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).

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bottom of the mercury column. A thin strip of shim stock along the axis of the tube prevented bumping. A slow flow of helium through the sample tube into the reflux vessel and out the manostat stabilized the pressure inside the system. An arrangement of Hoke toggle valves made it possible to evacuate the sample chamber, which was maintained at 50° then connect the sample chamber to the reflux vessel to obtain a sample, and then to force the sample into the chromatographic column with a stream of helium.

During the reaction the solution was kept refluxing at 40°.

Materials. A solution of *phenylmagnesium bromide* was prepared from redistilled phenyl bromide and magnesium (Fisher, Grignard Reagent) by the usual method using a cover of oil-pumped nitrogen which had been dried with sulfuric acid after being passed through a Fieser solution and a lead acetate solution. The concentration of basic magnesium was 1.7 molar and the ratio of bromide to basic magnesium was 1.03. The amount of benzene in the new reagent was negligible.

One other ether solution of *phenylmagnesium bromide* had been prepared by the usual method several years prior to its use in these experiments. It has been stored under nitrogen in an amber colored bottle with a serum cap, which was coated with wax. Some precipitate which had formed was removed by filtering under nitrogen through a glass wool plug. Acid titration gave, for the basic magnesium, 2.3 moles per 1000 g. of solution. By a gas chromatographic analysis of the type previously described,[6] but in which cyclohexane was used as an internal standard and direct vapor sampling was employed, the amount of benzene in the reagent (probably the result of reaction with moisture during storage) was found to be 0.361 mole per 1000 g. of solution, and the still active reagent was 1.48 moles of phenylmagnesium bromide per 1000 g. of solution. The bromide concentration was not determined for this reagent.

Ethyl ether (Mallinckrodt, analytical reagent grade, anhydrous) was stored over sodium. *Tetrahydrofuran* was distilled from ferrous sulfate solution, dried over calcium chloride, distilled in the presence of ethylmagnesium bromide, and stored over sodium.

1-Hexyne is described elsewhere.[7]

Procedure. The oven-dried reaction vessel was purged with dry nitrogen and then placed in the system. After further purging with nitrogen, the cold finger was filled with a Dry Ice–acetone slurry which was maintained at a constant level during the course of the experiment. Ether, Grignard reagent, and hexyne were added through the capillary stopcock from a hypodermic syringe. Tetrahydrofuran was added prior to the addition of 1-hexyne in some of the experiments. To measure the Grignard reagents, the syringe was used as a weighing pipette; the barrel of the syringe was lubricated with a silicone oil and, during weighing operations, the needle tip was inserted in a silicone rubber plug. A timer was started at the time of injection of the 1-hexyne and samples of vapor were withdrawn periodically and analyzed chromatographically.

RESULTS AND DISCUSSION

The reactions of phenylmagnesium bromide in ether with 1-hexyne could be followed readily through the disappearance of 1-hexyne or the appearance of benzene in the vapor phase above the refluxing solution. In an independent experiment it was established that the vapor pressure of benzene followed Henry's law in mixtures containing diethyl ether and phenylmagnesium bromide. Within experimental error the rates were the same whether followed by the appearance of benzene or the disappearance of 1-hexyne but the latter gave higher precision. Plots of appropriate functions of the peak area of hexyne versus time indicate that the reaction of 1-hexyne with both the old and the freshly prepared phenylmagnesium bromide in ether solution was first order, which is in disagreement with the results reported in the literature[5] and is in contrast to the reaction of 1-hexyne with alkylmagnesium bromide in ether which is nearly second order.[4f] Figure 1 is an example of the straight line obtained for a plot of log A *vs.* t as compared with the curved line for $1/A$ *vs.* t (where A is the peak area for 1-hexyne and t is the reaction time). Old and new reagents gave the same result. The rate constants and other information are given in Table I. Since the reactants were present in equivalent amounts in all experiments (see Table I), the results give only the over-all order of the reaction; that is, they do not give the dependence of the rate upon the concentrations of the individual reactants.

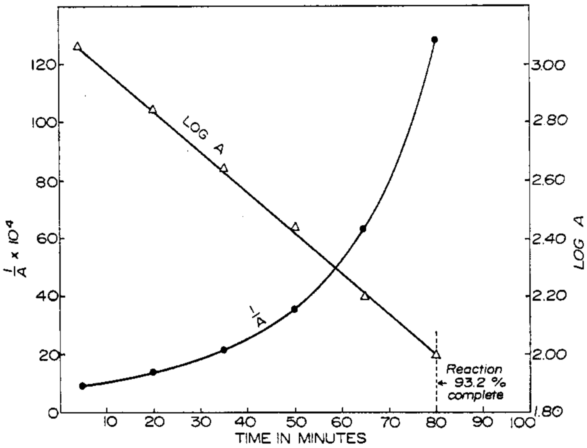

Fig. 1. Graphs of 1-hexyne peak areas (sq. mm.) as a function of the time for experiment No. 1. No tetrahydrofuran present

It seemed possible that the explanation of the first-order kinetics might be that these Grignard reagents were colloidal. Evans and Pearson[8] concluded on the basis of the behavior during electrolysis, Tyndall beam observations, and the color of the solutions that phenylmagnesium bromide in ethyl ether is, at least in part, colloidal. Slough and Ubbelohde[9] found, from vapor pressure data that trace amounts of oxygen in ethyl ether solutions caused the apparent molecular weight of phenylmagnesium to increase.

