

hydrolysis of uranium dicarbide agree as to the major product, even though the two studies were carried out at widely different temperatures.

In the case of the thorium and uranium carbides, the final oxidation state is plus four. The two-electron oxidation in the hydrolysis reaction

is expected to produce more hydrogen and hydrogenated hydrocarbons than in the case of the rare earth dicarbides. The hypothesis given above can be tested only when additional data are available on the thorium and uranium carbide hydrolyses.

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Dimethylaminomethylchloroborane and Related Compounds¹

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The dimerization of $(\text{CH}_3)_2\text{NBCl}_2$ and non-dimerization of $(\text{CH}_3)_2\text{NB}(\text{CH}_3)_2$ have been investigated by preparing $(\text{CH}_3)_2\text{NBCH}_2\text{Cl}$. It is made in high yield by heating $(\text{CH}_3)_2\text{NBCl}_2$ and $(\text{CH}_3)_2\text{NB}(\text{CH}_3)_2$ together at 170° . It is very stable to disproportionation. It slowly forms a solid dimer like that of $(\text{CH}_3)_2\text{NBCl}_2$. The dimerization is shown to be a non-equilibrium process resembling freezing which occurs at a higher temperature than the true melting point. This can be located by observation of the kinetics of freezing and by finding the intersection of vapor pressure curves. Solid adducts $[(\text{CH}_3)_2\text{NBCl}_2][(\text{CH}_3)_2\text{NB}(\text{CH}_3)_2]$ and $[(\text{CH}_3)_2\text{NBCl}_2][(\text{CH}_3)_2\text{NBCH}_2\text{Cl}]$ also are described.

This study arose from the observation in the literature that two apparently similar boron amines have dramatically different properties. Dimethylaminodichloroborane, $(\text{CH}_3)_2\text{NBCl}_2$, is a mobile, fuming liquid that deposits a solid on standing, referred to as a "dimer" because of the molecular weight of its solutions in benzene.² This substance has remarkable resistance to hydrolysis by water. Dimethylaminodimethylborane, $(\text{CH}_3)_2\text{NB}(\text{CH}_3)_2$, on the other hand, is a mobile, oxidizable liquid that does not deposit a solid or undergo any detectable changes in properties, no matter how long it stands in the absence of oxygen.

In an attempt to determine the reason for this behavior, we prepared the compound intermediate between these two, dimethylaminomethylchloroborane, $(\text{CH}_3)_2\text{NBCH}_2\text{Cl}$, observed some of its physical and chemical properties, and compared the properties of all three compounds.

In this paper the term "dimer" will be used for the solids that deposit from pure, monomeric liquids, and the term "adduct" for solids that de-

posit from mixtures of monomers. The solids may be more complex than "dimer" implies.

Experimental

(1) **Preparation and General Properties.**—All monomeric aminoboranes were handled in dry nitrogen atmospheres. Samples for analysis were subjected to basic peroxidation at 100° . After neutralization, boric acid was determined by titration in the presence of mannitol, and chlorine was determined by the Mohr titration. Molecular weights were measured cryoscopically in *p*-xylene.

(a) $(\text{CH}_3)_2\text{NBCl}_2$ was prepared by using a slight modification of the method of Goubeau.³ The separation of $[(\text{CH}_3)_2\text{N}]_2\text{B}$ and $[(\text{CH}_3)_2\text{N}]_2\text{BCl}$ was found to be unnecessary, since both reacted readily with BCl_3 to give the desired product. Each sample was purified by fractional distillation through a 45.8-cm., wire-spiral column at 30–40 mm., collected in a receiver chilled to -25° , and stored at -25° until used. Yields ranged up to 75%.

(b) $(\text{CH}_3)_2\text{NB}(\text{CH}_3)_2$ was prepared by the action of methyl Grignard reagent on $(\text{CH}_3)_2\text{NBCl}_2$, as described elsewhere.⁴

(c) $[(\text{CH}_3)_2\text{NBCl}_2][(\text{CH}_3)_2\text{NB}(\text{CH}_3)_2]$ was prepared by mixing approximately equimolar amounts of the monomers at -25° and allowing the mixture to stand for 4–8 hr. at this temperature. The reaction at room temperature was too violent. Unreacted starting materials then were removed *in vacuo*, and the crystals were washed with water and dried in a vacuum desiccator for several hours. Yields

(1) Based in part on a thesis submitted by Frank Gunderloy in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Rutgers, the State University, September, 1957. Presented at the 135th National Meeting, American Chemical Society, Atlantic City, N. J., Sept., 1959.

(2) E. Wiberg and K. Schuster, *Z. anorg. u. allgem. Chem.*, **213**, 89 (1933).

(3) J. Goubeau, M. Rabtz, and H. J. Becher, *ibid.*, **275**, 162 (1954).

