the volumes of activation. Empirically, the pressure dependence is adequately described by equation 14, where $\Delta V^{\ddagger}$ is constant. This result implies the existence of a $p\Delta V^{\ddagger}$ term in the free energy of activation.

Eyring and his co-workers have discussed the volume of activation associated with the viscosity of simple liquids.[23-26] They were able to relate (empirically) the energy of activation for viscosity to the heat of vaporization, for some *n*-alkanes: $E_{\text{vap}}/E_{\text{vis}} = 4$. Volumes of activation were related to the molar volume by $V_{\text{M}}/\Delta V^{\ddagger}_{\text{vis}} = 8$, this conclusion being based on very limited experimental data. From these considerations they concluded that the volume of activation is the extra volume required to form the activated state and that the energy of activation is the energy required to form a hole of this size.

Our results for diffusion in polyethylene do not seem to fit the interpretations of the Eyring model, for we find that the activation energy is independent of the volume of activation. It would be interesting to investigate the volumes of activation for diffusion in pure liquid *n*-alkanes to ascertain whether the finding in the present case is a consequence of the diffusion process (*versus* that involved in viscosity) or of the fact that we are concerned here with polymers. For the present we prefer to retain the Eyring interpretation of the activation energy and simply supplement it with the assumption that above a certain volume the energy of hole formation is independent of hole size.

In any case, some conclusions regarding the details of the diffusion process can be drawn from the volumes of activation. In the series *n*-hexane, *n*-octane, *n*-decane, $\Delta V^{\ddagger}$ is essentially constant, = 50 cm.^{3}. In the initial state the chains of polymer and solvent are presumed to lie parallel to one another. Thus a volume of about two chain segments is swept out when a molecule moves parallel to its chain axis from one site to the next. This model accounts for the magnitude of $\Delta V^{\ddagger}$ and offers a simple explanation for the fact that $\Delta V^{\ddagger}$ in the *n*-alkanes studied does not depend upon chain length. Furthermore, the addition of side groups would be expected to increase $\Delta V^{\ddagger}$ as is observed for 3-methylpentane and neohexane. The magnitude of the increment in $\Delta V^{\ddagger}$ does not equal the volume of a methyl group: the observed increment is about 10 cm.^{3} per methyl group, whereas the molar volume of a methyl group is about 25 cm.^{3}. Probably the disparity for the branched solvents has to do with the fact that there is unoccupied space even when the molecule resides in a site. It is interesting to note that benzene requires a volume of activation equal to the molar volume of the solvent, which reflects the lack of conformity of benzene with the polymer chains.

V. Acknowledgments.—It is a pleasure to acknowledge the assistance of Miss E. R. Mandell and N. A. Kuebler in making the measurements; the contribution of H. L. Frisch in discussions; and the aid of V. L. Lanza in preparation of samples and of P. D. Garn in installing the automatic balance.

MURRAY HILL, NEW JERSEY

---

[23] J. O. Hirschfelder, D. Stevenson and H. Eyring, *J. Chem. Phys.*, **5**, 896 (1937).

[24] D. Frisch, H. Eyring and J. F. Kincaid, *J. Appl. Phys.*, **11**, 75 (1940).

[25] J. F. Kincaid, H. Eyring and A. E. Stearn, *Chem. Revs.*, **28**, 301 (1941).

[26] R. E. Powell, W. E. Roseveare and H. Eyring, *Ind. Eng. Chem.*, **33**, 430 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

The Reaction of O-Methylhydroxylamine and its N-Methyl Derivatives with Diborane

BY T. C. BISSOT, D. H. CAMPBELL AND R. W. PARRY

RECEIVED SEPTEMBER 10, 1956

The borane adducts of O-methyl-, O,N-dimethyl- and O,N,N-trimethylhydroxylamine have been prepared. Their thermal decomposition and hydrolysis have been studied. An internal oxidation–reduction reaction involving shift of a methoxy group from nitrogen to boron and of hydrogen from boron to nitrogen is described and discussed.

Many of the reactions of the boron hydrides are assumed to occur through the addition of a Lewis base to the borane group followed by decomposition of the adduct.[1] A study of the decomposition of the borane adducts of the methylhydroxylamines has provided interesting possibilities for processes of this type and has been of further interest because of the possibility of obtaining ring and chain structures with the –B–N–O– linkage.

The O-methyl- or methoxyamines (CH_3ONR_2, R = H or CH_3) differ appreciably from the hydroxylamines ($HONR_2$) in their reactions with diborane as well as in their other physical and chemical properties.[2] Since the reactions between diborane and the O-methylhydroxylamines are somewhat easier to interpret than the corresponding reactions involving the hydroxylamines, the preparation, properties and chemistry of the O-methylhydroxylamine–boranes are considered herein.

O-Methylhydroxylamine–Borane, $(CH_3O)NH_2 \cdot BH_3$. **a. Preparation and Characterization.**—In the presence of diethyl ether pure O-methylhydroxylamine and pure diborane react at −112° to produce O-methylhydroxylamine–borane.[3]

The pure white solid addition compound melts sharply at 55°, with rapid evolution of hydrogen gas (see Table I). Its solubility in ether is appreciable at room temperature but falls off as the tem-

---

[1] H. G. Weiss and S. Shapiro, THIS JOURNAL, **75**, 1221 (1953).

[2] T. C. Bissot, R. W. Parry and D. H. Campbell, *ibid.*, **79**, 796 (1957).

[3] Because of the relatively low stability of dimethyl ether-borane and the relatively high stability of the amine-boranes, coördination through nitrogen rather than oxygen is assumed.

