as a definite confirmation of a special case of Brönsted's theory. We shall continue this investigation by direct measurement of the activities involved and by further rate measurements.

## Summary

1. The steady-state rate of the bromine-bromide catalysis of hydrogen peroxide has been measured in dil. solutions of sulfuric acid and potassium bromide, and it has been shown that the rate constant approaches a definite finite value as the sulfuric acid is indefinitely decreased.

2. The steady-state rate has also been measured in the following solutions: hydrobromic acid, hydrobromic-perchloric acid, hydrobromic acid-potassium bromide, hydrobromic acid-barium bromide, and perchloric acid-potassium bromide. The rate constants obtained from measurements in these various solutions are all slightly larger than those obtained from measurements in dil. sulfuric acid solutions, and are about twice as great as those obtained in sulfuric acid solutions above 0.2 *N*.

3. At the steady state, in hydrobromic acid and hydrobromic-perchloric acid solutions of ionic strength less than 0.25 and in 8 out of the 12 remaining experiments in the absence of sulfate, the rate of decomposition of peroxide is represented by the following expression within the limits of experimental error, 1% to 2% (the discrepancy in the 4 excepted experiments lies between 4% and 9%):

$$-d(H_2O_2)/dt = 0.0437\ (H_2O_2)\ (H^+)\ (Br^-)\gamma^2_{HBr} \qquad (7)$$

4. The activity coefficient of hydrobromic acid in solutions containing sulfuric acid and potassium bromide has been estimated from the rate measurements in these solutions, by the assumption that Equation 7 holds.

5. The application of the "activity-rate" theory and of Brönsted's theory to the experiments presented here has been briefly discussed.

BERKELEY, CALIFORNIA

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[CONTRIBUTION FROM THE CHEMICAL AND PHYSICAL LABORATORIES OF THE UNIVERSITY OF MISSOURI]

# LUMINESCENCE OF ORGANO-MAGNESIUM HALIDES

BY R. T. DUFFORD, S. CALVERT AND DOROTHY NIGHTINGALE

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Apparently the first notice of luminescence associated with a Grignard reagent dates from 1906, when Wedekind[1] found that phenylmagnesium bromide and phenylmagnesium iodide give a bright light when reacting with chloropicrin. This reaction has become widely known as the "Wedekind Reaction."

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[1] Wedekind, *Ber.*, **4**, 417 (1906); *Physik. Z.*, **7**, 805 (1906); *Chem. Zentr.*, **30**, 921 (1906); *Z. wiss. Phot.*, **5**, 29 (1907).

Heczko,[2] in repeating the experiment, noticed that these compounds are luminous when oxidized in air. He thought moisture necessary to produce the light, but this idea was shown to be wrong by Moeller; in fact, tests by the writers have shown definitely that the presence of moisture tends to inhibit the light. Other workers occasionally have noted, incidental to synthetic work, that certain Grignard compounds give light. Thus, Schmidlin[3] reports light from diphenylmagnesium bromide, but wrongly reports several other compounds to be non-luminous. Späth[4] mentions *p*-chlorophenylmagnesium bromide and *m*-*p*-xylylmagnesium bromide as brightly luminescent. These are isolated references that came to the attention of the writers only after most of their work had been done.

Moeller,[5] in 1914, reported a systematic investigation of 10 such compounds. The original Danish article is practically unavailable in this country, and it has not been adequately abstracted. The growing interest in these compounds makes it seem desirable to give here a summary of his results, although several of his statements have been shown by later workers to be incorrect. The writers, on finally obtaining a photostatic copy of the article, found that they had already rediscovered all but one of the compounds mentioned, and would have recorded their results on that one also within a few days more. It is hoped that others will be saved this experience. The results reported by Moeller are as follows.

| "Good" | "Weak" | "No reaction" | |
|---|---|---|---|
| $C_3H_7MgBr$ (wrong) | $C_2H_5MgBr$ (wrong) | $C_3H_7Cl$ | and Mg |
| $C_6H_5MgBr$ | $C_5H_{11}MgBr$ (wrong) | $C_5H_{11}Cl$ | |
| *p*-$BrC_6H_4MgBr$ | $C_6H_5MgI$ | $C_6H_5Cl$ | |
| α-$C_{10}H_7MgBr$ | $C_6H_5CH_2MgBr$ (wrong) | $C_6H_3Br_3$ | |
| α-α-$C_{10}H_6Br_2$ and Mg | | | |
| *p*-$CH_3C_6H_4MgBr$ | | | |

Moeller also pointed out that oxygen, not moisture, is needed to produce luminescence.

An attack on the problem from quite another angle was made by Lifschitz,[6] whose early work seemed to indicate that differences in the stabilities of the etherates might account for the difference in behavior between aliphatic and aromatic Grignard compound in ether solution. Later work[7] showed that the differences were less than at first was supposed, and that his original explanation was inadequate. The work is, nevertheless, an exceedingly valuable contribution to the chemistry of these compounds. A connection with unsaturation is suggested.

The luminescence of *p*-$BrC_6H_4MgBr$ was independently discovered by W. V. Evans, and investigated with one of the writers,[8] who pointed out also that an interesting fluorescence is shown by the product of oxidation of this compound, and that the fluorescence and the chemiluminescence are not identical. The oxidation of *p*-$C_6H_4MgBr$ gives about as much light as any of the older classical chemiluminescent reactions. The writers suggest the name "Moeller-Evans Reaction" for it in honor of the discoverers. It has been used frequently in the present work for comparison with other reactions, and the name will be convenient for reference. In the course of this work, all the classical chemiluminescent reactions were repeated for comparison.

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

[3] Schmidlin, *Ber.*, **45**, 3172 (1912).

