3. It is shown that it is doubtful if a pure preparation of aurous oxide has ever been prepared.

CAMBRIDGE A, MASSACHUSETTS

[CONTRIBUTION FROM THE LABORATORIES OF PHYSICS AND OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF MISSOURI]

LUMINESCENCE OF GRIGNARD COMPOUNDS IN ELECTRIC AND MAGNETIC FIELDS, AND RELATED ELECTRICAL PHENOMENA

BY R. T. DUFFORD, DOROTHY NIGHTINGALE AND L. W. GADDUM

RECEIVED SEPTEMBER 16, 1926 PUBLISHED AUGUST 5, 1927

Previous work by the authors and their colleagues[1] has shown the existence of interesting and remarkable regularities in the relations between chemical structure and the brightness and spectral distribution of the light emitted when ether solutions of Grignard compounds, having the general formula RMgX, are oxidized with air or oxygen. The behavior of this group of compounds raises many questions regarding the molecular structures involved.

It seemed possible that some light in this direction might be obtained from experiments with strong magnetic and electric fields. If the radiators are electrons in orbits, as current ideas go, it seemed barely possible that the application of a strong field might bring about a uniform orientation of the molecules, or of the orbits within the molecules, and that this condition might result in polarization of the light emitted in such a field.

The experiment was therefore made of oxidizing certain of the brighter compounds in magnetic fields of about 15,000 gauss; but in every case, polarization appeared to be completely lacking. If it existed, it could not have exceeded one or two per cent. However, one effect was clearly visible; in the strongest fields, there was a distinct tendency for the most of the emission to occur in the most intense parts of the field, near the pole pieces. Immediately on applying the field, a streaming appeared in the solution, with the brightening at the sides of the crucible containing the solution. It appeared as if the effect were mechanical, either the Grignard or, more probably, the oxidation product, being sufficiently paramagnetic to be drawn to the poles. If the solution were very clear to begin with, it would soon show minute black specks being drawn to the poles with the streams. Most of the oxidation product collected near the poles. The effect is shown well by p-BrC_6H_4MgBr. It does not, however, appear in weak fields.

---

[1] Dufford and co-workers, THIS JOURNAL, **47**, 95 (1925); **45**, 2058 (1923); **45**, 278 (1923); *J. Optical Soc. Am.*, **9**, 405 (1924); *Phys. Rev.*, **21**, 203 (1923); **27**, 247 (1926).

The similar study of these compounds in strong electric fields is impossible, because of the remarkably high conductivity of their solutions which are, indeed, quite comparable with aqueous solutions in showing the properties of electrolytes.[2] Tests were made with voltages up to 1500. The experiments at once brought out what appears to be a quite distinct type of luminescence, which occurs at one or both electrodes, and is not due to oxidation at the surface of the liquid. Usually the light appears at the anode but sometimes it is at the cathode, or at both electrodes. The effect is not always visible at low voltages. A surprising fact is that the brightness of the light appears to have little if anything to do with the brightness obtained on reaction with oxygen. In no case was any trace of polarization observed in the light. Table I gives a list of typical examples and it will be noted that some compounds that give no light on oxidation with oxygen show the effect, while the brightest of the oxyluminescent substances hardly show the present effect at all.

TABLE I

LUMINESCENCE DURING ELECTROLYSIS OF GRIGNARD COMPOUNDS

Grignard compound from	Light during electrolysis	Remarks
Methyl iodide	None	
Ethyl iodide	None	
n-Butyl bromide	None	
iso-Amyl bromide	None	
n-Lauryl bromide	Faint	Seen only above 1000 v.
Trimethylene bromide	Faint	Seen only above 500 v.
Bromocyclohexane	Faint, momentary	Seen only above 1000 v.
Benzyl chloride	None	
β-Bromostyrene	Faint	Less than with oxygen
Phenyl bromide	Fair	About equal to light with O_2; easily visible at 110 v.
Phenyl iodide	Faint	Visible with 110 v.
p-Iodotoluene	Fair	Stronger at 1500 v. than oxidation
p-Chloro-bromobenzene	Very faint	Much less than with O_2 even at 1500 v.
p-Dibromobenzene	Faint	Less than with oxygen
1,2,4-Chloro-bromotoluene	Faint	Visible above about 500 v.
α-Bromonaphthalene	Very faint	
β-Bromonaphthalene	Faint	At cathode
1,4-Chloro-bromonaphthalene	Fair	At anode; appears between 500 and 600 v.
	Faint	At cathode; appears between 600 and 700 v.
β-Iodonaphthalene	None	

In a recent article, Evans and Diepenhorst[3] have questioned the conclusion of the writers that luminescence on oxidation of a Grignard com-

---

[2] Nelson and Evans, THIS JOURNAL, **39**, 82 (1917). Kondyrew, *Ber.*, **58**, 459 (1925).