TABLE I

SUMMARY OF THE PROPERTIES OF THE BORANE ADDITION COMPOUNDS OF O-METHYLHYDROXYLAMINE AND ITS N-METHYL DERIVATIVES

Compd.	M.p., °C.	Volatility	Ratio amine/B_2H_6 in preparation	Approx. temp. at which 50% dec. in 24 hr., °C.
$(CH_3O)NH_2BH_3$	55	Slightly volatile 40°	2.00 ± 0.02	55
$(CH_3O)NHCH_3BH_3$	−23 to −21	Slightly volatile 25°	1.97 ± .03	65
$(CH_3O)N(CH_3)_2BH_3$	−16.5	3.8 mm. 26°	1.99 ± .02	90

perature is lowered. Some of the solid could be sublimed slowly and with difficulty at 40° in high vacuum. Hydrogen loss was a competing process. Homogeneity of this solid and of the other O-methylhydroxylamine–boranes was indicated by the fact that the melting point of a small fraction which sublimed or distilled from the mass was identical to that of the original sample. The volatility of the solid under low pressures argues in favor of a monomeric formulation. A rather rough estimate of its molecular weight based on vapor pressure depression of a diethyl ether solution gave a molecular weight of 75 to 83 in the concentration range of 1.1 to 1.9 molal. The values extrapolate to a molecular weight of about 65 at infinite dilution. The theoretical value for the monomer $(CH_3O)NH_2BH_3$ is 61. Precise measurements in dilute solution were rendered difficult by slight decomposition of the compound, but the data support a monomeric rather than a dimeric formula.

After hydrolyzing $(CH_3O)NH_2BH_3$ with dilute hydrochloric acid, the following analytical data were obtained: hydridic hydrogen: obsd. 4.63%, theor. 4.96%; boron: obs. 17.8%, theor. 17.77%. The amount of O-methylhydroxylamine hydrochloride in the hydrolysis product was estimated roughly from a titration curve on an aliquot. *At least* 93% of the nitrogen was still present as CH_3ONH_2.

When an *ethereal solution* of $(CH_3O)NH_2BH_3$ was treated with a slight excess of gaseous BF_3 at 0°, no B_2H_6 was released, but hydrogen loss was accelerated. Excess B_2H_6 was without effect on the pure adduct. Attempts to displace CH_3ONH_2 from the complex by the stronger base[2] $N(CH_3)_3$ gave only a 22% yield of $(CH_3)_3NBH_3$. A competing reaction was loss of hydrogen from the complex, a process which appeared to be catalyzed by the presence of trimethylamine. Thirty-three per cent. of the original complex decomposed through hydrogen loss in 17 hours. Ammonia had a similar effect. The foregoing observation was of importance in interpreting the poor stoichiometry obtained in early attempts to synthesize $(CH_3O)NH_2BH_3$ from CH_3ONH_2 containing ammonia as a contaminant.

b. Pyrolysis of O-Methylhydroxylamine–Borane.—The thermal decomposition of pure $(CH_3O)NH_2BH_3$ occurred in two ways. If it was heated rapidly to approximately 90°, a violent detonation resulted. If it was heated slowly, hydrogen was evolved at a slow rate. The rate of H_2 evolution increased markedly when the liquid phase appeared at 55°; within ten minutes or less the amount of hydrogen evolved was such that the ratio $H_2/(CH_3O)NH_2BH_3$ amounted to 0.66. At this point the liquid became increasingly viscous and the rate of hydrogen evolution dropped sharply. After four days at 55° the last one-third of a mole of H_2 was obtained. The sharp break in the rate of hydrogen evolution after loss of only two-thirds of one mole of hydrogen is difficult to correlate with detailed structural or mechanistic arguments for the process. During heating at 55° a complex solid mixture of NH_3, $B(OCH_3)_3$, and in some cases CH_3OH, sublimed from the reaction vessel. The chief component of the mixture was the weakly associated solid $H_3NB(OCH_3)_3$. In the vapor phase the complex dissociated completely to H_3N and $B(OCH)_3$.

Hydrogen evolution from the original viscous mass did not stop at one mole but continued at a slow rate. After the loss of one mole of hydrogen and the evolution of considerable trimethyl borate from the system, the residue could be heated safely above 90°. The viscous mass changed slowly into a white solid as the temperature was raised. After heating to 300°, the residue was analyzed. The empirical formula for the solid was $BN_{1.12}(OCH_3)_{0.1}H_{1.3}$. It is important to note that more than 90% of the original methoxy content of the compound was sublimed from the system, largely as trimethyl borate.

The rate of decomposition of pure O-methylhydroxylamine–borane was studied in solution at 55°. Diethylene glycol dimethyl ether was chosen as a suitable solvent. Figure 1 shows decomposition rate data for (1) the pure compound, (2) a 50% solution of the complex in the polyglycol ether, and (3) a 10% solution. The previously unexplained sharp break in rate after loss of only two-thirds of a mole of hydrogen disappeared when the solvent was introduced. Such an observation suggests that the break may be associated with the observed rapid increase in viscosity of the decomposing mass.

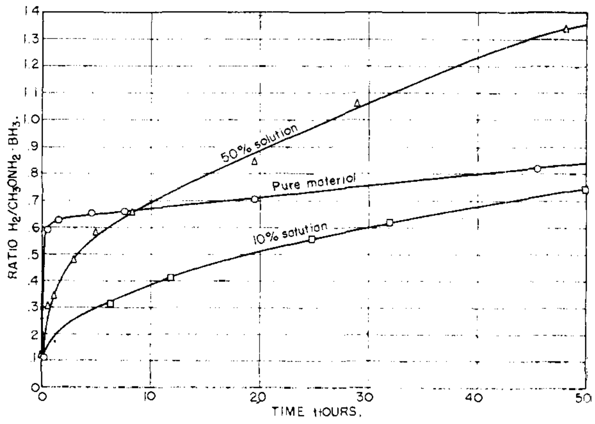


Fig. 1.—Rate of hydrogen loss from $(CH_3O)NH_2BH_3$ at a temperature of 55°. Solvent was diethyleneglycoldimethyl ether.

