According to Smiles,[6] in a homologous series the specific refractive power increases with the molecular weight but the increment decreases as the series is ascended. On the other hand, the increase in molecular refractivity appears to be constant. The data on the polyethylene glycols (Table IV) appear to show that both these statements are true for this series, though the increment in molecular refraction exhibits a slight increase with increase in molecular weight.

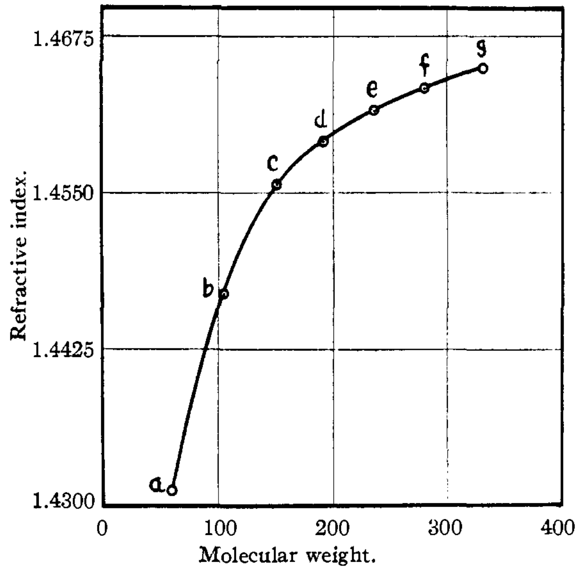

Fig. 2.—Refractive indices of polyethylene glycols: a, ethylene glycol; b, diethylene glycol; c, triethylene glycol; d, tetraethylene glycol; e, pentaethylene glycol; f, hexaethylene glycol; g, heptaethylene glycol.

Summary

The molecular weights (cryoscopic) in ethylene dibromide of tri-, tetra-, penta-, hexa- and heptaethylene glycols and of certain of their derivatives have been measured. Abnormalities in the variation of the degree of association with the concentration have been observed in the case of the glycols.

From the freezing point data on the polyethylene glycols it may be predicted that pure decaethylene glycol and possibly pure nonaethylene glycol will be solids at room temperature.

An indication of the formation of chelate rings was observed with ethylene and trimethylene glycols, and to a lesser degree with ethylene dichloride and ethylene glycol monomethyl ether, when these compounds were treated with anhydrous copper sulfate.

An approximately constant increase in molecular refraction with increasing molecular weight has been observed in the polyethylene glycol series.

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[6] Smiles, "Relations between Physical Properties and Chemical Constitution," Longmans, Green and Co., London, 1910, p. 257.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

The Catalyzed Reaction of Ethylmagnesium Bromide with Ethyl Bromide

BY C. B. LINN AND C. R. NOLLER

One of the side reactions encountered during the preparation of Grignard reagents from alkyl halides leads to the formation of saturated and unsaturated hydrocarbons in equivalent amounts.[1] Jolibois[2] was the first to discover the cause of this type of side reaction when he showed that the formation of ethylene and ethane was due to the reaction of ethyl iodide with ethylmagnesium iodide according to equation I.

$$C_2H_5MgX + C_2H_5X \longrightarrow C_2H_4 + C_2H_6 + MgX_2 \quad \text{(I)}$$

In the following year Späth[3] reported on a number of reactions between alkylmagnesium halides and alkyl halides in which coupling and disproportionation were observed.

More recently Job, Reich and Dubien[4] found that the evolution of gases during the preparation of ethylmagnesium iodide does not occur if the magnesium is pure, but that the side reaction is vigorously catalyzed by copper and iron. In a second note Job and Dubien[5] reported that the rate of reaction between ethylmagnesium bromide and ethyl bromide can be studied by adding a trace of cuprous or ferric chloride to catalyze the reaction. No velocity data or details of the procedure are given but they state that when the Grignard reagent is in excess, the reaction is

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[1] Bouveault, *Compt. rend.*, **138**, 1108 (1904); Tschelinzeff, *J. Russ. Phys.-Chem. Soc.*, **36**, 549 (1904); *J. Chem. Soc.*, **86**, 641 (1904).

