861. *Dimethylberyllium. Part I. Vapour Pressure and Vapour-phase Association.*

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The vapour pressure of dimethylberyllium has been measured between 100° and 180°, and the vapour density between 160° and 200°. The extrapolated sublimation temperature is 217°. From a study of the pressure dependence of the vapour density it is concluded that the vapour contains monomer, dimer, trimer, for which structures are proposed, and higher polymers, the last only becoming important under near-saturation conditions. Heat and entropy terms have been obtained for the monomer–dimer and the monomer–trimer equilibria. The significance of the apparent heat of sublimation is discussed in the light of the association equilibria, and the heat of sublimation of the solid polymer into monomer is deduced.

The energy difference between two half bonds and one whole bond is 9—12 kcal., depending on the degree of polymerisation; this is compared with the value of 10 kcal. for the similar quantity in trimethylaluminium and its dimer. The entropy change on dimerisation is discussed in relation to the use of 3*d* orbitals by carbon in compounds of this type.

THE dialkyl derivatives of beryllium present structural and valency problems similar to those which have developed from the study of the alkyls and hydrides of its neighbours in the Periodic Table, *viz.*, lithium, boron, aluminium, and gallium. Very few organo-beryllium compounds have been properly characterised, but all of these have properties which preclude their formulation as salts and indicate covalent but polymeric structures. For example, dimethylberyllium (Gilman and Schulze, *J.*, 1927, 2663) is a white crystalline solid, sublimation temperature 217°/760 mm., and diethyl- (Goubeau and Rodewald, *Z. anorg. Chem.*, 1949, **258**, 162) and di*iso*propyl-beryllium (Coates and Glockling, unpublished) are colourless, rather viscous * liquids which may be distilled slowly in a high vacuum at room temperature. Since these compounds are covalently saturated in their monomeric forms, any polymerisation involving the formation of additional covalent bonds requires their classification as electron-deficient molecules, *i.e.*, the total number of electrons available for valency-bond formation is less than twice the minimum number of bonds required to hold any reasonable structure together. Other examples of electron-deficient molecules are ethyl-lithium, m. p. 95° to a non-conducting liquid, which may easily be distilled in a high vacuum and is strongly associated in benzene solution (Hein, Petzchner, Wagler, and Segitz, *ibid.*, 1924, **141**, 161), all the hydrides of boron, trimethyl-aluminium which is dimeric (Pitzer and Gutowsky, *J. Amer. Chem. Soc.*, 1946, **68**, 2204; Rundle, *ibid.*, 1947, **69**, 1327), and digallane Ga_2H_6 (Wiberg and Johannsen, *Angew. Chem.*, 1942, **55**, 38).

A recent *X*-ray analysis (Snow and Rundle, *Acta Cryst.*, 1951, **4**, 348) has shown that solid dimethylberyllium has a polymeric structure similar to that of silicon disulphide, beryllium and methyl groups replacing silicon and sulphur respectively. All the beryllium–carbon bonds are equivalent, with an approximately tetrahedral distribution of methyl groups round each beryllium atom; one of the most significant features of the structure is the small Be–C–Be angle (66°), which will be mentioned again below. In the present work we have investigated the nature of gaseous dimethylberyllium which is also associated, the heat of sublimation of monomer from the solid, and the heat of formation of dimer and trimer from monomer, by means of vapour-pressure and vapour-density measurements.

EXPERIMENTAL

Dimethylberyllium.—For both vapour-pressure and vapour-density measurements the preparative method of Burg and Schlesinger (*J. Amer. Chem. Soc.*, 1940, **62**, 3425) was preferred to the Grignard method of Gilman and Schulze (*loc. cit.*), since ether co-ordinates to dimethyl-beryllium and it was found that samples prepared by high-vacuum sublimation of the solid

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* Their viscosity is of the same order as that of concentrated sulphuric acid.

