735. *Heats of Formation and Bond Energies. Part V.** n-*Butyl-lithium.*

By P. A. Fowell and C. T. Mortimer.

The heats of the following reactions of n-butyl-lithium have been measured calorimetrically: LiC_4H_9(liq.) + H_2O(g.) $\longrightarrow$ LiOH(cryst.) + C_4H_{10}(g.), $\Delta H = -57{\cdot}4 \pm 0{\cdot}7$ kcal./mole and LiC_4H_9(liq.) + $C_6H_5{\cdot}CH_2Br$(liq.) $\longrightarrow$ LiBr(cryst.) + $C_6H_5{\cdot}C_5H_{11}$(liq.), $\Delta H = -80{\cdot}8 \pm 2{\cdot}6$ kcal./mole. From these, the heats of formation are calculated: $\Delta H_f^\circ(LiC_4H_9,liq.) = -31{\cdot}4 \pm 0{\cdot}7$ kcal./mole, and $\Delta H_f^\circ(C_6H_5{\cdot}CH_2Br,liq.) = +7{\cdot}1 \pm 3{\cdot}3$ kcal./mole. The value $D(Li\text{–}C_4H_9) = 54 \pm 9$ kcal./mole is derived.

THERE is very little information about the strength of metal–carbon bonds in the organometallic compounds MR_n where M is one of the lighter metals lithium, beryllium, or aluminium and R is an alkyl radical. The *mean* bond dissociation energy $\bar{D}$(M–C) is an expression of the strength of these bonds and is readily calculated from the relation $\bar{D}(M\text{–}C) = \Delta H_f^\circ(R,g.) + \frac{1}{n}\Delta H_f^\circ(M,g.) - \frac{1}{n}\Delta H_f^\circ(MR_n,g.)$. In the particular case of the lithium alkyls, LiR, $\bar{D}$(M–C) refers to the bond dissociation energy, since there is only one metal–carbon bond. The heats of formation of the gaseous metal atoms and alkyl radicals are known, so it remains only to determine the heat of formation of the compounds MR_n.

This paper reports the measurement of the heat of formation of n-butyl-lithium and the calculation of the bond dissociation energy $D(Li\text{–}C_4H_9)$.

The most convenient method of determining the heat of formation of this compound is to measure the heat of a reaction in which it takes part, provided that the heats of formation of all the other reactants and products are known. The reaction should be rapid and well defined. Combustion in oxygen is such a reaction, but since the heat of combustion is large it requires the preparation of a very pure sample of n-butyl-lithium to give a moderate accuracy in the derived heat of formation. Because of the difficulty of obtaining a pure sample, which is solvent-free, this reaction was rejected. Two reactions which are suitable are (i) hydrolysis and (ii) that with benzyl bromide, both rapid and quantitative. The heats of these two reactions have been measured:

$$LiC_4H_9(liq.) + H_2O(g.) \longrightarrow LiOH(cryst.) + C_4H_{10}(g.) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (i)$$

$$LiC_4H_9(liq.) + C_6H_5{\cdot}CH_2Br(liq.) \longrightarrow LiBr(cryst.) + C_6H_5{\cdot}C_5H_{11}(liq.) \quad . \quad . \quad . \quad . \quad . \quad . \quad (ii)$$

It has been suggested[1] that n-butyl-lithium also reacts with benzyl bromide to give bibenzyl: $LiC_4H_9 + 2C_6H_5{\cdot}CH_2Br \longrightarrow LiBr + C_4H_9Br + C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$. This reaction was shown to be unimportant under the conditions in the calorimeter, in the following way. A weighed ampoule of benzyl bromide was added to an excess of n-butyl-lithium in light petroleum. Water was then added to hydrolyse unchanged butyl-lithium to lithium hydroxide, and the aqueous portion was analysed for bromide ions. All the bromine appeared as bromide ions, and it was assumed that reaction (ii) occurs quantitatively.

EXPERIMENTAL

Compounds.—n-Butyl-lithium was prepared[2] by adding a solution of n-butyl bromide in light petroleum dropwise to an excess of freshly cut lithium, suspended in sodium-dried petroleum, with rapid stirring, in an atmosphere of dry nitrogen. The solution of butyl-lithium in petroleum was filtered from the precipitated lithium halide by forcing it, with a pressure of

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* Part IV, *J.*, 1960, 4649.

