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THE SCHLENK EQUILIBRIUM AND THE RELATIVE REACTIVITY OF BUTYLMAGNESIUM COMPOUNDS IN DIETHYL ETHER AND IN TETRAHYDROFURAN

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The addition of the various butylmagnesium compounds to acetone in ether and in tetrahydrofuran has been studied kinetically by means of a thermographic method (1,2). The use of a flowing stream reactor permitted the study of fast reactions with half lives from 0.002 to 10 seconds. By using a calorimeter and automatic recording of the temperature the range of the method may be extended to reactions with half lives from 10 to 10^4 seconds.

A comparison has been made between the initial rates of reaction of butylmagnesium compounds and six different types of substrate. The substrates were chosen in an attempt to pick reactions which are known to give a relatively high yield of just one main product, and which must be assumed to react by mechanisms of widely different type. The substrates were: acetone (2), methyl acetate (3), methyl trifluoroacetate (4), sec.butyl crotonate (5), azobenzene (6), and 1-hexyne (7).

Since it has been found (1) that reaction products like magnesium alkoxides etc. may coordinate with unreacted Grignard reagent, only initial rates were compared. The value was obtained from the slope of the plot of temperature versus time. Obtaining the true value of initial rate may require a certain amount of interpretation since a small more or less sudden "jump" in temperature is usually observed when mixing Grignard solution and substrate. The rates were expressed in °C per second but with knowledge of Δ T for total reaction of 1 molar substrate the values may be converted into moles liter^{-1} sec^{-1}.

The method has been used to study details of the kinetics of some of the reactions to be published elsewhere (3). In general the reactions when judged by the initial rates, seem to be second order in tetrahydrofuran, while the reaction order in ethyl ether may vary depending on the ratio of the concentrations of Grignard reagent and substrate. When the Grignard reagent is in excess the addition to acetone and methyl acetate tends to be zeroth or very low order in Grignard reagent and 1. order in substrate, but when these substrates are in excess, second or higher order in substrate concentration is observed. The remaining four substrates react in ether according to straight second order kinetics or they represent a compromise between second order kinetics and "acetone kinetics".

One tenths molar concentrations of substrate were used throughout. The Grignard reagent was used in a concentration of 0.5 normal as determined by titration with standard acid, dibutylmagnesium solutions being 0.25 molar. The reaction mixtures were obtained by mixing equal volumes of reagents of twice this strenght. The solutions were kept at 20° until mixing, which occurred in the flowing stream reactor for fast reactions and for slow reactions in a light-weight Dewar flask. The results were not corrected for heat uptake by the calorimeter or by the reaction tube, or for exchange of heat with the surroundings. The temperature was measured with a copper-constantan thermocouple. The results are shown in Table 1.

It is seen that there is a remarkable consistency in the relative reactivity of the various butylmagnesium reagents toward the different substrates.Except for the 1-hexyne reaction there is a tendency to a 400 fold greater reactivity of dibutylmagnesium than of butylmagnesium iodide in ether solution toward all substrates. Butylmagnesium bromide in ether solution reacts 4 times faster than the iodide and the chloride (less regularly) 20-30 times faster than the bromide. In tetrahydrofuran the reactivity varies much less being only 40 % increased from butylmagnesium bromide to dibutylmagnesium.

It seems an obvious possibility to explain these results in terms of the Schlenk (8) equilibrium:

$$R_2Mg + MgX_2 \rightleftharpoons 2\ RMgX$$

TABLE 1.

Initial reaction rates at 20° expressed in °C per second for 0.5 molar substrate with 0.5 molar butylmagnesium reagent.

