Reaction of $Ni[P(OC_2H_5)_3]_4$ with I_2 in pyridine in a closed, evacuated flask released no gas. Determination of excess I_2 in the pyridine after this reaction showed that 5 moles of I_2 per mole of $Ni[P(OC_2H_5)_3]_4$ was used. Known bis(triphenylphosphine)platinum hydride, $[(C_6H_5)_3P]_2PtH_2$, exhibits infrared M–H stretching bands at 1670 and 815 cm.$^{-1}$.[5] The infrared spectra of tetrakis(triethyl phosphite)nickel(0) in Nujol and in a KBr pellet are practically identical with the spectrum of purified triethyl phosphite over the range 4000 to 670 cm.$^{-1}$ showing no indication of M–H stretching frequencies. The most plausible equation which fits this stoichiometry is

$$Ni[P(OC_2H_5)_3]_4 + 5I_2 \longrightarrow NiI_2 + 4(C_2H_5O)_3PI_2$$

We anticipate that this new preparation will provide a more convenient route to other Ni(0) complexes and will help clarify aspects of other reactions involving Ni(II) organophosphorus complexes.

(5) L. Malatesta and R. Ugo, *J. Chem. Soc.*, 2080 (1963).

CONTRIBUTION FROM THE CHEMISTRY SECTION,
ROCKETDYNE, A DIVISION OF NORTH AMERICAN
AVIATION, INC., CANOGA PARK, CALIFORNIA

Synthesis of Nitrogen Trifluoride from the Elements

BY WALTER MAYA

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It has been reported that nitrogen trifluoride cannot be synthesized from the elements by the action of an electrical discharge at low temperatures.[1] We have found that nitrogen trifluoride can be synthesized in substantial yields by the action of an electrical discharge at liquid nitrogen temperature on a gaseous mixture of fluorine and nitrogen. The synthesis of nitrogen trifluoride appears analogous to the synthesis of fluorine oxides from the elements under essentially the same conditions.[2,3] However, unlike the fluorine oxides, variations of the stoichiometry of the fluorine–nitrogen mixtures did not lead to other nitrogen–fluorine compounds such as N_2F_2.

Experimental

A 15-kv., 30-ma. luminous tube transformer was used as the power source for the discharge. The discharge cell consisted of a glass U-tube, with each leg of the U equipped with copper electrodes. The electrodes were 8 cm. apart. The whole cell was immersed in liquid nitrogen during the discharge. A mixture of fluorine and nitrogen was prepared by admitting the requisite amount of gas into an evacuated 2-l. glass bulb; the fluorine is storable in glass for days, if the glass is thoroughly dry. Mixtures of the two gases investigated were 25% F_2, 75% N_2 and 75% F_2, 25% N_2. The best yields of NF_3 were obtainable with the latter mixture. The gaseous mixture was admitted into the discharge cell at a rate that allowed the pressure in the cell to remain between 20 and 40 mm. After leaving the discharge cell, the noncondensable gases were pumped off through a bubbler manostat filled with Fluorolube oil, through a fluorine absorber made of sodium chloride–soda lime, and to a vacuum pump.

At the end of the reaction, the discharge cell was allowed to warm gradually to room temperature, and its contents were fractionated in a high-vacuum line by pumping through a −196° and a −210° (solid nitrogen) trap. In the latter trap, nitrogen trifluoride in yields of 30% was found. The NF_3 was characterized by infrared[4] and mass spectra.

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(2) O. Ruff and W. Menzel, *Z. anorg. allgem. Chem.*, **211**, 204 (1933).

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(4) J. H. Simons, Ed., "Fluorine Chemistry," Academic Press Inc., Vol. II, New York, N. Y., 1954, p. 498.

