$ClOSO_2F$. Cleavage of the Cl–O bond by ultraviolet radiation has been generally observed[6,7] to produce the respective peroxide in good yield.

The reactions of HNO_3 or HNF_2 with ClF have been demonstrated[3,4] to be fast and efficient methods of forming the respective chlorine-substituted compounds $ClNO_3$ and $ClNF_2$. However, fluorosulfonic acid and ClF reacted more slowly and with appreciable formation of the by-products Cl_2, $FClO_2$, and ClO_2. These compounds are indicative of a $ClF–H_2O$ reaction,[26] the latter being an impurity in the commercial HSO_3F used. Nevertheless, $ClOSO_2F$ was obtained in at least 30% yield. Chlorosulfonic acid and an equivalent amount of ClF reacted as shown by

$$HSO_3Cl + ClF \longrightarrow HSO_3F + Cl_2$$

rather than giving the unknown compound, chlorine chlorosulfate. Thus, only fluorination occurred through halogen exchange and no evidence for chlorination of the OH group was obtained.

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Hydrogen Elimination in Dimethylamine–Borane

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The elimination of hydrogen from dimethylamine–borane was studied at 100° by observing the hydrogen isotope distribution in the products resulting from reactants with different hydrogen isotopes on nitrogen and/or boron. The results clearly eliminate the possibility of a unimolecular elimination and favor a bimolecular reaction. Different deuterium isotope effects on the elimination rates were deduced, depending on whether the nitrogen atom or the boron atom was substituted ($k_{N-H}/k_{N-D} = 3.5$; $k_{B-H}/k_{B-D} = 1.2$). Various possible isotopic exchange reactions which could have complicated the study were investigated.

Introduction

Dimethylamine–borane and other borane adducts of primary and secondary amines have been reported to lose hydrogen at elevated temperature to yield aminoboranes, borazine, and redistribution products or substituted boranes.[1–3]

The first step in these reactions has been demonstrated to follow the stoichiometry expressed by

$$R_2NHBH_3 \longrightarrow R_2NBH_2 + H_2 \qquad (1)$$

It would be of interest to determine whether this reaction proceeds *via* a unimolecular elimination, as is the case in a number of organic systems, or whether elimination occurs between more than one molecule. The normal experimental approach, where the rate law would be established from concentration measurements, seemed inappropriate since the amine–boranes are not very volatile nor are they, as mixtures of the products, readily susceptible to quantitative analysis. Moreover, the aminoborane products may dimerize, trimerize, or redistribute to give bis(aminoboranes) and aminodiboranes.[3] Therefore, the problem was approached by labeling boron and/or nitrogen bonds with deuterium and following the reaction by isotopic analysis of the noncondensable products.

Discussion

It was proposed to answer two basic questions in this study. (1) Is the hydrogen elimination reaction in dimethylamine–borane unimolecular or not? (2) What is the magnitude of the hydrogen isotope effect?

The first question was answered by the first two experiments in Table I, where mixtures of about equal proportions of undeuterated and completely deuterated compounds were heated or where mixtures of $(CH_3)_2NHBD_3$ and $(CH_3)_2NDBH_3$ were heated. Intramolecular hydrogen elimination should, in the first instance, produce only H_2 and D_2, whereas in the second instance, only HD should be formed. Incomplete deuteration might in either set introduce a small quantity of the missing isotopic variety of molecular hydrogen. On the other hand, intermolecular hydrogen elimination should produce all three hydrogen species in propor-

TABLE I

DECOMPOSITION OF DEUTERATED DIMETHYLAMINE–BORANES

Isotopic species	Amt of species, mmol	% reaction	% products D_2	HD	H_2
$(CH_3)_2NDBD_3$	0.82	31.3	11.0	47.7	41.3
$(CH_3)_2NHBH_3$	0.77				
$(CH_3)_2NDBH_3$	0.50	32.8	12.9	46.5	40.6
$(CH_3)_2NHBD_3$	0.48				
$(CH_3)_2NDBD_3$	1.05	38	83.1	16.9	. . .
$(CH_3)_2NDBD_3$	1.47	3.9	60.5	39.5	. . .

(1) E. Wieberg, A. Bolz, and P. Buchheit, *Z. Anorg. Chem.*, **256**, 285 (1948).

(2) H. I. Schlesinger, D. M. Ritter, and A. B. Burg, *J. Am. Chem. Soc.*, **60**, 1296 (1938).

