

Found: K, 12.6; Ti, 7.8; Br, 78.9. Calcd. for  $\text{Rb}_2\text{-TiBr}_6$ : Rb, 24.48; Ti, 6.86; Br, 68.66. Found: Rb, 24.2; Ti, 6.8; Br, 68.3. Calcd. for  $\text{Cs}_2\text{-TiBr}_6$ : Cs, 33.51; Ti, 6.04; Br, 60.45. Found: Cs, 33.1; Ti, 5.9; Br, 60.2. All compounds obtained were dark wine-red. The rubidium salt was darker than the potassium and cesium salts.

The alkali hexabromotitanates appear to be stable in dry air. However, they are rapidly decomposed when exposed to the atmosphere in the laboratory ( $\sim 60\%$  relative humidity). The alkali hexabromotitanates are considerably more hygroscopic than the corresponding hexachlorotitanates. The hygroscopicity decreases from the potassium to the cesium salt.

In preliminary X-ray studies it was found that the potassium, rubidium, and cesium hexabromotitanates are isomorphous with potassium hexachloroplatinate. The lattice constants of the potassium, rubidium, and cesium hexabromotitanates were found to be  $a_0 = 10.35, 10.46, \text{ and } 10.66 \text{ \AA}$ , respectively.

The formation of the alkali hexabromotitanates in fused antimony tribromide and the formation of the monovalent metal hexachlorotitanates in fused antimony trichloride<sup>1</sup> are based on a similar acid-base reaction. Another type of acid-base reduction in fused antimony tribromide was described by Jander and Weis.<sup>5</sup>

**Acknowledgment.**—Miss Irene Corvin performed the X-ray analyses.

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## Infrared Spectra of Vanadium Fluorides

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Although the chemistry of the higher fluorides of vanadium has been extensively investigated<sup>1,2</sup> and certain physical properties have been determined,<sup>3,4</sup> little structural information has yet been obtained. The structure of vanadium pentafluoride is of some considerable interest since the liquid is thought to be associated<sup>1,5</sup> by fluorine bridge bonds, while the normal vapor density<sup>1,6</sup> suggests that the pentacoordinate monomer is present in the gas phase. Moreover, the geometry of this monomer, either trigonal bipyramidal or perhaps square pyramidal, is itself of great interest.

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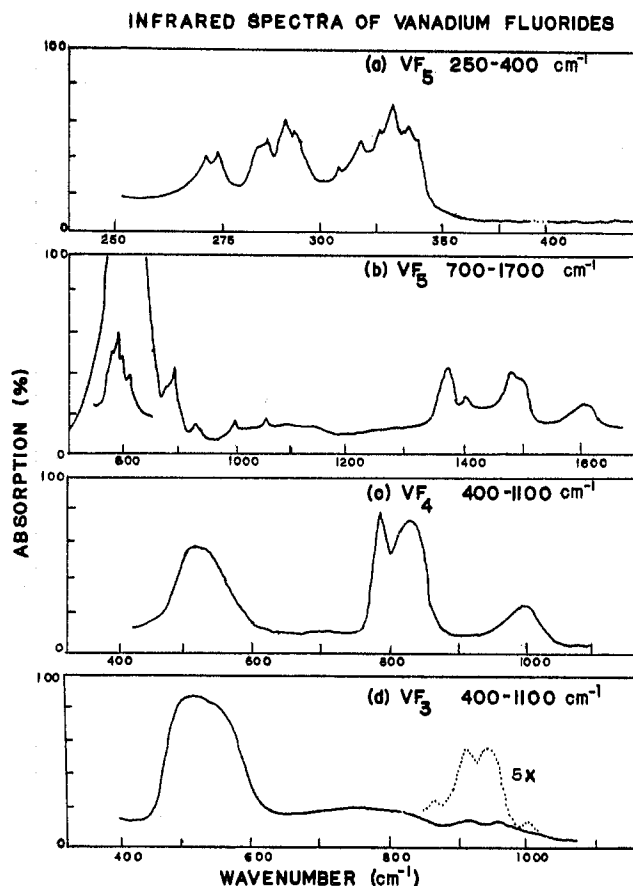


Figure 1.

