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Physical Properties of Decaborane(14) Derivatives

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Enthalpy and entropy of vaporization for 2-ethyldecaborane(14) are 13.8 kcal. and 28.0 cal. per deg. per mole, respectively. Similar values for 1,2-diethyldecaborane(14) are 18.1 kcal. and 39.0 cal. per deg. per mole. Activation energies for flow are 4.8 kcal. for the monoethyl and 3.0 kcal. for the diethyl derivative. The former demonstrated a distribution of free volumes double that of the latter. These results are interpreted as changes from somewhat associated, spherical molecules for the 2-ethyldecaborane(14) to highly asymmetric, strongly associated 1,2-diethyldecaborane(14) molecules.

PHYSICAL MEASUREMENTS on 2-ethyldecaborane-(14), I, and 1,2-diethyldecaborane(14), II, are given in Table I. These materials were prepared by reactions between decaborane(14) and ethyl chloride, catalyzed by anhydrous aluminum trichloride, then purified by reduced pressure fractionation to 99.9% assay of boron, carbon, and hydrogen.

METHODS

Kinematic viscosities were obtained with Cannon-Fenske viscometers operated under high purity nitrogen atmospheres; these values are means of at least 11 determinations

and of 0.5% precision. Densities were determined pycnometrically with 0.3% precision. Vapor pressures were determined with the Reid micro vapor pressure apparatus operated under high purity nitrogen atmospheres, with a precision of 0.5%.

THERMODYNAMICS

Enthalpies of vaporization calculated from the Clapeyron-Clausius equation gave values of 13.8 kcal. for I and 18.1 kcal. for II. Moreover, this value for I correctly predicts the extrapolated boiling temperature for I at 217° C. (*1*), and gives $\Delta S_{vap.}$ = 28.0 cal. per degree per mole.

Table I. Physical Measurements on Decaborane(14) Derivatives

	Temperature, ° C.											
	0	20	30	40	45	50	55	60	65	70	75	80
I. 2-ETHYLDECABORANE(14), $C_2H_5B_{10}H_{13}$												
Kinematic viscosity, centistokes	13.59	7.62	6.10			4.56		3.43				
Density, grams/cc.	0.8296	0.8164	0.8099			0.7967		0.7903				
Absolute viscosity, centipoises	11.28	6.22	4.94			3.63		2.71				
Vapor pressure, mm. of Hg					0.34	0.49	0.68	0.84	1.26	1.67	2.19	
Free volume, $\dfrac{V_o^a}{V - V_o}$	5.43	4.94	4.64			4.25		4.08				
II. 1,2-DIETHYLDECABORANE(14), $(C_2H_5)_2B_{10}H_{12}$												
Kinematic viscosity, centistokes	11.80	6.35	5.20	4.19		3.55		3.17				
Density, grams/cc.	0.8410	0.8283	0.8215	0.8150		0.8088		0.8025				
Absolute viscosity, centipoises	9.84	5.26	4.27	3.42		2.87		2.54				
Vapor pressure, mm. of Hg								0.27	0.30	0.49	0.72	1.03
Free volume, $\dfrac{V_o^a}{V - V_o}$	2.60	2.43	2.38	2.32		2.24		2.20				

^{a} Based upon d = 0.8 gram/cc./$B_{10}H_{14}$ (solid).

