Journal of Organometallic Chemistry, 56 (1973) 87–93

THERMOCHEMISTRY OF GRIGNARD REAGENTS. ENTHALPIES OF FORMATION OF ALKYLMAGNESIUM BROMIDES AND OF ALKYL BROMIDES

TORKIL HOLM
Institute of Organic Chemistry, Technical University of Denmark, DK-2800, Lyngby (Denmark)
(Received December 5th, 1972)

SUMMARY

The enthalpies of reaction of 17 alkyl halides with magnesium metal in diethyl ether were measured by use of a steady-state heat flow calorimeter. Enthalpies of formation of the alkyl bromides were determined via the enthalpies of reaction of the alkylmagnesium bromides with hydrogen bromide. The carbon–magnesium bond dissociation energies in alkylmagnesium bromides increases in the order: tert-butyl, allyl, benzyl, sec-butyl ≃ isopropyl, ethyl, isobutyl, n-butyl, methyl, and phenyl.

INTRODUCTION

Thermochemical data for organomagnesium compounds are scarce, although they should be useful in view of the versatility of the Grignard reagent. Carson and Skinner[1] observed an enthalpy of reaction for methyl iodide and magnesium in ether of 65.4 kcal/mole by use of an adiabatic calorimeter *in vacuo*. Smith and Becker[2] measured the enthalpy of reaction of magnesium bromide and magnesium iodide with diethylmagnesium and diphenylmagnesium in ether (the Schlenk equilibrium). Recently Hull *et al.*[3] determined the enthalpy of formation of dicyclopentadienylmagnesium.

In the present investigation a simple reaction calorimetric arrangement has been developed which allows the measurement of the reaction of magnesium with alkyl halides with a reproducibility of 0.2–0.4%. A series of 17 alkyl halides was studied. The purpose of the investigation was to survey the effect of structure on the enthalpy of reaction and to study the variation of the bond dissociation energies of the carbon–magnesium bond.

RESULTS AND DISCUSSION

The principle of the calorimetric procedure was the addition of an alkyl halide to an excess of magnesium in ether at a constant rate. The temperature of the thermostat water surrounding the calorimeter was adjusted until a steady state was obtained in which the temperature of the calorimeter remained constant. The flow of alkyl halide was then stopped, and from a regulated power supply the exact current which maintained the temperature of the calorimeter was passed through a heating coil. From the relation between the feed rate of the halide and the equivalent electrical effect, the enthalpy of reaction was calculated. The precision of the determination of the electrical effect was 0.2–0.4 %, but for reasons mentioned below the accuracy of the results is considered to be ±1%.

The formation of Grignard reagents from magnesium and alkyl halide [eqn. (1) below] is accompanied by some "Wurtz" reaction, in which alkyl halide is converted directly into hydrocarbons and magnesium halide as shown in eqns. (2) and (3). The extent to which the side reactions have taken place is measured by comparing the halide ion titration of the Grignard reagent (after decomposition with water) with the base equivalent. The value of [(halide − base)/halide] × 100 is the percentage of the halide which has undergone the "Wurtz" reaction. In order to be able to establish the true value of the enthalpy of reaction of (1), it is necessary to know both the extent and the true nature of the side reactions. The three main schemes for the reaction of alkyl halides with magnesium in ether are the following:

$$\mathrm{RX(liq)+Mg\rightarrow RMgX(sol)} \tag{1}$$

$$\mathrm{RX(liq)+\tfrac{1}{2}Mg\rightarrow \tfrac{1}{2}R{-}R(liq)+\tfrac{1}{2}MgX_2(sol)} \tag{2}$$

$$\mathrm{RX(liq)+\tfrac{1}{2}Mg\rightarrow \tfrac{1}{2}R(-H)(liq)+\tfrac{1}{2}R(+H)(liq)+MgX_2(sol)} \tag{3}$$

Very small amounts of other side products may occur in some cases. A detailed analysis of the hydrocarbon reaction products was not carried out in the present work since there is evidence[4,5] indicating that reaction (3) is the predominant side reaction in the case of alkyl halides branched in the α-position, while reaction (2) prevails if the alkyl is primary or devoid of hydrogen in the β-position, and these generalizations were assumed to apply in the cases under study.

The enthalpy of reaction of the side reactions of each alkyl bromide used was calculated from the known enthalpy of formation of the hydrocarbons in the liquid state, and the value −133.6 kcal/mole for the enthalpy of formation of magnesium bromide in ether solution (the determination of this value is described below). Neither the small contributions of the enthalpy of solution of alkyl halides and hydrocarbons in ether nor the enthalpy of vaporization of the very small fraction of alkane present in the gas phase were taken into account. The enthalpy of reaction for the isolated Grignard reagent formation [eqn. (1)] could now be calculated. The values of ΔH_r for reaction (1), (2), and (3) are given in Table 1. Except for tert-butylmagnesium bromide, the correction from $\Delta H_{r(\mathrm{obs})}$ to $\Delta H_r(1)$ is seen to be much less than 1 %.

