[Contribution from the Department of Chemistry, University of Pittsburgh]

Reaction of 1-Alkynes with Organometallic Compounds. IX.[1a] The Reactivity of Mixed Grignard Reagents toward 1-Hexyne[1b]

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The rates of reaction with 1-hexyne of methylmagnesium iodide, isopropylmagnesium iodide, a mixture of these two reagents, and a reagent prepared from a mixture of methyl iodide and isopropyl iodide indicate that the reactivity of either alkylmagnesium iodide is independent of the presence of the other.

The rates of reaction of the following Grignard reagents with 1-hexyne were determined: methylmagnesium iodide, isopropylmagnesium iodide, a mixture of these two reagents, and a Grignard reagent prepared from a mixture of methyl iodide and isopropyl iodide. It was found that isopropylmagnesium iodide reacts about forty-seven times as rapidly as methylmagnesium iodide. This is in line with results previously reported[2] that isopropylmagnesium bromide reacts about thirty-five times as rapidly with 1-hexyne as does methylmagnesium bromide or iodide. It was also found that in both of the "mixed" Grignard reagents the reactivity of either alkyl group was essentially independent of the presence of the other as is evident from Fig. 1, where the total volume of gas evolved is shown as a function of the time for the first 1100 seconds of the reaction. The experiment numbers are those given in Table I. In this time the reaction of isopropylmagnesium iodide was 95% complete, but the reaction of methylmagnesium iodide was only 13% complete. The rate of evolution of gas from the two "mixed" Grignard reagents is the same for about the first 225 seconds. Comparison of the curves for experiments 1, 2, and 3 shows that the difference in the results of experiments 2 and 3 can be explained in terms of independent evolution of propane and methane in experiment 3. This interpretation is confirmed by the results of experiment 5, in which the propane was prevented from escaping from the reaction mixture by using Dry Ice and acetone in the reflux condenser. The presence of an increasing amount of propane in the reacting system caused the reaction temperature, which was the reflux temperature, to decrease to 23° during the first 700 seconds of the reaction. The temperature then remained constant at 23°, and the rate decreased accordingly. The fact that gas was evolved more rapidly during the first minute in experiment 5 than in experiment 1 can be explained by the fact that the propane produced in experiment 5 displaced more volume in the reflux condenser than was occupied by the ether before the reaction started. This could account for the extra 15 ml. of gas which appeared to be evolved

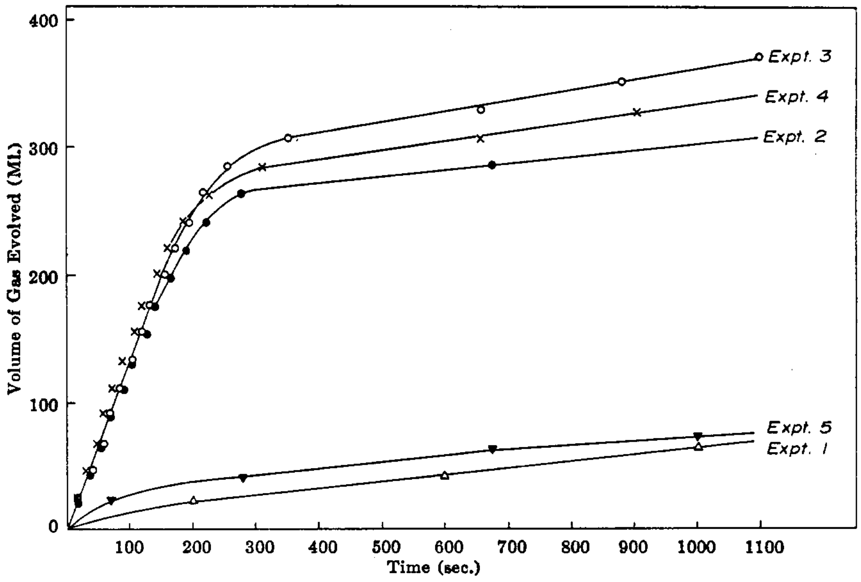

Fig. 1. Volume of gas as a function of the time—experiment numbers are those given in Table I

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[1] (a). Part VIII, J. H. Wotiz, C. A. Hollingsworth, and A. W. Simon, *J. Org. Chem.*, 24, 1202 (1959). (b) This work was supported by the National Science Foundation.

[2] J. H. Wotiz, C. A. Hollingsworth, and R. Dessy, *J. Am. Chem. Soc.*, 77, 103 (1955).