Table II. Comparison of Physical Properties of Decaborane (14) Derivatives

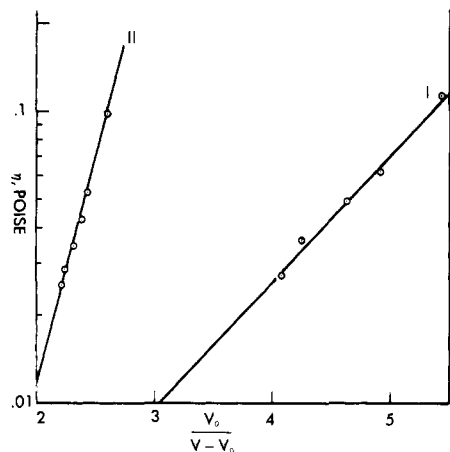|	$V_f(1)$, Cc.	V_f/V	$\dfrac{(V_o)}{(V-V_6)}$, 30°C.	$\Delta H_{vap.}$, Kcal./ Mole	$\Delta S_{vap.}$, Cal./ Mole/Deg.	$\dfrac{\Delta H_{vap.}}{\Delta S_{vap.}}$, Deg.	E_v^*, Kcal.	$\dfrac{\Delta H_{vap.}}{E_v^*}$	$\dfrac{E_v^*}{\Delta S_{vap.}}$, °K.	$T_{b.p.}$, °K.
I	2.22×10^{-25}	0.00072	4.64	13.8	28.0	494	4.8	2.88	126.5	490
II	1.11×10^{-25}	0.00031	2.38	18.1	39.0	465	3.0	6.05	77.0	465
I/II	2/1	2/1	2/1	3/4	3/4	1/1	3/2	1/2	5/3	1/1

Figure 1. Hybrid viscosity plots for decaborane(14) derivatives

The boiling temperature of II is calculated at 192° C., with $\Delta S_{vap.} = 39.0$ cal. per degree per mole.

With these values, estimates of free volumes for assumed close-packed lattices are possible with Equation 1 (4), and are given in Table II.

$$V_f = \frac{8(V^*/N)}{\left(\dfrac{\Delta H_{vap.}}{RT} - 1\right)^3} \qquad (1)$$

KINETICS

By using the reaction-rate theory with simplifying assumptions that the probability of a molecule, vibrating in an imperfect quasicrystalline liquid, jumping between equilibrium positions is proportional to both its energy, E_v^*, and the existence of a vacancy (the free volume term) (3):

$$\eta = A_o \text{ exptl.} \left[\frac{E_v^*}{RT} \right] \qquad (2)$$

Plots of log η against $1/T$ for these data gave decided curvature, as is typical for many associated and polymeric liquids.

By incorporating the concept that a distribution of the sizes of vacancies exists, the hybrid equation for well-known close-packed volumes without overlap can be written (5):

$$\eta = A_o \left[\text{exptl.} \frac{(V_o)}{(V - V_o)} + \frac{(E_v^*)}{(RT)} \right] \qquad (3)$$

Although this equation is not entirely free from theoretical objections (2), its utility is demonstrated with these data in Figure 1, from which values of E_v^* are readily calculated. The activation energy for flow of I is 4.8 kcal., and that of II is 3.0 kcal. Free volume distribution of I is double that of II, as might be expected for one pendent ethyl grouping on the bottom of the partial icosahedron of decaborane(14). Two pendent ethyl groupings on the bottom of this partial icosahedron, however, restore one plane of symmetry for better intermolecular association,

thereby possibly augmenting the total molecular asymmetry.

ACKNOWLEDGMENT

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CORRECTION

In the article "The Ternary Systems Cobalt Chloride–Dioxane–Water and Nickel Chloride–Dioxane–Water at 25° C." by Hans Schott and Cecil C. Lynch [J. CHEM. ENG. DATA 11, 215 (1966)], the following corrections should be made:

In Table III, p. 218, the superscript b in the column "Heavy Layer NiCl$_2$" at Designation 16 should be changed to a superscript d.

The following appendix was omitted:

Table V. X-Ray Powder Diffraction Pattern of Cobalt Chloride Diaquomonodioxanate

Bragg Spacing[a] d/n, A	Relative Intensity I/I_0
6.20[b]	0.13
5.68	1.00
4.58	0.18
3.67	0.22
3.22	0.07
3.10[c]	0.08
3.02	0.07
2.93	0.05
2.87	0.07
2.82	0.13
2.75	0.12
2.70	0.04
2.59	0.06
2.36	0.06
2.29	0.16
2.15	0.09
2.02	0.06
1.99	0.06
1.95	0.06
1.91	0.04

[a] Down to 1.88 A. [b,c] Coincides with the position at which the 5.7 A[b] or 2.82 A[c] spacings would diffract the $K\beta_1$ line of cobalt, respectively, but since most, if not all, $K\beta_1$ radiation was filtered out, these lines are too intense to be due to it.