[4] Späth, *Monatsh.*, **36**, 4 (1915).

[5] S. Moeller, *Arch. Pharm. Chem.*, **21**, 449, 466 (1914).

[6] Lifschitz. *Helvetica Chim. Acta*, **1**, 482 (1918).

[7] Lifschitz and Kalberer, *Z. physik. Chem.*, **102**, 393 (1922).

[8] Evans and Dufford, THIS JOURNAL, **45**, 278 (1923).

An extensive examination of over 60 Grignard compounds has been carried out by the present writers,[9] in which more than 40 luminous compounds have been studied. The effects on the color and the brightness of the chemiluminescence have been determined for several factors, such as the chemical nature of the reacting atoms, the position, the mass and the chemical nature of substituents, unsaturation and molecular structure. Certain fluorescent effects have been noted, also. We shall discuss first the chemiluminescence in ether solution on oxidation with oxygen.

## Experimental Methods

Where possible, the compounds used were purchased from a commercial source. The majority of the aromatic halogen bodies were synthesized in the Organic Laboratory of the University of Missouri, from materials so purchased. The methods of synthesis chosen were those which seemed calculated to yield the purest products, and in these cases, the products were tested carefully. The results, it is believed, are therefore entitled to confidence in this respect.

In preparing the Grignard reagents, in most cases the attempt was made to use equivalent quantities of material, so that the results would be as nearly comparable as possible with such unstable compounds. With certain of the less soluble compounds it was necessary to work at greater dilutions than usual. The concentrations used were near the optimum.

For studying the spectral distribution of light, the Weiser[10] method of color filters was used, much as in the preliminary work by Evans and Dufford, but with a slightly improved set of filters, as described in Table I. The photographic method is unreliable at the red end of the spectrum and was, therefore, supplemented by visual observations through a second set of filters. The photographs are more reliable than the eye at the violet end of the spectrum, however. For accuracy, both methods are necessary.

TABLE I

TRANSMISSIONS OF MONOCHROMATIC FILTERS

| Window No. | Mfr's. No. | Color | Approximate spectral range | Wave length of max. transmission |
|---|---|---|---|---|
| 1 | α | red | limit of visible to λ 6450 | λ 6690 |
| 2 | γ | orange | λ 6450–5800 with faint band λ 7300–6700 | λ 6050 |
| 3 | δ | yellow-green | λ 6250–5500 with faint band λ 7330–6760 | λ 5830 |
| 4 | ε | green | λ 5700–5100 | λ 5340 |
| 5 | η | blue | λ 5400–4600 | λ 4870 |
| 6 | θ | violet | λ 4800–4100, and faintly to λ 3500 | λ 4550 |
| 7 | G586A | ultraviolet | λ 4200–3000 | λ 3600 |

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[9] Dufford, Calvert and Nightingale, *Phys. Rev.*, **21**, 203 (1923), (abstract); a paper on this work was read at the New Haven Meeting of The American Chemical Society, April 5, 1923.

[10] Weiser, *J. Phys. Chem.*, **22**, 439, 480, 576 (1918).

For gaging the brightness of the luminescence of the compounds, several methods were used. In the earlier work, compounds were compared with the Moeller-Evans reaction. In later work, the fainter compounds were compared with a set of radio-luminous disks, which were carefully protected from light to prevent phosphorescence. These disks were calibrated by the Bureau of Standards; their brightness ranged from 1 to 8 microlamberts. The brighter compounds were compared by the optical pyrometer method described by Nichols.[11] The ranges of the two methods overlap, so that it is possible to determine, at least approximately, the surface brightness of any luminescence. Another method of estimating brightness is given by Ives.[12] The writers hope to say more concerning such measurements in a later article.

## Factors not Determinative of Luminescence

It is very clear, as Lifschitz has pointed out, that reaction velocity is not the factor that determines the luminescence. The oxidations studied are all very slow compared to ordinary ionic reactions, which are not chemiluminescent at all. But if a given Grignard compound is luminescent, increased speed of reaction will brighten the light; for example, pure oxygen gives much more light than air with such Grignard compounds. The quantitative work of Amberson[13] on luciferin, the luminescent material studied by Harvey, tends strongly to indicate that the brightness is closely proportional to the speed of oxidation. Results of the writers indicate further that the spectral band of a compound widens somewhat when the intensity is high. Thus the radiation from the Moeller-Evans reaction ordinarily photographs as if it were confined to the range 5200–3500, and was so reported by Evans and Dufford. But it is easy to show, when the intensity is high, that the band really extends to about 6200, on the red end, and probably beyond 3000 on the short-wave-length end.

The heat of oxidation of the compounds is also not determinative. Qualitative observations by the writers are in accord with the careful quantitative work of Lifschitz and Kalberer. In certain series of compounds the brightest become hottest during oxidation. But the reverse is more often true; the most of the remarkably bright compounds actually become cooler while oxidizing and radiating, because not enough heat is given off to compensate for the cooling due to the evaporation of ether.

It appears that slight changes in temperature do not affect the brightness of the luminescence appreciably.

## Effect of Solvents

While much remains to be done in this line, enough evidence has been secured to establish clearly that the ethyl ether in which such compounds

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[11] Nichols, *Science*, **55**, 157 (1922).

[12] Ives, *J. Franklin Inst.*, **194**, 213 (1922).

