Results and Discussion

Vibrational Spectra of Oxotetrakis(fluorosulfato)tungsten(VI).—To obtain the Raman spectrum of the compound, a sample was prepared in a tube (12-mm o.d.) and sealed. A Spex 1401 double spectrometer equipped with a Model 52 argon–krypton ion laser was used. The prominent vibrational peaks are tabulated in Table I. Satisfactory infrared spectra were not obtained, because of the reaction of $WO(SO_3F)_4$ with the cell windows or the mulling agents.

TABLE I
VIBRATIONAL SPECTRA OF
OXOTETRAKIS(FLUOROSULFATO)TUNGSTEN(VI)

Bands, cm^{-1}	Assignment (tentative)	Bands, cm^{-1}	Assignment (tentative)
1464	SO_2 asym str	644	SO_3 sym str
1416			
		552	SO_2 bend (bridging SO_3F)
1240	SO_2 sym str		
1163	SO_2 asym str (bridging SO_3F)	455	S—F wag
1044		421	S—F def
964	W=O str		
944		280	W—O str
		273	
873	S—F str	214	
853			
826		184	W—O bend modes
801		154	
707	SO_3 asym bend (bridging SO_3F)	141	
700			

The viscous nature of the compound and the large number of Raman bands, all of which were polarized, indicated the polymeric nature of the compound. Polymerization can be thought to occur *via* bridging fluorosulfate groups, as shown in Figure 1.

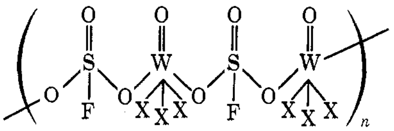

Figure 1.—Structure of oxotetrakis(fluorosulfato)tungsten(VI) (X = OSO_2F).

The SO_3F^- ion has C_{3v} symmetry. Covalent unidentate and bidentate fluorosulfate groups are both expected to have C_s symmetry.[8] For the fluorosulfate ion,[9] the symmetric SO_2 stretching mode is found at 1080 cm^{-1}, and the doubly degenerate antisymmetric stretching mode, at 1290 cm^{-1}. The vibrational frequencies given in Table I rule out the possibility of the SO_3F^- ion. The SF stretching frequencies around 800–873 cm^{-1} may be due to the fluorosulfate groups in different environments. The W=O stretching frequency has been reported at ~960 cm^{-1} in some of the complexes of tungsten oxyhalides with phosphine oxide.[10] We therefore, assign the vibrational band around 944 and 964 cm^{-1} to be due to W=O stretching motion.

^{19}F Nmr Spectrum of Oxotetrakis(fluorosulfato)tungsten(VI).—The polymeric structure *via* bridging fluorosulfate groups is further supported by the ^{19}F nmr spectrum of the compound. A sample of $WO(SO_3F)_4$ was prepared in an nmr tube having a capillary containing CCl_3F. The compound was dissolved in $S_2O_6F_2$. Its spectra at room temperature and at −45° were much alike. In a polymeric chain (Figure 1), the bridging fluorosulfate groups may either be cis or trans to each other, as has been argued for the compound $SbF_4(SO_3F)$.[11] A peak observed at a chemical shift −42.4 ppm with respect to CCl_3F may be attributed to the terminal fluorosulfate groups, while the peaks at chemical shifts −41.9, −41.6, and −41.1 ppm with respect to CCl_3F may be attributed to the bridging fluorosulfate groups, which can be in different environments, *i.e.*, cis–cis, trans–trans, or cis–trans with respect to the neighboring fluorosulfate groups. It is also possible that cyclic polymers may exist.

Acknowledgment.—This work was performed in part under contract with the office of Naval Research. The authors thank Dr. J. W. Macklin and Mr. B. J. Nist for taking the Raman and ^{19}F nmr spectra, respectively.

---

[8] P. A. Yeats, B. L. Poh, B. F. E. Ford, J. R. Sams, and F. Aubke, *J. Chem. Soc.*, 2188 (1970).