[2] Jolibois, *Compt. rend.*, **155**, 213 (1912).

[3] Späth, *Monatsh.*, **34**, 1965 (1913).

[4] Job, Reich and Dubien, *Bull. soc. chim.*, [4] **37**, 976 (1925).

[5] Job and Dubien, *ibid.*, [4] **39**, 583 (1926).

pseudomonomolecular according to equation I and advance this as conclusive evidence that the formula for the Grignard reagent is RMgX and not $R_2Mg{\cdot}MgX_2$. This view was concurred with by Grignard.[6]

Jolibois,[7] who has long advocated the double formula, attacked this deduction. His most valid argument against it was that the catalysis was heterogeneous and hence the rate determinations have no significance. Job and Dubien[8] replied that the reaction was homogeneous but again no experimental details were given. In this paper they admitted the possibility of a step-wise reaction but considered this improbable.

The reactivity of heavy metal halides with Grignard reagents is well known and Konduirov and Fomin[9] have reported that ethylmagnesium bromide reacts with cuprous bromide with the formation of ethylene, ethane, magnesium bromide and copper. An interest in the constitution of the Grignard reagent prompted us to reinvestigate this reaction. It was found at once that cuprous chloride is reduced to metallic copper by ethylmagnesium bromide in ether solution at room temperature. The white cuprous chloride was converted into a black solid which was free of halogen and underwent reactions such as dissolving in nitric acid with evolution of oxides of nitrogen and precipitating silver from silver nitrate solution. The gaseous products of the reaction of cuprous chloride and ethylmagnesium bromide were found to contain hydrogen in addition to the ethylene and ethane reported previously.[9] No butane could be detected. To account for the reaction products equations II and III may be proposed.

$$2CuCl + 2C_2H_5MgBr \longrightarrow 2Cu + C_2H_4 + C_2H_6 + MgBr_2 + MgCl_2 \quad (II)$$

$$2CuCl + 2C_2H_5MgBr \longrightarrow 2Cu + 2C_2H_4 + H_2 + MgBr_2 + MgCl_2 \quad (III)$$

In accordance with these equations the excess of ethylene over ethane was equal within experimental error to twice the volume of hydrogen. The total volume of gas evolved from a given weight of cuprous chloride corresponded to that expected from the equations II and III. Similar results were obtained in both ethyl ether and *n*-butyl ether solutions but the latter was more convenient to use because of its lower volatility. Cuprous bromide behaved in every way like cuprous chloride. Ferric chloride reacted much more vigorously than the cuprous halides and no hydrogen was detected in the gaseous products.

In agreement with the work of Job, Reich and Dubien[4] no noticeable reaction was observed between a solution of ethylmagnesium bromide and ethyl bromide in the absence of a catalyst. Cuprous chloride cannot be the catalyst, however, since it reacts completely with ethylmagnesium bromide. Moreover, the solubility of cuprous chloride in absolute ether is so low that saturated solutions do not show any catalytic activity. The catalytic action of the copper formed in the reaction of cuprous chloride with an excess of ethylmagnesium bromide was readily shown. As soon as ethyl bromide was added a vigorous evolution of gases took place from the surface of the copper whereas when added to solutions decanted from the copper, no evolution of gas was detected. Although ordinary copper does not catalyze the reaction, copper prepared by reducing powdered copper oxide in a current of hydrogen was a fairly active catalyst. Metallic silver prepared by reducing silver oxide had some catalytic activity also.