[13] Amberson, *J. Gen. Physiol.*, **4**, 517 (1922).

are usually made is by no means necessary. Much evidence indicates that these compounds exist as etherates in such solutions. Other ethers may be substituted, however, without destroying the luminescence; normal ethers appear slightly better than *iso* ethers, or than diphenyl ether, at least for bromine compounds. Chlorine Grignard compounds are usually best in *iso*-amyl ether. Dimethylaniline can be substituted for ether, though the light is less intense than with ethyl ether, as was shown by Lifschitz. Toluene containing some ether has been used also. Lifschitz states that the pure, ether-free Grignard compounds, even the aliphatic compounds, give light. The writers have not yet been able to verify this statement, but it is very clear that the nature of the solvent affects the intensity of the light. The writers have failed to find any effect on the spectral distribution, however, though several tests were made. The question should be investigated further before any final decision can be reached.

## Effects of Other Oxidizers

The light is brightest when pure oxygen is used; air is much less effective. Other reagents, such as sodium peroxide, hydrogen peroxide, etc., react more violently, but they give no light. Water hydrolyzes these compounds instantly, but without evolution of light. Other gases, such as sulfur dioxide, carbon dioxide, nitric oxide, and nitrogen dioxide also give no light, although some of them react. Lifschitz and Kalberer reported evolution of light with benzene triozonide and also with nitrous oxide, but the writers failed repeatedly to observe light with this gas when particular care was first taken to remove all traces of atmospheric oxygen from the apparatus.

## Effect of Other Metals

The magnesium of the Grignard compounds appears to be necessary for chemiluminescence. Several of the analogous zinc compounds, including phenylzinc bromide and iodide, and *p*-bromophenylzinc bromide, showed no light. Evans, in a private communication, has stated that he found no light with phenylmercuric bromide. The writers plan to try certain other compounds later.

## Effect of Concentration

These compounds evolve most light when the concentration is fairly high; but when the concentration becomes too great, an optimum value is passed. For phenylmagnesium bromide the optimum lies near 2.5 moles per liter. For some other compounds the optimum is at higher concentrations. However, in at least one case, that of the Grignard compound from $\alpha$-bromonaphthalene, the optimum is lower. This compound has a remarkable tendency to crystallize from solution. When its brightness has died down, successive additions of ether increase the brightness again.

## Effect of Reacting Halogen

The identity of the reacting halogen definitely affects both the color and the intensity of the radiation. To test this point, solutions were prepared of the following Grignard compounds: $C_6H_5MgI$, $p$-$CH_3C_6H_4MgI$, $C_6H_5MgBr$, $p$-$CH_3C_6H_4MgBr$, $C_6H_5MgCl$, and $p$-$CH_3C_6H_4MgCl$. In these series the iodine compounds give the faintest light, while the chlorine compounds give the most. Further, the chlorine compounds give light that is distinctly greener than that from the other compounds, while the iodine compounds are bluest, that is, chlorides give off the longest effective wave length, and iodides the shortest. Fig. 1 shows the shift in wave length for phenylmagnesium chloride and bromide; the light from the iodide was too faint to photograph in the same time of exposure. A somewhat similar effect is observed in the dihalogen derivatives, $p$-$IC_6H_4MgI$, $p$-$BrC_6H_4MgBr$, $p$-$ClC_6H_4MgCl$; the same shift in wave length is observed. The same brightness relations exist, except that the dichloro compound gives less light than the dibromo compound. The effect is due partly to the lower yields obtained from the dichloro compound; the point is being investigated further, to determine whether this is the only reason.

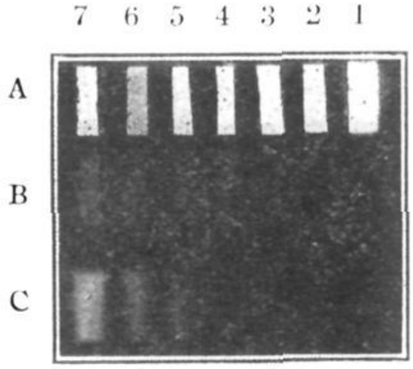

Fig. 1.—Luminescence of Monohalogen benzene Grignard compounds. A, white light; B, $C_6H_5MgCl$; C, $C_6H_5MgBr$. The numbers refer to the filters described in Table I

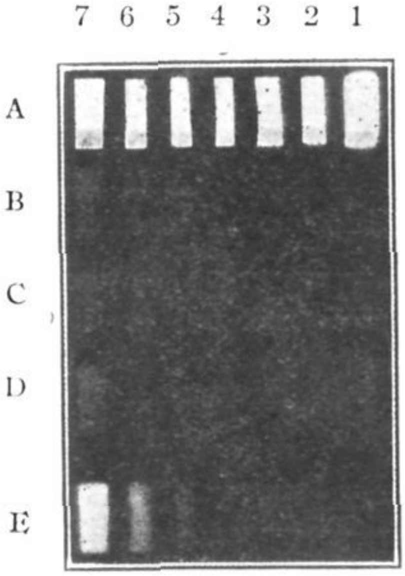

Fig. 2.—Luminescence of Grignard compounds from bromine derivatives of benzene with alkyl side-chains *para* to the reacting halogen. A, white light; B, $C_6H_5MgBr$; C, $CH_3C_6H_4MgBr$; D, $C_2H_5C_6H_4MgBr$; E, $C_4H_9C_6H_4MgBr$

## Method of Preparing Grignard Compounds Containing Chlorine

None of the chlorine compounds mentioned above can be prepared by the usual methods, in ordinary ether, at least not in any reasonable length of time. The di-iodo compound is also difficult to prepare. Evans[8] has described a method for preparing the latter, using the analogous dibromo compound as a catalyst; but this method is open to the objection that the catalyst is itself luminescent and, hence, makes the tests unreliable. Hesse[14] patented a method of making chlorine Grignard compounds using pinene hydrochloride as catalyst. The writers found that the compounds formed in *iso*-amyl ether with iodine or ethyl bromide as catalyst; this method works with the di-iodo compound also. The yields are probably somewhat less than with pinene hydrochloride, but the products give a brighter light, as if the pinene hydrochloride tended to inhibit the luminescence.