[9] J. Goubeau and B. J. Milne, *Can. J. Chem.*, **45**, 2321 (1967).

[10] J. Lewis and R. Whyman, *J. Chem. Soc.*, 6027 (1965).

[11] R. J. Gillespie and R. A. Rothenbury, *Can. J. Chem.*, **42**, 416 (1964).

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY, THE OHIO STATE
UNIVERSITY, COLUMBUS, OHIO 43210

Tetra-*n*-butylammonium Salts of $B_5H_8^-$ and $B_6H_9^-$ and Decomposition Products of the Anions

BY V. T. BRICE, H. D. JOHNSON, II, D. L. DENTON,
AND S. G. SHORE*

Received July 12, 1971

The deprotonation of pentaborane(9)[1-3] and hexaborane(10)[3,4] has been established and the physical properties and thermal stabilities of the alkali metal salts have been reported.[3] In our studies of the $B_5H_8^-$ and $B_6H_9^-$ anions, we have found that the tetra-*n*-butylammonium salts are thermally more stable than their alkali metal counterparts. Furthermore they are readily soluble in nonbasic solvents such as methylene chloride, while the alkali metal salts are insoluble. In view of the possible advantages afforded by tetra-*n*-butylammonium salts, we report herein metathesis reactions for the preparation of $(n\text{-}C_4H_9)_4NB_5H_8$ and $(n\text{-}C_4H_9)_4NB_6H_9$ and the thermal decomposition products of these anions. We also wish to report that the previously claimed $(CH_3)_4N$-*i*-B_5H_8[2,3] was in fact a mixture of decomposition products of $(CH_3)_4NB_5H_8$.

Results and Discussion

Metathesis Reactions.—Tetra-*n*-butylammonium salts of $B_5H_8^-$ and $B_6H_9^-$ were prepared by means of

---

[1] D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, **89**, 3375 (1967).

[2] R. A. Geanangel and S. G. Shore, *ibid.*, **89**, 6771 (1967).

[3] H. D. Johnson, II, R. A. Geanangel, and S. G. Shore, *Inorg. Chem.*, **9**, 908 (1970).

[4] H. D. Johnson, II, S. G. Shore, N. L. Mock, and J. C. Carter, *J. Amer. Chem. Soc.*, **91**, 2131 (1969).

the following metathesis reactions in which KI precipitated from solution and the borate salt was isolated from the filtrate

$$(n\text{-}C_4H_9)_4NI + KB_5H_8 \xrightarrow[-22.5°]{CH_2Cl_2\text{-}THF} KI + (n\text{-}C_4H_9)_4NB_5H_8 \quad (1)$$

$$(n\text{-}C_4H_9)_4NI + KB_6H_9 \xrightarrow[-22.5°]{CH_2Cl_2\text{-}THF} KI + (n\text{-}C_4H_9)_4NB_6H_9 \quad (2)$$

A similar metathesis procedure has been used to prepare $(n\text{-}C_4H_9)_4NB_6H_9$ from $NH_4B_6H_9$;[5] however, for quantities of $(n\text{-}C_4H_9)_4NB_6H_9$ larger than 2 or 3 mmol, reaction 2 represents the preferred procedure.

The ^{11}B nmr spectrum of $(n\text{-}C_4H_9)_4NB_5H_8$ at low temperature (0 to $-50°$) consists of doublets at 16.3 ppm (J = 135 Hz) and 52.6 ppm (J = 152 Hz) and for $(n\text{-}C_4H_9)_4NB_6H_9$ the ^{11}B nmr spectrum (0 to $-30°$) consists of doublets at -10.0 ppm (J = 120 Hz) and 49.0 ppm (J = 140 Hz). (Chemical shifts are with respect to $BF_3 \cdot Et_2O$.) These values are slightly lower than those reported for the alkali metal salts in THF.[3] The boron-11 nmr spectra of tetra-*n*-butylammonium salts show the same general temperature dependence as reported for the alkali metal $B_5H_8^-$ and $B_6H_9^-$ salts.[3] That is, with decreasing temperature there is a loss of resolution and broadening of the basal peaks while apical peaks sharpen. Sharpening of apical peaks of pyramidal boranes has been suggested by Onak and Leach[6] as being due to loss of coupling between the apical and basal borons due to more effective and rapid nuclear quadrupolar relaxation of the basal borons.