Reduced mobility of interacting groups would reduce the rate of gas evolution.

The rate data of Fig. 1 can be used to differentiate between intramolecular and intermolecular loss of hydrogen from the complex in solution. If the liberated hydrogen were produced by an intramolecular reaction comparable to that proposed in the hydrolysis of B_2H_6(1), (*i.e.*, $H_2OBH_3 \rightarrow HOBH_2 + H_2$), the process would be first order and one mole of hydrogen would be evolved per mole of borane adduct

$$(CH_3O)NH_2BH_3 \longrightarrow H_2 + (CH_3O)NHBH_2$$

The resulting "unsaturated" product would be expected to polymerize. If the hydrogen were produced by an intermolecular process, the kinetics should be higher than first order, but the stoichiometry would be the same as for the first-order process

$$n(CH_3O)NH_2BH_3 \longrightarrow nH_2 + [(CH_3O)NHBH_2]_n$$

Further reaction between the monomer and the dimer or polymer should give long chains or rings. Both intra- and intermolecular processes would be complicated by the partial loss of a second mole of hydrogen, since hydrogens are still available on boron and nitrogen. Crosslinking of chains or rings might thus be expected.

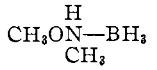
In Fig. 1 the fraction of complex decomposed, x/a, is plotted as a function of time, where x is the number of moles of hydrogen at time t, and a is the initial number of moles of $(CH_3O)NH_2BH_3$. The first-order rate equation can be converted to the form

$$\frac{d(x/a)}{dt} = \frac{k(a - x)}{a}$$

From this form it is apparent that the fraction decomposed at any time would be independent of the volume of the solution if the reaction were first order. The data in Fig. 1 thus provide strong evidence against intramolecular loss of hydrogen in the polyether solutions used. If one uses the normal simplified processes for treating rate data, such as calculation of rate constants at different concentrations and plotting of functions of the methoxyamine–borane concentration against time, an apparent order of about 2 is obtained for the early stages of the process in solution. This fact would be consistent with an intermolecular, but not with an intramolecular process for hydrogen loss.

c. Hydrolysis of O-Methylhydroxylamine–Borane.—Acidic hydrolysis of $(CH_3O)NH_2BH_3$ gave the expected hydrochloride salt of the base along with boric acid; in contrast, basic hydrolysis of the complex gave reduction of the O-methylhydroxylamine to ammonia, and only two of the expected three hydridic hydrogens of the borane group were recovered. A shift of hydrogen from boron to nitrogen and of a methoxy group from nitrogen to another atom (presumably boron) is implied by the data for the basic hydrolysis. The shift is comparable to that observed in the thermal decomposition process. In order to eliminate the possibility that O-methylhydroxylamine itself could be hydrolyzed to ammonia in the presence of a strong base, 3.23 millimoles of base and one ml. of 50% KOH were heated in a sealed tube at 100° for one hour. No ammonia was obtained and the original amine was recovered.

O,N-Dimethylhydroxylamine–Borane, $(CH_3O)NCH_3HBH_3$. **a. Preparation and Characterization.**—O,N-Dimethylhydroxylamine will react with diborane to produce



$$CH_3O\overset{H}{\underset{CH_3}{N}}—BH_3$$

Ether was acceptable but not necessary as a solvent. In contrast to the case of O-methylhydroxylamine, good stoichiometry and a pure liquid product resulted from the interaction of diborane and the free, non-solvated base. Data are summarized in Table I. Vapor pressure of O,N-dimethylhydroxylamine–borane at room temperature could not be measured with the mercury manometer on the system, but the liquid could be distilled at room temperature under high vacuum without decomposition. Analysis gave a B/N/hydridic H ratio of 1/0.97/2.92. Upon hydrolysis with hydrochloric acid the original amine was recovered and identified as the hydrochloride salt. As before, the slight volatility of the compound suggested a monomeric formula which was supported by a rough molecular weight value of 90 obtained from vapor pressure depression of an 0.8 molal diethyl ether solution. Since with dilution the value should decrease toward the theoretical monomeric value of 75, a monomeric rather than a dimeric formula is indicated.

When an ether solution of $(CH_3O)NCH_3HBH_3$ was stirred overnight with an excess of $N(CH_3)_3$ at 0°, an 86% yield of $(CH_3)_3NBH_3$ was recovered. There was no hydrogen evolution in this displacement reaction, as there was in the similar experiment with $(CH_3O)NH_2BH_3$.

b. Hydrolysis of O,N-Dimethylhydroxylamine–Borane.—$(CH_3O)NCH_3HBH_3$ is more stable than the O-monomethylhydroxylamine adduct. Only traces of H_2 were liberated in its preparation and storage at room temperature. As in the previous case, both explosive and non-explosive decompositions were observed. Explosive decomposition, brought about by heating the compound rapidly to 100°, is obviously a very complex process. The stoichiometry for one sample was obtained from an over-all analysis of explosion products. The process was approximated by the empirical equation

$$(CH_3O)NCH_3HBH_3 \longrightarrow 2.3H_2 + 1.1CH_4 + 0.03C_2H_6 + 0.08N_2 + 0.21HCN + \underbrace{\text{solid of approx. composition}}_{BN_{0.65}OH_{0.6} + 0.6C}$$

The quantitative features of the above equation undoubtedly vary from one explosion to another, but the qualitative features are of interest. Hydrogen is to be expected in view of the ease with which hydrogen evolution occurs from compounds of this type; nitrogen is a normal explosion product of nitrogen compounds. The appearance of methane and ethane suggests methyl radicals as an intermediate; their reduction gives methane, their combination gives ethane. The appearance of HCN was rather unexpected, but can be rationalized in terms of the original HCN linkage in the molecule.

