Thermochemical Bond Dissociation Energies of Carbon–Magnesium Bonds

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The heats of formation of 29 alkylmagnesium bromides, isobutyl bromide, and neopentyl bromide have been determined, and bond dissociation energies have been derived for the Grignard reagents. For saturated alkyl derivatives the C–Mg bond strength decreases with an increasing number of β-hydrogens in the series methyl, neopentyl, isobutyl, butyl, ethyl, 1-ethylpropyl, 1-methylpropyl, isopropyl, and t-butyl. Bonding in alkyl bromides and alkylmagnesium bromides is discussed.

THOUGH Grignard reagents have been in use for 80 years, the thermochemistry of alkylmagnesium reagents still represents a rather undeveloped field.[1-7] Various problems in the preparation and handling of these reagents, paired with a tendency to by-product formation in their reactions, may explain this in part; nevertheless the reagents are in many ways ideal from the thermochemists point of view, since suitable reactions are clean, fast, complete, and highly exothermic.

The heats of formation of a series of 12 alkylmagnesium bromides were previously obtained from a study of reactions (1) and (2) using a heat flow calorimeter.[4] The

$$\mathrm{RBr(l) + Mg(s) = RMgBr(soln\ in\ ether)} \quad (1)$$

$$\mathrm{RMgBr(soln\ in\ ether) + HBr(g) =} \\ \mathrm{RH(soln\ in\ ether) + MgBr_2(soln\ in\ ether)} \quad (2)$$

agreement obtained between the two series of reactions was usually within 4—8 kJ mol^{-1}. Occasional discrepancies larger than those were attributed to systematic errors. Most of the work has now been repeated with a view to improving the accuracy. Seventeen alkyl bromides not previously studied have been included and an attempt has been made to derive values for the bond dissociation energy for the various types of carbon–magnesium bonds.

RESULTS

It was found that in the study of reaction (2) the most important source of error when using the calorimetric procedure described in ref. 4 was the change of vapour pressure in the calorimeter caused by the formation of gases. This resulted in a significant change in the heat transfer coefficient for the heat flow calorimeter due to a change in rate of reflux of the ether solvent from the uncovered walls. The error was almost eliminated by filling the calorimeter with ether, leaving only 10% empty space. Errors were introduced also by assuming that gaseous alkanes dissolve in ether with evolution of the full heat of vaporization. By measurements this was found to be true within experimental uncertainty for C_5 alkanes and higher, but incorrect for the lower alkanes. Corrections were made for C_1—C_4 alkanes. Several improvements were made in the construction of the calorimeter and in the thermochemical procedure and, benefitting from these, the results were usually reproducible to within ± 1 kJ mol^{-1} when using liquid alkanes, and ± 2.2 kJ mol^{-1} when using gaseous alkanes. The results are presented in the Table as values of $\Delta H_r(2)$ and as values of ΔH_f (RMgBr, soln) calculated from (2) using enthalpies of formation of R–H(l) from ref. 8. ΔH_f° ($MgBr_2$, soln in ether) $= -559$ kJ mol^{-1} was taken from ref. 4.

Included in the Table are enthalpies of reaction (1). The results for this reaction were less reproducible and probably less accurate. The 'Würtz'-like side reactions were estimated by titration of the excess bromide ion, but no determination was made of the hydrocarbons produced. However, it was assumed that (3) was the most important side reaction using primary alkyl derivatives whereas (4) became important in the case of secondary and tertiary alkyl bromides.

$$\mathrm{RBr(l) + \tfrac{1}{2}Mg(s) \longrightarrow} \\ \mathrm{\tfrac{1}{2}R{-}R(l) + \tfrac{1}{2}MgBr_2\ (soln\ in\ ether)} \quad (3)$$

$$\mathrm{RBr(l) + \tfrac{1}{2}Mg(s) \longrightarrow} \\ \mathrm{\tfrac{1}{2}R_{+H}(l) + \tfrac{1}{2}}R_{-\mathrm{H}}\mathrm{(l) + \tfrac{1}{2}MgBr_2\ (soln\ in\ ether)} \quad (4)$$