Properties of the Solid Salts.—The tetra-*n*-butylammonium salts of $B_5H_8^-$ and $B_6H_9^-$ are fine white crystalline materials which are soluble not only in tetrahydrofuran and 1,2-dimethoxyethane as are the alkali metal salts[3] but also in methyl chloride, methylene chloride, and chloroform. They precipitate from these solvents upon addition of diethyl ether or pentane. In the solid state these salts are appreciably more thermally stable at room temperature than the potassium salts and could be "fingerprinted" by means of infrared spectroscopy and X-ray powder patterns.

The first sign of decomposition of $(n\text{-}C_4H_9)_4NB_5H_8$ appears in the infrared spectrum 8 hr after isolation of the compound at room temperature; a shoulder appears near the original B-H terminal stretch. Even 24 hr later the very weak absorption at 1780 cm^{-1}, tentatively assigned to the bridge hydrogen stretching motion, is still in evidence whereas, for KB_5H_8, decomposition becomes evident from its infrared spectrum within 15 min after warming the isolated solid to room temperature.[3] X-Ray powder pattern data suggest essentially total decomposition of KB_5H_8 within 24 hr. On the other hand, infrared and X-ray powder pattern data of $(n\text{-}C_4H_9)_4NB_5H_8$ still show evidence of the presence of some of the tetra-*n*-butylammonium salt after a period of 4 days.

There is no change in the infrared spectrum of $(n\text{-}C_4H_9)_4NB_6H_9$ (Nujol mull) over a period of 5 days at room temperature while KB_6H_9 is extensively decomposed after this period under the same conditions.

The primary decomposition products of the solid salts are the same as those of the salts in solution and are discussed below in the section on thermal decomposition in solution.

Treatment of solid $(n\text{-}C_4H_9)_4NB_5H_8$ with liquid HCl produced the parent hydride B_5H_9 in 96% yield. On the other hand attempts to regenerate B_6H_{10} from solid $(n\text{-}C_4H_9)_4NB_6H_9$ with liquid HCl did not yield B_6H_{10} quantitatively. The volatile product contained approximately half of the boron in the system and consisted of about 75 mol % B_5H_9 and 25 mol % B_6H_{10}. The remaining solid was not characterized. Essentially the same results were obtained in $(CH_3)_2O$. The yield of B_6H_{10} obtained was significantly lower than from the reaction of HCl with KB_6H_9 in $(CH_3)_2O$.[3]

Thermal Decomposition in Solution.—Monitoring the ^{11}B nmr spectrum of KB_5H_8 in THF and $(n\text{-}C_4H_9)_4NB_5H_8$ in CH_2Cl_2 showed that decomposition begins at about 20°. On the average, samples were completely decomposed in 30 hr at room temperature. When B_5H_9 is present in the solution (5 mol %), decomposition is accelerated and becomes evident at $-10°$. Analogous salts of $B_6H_9^-$ are significantly more stable. Only slight decomposition is evident after 24 hr at ambient temperature and decomposition is not complete even after 5 days.

The primary decomposition products of KB_5H_8 and $(n\text{-}C_4H_9)_4NB_5H_8$ in solution are BH_4^-, $B_3H_8^-$, and $B_9H_{14}^-$. In the case of the THF solution of KB_5H_8, tetrahydroborate(1−) precipitated as the potassium salt and was identified by X-ray powder pattern and infrared spectra. The $B_9H_{14}^-$ anion was also isolated as the tetramethylammonium salt. An authentic sample of $(CH_3)_4NB_9H_{14}$ was prepared.[7] Its ^{11}B nmr spectrum was in agreement with that reported for CsB_9H_{14}[8] and also with that of the material isolated from the decomposition products. The X-ray powder pattern and infrared spectrum of the authentic sample of $(CH_3)_4NB_9H_{14}$ were identical with those of $(CH_3)_4NB_9H_{14}$ which was isolated from the decomposition product. The previously reported $i\text{-}B_5H_8^-$ [2,3] was found to be a mixture of $B_3H_8^-$ and $B_9H_{14}^-$. A doublet at -10.3 ppm (J = 130 Hz) and one arm of a doublet or triplet at 36.7 ppm (the other being hidden by the absorption due to $B_3H_8^-$) cannot be assigned to any known species at the present time.