(4) F. C. Gunderloy, Jr., and C. E. Erickson, *J. Org. Chem.*, **24**, 1161 (1959).

were 70–90% of theory, based on the component not in excess. *Anal.* Found: B, 10.44; Cl, 33.10; mol. wt., 211, 214. Theory: B, 10.27; Cl, 33.64; mol. wt., 210.8.

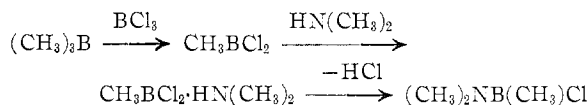
The adduct is a white crystalline solid, melting at 63–65° by instant immersion in sealed capillaries. Slower heating will not give clean melts, since the adduct reverts to the monomers, and the solid dimer of $(\text{CH}_3)_2\text{NBCl}_2$ then will form to some extent. After 24 hr. at 60–70° (under a reflux condenser) the reaction $[(\text{CH}_3)_2\text{NB}(\text{CH}_3)_2] \rightarrow \frac{1}{2}[(\text{CH}_3)_2\text{NB}(\text{CH}_3)_2]_2 + (\text{CH}_3)_2\text{NB}(\text{CH}_3)_2$ is quantitative.

The adduct slowly develops a pressure of monomeric vapor at room temperature, and must be stored at –25° in order to inhibit this. After four days of immersion in water at ambient temperature, about 70% of a sample was found to have hydrolyzed.

(d) $(\text{CH}_3)_2\text{NB}(\text{CH}_3)\text{Cl}$ was prepared by heating $[(\text{CH}_3)_2\text{NB}(\text{CH}_3)_2][(\text{CH}_3)_2\text{NB}(\text{CH}_3)_2]$ in a sealed tube at 160–170° for 36 hr. The tube then was chilled rapidly to –25°, and the liquid portion of the contents removed and fractionally distilled at 150 mm. The purified product was received and stored at –25°. The yield of monomer was 60–70%, and recovery of dimer from the apparatus showed an essentially quantitative conversion of the adduct.

The infrared spectrum of $(\text{CH}_3)_2\text{NB}(\text{CH}_3)\text{Cl}$ has a strong band at 9.8 μ , missing from that of the parent compounds, and no absorption in the range 10.4–11.0 μ , where the parent compounds show strong absorption. *Anal.* Found: B, 10.38; Cl, 33.29; mol. wt., 110. Theory: B, 10.27; Cl, 33.64; mol. wt., 105.4.

Some $(\text{CH}_3)_2\text{NB}(\text{CH}_3)\text{Cl}$ for kinetic studies was prepared by treating accumulated dimer in the same manner as just described for the adduct conversion. A trace of $(\text{CH}_3)_2\text{NB}(\text{CH}_3)\text{Cl}$ also was obtained by the route



but the over-all procedure is tedious and the yield extremely low.

$(\text{CH}_3)_2\text{NB}(\text{CH}_3)\text{Cl}$ is a water-white mobile liquid, freezing to a white solid at roughly –70°. It fumes in moist air, and hydrolyzes violently in contact with water, but is not spontaneously inflammable. More detailed studies of its properties are given below.

(e) $[(\text{CH}_3)_2\text{NB}(\text{CH}_3)\text{Cl}]_2$ was prepared by allowing the monomer to stand at ambient temperature for varying periods. Unreacted monomer then was taken off, and the crystals were washed with water and dried in a vacuum desiccator. *Anal.* Found: B, 10.31; Cl, 33.30; mol. wt., 215. Theory: B, 10.27; Cl, 33.64; mol. wt., 210.8.

The white crystals melt at 100–102° in a sealed capillary. From bulk monomer, the solid crystallizes as large rhombohedra. Thin diamonds corresponding to one face of the rhombohedron appear when thin films crystallize. All faces appear to be identical under the petrographic microscope, with angles of 67°30' and 112°30', and an extinction angle of 3°45' with the long diagonal.

The dimer is readily soluble in C_6H_6 , CCl_4 , and CHCl_3 , but only sparingly soluble in aliphatic hydrocarbons. It may be recrystallized from a solvent pair chosen from these groups, yielding small crystals identical with those formed directly from monomer, but it must not be heated above

45° in the process, or excessive reversion to monomer occurs.

(f) $[(\text{CH}_3)_2\text{NB}(\text{CH}_3)_2][(\text{CH}_3)_2\text{NB}(\text{CH}_3)\text{Cl}]$ formed from a mixture of the monomers at room temperature but was not obtained pure, since the corresponding dimers formed concurrently. The crystals showed major melting at 106–108°, and the infrared spectrum established the existence of a new adduct. *Anal.* Found: B, 9.26; Cl, 45.40. Theory: B, 9.36; Cl, 46.00.