## Effect of the Organic Radical

The character of the radiation during oxidation is profoundly affected by the nature of the organic radical involved. It may be true that ordinary saturated aliphatic compounds give light when crystallized, free from ether, but it is very certain that they do not do so in any ordinary solvent. It was thought at first that the luminescence was confined to aromatic compounds.

Certain theories regard the benzene ring as being in vibration. It appeared possible that the luminescence might be associated with some sort of vibration of the ring. If so, certain effects may be expected: first, that if the ring were loaded with a substituent group, the light should be affected regularly as the mass of the loading group increases, probably in the direction of an increase in wave length; and second, that symmetrical loading should not produce the same effect as unsymmetrical; probably the unsymmetrical (*ortho* and *meta*) compounds should show shorter wave lengths than the symmetrical (*para*) compounds, but without much difference in intensity. Other questions concerning the effect of structure and unsaturation also are suggested. The following paragraphs will show how these compounds actually behave.

## Effect of Position of Substituted Group

In order to test carefully the effect of the position of the substituted group, a number of series of compounds were prepared which would form Grignard compounds differing only in the position of the substituted group. They included the *ortho*, *meta* and *para* derivatives of methylphenylmagnesium chloride, bromide and iodide, chlorophenylmagnesium chloride and bromo- and chlorophenylmagnesium bromide. The light

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[14] Hesse, *Ber.*, **39**, 1147 (1906); *Chem. Zentr.*, **1906**, I, 1424; **1908**; Ger. Pats. 189,476 and 193,177.

from these compounds was studied carefully, both visually and photographically.

The results show that the *para* compounds are always very much brighter than the corresponding *ortho* or *meta* compounds, though neither of the latter classes is consistently brighter than the other. The differences in wave length are slight—rather less than might have been expected. Indeed, after examining the toluenes, the writers were in doubt whether the observed differences were real at all. The dichlorobenzene derivatives are so faint that their evidence is inconclusive. But the dibromobenzene and chlorobromobenzene derivatives show the same effect as the toluenes, and in so pronounced a form as to be unmistakable. While the differences are small, they are quite regular. Each compound radiates a spectrum made up of a wide continuous band. The spectra of the *para* compounds always extend farther toward the red than is the case with the other isomeric compounds; the *ortho* and *meta* compounds are more nearly alike, but the *meta* compounds regularly show the shortest wave lengths. Light from *para* compounds is, therefore, always greener than that from the others, and from *meta* compounds more violet. The differences show best in the dibromo and chlorobromo compounds; these are illustrated in Figs. 2 and 3, respectively

## Mass and Chemical Nature of Loading Group

Moeller[5] concluded that the brightness of the luminescence is proportional to the molecular weight of the halogen derivatives. This statement is not true, even of the few compounds which he studied. To test this point, the writers studied a large number of compounds.

When the group added to the benzene ring is an aliphatic side-chain, then the brightness does increase with the weight of the added group or, what is the same thing, with the molecular weight of the compound. Thus, in the series $C_6H_5MgBr$, *p*-$CH_3C_6H_4MgBr$, *p*-$C_2H_5C_6H_4MgBr$ and *p*-$C_4H_9$-$C_6H_5MgBr$, the brightness increases with the weight and, at the same time, the wave length shifts steadily toward the violet and not toward the red, as might be expected if mass were the determining factor (by analogy with the vibration of a loaded spiral spring). Fig. 4 shows the effect fairly well, except that the exposure for the toluene derivative was too short.

When the loading group is a halogen, however, the result is different. This was tested by studying series in which the loading halogen alone was varied, as in the following: *p*-$IC_6H_4MgBr$, *p*-$IC_6H_4MgI$, *p*-$BrC_6H_4MgBr$, *p*-$ClC_6H_4MgBr$, and *p*-$ClC_6H_4MgI$. In these compounds, the brightness of the radiation increases in most remarkable fashion as the weight of the loading halogen decreases, and with this, there is an increase in the effective wave length.

In the series $p$-$C_2H_5C_6H_4MgBr$, $p$-$ClC_6H_4MgBr$ and $p$-$(CH_3)_2NC_6H_4MgBr$, the masses of the loading groups are comparable, being 29, 35 and 44, respectively. The brightness shows no regularity; the chlorine derivative is by far the brightest, and the dimethyl-aniline derivative the faintest.

It has already been shown that in the case of Grignard compounds from monohalogen benzene derivatives, the brightness increases as the molecular weight decreases, and the wave length increases at the same time. Certain dihalogen derivatives were shown to behave likewise.

Among diphenyl derivatives, Schmidlin[3] reports $p$-$C_6H_5C_6H_4MgBr$ as giving a bright blue light; the writers find that $p$-$p$-$BrC_6H_4C_6H_4MgBr$ gives a bright green light.

These results seem to indicate that mass is not at all the controlling factor in these compounds; if it has any effect, it is so small that it is completely masked by other factors depending on the chemical nature of the loading groups. Further evidence on this point will be given later.

