3. Incidental to the above, the arrangements of molecules, atoms, and electrons in the crystals considered have been partially determined.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

LUMINESCENCE OF COMPOUNDS FORMED BY THE ACTION OF MAGNESIUM ON PARA-DIBROMOBENZENE AND RELATED COMPOUNDS

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The ethereal solution formed by the action of magnesium on *p*-dibromobenzene, when exposed to the action of air or oxygen, is strongly chemiluminescent. Since this reaction is more luminescent than the oxidation of pyrogallol, or the chloropicrin and phenylmagnesium iodide (Wedekind)[1] reaction, and can be maintained for some time, it was thought worthy of investigation. Furthermore, both light emission and light absorption promise to show us a relation between radiation and chemical energy. Heczko[2] has shown that ethereal Grignard solutions react with oxygen with light emission, and Moeller[3] shows later that this luminescence appears only with aromatic compounds.

Previous work on the action of magnesium on dihalogen aromatic compounds points to the fact that with dibromobenzene but one halogen reacts, while with di-iodo-benzene both halogens are active. Tschitschibabin,[4] who used the reaction in the preparation of *p*-bromobenzaldehyde, claims that only one halogen reacts. F. Bodroux[5] in his work on nuclear dihalogen aromatic compounds found only one halogen active. Gomberg and Cone[6] also obtained the monohalogen derivative. On the other hand, E. Votocek and J. Kohler[7] find that with *p*-di-iodobenzene both halogens react.

Experimental Part

The *p*-bromophenylmagnesium bromide was prepared by the usual method.

The best results were obtained when 2.4 g. of magnesium and 23.6 g. of *p*-dibromobenzene were mixed in 130 cc. of dry ether in a flask connected with a reflux condenser. If the materials are perfectly dry, and iodine is used as a catalyst, the reaction begins at once and progresses smoothly. At the conclusion the flask was heated and a slight

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[1] Wedekind, *Z. wiss. Phot.*, **5**, 29 (1907).

[2] Heczko, *Chem.-Ztg.*, **35**, 199 (1911).

[3] Moeller, *Arch. Pharm. Chem.*, **1914**.

[4] Tschitschibabin, *Ber.*, **37**, 186 (1904).

[5] Bodroux, *Compt. rend.*, **136**, 1138 (1903).

[6] Gomberg and Cone, *Chem. Centr.*, **1906**, II, 1612.

[7] Votocek and Kohler, *Ber.*, **47**, 1219 (1914).

excess of magnesium added to insure the reaction of all of the *p*-dibromobenzene. After completion a black sediment that usually accompanies a Grignard reaction remained in the bottom of the flask, covered by a yellowish liquid which contained the luminescent material dissolved in ether. Because of the avidity of the compound for oxygen, the material was also made in an atmosphere of nitrogen, but the same results were obtained.

When the solution is cooled with ether and solid carbon dioxide, two layers appear at a temperature of about —30°, and upon further cooling, crystals appear in the lower layer. Upon warming the solution, these phenomena are reversed. Attempts were made to analyze the compound separating, but no constant proportion of ether could be obtained, due to efflorescence. Upon standing for 2 weeks, in an atmosphere of nitrogen, the solution deposits crystals at ordinary temperature. This phenomenon has been observed by Zerewitinoff[8] who made direct analysis of the crystalline compound of methylmagnesium iodide containing one molecule of amyl ether.

Chemiluminescence

The ethereal solution of *p*-bromophenylmagnesium bromide is so chemiluminescent that its light can be observed by day when the liquid is dropped from a tip in air, or when it is stirred in a test-tube in an atmosphere of oxygen. Poured from a test-tube, it glows with a greenish-blue light, in such a way as to suggest molten metal; 100 cc. of the solution in a 500cc. flask, opened to the air and shaken, gives enough light to read print and can be seen easily by an audience in a large auditorium if the room is well darkened.