obtained from ethereal solution had somewhat higher vapour pressures, particularly at lower temperatures, than samples obtained from metallic beryllium and dimethylmercury (*e.g.*, 1·6 and 0·6 mm. respectively at 100°). Burg and Schlesinger's method was modified slightly in that beryllium powder was found to react faster than small lumps of metal, and instead of being heated in a sealed tube the reactants were refluxed together under slightly greater than atmospheric pressure in an apparatus sealed to a vacuum-system. In a typical preparation beryllium powder (1 g.) was placed in the reaction tube, which was then sealed into the vacuum-system and pumped and baked out at 400°; dimethylmercury (4·3 ml.) was condensed on the beryllium, the apparatus filled with oxygen-free dry nitrogen to atmospheric pressure, and the mixture refluxed for 36 hours, whereafter very little dimethylmercury remained. The residue of it was removed *in vacuo* at room temperature and the dimethylberyllium was then sublimed *in vacuo* from any excess of metal. The light metal is readily carried by a stream of dimethylberyllium vapour, but was easily separated by means of a small, grade 3, sintered disc sealed into the apparatus. This method gave a product which was slightly contaminated with metallic mercury, which could not be removed by sublimation over gold foil since the latter parts with mercury even at the lowest temperatures (about 100°) at which the alkyl may be sublimed. For vapour-pressure and vapour-density measurements the presence of mercury does not matter since its vapour pressure is accurately known and appropriate corrections were included. For experiments (particularly some of those described in Parts II and III) in which it was necessary to weigh samples of dimethylberyllium, the presence of mercury was serious while a trace of ether did not matter; in such cases the sample was dissolved in pure dry ether and either filtered through a sintered disc or, more conveniently, siphoned from the residual mercury. These operations were all carried out in the vacuum-apparatus with rigorous exclusion of oxygen and water vapour, both of which react with dimethylberyllium with considerable vigour.

Vapour Pressure and Vapour Density.—These measurements were carried out in the "high-temperature bulb" of known volume, described by Burg and Schlesinger (*ibid.*, 1937, **59**, 780) and by Sanderson ("The Vacuum Manipulation of Volatile Compounds," Wiley, 1948); the bulb was immersed in an oil-thermostat containing a resistance thermometer connected to an a.c. bridge thermo-regulator (Coates, *J. Sci. Instr.*, 1944, **21**, 86). Temperatures were measured by standardised mercury thermometers reading to tenths of a degree. Vapour-density measurements required accurate determination of the quantity of dimethylberyllium present in the high-temperature bulb; these quantities were determined, not by weighing (on account of mercury contamination and the small weights involved), but by hydrolysis after each experiment, and removal of the liberated methane by a Töpler pump through a liquid-oxygen trap into a gas-burette. The direct hydrolysis of dimethylberyllium is so vigorous and exothermic that some carbon, hydrogen, and other products are sometimes formed; therefore it was moderated by first adding a slight excess of trimethylamine, which formed a less reactive co-ordination compound (see Part II), and then water. Vapour densities were not measured above 200° since thermal decomposition then becomes quite appreciable, and is shown by the deposition of colourless glistening crystals unlike dimethylberyllium in appearance, a decrease of pressure, and a residual pressure on cooling to room temperature after an experiment.

RESULTS

Vapour Pressure.—Over the temperature range studied, 100—180°, the plot of log p against temp.$^{-1}$ (K) was not quite linear, but the observed vapour pressures are represented closely by two linear equations :

$$100\text{—}155^\circ : \log_{10} p_{\text{mm.}} = 12{\cdot}530 - 4771/T$$

$$155\text{—}180^\circ : \log_{10} p_{\text{mm.}} = 13{\cdot}292 - 5100/T$$

Observed vapour pressures are compared in Table 1 with those calculated from the above equations.

TABLE 1.