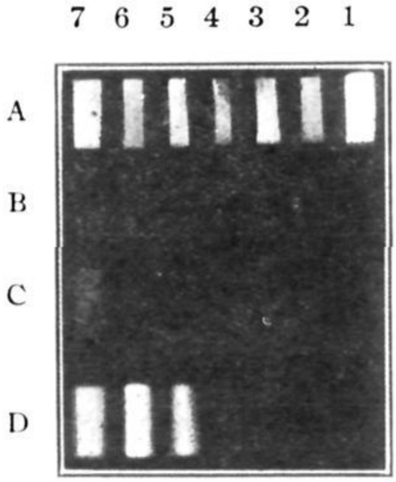

Fig. 3.—Luminescence of Grignard compounds from dihalogen derivatives of benzene. A, white light; B, $o$-$BrC_6H_4MgBr$; C, $m$-$BrC_6H_4MgBr$; D, $p$-$BrC_6H_4MgBr$

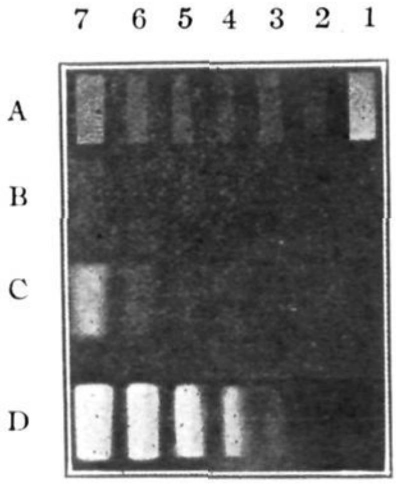

Fig. 4.—Luminescence of Grignard compounds from bromochlorobenzenes. A, white light; B, $o$-$ClC_6H_4MgBr$; C, $m$-$ClC_6H_4MgBr$; D, $p$-$ClC_6H_4MgBr$

In this discussion it has been assumed that in dihalogen derivatives of benzene only one of the halogens reacts with magnesium to form a Grignard compound, and that when the 2 halogens are different, the magnesium reacts with bromine, if present, in preference to the other halogens, or with iodine in preference to chlorine. It is believed that these assumptions are in accord with the experience of most other workers in the field, as well as with many incidental observations by the writers.

## Derivatives of Naphthalene, Anthracene and Xylenes

The Grignard compound from $\alpha$-bromonaphthalene gives a blue light, nearly as bright as that formed in the Moeller-Evans reaction. That from

$\beta$-bromonaphthalene is much brighter, and is at least as bright as that from the Moeller-Evans reaction. By analogy with the benzene derivatives, one might expect the Grignard compound from 1,4-dibromonaphthalene to be still brighter and bluer. In fact, it is much fainter, and greener. The Grignard compound formed from 1,4-chlorobromonaphthalene is, however, much brighter and bluer than that from the 1,4-dibromonaphthalene compound. It, also, is about as bright as the light from the Moeller-Evans reaction. $\alpha$-Chloronaphthalene forms a compound giving a light much weaker than the other compounds just mentioned, and too faint to photograph well. Some of these effects are shown in Fig. 5.

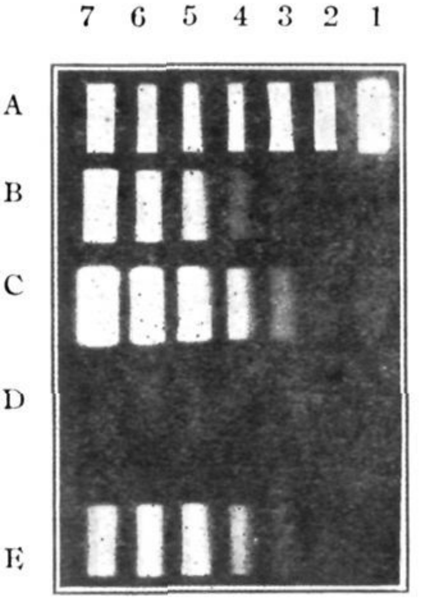

Fig. 5.—Luminescence of Grignard compounds from naphthalene derivatives. A, white light; B, $\alpha$-$C_{10}H_7MgBr$; C, $\beta$-$C_{10}H_7MgBr$; D, (1,4)$BrC_{10}H_6MgBr$; E, (1,4) $ClC_{10}H_6MgBr$

9,10-Dibromo-anthracene forms a Grignard compound showing a greenish-blue light whose faintness can hardly be due entirely to poor yields. Since this has a bearing on the probable structure of anthracene we intend to study the matter further.

If Moeller's conclusion as to the effect of mass were correct, the results obtained with the compounds just described would necessarily have been very different. Further, it is evident that the behavior of these multiple-ring compounds, and perhaps also of the diphenyl compounds, is not altogether analogous to the behavior of the benzene derivatives. Perhaps a more useful and fruitful point of view is to regard the $\alpha$-bromonaphthalene Grignard compound as a bromobenzene derivative with its *ortho* and *meta* positions both loaded; and the $\beta$-bromo compound as a similar derivative with the *meta* and *para* positions substituted. According to this view, the Grignard compound from 1,2-dimethyl-4-bromobenzene should be brightly luminescent. The writers were preparing to test this point, but came across the statement by Späth[4] that the light from this compound is very bright. Other xylene compounds give less light; for example, those from 1,3-dimethyl-4-bromobenzene, and 1,4-dimethyl-2-bromobenzene. It is hoped that other experiments in this direction will be ready for reporting soon.

## Effect of Structure and Unsaturation

It will be noted that all the compounds so far mentioned as luminescent are cyclic in structure, and unsaturated. It is of interest to inquire whether the cyclic structure, or the unsaturation, or both, are necessary to produce luminescence.

Further evidence pointing toward unsaturation as being an important factor is the complete failure of saturated aliphatic Grignard compounds to show luminescence in ether solution. The following list of saturated non-luminescent compounds, containing both halogen-substituted and simple aliphatic derivatives, shows how widespread is the lack of luminescence: $C_2H_5MgBr$, $C_2H_5MgI$, $C_3H_7MgBr$, $C_4H_9MgBr$, *i*-$C_5H_{11}MgBr$, $C_7H_{15}MgBr$, $ICH_2MgI$, $BrC_2H_4MgBr$, $IC_2H_4MgI$. If molecular weight had anything to do with luminescence, some of the heavy molecules at the end of the list should give light, for they are comparable with the benzene ring in mass. This is one more reason for thinking that mass has nothing to do with the question, but suggests that unsaturation or cyclic structure may have some influence.