CONTRIBUTION FROM THE NORTH AMERICAN AVIATION
SCIENCE CENTER, CANOGA PARK, CALIFORNIA

Matrix Isolation Spectra of $HBCl_2$ and $DBCl_2$

BY C. D. BASS, L. LYNDS, T. WOLFRAM, AND R. E. DEWAMES

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In a recent paper, DeWames and Wolfram have developed a method of vibrational analysis of substituted and perturbed molecules utilizing the Green's function and partitioning techniques.[1] We have applied this method to planar XY_3 molecules and calculated the spectra of $HBCl_2$ and $DBCl_2$ from the observed frequencies of BCl_3, without invoking a force constant model.[2] Since the gas phase spectra of $HBCl_2$ and $DBCl_2$ are complicated by interference from BCl_3, which cannot be eliminated,[3] we obtained the matrix isolation spectra of $HBCl_2$–BCl_3 and $HBCl_2$–$DBCl_2$–BCl_3 mixtures in a large excess of argon at $\approx$ 10°K.[4] Although the matrix spectra are also quite complex, they have provided us with additional evidence in support of our gas phase calculations and assignments, as well as showing some interesting features.

Figure 1 shows some of the typical matrix isolation spectra which were observed. Table I lists the results of our calculations, and the gas phase assignments. The following correlations from the $HBCl_2$–BCl_3 spectrum are immediately apparent: a triplet with peaks at 2647, 2639, and 2625 cm.$^{-1}$ in the region where the B–H stretching band is observed (2617 cm.$^{-1}$); two bands at 1116 and 1099 cm.$^{-1}$, which are near the frequencies of the B^{10} and B^{11} components of the B–Cl asymmetric stretch (1100 and 1089 cm.$^{-1}$); and a doublet centered at 895 cm.$^{-1}$, which correlates with the frequency assigned to the B^{11}–H in-plane deforma-

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(1) R. E. DeWames and T. Wolfram, *J. Chem. Phys.*, **40**, 853 (1964).

(2) C. D. Bass, L. Lynds, T. Wolfram, and R. E. DeWames, *ibid.*, in press.

(3) $6HBCl_2 \rightleftarrows 4BCl_3 + B_2H_6$.

(4) G. C. Pimentel, *Spectrochim. Acta*, **12**, 94 (1958).

Table I

Calculated and Observed Gas Phase Spectra and Assignments[d]

Mode	Symmetry type	Band type[a]		$HB^{10}Cl_2$	$HB^{11}Cl$	$\Delta\nu$ ($B^{10}-B^{11}$)	$DB^{10}Cl$	$DB^{11}Cl$	$\Delta\nu$ ($B^{10}-B^{11}$)
ν_1	A_1	B (⊥)	Calcd.	752	729	23	735	714	21
B–Cl stretch			Obsd.	762[b]	740[b]	22			
ν_2	A_1	B (⊥)	Calcd.	2614	2607	7	1913	1902	11
B–I stretch			Obsd.	2617	[c]		1969[b]	[c]	
ν_3	A_1	B (⊥)	Calcd.	289	287	2	287.5	285	2.5
B–Cl sym.			Obsd.						
ν_4 deformation	B_1	A (∥)	Calcd.	1032	1000	32	1002	962	40
B–Cl asym. stretch			Obsd.	1100[b]	1089[b]	11	1050[b]	1005[b]	45
ν_5	B_1	A (∥)	Calcd.	859.5	851.2	8.3	640.6	639.7	0.9
B–H in-plane deformation			Obsd.		892[b]				
ν_6	B_2	C (⊥)	Calcd.	667.2	654.0	13.2	576.1	560.4	15.7
Out-of-plane deformation			Obsd.	795[b]	784[b]	11	661[b]	645[b]	16

[a] Type A, B, and C refer to vibration–rotation bands whose dipole moment changes are along the axes of least, intermediate, and greatest moments of inertia, respectively. In this case, $I_B \approx I_C$, and ∥ and ⊥ refer to band types of the accidentally symmetric top whose dipole moment changes are along and perpendicular to the top axis, A. [b] Band centers estimated from positions of the observed vibration–rotation envelopes. [c] No B^{10}–B^{11} splitting was observed for this mode. [d] All frequencies are in cm.$^{-1}$.

tion (892 cm.$^{-1}$). In the matrix, a doublet centered at 917 cm.$^{-1}$ is also observed and can be assigned to the B^{10} species. (Interference from ν_3 (958 cm.$^{-1}$) of $B^{11}Cl_3$ prevented observation of this band in the gas phase.) Two bands at 801 and 788 cm.$^{-1}$ can be assigned to the B^{10}–B^{11} splitting of the out-of-plane deformation, which occurs at 795 and 784 cm.$^{-1}$ in the gas phase. The behavior of the remaining bands from 760 to 700 cm.$^{-1}$ cannot yet be correlated with the gas phase observations. (The two intense bands at 995 and 955 cm.$^{-1}$ are ν_3 of B^{10} and $B^{11}Cl_3$.)