Before studying the kinetics of the reaction it was necessary to determine definitely the reaction products. Job and Dubien[5] advanced equation I for the reaction but published no data concerning the products of the reaction. Besides ethylene and ethane two other gases, butane and hydrogen, might be expected but we have not been able to detect the formation of either substance in this reaction. Since hydrogen was formed in the reaction of ethylmagnesium bromide with cuprous chloride, it would seem unlikely that a single mechanism, such as the intermediate formation of free radicals, can explain both reactions. Quantitative determinations showed that the amount of ethane formed was that expected from equation I but that the amount of ethylene was always somewhat low. The amount of ethylene more closely approached the theoretical the faster the gases were evolved, indicating a side reaction after the formation of the ethylene, probably polymerization in the reaction mixture.

The kinetics of the reaction confirms the view that it is one of heterogeneous catalysis. As shown in Curves I and II the first part of the reaction, using an excess of ethylmagnesium bro-

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[6] Grignard, *Bull. soc. chim.*, [4] **39**, 1288 (1926).

[7] Jolibois, *Compt. rend.*, **183**, 971 (1926).

[8] Job and Dubien, *ibid.*, **184**, 155 (1927).

[9] Konduirov and Fomin, *J. Russ. Phys.-Chem. Soc.*, **47**, 190 (1915); *C. A.*, **9**, 1473 (1915).

mide, is of zero order. The concentration of ethyl bromide is sufficient to cover the surface of the catalyst with reactants and hence the rate is independent of the concentration. As the reaction proceeds this is no longer true and the rate is dependent on the rate of diffusion of ethyl bromide, giving rise to an apparent first order reaction. The view that no conclusions concerning the constitution of Grignard reagents can be drawn from these rate studies has been confirmed by following the rate of reaction of diethylmagnesium with ethyl bromide. The results are shown in Curve III which is indistinguishable from those using ethylmagnesium bromide.

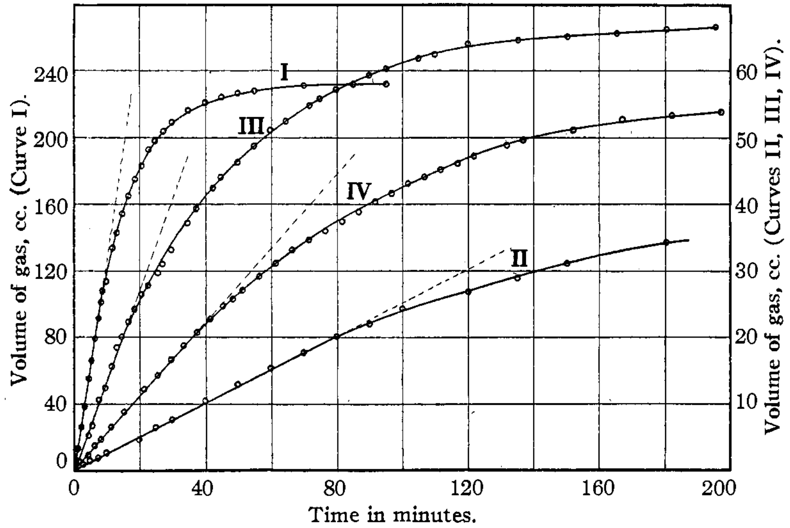

Fig. 1.—Rates of reaction of ethylmagnesium bromide and of diethylmagnesium with ethyl bromide: Curves I and II, ethylmagnesium bromide, ethyl bromide and cuprous chloride; Curve III, diethylmagnesium, ethyl bromide and cuprous chloride; Curve IV, ethylmagnesium bromide, ethyl bromide and colloidal copper.

A possible explanation for the belief of Job and Dubien[8] that the reaction is homogeneous was found toward the end of these experiments. It had been observed that after cuprous chloride has reacted with solutions of ethylmagnesium bromide the supernatant liquid is colored from blue to red. By using larger amounts of cuprous chloride, clear solutions which were black by reflected light but red by transmitted light could be obtained. These solutions definitely catalyzed the reaction of ethylmagnesium bromide with ethyl bromide but as shown by Curve IV the reaction is still of the heterogeneous type. It is assumed that the red solutions are solutions of colloidal copper, an assumption which is borne out by the fact that they show a much stronger Tyndall cone than the solutions of ethylmagnesium bromide from which they were prepared.