A mixture of $(\text{CH}_3)_2\text{NB}(\text{CH}_3)_2$ and $(\text{CH}_3)_2\text{NB}(\text{CH}_3)\text{Cl}$ yielded $[(\text{CH}_3)_2\text{NB}(\text{CH}_3)\text{Cl}]_2$ after prolonged standing. $(\text{CH}_3)_2\text{NB}(\text{CH}_3)_2$ failed to form a dimer over the temperature range –25 to 65°.

(2) Properties of $(\text{CH}_3)_2\text{NB}(\text{CH}_3)\text{Cl}$. (a) Vapor Pressure of Monomer.—Samples were introduced into a small manometer by conventional vacuum techniques. The manometer then was sealed and immersed in various constant-temperature slush baths. Readings were made with a brass scale cathetometer and corrected accordingly. The results of two determinations in Table I showed a slight deviation from linearity at the lowest temperature. Exclusive of this point, the values fit the equation $\log P$ (mm.) = 8.377 – (1995/ T (°K.)). Extrapolated to 760 mm., this yields b.p. = 90°, and $\Delta H_{\text{vap}}^\circ = 9.1$ kcal./mole, $\Delta S_{\text{vap}}^\circ = 25.2$ cal. mole^{–1} °K.^{–1}.

TABLE I

VAPOR PRESSURE OF $(\text{CH}_3)_2\text{NB}(\text{CH}_3)\text{Cl}$

T (°C.)	$P_{\text{obsd.}}$ (mm.)	$P_{\text{calcd.}}$ (mm.)
–22.9	2.2, 2.2	...
0.0	11.8, 11.8	11.8
4.8	16.0, 15.9	15.8
12.8	25.2, 25.0	25.1
16.7	31.2	31.2
18.2	33.7	33.8

(b) Density.—A Lipkin pycnometer calibrated with purified water was employed. Samples were introduced by applying a nitrogen-operated aspirator to one leg of the pycnometer while the other was immersed in a storage reservoir of $(\text{CH}_3)_2\text{NB}(\text{CH}_3)\text{Cl}$. The pycnometer then was closed with a loop of tubing and removed to various constant-temperature baths for determinations. The results of two runs in Table II give the equation

$$d \text{ (g./ml.)} = 0.9518 - 0.001082 t \text{ (}^\circ\text{C.)}$$

TABLE II

DENSITY OF $(\text{CH}_3)_2\text{NB}(\text{CH}_3)\text{Cl}$

T (°C.)	$d_{\text{obsd.}}$ (g./ml.)	$d_{\text{calcd.}}$ (g./ml.)
0.00	0.9518, 0.9518	0.9518
15.00	.9355, .9355	.9356
25.05	.9238, .9248	.9247
37.90	.9110, .9110	.9108
43.75	.9044	.9045

(3) Kinetic Studies. (a) Dimerization of Pure Liquid $(\text{CH}_3)_2\text{NB}(\text{CH}_3)_2$.—Each point of the rate study was determined on an essentially independent sample by weighing 0.5–1.5 g. of $(\text{CH}_3)_2\text{NB}(\text{CH}_3)_2$ into screw-cap vials, immersing these in a constant-temperature bath, and then removing

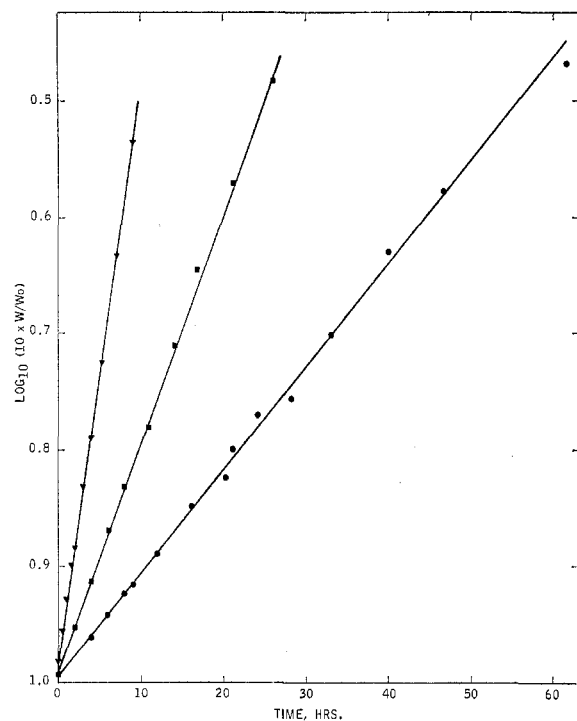


Fig. 1.—Dimerization of pure liquid $(\text{CH}_3)_2\text{NBCl}_2$: w_0 = initial weight of monomer; w = weight of monomer after t hr.; ●, 25°; ■, 35°; ▼, 45°.

one vial at a time for analysis. The amount of dimer formed was determined by hydrolyzing unreacted monomer in a stream of moist air at -25° , followed by exhaustive washing with water and quantitative weighing of the remaining dimer. The data so obtained are plotted in Fig. 1, and give the equations

$$\log (10w/w_0) = 0.992 - 0.0087t \quad (25^\circ)$$

$$\log (10w/w_0) = 0.991 - 0.0198t \quad (35^\circ)$$

$$\log (10w/w_0) = 0.980 - 0.0488t \quad (45^\circ)$$

Failure of the equations to give lines through the origin reflects the handling and weighing of samples prior to their introduction into the bath, since $t = 0$ was arbitrarily assigned to the time of such introduction.