The non-explosive decomposition which results from storage of the compound at 65° for several hours differs markedly from the explosive decomposition. The over-all stoichiometry is approximated by the equation

$$3(CH_3O)NCH_3HBH_3 \xrightarrow[\text{Several hours}]{65^\circ} \left\{ \begin{array}{c} (CH_3)_2HNB(OCH_3)_3 + \frac{1}{x}(HNBH)_x + \frac{1}{3}(CH_3HNBH_2)_3 + 3H_2 \\ \text{and} \\ \text{small amount} \\ (CH_3)H_2NB(OCH_3)_3 + \frac{1}{x}(CH_3NBH)_x + \frac{1}{3}(CH_3HNBH_2)_3 + 3H_2 \end{array} \right.$$

The compound $(CH_3NHBH_2)_3$, first prepared as a definite compound by the above process, has been described elsewhere.[4] By vapor pressure and molecular weight measurements it was established that the amine liberated from the methyl borate was largely dimethylamine. Much smaller amounts of methylamine were found. A shift of methyl groups from one nitrogen to another in a controlled disproportionation reaction is implied.

c. Hydrolysis of O,N-Dimethylhydroxylamine–Borane.—Hydrolysis reactions followed closely the pattern set in the hydrolysis of O-methylhydroxylamine–borane. Acid hydrolysis produced boric acid and the salt of O,N-dimethylhydroxylamine. Hydrolysis with 50% KOH in a sealed tube at 100° produced a shift of methoxy and hydrogen to give methylamine as the principal basic product recovered from a complex mixture of amines (27% yield). Pure CH_3ONHCH_3 was not decomposed when heated under similar conditions with 50% KOH. Only two of the three hydridic hydrogens on the borane group of $(CH_3O)NHCH_3BH_3$ were ever released as H_2.

O,N,N-Trimethylhydroxylamine–Borane. a. Preparation and Characterization.—$CH_3ON(CH_3)_2$ reacted with diborane without a solvent to give $CH_3ON(CH_3)_2BH_3$. Stoichiometry of the process was excellent. The pure addition compound melts at −16.5 to −16.0° and has a vapor pressure of 3.8 mm. at 25°. An equimolar mixture of $CH_3ON(CH_3)_2BH_3$ and trimethylamine, $N(CH_3)_3$, reacted as indicated

$$CH_3ON(CH_3)_2BH_3 + N(CH_3)_3 \xrightarrow[Et_2O]{0^\circ} (CH_3)_3NBH_3 + CH_3ON(CH_3)_2$$

Ninety-eight per cent. of the original $CH_3ON(CH_3)_2$ was recovered. No H_2 was evolved. Although no direct measurement of the molecular weight of $CH_3ON(CH_3)_2BH_3$ was made, its volatility and the observations on two earlier members of the series leave little real doubt as to its monomeric nature.

b. Pyrolysis of O,N,N-Trimethylhydroxylamine–Borane.—In contrast to the behavior of O-methyl- and O,N-dimethylhydroxylamine boranes, O,N,N-trimethylhydroxylamine–borane did not undergo an explosive decomposition when heated rapidly to 100° in a sealed tube. At this temperature slow decomposition took place. All products were volatile. The molar ratio of hydrogen produced to O,N,N-trimethylhydroxylamine–borane used was 0.64. Trimethyl borate, $B(OCH_3)$, was isolated as one of the products. The remainder of the volatile components was fractionated extensively, but no pure compounds could be separated.

c. Hydrolysis of O,N,N-Trimethylhydroxylamine–Borane.—Hydrolysis of $CH_3O(CH_3)_2NBH_3$ with 50% KOH for two hours at 100° in a sealed tube gave no evidence for a shift of methoxy or hydrogen as had been observed in the two preceding cases. About 92% of the original base and 90% of the hydridic hydrogen in the compound were *recovered* after hydrolysis.

Discussion

a. Loss of Hydrogen from the Borane Adducts of the Methylhydroxylamines.—If one makes the logical assumption that hydrogen evolution in the impure complex results from the interaction of a protonic hydrogen on the amine and a hydridic hydrogen on the attacking borane group, then the temperature for loss of hydrogen from the complex should correlate with the relative acidity of the hydrogen atoms on the amine.[5]

Table I gives the temperature required to effect loss of $^1/_2$ mole of H_2 per mole of addition compound over a 24-hour period. If one assumes the usual electron-donating power attributed to alkyl radicals, the inductive effect of the methyl groups would reduce the acidic character of the remaining hydrogen atoms on the amine whenever a hydrogen is replaced by an alkyl radical. The expected increase in decomposition temperature when a methyl group replaces a hydrogen attached to nitrogen is apparent in Table I. Other factors such as entropy of activation would also contribute to this result.

b. The Hydride–Methoxy Shift in Pyrolysis.—Rapid heating of the O-methyl- and O,N-dimethylhydroxylamine–boranes invariably led to a violent explosion, which appeared to be triggered by the sudden exothermic shift of methoxy groups from nitrogen to boron. Slower, more gentle heating of the O,N-dimethylhydroxylamine–borane adducts led to a controlled shift of methoxy groups from nitrogen to boron and of hydrogen from boron to nitrogen. Loss of gaseous hydrogen from the compound always preceded the low-temperature shift. Prior to the loss of hydrogen from the borane adduct, acid hydrolysis always yielded the original O-methylhydroxylamine and three molecules of hydrogen per borane group. After loss of hydrogen, $B(OCH_3)_3$, ammonia, methyl and dimethylamines were obtained. Clearly, group transfer had occurred after, or concurrent with, hydrogen loss. The difficult pyrolysis of $(CH_3O)(CH_3)_2NBH_3$ below 100° also suggested that hydrogen loss

---

[4] T. C. Bissot and R. W. Parry, THIS JOURNAL, **77**, 3481 (1955).

