$$\begin{tikzcd}
[NbCl(OC_2H_5)_3(C_5H_5N)]_2 \arrow[rr, "NaOC_2H_5"] \arrow[dr, "HCl"'] & & Nb(OC_2H_5)_4 \arrow[dl, "C_5H_5N,\ HCl"] \\
& (C_5H_6N)_2[Nb(OC_2H_5)Cl_5] &
\end{tikzcd}$$

This cycle demonstrates the equivalence of the oxidation state of niobium in each compound and thus proves the tetravalent state in $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ and $Nb(OC_2H_5)_4$ since the pentachloroethoxoniobate anion is known to contain niobium(IV).

Acknowledgment.—R. A. D. W. wishes to thank the National Science Foundation for fellowship aid in 1962–1963.

Contribution from the Institute for Atomic Research and
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Transport Reactions of Some Vanadium(III) Halides. Mixed Halide Formation[1a]

By ROBERT E. McCARLEY, JAMES W. RODDY,[1b] and KEITH O. BERRY

Received September 8, 1962

The reactions of VCl_2, VCl_3, and VCl_3–VBr_3 mixtures with bromine vapor at 350 to 450° led to vaporization of the halides and deposition of mixed halides of vanadium(III) at lower temperatures. A study of solid solution formation in the system VCl_3–VBr_3 showed that the two components were miscible in the solid state, and that the mixed halide VCl_2Br should be regarded as such a solid solution. The pure compounds VCl_3 and VBr_3, the mixed halides VCl_2Br and VBr_2I, and solutions of all compositions in the system VCl_3–VBr_3 were hexagonal solids with the BiI_3 layer structure; lattice constants for all of the compounds are given. Vaporization of VBr_2 in iodine vapor at 350 to 400° resulted in the transport and deposition of VBr_2I, but the analogous reaction between VCl_2 and iodine yielded only a deposit of VCl_2. Vanadium(IV) mixed halides containing iodine were postulated to account for the vaporization at these temperatures.

Introduction

Sublimation of the vanadium(III) halides VX_3 (where X = Cl, Br, I) as a means of purification is not practical because of the stability relationships to the respective lower and higher halides. For example, it has been shown[2] that VCl_3 is unstable at high temperature with respect to reaction 1

$$2VCl_3(s) = VCl_2(s) + VCl_4(g) \tag{1}$$

whereas VBr_3 is decomposed[3a] *via* reactions 2 and 3

$$VBr_3(s) = VBr_2(s) + {}^1/_2Br_2(g) \tag{2}$$

$$2VBr_3(s) = VBr_2(s) + VBr_4(g) \tag{3}$$

Simple vaporization of the trihalides is not feasible because at the temperatures required for sublimation of the solids the decomposition pressures are comparable in magnitude to the vapor pressures.

However, vaporization and deposition of compounds which are unstable in this manner frequently may be performed by means of chemical reactions. In this connection, a volatile species containing the metallic element must be formed in a reversible reaction of the type

$$A(s) + B(g) = C(g)$$

The conditions necessary for the transport of a crystalline phase through a temperature gradient T_1 to T_2 have been outlined and demonstrated by Schäfer, *et al.*[4] Reactions of this type will be referred to as transport reactions in this work.

Based on these considerations some transport reactions of the crystalline vanadium halides have been studied, and the decreased stability of the higher-valent vanadium bromides and iodides has been utilized. For example, reactions of types 4 and 5 have been performed where X = Cl or Br and X′ = Br or I.

$$VX_3(s) + {}^1/_2X_2'(g) = VX_3X'(g) \tag{4}$$

$$VX_2(s) + n/2X_2'(g) = VX_2X_n' \tag{5}$$

In the case of (4), equilibrium studies previously have been completed where X = X′ = Cl[5] or Br.[3a] As a result of the work reported here some new, mixed halide compounds of vanadium(III) were prepared and characterized, while indirect evidence was obtained for the formation of some mixed halides of vanadium(IV) in the vapor phase.