For the first-order equation $\ln w_0/w = k_1 t$, the above equations yield the k_1 values $5.58 \times 10^{-6} \text{ sec.}^{-1}$ (25°), $1.27 \times 10^{-5} \text{ sec.}^{-1}$ (35°), and $3.12 \times 10^{-5} \text{ sec.}^{-1}$ (45°). Times required to convert half the sample to solid were, respectively, 35, 15, and 6 hr.

(b) **Dimerization of $(\text{CH}_3)_2\text{NBCl}_2$ in Solution.**—At 35° , 2.0214 g. $(\text{CH}_3)_2\text{NBCl}_2$ was diluted to the mark in a 10-ml. volumetric flask with 7.0689 g. C_6H_6 . (Using the density values for $(\text{CH}_3)_2\text{NBCl}_2^5$ and C_6H_6 ,⁶ the calculated total volume is 9.997 ml., which indicates no interaction of the components.) The solution then was subdivided into vials and handled essentially as described for the pure monomer above, except that the final isolation of dimer required evaporation of the benzene after hydrolysis of monomer.

(5) C. A. Brown and R. C. Osthoff, *J. Am. Chem. Soc.*, **74**, 2340 (1952).

(6) E. W. Washburn (Ed.), "International Critical Tables," McGraw-Hill, New York, N. Y., 1928, Vol. III, p. 29.

Data from the run are given in Table III. The values fit the second-order equation $1/c = (2.53 \times 10^{-6}) t + 0.575$ where c = concentration of unreacted monomer (moles/l.) and t = seconds. In this run the t_0 value represents an actual determination.

TABLE III
DIMERIZATION OF $(\text{CH}_3)_2\text{NBCl}_2$ IN C_6H_6 (35°)

Time (sec.)	c (moles/l.)	$1/c$	$1/c$ (calcd.)
0	1.711	0.585	0.575
4.32×10^4	1.439	.695	.684
8.64×10^4	1.266	.790	.793
12.96×10^4	1.176	.855	.903
17.28×10^4	0.970	1.031	1.012
21.60×10^4	.882	1.134	1.121

(c) **Dimerization of Pure Liquid $(\text{CH}_3)_2\text{NB}(\text{CH}_3)\text{Cl}$.**—With the exception that sample sizes were only 0.2 to 0.6 g., the techniques for this study were identical with those described in part (a). Data are presented in Fig. 2 from which may be obtained the equations

$$\log (10w/w_0) = 0.980 - 0.0042t \quad (15^\circ)$$

$$\log (10w/w_0) = 0.984 - 0.0137t \quad (25^\circ)$$

$$\log (10w/w_0) = 0.976 - 0.0154t \quad (35^\circ)$$

These lead to the first-order rate constants $2.67 \times 10^{-6} \text{ sec.}^{-1}$ (15°), $8.76 \times 10^{-6} \text{ sec.}^{-1}$ (25°), and $9.86 \times 10^{-6} \text{ sec.}^{-1}$ (35°). Based on the slopes, the times required for half the reaction to occur were 72, 22, and 20 hr., respectively.

At 45° , erratic results were obtained. At 46° , a sample of $(\text{CH}_3)_2\text{NB}(\text{CH}_3)\text{Cl}$ remained totally liquid. This is taken to signify that 45° is a melting point.

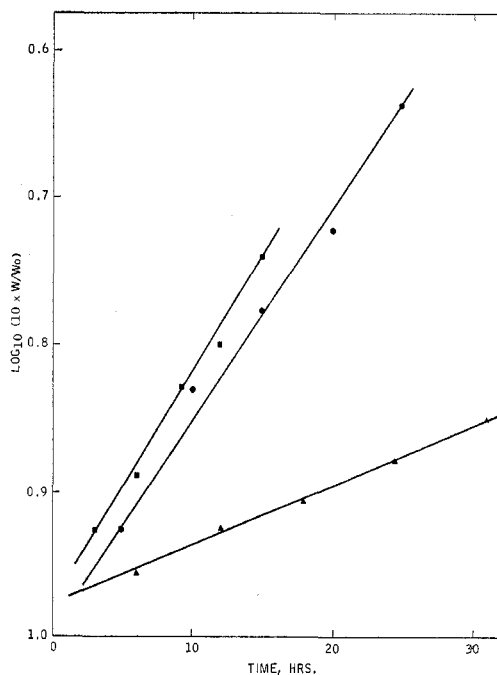


Fig. 2.—Dimerization of pure liquid $(\text{CH}_3)_2\text{NBCH}_2\text{Cl}$: w_0 = initial weight of monomer; w = weight of monomer after t hr.; ▲, 15°; ●, 25°; ■, 35°.