The enthalpies of reaction of the two types of side reactions were calculated using the literature values for the enthalpies of formation for the individual compounds.[4,8] When the excess of bromide over base in the Grignard reagent was found by titration as $r_{\text{Würtz}} = (T_{\text{Br}} - T_{\text{base}})/T_{\text{Br}}$ corrections were made for primary alkyls including phenyl according to equation (5). For secondary and tertiary alkyls $\Delta H_r(4)$ was used instead of $\Delta H_r(3)$.

$$\Delta H_r(1) = \Delta H_r(1)_{\text{obs}} - [\Delta H_r(3) - \Delta H_r(1)_{\text{obs}}]r_{\text{Würtz}} \quad (5)$$

The Würtz side reactions (3) and (4) were <4—5% of the total reaction except for secondary and tertiary alkyls and for allyl, which caused up to 30% Würtz-like side reactions.

Uncertainty in $\Delta H_r(1)$ was also introduced by impurities in the alkyl bromides. This problem was eliminated in the determination of $\Delta H_r(2)$ since here the Grignard reagent was in large excess. An idea of the accuracy of the measurements was obtained by using the results to calculate the heat of formation for the alkyl bromides, and comparing this with the values found in the literature.[8] Deviations were usually <2.2 kJ mol^{-1}.

DISCUSSION

One of the intentions of the investigation was to derive bond dissociation energies for the Grignard reagents. The enthalpy of reaction of (2) may be obtained as from equation (6). For the purpose of comparing the values of $\Delta H_r(2)$ when R is varied all enthalpy contributions involving magnesium bromide and hydrogen bromide may be represented by a constant (c_1). The enthalpy of sublimation of a Grignard reagent is unknown, but it seems reasonable to assume, as a first approximation, that ΔH_{sub} (RMgBr,c) and ΔH_{vap} (RH) will have the same increment for each added CH_2, and that the difference may therefore be represented by a constant (c_2). Likewise one may assume that the difference between the enthalpies of solution of RH,l and RMgBr,c will have a constant value (c_3). Equation (6) may then reduce to (7) where $c = c_1 - c_2 - c_3$.

$$\begin{aligned}\Delta H_r(2) = {} & D(\text{R–MgBr}) - D(\text{R–H}) + \\ & \Delta H_{sub}(\text{RMgBr,c}) - \Delta H_{soln}(\text{RMgBr,c}) + \\ & \Delta H_{soln}(\text{RH,l}) - \Delta H_{vap}(\text{RH}) + \\ & \Delta H_f(\text{MgBr}_2\text{,soln}) + \Delta H_f(\text{H}) - \\ & \Delta H_f(\text{MgBr,g}) - \Delta H_f(\text{HBr,g}) \qquad (6)\end{aligned}$$

$$D(\text{R–MgBr}) = D(\text{R–H}) + \Delta H_r(2) + c \qquad (7)$$

Enthalpies of reaction of alkyl bromides with magnesium in diethyl ether [$\Delta H_r(1)$] and of alkylmagnesium bromides with hydrogen bromide [$\Delta H_r(2)$]. Enthalpies of formation of alkylmagnesium bromides in diethyl ether and of liquid alkyl bromides. Bond dissociation energies of the carbon–magnesium bond derived from reaction (1), a, and from (2), b. Also given are the densities for the alkyl bromides used

