Boron trichloride and hydrogen also reacted with crushed calcium hydride to produce spontaneously inflammable gaseous products which responded to the conventional tests for diborane. Calcium chloride was formed in the charge.

3. It is of interest to note in passing that some chemical evidence has been obtained for the formation of boron hydrides in the violent reaction that ensues upon heating mixtures of powdered anhydrous boric oxide and lithium hydride or sodium hydride. This hardly seems desirable as a preparative method, however.

Discussion

It indeed appears surprising that a substance as thermally unstable as diborane can be synthesized under conditions that ordinarily would result in a rather rapid pyrolysis of this material. Several factors, however, may explain why so little pyrolysis actually does occur and why the losses of boron are small.

The actual contact time during which a unit of gas remained at elevated temperatures was in most cases rather short (Table I). This would tend to minimize pyrolysis losses. Also, there generally has been present in the reaction zone a large excess of hydrogen over the amount actually needed for the formation of boron–hydrogen compounds. Although the effect of hydrogen in inhibiting the decomposition of hydroborons at room temperature is well known, it well may be that this effect is not operative at elevated temperatures and the hydrogen may be effective largely by diluting the diborane product.

TABLE I

DIBORANE PREPARATIONS

	T, °C.	H_2/ BCl_3	C. T.[a]	Al_{size}	Condensed product, mole per cent. B_2H_6	HCl	BCl_3	Conversion, %[b]
1	360	4–1	5″	−12	2.9	4.1	93	6
2	320	3–1	12″	−40	3.5	1.3	95.2	6.7
3	350	3–1	12″	−40	5.8	0	94.2	11
4	350	6–1	15″	−40	8.8	1.7	89.5	16.4
5	475	6–1	6″	−30	12.4	1.7	85.9	20.4
6	500	6–1	4″	−30	6.7	0.9	92.4	12.5
7	450	6–1	6″	−30	17.2	3.9	78.9	30

[a] C.T. Calculated contact time in hot zone, 1″ dia. reactor. [b] Per cent. BCl_3 converted to B_2H_6, assuming no boron loss in the reactor.

In addition it may be possible that more stable monoboron compounds, *e. g.*, $BHCl_2$, BH_2Cl, may be the primary products of a stepwise reaction and that these transient compounds later undergo rearrangement into diborane and boron trichloride when out of the reactor hot zone.

In the runs where boron fluoride was used no inflammation was noticed even though large quantities of diborane were present at times in the exit gas. This may indicate either that diborane monofluoride (B_2H_5F) is not formed in the reaction or is not spontaneously inflammable if it is formed.

Reasoning from the experiments with metal hydrides, the reduction of boron halides with hydrogen over metals similarly may appear at first glance to involve the initial formation of reactive hydrides on the surface of the metal followed by replacement reactions. There is, however, little direct evidence to support this over other possible mechanisms, and at the present time the exact nature of the reaction is not known.

Summary

Diborane and diborane monohalides have been produced by the reduction of boron halides with hydrogen over active metals at elevated temperatures.

The reaction of gaseous boron halides with active metal hydrides also has been found to produce diborane.

SCHENECTADY, NEW YORK RECEIVED JUNE 24, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Liquid–Liquid Solubility of Perfluoromethylcyclohexane with Benzene, Carbon Tetrachloride, Chlorobenzene, Chloroform and Toluene

BY J. H. HILDEBRAND AND D. R. F. COCHRAN

The extraordinary solvent properties of fluorocarbons which have come to light during the last few years have been considered in two recent papers from this Laboratory, one by R. L. Scott,[1] who gave "solubility parameters" for a number of fluorocarbons and showed their general harmony with available solubility data, and another by Benesi and Hildebrand[2] who reported a figure for the solubility of iodine in normal perfluoroheptane at 25° and showed that the remarkably small solubility, only 0.007 the solubility in an ideal solution, does not overstrain existing solubility theory for regular solutions.[3] This instance of the adequacy of theory to cope with an extreme departure from Raoult's law encouraged us to measure other fluorocarbon solubilities in the expectation that they would have much more than merely empirical value and could be used in connection with refinements in the general theory.

The large molal volumes of the fluorocarbons compared with the corresponding hydrocarbons leads to unusually low "internal pressures" or "cohesive energy densities," while their high

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(1) R. L. Scott, THIS JOURNAL, **70**, 4090 (1948).