Temp. (c)	100·2°	115·0°	125·4°	130·2°	135·1°	140·6°	145·3°
$p_{\text{obs.}}$	0·62	1·72	3·39	4·98	6·81	9·82	13·1
$p_{\text{calc.}}$	0·56	1·71	3·59	4·98	6·92	9·89	13·3
Temp. (c)	151·5°	155°	160°	165°	170°	175°	180°
$p_{\text{obs.}}$	19·8	24·4	33·1	45·1	61·0	82·4	110·0
$p_{\text{calc.}}$	19·8	24·2	33·2	45·1	61·1	82·0	109·9

Vapour-phase Association.—Preliminary experiments having indicated a degree of association between 1 and 2 under conveniently accessible conditions of temperature and pressure, it was clear that monomeric dimethylberyllium was present in the vapour. It was then necessary to decide whether the equilibrium involved dimeric or trimeric molecules or both; this was done by calculating equilibrium constants K_D and K_T on the respective assumptions of monomer–dimer and monomer–trimer equilibria, where

$$K_D\ (\text{atm.}^{-1}) = p_{\text{dimer}}/p^2_{\text{monomer}}$$

and

$$K_T\ (\text{atm.}^{-2}) = p_{\text{trimer}}/p^3_{\text{monomer}}$$

Eight series of vapour-density determination were carried out with quantities of dimethylberyllium from 1·26N-c.c. (*i.e.*, c.c. calculated as monomer at N.T.P.) to 27·3N-c.c., pressure readings being taken at 5° intervals from about 10° above the temperature at which all the solid disappeared to 200°. In this way it was possible to examine the variation of K_D and K_T with pressure at any chosen constant temperature, the latter in practice being restricted to 160° to 200°. Table 2 indicates that K_D slowly increases with pressure, while K_T rapidly diminishes;

TABLE 2. *Variation of* K_D *and* K_T *with pressure at* 190° C.

$p_{\text{mm.}}$	25	31	52	81	101	151
K_D (atm.$^{-1}$)	4·4	4·6	4·8	5·5	6·2	6·6
K_T (atm.$^{-2}$)	0·62	0·51	0·28	0·20	0·17	0·11

thus it follows that the equilibrium primarily involves monomer and dimer but that some trimer is also present. Hydrogen cyanide behaves in much the same way (Giauque and Rührwein, *J. Amer. Chem. Soc.*, 1939, **61**, 2626), the association being due to hydrogen bonding. The present probem was solved by making the same assumption that led to the solution of the hydrogen cyanide case, namely, that as the pressure approaches zero the trimer equilibrium becomes negligible, hence the true dimer constant for any temperature may be obtained by plotting the apparent K_D (as given in Table 2 for 190°) against p and extrapolating to $p = 0$. In this way the values of K_D (true) given in Table 3 were obtained.

The values of K_T were calculated as follows. Let x^{-1} = mean degree of association of the vapour; then $x = PV/\boldsymbol{R}T(1 + \lambda P)$. The compressibility factor λ, if taken as equal to that of hydrogen chloride (M for HCl = 36·5; M for Me_2Be = 39·1), has an insignificant effect on the results over the temperature and pressure range investigated, and was therefore ignored. Let α = fraction of the dimethylberyllium present in dimeric form, and let β = fraction in trimeric form; then the fraction of the dimethylberyllium in the monomeric form is $1 - \alpha - \beta$, and $x = 1 - \alpha/2 - 2\beta/3$.

Since

$$p_{\text{monomer}} = p \cdot \frac{1 - \alpha - \beta}{1 - \alpha/2 - 2\beta/3} = p \cdot \frac{1 - \alpha - \beta}{x}$$

and

$$p_{\text{dimer}} = p \cdot \frac{\alpha/2}{1 - \alpha/2 - 2\beta/3} = p \cdot \frac{\alpha}{2x}$$

then

$$pK_D(\text{true}) = \alpha x/2(1 - \alpha - \beta)^2 = 2\alpha x/(3x - 1 - \alpha/2)^2$$

The solution to this equation is

$$\frac{\alpha}{2} = \frac{8x}{q} + 3x - 1 - 4\sqrt{\frac{x}{q}\left(\frac{4x}{q} + 3x - 1\right)}$$

where $q = 4pK_D$ (true). Since K_D (true) has been found as described above, it is now possible to calculate α for experimentally observed values of temperature and pressure, and hence $\beta(= 1 - 3x - \alpha/2)$. Then, since

$$p_{\text{trimer}} = p \cdot \frac{\beta/3}{1 - \alpha/2 - 2\beta/3} = p \cdot \frac{\beta}{3x}$$

$$p^2K_T = \beta x^2/3(1 - \alpha - \beta)^3$$

Value of α, β, and K_T were calculated for a pressure of 0·1 atm. from 170° to 200°.

