

Diphenylberyllium: Electron Impact and Calorimetric Studies

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Diphenylberyllium, at 200—240 °C, produces parent trimer- and monomer-ions ($\text{Ph}_6\text{Be}_3^{++}$ and Ph_2Be^+) in a mass spectrometer, with $A(\text{Ph}_2\text{Be}^{++}) = 9.2 \pm 0.1$ and $A(\text{PhBe}^+) = 13.4 \pm 0.2$ eV. Acid hydrolysis leads to $\Delta H_f^\circ \text{Ph}_2\text{Be}(s) = 153.1 \pm 2.5$ kJ mol⁻¹.

ORGANO-DERIVATIVES of beryllium, like those of aluminium, are commonly associated by electron-deficient bridging bonds.¹ For beryllium alkyls the extent of association is determined mainly by the steric requirements of the organic group (Me_2Be , polymeric; Pr_2Be , dimeric; Bu_2Be , monomeric). The heat formation of two (bridging) half bonds from one whole bond is about -42 kJ mol⁻¹, but no values have been reported for the beryllium-carbon bond strength. Electron impact studies on various beryllium dialkyls give values for the Be-C bond energy in the parent monomer ions, $D(\text{RBe}^+-\text{R})$, in the range 180—192 kJ mol⁻¹. Since ionization probably removes a Be-C bonding electron these bond energies are likely to be considerably lower than in the neutral molecules.^{2,3}

Less information is available on electron-deficient aryl compounds, though crystalline triphenylaluminium contains discrete Ph_6Al_2 units in which two phenyl groups

¹ G. E. Coates and K. Wade, 'Organometallic Compounds,' vol. 1, Methuen, 1967.

² D. B. Chambers, G. E. Coates, and F. Glockling, *J. Chem. Soc. (A)*, 1970, 741.

function as bridging ligands, and there is evidence that phenyl ligands form stronger bridging bonds than alkyl groups.¹ Diphenylberyllium, prepared from powdered beryllium and diphenylmercury, is a white crystalline solid soluble in hot benzene or xylene. It decomposes at its melting point (248—250 °C) and its extremely low volatility suggests a polymeric phenyl-bridged structure analogous to that of $(\text{Me}_2\text{Be})_n$. The present work has been concerned with examining mass spectroscopically the state of diphenylberyllium vapour and deriving bond energy data from its heat of hydrolysis and from appearance potential measurements.

EXPERIMENTAL

Diphenylberyllium was prepared by the method of Coates and Tranah⁴ and recrystallized from hot benzene (Found C, 87.9; H, 6.2. Calc. for $\text{C}_{12}\text{H}_{10}\text{Be}$: C, 88.3; H, 6.1%).

Electron Impact Studies.—Attempts to introduce Ph_2Be into an MS 902 mass spectrometer via a heated all-glass

³ D. B. Chambers, G. E. Coates, and F. Glockling, *Discuss. Faraday Soc.*, 1969, 47, 157.

⁴ G. E. Coates and M. Tranah, *J. Chem. Soc. (A)*, 1967, 236.

inlet system required a temperature in excess of 250 °C and produced mainly hydrocarbon ions. Reproducible mass spectra could only be obtained by introducing the sample on a direct insertion probe, all operations being carried out in a nitrogen atmosphere with the source temperature held between 200–245 °C. Abundance measurements were recorded at a resolution of 1:1000 and accurate mass measurements at a resolution of 1:10,000. Other spectrometer conditions were: ionizing voltage, 70 eV; trap current, 100 mA; ion repeller voltage, +4 V; accelerating voltage, 6 kV. Appearance potentials were measured at the highest possible sample pressure and evaluated as previously described.⁵

