methyl signals from the 2,4-pentanedione residues occur at 1.78 and 1.90 ppm downfield from TMS as an internal standard and at 1.83 and 2.22 ppm downfield, respectively. From a comparison of these spectra with the pmr spectrum of Ni(sacsac)(sacac)[10] and a consideration of the bond anisotropies of the C=N and C=O linkages, we have tentatively assigned the methyl signal at lower field to the group adjacent to the C=O bond. The proton (2), structures I and II, occurs at about 5 ppm downfield from TMS as a consequence of the deshielding effect of the pseudoaromatic chelate ring.

The spectra of the two compounds containing the 2-mercaptoethylamine residue show only very diffuse signals (if any) for the ABCD protons of the ethylene moiety. The proposed structure, like that of di-μ-(bis-(2-mercaptoethyl) sulfide)-dinickel(II),[11] possesses a C_2 axis as its only element of symmetry. The molecule is therefore optically active, with the enantiomers related by inversion of the dihedral angle about an axis joining the bridging sulfur atoms. For a stable optical isomer, a complex ABCD pattern should appear in the vicinity of the observed methyl signals of the 2,4-pentanedione residue. We have made no attempt to assign the signals observed in this region, but we note significant and reversible enhancement of the intensities (relative to the methyl signals) as temperature is lowered from 30 to −60°. This observation is consistent with a decreased rate of intramolecular racemization at lower temperatures.

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[10] C. G. Barraclough, R. L. Martin, and I. M. Stewart, *Aust. J. Chem.*, **22**, 891 (1969).

[11] D. J. Baker, D. C. Goodall, and D. S. Moss, *Chem. Commun.*, 325 (1969).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
RUTGERS, THE STATE UNIVERSITY,
NEW BRUNSWICK, NEW JERSEY 08903

The Pyrolysis of Pentaborane(9)

BY A. C. BOND* AND G. HAIRSTON

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Although the pyrolysis of diborane has been studied extensively, very few data are available on the pyrolysis of other boron hydrides. Pentaborane(9) is known to be thermally stable up to 200° but to undergo considerable decomposition at 250° to give hydrogen and nonvolatile solids.[1] A short study by Houser and Greenough[2] of the pyrolysis of pentaborane(9) in a flow system at 590–645°K concluded that the decomposition was first order. A study was made by Cheney, *et al.*,[3] at 100–300 mm pressure and a temperature range of 194–243° by measuring initial rates of pressure increase. They also found the reaction to be first order. Hydrogen and nonvolatile solids were the only products found in both of these studies. The work reported here is a study of the pyrolysis of pentaborane(9) at 40–80 mm pressure and 202–228° in which pentaborane(9) was heated in sealed glass bulbs and gaseous products were analyzed in a vacuum line.

Experimental Section

Pentaborane(9) was prepared by introducing 440 mm of diborane and 100 mm of dimethyl ether into a reaction vessel to which a water condenser had been sealed at the top. The vessel was heated to 150° for 20 min.[4] The products were fractionated and pure pentaborane(9) was isolated. The 0° vapor pressure was 66 mm (lit.[5] 66 mm) and a fractionation–codistillation chromatograph[6] showed only one peak.

Using standard high-vacuum techniques, samples of pentaborane(9) were measured and condensed into 40-ml Pyrex glass bulbs which had been previously exposed to diborane at 0.5 atm pressure for at least 24 hr at room temperature to season the walls. The bulbs were then sealed off under vacuum and placed in a temperature bath of glycerin covered with General Electric SF-1017 silicone fluid to reduce evaporation. The bath was heated by a thermostated, stirring hot plate, which held the temperature of the bath constant to within ±1.0° during the time that the data were taken. A bulb was removed from the bath every 10 or 15 hr, cooled to room temperature, and then opened into vacuum with a tube breaker.[7] The hydrogen was transferred by a Toepler pump into a standard volume and measured. The gas which condensed at −196°, which was shown to be pure pentaborane(9) by fractionation–codistillation chromatography, was then measured.