(2) H. A. Benesi and J. H. Hildebrand, *ibid.*, **70**, 3978 (1948).

(3) *Cf.* J. H. Hildebrand and R. L. Scott, "Solubility of Non-Electrolytes," 3rd edition, 1949, Reinhold Publ. Corp., New York N. Y.

TABLE I

CONSOLUTE TEMPERATURES, °C., OF SOLUTIONS OF PERFLUOROMETHYLCYCLOHEXANE AT VARIOUS VOLUME FRACTIONS ϕ_2, AND MOLE FRACTIONS, x_2, OF THE OTHER COMPONENT

	CCl_4		$CHCl_3$		C_6H_6		$C_6H_5CH_3$		C_6H_5Cl	
ϕ_2	x_2	t	x_2	t	x_2	t	x_2	t	x_2	t
0.909	0.953	3.0	0.960	26.3	0.956	61.1	...	..	0.950	86.9
.900	...	...	...	..	...	..	0.943	63.7	...	...
.833	.910	17.5	.916	41.0	.916	76.1	...	..	.905	110.4
.800	...	...	...	..	...	..	.880	83.1	...	...
.769	.870	23.4	.890	46.6	.876	81.6	...	..	...	...
.714	.834	25.5	.858	48.9	.845	83.9	...	..	...	...
.700	...	...	...	..	...	..	.810	87.7	...	...
.667	...	...	...	..	.814	84.7	...	..	...	...
.625	...	...	...	..	.785	85.1	...	..	...	...
.600	.752	26.8	.784	50.2	.767	85.3	.733	88.9	.742	126.8
.500	.669	26.7	.708	50.1	.687	84.9	.647	88.6	.657	126.7
.400	.574	25.2	.618	49.0	.593	82.7	.550	87.2	.561	123.5
.333	...	...	...	..	.523	79.2	...	..	...	...
.300	...	...	...	..	...	..	.440	82.0	...	...
.286	.447	19.9	...	..	.467	75.7	...	..	...	...
.231	.377	14.4	.422	38.6	.397	69.3	...	..	.365	108.1
.200	...	...	...	..	...	..	.314	68.7	...	...
.167	.288	4.0	.327	28.9	.305	58.9	...	..	.277	92.9
.100	...	...	...	..	...	..	.169	42.8	...	...
.091	.168	−8.0	.195	7.2	.190	35.0	...	..	.161	65.7

molecular weights aid in maintaining them in the liquid state; the net result of which is to make many of their solutions with ordinary liquid hydrocarbons deviate from Raoult's law to such an extent as to form two liquid phases, a state of affairs comparatively rare among non-polar liquids. Since liquid–liquid solubilities are easily determined, we have used this means of further comparing theory with experiment.

Materials.—We are indebted to the Jackson Laboratory, du Pont de Nemours Co., for the supply of perfluoromethylcyclohexane. The benzene, "reagent grade, thiophene free," showed no color with concentrated sulfuric acid. It was dried with calcium chloride and distilled. The carbon tetrachloride, "reagent grade," was washed with concentrated sulfuric acid, then with water, and dried over calcium chloride. The chloroform, also "reagent grade," was washed successively with concentrated sulfuric acid, sodium carbonate aq., water, and dried over calcium chloride. The toluene was that used by Benesi and Hildebrand.[2] The chlorobenzene, "reagent grade," was dried over phosphorus pentoxide and distilled. All the above distilled within 0.1°.

Procedure.—The two liquids were measured by means of a carefully calibrated pipet made of 2-mm. capillary tubing into tubes 10 cm. long and 7 mm. diameter through capillary stems at right angles. The liquids were frozen in liquid nitrogen after introduction and sealed in. These tubes were heated above the consolute temperatures in a water-bath for 0 to 90° and in sulfuric acid for the range 90 to 130°. On slowly lowering the temperature while rocking a tube, the unmixing temperature of a solution could be accurately determined.

Results.—Table I gives the consolute temperatures of the different solutions together with the corresponding volume fractions of the fluorocarbon as measured at 25°, and the corresponding mole fractions. These temperatures are plotted against mole fraction in Fig. 1 and against volume fraction in Fig. 2. In Table II are given the critical mixing temperatures read from the maxima of these curves, also the critical compositions determined by aid of the assumption of rectilinear diameter, as in the analogous case of liquid–gas equilibrium.