The cyclic structure alone, however, is not sufficient to give luminescence. Several saturated cyclic compounds which form Grignard compounds easily prove to be quite inactive, photochemically. Examples are: *cyclo*-$C_6H_{11}Br$, $C_{10}H_{15}OBr$ (camphor), $C_{10}H_{17}Cl$ (pinene hydrochloride).

Unsaturation alone is likewise not a sufficient condition for luminescence. Thus the following substances which are really phenyl-substituted aliphatic compounds give no light, though highly unsaturated: $C_6H_5CH_2MgCl$, $C_6H_5CH_2MgBr$, *p*-$ClC_6H_4CH_2MgBr$, $(C_6H_5)_3CMgCl$.

Careful scrutiny of the lists seems to indicate that the determining difference lies in the fact that *in the luminescent compounds, the magnesium is attached directly to an unsaturated carbon atom*, while in the others it is not. No exceptions to this statement are known at present.

To test this supposition further, the compound $ClHC{:}CHMgCl$ was prepared, as an aliphatic compound with the supposedly necessary grouping. This compound is faintly but unmistakably luminescent. It is believed to be the first aliphatic compound discovered to be luminescent in ether solution. The analogous bromine compound, $BrHC{:}CHMgBr$, shows so much fainter luminescence that it is to be regarded as doubtful, but this is what would be expected if these compounds are like the mono-halogen benzene Grignard compounds in their behavior. The Grignard compound from $\beta$-bromostyrene, ($C_6H_5CH{:}CHBr$), is fairly bright, however, thus substantiating the view. On the other hand, allyl bromide and iodide, which are unsaturated, but which have the halogen attached to a saturated carbon, give non-luminescent Grignard compounds. The final product of this reaction is claimed to be diallyl. As the reaction was in progress, oxygen was passed into the solutions in the dark, so that any allylmagnesium bromide or iodide present as an intermediate product would be oxidized. No light was observed. It is hoped to make other tests later.

### Especially Bright Reactions

Several of the compounds are bright enough to be worthy of special mention. The Moeller-Evans reaction has been mentioned already;

it is as bright as any of the classical chemiluminescent reactions, except the oxidation of luciferin. The Grignard compounds derived from $\alpha$-bromonaphthalene, from 1,4-bromochloronaphthalene, and from *p,p*-$BrC_6H_4C_6H_4Br$, are nearly as bright. That derived from $\beta$-bromonaphthalene is at least as bright as the Moeller-Evans reaction, and probably brighter at its best. The compound *p*-$ClC_6H_4MgBr$ is much brighter than any other so far found. Careful pyrometric measurements show that it is brighter even than luciferin, except possibly for the bright specks in the luciferin solution and, therefore, probably the brightest case of chemiluminescence on record. The comparisons were made at the wave length corresponding to the maximum of the emission of the luciferin. The light from the luciferin is greenish-blue, while that from the Grignard compound is deep blue. The ease of preparation of this compound and the high intensity of its light make it an ideal demonstration material for illustrating the phenomenon of chemiluminescence.

## Reactions with Chloropicrin and Bromopicrin

Many of the luminescent Grignard compounds studied show light also when reacting with chloropicrin or with bromopicrin, as in the well-known Wedekind reaction.[1] These cases are of interest as being probably not oxidations, though the precise nature of the reactions is not known. Thus far, the work of the writers has established several important facts regarding this type of luminescence. (1) No compound has been found to give light in these reactions that does not also give light on oxidation with oxygen. (2) The light obtained from chloropicrin is always stronger than that obtained with bromopicrin. (3) The light from these reactions is clearly not identical with that from the oxidation of the same Grignard compounds with oxygen. It is always of somewhat longer wave length, although its spectrum is always a single continuous band. (4) The order of brightness in these reactions is precisely the reverse of that for oxidation with oxygen; that is, with chloropicrin, iodides are the brightest, and chlorides the least bright.

An attempt was made to determine the part of the chloropicrin molecule that is essential for the production of light. Aliphatic nitro compounds, picryl chloride, chloroform and other compounds were tried, but none of these gave light, although some of them reacted violently with the Grignard reagent. Apparently there is something about the particular chloropicrin grouping that is necessary for the production of light in these reactions.

## Fluorescence

A very large number of the oxidation products of these Grignard compounds show fluorescence in "near" ultraviolet light. Apparently little regularity is to be found in most cases. Several new multiple-banded spectra have been observed. A few of these fluorescences are extremely bright; curiously, these all come from compounds that show very bright chemiluminescence with oxygen. In spectral distribution, the fluorescence is clearly not the same as the related chemiluminescence. These results the writers hope to discuss more fully in a later article.

## List of Luminescent Grignard Compounds

Tables II and III give lists of the Grignard compounds studied by the writers, together with 2 or 3 others on which observations have been published by other workers. The list is believed to contain all known luminescent Grignard compounds except certain triple bond compounds investigated by Evans, on which the results have not yet been published. The notes indicate the cases where other investigators have studied any of these compounds, so far as is known. While most of the formulas as written are those generally accepted, they are written in this form here chiefly for reasons of brevity, and not because it is desired to claim that any particular structure has been proved. It may be that such results will come to be of aid in determining chemical structure later.