Experimental

Materials.—Commercial chlorine was taken from the cylinder and purified by passing the gas through a potassium permanganate solution to remove hydrogen chloride and then through sulfuric acid and over phosphorus(V) oxide to remove moisture. Reagent grade bromine was vacuum distilled from phosphorus (V)

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[1] (a) Contribution No. 1215. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission; (b) this paper was taken in part from a thesis submitted by J. W. Roddy to the Iowa State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] (a) O. Ruff and H. Lickfett, *Ber.*, **44**, 506 (1911); (b) V. Funk and C. Muller, *Z. anorg. allgem. Chem.*, **244**, 94 (1940); (c) W. Blitz, *ibid.*, **109**, 132 (1919); (d) M. Oranskaya, Y. Lebedev, and I. Perfilova, *Zh. Neorgan. Khim.*, **6**, 259 (1961).

[3] (a) R. E. McCarley and J. W. Roddy, *Inorg. Chem.*, **3**, 54 (1964); (b) R. E. McCarley and J. W. Roddy, *ibid.*, **3**, 60 (1964).

[4] (a) H. Schäfer, H. Jacob, and K. Etzel, *Z. anorg. allgem. Chem.*, **286**, 42 (1956); (b) *ibid.*, **286**, 27 (1956); (c) H. Schäfer, E. Weiss, and F. Wartenpfull, *ibid.*, **295**, 268 (1958); H. Schäfer, E. Weiss, and F. Wartenpfull, *Angew. Chem.*, **69**, 479 (1957).

[5] J. Simons and M. Powell, *J. Am. Chem. Soc.*, **67**, 75 (1945).

oxide and stored in an evacuated flask which was connected to the vacuum system by a stopcock lubricated with fluorocarbon grease. Iodine was purified by grinding the solid with potassium iodide and subliming from phosphorus(V) oxide. All other reagents were of reagent grade quality and were used without further purification.

The vanadium halides used in the reactions reported here were prepared by methods described elsewhere.[3b] They always were stored in sealed vials and handled in a glove box under argon, which was maintained at low humidity (at a dewpoint of *ca.* −75°) by circulation of the gas through Linde 4A Molecular Sieves.

Analytical Procedures.—Vanadium was determined by titration with standard permanganate solution.[6] Samples were dissolved in 1:1 nitric acid, sulfuric acid was added, and the solution was evaporated to fumes of sulfur trioxide. Water then was added until the solution contained about 5% acid and the analysis was completed in the usual manner after reduction of the vanadium(V) to VO^{+2} with sulfur dioxide.

Chlorine in samples containing both chloride and bromide was determined by a procedure given by McAlpine.[7] The method consisted of forming a compound of acetone with bromine which was unreactive toward silver nitrate. Subsequently, best results were obtained when chloride was determined gravimetrically.

For the determination of bromide in the presence of chloride, the procedure given by Kolthoff and Yutzy[8] yielded excellent results. Accuracy and precision of the method were on the order of 0.3%.

Iodine in the mixed halides was determined by oxidation of iodide to the free element with bromine water. Excess bromine was destroyed by addition of sodium formate and the iodine determined by the usual titrimetric method.

Transport Reactions.—All reactions of this type were performed using sealed, evacuated tubes which contained the vanadium halide, and in some instances free halogen. In those experiments where a fixed temperature gradient was maintained during the reaction, and where the lower temperature was well above ambient temperature, the reaction vessel was heated in a double, tubular furnace provided with separately controlled heating elements at each end. This arrangement permitted a uniform temperature gradient to be maintained over the length of the reaction tube.

Equilibrium Pressure Measurements.—For determination of the equilibrium pressures in the VCl_3–Br_2 and VCl_2Br–Br_2 reactions the total pressures were measured in a Pyrex diaphragm gage. With the initial bromine pressure in the gage at room temperature known, it was possible to calculate the equilibrium constant for the reaction of the type

$$VX_3(s) + {}^1/_2X_2(g) = VX_4(g)$$

at any given temperature from the value of the total pressure in the gage at that temperature. The measured total pressures were corrected for a small residual pressure (3–6 mm.) which developed in the gage after heating the gage and contents near the reaction temperature. A more detailed description of the correction of the pressure data, of the experimental apparatus and procedure, and of the method of calculation of the equilibrium pressures and equilibrium constants has been given in another paper.[3a]

Preparation of Solid Solutions in the System VCl_3–VBr_3.—Three methods of preparing solid solutions of VCl_3 and VBr_3 were used; each method appeared to give equally satisfactory results. The methods were the following:

(1) Weighed samples of the two components were thoroughly mixed by grinding in the glove box. The powder then was sealed *in vacuo* in a Vycor tube and heated at 700° for at least 12 hr. Subsequently, the tube was quenched in ice-water, annealed at 200° for 24 hr., and cooled slowly to room temperature. After grinding the material thus treated, samples were taken for analysis and X-ray powder diffraction data.