The enthalpies of reaction measured in this way permit an estimate of the differences between the carbon–magnesium bond dissociation energies of various types of alkylmagnesium bromides.

From the reaction schemes

$$\mathrm{R{\cdot}(g)+Br{\cdot}(g)\xrightarrow{D(\mathrm{RBr})}RBr(g)\xleftarrow{\Delta H_v(\mathrm{RBr})}RBr(liq)}$$

it follows that:

$$\Delta H_f^0[\mathrm{R{\cdot}(g)}]=D(\mathrm{R{-}Br})-\Delta H_f^0[\mathrm{Br{\cdot}(g)}]+\Delta H_f^0[\mathrm{RBr(liq)}]+\Delta H_v(\mathrm{RBr})$$

From the equations

$$\mathrm{R{\cdot}(g)} + \mathrm{{\cdot}MgBr(g)} \xrightarrow{D(\mathrm{R-Br})} \mathrm{RMgBr(g)} \xleftarrow{\Delta H_v(\mathrm{RMgBr})} \mathrm{RMgBr(liq)}$$

it follows that

$$\Delta H_f^0[\mathrm{R{\cdot}(g)}] = \Delta H_f^0[\mathrm{RBr(liq)}] + \Delta H_r(1) + \Delta H_v(\mathrm{RMgBr}) - \Delta H_f^0[\mathrm{{\cdot}MgBr(g)}] + D(\mathrm{R-MgBr})$$

For the purpose of calculating the difference in the bond dissociation energy on going from one alkyl to another, all terms which are invariant with R can be ignored and the following expression for the bond dissociation energy is arrived at:

$$D(\mathrm{R-MgBr}) = D(\mathrm{R-Br}) - \Delta H_r(1) + \Delta H_v(\mathrm{RMgBr}) - \Delta H_v(\mathrm{RBr}) + \mathrm{Constant}$$

The difference between the enthalpies of vaporization of RBr and RMgBr, although unknown and presumably inaccessible, may be expected to be relatively constant, and thus the value of $D(\mathrm{R-Br}) - \Delta H_r(1)$ should be useful for calculating the increments in the bond dissociation energies of alkylmagnesium bromides when changing from one R to another. The values of $D(\mathrm{R-Br}) - \Delta H_r(1)$ for various R groups are given in Table 1.

From the values of $D(\mathrm{R-Br}) - \Delta H_r(1)$ it can be concluded that the R–MgBr bond strength is constant for the various primary alkyl groups such as ethyl, butyl, and isobutyl. For methyl and phenyl the value is 11–12 kcal/mole higher, and for isopropyl, sec-butyl, and tert-butyl it is lower by 5, 5, and 15 kcal/mole respectively. The carbon–magnesium bond dissociation energy for R = tert-butyl is thus lower than for benzyl and allyl even though these groups form bonds to magnesium which are 8 kcal/mole weaker than the bonds formed with primary alkyls.

Whether steric or electronic factors are the cause of the low bond energy in tert-butyl and sec-butylmagnesium bromide remains undecided. No serious increase in steric inhibition should result, however, on going from methyl- to ethylmagnesium bromide and thus the large decrease in bond energy in this case may be due to the electron-donating ability of the α-methyl group. Increased electron density at the carbon attached to magnesium undoubtedly accounts for the indicated decrease in bond strength in *p*-methylphenylmagnesium bromide as compared with that in phenyl- or *p*-chlorophenylmagnesium bromide. The extremely low bond dissociation energy in tert-butylmagnesium bromide is not surprising, since both electronic and steric factors operate to weaken the bond.

The correction of the values of $\Delta H_{r(\mathrm{obs})}$ for the heat produced in the side reactions (2) and (3) as mentioned above, required the determination of the enthalpy of formation of magnesium bromide when dissolved in diethyl ether. This was attempted in three different ways. The direct attack of bromine on magnesium in ether was carried out in the calorimeter and an enthalpy of reaction of −133.3 kcal/mole was measured. However, since hydrogen gas was also produced it was concluded that side-reactions were taking place. Next measurement of the enthalpy of reaction of Grignard reagents with bromine was examined; this reaction combined with the formation reaction (1) is equivalent to the formation of magnesium bromide from magnesium and bromine:

TABLE 1

ENTHALPIES OF REACTION, $\Delta H_{r(obs)}$ OF MAGNESIUM METAL WITH ALKYL HALIDES IN DIETHYL ETHER

Extent of Wurtz-like side reactions given as % X^-. Calculated values of ΔH_r of side reactions. Enthalpies of reaction of Grignard reagents with bromine [$\Delta H_r(4)$] and with hydrogen bromide [$\Delta H_r(5)$]. Enthalpies of formation of Grignard reagents (ca. 0.5 *M*) in diethyl ether. Relative strengths of carbon–magnesium bonds. Enthalpies of formation of RBr. All values in kcal/mole.