(4) **Properties of Solid Dimers.** (a) **Vapor Pressure.**—Solids were introduced into a bulb attached to a U-tube manometer having a side reservoir in which mercury could be contained until the system was evacuated and sealed. Constant-temperature baths filled with water or oil were used for heating. Control of temperature was within 0.10°. Pressure readings were corrected to the density of mercury at 0°. They were reproducible to within 0.05 mm., but may have absolute errors of several tenths of a mm. ΔH and ΔS may be in error by several per cent. Since the vapors are monomeric, both ΔH and ΔS refer to a monomeric unit. Results are shown in Tables IV and V.

TABLE IV
VAPOR PRESSURE OF $(\text{CH}_3)_2\text{NBCH}_2\text{Cl}$ DIMER

<i>T</i> , °C.	<i>P</i> _{obsd.} , mm.	<i>P</i> _{calcd.} , mm.	Equili- bration, days
34.20	34.65	34.55	10
39.00	55.85	56.15	11
43.70	89.30	89.05	15

$$\log p \text{ (mm.)} = 15.261 - 4218/T$$

$$\Delta H^0 = 19.3 \text{ kcal.}$$

$$\Delta S^0 = 57 \text{ cal. mole}^{-1} \text{ } ^\circ\text{K.}^{-1}$$

TABLE V
VAPOR PRESSURE OF $(\text{CH}_3)_2\text{NBCl}_2$ DIMER

<i>T</i> , °C.	<i>P</i> _{obsd.} , mm.	Equili- bration, days
68.55	42.0	142
75.00	71.8	127

$$\log p \text{ (mm.)} = 14.175 - 4289/T$$

$$\Delta H^0 = 19.6 \text{ kcal.}$$

$$\Delta S^0 = 52 \text{ cal. mole}^{-1} \text{ } ^\circ\text{K.}^{-1}$$

Equilibration was very slow, and a number of observations were discarded because it was almost certain that equilibrium had not been reached. The times given in the tables include only consecutive time at the stated temperature. The changes in pressure from day to day often were small enough to be masked by reading error or temperature fluctuation.

(b) **Melting Point.**—As shown in Table VI, there are two sets of values differing by 40° or more. The capillary observations always involve some decomposition. Results determined in air generally are very dependent on conditions. Once melted, the dimer does not form again until the temperature is lowered. This is not a supercooling phenomenon, as the dimer always forms rather slowly even after crystallization begins. The lower values represent thermodynamic equilibrium temperatures.

Vapor pressures were taken from this paper and, in the case of monomeric dimethylaminodichloroborane, from Wiberg and Schuster.²

Discussion

(1) **Phase Relations.**—If one excludes the dimers from consideration, the boron amines behave very much like other covalent, molecular substances. The boiling points of $(\text{CH}_3)_2\text{NBCl}_2$, $(\text{CH}_3)_2\text{NBCH}_2\text{Cl}$, and $(\text{CH}_3)_2\text{NB}(\text{CH}_3)_2$ are 112,³

TABLE VI
MELTING POINTS OF DIMERS

Method	$(\text{CH}_3)_2\text{NBCH}_2\text{Cl}$ dimer	$(\text{CH}_3)_2\text{NBCl}_2$ dimer
In sealed capillary	100-102°	142°
Intersection of vapor- pressure curves	50°	103°
Kinetics of dimer formation	45°	Between 99 and 102°

90, and 65°,⁷ respectively. The melting points in the same order are -43,⁵ about -70, and -92°.⁷ The values are what would be expected for a series of related, polar compounds with molecular weights of roughly 100. The entropies of vaporization, 22.5,² 25.2, and 19.8⁷ cal. mole⁻¹ °K.⁻¹, in the same order, indicate that the vapor and liquid have the same molecularity. Since the vapors all appear to be monomeric, the liquid phases are monomeric, too. The melting point at low temperature is readily reversible. Hence the solid probably has monomeric molecular units as well.

The solid called dimer is superimposed on an otherwise normal phase diagram. Below the melting point of dimer, all monomeric phases are metastable, and exist only because the rate of conversion to dimer is slow. Above the melting point the dimer is metastable.