The decomposition of $B_6H_9^-$ in solution yields primarily $B_{11}H_{14}^-$, identified by ^{11}B nmr spectra and X-ray powder pattern, and BH_4^-, identified by its infrared spectrum and X-ray powder pattern.

It is of interest to note that the decomposition products of $B_5H_8^-$ observed in this investigation are in accord with products reported from the reaction of B_5H_9 with BH_4^- in a recent investigation.[9] It was suggested[9] that the reaction between B_5H_9 and BH_4^- is essentially different from that involving B_5H_9 and H^- since no $B_5H_8^-$ was observed in the reaction with BH_4^-. On the other hand it is possible that the following sequence occurred

$$B_5H_9 + BH_4^- \longrightarrow H_2 + B_5H_8^- + BH_3 \longrightarrow B_6H_{11}^- + H_2$$

since the existence of $B_6H_{11}^-$ is now established.[10] However, under the conditions reported for the ^{11}B nmr spec-

---

[5] G. L. Brubaker, M. L. Denniston, S. G. Shore, J. C. Carter and F. Swicker, *J. Amer. Chem. Soc.*, **92**, 7216 (1970).

[6] J. B. Leach and T. Onak, *J. Magn. Res.*, **4**, 30 (1971).

[7] L. E. Benjamin, S. F. Stafiej, and E. A. Takacs, *J. Amer. Chem. Soc.*, **85**, 2674 (1963).

[8] N. N. Greenwood, H. J. Gysling, J. A. McGinnety, and J. D. Owen, *Chem. Commun.*, 505 (1970).

[9] C. G. Savory and M. G. H. Wallbridge, *Inorg. Chem.*, **10**, 419 (1971).

[10] H. D. Johnson, and S. G. Shore, *J. Amer. Chem. Soc.*, **92**, 3789 (1971).

tra (0 and 25°)[9] $B_6H_{11}^-$ would go undetected, since we have found that it decomposes above $-15°$ to form similar decomposition products as $B_5H_8^-$.

Experimental Section

A conventional vacuum line system was used in handling air-sensitive materials. Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer. X-Ray powder patterns were obtained using a Debye–Scherrer camera and Cu Kα radiation. Boron-11 nmr spectra were obtained on a Varian Associates HA-100 spectrometer with a 32.1-MHz probe.

Materials.—Potassium hydride was obtained from ROC/RIC as a 50% suspension in mineral oil. The mineral oil was removed by washing with pentane. Pentaborane(9) was obtained from Callery Chemical Co. Hexaborane(10) was prepared according to the literature.[11] Tetra-*n*-butylammonium iodide was obtained from Matheson Coleman and Bell.

Preparation of $(n\text{-}C_4H_9)_4B_5H_8$ and $(n\text{-}C_4H_9)_4B_6H_9$.—In a standard drybox 2.00 mmol (0.738 g) of $(n\text{-}C_4H_9)_4NI$ and 2.00 mmol (0.08 g) of KH were weighed in a reaction vessel containing a Teflon-covered magnetic stir bar. The vessel was attached to the vacuum line and approximately 3 ml of dry THF was condensed in and KB_5H_8 or KB_6H_9 was prepared as described elsewhere.[3] The reaction mixture was frozen and 6 ml of methylene chloride was condensed in. The mixture was stirred and allowed to warm to $-22.5°$ at which temperature it was kept for 30 min. Diethyl ether was added to precipitate the salt. The mixture was frozen and transferred under nitrogen to an extractor and filtered at $-78°$. Under nitrogen a new vessel was placed under the extractor and the precipitate was washed with CH_2Cl_2 dissolving the borate salt. The product on the frit was identified by its X-ray powder pattern as KI. A portion of the solution was tipped into an nmr tube side arm attached to the vessel, which was sealed and removed. The remainder of the compound was precipitated with ether and filtered. The infrared spectrum of $(n\text{-}C_4H_9)_4NB_5H_8$ showed an absorption in the B–H terminal region at 2500 cm^{-1} and a very weak, very broad peak in the B–H–B stretching region centered at 1780 cm^{-1}.