Results and Discussion

Kinetics.—The pyrolysis of pentaborane(9) was studied at 202, 213.5, and 228° at a pressure of about 40 mm and at 204° at a pressure of about 80 mm. The reaction was found to be first order and rate constants are $1.68 \pm 0.03 \times 10^{-6}$, $1.79 \pm 0.05 \times 10^{-6}$, $2.62 \pm 0.2 \times 10^{-6}$, and $8.23 \pm 0.1 \times 10^{-6}$ sec^{-1} at 202, 204, 213.5, and 228°, respectively. The activation energy is 31.1 ± 1.5 kcal/mol. These results agree relatively well with the values reported by Cheney, *et al.*[3] They obtained first-order rate constants of 0.376×10^{-2}, 1.73×10^{-2}, 4.18×10^{-2}, and 11.6×10^{-2} hr^{-1} at 194.5, 216, 228.5, and 243°, respectively, and an activation energy of 33.9 ± 1 kcal/mol. Converting the rate constants to common units gives rate constants of 4.8×10^{-6} and 1.16×10^{-5} sec^{-1} at 216 and 228.5°, respectively, which are approximately 20% larger than the rate constants reported in this paper. The rate expression $k = 10^{8.1} \exp((-25{,}000 \pm 2000)/RT)$ sec^{-1} obtained by Houser and Greenough[2] is inconsistent with both this study and the study by Cheney, *et al.*, and

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* To whom correspondence should be addressed.

[1] I. Shapiro and B. Keilin, *J. Amer. Chem. Soc.*, **73**, 2663 (1955).

[2] T. J. Houser and R. C. Greenough, *Chem. Ind.* (*London*), 323 (1967).

[3] S. H. Cheney, Jr., G. M. Kibler, and R. C. Williamson, "Summary Report No. 4 on Combustion, Decomposition, and Thermal Decomposition Studies," General Electric Co., June 30, 1955. This document can be obtained as No. AD-142624 from the Defense Documentation Center for Scientific and Technical Information, Cameron Station, Alexandria, Va.

[4] W. DeAcetis and S. J. Trotz, U. S. Patent 2,983,581 (May 9, 1961); *Chem. Abstr.*, **56**, 2134*e* (1962).

[5] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p 207.

[6] G. H. Cady and D. P. Siegworth, *Anal. Chem.*, **31**, 618 (1959).

[7] Reference 5, p 180.

with the fact that pentaborane(9) is thermally stable up to 200°. It may have included heterogeneous reactions, since they made no mention of seasoning the reaction chamber. To determine whether heterogeneous reactions took place in this study, additional pyrolyses were done using vessels packed with Pyrex glass tubing, which increased the surface to volume ratio by a factor of 10. Pyrolyses were done in these vessels as previously described and no increase in decomposition rate was observed.

Hydrogen Evolution.—In the previously mentioned pyrolyses at 202, 204, 213.5, and 228° and in another pyrolysis in which the temperature varied between 228 and 235°, the hydrogen evolution was measured. A 2.9-mol amount of hydrogen was evolved for each mole of pentaborane(9) decomposed in all pyrolyses, in spite of variations in reaction temperature, reaction time, and amount of decomposition. The overall pyrolysis reaction is

$$B_5H_9 \longrightarrow 5BH_{0.6}(s) + 3H_2 \qquad (1)$$

No attempt was made to analyze this reddish orange $BH_{0.6}$ solid because of the extremely small amount produced. In the study by Cheney, *et al.*,[3] the reaction is described by the equation

$$B_5H_9 \longrightarrow 2H_2 + 5(BH)_x \qquad (2)$$

However, this value was obtained by studying the volatile contents of the reaction vessel after pyrolysis by infrared absorption techniques. Hydrogen was not analyzed for but was computed by difference.

When Stock and Pohland[8] heated decaborane(14) to 250° for 24 hr, they found as products only hydrogen and a nonvolatile solid of composition $BH_{0.6}$. Beachell and Haugh[9] observed the same overall stoichiometry for the pyrolysis of decaborane(14). Unlike the pentaborane(9) pyrolysis, the pyrolysis of decaborane(14) initially yields less than 1 mol of hydrogen per mole of decaborane(14) decomposed. This produces a relatively hydrogen-rich solid, which then yields more hydrogen until the composition of the solid becomes $BH_{0.6}$.[9,10] In the early part of the pyrolysis of decaborane(14), Beachell and Haugh[9] found the molecular weight of the decomposition product to be 375 and observed some whitish materials that were slightly volatile and could be sublimed with gentle warming. Owen[10] isolated a small quantity of viscous liquid by vacuum distillation, which he said could be $B_{20}H_{24}$.

