diate, which would be expected to lead to rearrangement. It is interesting that this proposal of a square-pyramidal geometry for the intermediate $[Ru(en)_2Cl]^{2+}$ is in accord with Pearson's theoretical prediction[9] that this is the most stable geometry for a five-coordinate low-spin d^5 complex.

Acknowledgments.—I thank Dr. R. G. Pearson for helpful discussions.

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Association of Group V Pentafluorides in the Gas Phase

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Received February 16, 1972

In a recent mass spectrometric study, Lawless[1] reported evidence for dimers of SbF_5 and BiF_5 in the gas phase but found no evidence for $(BiF_5)_n$, $n = 3$ or 4, nor presumably for $(SbF_5)_n$, $n > 2$. From these observations Lawless suggested that the dimers have a double fluorine bridge structure and that the preferred interpretation[2] of the ^{19}F nmr spectrum of liquid SbF_5 should be in terms of dimeric units. Müller, *et al.*,[3] have also shown that the mass spectrum of gaseous SbF_5 contains small amounts of dimeric ions. However, a number of recent studies suggest higher concentrations of SbF_5 dimer than were found in either of these mass spectrometric studies;[4-7] some also find evidence for higher agglomerates.[5,7]

The concentration of associated species will be greatest in the saturated vapor which is in equilibrium with either the solid or liquid phase. In the work of Lawless,[1] this condition will be more nearly approached for BiF_5 than for SbF_5. Using a molecular beam source mass spectrometer,[7] we were able to find substantially more dimer in SbF_5 vapor than either Lawless[1] or Müller, *et al.*,[3] as well as higher agglomerates up to the pentamer. Therefore we have studied the saturated vapors of PF_5, AsF_5, and BiF_5 to gain insight into the vapor-phase structure of the group V pentafluorides.

The molecular beam sources and collimating orifices were fabricated from Monel and heavily prefluorinated. Effusion took place from either a 0.025- or a 0.038-cm diameter orifice. The temperature of the gas inlet was maintained by melting slush baths, and the solid sources were heated with resistive windings. Source temperatures were monitored continuously with thermocouples. The mass spectrometer was a modified EAI quadrupole with an Extranuclear Laboratories power supply. The electron energy in the ion source was 70 eV. The molecular beam, electron beam, and resultant ions were on mutually perpendicular axes.

PF_5 was obtained from Matheson, AsF_5 and BiF_5 were supplied by Ozark-Mahoning, and SbF_5 was from Allied Chemicals. All were used without further purification. PF_5 and AsF_5 were handled on a Monel vacuum line; BiF_5 was loaded into the solid effusion source in a dry, oxygen-free helium atmosphere (O_2 + H_2O concentration below 1 part in 10^6).

PF_5 vapor was sampled effusively from a gas–solid equilibrium at 162°K; AsF_5 was similarly studied at 191°K. In neither case could any association be detected, which means an upper limit of dimeric ions of less than 1 part in 10^4.

For BiF_5 a satisfactory molecular beam was obtained between 341 and 361°K, corresponding to vapor pressures between 1.2 and 2.1 Torr. The fragmentation pattern for BiF_5 at an effusion source temperature of 360°K obtained in this study and that due to Lawless are given in Table I. Similar data, for SbF_5, including a comparison with the work of Müller, *et al.*, are given in Table II. The data obtained in this study for SbF_5 were for an effusion source at room temperature (~298°K, vapor pressure of $SbF_5 \cong 2$ Torr). Abundances of associated ions were independent of the effu-

TABLE I

RELATIVE INTENSITIES OF FRAGMENT IONS FROM BiF_5

Mass	Ion	Rel intensity	
		Ref 1	This work[a]
209	Bi^+	13	24
228	BiF^+	10	26
247	BiF_2^+	38	62
266	BiF_3^+	10	2
285	BiF_4^+	100	100
418	Bi_2^+	0.3	0.3
437	Bi_2F^+	0.3	0.3
456	$Bi_2F_2^+$	0.2	0.2
475	$Bi_2F_3^+$	0.5	0.1
494	$Bi_2F_4^+$	0.3	0.2
513	$Bi_2F_5^+$	3.4	4.0
551	$Bi_2F_7^+$	3.5	2.6
589	$Bi_2F_9^+$	18.0	13.5
857	$Bi_3F_{12}^+$	ND[b]	0.05
895	$Bi_3F_{14}^+$	ND	0.07

[a] Not corrected for transmission. Oven temperature 360°K. [b] ND, not detected.

TABLE II

RELATIVE INTENSITIES OF FRAGMENT IONS FROM SbF_5

Mass	Ion	Rel intensity		
		Ref 3[a]	Ref 1[b]	This work[c]
121	Sb^+	10.8	8.0	4
140	SbF^+	10.0	7.0	23
159	SbF_2^+	18.8	25	47
178	SbF_3^+	10.8	20	26
197	SbF_4^+	100	100	100
216	SbF_5^+	0.72	NR[d]	ND[e]
413	$Sb_2F_9^+$	0.24	0.2	8.9
415	$Sb_2F_9^+$	0.40	NR	13.7
417	$Sb_2F_9^+$	0.13	NR	4.7
629	$Sb_3F_{14}^+$	NR	ND	0.06
631	$Sb_3F_{14}^+$	NR	ND	0.10
633	$Sb_3F_{14}^+$	NR	ND	0.07
635	$Sb_3F_{14}^+$	NR	ND	0.02

[a] Conventional inlet and ion source (source temperature not quoted). [b] Conventional inlet, temperature 363–383°K. [c] Beam inlet at room temperature—not corrected for transmission. [d] NR, not reported. [e] ND, not detected.