	d_4^{20}(RBr)/ g cm^{-3}	$-\Delta H_r(1)$/ kJ mol^{-1} (± 4.4)	$-\Delta H_r(2)$/ kJ mol^{-1} (± 2.2)	$-\Delta H_f^\circ$(RMgBr) (soln in ether)/ kJ mol^{-1} (± 2.2)	ΔH_f°(RBr, l) [a]/ kJ mol^{-1} (± 4.4)	D(R–MgBr)/ kJ mol^{-1}	
						a	b
Methyl		267.8	274.5	331.8		251	255
Ethyl	1.4646	231.0	299.2	323.0		205	205
Propyl	1.3344	232.2		360.7		209	209
1-Methylethyl	1.3146	210.0	305.9	339.7		184	184
Butyl	1.2762	233.9	292.5	378.2		213	213
1-Methylpropyl	1.2616	211.7	305.9	368.2		187	184
Isobutyl	1.2698	237.3	289.1	391.6	154.3	213	
t-Butyl	1.2183	209.2	306.7	370.7		176	172
Pentyl	1.2177	236.4		406.7		209	209
1-Ethylpropyl	1.2149	215.5	306.3	389.9		190	184
Neopentyl	1.2073	251.5	286.6	430.1	−176.6	226	
Hexyl	1.1693	233.5		427.6		209	
Heptyl	1.1350	233.9		452.3		209	
Octyl	1.1090	233.5		478.6		209	
Nonyl	1.0866	231.0				205	
Cyclopropyl	1.5050		282.8	211.3	27.6		234
Cyclobutyl	1.4208	223.4	289.1	229.7	−6.3	205	205
Cyclopentyl	1.3875	223.0	291.6	336.8	−113.8	197	201
Cyclohexyl	1.3281	210.9	298.7	380.3	−169.5	188	192
Cycloheptyl			299.6	379.5		192	
Cyclo-octyl			295.0	395.4		197	
Vinyl			294.1 *	264.4 *		289	285
Allyl	1.4289	271.1	259.4	265.7		201	201
Benzyl	1.438	275.7	256.5	252.3		197	201
Phenylethynyl			169.9	69.5			
4-Methylphenyl		256.9	262.3	244.8			
Phenyl	1.4931	269.0	263.2	208.4		289	289
4-Chlorophenyl		279.9	260.2	251.5			
Triphenylmethyl			231.0	120.5			180

* THF.

[a] Values used in the calculations were usually taken from ref. 8. Values missing in ref. 8 were calculated from $\Delta H_r(1)$ and $\Delta H_r(2)$ and given in this column.

The values for $\Delta H_r(1)$ combined with the known values[9] for D(R–Br) allow the arrangement of a similar scale since equation (8) holds. In this case the increment in ΔH_{sub} (RMgBr,c) and ΔH_{soln} (RMgBr,c) are assumed to vary like the increments in ΔH_{vap} (RBr) and ΔH_{soln} (RBr,l). Since by comparison (Table) the two scales do not deviate seriously the assumptions seem justified.

$$D(\text{R–MgBr}) = D(\text{R–Br}) - \Delta H_r(1) + \text{constant} \qquad (8)$$

Determination of the constants in (7) and (8) and fixation of the scales required the determination of at least one value of D(R–MgBr) by an independent method. Since it is impossible to determine the absolute value of ΔH_v (RMgBr) an attempt was made to find a reaction in which fission of the carbon–magnesium bond is rate-limiting. This seems to be the case when t-butylmagnesium bromide is heated in ether to form isobutene and bromomagnesium hydride [reaction (9)]. The reaction was followed at temperatures between 140 and 200 °C and from an Arrhenius plot (Figure 1) an energy of activation of 166.5 kJ mol^{-1} and an entropy of activation of 50 J K^{-1} mol^{-1} were obtained. The high positive value of $\Delta S^\ddagger$ strongly suggests a fission in the rate-determining step and excludes any alternative, concerted mechanism. Addition to the reaction mixture of the radical scavenger styrene produced the addition product 3,3-dimethyl-1-phenylbutane, which is best explained as the result of homolysis of the reagent. D(Bu^t–MgBr) must then be larger or equal to 166.5 kJ

$$\text{Bu}^t\text{–MgBr} \xrightarrow{\Delta} \text{Bu}^{t}\cdot + \cdot\text{MgBr} \xrightarrow{\text{fast}} \text{isobutene} + \text{BrMgH} \qquad (9)$$

mol^{-1}. A theoretical calculation by Astier and Millié of the C–Mg bond strength in solvated MeMgF gave a value[10] of 263.6 kJ mol^{-1}. Considering both this theoretical value for D(Me–MgF) and the experimental value for D(Bu^t–MgBr) a correlation of the two scales was achieved by the use of +93.3 and −309.6 kJ mol^{-1} as the values of the constants in expression (7) and (8), respectively.