(3) A. B. Burg and C. L. Randolph, Jr., *ibid.*, **73**, 958 (1951).

tions determined by: (a) the relative number of bonds of each kind; (b) a statistical factor favoring the formation of HD by a factor of 2 over the formation of either H_2 or D_2; (c) an isotope effect arising at the bonds to nitrogen and boron. Again, the results would be slightly modified if there were incomplete deuteration.

The data pertinent to these experiments clearly show that HD was the species produced in the largest amount when an intramolecular mechanism had predicted none, and H_2 and D_2 were produced when the intramolecular mechanism had predicted none of these gases. Moreover, the close agreement in the two experiments for the distribution of isotopes among the molecular species suggests that the production of each molecular species is independent of the particular combination of bonds to nitrogen and boron which might exist in a molecule and instead depends only on the total concentration of N–H and B–H bonds in the mixture. Barring the possibility of exchange of hydrogen and deuterium in the reactants prior to reaction, or between products after reaction, one is forced to the conclusion that the elimination is intermolecular and therefore a unimolecular reaction must be ruled out as an important reaction path under these conditions.

There are, however, serious *a priori* doubts whether various exchange reactions might not occur and thus vitiate this conclusion. Therefore, the possibility of isotopic exchanges which could reasonably be expected in this system was tested critically. The types of these reactions are

$$H_2 + D_2 \rightleftharpoons HD \tag{2}$$

$$(CH_3)_2NHBH_3 + D_2 \rightleftharpoons (CH_3)NHBH_2D + HD \tag{3}$$

$$(CH_3)_2NDBH_3 \rightleftharpoons (CH_3)_2NHBH_2D \tag{4}$$

$$(CH_3)_2NHBH_2 + (CH_3)_2NDBD_3 \rightleftharpoons (CH_3)_2NDBH_3 + (CH_3)_2NHBD_3 \tag{5}$$

Direct isotopic exchange within gaseous hydrogen (eq 2) did not occur since no HD was found when H_2 and D_2 were heated with mercury. Moreover, the relative quantities of H_2, D_2, and HD resulting from the elimination experiments do not agree at all with values calculated for the experimental isotopic composition from the equilibrium constant determined by Urey.[4]

Exchange between gaseous hydrogen and amine–borane was not noticeable after 1 hr at 100° and produced only a small amount of exchanged product after 24 hr. Reaction 3 was thus insignificant.

In order to test the importance of exchange between N–D and B–H bonds (eq 4), the change in the N–H concentration was determined on heating $(CH_3)_2NDBH_3$. Since the proportion of N–H bonds actually decreased markedly without a significant decrease in the B–H concentration, the extent of the self-exchange reaction must have been negligible.

Finally, amine exchange (eq 5) also proved insignificant since the mass spectrum of heated mixtures of $(CH_3)_2NDBH_3$ and $(CH_3)_2NHBD_3$ did not reveal the presence of $(CH_3)_2NDBD_3$, a material which should have been produced and which should have been enriched in the sample because of the reduced hydrogen elimination rate on deuterium substitution.

It is therefore concluded that the various isotopic exchange reactions, if they occurred at all, did not interfere with the interpretation of the data.

The deviation of the proportions of H_2, HD, and D_2 from the 1:2:1 ratio expected on statistical grounds now clearly indicates the existence of an isotope effect which favors elimination of H. The same conclusion is reached from the last two experiments in Table I. As in the first two experiments, the concentration of deuterium is lower in the product than in the reactants and is lowest in the gas produced in the initial portion of the reaction. Experiments to establish the magnitude of this effect were made. Mixtures of amine–boranes were prepared such that either the boron atom or the nitrogen atom was bonded to only one kind of hydrogen isotope while the other atom was bonded to hydrogen or deuterium. Approximately equal proportions of the two labeled amine–boranes were mixed. The mixture was heated and then quenched after only a few per cent reaction. Under these circumstances, the relative amounts of the hydrogen species produced were a measure of the relative magnitudes of the specific rate constants associated with the process.

