[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, UNIVERSITY OF MISSOURI]

Photo-voltaic Effects in Grignard Solutions

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It has previously been reported that metallic electrodes in ether solutions of Grignard compounds form a voltaic cell and that the potential difference between the electrodes changes when one or both electrodes are illuminated.[2] Both electrodes may be made from the same metal or from different metals. An extensive list of metals and a number of both aliphatic and aromatic Grignard compounds have been investigated.[3] In all cases both the dark voltage and the photovoltaic response were only roughly reproducible or completely non-reproducible. Several cases, however, indicated that the magnitude and direction of the response might be dependent upon the Grignard compound.

This investigation was undertaken in an attempt to obtain reproducible results so that this effect might be used in the study of homologous series of organic groups. Magnesium amalgam electrodes were studied first since these would have a liquid surface which could be changed by shaking and since magnesium would be present to establish equilibrium with the ions of the Grignard compound.

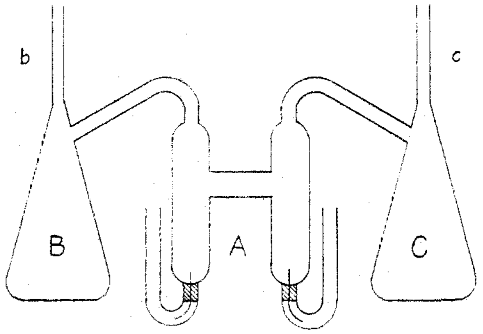

Fig. 1.

Experimental.—Each cell was kept in a separate compartment of a black light-proof box and was illuminated through a small window by a thousand-watt lamp. The temperature was controlled by a water-bath and the voltage was measured by a potentiometer which was sensitive to a few tenths of a millivolt. Ordinary laboratory reagents were used. All organic compounds were dried over calcium chloride and all liquids were distilled. The ether was dried over and distilled from sodium. Freshly sanded magnesium ribbon was used both in the reactions and as electrodes.

The apparatus shown in Fig. 1 was filled with nitrogen and kept closed as much as possible while 15 mg. of fluorenone, 25 cc. of ether and 5 cc. of saturated sodium amalgam were placed in B and 5 cc. of 1% magnesium amalgam and 25 cc. of the Grignard solution in C. The Grignard compound had been synthesized previously in a nitrogen atmosphere. Concentrations ranged from one-half to two molar. The magnesium amalgam had been made in a partial vacuum and the sodium amalgam under dry kerosene. The cell was again filled with nitrogen, evacuated, and openings b and c sealed. After shaking for several hours, the sodium fluorenone produced in B was decanted into the cell, A, and after standing for at least two hours to allow complete drying,[4] was returned to B. After rinsing A several times with ether distilled from B, this side bulb was sealed off. The Grignard solution and the electrode material were transferred to the cell and C sealed off. Electrical connections were made to the magnesium amalgam through very fine platinum ribbon which had been worked into a section of glass tubing at the bottom of each arm of the cell. Mercury contacts were made on the outside. With the exception of the lower part of one arm, the cell was well covered with black friction tape so that only one electrode could be exposed to light.

Similar cells were constructed with metallic magnesium electrodes. These electrodes were suspended by a platinum wire from the platinum connection through the glass at the top of the cell. The platinum–magnesium connection was high enough to be above the solution in the cell. In these cells, the Grignard compound was synthesized in the side bulb after the apparatus had been sealed. In order to avoid any possible reaction between the sodium fluorenone and the magnesium electrodes, the cell was dried with ether distilled from the sodium fluorenone solution rather than by transferring sodium fluorenone into the cell. After the sodium fluorenone side bulb, B, had been removed, a mixture of the Grignard reagent and excess alkyl halide was transferred into the cell to allow the alkyl halide to react with the magnesium electrodes for a short time to ensure a clean electrode surface. The Grignard solution was then returned to its side bulb and ether distilled into the cell to rinse it. The cell was filled with Grignard reagent and the reaction bulb removed. Both types of cells were prepared with phenylmagnesium bromide and with ethylmagnesium bromide.

Results.—Typical results obtained are given in Fig. 2. In this the potential difference in millivolts is plotted against the time in minutes. The sign is that of the electrode in the untaped arm

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[1] Abstract of a dissertation presented by Anna Jane Harrison in partial fulfilment of the requirements for the degree of Master of Arts at the University of Missouri.

