Volume Changes for Metal Solutions in Liquid Ammonia

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RECEIVED MARCH 30, 1955

In the course of recent research it was necessary to obtain the volume change associated with the solution of lithium, sodium and potassium in liquid ammonia. That the solution of these metals in liquid ammonia is accompanied by a relatively large increase in volume has long been known. From the densities of sodium and potassium solutions it has been shown that these volume changes pass through a maximum at about 3 *N*.[2]

However, the more recent publication of the densities of lithium solutions[3] did not include values for the accompanying volume changes. The mole fractions of lithium and the densities of these solutions as given in the above article are shown in Table I along with the volume changes calculated from these data. Since many properties of these solutions have been shown to be the same or at least quite similar it seems significant to note that the lithium solutions, at least according to the available data, do not exhibit a maximum. As is shown in Fig. 1 the volume change increases steadily as the solutions become more dilute.

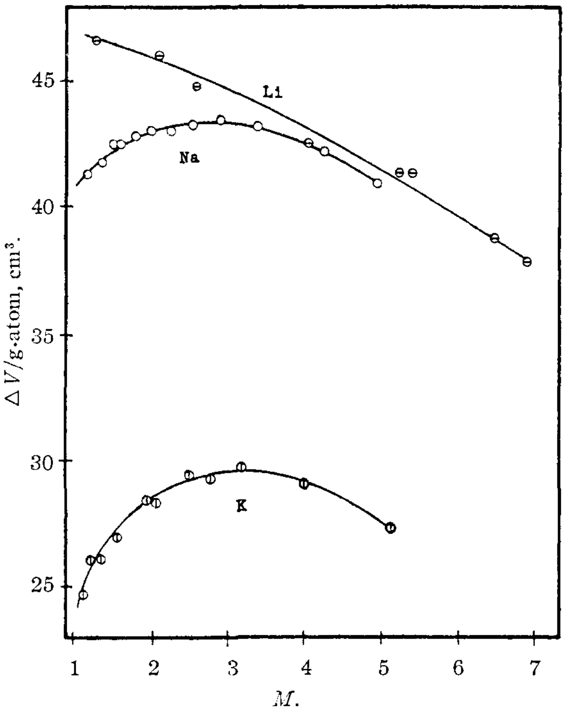

Fig. 1.—Volume changes accompanying the solution of the alkali metals in liquid ammonia, the increase in volume, Δ *V*/g. atom, as a function of the normality, *N*.

TABLE I

VOLUME CHANGES FOR LITHIUM SOLUTIONS IN LIQUID AMMONIA[a]

X_2	*d*, g./cc.	Δ*V*/g. atom, cc.	X_2	*d*, g./cc.	Δ*V*/g. atom, cc.
0.0331	0.639	46.7	0.1557	0.523	41.4
.0571	.611	46.1	.1616	.518	41.4
.0713	.597	44.8	.1958	.498	38.8
.1180	.554	42.5	.2105	.490	37.9

[a] Lithium densities determined at −33.2° by Johnson, Meyer and Martens.[3]

It should be noted, as pointed out by Johnson, *et al.*, that the volume changes in the dilute range are extremely sensitive to errors in the density determinations. Errors of 0.1% in the densities would be sufficient to give a somewhat flat maximum to the curve and errors of the order of 0.5% could give a curve quite similar to those obtained previously for sodium and potassium.

However, at the present time the conclusion that these metal–ammonia solutions are the same or even quite similar in this respect does not seem to be a fair statement. It would seem that further and more precise data, especially in the dilute solutions, is desirable.

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[2] C. A. Kraus, E. S. Carney and W. C. Johnson, THIS JOURNAL, **49**, 2206 (1927); W. C. Johnson and A. W. Meyer, *ibid.*, **54**, 3621 (1932).

[3] W. C. Johnson, A. W. Meyer and R. D. Martens, *ibid.*, **72**, 1842 (1950).

