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THE THERMOCHEMISTRY OF ALKYLLITHIUM REAGENTS

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Summary

The enthalpies of formation of twelve alkyl- and aryl-lithium reagents have been determined by measurement of the enthalpies of reaction of the reagents with hydrogen bromide using a steady-state heat flow calorimeter. Approximate values for the bond dissociation energies of the carbon—lithium bond are derived.

Introduction

During the study of the enthalpies of formation of alkylmagnesium reagents [1] it became of interest to compare the values obtained with those for alkyllithium reagents. Only two earlier reports were found on this subject. Fowell and Mortimer [2] determined the heat of reaction of benzyl bromide with butyllithium and of butyllithium with water vapour, and from the results calculated an enthalpy of formation for butyllithium of — 31.4 ± 0.7 kcal/mol. Lebedev et al. [3] obtained a value of —32.0 ± 1.7 kcal/mol from combustion in a bomb of a syrupy butyllithium concentrate. The same workers found the enthalpy of formation of sublimed ethyllithium to be —14.0 ± 1.3 kcal/mol.

The three procedures described in the literature were all considered inaccurate and inconvenient, since they depended either on preparation and weighing of the isolated pure alkyllithium and/or on reactions which may yield unknown amounts of side products. As an alternative the reaction with hydrogen bromide, which was used previously with Grignard reagents [1], was found to be very suitable, since the limiting reactant was hydrogen bromide and the sole products were hydrocarbon and lithium bromide (eqn. 1).

$$\text{R—Li (s or c)} + \text{HBr(g)} \rightarrow \text{RH(l)} + \text{LiBr(c)} \qquad (1)$$

Results and discussion

The procedure was essentially the same as used with Grignard reagents and the reproducibility was within ± 0.2 kcal/mol. The reactions were usually carried out in petroleum ether in which the alkyllithium was either dissolved or dispersed. The enthalpy of formation of the alkyllithium was found from the enthalpy of reaction 1 according to:

$$\Delta H_f^0[\text{R—Li(c)}] = \Delta H_f^0[\text{R—H(l)}] + \Delta H_f^0[\text{LiBr(c)}] - \Delta H_f^0[\text{HBr(g)}] - \Delta H_r(1) \quad (2)$$

The results are given in Table 1.

By means of a few approximations, the enthalpy of reaction 1 allows an estimate of the relative strength of the carbon—lithium bond in alkyllithium, since:

$$\Delta H_r = D(\text{R—Li}) + D(\text{H—Br}) - D(\text{R—H}) - D(\text{Li—Br}) + \Delta H_v(\text{LiBr}) + \Delta H_v(\text{RH}) - \Delta H_v(\text{R—Li}) \quad (3)$$

As an approximation this expression omits terms connected with aggregation or solvation of the alkyllithium. As further approximation one may assume a constant value of $\Delta H_v(\text{RH}) - \Delta H_v(\text{R — Li})$ from one alkyl to the other, which reduces eqn. 3 to:

$$D(\text{R—Li}) = \Delta H_r(1) + D(\text{R—H}) + \text{constant} \quad (4)$$

The value of $D(\text{C}_2\text{H}_5\text{—Li})$ was determined by Lebedev et al. to be 47.5 kcal/mol, and combination of this with the $D(\text{C}_2\text{H}_5\text{—H})$ value of 98 kcal/mol gives the constant in eqn. 4 as 34.5 kcal/mol. The approximate bond strengths calculated from eqn. 4 are given in Table 1.

TABLE 1

ENTHALPIES[a] OF REACTION 1, RLi(s or c) + HBr(g) → RH(l) + LiBr(c); ENTHALPIES OF FORMATION OF SOLVENT-FREE ALKYLLITHIUM; APPROXIMATE BOND DISSOCIATION ENERGIES FOR ALKYL—LITHIUM BOND (SEE TEXT)

R in RLi	State	$-\Delta H_r(1)$	ΔH_f^0[RLi] (l or c)	D(R—Li)
CH_3	Soln. ether	77.1	−17.9	61.4
C_2H_5	Susp. pet.-ether	85.0	−13.2	47.5
$(CH_3)_2CH$	Soln. pet.-ether	86.0	−13.8	43.0
C_4H_9	Soln. ether	84.3	−26.1	48.2
C_4H_9	Soln. pet.-ether	84.3		
s-C_4H_9	Soln. pet.-ether	89.4	−21.0	39.6
t-C_4H_9	Soln. pet.-ether	90.0	−22.0	35.5
C_3H_5	Susp. pet.-ether	73.4	−1.4	46.1
$C_6H_5CH_2$	Susp. pet.-ether	76.3	4.2	43.3
p-$CH_3C_6H_4$	Susp. pet.-ether	73.5	1.4	
C_6H_5	Susp. pet.-ether	75.6	12.3	62.9
p-ClC_6H_4	Susp. pet.-ether	74.2	1.8	

[a] All values in kcal/mol.