Analyses.—Boron and hydrolyzable hydrogen analyses for $(n\text{-}C_4H_9)_4NB_5H_8$ and $(n\text{-}C_4H_9)_4NB_6H_9$ were carried out by acid hydrolysis. *Anal.* Calcd for $(n\text{-}C_4H_9)_4NB_5H_8$: B, 17.76%; H, 12.00 mol/mol of sample. Found: B, 17.14%; H, 11.64 mol/mol of sample. Calcd for $(n\text{-}C_4H_9)_4NB_6H_9$: B, 20.49%; H, 14.00 mol/mol of sample. Found: B, 20.37%; H, 13.37 mol/mol of sample.

X-Ray Powder Patterns.—$(n\text{-}C_4H_9)_4NB_5H_8$: d (Å) = 10.8 (s), 8.63 (m), 7.46 (m), 6.71 (m), 5.38 (m), 5.01 (w), 4.75 (m), 4.47 (w), 4.29 (s), 4.15 (w), 3.78 (w). $(n\text{-}C_4H_9)_4NB_6H_9$: d (Å) = 10.0 (m), 9.12 (m), 8.22 (m), 7.70 (m), 7.16 (m), 6.79 (s), 6.19 (w), 5.82 (vw), 5.31 (m), 4.77 (s), 4.53 (s), 4.29 (m), 4.05 (m), 3.79 (m), 3.49 (w), 3.39 (w).

Regeneration of B_5H_9 and B_6H_{10}.—Into a test tube type vessel was placed 0.154 g (0.505 mmol) of $(n\text{-}C_4H_9)_4NB_5H_8$. Approximately 1 ml of liquid HCl was condensed in at $-196°$. The vessel was warmed to $-111°$ and the solution was stirred for 45 min. The mixture was fractionated and 0.485 mmol (96%) of B_5H_9 was recovered.

Reaction of $(n\text{-}C_4H_9)_4NB_6H_9$ with liquid HCl was carried out using a similar procedure. Regeneration of B_6H_{10} was also attempted in $(CH_3)_2O$. In a vessel 0.321 g (1.52 mmol) of $(n\text{-}C_4H_9)_4NB_6H_9$ was weighed. About 3 ml of dimethyl ether and 1.55 mmol of HCl passed through P_2O_5 were condensed in at $-196°$. The vessel was warmed to $-78°$ and stirred overnight. Fractionation of the volatiles yielded B_5H_9 and B_6H_{10} in both procedures. B_5H_9 and B_6H_{10} were condensed in on excess KH in $(CH_3)_2O$ at $-78°$. The H_2 evolved was collected and measured as 0.785 mmol representing 52% of the original $B_6H_9^-$. The solid residue in the vessel was dissolved in CH_2Cl_2 and the ^{11}B nmr showed the presence of $B_6H_9^-$ and $B_5H_8^-$.