[1] Gilman and Jones, " Organic Reactions," Wiley, New York, 1951, Vol. VI, p. 350.

[2] Gilman, Beel, Branne, Bullock, Dunn, and Miller, *J. Amer. Chem. Soc.*, 1949, **71**, 1499.

dry nitrogen, through a U-shaped tube in which a glass sinter was sealed. This petroleum solution was used for the benzyl bromide investigation. For the hydrolysis, most of the petroleum was removed under reduced pressure. During this distillation the temperature was not allowed to rise above 25°. This sample of n-butyl-lithium contained about 10% of petroleum. Most of the remaining petroleum could be removed by reducing the pressure considerably more, and these samples were used for measurement of heats of solution. It seems most likely that the solution of n-butyl-lithium in petroleum and liquid n-butyl-lithium contain " cluster " polymers. Rogers and Young [3] measured the dipole moment of butyl-lithium in benzene solution and the value of *ca.* 1 D for μ is much smaller than one would expect for a polar monomeric structure, but is consistent with " cluster " polymers in solution. Although no cryoscopic measurements are available for n-butyl-lithium, Hein and Schramm [4] conclude that ethyl-lithium is a 6-polymer in benzene solution.

Benzyl bromide was distilled through a 6 in. Fenske column.

Calorimeters.—Because of the thermochemical difficulties of measuring the heat of a reaction in which a large volume of gas is suddenly liberated, and the chemical difficulty of preparing pure n-butyl-lithium, it was thought inadvisable to measure the heat of hydrolysis by breaking weighed ampoules of n-butyl-lithium into water or wet petroleum. The reaction was therefore carried out by adding a known weight of water vapour, in a stream of nitrogen, to the sample of butyl-lithium.

The calorimeter used was similar to that described by Pedley, Chernick, and Skinner [5] for the bromination of hexamethyldistannane. It consisted of a cylindrical, silvered Dewar vessel of 250 ml. capacity, inserted into a flanged brass can. The calorimeter cap was a brass plate, with five chimneys, screwed to an ebonite bung which fitted tightly into the Dewar vessel. The cap was screwed to the flange of the brass can, a water-tight joint being formed with a rubber washer. The calorimeter was immersed in a thermostat-bath, at 25°, to a level near the top of the chimneys. These chimneys allowed connection to a stirrer, a calibration heater, a thermistor (used to measure the temperature change inside the calorimeter), and an inlet to and an outlet from a reaction vessel. The Dewar vessel was filled with water. A stream of oxygen-free nitrogen, at 25°, entered the calorimeter, bubbled through the liquid n-butyl-lithium in the reaction vessel, and then passed through a spiral heat-exchanger before leaving the calorimeter. The nitrogen stream was saturated with a known weight of water vapour and the temperature rise accompanying the hydrolysis was measured.

The calorimeter used to measure the heat of reaction of n-butyl-lithium with benzyl bromide has been described previously.[6] It was similar to that used for the hydrolysis. In this case the Dewar vessel was filled with a solution of n-butyl-lithium in light petroleum under a slight pressure of nitrogen. The reaction vessel was replaced by a weighed ampoule of benzyl bromide and some glass teeth on which it was crushed.

Units.—All reactions were initiated at 25°. Heat quantities are given in units of the thermochemical calorie, 1 cal. = 4·1840 abs. J.

Results.—Typical results for the heat of reaction of n-butyl-lithium with water and with benzyl bromide are shown in the Table.

Heats of reaction of n-butyl-lithium.

With water				With benzyl bromide			
Wt. water (g.)	$-\Delta H$ (kcal./mole)	Wt. water (g.)	$-\Delta H$ (kcal./mole)	Wt. benzyl bromide (g.)	$-\Delta H$ (kcal./mole)	Wt. benzyl bromide (g.)	$-\Delta H$ (kcal./mole)
0·0179	57·9	0·0306	56·3	0·5651	81·4	0·1908	83·6
0·0268	56·6	0·0236	57·9	0·1566	77·1	0·2008	78·4
0·0147	55·7	0·0294	56·5				

Mean $\Delta H = -56{\cdot}8 \pm 0{\cdot}5$ kcal./mole. Mean $\Delta H = -80{\cdot}1 \pm 2{\cdot}5$ kcal./mole.