TABLE I

REACTANTS AND CONDITIONS

Expt.	Initial Molarities							Reaction Temp. °[a]		
No.	CH_3MgI	i-C_3H_7MgI	Hexyne	Total Gas	(Ml., STP)	$t_{1/2}$ (Sec.)		max	min	$t_{1/2}$
				CH_4	C_3H_8	CH_4	C_3H_8			
1	1.00	0	1.63	526	0	6,550	—	35	34	34
2	0	0.64	1.93	0	334	—	140	37	37	37
3[b]	1.00	0.64	1.93	526	334	6,330	140	37	36	36
4[c]	0.66	0.64	1.93	346	334	6,240	130	37	36	36
5[d]	1.00	0.64	1.63	526	0	21,800	—	35	23	23

[a] Maximum and minimum temperatures observed and the temperature at half-life. [b] This reagent was made by mixing two Grignard reagents. [c] This reagent was made from the mixed alkyl iodides. [d] Because a Dry Ice–acetone mixture was used in the condenser, the propane was condensed back into the reaction flask.

in the beginning of experiment 5. Because of the decrease in temperature and because the concentration of hexyne had been decreased by reaction with the isopropylmagnesium iodide, the rate of reaction in experiment 5 eventually became much slower than that in experiment 1 (compare the half-lives in Table I); the two curves intersect at a time greater than that shown in Fig. 1. The rate of evolution of methane is less in experiment 4 than in experiment 3 (see Fig. 1) because the concentration of the methylmagnesium iodide is greater in the latter experiment (see Table I).

These results suggest that a mixture of Grignard reagents reacts with 1-hexyne in a manner which is the sum of the activities of its components. This is not contradictory to evidence[3] that the Grignard reagents, at least in the cases of ethyl and phenylmagnesium bromides, are best represented by $R_2Mg{\cdot}MgX_2$. The independence of activities might mean that no exchange of alkyl groups takes place, and the mixture of Grignard reagents is best represented as $(CH_3)_2Mg{\cdot}MgI_2$ and $(i\text{-}C_3H_7)_2Mg{\cdot}MgI_2$. This possibility would require that the products in the formation of a mixture of Grignard reagents by the reaction of magnesium with a mixture of alkyl iodides are independent of each other. At this time the mechanisms of reaction of magnesium with alkyl halides are too speculative[4] to be of much help.

An alternative explanation for the observed rates is that $i\text{-}C_3H_7\text{—}Mg\text{—}CH_3.MgI_2$ is formed. In this case the reactivities of the alkyl groups must be the same as in the "pure" Grignard reagents. There are some kinetic results that suggest this possibility as follows: To a fairly good approximation, the reaction with 1-hexyne is a one-step, second-order reaction. This was previously[5] found to be true for ethylmagnesium bromide, and the present data show this for methylmagnesium iodide. The data for the isopropylmagnesium iodide are not sufficiently accurate to determine a reliable rate law for the reaction, because of the behavior of the alcohol-ice condenser (see Experimental). Although this kinetic behavior suggests the species RMgX, the species $R_2Mg{\cdot}MgX_2$ could behave this way also if the reactivities of the R-groups in $RMgC{\equiv}CC_4H_9{\cdot}MgX_2$ and $R_2Mg{\cdot}MgX_2$ are approximately the same.

EXPERIMENTAL

Grignard reagents were prepared from the alkyl iodide, which had been freshly distilled, and magnesium turnings (Fisher "Grignard Reaction") in ethyl ether (Mallinckrodt, anhydrous, analytical reagent, stored over sodium) under dry nitrogen by the usual procedure. The ratios of iodide to basic magnesium were as follows: methylmagnesium iodide, 0.96; isopropylmagnesium iodide, 2.5; the reagent prepared from a mixture of 50 mole per cent methyl iodide and isopropyl iodide, 1.05. In the last reagent the ratio of methyl to isopropyl groups was 1.03. The high iodide to basic magnesium ratio of the isopropylmagnesium iodide is consistent with the fact that the yield of this Grignard reagent has been reported[6] to be only 57.5%. The excess magnesium iodide may not necessarily affect the rate of the reaction with 1-hexyne to an appreciably extent, as it has been shown[5,7] that the rate of reaction of ethylmagnesium bromide with 1-hexyne is only slightly affected by the presence of *excess* magnesium bromide. Also, for the reaction of methylmagnesium bromide with 1-hexyne it was found[8] that the presence of moderate amounts of additional magnesium bromide decreases the rate slightly, but in the presence of larger amounts (bromide to basic magnesium about 3) the rate is the same as that when no excess magnesium bromide is present.

1-Hexyne (Farchan) was washed with aqueous hydrochloric acid, dried over calcium chloride, and redistilled, b.p. 69.8–70.5°.

Rate measurements. The rates were measured by a method which has been previously described.[9] The reactions were followed by measuring the volume of gas evolved as a function of the time. The ether was removed from the gaseous

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[3] R. E. Dessy, G. S. Handler, J. H. Wotiz, and C. A. Hollingsworth, *J. Am. Chem. Soc.*, 79, 3476 (1957); R. E. Dessy, and G. S. Handler, 80, 5824 (1958).

[4] See for example, M. S. Kharash and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, New York, 1954, p. 61. See also, R. Hamelin, *Bull. soc. chim. France*, 684 (1961).

[5] R. E. Dessy, J. H. Wotiz, and C. A. Hollingsworth, *J. Am. Chem. Soc.*, 79, 358 (1957).

[6] See for example, M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Monmetallic Substances*, Prentice-Hall, Inc., New York, 1954, p. 32.

[7] J. H. Wotiz, C. A. Hollingsworth, and R. E. Dessy, *J. Org. Chem.*, 21, 1063 (1956).