	Acetone		Methyl acetate		Azobenzene		Methyl trifluoro-acetate		1-Hexyne		sec.Butyl crotonate	
	Ether	THF	Ether	THF	Ether	THF	Ether	THF	Ether	THF	Ether	THF
$(C_4H_9)_2Mg$	2000	25	23	0.30	1.02	1.40	3000	15	0.0080		15.5	0.27
C_4H_9MgCl	390	19	6.5	0.28	1.02	1.40	600		0.0029		1.7	
C_4H_9MgBr	21.6	18	0.23	0.23	0.025	1.0	30	11	0.00033		0.28	0.24
C_4H_9MgJ	6.0		0.053		0.0023		7.2		0.00040		0.07	
Δ T, 1 molar	150°		250°		140°		160°		60°		120°	

Like House and Traficante (9) one may assume that dialkylmagnesium is the only active entity in a Grignard solution, and that the Schlenk equilibrium is so fast that the dissociation of RMgX into R_2Mg and MgX_2 is never limiting the rate of reaction. In this way the dibutylmagnesium content of a 0.5 M Grignard reagent in diethyl ether may be estimated to be the following percentage of the maximal possible: butylmagnesium iodide 0.25 %, butylmagnesium bromide 1.0 %, butylmagnesium chloride 20 %*. The corresponding concentrations of dibutylmagnesium for Grignard reagents in tetrahydrofuran solution would be: butylmagnesium bromide 70 %, butylmagnesium chloride ca. 90 %.

Estimation of the position of the Schlenk equilibrium has been attempted by means of precipitation of magnesium bromide with dioxane (10), but the results of course give no information about the equilibrium before the dioxane addition. The results obtained by Becker and Smith (11) by thermometric titration indicate an 8 % content of diethylmagnesium in a 0.1 M solution of ethylmagnesium bromide in diethyl ether, while the results obtained by Mosher and Salinger (12) by infrared analysis seemed to indicate the presence of 25 % dimethylmagnesium in solutions of methylmagnesium bromide or methylmagnesium chloride in tetrahydrofuran.

In order to test the validity of the theory presented

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*For dimerized organomagnesium compounds like butylmagnesium chloride in ether solution (13), the equilibrium between active and inactive reagent may be: $R_2MgMgX_2 \rightleftharpoons (RMgX)_2$.

above thermometric titrations of 0.2 M magnesium bromide solution with 0.2 M dibutylmagnesium solution were undertaken in ether and in tetrahydrofuran using the principle of Smith and Becker (11). The results indicated approximately 98 % conversion to butylmagnesium bromide in ether ($K_{Eq} = 4 \cdot 10^4$). ΔH for the reaction was 2.2 kcal/mole. In tetrahydrofuran ΔH was negative being -3.3 kcal/mole. The extent of the reaction between dibutylmagnesium and magnesium bromide at 0.1 M concentration in tetrahydrofuran was found to be ca. 60 % ($K_{Eq} = 9$).

These results are consistent with the theory of inactivity of RMgBr in ether solution, while the same species in tetrahydrofuran solution must be reactive to some extent.

It was observed that equilibrium by reaction of dibutylmagnesium with magnesium bromide was established within a fraction of a second. For determination of the actual rate a special technique must be applied. Details of the thermometric titrations will be published elsewhere (3).

While the reactivity of dibutylmagnesium towards acetone, methyl acetate, methyl trifluoroacetate, and sec.butyl crotonate is about 100 times lower when dissolved in tetrahydrofuran than when dissolved in diethyl ether, it is interesting to note that the reactivity of dibutylmagnesium toward azobenzene is increased in tetrahydrofuran, and butylmagnesium bromide is even 40 times more reactive in tetrahydrofuran than in diethyl ether. Addition of 5-10 % of tetrahydrofuran shortly after mixing equal volumes of 0.2 M azobenzene with 1.0 M butylmagnesium bromide in diethyl ether caused an instantaneous 3-12 fold increase in rate. This extraordinary reactivity of butylmagnesium compounds in tetrahydrofuran may be connected with the specific (radical-type ?) mechanism for this reaction.

The rates observed for the reaction between 1-hexyne and butylmagnesium reagents in ether vary only 20 times from 0.5 M butylmagnesium iodide to 0.25 M dibutylmagnesium and the bromide is less active than the iodide. This suggests a role for the magnesium halide in the reaction.

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