The bond strengths are seen to be related to the relative stabilities of the anions, and if there is no resonance stabilization of the anion then the more acidic the hydrocarbon, the stronger the carbon—lithium bond. For allyl and benzyl the carbon—lithium bond is weak since the radicals are resonance stabilized. It is interesting to note, however, that the $CH_2=CHCH_2$—MgBr bond is 10 kcal/mol weaker than primary alkyl—Mg [1] while C_3H_5—Li is only 2 kcal/mol weaker than primary R—Li. This probably means that sp^2 hybridization and formation of the planar anion is far advanced in allyllithium, while much less important in allylic Grignard reagent.

The enthalpy of reaction of hydrogen bromide with phenyllithium is lower than the value observed with either *p*-methyl- or *p*-chloro-phenyllithium. This is an indication that the ionic character of the carbon—lithium bond is increased with *p*-substitution, whether the substituent is chlorine or methyl, meaning that the resonance interaction of the chlorine is more important than the inductive interaction in this compound. This conclusion has previously been reached on the basis of NMR observations [4].

Reaction of butyllithium with hydrogen bromide was performed in diethyl ether as well as in petroleum ether and the enthalpies of reaction were found to be identical within experimental error. This means that the enthalpy of coordination of ether and butyllithium is almost the same as the enthalpy of coordination of the lithium bromide formed in the reaction. In the calculation of enthalpies of formation of methyl- and benzyl-lithium (which were prepared only in diethyl ether) it was assumed by analogy that the enthalpy of coordination of the alkyllithium was equal to the enthalpy of coordination of LiBr. The absolute value of the enthalpy of coordination of ether and butyllithium was estimated to approximately 2 kcal/mol by mixing butyllithium with pure diethyl ether.

Reaction of hydrogen bromide with methyl- and ethyl-lithium caused a slight excess of pressure in the calorimeter, and the distribution of methane and ethane between the liquid and the gas phase was estimated by experiment to be 1/2 and 4/1 respectively. The observed enthalpies of reaction 1 were accordingly corrected by amounts corresponding to 0.66 to 0.20 times the relevant enthalpy of evaporation.

Experimental

Materials

Isopropyl-, sec-butyl-, butyl-, and t-butyl-lithium in pentane solution, as well as ethyllithium in benzene suspension were commercial products (Fluka). Methyllithium was prepared from methyl bromide and lithium in diethyl ether. Aryllithiums were prepared from the appropriate aryl iodides in pentane by halogen—metal exchange with butyllithium [5]. The products were washed three times with petroleum ether and used as suspensions. Allyllithium was prepared from tetraallytin by reaction with butyllithium [6]. Benzyllithium was prepared from tetrabenzyltin by reaction with butyllithium in petroleum ether overnight [7]. The product was a sticky yellow-brown residue which was washed with petroleum ether and used in diethyl ether solution.

Calorimetry

A steady state heat flow calorimeter was used as described [1]. The evacuated calorimeter was half filled through a rubber stopper with 300 ml of a ca. 0.2 *M* solution or suspension of the alkyllithium at room temperature. A slight pressure of argon was applied while the stopper was replaced with the adapter. The adapter held the Beckmann thermometer, the manganine heating coil, and the polyethylene feeding tube for hydrogen bromide. The calorimeter, which was "half insulated" by means of an air filled glass jacket, was placed in a precision water thermostat and stirred magnetically. A steady temperature difference of ca. 10° between the calorimeter contents and the thermostat water was established by applying an electrical effect of 5.000 W to the heating coil, and adjusting the water thermostat to 21°. The electrical heating was switched off, and a constant stream of hydrogen bromide (ca. 17 μmol/s) was lead into the alkyllithium, while the temperature of the calorimeter was controlled continuously. A new steady state was established by changing the temperature of the water thermostat, and the steady state temperature was read to 0.001°. After disconnecting the hydrogen bromide, the steady state was sustained by adjusting the electrical effect in the heating coil. A Fluka 382 A current calibrator was used, and the voltage was read on a Takeda—Riken digital voltmeter. The effect necessary to keep the temperature exactly divided by the rate of the stream of HBr (checked by titration) gave the enthalpy of reaction.

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