(2) Weighed samples of VBr_3 were equilibrated with chlorine of known pressure and volume at 400–450° for periods of *ca.* 40 hr.

(3) Weighed samples of VCl_3 and VBr_3 were intimately mixed and sealed in a tube into which bromine had been introduced. When the solids were heated to 325°, while the opposite end of the tube was maintained at room temperature, a transport reaction occurred and yielded the desired solid solution in a region of the tube near the cool end. Under these conditions the bromine partial pressure in the tube was about 220 mm.

X-Ray Diffraction Data.—Samples on which diffraction data were desired were sealed in 0.2-mm. Lindemann glass capillaries and exposed to Ni-filtered, Cu Kα radiation in a 11.46-cm. camera. All data were corrected for film shrinkage. After indexing of the powder patterns, the final lattice parameters were calculated by the refinement method of Taylor and Sinclair[9a] and Nelson and Riley.[9b]

Results and Discussion

Transport of VCl_3 in Bromine.—When samples of VCl_3 were maintained at any temperature from 325 to 450° in the presence of bromine vapor a rapid transport reaction occurred. In these experiments a 4–5 g. sample could be vaporized in a 24-hr. period; deposition of the solid occurred in a portion of the tube that was near room temperature. Products of the reaction at 400° and the indicated pressure of bromine gave the following analytical data.

P_{Br_2}, mm.	Percentage Composition V	Cl	Br	Cl/V	(Cl + Br)/V	Lattice constants, Å. a_0	c_0
220	31.8	65.5	2.5	2.96	3.01	6.06	17.46
67	32.1	66.2	1.6	2.97	3.00	6.08	17.47

Thus in the reaction a volatile, higher halide was formed; the volatile species migrated to the cool end of the tube and decomposed to a solid having the composition $VCl_{2.97}Br_{0.03}$. The lattice constants of the products of these reactions showed that the solid was a solid solution of VBr_3 in VCl_3, as discussed in a later section. Adequate thermodynamic data are not available to make an estimate of the extent to which bromine should replace chlorine in a reaction of the type

$$VCl_3(s) + {}^3/_2Br_2(g) = VBr_3(s) + {}^3/_2Cl_2(g) \qquad (6)$$

However, since VCl_3 and VBr_3 do form solid solutions reaction 6 is expected to proceed until the activity of VBr_3 becomes significant. The extent of replacement of chlorine with bromine observed in the transport reactions does not seem unreasonable.

It is certain that the vapor species in these experiments was not the vanadium(III) halide since it has been shown in another paper[3b] that the vapor pressures of $VCl_3(g)$ and $VBr_3(g)$ are too low to account for the rapid transport. Because both VCl_4[2d] and VBr_4[3a] have been shown to exist as stable compounds in the vapor state at elevated temperature, the major volatile species in these experiments is formulated as a mixed

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(6) W. Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, N. Y., 1948.

(7) R. McAlpine, *J. Am. Chem. Soc.*, **51**, 1065 (1929).

(8) I. Kolthoff and H. Yutzy, *Ind. Eng. Chem., Anal. Ed.*, **9**, 75 (1937).

(9) (a) A. Taylor and H. Sinclair, *Proc. Phys. Soc.* (London), **57**, 126 (1945); (b) J. Nelson and D. Riley, *ibid.*, **57**, 160 (1945).

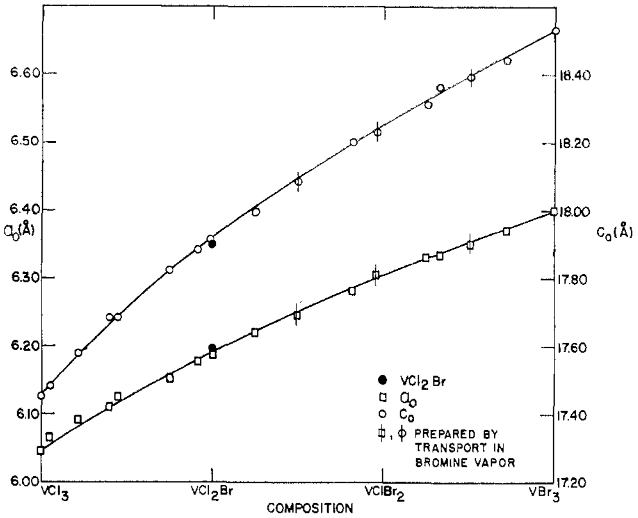

Fig. 1.—Lattice parameters of solid solutions in the system VCl_3–VBr_3.