Since there are no nonbonding, valence-shell electron pairs in vanadium pentafluoride, the trigonal bipyramidal structure is reasonably expected, but this has not yet been established for this or any other transition metal fluoride. As one approach, we have now investigated the infrared spectrum of vanadium pentafluoride, and also of the tetra- and trifluorides.

### Experimental

The preparations of vanadium pentafluoride and tetrafluoride have been described previously,<sup>1,2</sup> as well as the techniques involved in their manipulation. Vanadium trifluoride was obtained by the thermal decomposition of the tetrafluoride.<sup>2</sup> The infrared spectra were measured on Perkin-Elmer Model 21 infrared recording spectrometers, fitted with NaCl optics for the 650–4000  $\text{cm}^{-1}$  region and cesium bromide optics for 200–650  $\text{cm}^{-1}$ . Spectra of the pentafluoride were taken using two different gas cells. The first was a 9-cm. long stainless steel cell fitted with polyethylene windows 0.5-mm. thick and held in place by stainless steel compression rings. With this cell, the 200–1000  $\text{cm}^{-1}$  region could be observed, since polyethylene has only two weak absorption bands at 720 and 730  $\text{cm}^{-1}$ . The other was a 10-cm. glass cell fitted with potassium bromide plates which previously had been coated with a thin film of paraffin wax to prevent attack by the pentafluoride. These windows were transparent from 350 to 4000  $\text{cm}^{-1}$ , except for the sharp paraffin absorption bands at approximately 2900, 1400, 730, and 720  $\text{cm}^{-1}$  which were weak because of the thinness of the wax film and hence did not obscure a large region of the spectrum.

Both cells were attached to glass fingers into which the pentafluoride was distilled. The pressure of pentafluoride vapor within the cell could be controlled by cooling the finger to various temperatures. Spectra were measured on two different samples in each cell over the entire accessible range for each cell, with no appreciable differences being observed.

Spectra of vanadium tetrafluoride and trifluoride were obtained using Nujol mulls which had been prepared in a drybox.

### Results and Discussion

The positions of the absorption bands for the pentafluoride and their estimated relative intensities are shown in Table I and Fig. 1. Four strong bands are

TABLE I  
INFRARED SPECTRUM OF VF<sub>5</sub> VAPOR

Frequency, cm. <sup>-1</sup>	Approx. intensity	Tentative assignment
271	1.1	{ e' fundamental (VF <sub>5</sub> in-plane bending)
274	1.3	
287	1.9	{ e' fundamental (VF <sub>5</sub> ' linear bending)
293	3.1	
320	2.5	{ a <sub>2</sub> '' fundamental (VF <sub>5</sub> out-of-plane bending)
326	sh?	
332	4.5	
339	3.0	
343	sh?	
351	sh?	
775	100	{ a <sub>2</sub> '' fundamental (V-F' antisym. stretch)
784		
791		
810	...	e' fundamental (V-F' antisym. stretch)
880	sh	
887	3.8	{ 273 + 290 + 332 = 895?
890		
930	0.6	
995	0.6	
1060	0.6	VOF <sub>3</sub> ?
1385	3.0	VOF <sub>3</sub> ?
1417	0.6	
1497	3.5	
1520	sh	
1615 br	0.8	

found in the 250–1200 cm.<sup>-1</sup> region. A trigonal bipyramid molecule (D<sub>3h</sub> point group) has eight fundamental frequencies of which only five, two of species a<sub>2</sub>'' and three of species e', are infrared active. The most prominent bands in the spectrum should be the antisymmetric vanadium-fluorine stretching frequencies, that of the axial fluorines being of a<sub>2</sub>'' symmetry and that of the equatorial fluorines of e' symmetry. These bands are generally observed in the 400–1000 cm.<sup>-1</sup> region in pentavalent halides and are usually within 15–150 cm.<sup>-1</sup> of each other.<sup>7–11</sup> In the present case only one strong band was observed in the region 400–1000 cm.<sup>-1</sup>, where the antisymmetric stretching frequencies are to be expected; however, the band shows more than the simple PQR structure expected for the a<sub>2</sub>'' fundamental, and it is possible that the two antisymmetric stretches are so close that resolution has not been completely achieved. The peak at 784 cm.<sup>-1</sup> may then be the Q branch of the parallel a<sub>2</sub>'' fundamental with the peaks at 775 and 791 cm.<sup>-1</sup> the P and R branches. The e' fundamental, a perpendicular band expected to show only a Q branch, is assigned to the in-