The relative rates characterizing the separate isotope effects associated with B–H and N–H bonds were obtained as follows. It was assumed that the rate of production of each isotopic hydrogen species was proportional to the concentration in the sample of the bonds to nitrogen and to the concentration of the bonds to boron from which this species could be formed. This implies a bimolecular, second-order reaction. Thus

$$\text{rate } (H_2) = k_{H_2}[NH][BH] \tag{6a}$$

$$\text{rate } (D_2) = k_{D_2}[ND][BD] \tag{6b}$$

$$\text{rate } (HD) = k_{HD}[NH][BD] + k_{HD}'[ND][BH] \tag{6c}$$

It was further assumed that each rate constant consisted of contributions of rate factors associated only with the kind of bond which was reacting and independent of the other constituents of the molecule. This assumption is justified by the experiments listed in Table I but neglects secondary isotope effects. In particular

$$k_{H_2} = k_{NH}k_{BH};\ k_{D_2} = k_{ND}k_{BD};\ k_{HD} = k_{NH}k_{BD};\ k_{HD}' = k_{ND}k_{BH} \tag{7}$$

with these assumptions the ratios k_{NH}/k_{ND} and k_{BH}/k_{BD} were calculated from the observed HD:H_2 and HD:D_2 ratios and from the known isotopic distribution in the starting material. Since reaction occurred only to a few per cent, possible changes in the isotope ratios in the starting material should have been insignificant.

Pertinent experimental data and the rate constant ratios are listed in Table II. In the first four experiments HD:H_2 ratios were used, and both rate factor ratios were obtained simultaneously with good precision by solving graphically. In the remaining experiments, one of the rate factors thus determined was used to calculate the other factor from the HD:D_2 ratio. The

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[4] H. C. Urey, *J. Chem. Soc.*, 562 (1947). $K = 3.48$; *e.g.*, obsd (mmol): H_2, 0.20; D_2, 0.06; HD, 0.22; calcd (mmol): H_2, 0.18; D_2, 0.036; HD, 0.27.

TABLE II

ISOTOPE EFFECTS IN HYDROGEN ELIMINATION

Mixture	% reacn[a]	Isotopic ratios		Percentage of products			Rate factor[d] ratios	
		NH:ND	BH:BD	D_2	HD	H_2	k_{NH}/k_{ND}	k_{BH}/k_{BD}
$(CH_3)_2NHBD_3$ $(CH_3)_2NHBH_3$	1.7	27.8	1.11	2.2	42.1	55.7	3.45	1.17
$(CH_3)_2NHBD_3$ $(CH_3)_2NHBH_3$	2.8	27.6	1.10	2.4	44.0	53.6		
$(CH_3)_2NDBH_3$ $(CH_3)_2NHBH_3$	2.8	1.47	67.9	...	17.4	82.6		
$(CH_3)_2NDBH_3$ $(CH_3)_2NHBH_3$	4.7	1.58	65.6	...	16.3	83.7		
$(CH_3)_2NDBH_3$ $(CH_3)_2NDBD_3$	9.7	0.282	1.06	23.6	45.7	30.6		1.16[b]
$(CH_3)_2NDBH_3$	4.9	0.282	31.2	4.0	54.3	41.7	3.15[c]	
$(CH_3)_2NDBD_3$	3.9	0.150	0.053	60.5	39.5	...	3.9[c]	

[a] At 100°. [b] Assuming $k_{NH}/k_{ND} = 3.45$. [c] Assuming $k_{BH}/k_{BD} = 1.17$. [d] As defined in eq 7.

agreement among the values is satisfactory in view of the experimental uncertainty involved in the isotope ratios in the starting materials. An additional check on self-consistency is provided from one experiment where both H_2 and D_2 were produced in significant quantities. The ratio H_2:D_2 was used to calculate a value for $k_{H_2}/k_{D_2} = 4.34$. The product of the individual rate factors, $(k_{NH}/k_{ND})(k_{BH}/k_{BD}) = k_{H_2}/k_{D_2} = 4.04$, is in reasonable agreement with this value.

The magnitudes of the isotope effects on boron as well as on nitrogen are rather small when compared to the value expected from complete loss of the stretching vibrations of the bonds to hydrogen in the transition state.[5] Low values for deuterium isotope effects have been attributed to loss of bending motions rather than stretching motions in a nonlinear transition state, or alternately to the retention of zero-point energy in a vibrational mode of the transition state involving motion of hydrogen.[6] In the present reaction, an intramolecular elimination of hydrogen surely would include bending of the bonds to boron and nitrogen in reaching the transition state; this should tend to produce small values of k_H/k_D. No ready prediction of the magnitude of k_H/k_D can be made for an intermolecular reaction on stereochemical grounds alone: it would appear that, *e.g.*, a linear arrangement B–H–H–N (large k_H/k_D possible) and a four-center arrangement, where boron–nitrogen bond making occurs simultaneously with hydrogen–hydrogen bond making (low k_H/k_D), are equally plausible. Since the observed kinetic isotope effect was small, this fact cannot be used to distinguish between the two reaction types.