halide of vanadium(IV) resulting from the reaction

$$VCl_3(s) + {}^1/_2Br_2(g) = VCl_3Br(g) \qquad (7)$$

The rapid rate of the reverse reaction at low temperature indicated that VCl_4 could not be an important species in the transport since its decomposition is normally slow. The transport of solid solutions of VCl_3–VBr_3 in bromine also indicated that the mixed halide was the most important vapor species.

Formation and Transport of VCl_2Br.—At temperatures above 300° VCl_2 reacted with bromine vapor (200 mm.) to produce the solid VCl_2Br, which was rapidly vaporized and condensed as a black sublimate of the same composition. *Anal.* Calcd.: V, 25.3; Br, 39.7. Found: V, 25.4; Br, 39.7. The lattice parameters given in Table I for this solid were in good agreement with the values expected for a solid solution of VCl_3–VBr_3 of the same composition, as shown in Fig. 1. Although the principal species in the vapor state in this reaction is indicated by the stoichiometry to be VCl_2Br_2, it is possible that other species are formed of the type $VCl_{4-x}Br_x$ ($x = 0, 1, 2, 3, 4$) either by halogen exchange in the vapor or by direct formation from the solid VCl_2Br. Additional evidence that all possible mixed halide species may occur in the reaction is provided by the experiments where solid solutions of VCl_3–VBr_3 were prepared by transport of simple mixtures of VCl_3 and VBr_3 in bromine vapor.

The evidence obtained here for mixed halide species in the vapor is similar to that obtained by Wilson and Gregory[10] in a study of the transport of $FeCl_2$(s) in bromine vapor. Their results differ in one important respect from those obtained in this work; in the $FeCl_2$(s)–Br_2 transport reaction the iron in the deposited halides was distributed between both an iron(II) halide phase and an iron(III) halide phase, because of the difference in stability of phases richer in $FeCl_3$(s) and those richer in $FeBr_3$(s). All of the vanadium transported in the reactions reported here was recovered in a vanadium(III) halide phase. This should be expected since both VCl_3 and VBr_3 are stable solids at the deposition temperatures involved in the experiments.

Table I

Lattice Constants of Vanadium(III) Halides and Mixed Halides

Compound	a_0, Å.	c_0, Å.	c_0/a_0
VCl_3	6.045	17.45	2.892
VBr_3	6.400	18.53	2.894
VCl_2Br	6.186	17.90	2.894
VBr_2I	6.589	19.30	2.933

Solid Solution Formation in the System VCl_3-VBr_3.—Because of the replacement of chloride with bromide in the solid formed by transport of VCl_3 in bromine, and the formation of the mixed halide VCl_2Br by reaction of VCl_2 with bromine, it was of interest to determine how extensive solid solution formation might be in the VCl_3–VBr_3 system. The X-ray powder diffraction data from solids treated by the methods given in the Experimental section showed that a continuous solid solution phase is formed over the entire composition range. Both of the pure compounds and all of the solid solutions prepared for this study gave powder patterns that were indexed on the basis of a hexagonal unit cell of the BiI_3 type. The results are presented in Fig. 1, where the lattice parameters are given as a function of the composition. It is to be noted particularly that the data for the solids prepared by transport of the mixtures of VCl_3 and VBr_3 in bromine fit smoothly onto the curves constructed from data for solutions which were prepared by the other methods. As indicated earlier VCl_4 was not thought to be an important species in the transport since none was recovered in the experiments, and the composition of the deposited solid corresponded closely to that calculated from the weights of the pure halides used in the reactions. It seems more likely that the vapor transport and deposition of the solid solution is caused by mixed halides of vanadium(IV) formed by rapid halogen interchange between species in the vapor or between vapor and the solid phases.