completely resolved peak at 810 cm.<sup>-1</sup>. The three remaining strong bands between 270 and 350 cm.<sup>-1</sup> are probably the other three infrared fundamentals, one of a<sub>2</sub>'' (VF<sub>5</sub> out-of-plane bending) and two of e' (VF<sub>5</sub>' linear bending and VF<sub>5</sub> in-plane bending) symmetry, of the trigonal bipyramid structure. The structures of these bands are somewhat more complicated than expected for the assignments and the additional structure may be due to overlapping of the fundamentals with combination bands involving inactive fundamentals or possibly the presence of "hot" bands. The information available here is not sufficient to establish a specific structure for vanadium pentafluoride vapor but assignments based on the square-pyramid structure, for which six infrared fundamentals are expected, do not yield better agreement with the observed spectrum. Clearly a Raman spectrum is necessary to establish the structure of vanadium pentafluoride.

In spectroscopic studies of highly reactive fluorides it is always possible that observed bands may be due to impurities, particularly to oxyfluorides. In this case partial hydrolysis would produce the oxyfluoride, VOF<sub>3</sub>. However, our results are very similar to those obtained by other workers<sup>12</sup> whose studies clearly show that our samples contained little or no VOF<sub>3</sub>, since this compound gives a very strong absorption band at approximately 1050 cm.<sup>-1</sup> associated with the V–O bond. Attempts to examine the spectrum of liquid vanadium pentafluoride were unsuccessful, because of its reactivity with all cell windows. It might be anticipated that other techniques, notably F<sup>19</sup> magnetic resonance studies, could successfully be applied to the determination of the structure of VF<sub>5</sub>, particularly in the liquid state. Unfortunately, all attempts at such studies<sup>13,14</sup> have been unsuccessful, only a broad resonance peak being observed.

TABLE II  
INFRARED SPECTRA OF VF<sub>3</sub> AND VF<sub>4</sub><sup>a</sup>

VF <sub>3</sub>		VF <sub>4</sub>	
Frequency, cm. <sup>-1</sup>		Frequency, cm. <sup>-1</sup>	
1060	w, br	1025	w, br
970, 940	doublet, w	837	s
890	vw	780	s
540 ± 20	s, br	530 ± 20	s, br

<sup>a</sup> s, strong; w, weak; vw, very weak; br, broad.

The results of infrared studies of vanadium tetrafluoride and vanadium trifluoride are shown in Table II. While both fluorides show strong bands of similar shape at approximately 530 cm.<sup>-1</sup>, the two spectra are otherwise markedly different. With VF<sub>3</sub>, only a few weak bands were observed from 600 to 4000 cm.<sup>-1</sup>, whereas the tetrafluoride shows a strong doublet at 780–837 cm.<sup>-1</sup>. This difference may be due to the different structures of the solid fluorides.

In vanadium trifluoride each vanadium atom is coordinated by six fluorine atoms forming a nearly regular

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octahedron.<sup>15</sup> The broad band at 540  $\text{cm}^{-1}$  can therefore be considered the  $\nu_3$  frequency arising from an octahedral species of  $O_h$  symmetry and is comparable to the value of 511  $\text{cm}^{-1}$  observed<sup>16</sup> for  $\text{K}_3\text{VF}_6$ . The suggestion was made previously<sup>2</sup> that vanadium tetrafluoride has an associated structure in which four fluorine atoms of each  $\text{VF}_6$  octahedral unit are shared with adjacent octahedra. The symmetry about the vanadium is therefore probably tetragonal rather than octahedral. A molecule of tetragonal ( $D_{4h}$ ) symmetry has three infrared active fundamentals (doubly degenerate  $E_u$  species) rather than the two triply degenerate infrared active fundamentals of an octahedral molecule. Assuming that small changes in symmetry such as this will not cause large shifts in the vibrational frequencies, the 780–837  $\text{cm}^{-1}$  band in vanadium tetrafluoride may be considered one of these three fundamentals. The strong band at 540  $\text{cm}^{-1}$  probably corresponds to the 583  $\text{cm}^{-1}$  band observed in  $\text{K}_2\text{VF}_6$ ,<sup>16</sup> and the remaining fundamental may be below 400  $\text{cm}^{-1}$ . The reason for the doublet structure of the 780–837  $\text{cm}^{-1}$  peak is not clear, but it may be due to crystal field effects or to differences in bonding.