The effect of passing different gases through this solution was tried. Dry nitrogen, carbon dioxide, hydrogen and sulfur dioxide did not effect luminescence. Air and oxygen, both dry and moist, caused the phenomenon to develop in marked form. The presence of moisture had no visible effect, although it was quite apparent that oxygen produced the more vivid light. The crystals that form in the solution upon long standing are also luminescent, but soon become coated with oxidation and hydrolytic products that must be removed in order to allow the chemiluminescence to appear.

The substance in solution was tested with 30% hydrogen peroxide, and although vigorous oxidation, accompanied with frothing, took place, much less chemiluminescence was observed, owing no doubt to the immediate hydrolysis, which is not accompanied by luminescence.

When the solution in a test-tube is opened in air and stirred, the temperature rises about 10°.

J. Lifschitz[9] has pointed out the importance of studying compounds of the type RMgX in regard to their light-giving properties. He has tried the effect of different gases on the aromatic Grignard compounds, but has made no attempts to determine the nature of the spectrum. His researches appear to connect the brilliancy of the luminescence with the stability of the etherates existing in the solution. He has also shown that addition compounds formed from organic magnesium compounds and dimethylaniline give faint

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[8] Zerewitinoff, *Ber.*, **41**, 2244 (1908).

[9] Lifschitz, *Helvetica Chim. Acta*, **1**, 472–4 (1918).

chemiluminescence when exposed to air or oxygen, but that this is true only with aromatic compounds. He further points out that chemiluminescence is not always due to oxidation, as some compounds when distilled in a current of hydrogen glow beautifully, and here the glow seems to be caused by an intramolecular change. That the luminescence does not necessarily accompany the fastest chemical reactions is apparent from the fact that few ionic reactions show this phenomenon. Thus we see that the connection of chemiluminescence with the presence of oxygen, or an exceedingly rapid reaction, is not necessarily established.

The reactions studied may be represented as follows: (1) $BrC_6H_4Br + Mg = BrC_6H_4MgBr$; (2) $BrC_6H_4MgBr + O = BrC_6H_4OMgBr$; (3) $BrC_6H_4OMgBr + H_2O = BrC_6H_4OH + Mg(OH)Br$.

The oxidation of the *p*-bromophenylmagnesium bromide probably produces the luminescence. When this material in a test-tube is stirred, the ether evaporates, and an oxidation product, insoluble in ether, appears. This product continues to grow darker in color until, when the ether has evaporated to about 5 cc., the mass is quite viscous and is dark green or blue. Chemiluminescence then gradually ceases; but this product is strongly fluorescent, and glows with a greenish color in ultra-violet light.

When water is added to this oxidized product, violent action takes place as the hydrolysis proceeds. The new compound formed is brown and is not fluorescent. From this water mixture, three compounds have been isolated: (1) unchanged *p*-dibromobenzene, (2) bromobenzene, (3) *p*-bromophenol. The main product is insoluble in all common solvents and could not be purified for analysis. No doubt the bromobenzene was formed by the hydrolysis of the unoxidized product.

For comparison, the luminescence of phenylmagnesium bromide, treated with chloropicrin, was tried. The phenylmagnesium bromide solution in ether has a faint luminescence when exposed to air. When dropped into chloropicrin, the solutions being of the same molecular strength as recommended for the Wedekind reaction, no increase in luminescence was noted.

On the other hand, repeating the Wedekind reaction as a check, the phenylmagnesium iodide was faintly luminescent in air, but became more so on treatment with the chloropicrin. It was thought that since a monohalogen compound gave a luminescence in chloropicrin greater than its luminescence when treated with air alone, the *p*-bromophenylmagnesium bromide treated with chloropicrin might also produce greater luminescence than this compound in air alone. The experiment was tried, but there was no luminescence.

p-Iodophenylmagnesium iodide was prepared in order to test its luminescence. The *p*-di-iodobenzene is less soluble in ether than is the dibromo compound and the reaction was not catalyzed by iodine but went quite smoothly when catalyzed with a trace of Grignard reagent. This was accomplished by allowing some of the *p*-dibromobenzene to react with magnesium in a flask. When the reaction was complete, the material was poured out, excepting what adhered to the flask. Dry ether, magnesium, and the *p*-di-iodobenzene were then added, and the reaction started at once. The *p*-iodophenylmagnesium iodide was not chemiluminescent, and showed no light when treated with chloropicrin. The results may be summarized as follows.