Structurally the solutions behaved almost ideally. The maximum deviation from a linear variation of the lattice constants with composition was 0.02 and 0.09 Å., respectively, for a_0 and c_0. However the ratio c_0/a_0 remained constant at 2.89 over the entire composition range. The lattice constants calculated for the pure compounds VCl_3 and VBr_3, and the mixed halides VCl_2Br and VBr_2I, are given in Table I. The values given for VCl_3 may be compared with those given by Klemm and Krose,[11] $a_0 = 6.012$ and $c_0 = 17.34$ Å. An explanation for the small discrepancy between the two sets of parameters cannot be given, but the difference does appear to be outside the limits of error of our results, which are estimated to be *ca.* ±0.005 Å. for a_0 and ±0.02 Å. for c_0. Klemm and Krose did not give analytical data for the material they used in their work; the analyses of VCl_3 and VBr_3 prepared by us are given below.

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[10] L. E. Wilson and N. W. Gregory, *J. Am. Chem. Soc.*, **80**, 2067 (1958).

[11] W. Klemm and E. Krose, *Z. anorg. allgem. Chem.*, **253**, 218 (1947).

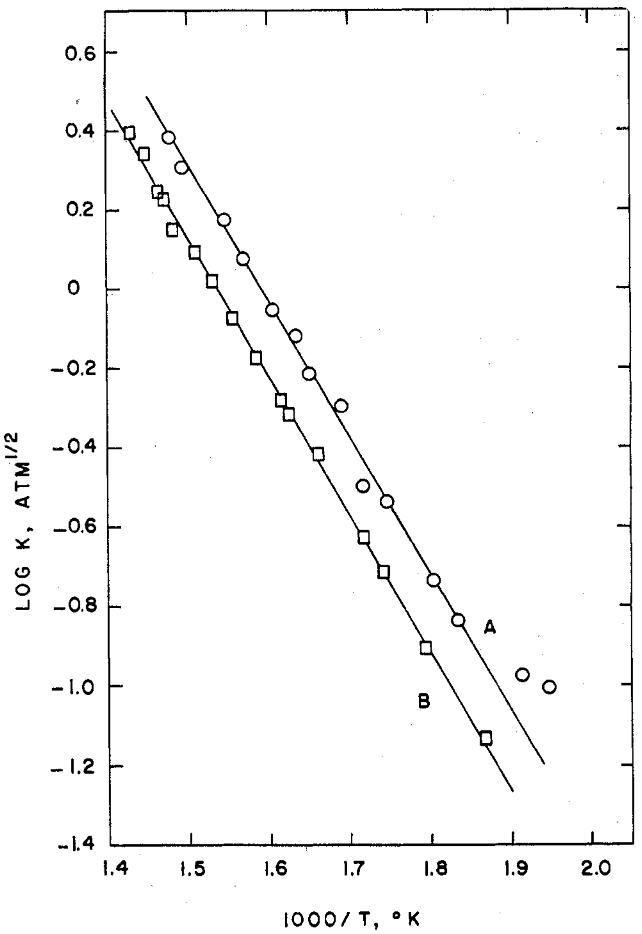

Fig. 2.—Apparent equilibrium constants for the reaction of bromine with VCl_3 and VCl_2Br: A, VCl_3; B, VCl_2Br.

Anal. Calcd. for VCl_3: V, 32.4; Cl, 67.6. Found: V, 32.2, 32.1, 32.3, 32.3; Cl, 67.7, 67.7, 67.8, 67.5. Calcd. for VBr_3: V, 17.5; Br, 82.5. Found: V, 17.5, 17.6, 17.4; Br, 82.4, 82.5, 82.5.

The solid solution formation in the system VCl_3–VBr_3 and formation of the mixed halides VCl_2Br and VBr_2I (see below) are closely analogous to the results of Handy and Gregory,[12] who made a study of the corresponding chroiumm(III) halides. In the work with chromium they also reported the mixed halide $CrCl_2I$, in addition to $CrBr_2I$ and $CrCl_2Br$. A point of interest here, though not easily explained, is the fact that the above chromium compounds all exhibited the $CrCl_3$ structure, while the vanadium compounds all exhibited the BiI_3 structure. The difference in the two structures is only in the type of closest packing of the halogen atoms[13] and is not otherwise important.