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## A New Polymorph of CrOOH

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Compounds in the system chromium–oxygen–hydrogen have been of interest in regard to magnetic properties,<sup>1</sup> catalytic action,<sup>2</sup> and pigment applications.<sup>3</sup> The chemistry of the system is complex, in view of the multivalence of chromium, and experimental work is hindered by the occurrence of poorly crystallized products. The present work involved reactions under hydrothermal conditions, using sealed platinum tubes inside Stellite pressure vessels,<sup>4</sup> and has yielded additional information concerning the solid phases and their interconversion. The use of hydrothermal reaction conditions is favorable in this type of system, both in order to promote crystallization and to permit retention of the higher valence states of

chromium. Previous investigations<sup>5–8</sup> have shown that, in addition to  $\text{CrO}_3$  and  $\text{Cr}_2\text{O}_3$ , the compounds  $\text{CrO}_2$  and  $\text{CrOOH}$  (I) can occur. Various hydrated oxides, usually poorly crystallized and of uncertain composition, have been described, and also a metastable "cubic  $\gamma\text{-Cr}_2\text{O}_3$ ," analogous to  $\gamma\text{-Fe}_2\text{O}_3$ .<sup>5</sup> The crystal lattice of the  $\text{CrOOH}$  compound (I) was deduced as rhombohedral by Thamer, Douglass, and Staritzky.<sup>7</sup> Their material was obtained as brown-red crystals by decomposition of  $\text{CrO}_3$  in water under hydrothermal conditions. They also observed coexistence of  $\text{CrO}_2$  in some experiments, but the conditions favoring formation of either product were not defined. Laubengayer and McCune<sup>5</sup> treated a precipitated hydrated chromium oxide in water or aqueous  $\text{NaOH}$  solution, at high temperature and pressure, and obtained a blue-gray compound (II). The chromium content of II was consistent with  $\text{CrOOH}$ , and the compound gave the same X-ray pattern as that subsequently reported for I. In the present work, treatment of  $\text{CrO}_3$ , either in the presence of water or nominally in the dry state, at 450° under a total pressure of 40,000 p.s.i., has yielded the black, magnetic  $\text{CrO}_2$ . This result is consistent with earlier reports.<sup>8–12</sup> Substitution of 0.25  $M$   $\text{K}_2\text{Cr}_2\text{O}_7$  solution for water in two experiments yielded the red  $\text{CrOOH}$  (I), although this has not been established as a consistent result. Treatment of  $\text{CrO}_2$ , obtained as described above, in water at 450° and 40,000 p.s.i., yielded a green product (III), which gave an X-ray pattern distinct from those of the known phases in this system. Emission spectrographic examination showed only chromium as a major constituent. Gravimetric determinations were consistent with the empirical formula  $\text{CrOOH}$  for III. The crystal lattice of III has been determined as orthorhombic, with  $a = 4.861$ ,  $b = 4.292$ ,  $c = 2.960$  Å.

### Experimental

The compound  $\text{CrO}_2$  was prepared by decomposition of  $\text{CrO}_3$ , by heating for 72 hr. at 450° and 40,000 p.s.i., using welded thin-walled platinum tubing as a reaction container. The pressure and temperature were provided by means of a Stellite pressure vessel heated in a tube furnace, according to conventional techniques. The  $\text{CrO}_2$  was removed from the reaction tube, washed in water, and ~0.2 g. was resealed in a new platinum tube, together with ~2 ml. of water. The  $\text{CrO}_2$ –water mixture was then heated for 72 hr. at 450° and 40,000 p.s.i. The reaction product was an olive-green powder (III) which gave the X-ray diffraction powder data shown in Table I.

X-Ray diffraction powder patterns were obtained using a 114.59-mm. Straumanis-loaded camera, with vanadium-filtered chromium radiation. Intensity measurements were made by visual estimation.

The powder pattern was indexed on an orthorhombic cell with  $a = 4.861$ ,  $b = 4.292$ , and  $c = 2.960$  Å. The indexing was done

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