TABLE 1

Mass spectrum of diphenylberyllium at 240°		
<i>m/e</i>	Ion ⁺	% Ion current
489 *	Ph ₆ Be ₃	0.4
396	C ₂₈ H ₂₁ Be ₃	0.4
380	C ₂₈ H ₂₆ Be ₂	<0.1
320	C ₂₁ H ₂₃ Be	0.2
319	C ₂₄ H ₂₂ Be	0.4
222	C ₁₇ H ₁₈	<0.1
198 *	C ₁₅ H ₁₈	0.2
197 *	C ₁₅ H ₁₇	0.3
182 *	C ₁₄ H ₁₄	0.5
167	C ₁₃ H ₁₁	<0.1
165	Ph ₂ BeH ₂	0.3
164 *	Ph ₂ BeH + ¹² C ₁₁ ¹³ CH ₁₀ Be	0.5
163 *	Ph ₂ Be	5.5
162	PhBeC ₆ H ₄	3.1
161	(C ₆ H ₄) ₂ Be	1.5
160	C ₁₂ H ₇ Be	0.2
155	C ₁₂ H ₁₁	0.2
154	C ₁₂ H ₁₀	3.2
153	C ₁₂ H ₉	1.2
152	C ₁₂ H ₈	1.6
137	C ₁₀ H ₈ Be	1.3
136	C ₁₀ H ₇ Be	1.0
128	C ₁₀ H ₈	1.0
110	C ₈ H ₅ Be	0.4
106	C ₈ H ₁₀	0.2
91	C ₇ H ₇	0.3
87	PhBeH	0.1
86 *	PhBe	1.0
85	C ₆ H ₄ Be	0.3
84	C ₆ H ₃ Be	1.0
81.5	Ph ₂ Be ²⁺	0.1
79	C ₆ H ₇	0.3
78	C ₆ H ₆	36.7
77	C ₆ H ₅	9.6
76	C ₆ H ₄	2.4
74	C ₆ H ₂	2.0
68.5	C ₁₀ H ₉ Be ²⁺	0.3
63	C ₅ H ₃	1.2
60	C ₄ H ₃ Be	0.4
52	C ₄ H ₄	6.3
51	C ₄ H ₃	6.2
50	C ₄ H ₂	4.3
43.5	PhBeH ²⁺	<0.1
39	C ₃ H ₃	3.8
9	Be	<0.1

* Confirmed by high resolution mass measurement; agreement better than 5 p.p.m.

Calorimetry.—The calorimeter has been described previously.⁶ Ampoules were loaded in a nitrogen filled glove box and sealed *in vacuo*. The hydrolysis proceeded without undue violence and was complete in less than 30 s. The calorimetric liquid, 1.16 *m* H₂SO₄ (H₂SO₄ 47.85 H₂O), was stored under a layer of benzene and benzene (1 ml) was added to the calorimeter before each run. This ensures

⁵ D. B. Chambers and F. Glockling, *Inorg. Chim. Acta*, 1970, **4**, 150.

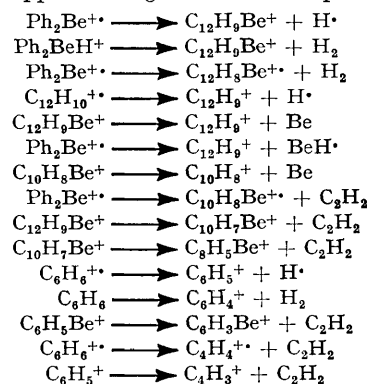
that the calorimetric liquid is saturated with benzene and therefore the benzene produced by the hydrolysis reaction is in its standard state. The uncertainty in ΔH_1 is expressed as the single standard deviation of the mean value. All weights were corrected for buoyancy.

RESULTS AND DISCUSSION

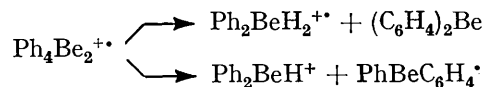
In a mass spectrometer, diphenylberyllium shows no beryllium-containing ions up to a source temperature of 200°. Hydrocarbon ions are present between 180–200° and the spectrum changes dramatically between 200–240° as beryllium-containing ions appear (Table 1). Above 250° the beryllium-containing ions disappear and the spectrum is then similar to that observed between 180–200°. Metastable supported fragmentation processes are listed in Table 2. For the beryllium containing ions these correspond to elimination of H, H₂, and acetylene and three processes are observed for the elimination of neutral Be or BeH.

TABLE 2

Metastable supported fragmentation of diphenylberyllium



Two molecular ions are observed (Ph₆Be₃³⁺ and Ph₂Be²⁺); both may be formed by the ionization of trimer and monomer molecules that evaporate from the crystal, although Ph₂Be²⁺ could be derived entirely from Ph₆Be₃³⁺. The absence of a parent dimer Ph₄Be₂²⁺ may not be significant in relation to the structure of the crystalline solid. The occurrence of ions (Ph₂BeH⁺ and Ph₂BeH₂²⁺) with more than two groups bonded to beryllium implies that these are formed from di- or tri-beryllium containing parent ions by processes such as



One feature of interest is the high proportion of the ion current carried by the C₆H₆⁶⁺ ion. It persists above 250 °C, and since there is no metastable supported process leading to its formation it seems likely that benzene is the main volatile product of the thermal decomposition of diphenylberyllium. This was confirmed by pyrolysis of Ph₂Be *in vacuo* at 240–250 °C. A high strength for the beryllium–phenyl bonds is

⁶ J. T. F. Fenwick and J. W. Wilson, *J.C.S. Dalton*, 1972, 1324.

indicated by the variety of ions that clearly involve fragmentation of phenyl groups (Table 1). Three doubly charged ions, $\text{Ph}_2\text{Be}^{2+}$, PhBe^{2+} , and $\text{PhBeC}_4\text{H}_4^{2+}$, were observed in contrast to the behaviour of diphenylmercury where only $\text{Ph}_2\text{Hg}^{2+}$ and Hg^{2+} are observed at very low intensity (0.1% total ion current).