[8] George B. Smith, Ph.D. thesis, University of Pittsburgh, 1959.

[9] J. H. Wotiz, C. A. Hollingsworth, and R. E. Dessy, *J. Org. Chem.*, 19, 1545 (1955).

product by a reflux condenser, which was charged with either a mixture of ethyl alcohol and ice or a mixture of acetone and Dry Ice, depending upon whether or not the propane evolution was to be measured. The reacting mixture was refluxed at barometeric pressure. The variation in the reflux temperature as the reaction proceeded was not large (see Table I) except in experiment 5, where the propane was condensed back into the reacting mixture. When the alcohol-ice mixture was used in the condenser some variation in the effective condenser temperature during the reaction could not be prevented because the alcohol became enriched with water as the ice melted, and it was necessary to remove the liquid and replace it with fresh alcohol at regular intervals. As this caused no difficulty in reproducing results, the results of different experiments can be reliably compared. However, because the errors thus introduced are of a systematic nature, they possibly do make the data unsuitable for determining the rate law for the reaction.

The initial concentrations of the reactants are given in Table I. The volumes given in the fifth and sixth columns are the total theoretical volumes of each gas that should be evolved. The experimental values for the total amount of gas evolved never differed by more than 6% from these calculated values. The values for the half-lives given in Table I were calculated assuming independent reactivities in those cases where both gases were evolved.

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[CONTRIBUTION NO. 1100 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Reaction of 1-Alkynes with Organometallic Compounds. X. A Kinetic Study by Gas Chromatography

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A method is described for measuring rates of reaction by gas chromatographic analysis of the vapor in equilibrium with the solution in which the reaction is taking place. The method is applicable to reactions in which one or more of the reactants or products is volatile. The method has been applied to the reaction of phenylmagnesium bromide with 1-hexyne in ethyl ether and in mixtures of ethyl ether and tetrahydrofuran. It was found that the presence of tetrahydrofuran had a marked effect upon the kinetics of the reaction and that this effect depended upon the age of the Grignard reagent.

Most of the previous studies of the kinetics of the reaction of Grignard reagents with 1-hexyne have involved the measurement of the rate of evolution of a gaseous product.[4] Recently a study has been reported[5] in which the rate of reaction of a series of substituted phenylmagnesium bromides with 1-hexyne had been studied by following the rate of change of the dielectric constant of the reacting mixture.

It is the purpose of the present paper to describe a gas chromatographic method of measuring rates of reactions in which nongaseous products are produced. The method is applied to the reaction of phenylmagnesium bromide with 1-hexyne. In this system sampling the vapor in equilibrium with the solution provided a self-quenching method of sampling, since one of the reactants is nonvolatile. Equilibrium between liquid and vapor was achieved by keeping the system under reflux. Gas chromatographic analysis of the vapor gave the relative changes in concentrations of all of the volatile components of the reacting mixture. This not only provided a check on the data by allowing a comparison between the rate of disappearance of 1-hexyne with the rate of production of benzyne, but gave some direct information about the interaction of the phenylmagnesium bromide and tetrahydrofuran, which was a cosolvent in some of the reactions.

The self-quenching aspect and the fact that a variety of different data are obtained from the same experiment may make this gas chromatographic method useful for kinetic studies of other systems in which at least one of the reactants or products is volatile.

EXPERIMENTAL

Apparatus. The reaction vessel was a modification of that used in earlier experiments in which the rate of evolution of gas was measured.[4a] It consisted of a manostated reflux vessel attached to a Dry Ice reflux condenser. The flask had three side arms: one contained a thermometer; one was a capillary stopcock sealed with serum stopper through which samples could be injected from a hypodermic syringe. A gas sampling tube, which was made of 17-gauge hypodermic tubing, passed through a silicone rubber seal in the third side arm and lead to a sample chamber which was in a bath at 50°. The sampling tube was heated electrically to prevent condensation of the vapor sample.

The manostat consisted of a mercury column in a glass tube. The mercury level was controlled by a leveling bulb. The top of the tube was open to the atmosphere, and at the bottom there was a one-way valve which consisted of a glass ball and ground socket. This valve permitted gas which passed through the reflux condenser to enter the

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[4] (a) J. H. Wotiz, C. A. Hollingsworth, and R. E. Dessy, *J. Am. Chem. Soc.*, **77**, 103 (1955); (b) *J. Org. Chem.*, **20**, 1545 (1955); (c) *J. Am. Chem. Soc.*, **78**, 1221 (1956); (d) *J. Org. Chem.*, **21**, 1063 (1956); (e) *J. Am. Chem. Soc.*, **79**, 358 (1957); (f) J. H. Wotiz, C. A. Hollingsworth, R. E. Dessy, and L. C. Lin, *J. Org. Chem.*, **23**, 228 (1958); (g) J. H. Wotiz, C. A. Hollingsworth, and A. W. Simon, *J. Org. Chem.*, **24**, 1202 (1959).

[5] R. E. Dessy and R. M. Salinger, *J. Org. Chem.*, **26**, 3519 (1961).