At much lower pressures the values of β are so small that accuracy is poor, and at higher pressures the available temperature range is limited by the vapour pressure of dimethylberyllium. Even at 170° the value of x had to be obtained by a short extrapolation, since the vapour pressure of dimethylberyllium at 170° is only 0·08 atm. The results are given in Table **3**.

TABLE 3.

Temp. (c)	K_D (true, atm.$^{-1}$)	K_T (atm.$^{-2}$) *	α *	β *	Temp. (c)	K_D (true, atm.$^{-1}$)	K_T (atm.$^{-2}$) *	α *	β *
170°	12·3	52	0·48	0·16	190°	3·7	6·1	0·338	0·063
175	9·1	29	0·454	0·132	195	2·8	3·6	0·298	0·045
180	6·7	21	0·408	0·126	200	2·1	2·4	0·256	0·036
185	4·9	11	0·376	0·090					

* p = 0·1 atm.

The values of β at the lower temperatures suggest that a small amount of tetramer is likely to be present; consequently the true values of K_T should be obtained by determining K_T as above for various pressures and extrapolating to zero pressure, but in fact the experimental restrictions (the vapour pressure at lower temperatures and thermal decomposition above 200°) did not allow this. The temperature dependence of K_D (true) and K_T is given by

$$\log_{10} K_D \text{ (true)} = 10{\cdot}92 - 532_5/T$$

and

$$\log_{10} K_T = 20{\cdot}3 - 977_0/T,$$

hence

$$\Delta H_D{}^\circ = -24{\cdot}4 \pm 1 \text{ kcal. per mole of dimer,}$$

$$\Delta G_D{}^\circ = -24400 + 50T \text{ cal.,}$$

$$\Delta S_D{}^\circ = -50 \pm 2 \text{ cal. per mole of dimer per degree;}$$

and

$$\Delta H_T{}^\circ = -44{\cdot}7 \pm 5 \text{ kcal. per mole of trimer,}$$

$$\Delta G_T{}^\circ = -44700 + 93T \text{ cal., and}$$

$$\Delta S_T{}^\circ = -93 \pm 10 \text{ cal. per mole of trimer per degree.}$$

Latent Heat of Sublimation.—Table 3 shows that at 174°, when the vapour pressure of dimethylberyllium is 0·1 atm., the vapour consists of about 14% of trimer, 46% of dimer and 40% of monomer. At other temperatures of saturated vapour the composition will clearly be different. Since the heats of association (given above) are quite large it is at first sight rather surprising that the logarithm of the vapour pressure is so nearly a linear function of T^{-1}. From the vapour pressure equation given above, for the temperature range 155—180° (over which the equilibrium data may be considered applicable), let $\boldsymbol{R}\mathrm{d}\log_e p/\mathrm{d}(1/T) = \Delta H_S' = 23{\cdot}3$. This may be regarded as an apparent heat of sublimation; it is, in fact, the quantity of heat, in kcal., required to obtain one mole of vapour *of mean molecular weight M/x* from the solid, where M is the molecular weight of monomeric dimethylberyllium. Then the heat required to obtain x moles of vapour is $\Delta H_S'.x$, but this amount of vapour contains $\alpha/2$ moles of dimer and $\beta/3$ moles of trimer. The heat required to convert $x = (1 - \alpha/2 - 2\beta/3)$ moles of mixed vapour into one mole of monomeric vapour is $-\Delta H_D.\alpha/2 - \Delta H_T.\beta/3$; hence the heat required to obtain one mole of monomeric vapour from the solid; which may be regarded as the true heat of sublimation ΔH_S, is given by

$$\Delta H_S = \Delta H_S'(1 - \alpha/2 - 2\beta/3) - \Delta H_D.\alpha/2 - \Delta H_T.\beta/3.$$