The values reported in this paper for the thermodynamic melting points of the dimers are likely to be in error a few degrees. The intersection of vapor pressure curves is the more uncertain of the two methods used to find the melting point, because the extrapolations needed are not very good. This especially is true of the dimer of dimethylaminodichloroborane, inasmuch as the vapor pressure is known for only two temperatures. Furthermore, possible curvature of the $\log p$ vs. $1/T$ relation has been ignored. Yet the agreement with observations by a kinetic method is very good.

The melting point obtained in the usual way in a sealed capillary looks like a normal observation, though there always is some decomposition. It is quite reproducible and can be used to characterize all the dimers and adducts that have been studied. Yet it is clear that the solid is not in equilibrium with liquid monomer.

One possible explanation is that this is the equilibrium melting of solid to a liquid of dimeric or larger molecules which immediately dissociate into the volatile monomers. It is more likely

(7) A. B. Burg and J. Banus, *J. Am. Chem. Soc.*, **76**, 3903 (1954).

that this is the temperature at which the rate of formation of monomer is rapid enough to be seen within the short time of observation. In typical melting point measurements the temperature is raised at a rate of 2–3° per min. Thus any process which is slow will not be observed at the true equilibrium temperature, but at a higher temperature that is determined by the rate. Such a measurement ought to be reproducible if the technique is always the same. It can give sharp results if the rate changes rapidly with temperature.

The vapor pressure of the dimer of the dichloro compound also has been reported by Brown and Osthoff.⁵ Their values are much lower—only 2 mm. at 96°. There is no indication of any error in their report, but their values can be discarded on the ground that they lead to 125 cal. mole⁻¹ °K.⁻¹ for the entropy of sublimation. This is an impossibly high value, much larger than the *total* entropy of gaseous compounds of similar molecular weight.

The thermodynamics of the phase changes are summarized in Table VII. The values for the melting process are calculated by difference from the other two sets, ignoring changes of ΔH^0 with temperature. The data for the dimer-liquid transition are not entirely consistent. If the melting points differ by roughly 50°, then ΔH^0 should differ by about 1.5 kcal., as long as ΔS^0 is roughly 30 cal. mole⁻¹ °K.⁻¹.

TABLE VII
THERMODYNAMICS OF PHASE CHANGES

	$-(\text{CH}_3)_2\text{NBCH}_2\text{Cl}-$		$-(\text{CH}_3)_2\text{NBCH}_2-$	
	$\Delta H^0,^a$ kcal.	$\Delta S^0,^a$ cal. mole ⁻¹ °K. ⁻¹	$\Delta H^0,^a$ kcal.	$\Delta S^0,^a$ cal. mole ⁻¹ °K. ⁻¹
Liquid-vapor	9.1	25.2	8.6 ²	22.5 ²
Dimer-vapor	19.3	57	19.6	52
Dimer-liquid	10.2	32	11.0	30

^a Per monomer formula unit.

The striking feature of these data is the extremely large entropy of fusion. The dimers are more nearly in the class of behavior represented by Al_2Cl_6 ($\Delta S^0_{\text{fus}} = 36.3$ cal. mole⁻¹ °K.⁻¹)⁸ than salts like alkali halides ($\Delta S^0_{\text{fus}} = 6$ cal. mole⁻¹ °K.⁻¹)⁹ or molecular materials where long chains are not involved ($\Delta S^0_{\text{fus}} = 2$ to 10 cal.

(8) F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, Washington, D. C., 1952, p. 731.

(9) A. S. Dworkin and M. A. Bredig, *J. Phys. Chem.*, **64**, 269 (1960).

mole⁻¹ °K.⁻¹).¹⁰ The fusion of Al_2Cl_6 involves a change from an ionic layer lattice to a liquid having Al_2Cl_6 molecules, introducing rotational freedom, perhaps some translational freedom, and a number of easily excited vibrational modes. The fusion of the boron amine dimers may be a somewhat similar process involving a profound structure change.

(2) **Reaction Rates.**—The dimerization from pure monomer leads to precipitation without change of concentration of the liquid phase. Hence the reaction gives no indication of concentration dependence. The kinetics as observed are strictly first order. Dimerization in benzene shows second order kinetics, but this may or may not be true when there is no inert solvent. The reaction may be characterized by the time for half of a sample to precipitate, as this depends only on temperature for a given substance. At 25° the half-times are about 35 hr. for $(\text{CH}_3)_2\text{NBCH}_2\text{Cl}$ and about 22 hr. for $(\text{CH}_3)_2\text{NBCH}_2\text{Cl}$.

The slowness of most of these reactions implies a high energy of activation of the order of 16 kcal. per mole. On the other hand, boron trichloride forms addition compounds rapidly and with low activation energy, and all the boron amines react rapidly with water or oxygen or both. Since the boron and nitrogen atoms of dimethylaminodichloroborane have steric and electronic environments resembling those in boron trichloride and trimethylamine, respectively, the attack of nitrogen on boron probably is not the rate determining step. Slowness of reaction may be the result of some subsequent step which involves bond breaking. We are not prepared to suggest what this reaction is.