The present work clearly refutes a recent suggestion that dimethylamine–borane eliminates hydrogen by an intramolecular route.[7] While the magnitude of the isotope effects could be reconciled with this view, the product distribution cannot. Ionic intermediates are apparently ruled out on the basis of Beachley's careful, but fruitless, attempts to isolate ionic intermediates, which are stable for analogous derivatives of methylamine. In this light, the most likely reaction path is a bimolecular hydrogen elimination which would be consistent with the magnitude of the isotope effect as well as with the distribution of isotopes in the product.

$$(CH_3)_2NHBH_3 + (CH_3)_2NHBH_3 \longrightarrow (CH_3)_2NHBH_2N(CH_3)_2BH_3 + H_2 \qquad (8)$$

A possible subsequent step, production of dimethylaminoborane by dissociation of dimethylamine and borane, would seem to be ruled out since such a reaction would provide a path for interchange of isotopically labeled species. An experiment designed to detect such an interchange failed to do so. A second possibility, which is considered now the most probable, is elimination of a second mole of hydrogen from the intermediate in eq 8, either by an intramolecular cyclization to produce the dimer of dimethylaminoborane or by reaction with another mole of amine–borane. Although the former step should produce a perturbation in the product isotope distribution not accounted for by our treatment of the data, our results are not sufficiently precise to allow a distinction to be made.

Experimental Section

Materials.—Dimethylamine–borane and trimethylamine–borane were supplied by Callery Chemical Co. and sublimed before use. Dimethylamine-*d* was produced by reaction of dimethylamine with butyllithium, followed by hydrolysis with 99.7% D_2O. It was purified by fractionation in the vacuum line. Diborane-d_6 was prepared in the vacuum line from $NaBD_4$ and BF_3. The deuterated amine–boranes were prepared by reaction of diborane with dimethylamine and were sublimed before use. Elemental analyses and infrared spectra agreed well with theory and available literature data.[8,9]

Isotopic Analyses.—The deuterium content of the amine–boranes was estimated from quantitative analysis of the infrared spectra of the compounds dissolved in carbon tetrachloride, using the intensities of the N–H and B–D stretching frequencies and the sum of the N–D and B–H intensities in the 2300–2500-cm^{-1} region.[10] The C–H deformation band near 1475 cm^{-1} was used as an internal standard to normalize the data.

Analyses of the samples from which the pyrolysis data in Tables I and II were obtained were as follows: for $(CH_3)_2$-

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[5] K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

[6] F. H. Westheimer, *ibid.*, **61**, 265 (1961).

[7] O. T. Beachley, Jr., *Inorg. Chem.*, **6**, 870 (1967).

[8] A. T. Webb, J. T. Neu, and K. S. Pitzer, *J. Chem. Phys.*, **17**, 1007 (1949).

[9] B. Rice, R. J. Galiano, and W. J. Lehmann, *J. Phys. Chem.*, **61**, 1222 (1957).

[10] R. C. Taylor, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D.C., 1964, p 59.

$NHBD_3$, NH:ND = 13.3, BH:BD = 0.053; for $(CH_3)_2NDBD_3$, NH:ND = 0.150, BH:BD = 0.053; for $(CH_3)_2NDBH_3$, NH:ND = 0.282, BH:BD = 31.2. Samples prepared from $(CH_3)_2ND$ and B_2H_6 always showed a small amount of B–D bonds, indicating that exchange of isotopes had occurred in the preparation. Once isolated, the amine–boranes were stable to further self-exchange. However, small changes in isotopic composition could be detected when the samples were sublimed.

Isotopic analysis of the molecular hydrogen species was carried out on a Bendix Time-of-Flight mass spectrometer. Sensitivity coefficients for H_2, D_2, and HD were determined on known mixtures and over the pressure range to be used for unknown mixtures. The data for H_2 were corrected, when necessary, for the presence of D^+.

Experiments to Test Exchange Reactions.—(a) Approximately equal amounts of hydrogen and deuterium were heated for 24 hr with mercury in a sealed glass tube. The mass spectrum of the gas showed no evidence of a peak at *m/e* 3, characteristic of HD.

