Solubility of Diborane

. . . in the Dimethyl Ether of Diethylene Glycol,
. . . in Mixtures of Sodium Borohydride and Dimethyl Ether of Diethylene Glycol
. . . and in Ditertiary Butyl Sulfide

S. YERAZUNIS, J. W. MULLEN, and B. STEGINSKY
Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, N. Y.

INCREASING recognition of the potential of diborane as a building block for the higher derivatives has resulted in major efforts to evaluate feasible separation processes. One of these, namely absorption, requires that suitable solvents for diborane be identified.

Although Elliot and others (*4*) had determined the solubility of diborane in diethyl ether and tetrahydrofuran, a knowledge of its solubility, particularly in the low pressure range, in an additional number of solvents was considered essential. In this research, the solubility of diborane was determined in the dimethyl ether of diethylene glycol, in a solution of sodium borohydride and the dimethyl ether of diethylene glycol, and in ditertiary butyl sulfide.

Diborane is sparingly soluble in the dimethyl ether of diethylene glycol at temperatures in the range of 0° C. to 30° C., the solubility increasing with lowering of the temperature. At the higher concentrations the dissolution process corresponds to physical absorption while a complexing or other chemical reaction appears to occur in the very dilute range.

The solubility of diborane in solutions of sodium borohydride and the dimethyl ether of diethylene glycol is considerably greater than in the pure ether, at 30° C. However, the enhanced solubility appears to be entirely attributable to the formation of an etherate complex and falls off markedly after a mole ratio of diborane to borohydride of 0.5, corresponding to saturation is reached.

The solubility of diborane in ditertiary butyl sulfide at 30° C. is considerably greater than in either of the other solvents investigated.

EXPERIMENTAL APPARATUS, MATERIALS, AND PROCEDURE

The equilibrium apparatus, which was designed to reduce to a minimum the need for introducing or removing diborane from the system, was composed of: three gas reservoirs in parallel, an automatic Toepler pump, closed end manometer, a cold finger, and the equilibrium cell. The components were arranged compactly so that the equilibrium cell and all but a small fraction of the gas volume would be immersed in a mineral oil bath for control of temperature. In practice, the equilibrium cell, having been charged with a known amount of solvent, was brought into contact with diborane whose quantity was calculated from the *P-T-V* relations. The Toepler pump was used to circulate the gas through the equilibrium cell forcing it to bubble through the solvent until steady pressures were attained, providing the experimental data required to calculate the concentration of diborane in the solvent. The shift to a new equilibrium measurement was accomplished by condensing the vapor phase diborane and modifying the system by isolating one or more of the gas reservoirs. A considerable range of solubility-pressure measurements was obtained with this equilibrium device by appropriately adjusting the available gas volume. When maximum pressure was attained, the procedure was reversed and solubilities can be determined by decompression.

Of two cylinders of diborane one was determined to be free of contaminants by infrared spectroscopy, the other was found to contain 6.0% ethane and 0.7% silane. Upgrading of this material without special low temperature fractionation equipment was out of the question and the material was used as received except for hydrogen removal.

The dimethyl ether of diethylene glycol was treated by fractionation in the presence of lithium hydride in a 4-foot Heli-grid, Hypercal Podbelniak distillation column under an atmosphere of high purity nitrogen.

The ditertiary butyl sulfide was used as received from the Phillips Petroleum Co.

Sodium borohydride was used as received and purified by recrystallization from diethylene glycol by the method described by Brown and others (*2*). No appreciable difference could be detected between the purified and unpurified material.

DISCUSSION OF RESULTS

Dimethyl Ether of Diethylene Glycol. The solubility of diborane in the dimethyl ether of diethylene glycol, Table I, was found to be a linear function of pressure at the higher concentrations with curvature being restricted to the low concentration regions. This behavior suggests that the diborane is complexing with solvent to a limited extent and that pure physical absorption is achieved only after the capacity of the system to form coordination complexes has been satisfied. The extent to which the complex is formed is temperature dependent and increases with decreased temperature.