[5] The relative acidic character of the secondary hydrogens on the amines is not necessarily the reverse of the primary basic strength of the amines as measured in water.[6]

was an important initial step in the shifting of groups.

These facts would be consistent with the following mechanism. In those cases where a hydrogen is still attached to the nitrogen of a methoxyamine the pyrolysis proceeds by an initial splitting out of hydrogen from boron and nitrogen followed by rapid CH_3O group transfer to the newly opened site on the boron. In explosive decomposition rapid heating produces more violent fragmentation, probably involving breaking of B, H and $O-CH_3$ bonds to give free radicals and atoms. This mode of decomposition undoubtedly involves a higher energy of activation, hence higher localized temperature. Temperatures may build up rather rapidly in small volumes of the solid as a result of the exothermic low-temperature process, hence the low-temperature shift in the O-methyl- and O,N-dimethylhydroxylamine boranes could be converted easily to the explosive decomposition process if heating were rapid and heat were not dissipated.

Although it was found that explosive decomposition of pure methoxyamine could be initiated by both spark and heat, it was shown that attachment of a non-oxidizable Lewis acid such as BF_3 to the base decreased its sensitivity to explosion. The compound $(CH_3O)NH_2BF_3$ was prepared in benzene as a white solid melting at 86–88°. The compound was heated in a sealed tube to 300°. There was no explosion, but at the higher temperature the solid turned dark. This evidence indicates that the explosive decomposition is associated with the reducing character of the BH_3 group and not alone with the properties of the coördinated amine.

The following equation was written for the low-temperature decomposition of O,N-dimethylhydroxylamine–borane

$$3(CH_3O)NCH_3HBH_3 \xrightarrow[\text{Several hr.}]{65°} (CH_3)_2HNB(OCH_3)_3 + \frac{1}{x}(HNBH)_x + \frac{1}{3}(HCH_3NBH_2)_3 + 3H_2$$

Data for the pyrolysis of O-monomethylhydroxylamine–borane suggest a similar process, but the trimeric compound $(H_2NBH_2)_3$, the inorganic analog of cyclohexane, was not isolated despite several experimental attempts. A polymerization beyond the trimer stage was probably responsible for the difference. The expected equation would be

$$3(CH_3O)NH_2BH_3 \xrightarrow[\text{several hr.}]{55°} H_3NB(OCH_3)_3 + 2/n(H_{1.5-x}NBH_{1.5-x})_n + (3 + 2x)H_2$$

The O,N,N-trimethylhydroxylamine–borane also underwent the methoxyl–hydride shift to give products which were rather similar in a formal sense to those outlined above

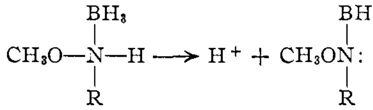
$$3(CH_3O)N(CH_3)_2BH_3 \longrightarrow (CH_3)_2HNB(OCH_3)_3 + 2/n[(CH_3)_2NBH_2]_n + 2H_2$$

Although all products of the reaction were volatile only hydrogen gas and trimethoxyborane could be isolated and characterized. The failure to isolate $[(CH_3)_2NBH_2]_n$ and $(CH_3)_2HN$ is understandable in terms of the properties of $[(CH_3)_2NBH_2]_n$ (see Experimental section).

Despite the formal similarity, the pyrolysis of O,N,N-trimethylhydroxylamine–borane must differ significantly from that suggested for the O-methyl and O,N-dimethyl derivatives. The absence of hydrogen attached to nitrogen renders impossible a low-temperature hydrogen loss followed by a shift of a methoxy group. Any mechanism which would impose a coördination number of five on boron or nitrogen is equally distasteful. Since the decomposition occurred at high temperatures, where there would be partial dissociation of the complex to give free BH_3 groups, it is suggested that the mechanism involved BH_3 groups. A temporary coördination of BH_3 with the oxygen on the amine would give an unstable intermediate which could shift a hydrogen over to the nitrogen while the boron retained the methoxyl group. A disproportionation of methoxyborane to trimethoxyborane and diborane would give the observed products. The rate for such a process, involving a high energy intermediate, would be slow compared to the shift over the unsaturated intermediate, and would not be expected to achieve explosive proportions even at 100°. Such was the case.

c. The Methoxy–Hydride Shift during Hydrolysis with a Strong Base.—Hydrolysis of $(CH_3O)NH_2BH_3$ and $(CH_3O)NCH_3HBH_3$ by 50% KOH invariably resulted in replacement of the methoxyl group on the nitrogen by a hydrogen from the boron. In contrast, hydrolysis of $(CH_3O)N(CH_3)_2BH_3$ simply liberated the base unchanged and produced hydrogen and borates from the BH_3 group. No shift of the methoxyl group was ever detected in the latter case. Clearly, the hydrogen attached to the nitrogen played a dominant role in group transfer. The following mechanism is suggested.