(b) Trimethylamine–borane or dimethylamine–borane was heated at 100° in sealed tubes containing 150 mm of D_2. After 1 hr no HD was found in the gas, nor was there any evidence for B–D bonds in the spectrum of the recovered boranes (1800 cm^{-1}). After 24 hr the trimethylamine–borane sample showed a small amount of B–D, estimated to be less than 5%. The dimethylamine–borane sample apparently produced, in addition to dimethylaminoborane, dimethylaminodiborane, whose absorption spectrum masked the 1800-cm^{-1} region. The B–D deformation around 900 cm^{-1}, however, was exceedingly weak.

(c) Dimethylamine–borane containing 78% N–D bonds and about 97% B–H bonds was heated as above. The remaining material after about 30% reaction contained 85% N–D bonds and more than 92% B–H bonds.

(d) Dimethylamine–borane-d_3 (mol wt 62) and N-deuteriodimethylamine–borane (mol wt 60) in approximately equal proportions were sublimed into a glass tube, and the sealed tube was heated as above. The solid remaining in the reaction was analyzed in the mass spectrometer. No peak at *m/e* 63 was found and the peaks at *m/e* 62 and 61 were at nearly the same intensity as for dimethylamine–borane-d_3. The mass spectrum of $(CH_3)_2NDBD_3$, independently obtained, showed low-intensity but easily detectable peaks at *m/e* 63 and 62 and a very intense peak at *m/e* 61, corresponding to loss of D^+.

Pyrolyses.—Samples of the desired amine–boranes were sublimed *in vacuo* into previously baked-out Pyrex tubes of about 50-ml capacity from tared storage containers. When mixtures were used, the quantities were very closely equimolar, approximately 1 mmol of each component. When small extents of reaction were desired, the sample was heated for 1 hr at 100–102° and quenched. The hydrogen produced was removed with a Toepler pump and measured and then subjected to mass spectroscopic analysis. After longer reaction times, the condensable materials revealed the presence of dimethylaminoborane and dimethylaminodiborane.

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Concerning the Existence of HMgX Compounds

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The preparation of "HMgX" compounds (where X = Cl, Br, and I) by hydrogenolysis and pyrolysis of Grignard compounds in diethyl ether has been previously reported. The authenticity of the "HMgX" product as distinguished from a physical mixture of MgH_2 and MgX_2 was shown by dta–tga analysis, but mainly by X-ray powder pattern data on the basis that the powder patterns for the "HMgX" compounds were different from those of MgH_2 and MgX_2. A repetition of the prior art plus additional work indicates that both hydrogenolysis and pyrolysis of Grignard compounds does *not* produce HMgX compounds, but a physical mixture of MgH_2 and MgX_2. The reason for the discrepancy was the comparison by prior workers of X-ray powder patterns for "HMgX" compounds containing 0.2–0.3 mol of ether of solvation with ether-free MgH_2 and MgX_2 containing 1.0 mol of ether. When comparison of X-ray powder pattern data was made for the "HMgX" compounds and MgH_2 and MgX_2 containing the same amount of ether of solvation, the "HMgX" compounds were found to exhibit the same X-ray powder lines as those found for a physical mixture of MgH_2 and MgX_2.

Introduction

The hydridomagnesium halides ("HMgX"[2] compounds) represent a novel new class of compounds which presumably can function as a selective reducing agent toward organic substrates[3] and as a starting material toward novel complex magnesium hydrides. The first comprehensive report of the preparation of "HMgX" compounds was made by Wiberg and Strebel[4] in 1957. These workers reported the preparation of crystalline soluble compounds of empirical formula $HMgX \cdot 2O(C_2H_5)_2$, where X = Cl, Br, and I, by the reaction of ethyl Grignard reagents and diborane

$$6C_2H_5MgBr + B_2H_6 \longrightarrow 6HMgBr + 2(C_2H_5)_3B \qquad (1)$$

Later we reported[5] that it was not possible to isolate these compounds under the exact conditions described earlier[4] or under a variety of other conditions that might be favorable for forming such compounds. Instead, only chloromagnesium borohydride could be ob-

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[2] "HMgX" in quotes will be used to represent the product formed from pyrolysis or hydrogenolysis of Grignard compounds which according to this report is actually a mixture of MgH_2 and MgX_2.

[3] R. A. Firestone, *Tetrahedron Letters*, **27**, 2629 (1967).

[4] E. Wiberg and P. Strebel, *Ann.*, **607**, 9 (1957).

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