[3] Evans and Diepenhorst, THIS JOURNAL, **48**, 715 (1926).

pound with oxygen, in ethyl ether solution, appears only if the —MgX group is attached directly to an unsaturated carbon atom. They state that they have obtained light from several Grignard compounds made from derivatives of saturated hydrocarbons, but do not state what solvent was used or whether the light was obtained from the crystallized compounds. The writers have carefully re-examined every such compound mentioned by Evans and Diepenhorst, without finding light in any case. Evidently the conditions for obtaining light, if it is emitted by such compounds, were not the same as used by the writers, that is, combination with oxygen while dissolved in ethyl ether.

Regarding the brightness of these compounds, Evans and Diepenhorst state that the "luminescence is proportional to the molecular weight of the halogen derivative so long as a definite series is considered without change in the chemical nature of the group or—in the case of the aromatic compounds—in position." So far as aliphatic compounds are concerned, Evans and Diepenhorst themselves appear to disprove the statement, by tabulating lauryl bromide as fainter than *iso*-amyl bromide. In the entire absence of quantitative measurements of brightness, the statement that a *proportionality* exists seems hardly justified. In the case of the aromatic compounds, it is true that the brightness increases when aliphatic groups of increasing formula-weight are substituted in the benzene ring, but this is the only case in which the brightness has been clearly shown to increase with molecular weight. On the other hand, there are several series, probably just as fairly called chemically similar, in which the brightness decreases when the molecular weight increases. This is the case in marked degree with the series C_6H_5MgCl, C_6H_5MgBr, C_6H_5MgI, with the series *p*-ClC_6H_4MgCl, *p*-BrC_6H_4MgBr, *p*-IC_6H_4MgI, and the series *p*-ClC_6H_4MgBr, *p*-BrC_6H_4MgBr, *p*-IC_6H_4MgBr. Other similar series are known. Evans and Diepenhorst have criticized the writers for concluding that mass is not the controlling factor, and that its influence is small compared with effects connected with the chemical nature of the compounds; but in view of the fact that only one series of compounds behaves in the way demanded by the "proportionality" of Evans and Diepenhorst, while there are several series which do not, and many more compounds which do differ chemically (for example, $(CH_3)_2NC_6H_4MgBr$) and which, when compared in molecular weight, seem to vary in brightness without much regard to molecular weight, the present writers feel that the effect of mass, if any, has not been clearly demonstrated. The question is simply one of interpretation of results, for with all these aromatic compounds the observations of Evans and Diepenhorst appear to repeat closely those of the writers.

The same authors criticize the writers for not noticing that the positions of the bands in the spectra from the oxidation of *p*-ClC_6H_4MgBr and *p*-BrC_6H_4MgBr are identical. They admit, however, that the light in the two cases differs in color. They attempt to explain the difference by saying that the light must be a mixture of fluorescence and chemiluminescence. The explanation is both untenable and unnecessary. In all known cases, the ratio between the intensities of fluorescent and of exciting light is so small that it is almost inconceivable that light as faint as chemiluminescence could produce perceptible fluorescence, and if it did, the spectra would show it, for the fluorescence spectra that would be observed are multiple-banded, and these bands do not appear on the photographs; they would be readily distinguishable if present. However, difference in color can mean only one thing—a difference in spectral distribution of energy; this is true no matter what the origin of the light may be. Now each of the chemiluminescence spectra shows a single, fairly symmetrical band, and the bands do not differ greatly in width. About the only possible difference would thus appear to be in the location of the maxima. Even a rough examination of the spectra, either in the articles by the writers or in those of Evans and Diepenhorst, will show that the maximum for p-BrC_6H_4MgBr lies somewhat on the violet side of the helium line at $\lambda 4472$, while for p-ClC_6H_4MgBr the maximum lies considerably on the long wave-length side of this line. The existence of such a difference was of course clearly indicated by the earlier work in which monochromatic filters were used.