The spectral distributions, where given, are in terms of the windows listed in Table I. The picture so given is very incomplete, but any other method would require an unreasonable amount of space. Because of the difference in sensibility of the eye and the photographic plate, the apparent maxima as found by both methods are given.

The following substances showed no chemiluminescence with oxygen nor, in those that were tested, with chloropicrin or bromopicrin. Their oxidation products, however, frequently exhibited fluorescence; references to the latter are given for each formula. Where chemiluminescence was tested for only in the presence of oxygen the symbol $O_2$ is also added.

TABLE II

NON-LUMINESCENT GRIGNARD COMPOUNDS

| Compound | Fluorescence of oxidation product | | Ref. | Compound | Fluorescence of oxidation product | | Ref. |
|---|---|---|---|---|---|---|---|
| $(C_6H_5)_3CMgCl$ | $O_2$ | Green | 3,7[b] | $i$-$C_5H_{11}MgBr$ | .. | .... | 5 |
| $ICH_2MgI$ | $O_2$ | .... | .. | *iso*-$C_5H_{11}MgI$ | $O_2$ | .... | 7[c] |
| $C_2H_5MgBr$ | .. | .... | 5,7 | $C_7H_{15}MgBr$ | .. | Bright blue | .. |
| $C_2H_5MgI$ | .. | .... | 3,7 | $C_6H_5ZnBr$ | $O_2$ | .... | .. |
| $BrC_2H_4MgBr$ | $O_2$ | Green, blue | .. | $C_6H_5ZnI$ | $O_2$ | .... | .. |
| $C_3H_7MgCl$ | $O_2$ | .... | 7[c] | $p$-$BrC_6H_4ZnBr$ | $O_2$[a] | .... | .. |
| $C_3H_7MgBr$ | $O_2$ | .... | 5,7 | $C_6H_5CH_2MgCl$ | $O_2$ | .... | 3 |
| $C_3H_7MgI$ | $O_2$ | .... | 7[c] | $C_6H_5CH_2MgBr$ | .. | .... | 5,7 |
| *iso*-$C_3H_7MgI$ | $O_2$ | .... | 7[c] | $p$-$ClC_6H_4CH_2MgBr$ | .. | Blue | .. |
| $H_2C=CHCH_2MgBr$ | .. | Blue, green | .. | *cyclo*-$C_6H_{11}MgBr$ | .. | .... | 7 |
| $H_2C:CHCH_2MgI$ | .. | Faint green | .. | $C_{10}H_{15}OMgBr$ (Camphor) | $O_2$[a] | .... | .. |
| $C_4H_9MgBr$ | $O_2$ | .... | .. | $C_{10}H_{16}HMgCl$ (Pinene hydr.) | .. | Blue | .. |
| *iso*-$C_4H_9MgI$ | $O_2$ | .... | 7[c] | | | | |

[a] Tested with chloropicrin also.

[b] In *iso*-amyl ether.

[c] Not prepared by the writers.

In Table III are listed the substances that showed chemiluminescence.

