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estimated visually. The results show good agreement between the observed and calculated $\sin^2 \theta$ values indicating the hexagonal system of the crystals of the complexes.

The densities by C_6H_6 displacement of the zirconyl and the thorium complexes were found to be 1.428 g/ml and 2.124 g/ml respectively, while the corresponding calculated values from the X-ray data were 1.448 and 2.104 g/ml. The number of molecules of zirconyl and thorium complexes per unit cell are found to be two.

Acknowledgment-The authors are thankful to Prof. M. R. A. RAO for his interest.

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J. Inorg. Nucl. Chem., 1965, Vol. 27, pp. 247 to 249. Pergamon Press Ltd. Printed in Northern Ireland

Reactions between diborane and some boron halides

(Received 10 March 1964; in revised form 5 August 1964)

WE HAVE studied the reactions between diboron tetrachloride and diborane in gas phase at 0°C. In the course of this study the nature of the unstable gaseous phase, previously mentioned by SCHLE-SINGER and coworkers,⁽¹⁾ was investigated. It was found that after 12 hours the system formed a

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B₁H₅Cl (cm ⁻¹)	B ₂ H ₄ Br (cm ⁻¹)	B₂H₄Me* (cm ⁻¹)	Assignment [†]
3580	3565	3623	-B _s H _s
_		3333	— B ₂ H ₄
2609	2615	2571	BH ₂ stretch. as.
2529	2530	2513	BH _s stretch. sym.
2300	2315	2299	-B ₁ H ₄
2132	2114	2110	BH' sym. in phase
2035		2062	-B ₂ H ₄
1915	1906	1919	B-H' sym. out of phase
1825	1822	1815	B-H' asym. out of phase
1733	1733	1710	-B ₁ H ₁
1578	1565	1592	B-H' as. in phase
1525	1490	1481	
1170	1163	1143	B-H, def.
1149	1150	1130	B-H in phase bend.
1092	1066	_	B—X
1073	1051	_	BX
966	956	946	BH, wag.
948	942		
913	907	901	—
847	818		B—X
831	807		B—X
748	683		
730	668	—	—

* Values obtained by SHAPIRO and coworkers.⁽²⁾ Only frequencies corresponding to -B₂H₅ group are given. † B-H' refers to bridge stretchings.

⁽¹⁾ G. URRY, T. WARTIK, R. E. MOORE and H. I. SCHLESINGER, J. Amer. Chem. Soc. 76, 5293 (1954).

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solid, so far not examined, and a gaseous phase in which the presence of B_2H_6 , BCl_2H , B_2H_6Cl and H_3 was established. The final amount of H_2 was always less than 2 per cent of the initial B_2H_6 , all expressed in moles. In a typical run, 0.74 mmoles of B_2H_6 , and 0.71 mmoles of B_2Cl_4 , formed 0.012 mmoles of H_2 as determined with a Töepler pump. It proved possible to isolate the relatively unstable B_2H_6Cl by fractional condensation in a conventional vacuum system with a purity greater than 99 per cent. Its molecular weight as determined by *PVT* measurements was 65.4 (calculated = 62.2). The nature of this compound was confirmed by comparing its spectrum with those of the monoalkyldiboranes.⁽²⁾ Taking advantage of the greater simplicity of B_2H_6Cl as compared with these compounds and the close analogy between them, it was possible to correlate their bands⁽³⁾ and to confirm the assignments given by SHAPIRO and coworkers⁽²⁾ for the $-B_2H_6$ group, (Table 1). Its IR



FIG. 1.—Infrared spectra of B₃H₃Br. Cell path length 61 mm pressure 41 mm Hg.

spectrum, at room temperature, did not show signs of decomposition. A similar result was obtained independently by MYERS and PUTNAM,⁽⁴⁾ who isolated $B_{1}H_{2}Cl$ by gaseous chromatography among the reduction products of BCl₂.

Since spontaneous decomposition of B_2Cl_4 to give BCl₂ takes place, the reaction between BCl₃ and B_2H_6 was studied simultaneously. At 0°C and after 18 hr, in the gas phase, no change was observed. At room temperature we found that the final system also contained BCl₃, B_2H_6 , $B_2H_6Cl_1$ and BCl₃H.

An IR spectrophotometric study of both reactions was carried out in a low temperature gas cell, employing various concentrations of reagents at a total pressure of aprox. 30 mm Hg and showed the formation of intermediaries common to both reactions. (The reaction with B_2Cl_4 was studied at 0°C, that with BCl₂ at 26°C.) Although it was not possible to isolate these intermediate compounds, the following evidence suggests they are BClH₂ (I) and asymmetric $B_2H_4Cl_2$ (II).

(I) Comparing the spectra of the series of compounds, BCl_s, BCl_sF, BCl_F already studied⁽⁵⁾ with BCl_s, BCl₄H,⁽⁶⁾ BClH_s, where one or two chlorine atoms are replaced by the lighter F and H atoms respectively, it was possible to assign one group of bands to the B—Cl and B—H stretching of BClH_s (v_1 :1305 (¹¹B), 1315 (¹⁰B) cm⁻¹; v_s : 1040 cm⁻¹; v_s : 2600 ± 50 cm⁻¹). Also it was shown that if a low concentration of B₂H₆ was used (initial ratio B₃Cl₄: B₃H₆ = 10:1) there was no formation

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⁽⁸⁾ S. B. RIETTI and J. LOMBARDO, Communication presented to the 8 Congreso Latinoamericano de Química, Buenos Aires, September, 1962, Argentina.

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of B_2H_6Cl in the first 3 hr of the reaction, while the above group of bands was observed during the whole period. When the concentration of B_2H_6 was increased (initial ratio 1:3), these bands disappeared and monochlorodiborane could be detected after the first hour of reaction. This may be due to the equilibrium: $B_2H_6Cl = BClH_2 + BH_3$, similar to that accepted for diborane, although in this case the weakening of the bridge structure due to the donor effect of Cl could displace the equilibrium towards the dissociation products.

(II) Another intermediary proved to be a substituted diborane, as indicated by a strong absorption band at 1575 cm^{-1} in the range attributable to bridge stretching of diborane and its derivatives. It



FIG. 2.—Infrared spectra of BBr_sH compensated with BBr_s (a) and without compensation (b). Cell path length 100 mm pressure 10 mm Hg.

must be a chlorinated derivative of diborane and the absorption due to the terminal B—H stretching was split appearing at 2500 ± 10 and 2600 ± 10 cm⁻¹; thus the possibility of tetra-, tri- or symmetric disubstitution,⁽⁷⁾ was eliminated. Furthermore, this compound is retained in the $-130^{\circ}/-150^{\circ}$ C fraction, excluding a heavier derivative and its decomposition takes place with formation of BCl₃H and B₃H₄, so that it is most likely an asymmetric dichlorodiborane.

The presence of the same intermediaries suggests that both reactions may have a common mechanism. We are now trying to isolate these compounds in the pure state.

The reaction which takes place between BBr₃ and B_2H_6 is also under study. In this case the formation of BBr₃H and B_3H_6 Br has been observed and the IR spectrum of pure monobromodiborane at 0°C obtained (Fig. 1, Table 1).

It has not been possible as yet to isolate $BBr_{a}H$ free from BBr_{a} , but its IR spectrum has been obtained by compensation using BBr_{a} in the reference beam, (Fig. 2).

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