This low molecular weight, hydrogen-rich solid gives off hydrogen at 230° at a rate similar to the rate of decomposition of decaborane(14) at 230°.[10] The first-order rate constant for the pyrolysis of decaborane(14) is 1.62×10^{-2} min^{-1} at 230°[9] which is 30 times the first-order rate constant for the pyrolysis of pentaborane(9) at this temperature. If the initial step in the pyrolysis of pentaborane(9) produced less than 3 mol of hydrogen per mole of pentaborane(9) decomposed and similar low molecular weight, hydrogen-rich solids, these solids would give off hydrogen at a rate 30 times more rapid than they were being produced until the composition reached $(BH_{0.6})_x$ and the stoichiometry of the reaction would be unaffected by their existence.

In an attempt to isolate any volatile molecular decomposition product, another pyrolysis was done in reaction vessels which had a cold finger (similar in design to a sublimater). About 40 mm of pentaborane(9) was introduced into the vessels and the exterior walls of the vessels were heated to 210° in the glycerine bath as previously described while cold tap water was circulated through the cold finger. After 40 hr of heating, there was nonvolatile solid on the exterior walls but no solid on the cold finger. Analysis of the volatile products showed the relative amount of hydrogen evoltuion to be unchanged from the pyrolysis without the cold finger. This indicates that unlike the decaborane(14) pyrolysis there is no volatile, molecular, intermediate decomposition product in the pyrolysis of pentaborane(9). Whether or not there exists a nonvolatile solid richer in hydrogen than $(BH_{0.6})_x$ in the pyrolysis of pentaborane(9) is open to speculation. It should be noted that the $(BH_{0.6})_x$ solid from the pyrolysis of pentaborane(9) or decaborane(14) has different composition than another boron hydride polymeric solid, which is stable in this temperature range (200–230°). Shapiro and Williams[11] prepared $(BH)_x$ solid by copyrolysis of decaborane(14) and diborane at 100°. They observed that this solid gives up slightly more than half of its hydrogen on heating to 200–230° resulting in a solid with the formula $(BH_{0.45})_x$.

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[8] A. Stock and E. Pohland, *Ber. Deut. Chem. Ges. B*, **62**, 90 (1929).

[9] H. C. Beachell and J. F. Haugh, *J. Amer. Chem. Soc.*, **80**, 2939 (1958).

[10] A. J. Owen, *J. Chem. Soc.*, 5438 (1961).

[11] I. Shapiro and R. F. Williams, *J. Amer. Chem. Soc.*, **81**, 4787 (1959).

CONTRIBUTION FROM THE
DEPARTMENT OF INORGANIC CHEMISTRY,
UNIVERSITY OF MELBOURNE, PARKVILLE, 3052, AUSTRALIA

A Carbonyl Fluoride of Molybdenum

BY T. A. O'DONNELL* AND K. A. PHILLIPS

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Molecular carbonyl halides of transition metals in which the halogen is chlorine, bromine, or iodine are well known. The formal oxidation states of the metals are usually I or II and only rarely III.[1] Some extremely reactive substances which may be carbonyl fluorides of transition metals have been reported[2,3] but they have not been characterized.

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* To whom correspondence should be addressed.

[1] J. Chatt, P. L. Pauson, and L. M. Venanzi in "Organometallic Chemistry," ACS Monograph No. 147, H. H. Zeiss, Ed., Reinhold, New York, N. Y., 1960, pp 509–513.

[2] N. Bartlett in "Preparative Inorganic Reactions," Vol. 2, W. L. Jolly, Ed., Interscience, New York, N. Y., 1965, pp 334, 337.

[3] R. D. W. Kemmitt, R. D. Peacock, and I. L. Wilson, *Chem. Commun.*, 772 (1968).