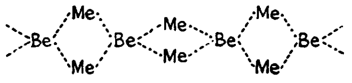
It is apparent that since $\Delta H_S' \approx -\Delta H_D \approx -\tfrac{1}{2}\Delta H_T$, $\Delta H_S \approx \Delta H_S'$. From the expressions for K_D and K_T given above, it follows that

$$\frac{2\beta}{3\alpha}\cdot\frac{(1 - \alpha/2 - 2\beta/3)}{1 - \alpha - \beta} = \frac{K_T.p}{K_D} \text{ and } \frac{4\beta}{3\alpha^2}(1 - \alpha - \beta) = K_T/K_D{}^2$$

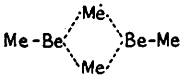
By solving these equations for α and β at various temperatures and pressures equal to the corresponding vapour pressures, the relation between the true and the apparent heat of sublimation may be examined more closely. The composition of the saturated vapour at 180°, calculated in this way, is 41% of monomer, 44% of dimer, and 14% of trimer, whence $\Delta H_S = 23{\cdot}4_8$ kcal. per mole of monomer. The results for 160° are 27% of monomer, 50% of dimer, and 23% of trimer, whence $\Delta H_S = 23{\cdot}4_6$. Clearly ΔH_S, which can be taken as 23·5 ± 1 kcal., is constant well within the accuracy with which $\Delta H_S'$ and the other data were measured, and, secondly, the high proportion of trimer at 160° indicates that tetramer and doubtless still higher polymers are present to an increasing extent at lower temperatures.

DISCUSSION

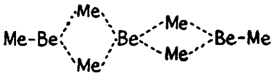
In view of the structure (I) of solid dimethylberyllium (Snow and Rundle, *loc. cit.*), in which broken lines represent half bonds, the following structures for the dimer (II) and trimer (III) present in the vapour would seem to be highly probable:



(I)



(II)



(III)

It is suggested that in (II) the Be–C–Be angle is about 60—70°, giving good overlap between the trigonal beryllium orbitals and the tetrahedral (sp^3) orbital of the methyl groups; the beryllium orbitals would be practically strainless with bond angles very close to 120°. In (III) the central beryllium atom would have a distorted tetrahedral configuration as in the solid polymer; thus one of the beryllium orbitals would appear to be more strained in the trimer and increasingly in higher polymers up to the solid "infinite" polymer, than in the dimer. Since the heat of formation of dimer from two monomer molecules is −24 kcal./mole, this represents mainly the heat change in the formation of four half bonds from two whole bonds, *i.e.*, 12 kcal. per whole bond. The corresponding value for the trimer, $\Delta H = 45$, is just over 11 kcal., since the trimer would contain eight half bonds. The heat of sublimation, 23·5 kcal./mole of monomer, can be resolved into two major parts, (*a*) the van der Waals energy which may be estimated at about 4—5 kcal. for a solid substance of molecular weight ~40, and (*b*) the energy required to form two whole bonds from four half bonds. Thus the second term is roughly 19 kcal., giving a value of 9—10 kcal. for the formation of two half bonds from one whole bond. Although the accuracy of the data and the assumptions involved do not permit very much significance to be attached to these figures, they are in agreement with the view that the strain in the dimer is least and that in the polymer greatest. It is interesting that the heat of formation of two half bonds from two whole bonds in the case of the trimethylaluminium dimer is nearly the same, *viz.*, 10 kcal., since the heat of dissociation (Laubengayer and Gilliam, *J. Amer. Chem. Soc.*, 1941, **63**, 477) is given as 20·2 ± 1 kcal./mole of dimer.

In the course of some experiments on the purification of dimethylberyllium, the solubility in benzene was found to be only just perceptible at the boiling point of benzene. Unlike solvents with donor properties, in which dimethylberyllium dissolves by chemical reaction, benzene is most unlikely to react chemically and the low solubility in this solvent agrees with the large amount of energy required to break the solid polymer into the smaller molecular units to be expected in a solution. In contrast, di*iso*propylberyllium, which is liquid at room temperature and certainly much less polymerised than dimethylberyllium, is readily soluble in benzene (unpublished observation by F. G.).