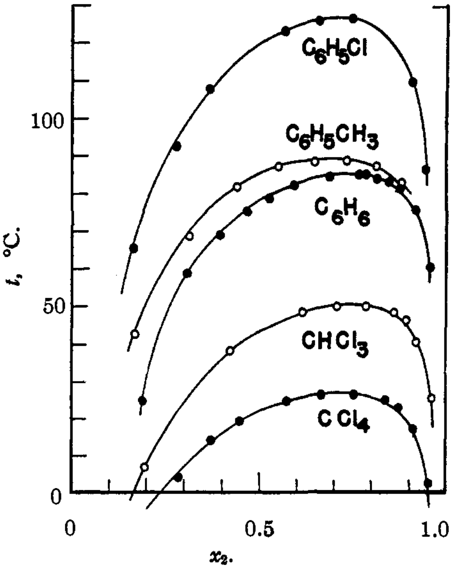

Fig. 1.—Consolute temperatures of perfluoromethylcyclohexane solutions *vs.* mole fraction of second component.

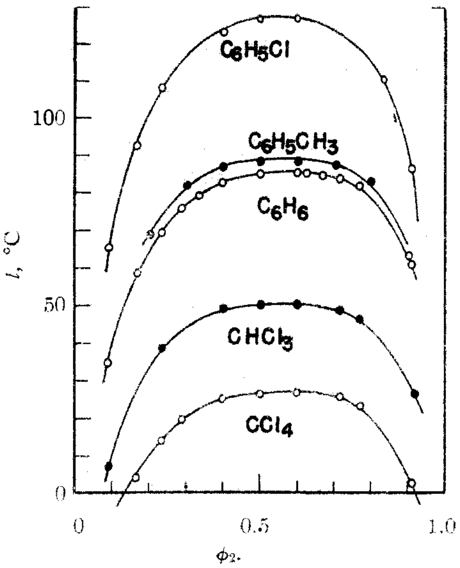

Fig. 2.—Consolute temperatures of perfluoromethylcyclohexane solutions *vs.* volume fraction of second component.

TABLE II

COMPARISON BETWEEN OBSERVED AND CALCULATED VALUES OF CRITICAL COMPOSITIONS AND TEMPERATURES FOR SOLUTIONS OF PERFLUOROMETHYLCYCLOHEXANE (COMPONENT 1)

	v cc., 25°	Crit. x_2		T_c			δ_1
		obs.	calcd.	obs.	calcd.	δ_2	calcd.
$C_6F_{11}CF_3$	195						
CCl_4	97	0.70	0.74	300.0	269	8.6[1]	5.8
$CHCl_3$	81	.74	.78	323.5	325	9.0[a]	6.0
C_6H_6	89	.73	.76	358.5	360	9.15[1]	6.0
$C_6H_5CH_3$	102	.69	.71	362.0	324	8.9[1]	5.8
C_6H_5Cl	107	.69	.72	400.0	464	9.5[1]	6.3

[a] This value is consistent with the solvent power of chloroform for other substances; the value of $(\Delta E^v/v)^{1/2}$ is 9.3. See J. H. Hildebrand, "A Critique of the Theory of Solubility of Non-electrolytes," *Chem. Revs.*, in press.

Comparison with Theory.—The regular solution equations[4] for liquid–liquid solubility are as follows, for the mole fraction at the critical point and the critical temperature, respectively

$$x_1 = \frac{(v_1^2 + v_2^2 - v_1v_2)^{1/2} - v_1}{v_2 - v_1} \tag{1}$$

and

$$RT_c = \frac{2x_1x_2v_1^2v_2^2}{(x_1v_1 + x_2v_2)^3}(\delta_1 - \delta_2)^2 \tag{2}$$

where the v's denote molal volumes, x's mole fractions, and δ's are what we have been calling the "solubility parameters," which are ordinarily the square root of the energies of vaporization per cc., *i. e.*, $\delta = (\Delta E^v/v)^{1/2}$. In this paper we shall distinguish the fluorocarbon by the subscript 1.