[2] Dufford, Nightingale and Gaddum, THIS JOURNAL, **49**, 1858 (1927).

[3] Dufford, *J. Phys. Chem.*, **34**, 1544 (1930); **35**, 988 (1931); **37**, 709 (1933).

[4] Bent and Irwin, THIS JOURNAL, **58**, 2072 (1936).

with respect to the electrode in the taped arm. An arrow pointed upward indicates the beginning and an arrow pointed downward the end of the exposure to light. All cells containing the magnesium amalgam electrodes gave a zero dark voltage with the exception of occasional temporary variations of the order of a millivolt Curve A shows the effect of light on the untaped arm. The illuminated electrode became positive with respect to the dark electrode to the extent of almost 2 mv. and then decreased slightly. Curve B shows the effect produced in the same cell by focusing the light on the taped arm instead of the untaped arm. The latter was unprotected from the large amount of diffused light. The response was in the opposite direction and somewhat larger. These responses must, therefore, be due to heating effects rather than any direct effect of the light. Similar curves of greater magnitude (12 to 20 mv.) were obtained when no water-bath was used. The curves were reproducible and after illumination ceased the voltage became smaller until zero was reached. Similar responses were obtained by placing the two arms of the cell in two water-baths which were not at the same temperature. Cells containing metallic magnesium electrodes gave the same type of results as is shown by curves C and D. In these the heating effect was slightly greater in the untaped arm than in the taped arm. This might be expected, however, since absorption was taking place on the electrode surface in one case and on the cell wall in the other case. Responses of this type will be referred to as no photo-voltaic effect.

Cells containing magnesium electrodes, which had not been cleaned with the reaction mixture but had been dried with ether distilled from the sodium fluorenone, showed variable dark voltages and variable photo-voltaic responses. For the most part these responses to light were rather large as is shown by curve E. The illuminated electrode always became positive with respect to the dark electrode. Responses of this magnitude could not be produced by temperature changes. Both the dark voltage and the light sensitivity could be destroyed by opening the cell and adding a few drops of the corresponding organic halide or by simply allowing the cell to stand for several days. The phenylmagnesium bromide solutions in two of these cells in which the photo-voltaic sensitivity had been destroyed by adding phenyl bromide were returned to the reaction bulbs. The Grignard solutions were kept cold with dry ice and ether while the cells were filled with oxygen, which had not been dried. After fifteen minutes the apparatus was evacuated and closed. After rinsing with ether distilled from the reaction flasks, the cells were filled. Both cells showed variable dark voltages and photo-voltaic responses. One such response is shown by Curve F. The Grignard solutions were clear and gave no evidence of having been oxidized. The dark voltage and the light sensitivity were destroyed in one cell by the addition of phenyl bromide and in the other by allowing it to stand.

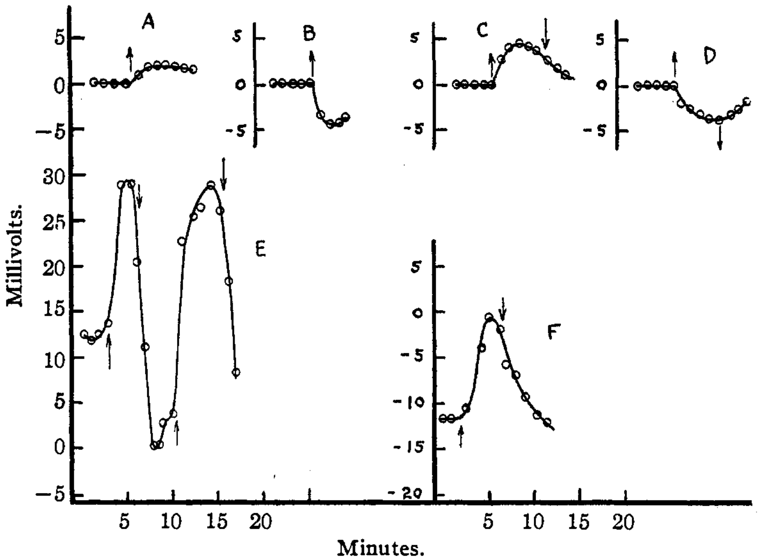

Fig. 2.—Curves A and B show the response of magnesium amalgam electrodes with the light focused on the untaped electrode (A) and on the taped electrode (B). Curves C and D are the same for magnesium electrodes which have been cleaned by the reaction with the organic halide. Curve E shows the response to light obtained with magnesium electrodes which had not been "cleaned." Curve F gives the response to light of cleaned magnesium electrodes which had been exposed to oxygen. An arrow pointed upward indicates the beginning and an arrow pointed downward the end of the exposure to light. In all cells one electrode was protected from light by tape. The sign of the voltage is that of the electrode in the untaped arm with respect to the electrode in the taped arm.