RX	$-\Delta H_r(1)$	$\%X^-$	$-\Delta H_{r(obs)}$	$-\Delta H_r(2)$	$-\Delta H_r(3)$	$-\Delta H_r(4)$	$-\Delta H_r(5)$	$D(C-Br)-\Delta H_r(1)$	$\Delta H_f^0[RBr(liq)]$		$\Delta H_f^0[RMgBr(s)]$
									Present work	*Literature*[8]	
CH_3Br	64.0	0.5	69.5	69.9		69.0		134.0		−15.1	−79.1
C_2H_5Br	53.6	4.4	54.1	64.0				122.6		−21.8	−75.4
$(CH_3)_2CHBr$	50.5	12.7	50.6		51.0	84.3	72.0	118.5	−30.9	−30.7	−81.4
C_4H_9Br	55.9	3.4	56.1	63.6		77.0	69.0	124.9	−35.4	−34.4	−91.3
i-C_4H_9Br	54.4	8.9	55.2	63.2			69.2	123.4	−38.3		−92.7
s-C_4H_9Br	50.3	16.0	50.7		52.6		72.8	118.3	−37.2	−37.2	−87.5
t-C_4H_9Br	47.3	30.0	48.7		51.9		75.4	110.3	−39.2	−39.3	−86.5
C_3H_5Br	67.3	14.5	66.7	63.1			60.5	114.3	4.7	3.0	−62.6
$C_6H_5CH_2Br$	65.9	3.3	65.8	63.9		68.9	61.3	116.9	5.2	5.6	−60.7
p-$CH_3C_6H_4Br$	61.4	4.0	61.8	(70.8)			62.7		2.9		−58.5
C_6H_5Br	64.3	1.9	64.4	70.8		70.0	62.9	135.3	14.0	14.5	−50.3
p-ClC_6H_4Br	66.9	4.7	67.1	(70.8)			62.2		6.8		−60.1
CH_3I		2.3	59.3								
C_2H_5I			52.6								
C_4H_9I			51.9								
C_4H_9Cl		1.6	51.3								
$C_6H_5CH_2Cl$			66.9								

$$\mathrm{RX(liq) + Mg \rightarrow RMgBr(sol)} \tag{1}$$

$$\mathrm{RMgBr(sol) + Br_2(liq) \rightarrow RBr(liq) + MgBr_2(sol)} \tag{4}$$

Several Grignard reagents were treated with bromine (Table 1), and the sums of $\Delta H_r(1) + \Delta H_r(4)$ were compared. An average value of -133.7 kcal/mole was found, but since some values deviated by 2–3% and the results were not very reproducible, it was again concluded that side-reactions occur and that $\Delta H_r(4)$ may be used only as a crude check of the values obtained for $\Delta H_r(1)$.

The best value for the enthalpy of formation of magnesium bromide was finally obtained by determining the enthalpy of reaction of hydrogen bromide with alkylmagnesium bromide:

$$\mathrm{RMgBr(s) + HBr(g) \rightarrow RH(liq) + MgBr_2(s)} \tag{5}$$

The calorimetric procedure was similar to that used in the determination of $\Delta H_r(1)$, a constant stream of HBr being passed into the calorimeter containing the Grignard reagent. Knowledge of $\Delta H_r(5)$, together with the known enthalpy of formation of the hydrocarbons, allowed the calculation of the enthalpy of formation of the alkyl bromide according to the equation:

$$\begin{aligned}\Delta H_f^0[\mathrm{RBr(liq)}] = -\Delta H_r(1) - \Delta H_r(5) + \Delta H_f^0[\mathrm{RH(liq)}]\\ +\Delta H_f^0[\mathrm{MgBr_2(s)}] - \Delta H_f^0[\mathrm{HBr(g)}]\end{aligned}$$

The enthalpy of formation of sec-butyl bromide has been determined accurately and with consistency by different methods[7], and must be considered known within ±0.3 kcal/mole. Since the reaction of Grignard reagents with hydrogen bromide is probably free of any side reactions, the value -37.2 kcal/mole for ΔH_f^0[sec-butyl bromide(liq)] was taken as the basis for the determination of the enthalpy of formation of magnesium bromide in ether solution, which by means of the equation above was found to be -133.6 ± 1 kcal/mole. By use of this value the enthalpies of formation of 9 other alkyl bromides were determined, and with a few exceptions satisfactory agreement with literature[8] values was obtained, as shown in Table 1. The accuracy of the determinations is probably of the order of ±1 kcal/mole. No corrections were made for the heat of mixing of alkyl halides and of hydrocarbons with ether, nor for the temperature difference between the calorimeter and the added reactant. It was estimated that these corrections would not exceed 0.3–0.4 kcal/mole.