The processes involved in the luminescence during electrolysis are probably different from those occurring during combination with oxygen. It is, therefore, not necessary to conclude that since one process gives luminescence, the other must also. The fact that the processes are different is shown by the following. It is found that while some Grignard compounds on electrolysis deposit magnesium immediately, others do not at first; the deposition potential of the magnesium varies for the different compounds, in some cases being high enough for other reactions to occur first. In such cases, it is often observed that a brown, oily liquid forms, which settles slowly. Some of this material seems to form in some cases even when magnesium is deposited. The liquid appears to be $MgBr_2.2(C_2H_5)_2O$. This substance can be prepared by methods not involving the use of Grignard compounds. However it is prepared, it is found to have the property of emitting light on electrolysis, just as many of the Grignard compounds do. The light emitted is so similar in the two cases that it seems probable that in many instances, especially with the saturated compounds, the formation of this substance, or possibly other etherates, may explain the entire luminescent effect.

Incidentally, it is worth pointing out that the magnesium which is deposited by electrolysis of these compounds is in a highly active state; it can be used to obtain good yields of some compounds, as C_6H_5MgCl, that are not easy to make.

The fact that ether solutions of Grignard compounds are closely comparable in their electrolytic properties with aqueous solutions of inorganic substances, opens a wide field for investigation. Some progress has been made by the writers and their colleagues in three directions: the study of decomposition potentials, the study of the complicated processes occurring in the electrolysis of these compounds, and the study of electrode potentials. The present article, however, will present only some important preliminary results from the last of these fields, that have shown a most interesting effect which is a converse of the luminescence on electrolysis. It is hoped that further results may be presented in later papers.

If a pair of strips of dissimilar metals is carefully cleaned and immersed in a solution of a Grignard compound, the strips will be found to have different potentials; they are the electrodes of a cell, a battery. Of course the cell must be sealed to prevent oxidation of the solution. A number of such cells have been studied, using a potentiometer outfit capable of measuring e.m.f.'s to 0.00005 volt.

The e.m.f. of such a cell varies greatly, for three reasons: (1) the cells have high temperature coefficients; (2) they are strikingly sensitive to changes in the illumination they receive; (3) the e.m.f. may be a periodic function of the time, dependng somewhat on the previous history of the cell. These facts make it extremely difficult to obtain results which are quantitative and reproducible and the following results are therefore regarded as only preliminary.

The luminescence, during electrolysis, having suggested the possibility of a converse effect, it did not take long to trace certain violent eccentricity in the behavior of the first such cell studied, to the flashing on and off of the thermostat lamp in the water-bath used for regulating the temperature of the cell. The cell was put in a light-proof box, in a liter beaker of water kept at 21° ± 0.1°. The mere opening of a shutter in the box, exposing the cell to the light from a 100-watt incandescent lamp a meter away, would instantly raise the voltage of the cell to several times its value in the dark. The incandescent lamp was kept running continuously. An experiment with colored water in the beaker indicated that red light was not the most effective, but the use of glass containers means that the effective light is either visible or near ultraviolet. Both aliphatic and aromatic Grignard cells show the effect.

Fig. 1 shows the effect of *continued* irradiation on a cell with gold and silver electrodes, in molal solution of phenylmagnesium bromide. The cell was kept in the dark until the e.m.f. was steady. On opening the window to the light from a mercury arc, a constant source, the e.m.f. is seen to rise suddenly, to oscillate about a final value, and finally to become steady after about four hours. As readings were made at short intervals, even one minute apart at the critical parts of the curve, the effect is not the result of accidental variations of a few readings. The second irradiation shows the same effect less prominently; also the less sudden drop in voltage when the light was excluded. Succeeding irradiations produced smaller effects, as shown. The temperature was constant to 0.05° in these experiments.

Other similar cells have given various similar curves (a number of these were shown at the Tulsa meeting of the American Chemical Society), some having a much greater oscillation in the e.m.f., and some showing the oscillations damped more quickly, some less quickly, than the example shown, but all showing the marked sensitivity to light. Similar oscillations were observed in deposition potentials taken with platinum electrodes. The work of Hedges[4] and associates indicates that such periodic functions of time may frequently be found in electrolysis of aqueous solutions of metal salts. No general theory of this effect has been given.