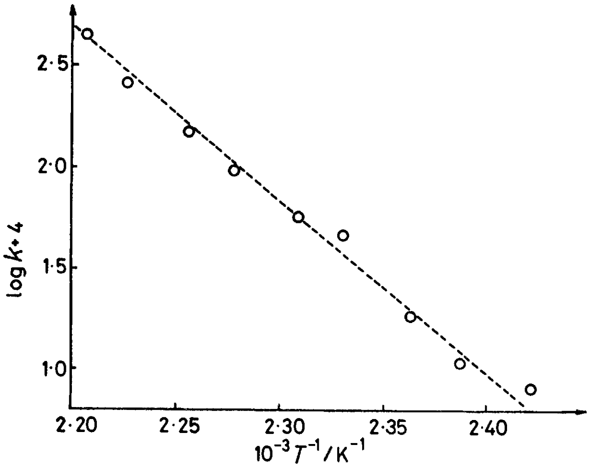

FIGURE 1 Arrhenius plot for the decomposition of t-butylmagnesium bromide in diethyl ether according to equation (7) (see text)

The resulting values of D(R–MgBr) are presented in the Table. A study of the Table shows that for saturated alkyl substrates the value of D(R–MgBr) decreases steadily with an increasing number of β-hydrogen atoms in the order: methyl (0), neopentyl (0), isobutyl (1), butyl (2), ethyl (3), cyclopentyl (4), cyclohexyl (4), 1-ethylpropyl (4), 1-methylpropyl (5), isopropyl (6), and t-butyl (9), as shown in Figure 2. This sequence is observed also, though less pronounced, for the bond strength of the carbon–hydrogen bond, and even for the carbon–bromine bond in which case the variation, however, is very low. Qualitatively these results may be explained by changes in hybridization during the homolysis. Considering the ground state of the molecules, both C–MgBr and C–Br bonds are polarized as compared with the C–H bond. The polarization causes changes in hybridization at the α- and β-carbons and the changes are more and more pronounced the more hydrogen atoms are placed at the β-carbons. By an instantaneous bond homolysis[11] of the bond to the α-carbon, a radical would be formed with bond angles and distances similar to those in the parent compound. The relaxation of this activated σ-radical to the radical in its normal state of hybridization represents a ' discount ' in the value of the bond dissociation energy.

The sequence of species arranged according to their decreasing electron deficiency or increasing negative charge at carbon is probably: alkyl radical, alkyl bromide, hydrocarbon, and alkylmagnesium bromide. This also represents a sequence of increasing s-character of the carbon orbital and of the resulting deviations in C–H and C–C bond lengths and bond angles. Since the electron deficiency in the bromide and the free radical are of the same order of magnitude, the rehybridization discount is low. In the hydrocarbon there is no deficiency of electrons at carbon and the rehybridization discount is more pronounced, but in Grignard reagents the negative charge on carbon causes a state of hybridization of the ground state which is further ' uphill ' from the hydrocarbon and a larger rehybridization effect is observed by homolysis.