## TABLE III

## LIST OF LUMINESCENT GRIGNARD COMPOUNDS

| Compound | Chemiluminescence with $O_2$ | | | | Chemiluminescence | | Fluorescence of oxidation product | Ref. |
|---|---|---|---|---|---|---|---|---|
| | Brightness color | Spectral range | Maximum vis. | Maximum photogr. | With chloropicrin | With bromopicrin | | |
| $ClHC:CHMgCl$ | Faint | | | | None | None | Pale blue | *a* |
| $BrHC:CHMgBr$ | Very faint | | | | | | | *a* |
| $C_6H_5CH:CHMgBr$ | Fair, blue | 3–7 | 5 | ... | | | Light blue | *b* |
| $C_6H_5MgCl$ | Bright green | 2–7 | 5, 6 | 5, 6 | Faint | Very faint | Green | *a* |
| $C_6H_5MgBr$ | Bright blue | 3–7 | 6 | 7 | Faint[1] | Very faint | Green | 2, 3, 5, 6, 7, 8 |
| $C_6H_5MgI$ | Fair, blue | 4–6 | 6 | ... | Bright green[1]<br>Windows 3–5 | Faint | | 2, 3, 5, 6, 7, 8 |
| *o*-$ClC_6H_4MgCl$ | Faint | | | | | | Blue | *a*, *d* |
| *m*-$ClC_6H_4MgCl$ | Faint | 3–6 | 5 | ... | | | Blue, green | *a*, *d* |
| *p*-$ClC_6H_4MgCl$ | Faint, green-blue | 3–7 | 5 | ... | | | Blue, green | *a* |
| *o*-$BrC_6H_4MgBr$ | Fair, bluish | 3–7 | 5, 6 | 6 | | | Yellow-green | |
| *m*-$BrC_6H_4MgBr$ | Fair, bluish | 3–7 | 6 | 7 | | | Yellow-green | |
| *p*-$BrC_6H_4MgBr$ | Very bright blue | 3–7 | 5, 6 | 6 | Very faint | None | Green, blue | 5, 6, 7, 8 |
| *p*-$IC_6H_4MgI$ | Faint | 3–7 | 6? | | None? | | | *b*, *d*, 8 |
| *o*-$ClC_6H_4MgBr$ | Bright blue | 3–7 | 5, 6 | 7 | | | Deep green | |
| *m*-$ClC_6H_4MgBr$ | Bright blue | 3–7 | 6, 7 | 7 | | | Yellow-green | |
| *p*-$ClC_6H_4MgBr$ | Exceedingly bright blue | 3–7 | 5, 6 | 6 | Faint | None | Very bright blue | 4 |
| *p*-$ClC_6H_4MgI$ | Bright blue | 3–7 | 6 | 6 | | | Bright green | |
| *p*-$IC_6H_4MgBr$ | Fair, deep blue | 3–7 | 6 | 7 | Faint | None | Green | *b* |
| *o*-$CH_3C_6H_4MgCl$ | Fair, greenish | 3–7? | 4–6 | ... | | | Green | *a* |
| *m*-$CH_3C_6H_4MgCl$ | Faint, greenish | 3–7 | 4, 6 | ... | | | Green | *a* |
| *p*-$CH_3C_6H_4MgCl$ | Fair, greenish | 3–7? | 4–6 | ... | None | | Blue, yellowish | *a* |
| *o*-$CH_3C_6H_4MgBr$ | Faint, green-blue | 3–7 | 4–6 | 7 | Faint | Faint | Green | 7 |
| *m*-$CH_3C_6H_4MgBr$ | Fair, green-blue | 3–7 | 4–6 | 7 | | | | |
| *p*-$CH_3C_6H_4MgBr$ | Bright, green-blue | 3–7 | 4–6 | 7 | Faint | | Green | 5, 7 |
| *o*-$CH_3C_6H_4MgI$ | Fair, bluish | 3–7 | 4, 5 | ... | Fair, bluish | None | Bright green | |
| *m*-$CH_3C_6H_4MgI$ | Fair, blue | 3–7 | 4–6 | ... | Bright yellow-green | Faint | Yellow-green | |
| *p*-$CH_3C_6H_4MgI$ | Bright, bluish | 1–7 | 4–6 | ... | Bright green | None | Bright blue-green | |
| *p*-$C_2H_5C_6H_4MgBr$ | Bright blue | 3–7 | 5 | 7 | Faint | Faint | Bright blue-green | |
| *p*-$C_4H_9C_6H_4MgBr$ | Bright blue | 3–7 | ... | 7 | | | Deep blue, bright | |
| *p*-$(CH_3)_2NC_6H_4MgBr$ | Faint blue | 3–6 | | | None | None | | |
| *p*-$C_6H_5C_6H_4MgBr$ | Bright blue | | | | | | | *c*, 3, 7 |
| *p*-p-$BrC_6H_4C_6H_4MgBr$ | Bright green | 3–7 | 5 | ... | | | Green, blue | |
| (1,2) $(CH_3)_2C_6H_3(4)MgBr$ | Bright yellow-white | | | | | | | *c*, 4 |
| (1,3) $(CH_3)_2C_6H_3(4)MgBr$ | Faint, blue | 3–7 | 5 | ... | | | Bright blue | |
| (1,4) $(CH_3)_2C_6H_3(2)MgBr$ | Faint, blue | | | | | | Deep green | |
| $\alpha$-$C_{10}H_7MgCl$ | Fair, green-blue | 3–6 | 5 | ... | | | Blue | *a* |
| $\alpha$-$C_{10}H_7MgBr$ | Bright greenish-blue | 3–7 | 5, 6 | 7 | None | None | Blue-green | 3, 5, 7 |
| $\beta$-$C_{10}H_7MgBr$ | Very bright, blue | 3–7 | 5, 6 | 7 | | | Very bright blue | |
| (1,4) $BrC_{10}H_6MgBr$ | Fair, green-blue | 3–7 | 4–6 | 6 | None | None | Blue-green | 5 |
| (1,4) $ClC_{10}H_6MgBr$ | Bright green-blue | 3–7 | 5, 6 | 5, 6 | | | Blue-green | |
| (9,10) $BrC_{14}H_8MgBr$ | Faint, green | | | | | | Green | |

[a] In *iso*-amyl ether.

[b] Investigated independently by W. V. Evans.

[c] Not prepared by the writers.

[d] Too faint to allow accurate measurement of the wave lengths.

## Summary

1. Grignard reagents in ether solution are chemiluminescent on oxidation by oxygen only if the magnesium is attached directly to an unsaturated carbon atom. This rule is shown to hold for both aliphatic and aromatic compounds, in all cases investigated.

2. The nature of the solvent affects the intensity of the luminescence, but apparently not the wave length.

3. No chemiluminescence is found when zinc or mercury is used instead of magnesium.

4. The wave length and intensity of the radiation are affected by the nature of the reacting halogen.

5. The wave length and the intensity are affected by the nature of the organic radical involved, and especially by the nature of substituted groups in the cyclic compounds. The effect depends on (a) the position of the substituent group; (b) the chemical nature of the substituent group. It is shown that the mass of the substituent is not the controlling factor.

6. Certain cases of very bright chemiluminescence are described; the luminescence of *p*-chlorophenylmagnesium bromide is believed to be the brightest yet recorded.

7. A method (apparently new) of preparing chlorine-containing Grignard compounds is described.

8. Many Grignard compounds give light when treated with chloropicrin and with bromopicrin. This light is not the same as that given out on oxidation with oxygen.

9. Many Grignard compounds and especially their oxidation-products are found to be fluorescent in ultraviolet light.

10. Two tables are given listing the luminescent properties of more than 60 compounds, of which over 40 are luminescent.

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[Contribution from the Chemical Laboratory of the University of Illinois]

# THE SEPARATION AND DETERMINATION OF POTASSIUM AND SODIUM. A PERCHLORATE PRECIPITATION PROCESS USING NORMAL BUTYL ALCOHOL

By G. Frederick Smith

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The perchlorate method for the separation and determination of potassium and sodium has been quite generally accepted as a satisfactory substitute for the chloroplatinate procedure. The use of absolute ethyl alcohol in the perchlorate procedure is a pronounced disadvantage. The method has the further disadvantage of being an extraction process. This method of extracting a mixture of salts with a solvent for one of them is necessarily inefficient, since the crystals of one may be more or less sur-