In a strongly alkaline solution the equilibrium shown below would be displaced to the right.



$$CH_3O-\overset{\overset{BH_3}{|}}{\underset{\underset{R}{|}}{N}}-H \longrightarrow H^+ + CH_3O\overset{\overset{BH_3^-}{|}}{\underset{\underset{R}{|}}{N}}:$$

The resulting anion could then rearrange by shift of a hydrogen to the nitrogen and of a methoxyl group to the boron.[6] Since the hydrolysis of such B–H bonds in alkaline solution is a rather slow reaction, the reduction of the amine would occur before the original compound was decomposed.

For the compound $(CH_3O)N(CH_3)_2BH_3$, acid ionization is impossible and no shift would be expected. This was observed.

Experimental

a. **Reagents.**—1. The O-methylhydroxylamines were prepared and purified as described earlier.[2] 2. Diborane was prepared from $LiAlH_4$ and BF_3 etherate and purified as described earlier.[7] 3. Ether—reagent grade diethyl ether was stored over CaH_2 for several days and distilled under

---

(6) Data now available provide no clear basis for outlining the detailed steps of the anion rearrangement. One route, kindly suggested by the reviewer, involves loss of an H^- from the anion, $CH_3ONRBH_3^-$, to give $CH_3ORN{=}BH_2$. The H^- lost to the solution would produce hydrogen. The unsaturated intermediate would undergo an internal shift of CH_3O from N to B and of H from B to N, just as was suggested in the thermal decomposition process.

(7) R. W. Parry and T. C. Bissot, This Journal, **78**, 1524 (1956).

low pressure before use. Commercial diethylene glycol dimethyl ether was handled in a similar fashion.

b. General Procedure for Compound Formation.—The reaction vessel was a 20-mm. Pyrex tube, about 8 inches long attached to the conventional high-vacuum system by means of a 20/40 ₸ joint. The tube was equipped with an automatic, electromagnetically operated, plunger-type stirrer. In a typical run an approximately 4-to-6 mmole sample of the pure amine was weighed out in an evacuated micro weighing tube and distilled into the reaction vessel. If ether was to be used as a solvent, a 1 to 6-ml. aliquot was distilled into the reaction tube at this point and the system was stirred until solution was obtained.

The system was then frozen with liquid nitrogen and a carefully measured amount of diborane, about 10 to 20% in excess of the stoichiometric amount, was distilled into the tube. For O-methylhydroxylamine the system was warmed to −112° by means of a CS_2 slush bath. Within 15 to 20 minutes a decrease in the pressure of the diborane and the appearance of a white precipitate indicated that the reaction had occurred at −112°. The system was warmed to −80°, stirred for another half hour, and the excess of B_2H_6 and ether removed and separated by careful vacuum line fractionation. The observed stoichiometric ratios of CH_3ONH_2 to B_2H_6 for five separate runs were in the range 1.98–2.01. In the absence of ether the stoichiometry was frequently poor and hydrogen gas was evolved at low temperatures.

The procedure for O,N-dimethylhydroxylamine and O,N,N-trimethylhydroxylamine was similar except that the frozen mixture of amine and B_2H_6 was warmed up in a somewhat different manner. The B_2H_6 was frozen in a ring above the amine then the liquid N_2 was poured out of the Dewar flask and the flask replaced on the reaction tube. The tube warmed up slowly to room temperature over a period of several hours. The contents of the tube were frozen with liquid N_2; any H_2 gas was pumped off and measured; then unreacted B_2H_6 was distilled out and the excess measured. Deviations from this general procedure are described in dissertation form.[8]

A small amount of ammonia present as a contaminant in O-methylhydroxylamine brought about hydrogen loss from the borane complex over the temperature range of −50 to 25°. The reality of the effect is illustrated by the following experiment. When 9 mole % ammonia was added to carefully purified O-methylhydroxylamine and the reaction with diborane was effected as described above, the resulting mixture of $(CH_3O)NH_2BH_3$ and $[H_3BNH_3]_n$ changed into a liquid at room temperature and evolved hydrogen such that the ratio $H_2/(CH_3O)NH_2BH_3$ was 0.48 after one hour at 26°. A weakly complexed 1:1 liquid mixture of $H_2NB_2H_5$ and $(C_2H_5)_2O$ was distilled from the system. Although the complexing of $H_2NB_2H_5$ with $(C_2H_5)_2O$ has not been reported previously, it is not unexpected since ammonia and trimethylamine adducts of $H_2NB_2H_5$ are known. If the 1:1 mixture is completely dissociated in the vapor state, it would have a molecular weight of 58.4. The observed values determined by vapor density were 61.5 and 63.7.

Essentially pure $H_2NB_2H_5$ was recovered from the mixture by complexing the ether with either $AlCl_3$ or BF_3. Both worked satisfactorily. A 7.7-mg. sample of aminodiborane purified by this technique, was characterized on the basis of the following evidence. The molecular weight by vapor density was 47 as compared to the theoretical value of 43. The vapor pressure values for the liquid at −23, 0 and 18.9° were 7.8, 32.4 and 85.4 mm. as compared to literature[9] values of 7.6, 32.2 and 86.8. The B/N/hydridic H ratio was 1/1.99/4.86 as compared to theoretical values of 1/2/5.

c. Reaction of Boron Trifluoride with Methoxyamine–Borane.—A 4.53-millimole sample of $(CH_3O)NH_2BH_3$ was dissolved in 4 cc. of diethyl ether at 0°. To this solution 4.85 mmoles of gaseous BF_3 was added. The mixture was stirred at 0° for about 12 hours. Hydrogen evolution was accelerated (1.56 mmoles in 12 hours) perhaps due to localized heating. Fractionation of the mixture produced ether and BF_3 etherate, but no diborane. A non-volatile viscous liquid typical of that produced by loss of H_2 from $(CH_3O)NH_2BH_3$ remained in the reaction tube. This was not $CH_3ONH_2BF_3$ since an authentic sample of $(CH_3O)H_2NBF_3$ made from methoxyamine and BF_3 in benzene, was a stable white solid with a melting point of 86–88°.