The dimerization of dimethylaminomethylchloroborane exhibits non-Arrhenius behavior below its melting point. A plot of the rate constant measured at 15, 25, and 35° against $1/T$ shows pronounced curvature. This indicates the onset of an opposing reaction. At 45° the two rates are equal. Above this the formation of monomer from dimer is faster. This is a rare case in which a thermodynamic melting point first was observed by measurement of rates of reaction.

Dimethylaminodichloroborane at 99° and below precipitates slowly in the course of several hours. The solid reverts to liquid at 102°. The true melting point is difficult to identify since the difference between forward and reverse rates is so

(10) A. R. Ubbelohde, *Quart. Revs. (London)*, **4**, 356 (1950).

small that a very long time would be required for an observable reaction. At these temperatures a small amount of another liquid forms irreversibly.

(3) **Stability of $(\text{CH}_3)_2\text{NBCH}_3\text{Cl}$.**—The formation of dimethylaminomethylchloroborane in excellent yield and with no evidence of disproportionation is somewhat surprising in view of the general tendency for boron compounds with three different substituents to disproportionate.

The postulate of additivity of bond energies implies that such reactions should have zero enthalpy change so that the yield of products depends on entropy only. In the reaction



statistical distribution of CH_3 and Cl groups should give a mixture with 50 mole % of the first substance, and 25 mole % of each of the other two. The experimental finding is that the equilibrium lies so far to the left that only one compound can be detected.

The stability of dimethylaminomethylchloroborane is clearly thermodynamic, since it is formed by the reverse of reaction 1, and the rate of reaction is rapid enough to lead to an equilibrium state. The equilibrium lies far to the left at 170° , and should be very nearly the same at room temperature.

The conclusion is that the reaction represented by eq. 1 is endothermic. This is equivalent to saying that one mole of the grouping $-\text{B}(\text{CH}_3)\text{Cl}$ has a greater bond energy than the total bond energy of a half-mole of $-\text{BCl}_2$ and a half-mole of $-\text{B}(\text{CH}_3)_2$. The difference must be at least several kilocalories per mole of $-\text{B}(\text{CH}_3)\text{Cl}$, though no quantitative measurements have been made in this work.

The compounds we have studied fit a pattern that can be supported by other data in the literature. Consider all possible mononuclear boron compounds with combinations of dimethylamino, chloro, and methyl groups. When the substituents are taken two at a time they fall into three series:

1. BCl_3 , $(\text{CH}_3)_2\text{NBCl}_2$, $[(\text{CH}_3)_2\text{N}]_2\text{BCl}$, $[(\text{CH}_3)_2\text{N}]_3\text{B}$.—Heats of formation as reported by Skinner and Smith¹¹ show that both of the mixed compounds are stable to disproportionation. Dimethylaminodichloroborane is the more stable of the two, by about 3 kcal. We have prepared

it in excellent yield from a mixture of two moles of boron trichloride and one of trisdiaminoborane.

2. $(\text{CH}_3)_3\text{B}$, $(\text{CH}_3)_2\text{NB}(\text{CH}_3)_2$, $[(\text{CH}_3)_2\text{N}]_2\text{BCH}_3$, $[(\text{CH}_3)_2\text{N}]_3\text{B}$.—Dimethylaminodimethylborane has been distilled in this work at its boiling point (65°) with no evidence of disproportionation. Bisdiaminomethylborane, on the other hand, is so unstable that it does not seem possible to prepare it.¹²

3. BCl_3 , CH_3BCl_2 , $(\text{CH}_3)_2\text{BCl}$, $(\text{CH}_3)_3\text{B}$.—The mixed compounds can be prepared from boron trichloride and trimethylborane, though it is not clear whether the yield is greater than the statistical yield.¹³

The evidence indicates that dimethylaminodichloroborane and dimethylaminodimethylborane are the most stable of their respective series, and it is from a mixture of these two compounds that dimethylaminomethylchloroborane is obtained. Hence compounds with only one dimethylamino group are preferred over mixtures of compounds having more than one or no dimethylamino groups. Of these, the most stable compound has all three substituents different, $(\text{CH}_3)_2\text{NBCH}_3\text{Cl}$.