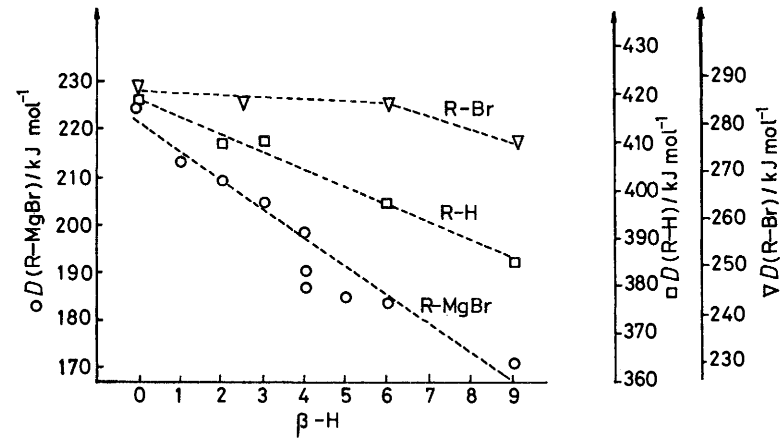

FIGURE 2 Bond dissociation energies in kJ mol^{-1} for alkanes, alkyl bromides, and alkylmagnesium bromides as a function of the number of β-hydrogens in the alkyl group

By an analogous reasoning the relative strong bond in allylmagnesium bromide may be explained by the similar geometries of the allylic anion and the allylic radical. The large rehybridization effect obtained by homolysis of allyl bromide and propene is not obtained by homolysis of allylmagnesium bromide because the anionic molecule is sp^2 hybridized almost like the radical.

$\Delta H_r(2)$ is a measure of the stability of an alkyl anion relative to the alkane if enthalpy is assumed to dominate over entropy factors. That this obtains is made likely by the linear correlation between $\Delta H_r(2)$ and known pK_a values for alkanes[12] (Figure 3). It seems safe to conclude that pK_a for alkanes increases in the order: methane, neopentane, isobutane, butane, ethane, cyclohexane, methylene of propane, and methine of isobutane. It may be possible even to use the relation in a quantitative manner.

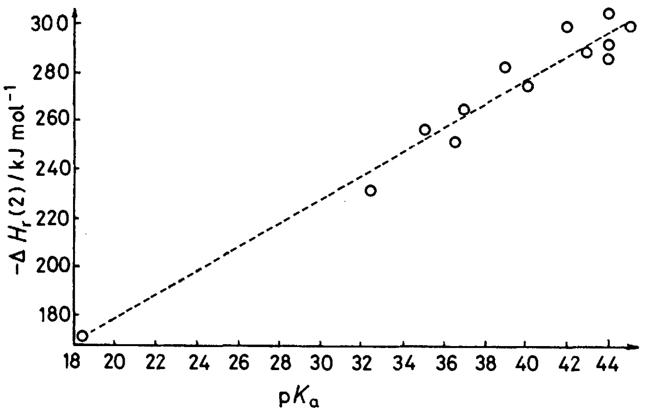

FIGURE 3 Enthalpy of reaction of alkylmagnesium bromides with hydrogen bromide as a function of the pK_a values of the alkanes

Many reactions of Grignard reagents are initiated by electron transfer. In the case of azobenzene and benzophenone it has been shown that the log rate is linearly correlated with the number of β-hydrogens in the Grignard reagent.[13] This means that single electron transfer is closely related to homolytic bond breaking.

EXPERIMENTAL

Materials and calorimetric procedure were as described,[4] with the improvements mentioned in the text. The kinetic measurements of the pyrolysis of t-butylmagnesium bromide in the ether were carried out by means of n.m.r. The reagent (*ca.* 1.0M) was sealed in an n.m.r. tube and heated in an oil thermostat in a protective metal tube which was half filled with ether. Determination of the Grignard concentration was performed by integration using the ether signals as an internal reference.

Scavenging of t-Butyl Radicals.—Heating 1M ethereal t-butylmagnesium bromide (10 ml) mixed with styrene (3 ml) to 180° for 30 min gave after work-up an oil (1.5 g) which according to n.m.r. and g.l.c.–m.s. contained 20% 3,3-dimethyl-1-phenylbutane and at least three isomeric diphenyl-t-butylbutanes, which are being studied further.

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