Discussion.—A surface film appears to be necessary for light sensitivity in the case of magnesium electrodes. Presumably, this film is removed by the reaction of the organic halide with the adjacent atoms of magnesium. If the film is magnesium hydroxide its disappearance on standing might be explained by the reaction with the magnesium bromide from the Grignard equilibrium to produce basic magnesium bromide which is soluble in ether.

Summary

(1) Magnesium amalgam electrodes gave zero dark voltage and no light sensitivity with ether solutions of either phenylmagnesium bromide or ethylmagnesium bromide. (2) Magnesium electrodes which had been cleaned by reacting with the organic halide gave the same results. (3) Magnesium electrodes which had not been cleaned in this manner showed variable dark voltages and variable photo-voltaic responses. Both of these could be destroyed by adding the organic halide or by allowing the cell to stand for several days. (4) "Cleaned" magnesium electrodes were made sensitive to light by exposure to oxygen.

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The Addition of Sulfur, Hydrogen Sulfide and Mercaptans to Unsaturated Hydrocarbons

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There have been many investigations of the action of sulfur and hydrogen sulfide on unsaturated hydrocarbons[2] and a few on the addition of mercaptans[3] but so many points have not been cleared up that further study seemed desirable.

Curiously enough the end-products are much the same whether an unsaturated hydrocarbon is treated with sulfur, hydrogen sulfide or a mercaptan. Thus with ethylene, sulfur gives hydrogen sulfide which reacts with more ethylene to form ethyl mercaptan which then adds to more ethylene to form ethyl sulfide.

Our results help to explain the presence of ethyl, *i*-propyl and other mercaptans and the corresponding sulfides in petroleum distillates but do not account for the presence of methyl mercaptan and methyl sulfide.

The Action of Sulfur.—Quite different results are obtained from the reaction with sulfur according to the conditions and whether free sulfur or a compound which readily liberates sulfur is used. When ethylene was passed over pyrites at 350° about 1% of thiophene was isolated along with hydrogen sulfide and ethyl mercaptan, while when it was bubbled through sulfur at 325° much hydrogen sulfide was formed along with 3% of ethyl mercaptan and small amounts of carbon disulfide and ethyl sulfide. We found it advantageous to use ethyl tetrasulfide as a sulfur donor. This is a liquid which mixes well with organic compounds and decomposes on heating, giving off what may be assumed to be atomic sulfur. The proportions were calculated on the basis of the tetrasulfide going down to the disulfide. A noteworthy difference is that with it, appreciable yields of the cyclic sulfides were obtained.

When ethylene was bubbled slowly through ethyl tetrasulfide kept at about 150°, the main product isolated was ethyl mercaptan with some ethyl sulfide and in addition some ethylene sulfide. The results of heating several hydrocarbons in a bomb with ethyl tetrasulfide are given in Table I.

TABLE I

Hydrocarbons with Et_2S_4, 10 hrs. at 180°

Hydrocarbon	Yields of products, %		
	Mercaptan	Sulfide	Cyclic sulfide
Ethylene	5	18	1
Propylene	6	20	15
Heptene-1	20	. .	. .
Octene-1	19	. .	. .
Cyclohexene	8	. .	8

The mercaptans, except from ethylene, and sulfides were all secondary.

The Addition of Hydrogen Sulfide.—The addition of hydrogen sulfide was effected by heating in the bomb for ten hours at 180°. Sulfur was added as a catalyst for without it there was little if any addition. The results are given in Table II. The sulfur is found on the secondary or tertiary carbon atom in accordance with Markownikow's rule.

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(1) Taken from the Ph. D. dissertation of S. O. Jones, R. J. Reynolds Tobacco Co. Fellow, The Johns Hopkins University, June, 1936.

(2) Mailhe and Renaudie, *Compt. rend.*, **195**, 391 (1932); Duffey, Snow and Keyes, *Ind. Eng. Chem.*, **26**, 91 (1934).

(3) Posner, *Ber.*, **38**, 646 (1905); Nicolet, THIS JOURNAL, **57**, 1098 (1935).