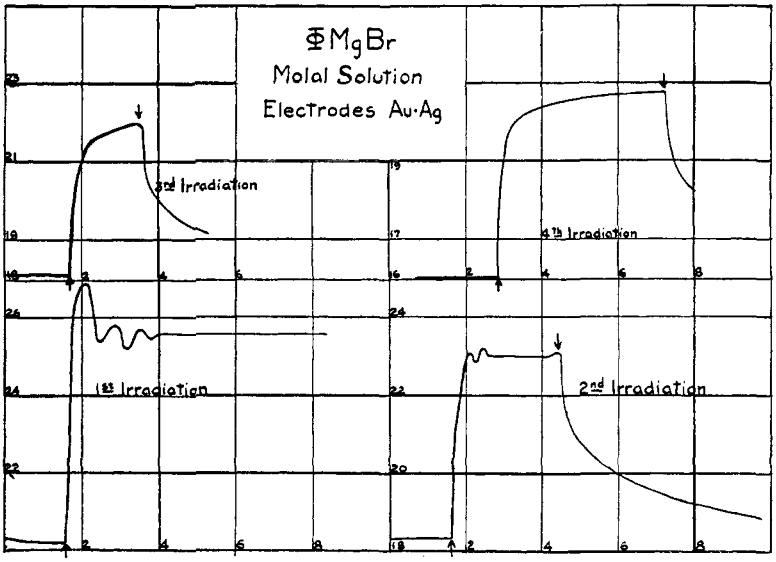

Fig. 1.

Cells with lead and copper electrodes gave erratic results, probably due to reactions at the electrodes; on standing, an oily liquid drips from the electrodes, and the solution shows a qualitative test for copper. While the values of the e.m.f. are not reproducible, the sensitivity to light appears to be always present, and the curves showing voltage variation with time have the same general shape. Magnesium-zinc cells, also sensitive, give much more closely reproducible e.m.f.'s.

Using a flowing junction method, with a cell made up of Mg | $MgBr_2 \cdot 2(C_2H_5)_2O$ (Sat. sol.) | C_2H_5MgBr (1.5 *M*) | Mg, e.m.f.'s are obtained

---

[4] Hedges, *J. Chem. Soc.*, **127**, 1013 (1925).

which are very steady and reproducible, readings checking repeatedly within one or two in the third significant figure. The cell used gave about 0.2 volt, but the numerical value is significant only in showing the order of magnitude of the effect measured, since the exact value of the concentration of the Grignard solution was not known.

Summary

1. It is shown that strong magnetic fields produce no polarization in the light from the oxy-luminescence of ether solutions of Grignard compounds, but may affect the brightness.

2. The application of electric fields often causes an unpolarized luminescence at one or both electrodes, accompanying the electrolysis of the solution. The process involved appears to be quite distinct from the oxy-luminescence.

3. Preliminary study of electrode potentials in cells containing ether solutions of Grignard compounds shows that the voltage of such cells is very sensitive to light and that, following a change in illumination, the voltage may be a periodic function of the time.

4. Using a flowing-junction method, closely reproducible voltages were observed.

Columbia, Missouri

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

A THERMODYNAMIC TREATMENT OF CERTAIN MAGNETIC EFFECTS. A PROPOSED METHOD OF PRODUCING TEMPERATURES CONSIDERABLY BELOW 1° ABSOLUTE

By W. F. Giauque

Received December 14, 1926 Published August 5, 1927

Some years ago the author's interest in cryogenic work led to a consideration of possible substitutes for the commonly used methods of producing low temperatures.

While a method of producing very low temperatures was devised, the lack of necessary facilities has caused a temporary delay in the actual experiment and it is desired to transmit the underlying ideas at this time.

The reversible transfer of heat from one temperature to another requires a working substance which is capable of undergoing an isothermal entropy change at the temperatures concerned.

From a practical standpoint, this entropy change must be considerable in view of the unavailability of those theoretically convenient, thermally non-conducting materials.

Compared to those of pressure, the effects ordinarily produced by obtainable electric and magnetic fields on the neutral states of matter are minute. However, a critical consideration indicated that while the latter