Thermochemistry.—The following data have been used in deriving the mean beryllium-carbon bond dissociation energy.

$$\Delta H_f^\circ(\text{H}_2\text{SO}_4, 47.85 \text{ H}_2\text{O}) = -886.7 \pm 0.2 \text{ kJ mol}^{-1}, \text{ ref. 7.}$$

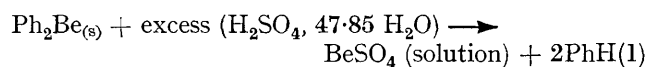
$$\Delta H_f^\circ(\text{BeSO}_4, \text{ solution in } 1.16 \text{ } m \text{ H}_2\text{SO}_4) = -1271.9 \pm 0.5 \text{ kJ mol}^{-1}, \text{ ref. 8.}$$

$$\Delta H_f^\circ\text{PhH}(1) = 49.0 \pm 0.4 \text{ kJ mol}^{-1}.$$

$$\Delta H_f^\circ\text{Be}(g) = 323.8 \pm 2.1 \text{ kJ mol}^{-1}, \text{ ref. 9.}$$

$$\Delta H_f^\circ\text{Ph}(g) = 325.9 \pm 8.4 \text{ kJ mol}^{-1}, \text{ ref. 10.}$$

For the reaction:



the enthalpy change (6 determinations) $\Delta H_1 = -440.6 \pm 2.5 \text{ kJ mol}^{-1}$. Hence $\Delta H_f^\circ\text{Ph}_2\text{Be}_{(s)} = 153.1 \pm 2.5 \text{ kJ mol}^{-1}$.

Since diphenylberyllium is associated its heat of sublimation to monomer will be high. We have attempted a direct measurement from the variation of

⁷ National Bureau of Standards, Technical Note 270-3, Washington, D.C., 1968.

⁸ A. R. Taylor, jun., B. B. Letson, and D. F. Smith, U.S. Bur. Mines, Rep. Invest. No. 6724, 1966 (*Chem. Abs.*, 1966, **64**, 13,463c).

source pressure *versus* probe temperature in a mass spectrometer without applying an electron voltage. This procedure is suspect because of thermal decomposition but it leads to the value: $\Delta H(\text{Ph}_2\text{Be})_{\text{sub}} = 150-200 \text{ kJ mol}^{-1}$. The lower value is close to that reported for Ph_3Al .¹¹ In deriving the mean beryllium-carbon bond dissociation energy we have taken

$$\Delta H(\text{Ph}_2\text{Be})_{\text{sub}} \approx 150 \text{ kJ mol}^{-1}$$

whence

$$\Delta H_f^\circ\text{Ph}_2\text{Be}_{(g)} \approx 303 \text{ kJ mol}^{-1}$$

and

$$\bar{D}(\text{Ph}-\text{Be}) = \frac{1}{2}(\Delta H_f^\circ\text{Be}_{(g)} + 2\Delta H_f^\circ\text{Ph}_{(g)} - \Delta H_f^\circ\text{Ph}_2\text{Be}_{(g)}) \approx 336 \text{ kJ mol}^{-1}$$

The ionization potential of diphenylberyllium, using argon as standard, is $9.20 \pm 0.10 \text{ eV}$ and this value is close to those reported for various beryllium dialkyls. The abundance of the PhBe^+ ion was rather low for appearance potential measurement and the value obtained ($13.4 \pm 0.2 \text{ eV}$) leads to $D(\text{PhBe}^+-\text{Ph}) = 412 \pm 20 \text{ kJ mol}^{-1}$, assuming that the threshold energy leading to the formation of PhBe^+ is cleavage of a phenyl radical from $\text{Ph}_2\text{Be}^{++}$.

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⁹ D. L. Hildenbrand and E. Murad, *J. Chem. Phys.*, 1966, **44**, 1524.

¹⁰ G. A. Chamberlain and E. Whittle, *Trans. Faraday Soc.*, 1971, **67**, 2077.

¹¹ N. N. Greenwood, P. G. Perkins, and M. E. Twentyman, *J. Chem. Soc. (A)*, 1967, 2109.