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[7] M. J. Vasile, G. R. Jones, and W. E. Falconer, *Chem. Commun.*, 1355 (1971).

sion orifice size. In parallel experiments with IrF_6, the orifice was varied from 0.012 to 0.100 cm without effect. Neither of the cracking patterns from this study given in the tables has been corrected for decreasing ion transmission through the quadrupole mass filter with increasing mass[8-10] (*i.e.*, increasing resolution since the mass filter scans in the constant ΔM mode), which under-represents the abundances of higher mass ions.

A comparison of the spectrum for BiF_5 by Lawless[1] and that obtained in this study shows that there are some differences in the monomer cracking patterns, but the dimer cracking patterns are quite similar. We also observed two ions due to trimeric BiF_5, *viz.*, $Bi_3F_{12}^+$ and $Bi_3F_{14}^+$. Making an approximate correction for the quadrupole transmission efficiency, the abundances of the associated ions relative to the monomeric ions for BiF_5 vapor are monomer:dimer:trimer::1:0.45:0.005.

Two alternate mechanisms by which the higher mass ions might have arisen may be considered: ion-molecule reactions in the ion source and condensation occurring by isentropic expansion at the beam source. With a typical neutral number density of 6×10^9 cm^{-3} and a path length in the ion source of 0.4 cm, and assuming an ionization cross section of 15 Å^2 and an ion-molecule reaction cross section of 100 Å^2, the ratio of secondary (dimer) ions to primary (monomer) ions would be 2×10^{-5}. The ion-molecule reaction

$$CD_4^+ + CD_4 \longrightarrow CD_5^+ + CD_3$$

known to have a large cross section, was not observed[7] in the present source configuration with a sensitivity of 1 part in 10^5. Termolecular ion-molecule reactions to yield trimer from monomer have very low probability since molecules in the neutral beam have directed rather than random velocities. Upper limit calculations for sequential ion-molecule reactions to yield timers from monomers predict a ratio of trimer ions to monomer ions of 1×10^{-9}. Similarly, the ratio of trimer to dimer ions resulting from ion-molecule reactions of dimer ions with monomer or dimer neutrals would be expected to be no greater than 10^{-4}.

Free-jet expansion would produce increasing concentrations of associated species as the pressure behind the orifice is increased.[11] In the case of BiF_5, the temperature of the oven was varied from 341 to 448°K, corresponding to a pressure increase from 1.2 to 100 Torr. The monomer ion signal increased by a factor of 11 (scattering losses in the vapor cloud immediately after the source aperture are responsible for the nonlinear behavior of beam intensity with source pressure),[12] while the dimer ion signal dropped to zero. If either free-jet expansion or ion-molecule reactions were responsible for the associated species observed in this study, one would certainly expect a substantial increase in dimer ion concentration with an 83-fold increase in oven pressure, or an 11-fold increase in number density in the ion source.

In the case of SbF_5, significant differences are found in the abundance of dimeric ions between the spectra obtained from our molecular beam source and those obtained from conventional inlets. The spectra reported in Table II for this study include the trimeric species $Sb_3F_{14}^+$; tetramer and pentamer ions were also found as well as trace amounts of $Sb_2F_8^+$, $Sb_2F_7^+$, $Sb_2F_6^+$, and $Sb_2F_5^+$. For SbF_5, the corrected relative abundances are monomer:dimer:trimer:tetramer:pentamer::1:0.5:0.09:10^{-4}:*ca.* 10^{-6}. The small concentration of tetramer ions is indicative that the tetrameric bridged ring structure known for crystalline[13] SbF_5 does not persist into the vapor phase.

The comparisons in mass spectra for SbF_5 and BiF_5 demonstrate the advantage of using a molecular beam source for the mass spectrometric study of reactive species and the necessity of considering the degree of vapor saturation for the detection of associated species. Although $(SbF_5)_2$ and $(BiF_5)_2$ may indeed be doubly fluorine bridged species, this conclusion should not be drawn from available mass spectrometric data. It should furthermore be stressed that in mass spectrometric studies one observes only ionic species. These do not necessarily arise *in toto* from the corresponding neutral agglomerates; an alternate possibility is that they might come from higher associated clusters as fragment ions from electron impact. Hence, the degree of association may well be underestimated due to the fragmentation of neutral clusters.

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A Dative-Bonded Sulfur-Boron-Nitrogen Heterocycle

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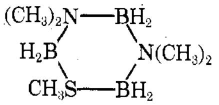
Received March 13, 1972

The dative-bonded dimer $[(CH_3)_2NBH_2]_2$ is known to exist in equilibrium with the monomer[1] or can be converted irreversibly to the cyclohexane-like dative-bonded trimer $[(CH_3)_2NBH_2]_3$ by the action of a transient catalyst derived from pentaborane(9).[2] This trimer has three axial methyl groups in close mutual contact, as proved by the infrared spectrum[2] and the crystallographically determined molecular parameters.[3] Such steric interference is the obvious reason that the trimer is not formed spontaneously from the monomer or dimer.

It now is found that omission of one methyl group from the trimer structure—by allowing a CH_3SBH_2 unit to take the place of one of the three $(CH_3)_2NBH_2$ units—so relieves the steric effect that the six-atom ring is easily formed. The resulting new white crystalline cotrimer



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