The ΔH values refer to the reactions

$$\mathrm{LiC_4H_9(soln.) + H_2O(g.) \longrightarrow LiOH(cryst.) + C_4H_{10}(g.)} \quad . \; . \; . \; . \; . \; . \; . \quad \text{(iii)}$$

$$\mathrm{LiC_4H_9(soln.) + C_6H_5{\cdot}CH_2Br(liq.) \longrightarrow LiBr(cryst.) + C_6H_5{\cdot}C_5H_{11}(soln.)} \quad . \; . \; . \; . \; . \quad \text{(iv)}$$

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[3] Rogers and Young, *J. Amer. Chem. Soc.*, 1946, **68**, 2748.

[4] Hein and Schramm, *Z. phys. Chem.*, 1930, *A*, **151**, 234.

[5] Pedley, Chernick, and Skinner, *Trans. Faraday Soc.*, 1957, **53**, 1612.

[6] Fowell and Mortimer, *J.*, 1959, 2913.

For the hydrolysis the n-butyl-lithium contained about 10% of petroleum; for the reaction with benzyl bromide the n-butyl-lithium was in a large excess of petroleum. The heat of solution of liquid n-butyl-lithium in an excess of petroleum, containing a small amount of n-butyl-lithium to ensure that it was dry and oxygen-free, was measured as $\Delta H = -0{\cdot}7 \pm 0{\cdot}1$ kcal./mole. The heat of solution of liquid n-butyl-lithium, containing 10% of petroleum, in an excess of petroleum was measured as $\Delta H = -0{\cdot}1 \pm 0{\cdot}1$ kcal./mole. By difference, the heat change when liquid n-butyl-lithium is diluted with 10% of its volume of petroleum is calculated as $\Delta H = -0{\cdot}6 \pm 0{\cdot}2$ kcal./mole. By incorporating these heats of solution, the heats of reactions (i) and (ii) are calculated as $\Delta H_1 = -57{\cdot}4 \pm 0{\cdot}7$, and $\Delta H_2 = -80{\cdot}8 \pm 2{\cdot}6$ kcal./mole, respectively. The heat of solution of pentylbenzene in petroleum was not measured. It is likely to be small compared with the uncertainty associated with ΔH_2.

DISCUSSION

The heat of formation of liquid n-butyl-lithium can be calculated from the thermochemical relation

$$\Delta H_1 = \Delta H_f^\circ(\text{LiOH,cryst.}) + \Delta H_f^\circ(\text{C}_4\text{H}_{10}\text{,g.}) - \Delta H_f^\circ(\text{LiC}_4\text{H}_9\text{,liq.}) - \Delta H_f^\circ(\text{H}_2\text{O,g.}).$$

The following heats of formation are then used: LiOH(cryst.), $-116{\cdot}45$; H_2O(g.), $-57{\cdot}80$ kcal./mole,[7] and C_4H_{10}(g), $-30{\cdot}15$ kcal./mole;[8] thus the value $\Delta H_f^\circ(\text{LiC}_4\text{H}_9\text{,liq.}) = -31{\cdot}4 \pm 0{\cdot}7$ kcal./mole, is derived. From this value, the heat of formation of liquid benzyl bromide can be calculated by means of the relation

$$\Delta H_2 = \Delta H_f^\circ(\text{LiBr,cryst.}) + \Delta H_f^\circ(\text{C}_6\text{H}_5\text{·C}_5\text{H}_{11}\text{,liq.}) - \Delta H_f^\circ(\text{LiC}_4\text{H}_9\text{,liq.}) - \Delta H_f^\circ(\text{C}_6\text{H}_5\text{·CH}_2\text{Br,liq.}),$$