Compound	Exposed to air Luminescence	Treated with chloropicrin Luminescence	Compound	Exposed to air Luminescence	Treated with chloropicrin Luminescence
C_6H_5MgBr	slight	none	BrC_6H_4MgBr	strong	none
C_6H_5MgI	slight	strong	IC_6H_4MgI	none	none

Studies of other related compounds are being carried out; these will be discussed in a later paper.

A number of attempts were made to photograph the spectrum of the chemiluminescence of the *p*-bromophenylmagnesium bromide, but these attempts were unsuccessful, even with long exposures (up to 10 hours). In this connection it may be noted that there are only two instances on record where direct photographs of chemiluminescence spectra have been obtained—the firefly pictures of Coblentz,[10] and the bacterial luminosity of Forsythe.[11] The latter did not publish his photographs.

A determination of the color of the light was made by the method due to Weiser.[12] For this purpose a plate holder was prepared with a series of colored gelatin windows, behind which a photographic plate could be moved. By comparing the effect on the plate of light from a given source with the effect of white light, a fair idea of the distribution of intensity with wave length can be obtained, since the windows have only narrow transmission bands, which in effect divide off the visible spectrum into strips, so that it is possible to tell at once whether any radiation, of wave length lying within the range of any of the filters, is given out by any source of light. The series of filters chosen is described in the following table; all but one of them were taken from the Wratten and Wainwright monochromatic filters.[13]

Good gelatin filters covering the violet end of the spectrum are difficult to obtain. The composite filter used in Window 6 was made from sheets of violet and blue-green gelatin superimposed, cutting off most of the long waves, but leaving a band covering the range of Window 5 and extending roughly twice as far into the violet. The low visibility of this part of the spectrum made it difficult to locate exactly the violet limit of the trans-

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[10] Ives and Coblentz, U. S. Bur. Standards, *Bull.*, **6,** 321 (1909).

[11] Forsythe, *Nature,* **83,** 7 (1910).

[12] Weiser, *J. Phys. Chem.,* **22,** 440 (1918).

[13] Made by the Eastman Kodak Company.

mission. The wide range of wave lengths, and high percentage of transmission, caused this filter to give images more heavily exposed than the

Window	Mfrs. designation	No.	Color	Range of Transmission
1	α	70	red	extreme red to λ6350
2	γ	72	orange	λ6350–λ5830 with faint band in red λ7400–λ6880
3	δ	73	yellow-green	λ6120–λ5530 with very faint band in red wider than above filter
4	ϵ	74	green	λ5640–λ5160
5	η	75	blue-green	λ5160–λ4700
6	composite		blue	λ5100–λ4300 approximately with band of red

others. The unequal transmissions make it necessary to compare any source with white light. Except for the last of the filters, however, it will be seen that the visible spectrum was well covered, without overlapping.

In addition to these filters, tests were made with a photographic plate partly covered by a piece of Corning glass G (586 Å.).[14] It has a narrow transmission band deep in the red, and a strong band reaching from about λ4200 to λ3000, with 90% transmission at λ3600; in other words the transmission of this glass is almost entirely in the ultra-violet.

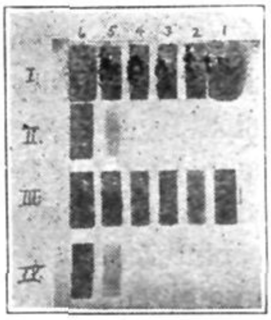

Fig. 1.—Color determination of chemiluminescence: I, white light; II, *p*-bromophenylmagnesium bromide; III, oxidation of phosphorus; IV, green fluorescent spectrum. Red window to right.