EXPERIMENTAL

Materials

Sublimed magnesium ("Specpure" Johnson, Matthey Chemicals Ltd.) was used. Commercial alkyl halides were fractionally distilled and checked for purity by NMR and GLC. Impurities were < 1.0%. Ether was freshly distilled from lithium aluminum hydride.

Apparatus

The calorimeter consisted of a jacketed 500 ml flask with magnetic stirrer and a 39.65 Ω Constantan heating coil made from 0.1 mm cotton insulated Constantan wire wound around a 1.5 mm polyethylene tube and sealed with "Araldite" epoxy resin. The calorimeter was closed with a B 29 standard-taper rubber-sealed adaptor which fitted the Beckman thermometer and the leads for the heating coil vacuum-tight to the flask. The adaptor had a glass capillary inlet for the halide (respectively bromine or hydrogen brodide). On the inside a piece of 1.5 mm polyethylene tubing led to the bottom of the flask and on the outside the capillary was connected to the motor burette by means of a glass capillary. The pure alkyl halide was contained in a 20 ml "Methrom" piston burette which was driven by a synchronous motor and delivered 20 ml/180 min, ≈ 1.8517 μl/sec.

Procedure

The calorimeter, containing a Teflon stirring bar and 15 g magnesium, was closed with a rubber stopper, evacuated, and filled with 300 ml absolute diethyl ether. It was then heated to 35°, and the rubber stopper was replaced with the B 29 adaptor containing the Beckman thermometer, heating coil, and feeding tube. The calorimeter assembly was placed in the plastic tank of the water thermostat over the magnetic stirring motor, which was then started. After 30–60 minutes the reaction had reached its equilibrium rate and the water thermostat was regulated until the reading of the Beckman thermometer was constant within ±0.005°. The adjustment required from 30 to 90 minutes. After obtaining the steady state the flow of halide was stopped and the heating coil was connected to a regulated DC power supply which had a 10-turn regulating potentiometer covering the range 5–21 V. The reading of the Beckman thermometer was kept constant by regulating the voltage, which was read to 0.01 V by means of a calibrated "Takeda-Riken" TR 6834 digital voltmeter. The regulation required 30–60 minutes and the electrical effect in cal/sec was calculated from the voltage and the resistance in the heating coil (39.65 Ω) and in the leads (0.06 Ω).

The molarity of the halide was found from the density at the working temperature, and the molecular weight and the molarity multiplied by the burette displacement per sec gave the rate of addition. The thermal effect divided by the rate of addition gave the heat of reaction of the liquid alkyl halide with magnesium in diethyl ether containing 0.3–0.6 *M* alkylmagnesium halide. The heat of dilution of 0.6 *M* Grignard reagent is insignificant.

Since methyl bromide boils at 3.6°, it was kept in an ampoule at 0° and was displaced through an inlet and an outlet capillary by mercury from the piston burette. The liquid methyl bromide passed through a 2 m stainless steel capillary heating coil which was placed in the thermostat water. In order to derive the heat of reaction of liquid methyl bromide, the heat of vaporization (5.5 kcal/mole) was subtracted from the value obtained for gaseous methyl bromide.

For addition of liquid bromine a piston burette with 5 ml displacement/180 min was used. For addition of HBr a cylinder was placed in ice water and fitted with a glass capillary which was filled with compressed glass fibres. A stream of 17 μmol/sec was obtained which was constant within ±0.1% for 30–60 min. The exact value was found by leading the HBr stream into water for 100 sec and titrating with sodium hydroxide. The determination was made before and after each experiment.

REFERENCES

1 A. S. Carson and H. A. Skinner, *Nature*, 165 (1950) 484.
2 M. B. Smith and W. E. Becker, *Tetrahedron*, 22 (1966) 3027.
3 H. S. Hull, A. F. Reid and A. G. Turnbul, *Inorg. Chem.*, 6 (1967) 805.
4 H. Gilman and R. E. Fothergill, *J. Amer. Chem. Soc.*, 50 (1928) 3334.
5 V. V. Chelintsev, *Zh. Russ. Fiz. Khim. Obshch.*, 36 (1904) 549.
6 J. C. Greenbank and B. B. Argent, *Trans. Faraday Soc.*, 61 (1965) 655.
7 L. Bjellerup, *Acta Chem. Scand.*, 15 (1961) 121.
8 J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London, 1970.