded spectra were hexaethylbenzene, styrene, fluorene, phenylfluorene, chlorobenzene, *p*-dichlorobenzene, α-chloronaphthalene, hexachlorobenzene, ψ-cuminol, diphenylcarbinol, quinol dimethyl ether, anthraquinone, phenanthraquinone, *p*-tolyl methyl ether, 1 : 5-dihydroxynaphthalene, and α-naphthyl methyl ether.

Discussion of Results.

On comparing the anticathodic luminescence spectra with the Tesla-luminescence, it is apparent that what has been noted and described as the Tesla green glow (Marsh, *Phil. Mag.*, 1925, **49**, 971), from its usual appearance in a number of vapours, is substantially identical with the anticathodic glow of the solids, although there may be a strong anticathodic glow and yet little sign of emission from the vapour, *e.g.*, in naphthalene. In the cooled solids, the glow usually extends further towards the red than was found with the Tesla glow, and is stronger; and, as would be expected, the bands are displaced a little towards the region of greater wavelengths. This shift amounts to 1/λ 40 or more.

The position of the abrupt blue end of the anticathodic glow varies in a manner parallel with the variation of the absorption and fluorescence regions of the substance. There is a fairly definite frequency interval between the fluorescence and anticathodic glow regions. This is seen in the accompanying table, and must indicate a more or less fixed energy difference between two levels of activation common to all the substances.

TABLE I.

Substance.	Absorption-fluorescence boundary.	Anticathodic luminescence (short λ end).	Difference.
Toluene	3749	2151	1598
o-Xylene	3731	2099	1632
m-Xylene	3759	2108	1651
p-Xylene	3741	2131	1610
p-Cymene	3690	2153	1537
Tetrahydronaphthalene	3678	2085	1593
Octahydroanthracene	3528	2035	1493
Naphthalene	3245	1840	1405
Acenaphthene	3264	1767	1497
α-Methylnaphthalene	3333	1825	1508
β-Methylnaphthalene	3333	1815	1518
Triphenylmethane	3546	1921	1625
Styrene	3475	1912	1563

With the exception of naphthalene, the differences found do not vary by more than 10%.

The atomic-group spectra found in the infra-red show bands to a large extent independent of the exact molecular structure from which they originate, and although absorption bands of this series have been traced as far down as 0·606μ, they seem to have no direct connexion with the anticathodic bands. The above-noted interval between absorption or fluorescence and the anticathodic spectra, on the other hand, tends to show that the origin of the last is similar to that of the first two. Moreover, between the absorption, fluorescence, and anticathodic luminescence there is a distinctly traceable resemblance in structural detail. The clearest example of this is in *p*-xylene. Mies (*Z. wiss. Phot.*, 1909, **7**, 357) has measured 16 absorption bands divisible into two series giving an average interval 1/λ 79·5, and the anticathodic luminescence (Fischer) shows ten bands in two series with an average interval of 81·2. The Tesla-luminescence bands are again divisible into two series with an average interval of 81.

It must be admitted that not all the anticathodic luminescence spectra examined show a degree of regularity approaching that of *p*-xylene, but in most instances some sort of order is apparent in the case of the stronger heads, which, however, are often so diffuse that the accuracy of measurement scarcely justifies much deduction. In the case of naphthalene the three strongest bands appear at 1/λ 1840, 1694, and 1542, giving intervals of 146 and 152, similar in size to those found in other naphthalene spectra (Marsh, *Phil. Mag.*, 1925, **49**, 971; László, *Z. physikal. Chem.*, 1925, **118**, 369). The four strongest bands of acenaphthene (1558, 1617, 1691, and 1748) show intervals of 133 and 131. α- and β-Methylnaphthalenes give spectra resembling that of the parent hydrocarbon, but more diffuse and having an average interval of about 135. The bands in the case of the β-derivative have undergone a shift towards the red region. In *p*-cymene, there is a regularity at intervals of 70 units, and so on. For a discussion of the significance of these intervals reference may be made to previous papers by the author (*Phil. Mag.*, 1925, **49**, 1206; J., 1926, 724).

Fischer found three equally-spaced broad bands between 4100 and 4700 Å. in very many of the substances he examined. Like several other workers, he has not recognised these as due to traces of anthracene. They belong to the ordinary fluorescence spectrum of this substance. On bombarding anthracene itself, they are produced, but not with particularly great intensity, and decomposition is rather rapid, but a mere trace of anthracene in another substance will give rise to them. The chemicals in which Fischer found these bands now ascribed to anthracene were: Naphthalene, β-naphthonitrile, α- and β-acetonaphthalide, α- and β-naphthol, α- and β-naphthylamine, dibenzyl, and phenanthrene.

It is worthy of note that benzaldehyde was found not to give an anticathodic glow. Most substances capable of light emission will give a fluorescence, a Tesla-luminescence, and an anticathodic glow. The Tesla glow of benzaldehyde, however, appears to be the only emission of which it is capable. This glow seems to bear some relation to the fluorescence, inasmuch as it occurs in the same position as the extra absorption band developed in concentrated sulphuric acid solutions, which, according to Baly, usually occurs in the fluorescence zone of the alcoholic solutions.

THE SIR DONALD CURRIE LABORATORIES, THE QUEEN'S UNIVERSITY,
BELFAST, NORTHERN IRELAND.
[*Received, June 28th,* 1926.]