In order to break up the colloid believed to be present, tetrahydrofuran was added as a cosolvent to the phenylmagnesium bromide in ether. This

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TABLE I

INITIAL CONCENTRATIONS AND OTHER DATA

Expt. No.	Initial Molarities		THF Conc.	Rate Constants[d]		Relative Reactivities
	C_6H_5MgBr	1-Hexyne		sec.$^{-1}$	l × mole^{-1} × sec.$^{-1}$	
1	0.60	0.60	0	5.2×10^{-4}	—	70–110
2[a]	0.36	0.36	2.4[b]	—	1.2×10^{-4}	4–8
3[a]	0.45	0.45	0.25[c]	—	0.86×10^{-4}	3–6
4[a]	0.45	0.45	0.25[c]	—	0.70×10^{-4}	4–8
5	0.46	0.46	0	5.5×10^{-4}	—	70–110
6	0.46	0.46	0.25[c]	—	3.8×10^{-4}	15–25

[a] Old reagent. [b]:Molarity. [c] Mole ratio, THF/ether. [d] For 40°. [e] Estimated for 35° and relative to the reactivity of ethylmagnesium bromide taken as 100 (*cf.* ref. 4a).

cosolvent was chosen since it is known to be an effective Grignard reagent solvent, being in most cases better than ether,[10–12] and also because previous study[4b] had shown the rate of reaction of ethylmagnesium bromide with 1-hexyne, is not influenced by the presence of tetrahydrofuran. In our study the presence of tetrahydrofuran as a cosolvent brought about a change in the kinetic order of the reaction between phenylmagnesium bromide and 1-hexyne as compared to the reaction in ether alone. Figure 2 shows plots of $1/A$ *vs.* *t* and *log A vs. t*. The former is very nearly linear and indicates that with tetrahydrofuran present the reaction is close to second order. It will be noted, however, that the rate of the reaction is decreased by the presence of tetrahydrofuran. Figure 2 shows some results for the old reagent; the new reagent showed the same change to second-order kinetics and a decrease in rate, though a much smaller decrease. In later experiments it was noted that some precipitate was formed when tetrahydrofuran was added to the aryl Grignard reagent. Analysis of the precipitate for basic magnesium and for halide content revealed that the precipitate was mainly magnesium bromide. At a similar ratio of tetrahydrofuran to ether (1:4), we found that a precipitate also forms in the ethylmagnesium bromide system. One might have expected that the effect of such a precipitation on the rates of reaction of Grignard reagents with 1-hexyne would be similar to that observed on adding dioxane,[4c] *i.e.*, the rate would be enhanced. However, the effect in this case was just the opposite. Also, the reduction in rate was not what would be expected if the role of the tetrahydrofuran were only to disperse a colloid, unless, for some unknown reason, colloid is more reactive than the dispersed solute.

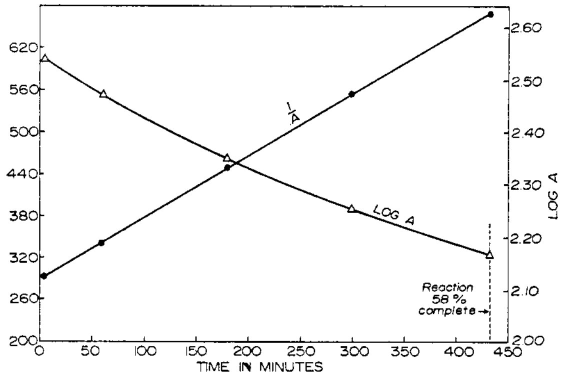

Fig. 2. Graphs of 1-hexyne peak areas (sq. mm.) as a function of the time for experiment No. 2. Tetrahydrofuran was present

That there was strong interaction between the tetrahydrofuran and phenylmagnesium bromide, but not between tetrahydrofuran and the product of the reaction with 1-hexyne, was evident by the following results: The concentration of tetrahydrofuran in the vapor in equilibrium with the solution of phenylmagnesium bromide in ether–tetrahydrofuran mixtures was less than that in the vapor in equilibrium with the same ether–tetrahydrofuran mixture when the phenylmagnesium bromide was absent. As the reaction with 1-hexyne proceeded the concentration of the tetrahydrofuran in the vapor increased until at the end of the reaction it was essentially the same as that in the vapor above the mixture that did not contain Grignard reagent.[13] These results were the same for both the new and old reagents.