The absolute accuracy of these solubility data is subject to some question particularly at the lowest concentrations, because of the evolution of a noncondensable gas at liquid nitrogen temperatures, observed whenever diborane and the ether solvent were brought together. Infrared spectroscopic analysis of the noncondensable failed to reveal any characteristic vibrational frequencies, suggesting that the gas could only be hydrogen, nitrogen, or some similar molecule. It was subsequently found that much of the evolution could be attributed to the reaction between diborane and unmethylated hydroxyls in the solvent, and a considerable reduction in the evolution was obtained by an intensive purification of the solvent. Nevertheless, some amount of hydrogen evolution was encountered even after purification supporting Hurd's (*7*) observation that the dissolution of diborane is frequently accompanied by hydrogen evolution.

The evolution of hydrogen can be explained by three mechanisms: reaction with residual hydroxyl groups on the solvent molecule, a slow reaction of diborane with the

Table I. Solubility of Diborane in Dimethyl Ether of Diethylene Glycol

0° C.		15° C.		30° C.	
Partial pressure, mm. Hg	Mole fraction solution	Partial pressure, mm. Hg	Mole fraction in solution	Partial pressure, mm. Hg	Mole fraction in solution
31.17	0.00929	26.76	0.00665	22.7	0.0035
33.47	0.00981	26.97	0.00657	49.6	0.0045
40.82	0.01055	29.47	0.00681	53.6	0.0057
51.09	0.01185	32.42	0.00699	74.0	0.0062
51.34	0.01177	41.84	0.00759	119.7	0.0076
56.25	0.01224	42.36	0.00746	142.3	0.0099
61.43	0.01270	56.59	0.00869	314.4	0.0158
61.43	0.01274	57.06	0.00864	...	...
77.96	0.01432	67.77	0.00988	...	...

stopcock grease, and the formation of a coordination complex between the ether and diborane in which the boron atom is bonded to an oxygen atom weakening boron-hydrogen bonds and inducing cleavage and subsequent evolution. It is likely that all three mechanisms occur to some extent, and it is in this respect that the question of accuracy of the data arises. That diborane producing hydrogen by cleavage can be properly considered as dissolved while that reacting with residual hydroxyls or system greases cannot be so considered. Since it was not possible to estimate what fraction of the diborane which takes part in the evolution process does so by any of the three mechanisms, it was decided to consider all diborane not accounted for in the vapor phase as being affectively dissolved in the ether. Fortunately, the potential error is quite small and at higher pressures the numerical effect is entirely negligible.

These solubilities in the low pressure range compare favorably with measurements reported by Goodell (*5*) in the range of pressure in excess of 600 mm. Hg. Although interpolation between the two sets of measurements is difficult because of the gap, the data seem compatible.

Solutions of Sodium Borohydride and the Dimethyl Ether of Diethylene Glycol. The solubility of diborane in 2% and 5.4% by weight solutions of sodium borohydride and ether solvent up to a pressure of 300 mm. Hg at 30° C. are presented in Table II. The observations of Goodell (*5*) and Gussow (*6*) and more recently Baker and others (*1*) that diborane was very soluble up to a point determined by the concentration of the sodium borohydride, beyond which diborane became relatively insoluble, were confirmed. These experimental results add support to the theory that diborane complexes with the sodium borohydride and the ether to form an etherate complex. Extrapolations of the pressure-concentration curves to zero pressure yield a ratio on a mole basis of diborane to sodium borohydride of approximately 0.48 corresponding closely to the values reported by Baker. Agreement is excellent with the theoretical ratio of 0.50 which would be expected if a complex consisting of one-half mole of diborane per mole of borohydride was formed.

Diborane is relatively insoluble after its concentration in the solvent exceeds a critical value determined by the concentration of the borohydride. In fact, the solubility is less favorable in this environment than in the ether solvent. This behavior may be attributed to an unavailability of ether molecules for direct complexing or to a relative insolubility of diborane in the etherate complex.

The solubility data are subject to a degree of uncertainty for two reasons: the evolution of hydrogen during the equilibrium process, and the presence of unremovable contaminants in the diborane.