Decomposition of $B_5H_8^-$ and $B_6H_9^-$.—A solution of KB_5H_8[3,4] in tetrahydrofuran (*ca.* 0.5 *M*) was stirred at room temperature for 2 days. The solution was filtered and the solid on the frit was identified as BH_4^- by its infrared spectrum and X-ray powder pattern. As much tetrahydrofuran as possible was removed under vacuum. The vessel was removed from the vacuum line and a solution containing excess $(CH_3)_4NCl$ in water was added to the gummy residue. The solution was stirred and filtered. The solid isolated was identified as $(CH_3)_4NB_9H_{14}$ by its ^{11}B nmr spectrum[8] and comparison of its infrared spectrum and X-ray powder pattern with those of an authentic sample. The yield of $(CH_3)_4NB_9H_{14}$ ranged from 0.15 to 0.20 mmol/mmol of KB_5H_8. The X-ray powder pattern of $(CH_3)_4NB_9H_{14}$ has the following d (Å) values: 7.18 (vw), 6.03 (w), 5.04 (vs), 4.12 (vw), 4.00 (vw), 3.56 (w), 3.19 (m). Concentration of the solution yielded another precipitate which was identified as $B_3H_8^-$ by its infrared spectrum and ^{11}B nmr spectrum.

Solutions of KB_6H_9 in tetrahydrofuran (*ca.* 1 *M*) were allowed to stir at room temperature for 2 weeks. Filtration of the solution and identification of the solid product by its infrared spectrum and X-ray powder pattern showed KBH_4. The boron-11 nmr spectrum of the resulting solution showed a doublet at 16.2 ppm (J = 138 Hz) which compares favorably with the literature value for $B_{11}H_{14}$.[12,13] Addition of dioxane to the solution precipitated a solid which exhibited the same infrared spectrum and X-ray powder pattern as an authentic sample of $KB_{11}H_{14}$ prepared in dioxane by the method previously reported for $B_{11}H_{14}^-$ salts.[12] The X-ray powder pattern of $KB_{11}H_{14}$ which has not been previously reported contains the following d (Å) values: 8.39 (m), 6.37 (m), 5.56 (m), 5.07 (s), 4.32 (m), 4.20 (s), 3.58 (m), 3.10 (vw), 2.98 (w), 2.80 (m), 2.70 (w), 2.56 (m), 2.49 (w), 2.41 (w), 2.36 (w).

Solutions of the tetrabutylammonium salts of these boranes in methylene chloride were monitored by ^{11}B nmr. The $B_5H_8^-$ salt was completely decomposed in 30 hr. The $B_6H_9^-$ species was completely decomposed after 2 weeks. The ^{11}B nmr spectra of the decomposition products of these salts appeared identical with those of their potassium counterparts.

Acknowledgments.—We wish to thank the National Science Foundation for its financial support. V. T. B. also wishes to thank the Stauffer Chemical Co. for financial support.

---

[11] R. A. Geanangel, H. D. Johnson, II, and S. G. Shore, *Inorg. Chem.*, **10**, 2363 (1971).

[12] V. D. Aftandilian, H. C. Miller, G. W. Parschall, and E. L. Muetterties, *Inorg. Chem.*, **1**, 734 (1962).

[13] R. Schaeffer and F. Tebbe, *ibid.*, **3**, 1638 (1964).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE FLORIDA STATE UNIVERSITY,
TALLAHASSEE, FLORIDA 32306

Preparation of *B*-Tris(cyclopentadienyl)-*N*-trimethylborazines and *B*-Tris(methylcyclopentadienyl)-*N*-trimethylborazines

BY BRADFORD L. THERRELL, JR., AND EDWARD K. MELLON*

Received July 15, 1971

Two reports have previously appeared concerning cyclopentadienyl reactions with borazines.[1,2] In view of their brevity, it was of interest to investigate the reactions of certain cyclopentadienides and methylcyclopentadienides with both *B*-trichloro-*N*-trimethylborazine and *B*-trichloroborazine in order to develop a preparative technique for obtaining cyclopentadienyl-substituted borazines. We were able to prepare methylcyclopentadienyl and cyclopentadienyl derivatives of *B*-trichloro-*N*-trimethylborazine while we were unsuccessful in similar attempts with *B*-trichloroborazine.

Experimental Section

General Information.—All preparations involved standard drybox and high-vacuum procedures with particular care being

---

[1] V. Gutmann, A. Meller, and E. Schaschel, *J. Organometal. Chem.*, **2**, 287 (1964).

[2] G. H. Dahl, Ph.D. Dissertation, Iowa State University, 1960.