It has been pointed out that eqn. 1 yields values of the critical composition not far from those obtained by the simpler assumption that the maximum occurs at equal volume fractions, *i. e.*, $\delta_1 = \delta_2 = 0.5$, as shown in Fig. 2. The curves are so flat at the top that this may suffice for ordinary purposes. It has been pointed out, further, that eqn. 2 yields values of T_c not seriously different from a greatly simplified equation

$$4RT_c = (v_1 + v_2)(\delta_1 - \delta_2)^2 \tag{3}$$

In Table II can be seen comparisons between observed and calculated values of the critical compositions and temperatures. The "observed" values of x_2 were taken from the solubility curves by aid of the assumption of rectilinear diameter, as in gas–liquid density curves. The curves are so flat around the maximum that these values are subject to an error of at least ±0.02. The "calculated" values were obtained from Equation 1 by substituting the molal volumes for 25°, given in the first column of figures. It would be preferable to use the molal volumes at the critical temperatures, but since we lack some of the necessary density data and in view of the uncertainty in fixing the "observed" values, a closer check is hardly to be desired.

We have found that values of $\delta_1 - \delta_2$ calculated from T_c by eqn. 3 agree within a few per cent., *i. e.*, well within the limit of the unavoidable errors and uncertainties of the method, with those derived by aid of the more complicated eqns. 1 and 2, therefore eqn. 3 has been used in the following calculations. Substituting the observed values of T_c and the v's for 25° gives $\delta_2 - \delta_1$, which, subtracted from the δ_2-values in the next to the last column gives the calculated values of δ_1 for perfluoromethylcyclohexane given in the last column. In so calculating we have neglected the effect of temperature upon both δ_1 and δ_2 and on this account alone we should not expect uniform values for δ_1 "calculated." In addition, the dipole moments of chloroform and chlorobenzene might be expected to cause some disturbance. It is sufficient to find that these values of δ_1 for the fluorocarbon derived from solubility data agree well with the value 6.0 at 25° set by Scott[1] long before this work was undertaken. Reversing the calculation, we have calculated T_c for each solution using this value of δ_1 in combination with the δ_2-values given in the table. It will be seen that while the result is far from precise it has value, nevertheless, in giving the general region in which two liquid phases can coexist. The high critical temperature with toluene is not what its δ-value, less than that of benzene, would lead us to expect. A similar reversal has been noted by Hildebrand and Jenks[5] in the solubilities of sulfur in these two liquids. An explanation of such facts must await refinements in the theory as well as additional data, such as partial molal volumes.

Acknowledgments.—We wish to express our appreciation to Dr. J. M. Tinker, Director of the Jackson Laboratory, E. I. du Pont de Nemours

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(4) *Cf.* ref. 3, Chap. XVI.

(5) J. H. Hildebrand and C. A. Jenks, THIS JOURNAL, **43**, 2172 (1921).

Co., for the sample of perfluoromethylcyclohexane, and the Office of Naval Research for financial support of this research.

Summary

Liquid–liquid solubility curves have been determined for binary mixtures of perfluoromethylcyclohexane with five other liquids, giving the following results for the critical solution temperatures in °C. and the mole fractions of the second components: carbon tetrachloride, 26.8°, 0.70; chloroform, 50.3°, 0.74; benzene, 85.3°, 0.73; toluene, 88.8°, 0.69; chlorobenzene, 126.8°, 0.69.

These values agree within the usual limits of error with those calculated by aid of the equations for regular solutions and the value 6.0, previously derived by Scott for the "solubility parameter" (the square root of the energy of vaporization per cc.) of the fluorocarbon.

BERKELEY, CALIF. RECEIVED AUGUST 23, 1948

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Kinetics of the Oxidation of 2-Deuteropropanol-2 by Chromic Acid

BY F. H. WESTHEIMER AND NICHOLAS NICOLAIDES

The rate of the chromic acid oxidation of isopropyl alcohol to acetone has been shown to be proportional to the concentrations of isopropyl alcohol and the acid chromate ion, and proportional to the square of the concentration of hydrogen ion.[1] Although these kinetics fix the composition of the activated complex in the oxidation, they leave unanswered many questions concerning the mechanism. Specifically, they do not show whether the oxidative attack upon the alcohol molecule is at the secondary hydrogen atom, at the hydroxyl hydrogen atom,[2] or elsewhere. This question can be answered by studying the rate of oxidation of 2-deuteropropanol-2.