It was pointed out in an earlier publication[14] that the logarithm of the relative reactivities of alkylmagnesium bromides toward 1-hexyne is a linear function of the decomposition voltages of those Grignard reagents. Because those relative reactivities were determined at 35 ± 2° and for $1M$ initial concentrations and because the present results were determined at 40° and initial concentrations between 0.36 and $0.60M$, accurate compari-

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(13) In another investigation in this laboratory a comparison of the concentration of tetrahydrofuran in the vapor in equilibrium with mixtures of ether and tetrahydrofuran, with and without solutes, has been used to obtain information about the interaction between these solutes and tetrahydrofuran. For the solute phenylmagnesium bromide the complex indicated by these results is $C_6H_5MgBr \cdot THF$ or $(C_6H_5)_2\ Mg \cdot MgBr_2 \cdot 2THF$.

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sons are not possible. It is possible to give the ranges of estimated values shown in Table I. These estimated relative reactivities are calculated for 35° and 1*M* initial concentrations and are on the same scale as those previously published,[4a] *i.e.*, with the reactivity of ethylmagnesium bromide taken as 100. The only value which is close to the value of 25 reported by Dessy and Salinger[5] for phenylmagnesium bromide in ether is that for experiment No. 6, which is the freshly prepared reagent in ether–tetrahydrofuran. The value calculated from decomposition voltages[15] by use of the empirical logarithmic plot[14] is 4, which is much lower than all values except those for the old reagent in the ether–tetrahydrofuran mixtures.

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[CONTRIBUTION FROM MELLON INSTITUTE]

Ozonolysis of Acenaphthene

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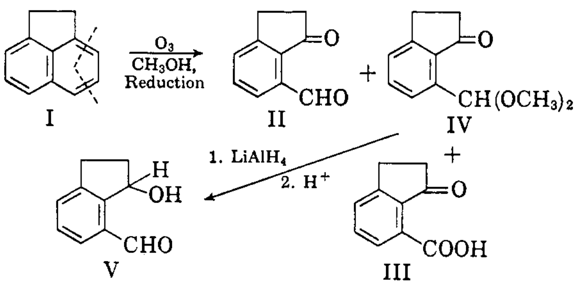
The ozonolysis of acenaphthene with two molecular equivalents of ozone was conducted in the participating solvents, methanol and *t*-butyl alcohol. By reduction of the primary ozonolysis products, 7-formyl-1-indanone was obtained as the major product along with a low yield of 1-indanone-7-carboxylic acid. The dimethyl acetal of 7-formyl-1-indanone was also prepared and characterized. Lithium aluminum hydride reduction of the acetal gave a good yield of material believed to be 7-formyl-1-indanol.

Previous work in this laboratory on the ozonolysis of acenaphthylene[1c] indicated that the use of excess ozone (more than one molecular equivalent) resulted in attack upon the naphthalene nucleus. It seemed of interest, therefore, to determine how the parent compound, acenaphthene, would behave when exposed to the action of ozone. The ozonolysis of acenaphthene has recently been reported by Copeland and associates.[2] By using two molecular equivalents of ozone and an oxidative work-up, which was not further described, they obtained a 24% yield of hemimellitic acid. No other products were identified. Our previous experience in the ozonolysis of fluoranthene[3] and Bailey's excellent work on the ozonolysis of naphthalene[4] indicated that 7-substituted derivatives of 1-indanone might be obtained from the ozonolysis of acenaphthene by using mild work-up procedures. To avoid the formation of unstable ozonides, methanol and *t*-butyl alcohol were used as participating solvents.

DISCUSSION

I. The ozonolysis reaction. It was anticipated that ozone would attack acenaphthene (I) at two bonds of one of the aromatic rings. The fact that ozone absorption was quantitative until almost two molecular equivalents of ozone were absorbed indicated the actual occurrence of such a reaction. A sharp decrease then occurred in ozone absorption. Such an attack would split off two carbon atoms from the aromatic nucleus and leave an indane skeleton substituted at the 1- and 7- positions. Research was directed toward determining ozonolysis conditions and work-up procedures that would yield optimum quantities of 7-formyl-1-indanone (II) and 1-indanone-7-carboxylic acid (III). These products, as well as the dimethyl acetal of 7-formyl-1-indanone (IV), were isolated, the isolation being dependent on the solvent used for ozonolysis and the method of work-up used.



Reduction of the product of the ozonolysis of acenaphthene in methanol was attempted to obtain a satisfactory yield of 7-formyl-1-indanone. When potassium iodide was the reducing agent, a mixture of 7-formyl-1-indanone and its dimethyl acetal was obtained. It was necessary to conduct the ozonolysis at a reduced temperature (−20° was effective) and to start the reduction while the solution was still cold to prevent undesirable side

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(1)(a) To whom requests for reprints should be mailed. (b) United States Steel Corp., Applied Research Laboratory, Monroeville, Pa. (c) R. H. Callighan, M. F. Tarker, Jr., and M. H. Wilt, *J. Org. Chem.*, 26, 1379 (1961).

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