In the $HBCl_2$-$DBCl_2$ mixture, all of the bands assigned to $HBCl_2$ show intensity decreases. In addition, two new bands appear at 1007 and 970 cm.$^{-1}$. Although the pattern of frequency shifts is not clear, these bands may be assigned to the B-Cl asymmetric stretch of $DB^{10}Cl_2$ and $DB^{11}Cl_2$ (observed at 1050 and 1005 cm.$^{-1}$ in the gas phase). Again the bands between 700 and 760 cm.$^{-1}$ cannot be assigned except for one possibility: a weak doublet, whose peaks are at 759 and 756 cm.$^{-1}$, which appeared in the $HBCl_2$ spectrum, has disappeared. The B^{10}–Cl symmetric stretch of $HBCl_2$ occurs at 762 cm.$^{-1}$ in the gas phase, and the calculations predict a shift to lower frequency for $DBCl_2$. The behavior of the doublet at 759 and 750 cm.$^{-1}$ indicates that it may be the B^{10} component of this mode.

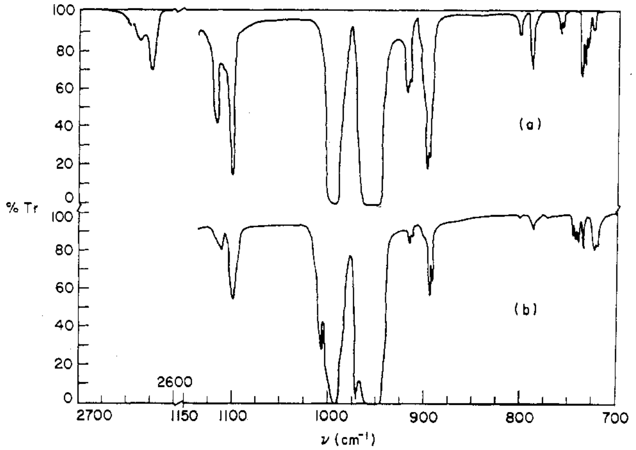

Fig. 1.—Matrix isolation spectra of $HBCl_2$–BCl_3 and $HBCl_2$–$DBCl_2$–BCl_3 mixtures in argon, at ≈10°K.; 700–1150 and 2600–2700 cm.$^{-1}$: (a) $HBCl_2$–BCl_3, ≈25% $HBCl_2$, and mole ratio of A to the mixture = 100; (b) $HBCl_2$–$DBCl_2$–BCl_3, ≈10% each of $HBCl_2$ and $DBCl_2$, and mole ratio of A to the mixture = 100.

Some of the bands observed in the matrix are multiplets, *e.g.*, the high-frequency triplet (B-H stretch), the doublets assigned to the B^{10}– and B^{11}–H in-plane deformation, and possibly the B^{10}–Cl symmetric stretching mode. Other spectra not shown (matrix isolation and mixed crystal) indicate that the relative intensities, frequencies, and line widths of the component of the high-frequency triplet are quite sensitive to concentration, temperature, and deposition effects. This behavior is characteristic of systems which are influenced by intermolecular interactions.[5] It is interesting to note that bands involving H motions are multiplets. Since $HBCl_2$ is the simplest compound available containing a single B-H bond, with refined methods of preparation and separation, it may provide a convenient species with which to investigate boron–hydrogen interactions.

(5) See, for example, D. Dows, *J. Chem. Phys.*, **31**, 1637 (1959).

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Nemours and Company, Wilmington 98, Delaware

Chemistry of Boranes. XVII.[1] Pyrolysis of $H_2B(NR_3)_2^+X^-$ Salts

By N. E. Miller, B. L. Chamberland,
and E. L. Muetterties

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Pyrolysis of the borane cation salts,[2] $H_2B(NR_3)_2^+X^-$, provides a good route to monosubstituted borane adducts, R_3NBH_2X.

(1) Paper XVI: N. E. Miller and E. L. Muetterties, *Inorg. Chem.*, in press.