The phenomenon of hydrogen evolution observed in the dissolution of diborane in the ether solvent was also encountered in this system. As in the previous case, it was not possible to differentiate between dissolved and reacted diborane, and the reported solubilities are based on the assumption that diborane unaccounted for in the vapor phase was effectively dissolved. Evolution of gas was also noted when sodium borohydride was dissolved in the ether solvent. Purity of the solvent or the borohydride did not seem to be a factor in this process. Although no effort was made to identify the gas it is believed that it was hydrogen being released from a borohydride-ether complex.

The silane and ethane contaminants were accounted for by assuming that their solubility was negligible. In addition, experimental measurements were obtained by a

Table II. Solubility of Diborane in Solutions of Sodium Borohydride and Dimethyl Ether of Diethylene Glycol at 30° C.

1.98 Weight %, 6.68 Mole % $NaBH_4$ in Diborane-Free Solution		2.00 Weight %, 6.75 Mole % $NaBH_4$ in Diborane-Free Solution		5.44 Weight %, 16.93 Mole % $NaBH_4$ in Diborane-Free Solution	
Partial pressure, mm. Hg	Mole fraction in solution	Partial pressure, mm. Hg	Mole fraction in solution	Partial pressure, mm. Hg	Mole fraction in solution
304.0	0.047	265.5[a]	0.047	221.1	0.085
176.4	0.047	23.7[a]	0.042	103.5	0.081
91.3	0.047	4.1[a]	0.041	38.5[a]	0.077
44.9	0.044	...	...	27.6	0.072
24.8	0.038	...	...	21.2	0.069
...	...	...	...	13.2[a]	0.074
...	....	...	...	5.4[a]	0.073
...	...	...	...	4.3[a]	0.072

[a] Obtained by a decompression sequence.

decompression sequence in which the saturated liquid phase was exposed to progressively larger gas volumes. The agreement between the corrected compression and the decompression measurements supports the assumption of negligible contaminant solubility.

The experimental data compare favorably with measurements at 25° C. reported by Baker and others (*1*). Modified Henry's Law constants representing the slope of the pressure *vs.* concentration curve expressed in units of mm. Hg. and weight fraction were calculated for the two cases reported by Baker to be 2.25×10^4 and 2.14×10^4 as compared to 2.26×10^4 and 0.8×10^4 obtained here. The latter figure is believed to be unduly biased by a single experimental value at high pressure.

Ditertiary Butyl Sulfide. The solubility of diborane was determined to be greater in ditertiary butyl sulfide, Table III, than in the ether or ether-borohydride solvent at 30° C. In order to account for the ethane and silane contaminants, gas samples were analyzed by infrared spectroscopy using a quantity of the original diborane mixture as a reference. Of the total measured pressure of 70.2 mm. Hg. in one instance, 52.4 mm. Hg. were attributable to ethane and silane and only 17.8 mm. Hg. to diborane. The alternate approach of assuming complete insolubility of ethane and silane, the method which was employed in the instance of the sodium borohydride-ether solvent, resulted in a calculated diborane partial pressure of 13.5 mm. Hg. The comparison between 17.8 and 13.5 is quite good (only a small error in the original analysis of the gas would be required to make the agreement exact) and lends support to the assumption that the contaminants are in fact sparingly soluble in the sulfide.

Table III. Solubility of Diborane in Ditertiary Butyl Sulfide at 30° C.

As Measured by Compression		As Measured by Decompression	
Partial pressure, mm. Hg	Mole fraction in solution	Partial pressure, mm. Hg	Mole fraction in solution
4.1	0.075	5.8	0.103
5.5	0.077	7.7	0.113
13.5	0.126	8.7	0.117
14.3	0.123	11.1	0.122
14.4	0.122	11.8	0.127
17.8	0.148	12.9	0.134
22.0	0.156	...	...
24.9	0.163	14.7	0.140

When the equilibrium data obtained during a compression sequence were corrected on the basis of insolubility of the contaminants, the diborane partial pressures were found to be internally consistent but somewhat higher by 2 to 3 mm. Hg than those measurements obtained during decompression for equivalent concentrations. As the corrections to the compression data were large and the decompression sequence believed to be more free of uncertainty, the use of the latter set is recommended.

The experimental data suggest the possibility that diborane-solvent complexes may have been formed. Coyle and others (*3*) have reported the existence of diborane complexes in these sulfide solvents.

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