Experimental

General.—Only pure sublimed magnesium, purchased from the Aluminum Company of America, was used. The solutions of ethylmagnesium bromide were filtered by nitrogen pressure through a layer of ignited kieselguhr and were colorless. They had a very slight opalescence which gave rise to a weak Tyndall cone in the ultramicroscope. These solutions were transferred in a pure nitrogen atmosphere and boiled under vacuum just before use to remove all gases formed during the preparation of the solution or formed by moisture on the glass. The reaction vessel was surmounted by a spiral condenser that could be cooled to as low as −80° to remove ether vapor from the evolved gases. These gases could be passed to a mercury-filled reservoir or to a mercury-filled gas buret. Gas analysis was by the slow combustion pipet. Ethylene was removed from ethane and hydrogen by washing with fuming sulfuric acid containing 20% sulfur trioxide, and ethane from hydrogen by passing the gases through a trap immersed in liquid air. Analyses of known mixtures of ethylene and ethane by these methods gave accurate results. The concentrations of the ethylmagnesium bromide and diethylmagnesium were determined by titration with standard acid.[10]

Cuprous chloride prepared as follows gave a pure product which was grayish-white and did not discolor on standing in a dry inert atmosphere. A solution of 25 g. of copper sulfate crystals and 7 g. of sodium chloride in 150 cc. of boiling water was filtered to remove a light yellow residue, and a second solution of 4 g. of sodium hydroxide and 6 g. of sodium bisulfite in 50 cc. of water was added slowly. After cooling, the cuprous chloride was filtered quickly, washed twice with a solution of sulfurous acid, and dried by heating for ninety minutes at 150° and 25 mm. pressure. It was placed in a desiccator in a nitrogen atmosphere over solid potassium hydroxide. Analysis showed 35.88% chlorine; calculated 35.82%.

The following detailed experiments are selected from a large number of trials and runs and the conditions given are those considered best for the type of reaction under consideration.

Reaction of Cuprous Chloride with Ethylmagnesium Bromide.—In a 25-cc. test-tube having a side-arm to admit nitrogen was placed 5 cc. (0.0095 mole) of ethylmagnesium bromide in *n*-butyl ether. The solution was freed from dissolved gases by warming under reduced pressure, cooled to −50° and 0.1617 g. of cuprous chloride added. The tube was connected to the condenser maintained at −80°

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[10] Gilman and co-workers, This Journal, **45**, 150 (1923); **51**, 1576 (1929).

which in turn was connected to the reservoir. No reaction was apparent at −50°. As the temperature was allowed to rise slowly the salt changed to a black solid, although at 0° there was still no evolution of gas and there was only a small layer of deep red solution around the catalyst. Gas evolution began between 15 and 20°. After the evolution of gas at room temperature was complete, the reaction mixture was warmed in a bath kept at 50° while a slow stream of nitrogen was passed through the apparatus and into the reservoir. The first reservoir was collected during a period of one hour and another collected over a period of two and one-half hours. At the end of this time the nitrogen passing through the reaction flask contained no combustible gas. Analysis showed the first reservoir to contain 11.4 cc. of ethylene, 8.7 cc. of ethane and 1.5 cc. of hydrogen.[11] The second reservoir contained 8.5 cc. of ethylene, 5.5 cc. of ethane and 1.4 cc. of hydrogen. The total volume of hydrocarbon gas was 34.1 cc. as compared with a value of 36.6 cc. calculated from equations II and III. The ethylene exceeded the ethane by 5.7 cc. making the calculated volume of hydrogen expected 2.85 cc. whereas 2.9 cc. was found. No butane was obtained on removing the cooling medium from the condenser and heating to 100°. Similar results were obtained using ethyl ether as a solvent.