The Thermal Decomposition of Tri-*n*-butylborane

BY LOUIS ROSENBLUM

RECEIVED JUNE 6, 1955

Sodium,[1] beryllium[2-4] and magnesium[5-7] alkyls thermally decompose under vacuum at 100 to 200°. The main products are a metal hydride or an alkyl metal hydride and an olefin of the same number of carbon atoms as the original alkyl group. Recently, we observed that a boron alkyl, tri-*n*-butylborane, decomposed upon heating under vacuum; the products were dibutyldiborane and butene. The similarity both in the nature of the products and the experimental conditions suggests that the same mechanism is involved in all of these metal alkyl decompositions.

The olefin product formed from the decomposition of $(n\text{-}C_4H_9)_3B$ is found to be either butene-1 or butene-2. This differs somewhat from the decomposition of $(n\text{-}C_4H_9)_2Mg$ where only butene-1 is observed.[6,7] Presumably, butene-1 is produced initially from both the boron and magnesium compounds, but under more vigorous experimental conditions, such as prolonged heating, it can rearrange to give the more stable isomer, butene-2.

The dibutyldiborane isolated probably arises *via* the formation of $(C_4H_9)_2BH$, which then dimerizes and disproportionates. This is comparable to the decomposition of $(i\text{-}C_3H_7)_4Be_2$ to yield $(i\text{-}C_3H_7\text{-}BeH)_n$.[3]

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[1] W. H. Carothers and D. D. Coffman, THIS JOURNAL, **51**, 588 (1929).

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[3] G. E. Coates and F. Glockling, *J. Chem. Soc.*, 22 (1954).

[4] G. E. Coates and F. Glockling, *ibid.*, 2526 (1954).

[5] P. Jolibois, *Compt. rend.*, **155**, 353 (1912).

[6] E. Wiberg and R. Bauer, *Z. Naturforsch.*, **5b**, [7] 396 (1950).

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Experimental

Tri-*n*-butylborane, prepared by the method of Johnson, *et al.*,[8] was refluxed at 125 to 130° at 10 mm. pressure for 10 days. The low boiling decomposition product was trapped in a −196° cold trap. At intervals small samples of the higher boiling product were tapped off.

The low boiling product from the cold trap was identified as *trans*-butene-2 from its infrared spectrum. Molecular weight calculated for C_4H_8, 56.10; found, 56.78.

When milder conditions were used (refluxing at 90 to 100° at 5 mm. pressure for 2 days) the low boiling decomposition product was identified as butene-1 by its infrared spectrum.

The high boiling decomposition product in the first case was identified as dibutyldiborane. This compound reduced silver nitrate solution and reacted vigorously with ethanol to give hydrogen. The infrared spectra showed absorption bands in the regions characteristically associated with CH, BH and BH (bridge) stretching frequencies (see Table I).

Anal. Calcd. for $C_8H_{22}B_2$: C, 68.68; H, 15.85; B, 15.47. Found: C, 68.79; H, 16.27; B, 15.27.

TABLE I

INFRARED ABSORPTION BANDS USED TO IDENTIFY DIBUTYLDIBORANE

Frequency, cm.$^{-1}$	Relative intensity	Motion
2930	VS	CH stretch
2840	VS	CH stretch
2530	S	BH stretch
2460	S	BH stretch
2020	W	BH (bridge) stretch
1915	VW	BH (bridge) stretch

A form of the Antoine equation may be used to give the vapor pressure–temperature relationship for this compound.

$$\log p = 5.374 - \frac{1233}{t + 230} \quad \begin{array}{l} p = \text{pressure in mm.} \\ t = \text{temp. in °C.} \end{array}$$

Since this compound begins to decompose at temperatures where any readable vapor pressures are exhibited, there was much difficulty in obtaining good vapor pressure data. This being the case, not too much reliance can be placed on the constants in the above equation.

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[8] J. R. Johnson, H. R. Snyder and M. G. Van Campen, THIS JOURNAL, **60**, 115 (1938).