by incorporating the following heats of formation: LiBr(cryst.), $-83{\cdot}72$ kcal./mole,[7] and $C_6H_5{\cdot}C_5H_{11}$(liq.), $-21{\cdot}39$ kcal./mole, which is calculated from the value $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{·C}_5\text{H}_{11}\text{,g.})$, $-8{\cdot}23$ kcal./mole [7] and a latent heat of vaporisation of $13{\cdot}16$ kcal./mole. The last figure is obtained from the formula given by Loeffler and Rossini [9] for the latent heats of vaporisation of normal alkylbenzenes, $C_6H_5{\cdot}[CH_2]_n{\cdot}CH_3$; $\Delta H_{\text{vap.}} = 7{\cdot}26 + 1{\cdot}18(n + 1)$ kcal./mole. The value $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{·CH}_2\text{Br,liq.}) = +7{\cdot}1 \pm 3{\cdot}3$ kcal./mole is derived. It may be that the lithium hydroxide and lithium bromide formed in these reactions are slightly soluble in the petroleum solution, and also that the salts are precipitated in a microcrystalline form which differs from the standard state. It must be admitted, therefore, that the heats of formation of the compounds formed under these particular conditions are not necessarily the same as the values quoted here, which refer to the standard states. This difficulty might have been overcome by measuring the heats of solution of the precipitated salts (*a*) in petroleum and (*b*) in aqueous solution. It would then have been possible to express the heats of formation of n-butyl-lithium and benzyl bromide in terms of heats for formation of the more well-defined states of lithium hydroxide and lithium bromide in aqueous solution. However, with the particular design of the calorimeter and the presence of unchanged n-butyl-lithium in the reaction vessel, it was not possible to extract the lithium hydroxide and bromide.

Two other values are available for the heat of formation of liquid benzyl bromide. These are $+5{\cdot}1 \pm 3{\cdot}0$ kcal./mole,[10] derived from a measurement of the heat of hydrolysis of benzyl bromide by Gellner and Skinner,[11] and $+8{\cdot}7 \pm 1{\cdot}0$ kcal./mole calculated by Benson and Buss [12] from equilibrium measurements of the reaction between bromine and toluene. Our value falls between the two heats of formation, both of which are within our limits of accuracy. The agreement helps to confirm that the heat of formation of liquid n-butyl-lithium which has been obtained is correct, within the quoted limits of error.

[7] National Bureau of Standards, Circular 500, Washington D.C., 1952.
[8] American Petroleum Research Institute Research Project 44, Carnegie Press, Pitt., Penn., 1952.
[9] Loeffler and Rossini, *J. Phys. Chem.*, 1960, **64**, 1533.
[10] Skinner, " Modern Aspects of Thermochemistry," *Roy. Inst. Chem.*, Monograph No. 3, 1958.
[11] Gellner and Skinner, *J.*, 1949, 1145.
[12] Benson and Buss, *J. Phys. Chem.*, 1957, **61**, 104.

The bond dissociation energy of the lithium–carbon bond, can be calculated from the relation:

$$D(\mathrm{Li{-}C_4H_9}) = \Delta H_f^\circ(\mathrm{C_4H_9,g.}) + \Delta H_f^\circ(\mathrm{Li,g.}) - \Delta H_f^\circ(\mathrm{LiC_4H_9,\ monomer,\ g.}).$$

In order to calculate a value for the heat of formation of monomeric, gaseous n-butyl-lithium, it is necessary to know the latent heat of vaporisation of liquid n-butyl-lithium to the gaseous state, at 25°, and also the heat of dissociation to monomer molecules, if this gas is associated. Taylor [13] has reported measurements of the variation of vapour pressure with temperature of liquid n-butyl-lithium. From the results of four experiments, which were not very reproducible, the calculated latent heat of vaporisation ranged from 25 to 38 kcal./mole. The average value is 33 kcal./mole. There is no evidence that the vapour of n-butyl-lithium is monomeric. It may still contain clusters of molecules. However, if we accept a value of $\Delta H = 33 \pm 5$ kcal./mole for the process $\mathrm{LiC_4H_9(liq.)} \longrightarrow \mathrm{LiC_4H_9}$ (monomer, g.), then we obtain the value $\Delta H_f^\circ(\mathrm{LiC_4H_9,\ monomer,\ g.}) = +1{\cdot}6 \pm 6$ kcal./mole. Using the heats of formation Li(g.) 37·07 kcal./mole,[7] and $\mathrm{C_4H_9(g.)}$ +18·5 ± 3 kcal./mole,[10] we derive the value $D(\mathrm{Li{-}C_4H_9}) = 54 \pm 9$ kcal./mole.

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UNIVERSITY COLLEGE OF NORTH STAFFORDSHIRE,
KEELE, STAFFS.

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[13] Taylor, M.Sc. Thesis, University of Manchester, 1946.