Kinetics of the Catalyzed Reaction of Ethylmagnesium Bromide and of Diethylmagnesium with Ethyl Bromide.—A weighed amount of cuprous chloride was treated with an excess of ethylmagnesium bromide and the reaction gases removed by boiling under reduced pressure. Sufficient ether was added to bring the total volume to 15 cc. and, with the condenser and reaction flask at the desired temperature, the system was brought to equilibrium. A known weight of ethyl bromide in 10 cc. of ether (ethyl or *n*-butyl) was added and the rate of gas evolution noted. During the velocity measurements, the contents of the reaction flask was agitated constantly by shaking. The results of a typical run in ethyl ether using 0.005 g. of cuprous chloride, 0.0435 mole of ethylmagnesium bromide and 0.00509 mole of ethyl bromide are given in Curve I. The volumes used in plotting these curves were not reduced to standard temperature and pressure. The experiment was carried out at the boiling point of the solution and a total gas volume of 213 cc. S. T. P. was obtained. The calculated value based on equation II is 228 cc. The ratio of ethylene to ethane was 0.869 at the beginning and 0.864 at the end of the run. Taking the average value of 0.866, the amount of ethane in the 213 cc. collected is 114 cc. which is the calculated amount. After removal of the ethylene, combustion showed the ethane to be pure. No trace of combustible gas could be detected after passage through a trap cooled in liquid air. In those runs made in *n*-butyl ether, removal of the cooling medium from the condenser and heating to 100° failed to give any butane. Curve II illustrates the data for the early portion of a reaction using 0.0002 g. of cuprous chloride, 0.0255 mole of ethylmagnesium bromide and 0.00188 mole of ethyl bromide in ethyl ether. The reaction is sufficiently slow so that the straight line portion of the curve cannot be due to errors in reading the gas volume.

Curve III illustrates the data for a run using 0.001 g. of cuprous chloride, 0.0140 mole of diethylmagnesium and 0.00144 mole of ethyl bromide in ethyl ether. The diethylmagnesium was prepared by the reaction of diethylmercury with magnesium. Analysis of the gases gave results identical with those for ethylmagnesium bromide. The same was true for the gases evolved during the reaction of the diethylmagnesium with the cuprous chloride.

In Curve IV are plotted the results of a run catalyzed by the colloidal solution of copper. This colloidal solution was prepared by adding 0.5 g. of cuprous chloride to 0.078 mole of ethylmagnesium bromide in 30 cc. of ethyl ether cooled to −15°. Reaction occurred on warming to room temperature. The reactants were allowed to stand for three days in an atmosphere of nitrogen and the solution filtered through a layer of ignited Kieselguhr. The filtrate was black by reflected light and dark red by transmitted light, and contained 0.00255 mole of ethylmagnesium bromide per cubic centimeter. To 0.5 cc. of this solution and 5 cc. of ethyl ether in the reaction flask was added 0.0299 mole of ethylmagnesium bromide in 10 cc. of ether. After the system came to equilibrium at 42°, 0.001293 mole of ethyl bromide in 2 cc. of ether was added and the rate of gas evolution determined. Analysis of the gases gave results identical with those using cuprous chloride as a catalyst. Saturated solutions of cuprous chloride in absolute ethyl ether did not cause a detectable reaction between ethylmagnesium bromide and ethyl bromide.

Summary

The reaction of ethylmagnesium bromide with ethyl bromide in the presence of cuprous chloride is heterogeneous, the catalyst being metallic copper either in the solid or colloidal state. Hence no conclusions concerning the mechanism of the reaction can be drawn from rate measurements. A careful study of the products of the reaction indicates that only ethylene and ethane are formed. The reaction of ethylmagnesium bromide with cuprous chloride at room temperature gives some hydrogen in addition to ethylene and ethane. No butane could be detected in either case. Solutions of diethylmagnesium behave in exactly the same way as solutions of ethylmagnesium bromide.

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(11) The amount of hydrogen was usually determined from the total contraction and carbon dioxide formed on combustion of the mixture of ethane and hydrogen after removal of ethylene. In several cases, however, the ethane was condensed at liquid air temperature and the residual gas shown to be hydrogen by combustion.