d. Reaction of NMe_3 with the O-Methylhydroxylamine–Boranes.—A sample of the desired pure O-methylhydroxylamine–borane was dissolved in diethyl ether. A slight excess of trimethylamine was added at 0° and the solution was stirred for periods of time ranging from 14 to 18 hours. At the end of the reaction period the solvent was removed and any $(CH_3)_3NBH_3$ was sublimed from the system and identified by melting point, and elementary analysis.

e. Low-Temperature Decomposition of Compounds.—Samples were maintained in the preparation vessel at the desired temperature and products were isolated, usually by sublimation or distillation, then characterized. The most difficult phase of the operation was the resolution of the resulting complex solid mixture of NH_3, $B(OCH_3)_3$, and, on occasion, CH_3OH.

Ammonia was identified by a potentiometric titration curve. Upon hydrolysis of the mixture, no hydridic hydrogen was found. Boron analysis indicated 9.22% B; nitrogen found was 7.52%. This is equivalent to 88.4% $B(OCH_3)_3$ and 9.15% NH_3, a mixture which should have a molecular weight of 70.0 when completely dissociated. The observed molecular weight by vapor density was 70.3.

Synthetic "mixtures" of H_3N, $B(OCH_3)_3$ and CH_3OH were identical to the solid mixtures in terms of physical appearance, vapor pressure and dissociation pressures in the vapor phase.

In a mixture resulting from the decomposition of $(CH_3O)NCH_3HBH_3$, the mixture of $R_2HN,B(OCH_3)_3$, and CH_3OH was separated by tying up the amines and alcohol with excess diborane, then separating the $B(OCH_3)_3$ and B_2H_6 by vacuum-line distillation. The purified $B(OCH_3)_3$ was characterized by vapor pressure at four temperatures, by melting point (−29.0° obsd. and −29.3° lit.), by molecular weight (114.6 *vs.* 103.9 literature), by absence of active hydridic H, and by boron analysis (10.05% *vs.* 10.41% theory). Despite extensive fractionation it was not possible to separate the compound $[(CH_3)_2NBH_2]_n$. This compound was expected from the decomposition of the original $(CH_3O)N(CH_3)HBH_3$ and from the $(CH_3)_2HNBH_3$ produced in the separation procedure. Such an observation is consistent with an earlier report by Burg and Randolph[10] to the effect that N,N-dimethylamine–borane, in addition to participating in a monomer–dimer equilibrium, can enter into the reaction

$$3/2[(CH_3)_2NBH_2]_2 \longrightarrow [(CH_3)_2N]_2BH + (CH_3)_2NB_2H_5$$

They reported that the mixture could not be separated into its components by conventional trap-to-trap distillation. The vapor pressure of the decomposition product in this investigation was in the same range as that expected for the mixture of the above compounds.

d. Explosive Decomposition.—Explosive decomposition was studied by heating a well-annealed bomb tube containing the sample to 100°. The tube was opened to the vacuum line by means of the vacuum-tube opener. Noncondensable gases such as H_2, N_2 and CH_4 were pumped off and separated by conventional techniques. C_2H_6 and HCN in the condensable products were separated by fractional distillation in the vacuum line. The HCN was characterized by molecular weight, melting point, vapor pressures and reaction with silver nitrate.

c. Analytical Methods.—1. Hydridic hydrogen was determined by heating the sample for several hours in a sealed tube with 6 *N* HCl. The hydrogen gas evolved was measured and identified in the vacuum system.

2. Boron—a modification[11] of the identical *p*H method of Foote[12] was applied to the micro-determination of boron in the presence of nitrogen compounds. The acid solution from hydrolysis was adjusted to a *p*H value very close to 7; the solution was then saturated with mannitol and the boric acid complex was titrated by bringing the system back to the same *p*H of 7. Excellent results were obtained when the method was applied to known standards.

---

[8] (a) D. H. Campbell, Ph.D. Dissertation, University of Michigan, Ann Arbor, Michigan, 1953; (b) T. C. Bissot, Ph.D. Dissertation, University of Michigan, Ann Arbor, Michigan, 1955.

[9] H. I. Schlesinger, D. M. Ritter and A. B. Burg, THIS JOURNAL, **60**, 2297 (1938).

[10] A. B. Burg and C. L. Randolph, *ibid.*, **73**, 953 (1951).

[11] R. W. Parry, D. H. Campbell, D. R. Schultz, S. G. Shore, T. C. Bissot and R. C. Taylor, "The Chemistry of Boron Hydrides," Eng. Res. Inst., Univ. of Mich., Annual Report Project 1966-1-P, 1954.

[12] F. J. Foote, *Ind. Eng. Chem., Anal. Ed.*, **4**, 39 (1932).

3. Nitrogen usually was determined by the micro-Kjeldahl method. The hydroxylamines were reduced to ammonia by digestion with glucose in the presence of K_2SO_4–$CuSO_4$ catalyst.