The rationalization of this observation must account for the behavior of both the dimethylamino group and the chloro group. Skinner and Smith,¹¹ writing about series 1, have suggested that the pi-character of the N-B and Cl-B bonds is responsible. In addition to the normal single bond, there is also some back coordination between p-electrons of an adjacent atom and a vacant p_z -orbital of boron. Two or three atoms on one boron compete for the same p_z -orbital. It is more satisfactory to have one B-X bond in each of many molecules than to have two or three bonds in each of fewer molecules. Skinner and Smith suggest that an amino nitrogen atom overlaps in this way to a greater extent than a chlorine atom, and therefore more energy is lost by having two amino groups in competition with each other. This agrees with the strong preference for only one dimethylamino group. However, a study of molecular models indicates a modification of this point of view. Dimethylamino groups crowd each other to such an extent that a second group would be forced out of the proper position for pi-overlap with boron. Hence the

(12) G. E. Coates, *ibid.*, 3482 (1950).

(13) J. Goubeau and W. Klemm, "FIAT Review of German Science, Inorganic Chemistry," Part I, 1948, p. 237.

(11) H. A. Skinner and N. B. Smith, *J. Chem. Soc.*, 2324 (1954).

total pi-bond energy is increased by dividing the dimethylamino groups between as many molecules as possible. This accounts equally well for the greater stability of monodimethylamino compounds. Competition between chlorine atoms accounts for the greater stability of dimethylaminomethylchloroborane.

(4) **Solid Adducts.**—Four different solids have been observed to precipitate from monomeric liquids and mixtures, and two more can be postulated. They are listed in Table VIII. All but the dimer of dimethylaminodichloroborane are new compounds. In an attempt to form $[(\text{CH}_3)_2\text{NB}(\text{CH}_3)_2][(\text{CH}_3)_2\text{NBCH}_2\text{Cl}]$, only the dimer of dimethylaminomethylchloroborane was obtained. This does not answer the question as to whether the desired compound exists; it means only that it did not form fast enough to be observed.

TABLE VIII
SOLID ADDUCTS OF BORON AMINES

	—Melting point, °C.—		Half-time at 25°, hr.
	Capillary	Thermo- dynamic	
$(\text{CH}_3)_2\text{NBCl}_2$ dimer	142	about 100	35
$(\text{CH}_3)_2\text{NBCH}_2\text{Cl}$ dimer	100-102	45	22
$(\text{CH}_3)_2\text{NB}(\text{CH}_3)_2$ dimer	(not observed)		
$[(\text{CH}_3)_2\text{NBCl}_2]$ $[(\text{CH}_3)_2\text{NB}(\text{CH}_3)_2]$	65	...	very short
$[(\text{CH}_3)_2\text{NBCl}_2]$ $[(\text{CH}_3)_2\text{NBCH}_2\text{Cl}]$	106-108	...	10 (est.)
$[(\text{CH}_3)_2\text{NBCH}_2\text{Cl}]$ $[(\text{CH}_3)_2\text{NB}(\text{CH}_3)_2]$	(not observed)		

The solid adducts, $[(\text{CH}_3)_2\text{NBCl}_2][(\text{CH}_3)_2\text{NB}(\text{CH}_3)_2]$ and $[(\text{CH}_3)_2\text{NBCl}_2][(\text{CH}_3)_2\text{NBCH}_2\text{Cl}]$, seem to be unique among boron compounds. The former was particularly well characterized in this work. It always formed in a 1:1 ratio, even when one or the other of the monomers was 50% in excess. This suggests that it is not a statistical copolymer in which the dimethyl compound substitutes for the dichloro compound. Presumably in this adduct the component molecules occur alternately. It is less stable than the dichloro

dimer and has an appreciable vapor pressure at room temperature.

The nature of these solids is still an open question. "Dimer" usually is taken to refer to four-membered rings of alternating boron and nitrogen atoms. However, the double molecular weight obtained cryoscopically in benzene or *p*-xylene solutions is not proof that the same molecules exist in the solid. Evidence such as the high entropy of fusion and the very slow solidification process point to something other than dimeric molecules.

The failure of dimethylaminodimethylborane to form a solid adduct may result from either or both of the following factors: (1) The thermodynamic melting point of the dimer is lower than the temperatures at which dimerization has been attempted. (2) The rate of forming dimer is so slow below its melting point that none has been observed to form during the periods the monomer has been allowed to stand.

Since the dimer of the methyl chloro compound reaches equilibrium with monomer at about 50° less than does the dimer of the dichloro compound, we may say that it is about 1.5 kcal. per mole of $(\text{CH}_3)_2\text{NBCH}_2\text{Cl}$ ($50^\circ \times 30 \text{ cal. mole}^{-1} \text{ }^\circ\text{K.}^{-1}$) less stable, relative to its monomer. If the dimer of the dimethyl compound is still less stable in the same degree, its melting point would be less than 0°. The reaction rates for dimer formation are so slow at this temperature that dimerization might not be observed. Furthermore, if this guess is correct, the difference in energy that must be explained is only 1.5 kcal. per mole of monomer. Our knowledge of electronic effects is not good enough to explain such a small difference, especially where the structures are not really known. Thus, the question as to why dimethylaminodimethylborane does not dimerize can be framed, but not answered.

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