The results obtainable are illustrated in Fig. 1. On the photographic plate here shown I shows the effect of white light from a 60watt tungsten bulb covered with 2 thicknesses of white paper; exposure, 1 second. II shows the effect of the chemiluminescence of the *p*-bromophenylmagnesium bromide, exposed 10 minutes, oxidizing in air. Five minutes with oxygen give the same effect. The exposure shows that the radiation is all confined to a narrow region of the spectrum, no perceptible amount of energy being radiated in wave lengths longer than about λ5200. The violet limit is not definitely indicated by this test; but supplementary tests, using the violet glass described above, showed that some energy is radiated in wave lengths shorter than λ4200. So far as possible these conclusions were verified by visual observations with the spectroscope; apparently the spectrum is continuous, and without structure in the band. It is thus quite similar to such other cases of chemiluminescence as are on record.

For comparison, the effect of the luminescence of phosphorus is shown in III. It will be seen that this reaction gives off light which is distributed.

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[14] The transmission curve for this glass is given by Gibsen, Tyndall and McNicholas in the *Bur. Standards Tech. Paper*, **148,** 23, Curve 82 (1920).

through the entire visible spectrum. The time of exposure was 10 minutes. IV shows the effect of the greenish fluorescence of the oxidation product of the *p*-bromophenylmagnesium bromide. This exposure, also for 10 minutes, shows distinctly the presence of radiation in the range λ5640–λ5160 through Window 4, in addition to shorter wave lengths, and may be regarded as establishing definitely that the fluorescence spectrum is not identical with the chemiluminescence spectrum.

Fluorescence

As indicated above, the oxidation products of *p*-bromophenylmagnesium bromide are strongly fluorescent, while the unoxidized compound is not photoluminescent in any notable degree. The fluorescence of the solution is, as nearly as can be judged, proportional to the degree of oxidation. The phenomena are more complicated than might be expected, however, two distinct types of fluorescence having been recognized, with notably different spectra.

The exciting light for these experiments on fluorescence may be most conveniently obtained by appropriate filters. In this work the intense beam of light from a 1000watt bulb in a stereopticon lantern was sent through the violet glass, Corning G, 586 Å., described above. It is desirable to include a cell containing a solution of copper sulfate, as this removes the red light transmitted by the glass, leaving an intense ultra-violet beam, with only a little of visible violet light, and also prevents the glass from heating and cracking. This beam was concentrated with a lens. The oxidation products under consideration glowed brightly when placed in such a beam. Their intensity is to be compared with that of fluorescent quinine sulfate or esculin solution. The luminescence does not persist noticeably when the exciting light is removed; the compounds are not notably phosphorescent.

A series of exposures by the color-filter method described above showed that the method was not sensitive enough to distinguish readily between the different types of fluorescence observed. It is not at all necessary, however, to depend on this process, since direct spectrum photographs can be taken. The ultra-violet beam is concentrated on a tube of fluorescent material, and an image of the luminous patch is thrown on the slit of the spectroscope by a second lens. The apparatus requires no further attention during the exposure, usually of several hours' length. The reflected exciting light will, of course, be photographed on a different part of the plate, since its shorter wave length throws it into a different region of the spectrum from that containing the fluorescent light. It can be identified, if desired, by an extra-exposure beside the other, with a mirror replacing the tube.

The instrument used had an optical system of quartz; panchromatic plates were used. For comparison, the spectrum of helium was photographed on each plate beside the fluorescent spectrum.