The entropy changes for the formation of one mole of dimer and trimer are −50 and −93 entropy units respectively. The translational entropy change being very readily calculated, the changes in internal entropy are −13 and −18 e.u. respectively (at 180° C). It is of some interest to enquire whether the value for the change of internal entropy on dimerisation is consistent with the proposed structure of the dimer (the data on the trimer equilibrium are not sufficiently accurate to be considered further). Beyond reasonable doubt the monomer has a linear structure, and by analogy with dimethylzinc and dimethylmercury (Boyd, Thompson, and Williams, *Discuss. Faraday Soc.*, 1950, **9**, 154) the methyl groups may be assumed to rotate freely. The Be–C bond length is calculated as 1·73 Å by applying the Schomaker–Stevenson electronegativity correction (*J. Amer. Chem. Soc.*, 1941, **63**, 37) to the beryllium and carbon single-bond radii given by Pauling (*ibid.*, 1947, **69**, 542). Taking the C–H bonds as $1{\cdot}09_3$ Å, the three rotational moments of inertia of the monomer are calculated as $I = I' = 169 \times 10^{-40}$, and $I'' = 10{\cdot}7 \times 10^{-40}$ g. cm.^{2}. On the free-rotation assumption the rotational entropy of the monomer becomes 23·6 e.u. at 180°, the total symmetry number being assumed to be 18. On the basis of structure (II) for the dimer and end Be–C bonds as 1·73 Å, bridge Be–C bonds as 1·92 Å (the value found for the solid polymer), and C–Be–C angles of 120°, the moments of inertia are $I = 167$,

$I' = 426$, and $I'' = 572 \times 10^{-40}$ g. cm.^{2}. Although it is highly probably that the end-methyl groups in the dimer can rotate freely, the matter of free rotation or a fixed configuration for the bridge-methyl groups is less easy to decide and is of considerable significance in view of the recent theory of Gillespie (*J.*, 1952, 1002) concerning the use of 3*d* orbitals by carbon in this type of compound. According to this theory the bridge-methyl groups should be fixed, whereas if the molecular orbital forming the Be–C–Be bond is derived from a carbon sp^3 tetrahedral orbital there appears to be no reason why the methyl groups should not rotate freely since steric interference would be very small. The rotational entropy is therefore calculated for the two situations, (*a*) fixed bridge-methyl groups, and (*b*) freely rotating bridge-methyl groups. In the former the symmetry number of the dimer is $4 \times 3^2 = 36$, and by the method given by Aston (Taylor and Glasstone, "A Treatise on Physical Chemistry," Vol. I, Van Nostrand, 1942), the rotational entropy at 180°, $S_r(a) = 33{\cdot}9$ e.u. In the latter case the symmetry number is $4 \times 3^4 = 324$, the number of rotational degrees of freedom is seven instead of five, and at 180° $S_r(b) = 42{\cdot}0$ e.u. From these results and the experimental value for the total internal entropy change on dimerisation (13 ± 2 e.u.), the quantity (vibrational entropy of the dimer — 2 × vibrational entropy of the monomer) becomes $0{\cdot}3 \pm 2$ e.u. on situation (*a*) and $-7{\cdot}8 \pm 2$ e.u. on situation (*b*). Since the number of bonds in the dimer is necessarily more than twice that in the monomer, and some of them must be half-bonds with relatively low force constants, it appears inevitable that the vibrational entropy of the dimer should be more than twice that of the monomer. Hence it is concluded (1) that the observed entropy change is reasonably consistent with the proposed structures, and (2) that, in support of the theory of Gillespie, the bridge-methyl groups are more likely to be fixed than free to rotate. This type of approach appears to provide one of the very few ways by which Gillespie's theory can be tested. Accurate equilibrium and calorimetric entropy data on trimethylaluminium (which is simpler to deal with experimentally than dimethylberyllium) are much to be desired in this connection.

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