Acknowledgment.—This research was conducted under Contract AF 23(616)-8 with the United States Air Force, the sponsoring agency being the Aeronautical Research Laboratory of the Wright Air Development Center, Air Research and Development Command.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

Low Temperature Oxidation of Solid Ferrous Sulfate Heptahydrate with Oxygen in the Presence of Solid Calcium Hydroxide

BY EDWIN ROIG, J. FRED HAZEL AND WALLACE M. McNABB

RECEIVED OCTOBER 10, 1957

The purpose of the present work was to study the oxidation of solid ferrous sulfate heptahydrate by oxygen in the presence of solid calcium hydroxide. An induction period preceded the oxidation. The amount of oxidation was directly proportional to the amount of calcium hydroxide present in the mixture. The rate of oxidation was increased by the presence of calcium chloride, and by the presence of excess calcium hydroxide. The induction period was decreased by a decrease in particle size of the ferrous sulfate, by addition of calcium chloride, and by shaking the mixture. It is suggested that the induction period consisted of a double decomposition reaction which was favored by the absorption of moisture on the solid calcium compound.

Introduction

Solutions of ferrous sulfate vary greatly in rate of oxidation depending on the *p*H of the medium.[1,2] Oxidation does not become significant until the *p*H is raised to the point where ferrous hydroxide begins to precipitate.[3]

The above behavior suggested to us the study of the oxidation of solid ferrous sulfate with oxygen in the presence of solid calcium hydroxide. Preliminary experiments conducted at room temperature revealed that ferrous sulfate monohydrate was not oxidized under these conditions unless the system was humid. The heptahydrate was oxidized by dry oxygen, on the other hand, and the reaction could be followed quantitatively by determining the residual ferrous iron in the mixture. The reaction was studied at room temperature at an oxygen pressure slightly greater than atmospheric using as variables the calcium hydroxide–ferrous sulfate heptahydrate ratio, agitation of the reaction mixture, particle size of ferrous sulfate, excess of reactants, and presence of calcium chloride.

Reagents.—Mallinckrodt ferrous sulfate granulated Analytical Reagent, Baker and Adamson Quality Calcium Hydroxide Powder (Lot No. Fa70) and C.P. Baker Analyzed anhydrous calcium chloride powder (12 mesh and finer) were employed as reagents. The ferrous sulfate and calcium chloride were ground and screened with Tyler's Standard Screens to obtain size fractionation. This operation was performed using a Ro-Tap Testing Sieve Shaker. The amount of sieved calcium chloride to be used in a given run was weighed approximately. It then was dried by heating at 325° for 12 hours and stored in a desiccator.[4,5] The preliminary weighing minimized handling of the dried material and its exposure to atmospheric moisture.

Apparatus and Experimental Technique.—Figure 1 is a diagram of the apparatus. A 250-ml. filtering flask (dried in an oven at 110°) was used as reaction vessel A. This flask was clamped to a high-frequency vibrator B used to obtain a thorough and uniform mixing of the reactants. The oxygen from a gas cylinder was admitted at C and on passing through the system was dried by magnesium perchlorate contained in towers D and E, and in drying tube F before entering the reaction vessel. The oxygen outlet was protected from atmospheric moisture by its immersion in dibutyl *o*-phthalate contained in graduated cylinder G. The reservoir H permitted an even distribution of the oxygen among six outlets at position I (only one is illustrated). Each outlet was supplied with a stopcock so that any number of samples up to a maximum of six could be oxidized at the same time. In case of simultaneous runs, regulation of the pinchcock attached to each outlet at position J permitted equalization of the oxygen pressure in the reaction vessels. This was shown by similar rates of bubbling through equal heights of the organic liquid.

The weighed reactants were added one at a time to the reaction vessel. A rapid stream of oxygen was passed through the system until the last reactant was added. This procedure assured the removal of any moisture in the system as well as a quick displacement of the air by the oxygen shortly after stoppering the flask.

If the mixture to be oxidized consisted of three substances, the vibrator was turned on for five minutes after the addition of the second reactant in order to obtain good mixing. In all cases the ferrous sulfate was added last. As soon as it was added the mixture was shaken for a certain time, the time depending on the particular mixture. Also, at this time the oxygen pressure was decreased by regulating the valve on the tank until it was only slightly higher than atmospheric pressure, so that no bubbling occurred. In this manner any water expelled from the hydrated salt remained in the system and was not removed as would have been the case had the stream of dry oxygen been continued. The level of the liquid within the outlet tube was kept constant during the oxidation in order to maintain the same oxygen pressure during the process. This was done by adjusting the valve on the tank since any change in the adjustment of the pinchcocks would result in different oxygen pressures in the reaction vessels with the possibility of reducing it greatly in any one vessel. At the end of the oxidation treatment of one sample, the reaction vessel could be removed from the apparatus after closing the stopcock on the particular line without disturbing the oxidation being carried out in other reaction vessels.

Analytical Procedures.—The course of the oxidation of solid ferrous sulfate heptahydrate with oxygen was followed by determining quantitatively the residual ferrous iron in the reaction mixture. The mixtures were warmed gently with an excess of standard 0.5 *N* potassium dichromate solution which was 3.4 *N* in hydrochloric acid. The excess dichromate was titrated electrometrically with standard ferrous sulfate using a Serfass Electron Ray Titration Assembly with polarized platinum electrodes. It was shown that no oxidation occurred in the air during the dissolving of the samples and that substitution of sulfuric acid for hydrochloric acid did not affect the results. The latter acid was used, however, because the mixtures dissolved more readily in it.

Approximately 700 samples were analyzed during the

---

[1] J. Cornog and A. Hershberger, *Proc. Iowa Acad. Sci.*, **36**, 264 (1929).

[2] O. Lievin and J. Herman, *Comp. rend.*, **200**, 1474 (1935).

[3] J. Herman, *ibid.*, **202**, 419 (1936).

[4] W. D. Cooke, Ph.D. Thesis University of Pennsylvania, Philadelphia, 1949.

[5] J. F. Hazel, W. M. McNabb and W. D. Cooke, THIS JOURNAL, **75**, 1552 (1953).