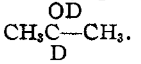
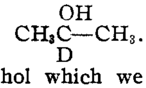
Both experimental and theoretical considerations show that, if the deuterium atom of 2-deuteropropanol-2 is removed in the rate-controlling step of the oxidation, the 2-deuteroalcohol will be oxidized much less rapidly than the corresponding hydrogen compound. On the other hand, if the rate determining step does not involve the removal of this deuterium atom, the oxidation rates for the hydrogen and deuterium compounds should be almost if not exactly identical. This test for the direct removal of a hydrogen atom depends upon the fact that C–H and C–D bonds differ in their zero-point energies. The method is completely general[3]; it has been strikingly applied by Reitz[4] in a study of the rate of enolization of acetone and of the deuteroacetones. In the present work, it has been found that 2-deuteropropanol-2 is oxidized by chromic acid only about one-sixth as fast as is ordinary isopropyl alcohol; it follows unambiguously that the secondary hydrogen atom is removed during the rate controlling step of the reaction.

Experimental

Deuterium.—The deuterium for these experiments was made by vaporizing 12.1 g. of Norwegian heavy water (Norsk Hydro Elektrish Kvaelstofaktieselskat 99.73% D_2O; d^{20}_4 1.10516) over Grignard magnesium heated electrically to 490 ± 25° in a heavy-walled combustion tube.[5] The resulting deuterium gas was passed through alkaline permanganate and stored over a saturated solution of sodium sulfate.

2-Deuteropropanol-2.—2-Deuteropropanol-2 was made by the catalytic deuteration of acetone according to the directions of Anderson and MacNaughton.[6] Eighty-six grams of acetone (J. T. Baker reagent grade, previously dried with potassium carbonate and distilled) was deuterated with 10.8 liters of deuterium gas, by means of 1.62 g. of Adams catalyst promoted with a few crystals of ferrous chloride. The deuteration required five days, during which time the catalyst was reactivated several times by briefly stirring the reaction mixture in air.

The reaction mixture was then fractionated through a small Podbielniak column (about 25 theoretical plates) to remove the large excess of acetone. When all the acetone had been removed, 54 cc. of water was added in order to exchange the hydroxylic deuterium of the isopropyl alcohol with the hydrogen of the water. Then the distillation (through the same column) was resumed. The fraction collected was 15 g. of the azeotropic mixture of isopropyl alcohol and water. Some of this azeotrope was used directly for rate measurements; some was re-equilibrated with water. The latter portion was prepared by adding 8.5 g. of the azeotrope to 100 g. of water, and then redistilling the mixture through the same Podbielniak column. The composition of the azeotrope was calculated as 90.1% deuteroisopropyl alcohol and 9.9% water from the combustion analysis of the material. (Microanalysis by Wm. Saschek, C, 53.40; H, 12.82.) Both portions of the azeotrope (that equilibrated once and that equilibrated twice) had the same rate of oxidation.

The work of Anderson and MacNaughton[6] suggests that in the deuteration all the deuterium gas is taken up at the carbonyl group, and the resulting product should be pure  $\mathrm{CH_3}\underset{\mathrm{D}}{\overset{\mathrm{OD}}{\mathrm{C}}}\mathrm{—CH_3}$. If this were the fact, the product after equilibration with water should have been pure  $\mathrm{CH_3}\underset{\mathrm{D}}{\overset{\mathrm{OH}}{\mathrm{C}}}\mathrm{—CH_3}$. Regrettably, however, the isopropyl alcohol which we prepared was a mixture containing only about 55% of the desired 2-deuteroalcohol. Fortunately the qualitative

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(1) Westheimer and Novick, *J. Chem. Phys.*, **11**, 506 (1943).

(2) Mosher, Abstracts, September, 1947, meeting of the American Chemical Society. Mosher and Whitmore, THIS JOURNAL **70**, 2544 (1948).

(3) Urey and Teal, *Rev. Mod. Phys.*, **7**, 34 (1935); *cf.* Taylor and Eyring, *Proc. Am. Phil. Soc.*, **72**, 255 (1933).

(4) Reitz, *Z. physik. Chem.*, **A179**, 119 (1937); *ibid.*, **A184**, 429 (1939); *cf.*, however, Wynne-Jones, *J. Chem. Phys.*, **2**, 381 (1934); Reitz, *Z. physik. Chem.*, **A176**, 363 (1936); and Maron and LaMer, THIS JOURNAL, **60**, 2588 (1938).

(5) Knowlton and Rossini, *Bur. Standards J. Research*, **19**, 605 (1937).

(6) Anderson and MacNaughton, THIS JOURNAL, **64**, 1456 (1942); see also Carothers and Adams, *ibid.*, **46**, 1675 (1924).