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Melt Viscosities of Dimethylpolysiloxanes

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RECEIVED MAY 24, 1955

Melt viscosities have been measured for four fractions obtained from a solution fraction of a high molecular weight dimethylpolysiloxane. Together with viscosity data for pure compounds, the linear dimethylpolysiloxanes,[1] the viscosity–molecular weight data for the fractions define two straight lines on a plot of log η_0 (zero shear viscosity) *vs.* log M_V. The high molecular weight branch has a slope of 3.64, quite close to the slope values found by Fox and Flory[2] for polyisobutylene and polystyrene. The low molecular weight branch has a slope of 1.43 which is only slightly greater than that suggested by Bueche.[3] The point of intersection lies at a molecular weight of 40,000. Bueche suggests this is the point of pseudo network formation due to polymer entanglements and in our case would represent a distance between entanglements of 1100 chain atoms.

The polymer used in the fractionation was prepared from pure octamethylcyclotetrasiloxane by an alkaline polymerization of the type described by Hyde.[4] The polymer was washed free of alkaline catalyst, dried and devolatilized at 1 mm. for 24 hours. During this period roughly 12% of volatile cyclic polymers were removed. The intrinsic viscosity of the polymer in toluene was 1.36. Barry's relationship[5] yielded a viscosity average molecular weight of 641,000. Fractionation of the polymer was carried out at 25° from a solution in ethyl acetate which was 2% by volume. Acetone was the precipitant. Fractions were obtained which were roughly one-fourth of the total sample in size. The procedure was repeated eight times taking a new sample of polymer each time with cuts removed at about the same precipitant volumes. All corresponding cuts were combined, redissolved, reprecipitated and dried. Solvent was removed at 1 mm. pressure at 50–70° for four to eight hours' pumping. This gave four fractions of roughly 200 g. each. These rather large samples were necessarv for rheological studies. It is recognized that effectively this was a single fractionation and did not yield the narrow range of molecular weights which a multiple fractionation would produce. However, the size of sample required by the extrusion type rheometer made such an extensive multiple fractionation prohibitive. The distribution of materials in the cuts is included in column 4 of Table I.

Viscosities at very low rates of shear (η_0 or zero shear viscosity) were obtained by measuring the rate of fall of $^1/_{16}''$ diameter steel balls in polymer held in one inch test-tubes. All polymer samples were centrifuged in the tubes to remove air bubbles. Viscosities of cuts 2, 3 and 4 were such that reasonable rates of fall for the balls were obtained. Faxen's equation[6] was used to calculate the viscosities from these rates of fall. Cut 1, however, was too viscous and it was necessary to increase the sedimenting force by centrifuging to roughly 2000 times gravity. To provide a basis for calculation cuts 1 and 2 were centrifuged simultaneously. The rate of fall of a $^1/_{16}''$ ball in cut 2, whose viscosity had been previously determined at unit gravity, gave a calibration of the sedimentation force. From this and the rate of fall of a $^1/_{16}''$-ball in cut one in the same centrifuge period, the viscosity of cut no. 1 was calculated. Molecular weights were obtained from intrinsic viscosities in toluene using Barry's value.[5] The data are summarized in Table I.

TABLE I

Cut	M_V	η_0, poise, 40°	% in fraction[a]
1	1,260,000	1.61×10^7	23.6
2	851,000	2.23×10^6	30.0
3	477,000	8.58×10^4	25.1
4	214,000	6.45×10^3	21.3

[a] Based on recovered polymer.

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[1] M. J. Hunter, E. L. Warrick, J. F. Hyde and C. C. Currie, THIS JOURNAL, **68**, 2284 (1946).

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[3] F. Bueche, *J. Chem. Phys.*, **20**, 1959 (1952).

[4] J. F. Hyde, U. S. Patent 2,490,357.

[5] A. J. Barry, *J. App. Phys.*, **17**, 1020 (1946).

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