One of the first things to attract attention was the color difference in the fluorescence. The viscous residue in the solution, after oxidation, gives off a sea-green light, but the material that splashes up on the walls of the tube, though coming from the same source, glows with a bright blue color resembling that of esculin. This latter effect is especially marked if the oxidation takes place very slowly in air; and the substance giving the fluorescence appears to be quite insoluble in the ether used as a solvent. Rapid oxidation with oxygen yields uniformly a material giving a greenish-blue fluorescence which is apparently intermediate in character between the two extreme types just described. It was thought at first that the difference might be due to the effect of the solvent, by analogy with the behavior of anthracene, which fluoresces blue when dissolved in organic solvents, but is greenish when dry, as when deposited by evaporation of the solvent. Apparently that is not the correct explanation, however, for the green color of the dissolved material persists for months, at least, after all the solvent has evaporated and the material is left hard and dry in the tubes. Although this fluorescent property is very lasting while the material is exposed only to air, the fluorescence is entirely and permanently destroyed once the material is thoroughly soaked with water. On the other hand, the blue fluorescent material loses its activity gradually in a few days or a week if exposed to air. It can be kept longer if tightly corked.

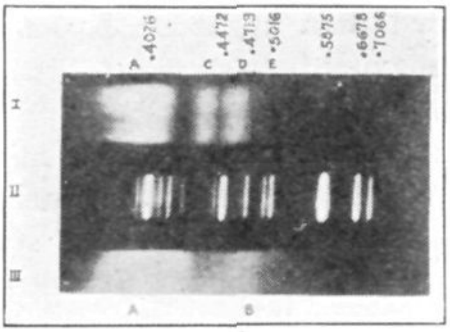

Fig. 2.—Fluorescence spectra from oxidation products of *p*-bromophenylmagnesium bromide: I, blue fluorescence, A, exciting light; C, D, E, fluorescence bands; II helium spectrum, red light to right, wave lengths given above; III, green fluorescence, A, exciting light; B, fluorescent band.

That there is a real difference between these two types of fluorescence is further indicated by the striking difference in the structure shown by their spectra. As shown in Fig. 2, the greenish fluorescence gives a spectrum containing a single continuous wide band (Fig. 2, III, B) extending from the blue-violet nearly to the yellow, with a diffuse maximum in the blue, near the green. The wave length can be judged approximately from the wave lengths of the lines in the helium comparison spectrum. Such single-banded spectra are quite the rule among fluorescent organic compounds; but the blue fluorescent spectrum, as shown in the figure (Fig. 2, I, C, D, and E) shows 3 distinct, narrow bands, none of which coincides exactly with the maximum of the green band, but with the stronger of them situated much farther into the violet. The band of longest wave length is much fainter than the others; for this reason we have not yet confirmed our belief that this band is really resolvable into two. This type of spectrum is exceptional among organic compounds, though certain (inorganic) uranium compounds show similarly banded fluorescence spectra, and a few organic compounds are known to show multiple-banded fluorescence spectra, also. Both types of spectra were photographed repeatedly, and could be produced at will.

These compounds were tested for fluorescence under the action of X-rays, but none was found.[15]

Summary

1. *p*-Bromophenylmagnesium bromide has been prepared and its properties in solution have been noted.

2. The luminescence of this substance has been compared with that of other aromatic halogen compounds when the substances are exposed to the action of air and oxygen.

3. No luminescence results from the action of other gases such as carbon dioxide, hydrogen sulfide, sulfur dioxide and nitrogen on these Grignard compounds.

4. The spectrum of the chemiluminescence of *p*-bromophenylmagnesium bromide has been investigated by the use of light filters and its lower and upper limits found to lie within the region λ5200–λ3500. This spectrum has been found to be distinct from the associated fluorescence spectra.

5. Photographs of two kinds of fluorescence have been obtained from the oxidation products, one giving a single-banded spectrum, the other a quite different multiple-banded spectrum.

EVANSTON, ILLINOIS

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[15] An incidental observation, however, is of sufficient interest to be worth mentioning. A pair of test-tubes containing a deposit of phosphorus on the walls, left by the evaporation of a CS_2 solution, was in the same rack with some other materials being tested. The tubes had been open to the air for several weeks, and the phosphorus was supposedly all oxidized. On exposure to X-rays, the deposit began to glow brightly; the glow died out gradually when the X-rays were turned off, but could be excited repeatedly by fresh exposure to the rays. The case is of interest from a photochemical viewpoint, being an example of a luminescent reaction accelerated by light of different wave length from that emitted.