Equilibrium Pressure Measurements.—For the reactions between VCl_3 and bromine, and VCl_2Br and bromine, equilibrium pressures were measured using a Pyrex diaphragm gage. Because the extent of displacement of chlorine by bromine in VCl_3 had been found to be slight (*ca.* 1 mole %) the reaction which occurred in the gage with VCl_3 and bromine was considered to be principally reaction 7. However, because other reactions could contribute to the over-all measured pressure, as discussed above, the equilibrium pressure of vanadium(IV) halide over the trihalide phase should be considered as the sum of the partial pressures of all species $VCl_{4-x}Br_x$ (x = 0, 1, 2, 3, 4). A similar argument may be applied to the pressures obtained from the reaction between VCl_2Br and bromine; in this case the preponderant vapor species should be expected to be VCl_2Br_2.

Using the equilibrium pressures of vanadium(IV) halide over VCl_3(s) at an initial pressure of bromine of 141.6 mm., and over VCl_2Br at an initial pressure of bromine of 120.0 mm., apparent equilibrium constants were calculated for the reactions. The two sets of data are given in Fig. 2. From these data the expressions $\log K$ (atm.$^{1/2}$) = $-3450/T + 5.48$ and $\Delta H° = 15.8 \pm 1.5$ kcal., $\Delta S° = 25.1$ e.u., were derived for the temperature interval 513 to 676°K. and the reaction

$$VCl_3(s) + {}^1/_2Br_2(g) = \overline{VCl_3Br}(g) \qquad (8)$$

where the barred formula indicates the average composition of the vanadium(IV) halide vapor. It is interesting and pertinent that the $\Delta H°$ for this reaction is the same as that found for the reaction between VBr_3(s) and bromine.[3a] The following calculations can be made for the reactions of chlorine with VCl_3 and bromine with VBr_3

Reaction	$\Delta H°$, kcal.	T, °K.	Ref.
$VCl_3(s) + {}^1/_2Cl_2(g) = VCl_4(g)$	6.9	440	5
$VCl_3(g) = VCl_3(s)$	−46.5	440	3b
$Cl(g) = {}^1/_2Cl_2(g)$	−29.0		14
$VCl_3(g) + Cl(g) = VCl_4(g)$ (9)	−68.6	440	
$VBr_3(s) + {}^1/_2Br_2(g) = VBr_4(g)$	15.8	600	3a
$VBr_3(g) = VBr_3(s)$	−43.3	600	3b
$Br(g) = {}^1/_2Br_2(g)$	−23.0		14
$VBr_3(g) + Br(g) = VBr_4(g)$ (10)	−50.5	600	

The heats of reactions 9 and 10 can be used as a rough measure of the heat of formation of an additional V–Cl bond and V–Br bond, respectively, from the gaseous trihalide. A similar calculation for the reaction

$$VCl_3(g) + Br(g) = VCl_3Br(g) \qquad (11)$$

yields a heat of −52.4 kcal. at 600°K., using 45.2 kcal. for the heat of sublimation of VCl_3 at this temperature[3b] and 15.8 kcal. for (7). The close agreement of the heats calculated for reactions 10 and 11 lends support to the assertion that VCl_3Br is the principal species formed in the reaction between VCl_3 and bromine in the diaphragm gage, since the heat change is close to that expected for the establishment of a V–Br bond.

From the equilibrium data for the reaction between VCl_2Br(s) and bromine are derived $\log K$ (atm.$^{1/2}$) = $-3460/T + 5.30$ and $\Delta H° = 15.8 \pm 1.5$ kcal., $\Delta S° = 24.2$ e.u., over the range 536 to 700°K. These data are relevant to the reaction

$$VCl_2Br(s) + {}^1/_2Br_2(g) = \overline{VCl_2Br_2}(g) \qquad (12)$$

where the barred formula again denotes the average

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[12] L. L. Handy and N. W. Gregory, *J. Am. Chem. Soc.*, **74**, 891 (1952).

[13] A. F. Wells, "Structural Inorganic Chemistry," Third Ed., Oxford at the Clarendon Press, London, 1962, p. 128.

[14] T. Cottrell, "The Strengths of Chemical Bonds," Butterworths Scientific Publications, London, 1958.

composition of the vanadium(IV) halide vapor. In this reaction no further replacement of chlorine by bromine in the solid VCl_2Br was noticed during the transport experiments. As indicated previously no evidence for the occurrence of undecomposed VCl_4 was found during the transport reactions and thus it is not considered to be an important species in the vapor generated by (12). The heat of this reaction also is consistent with the formation of mixed halides, of which VCl_2Br_2 should be the most important. Because the heat of sublimation of VCl_2Br is not known, a detailed calculation of the type shown for (9), (10), or (11) is not possible. However, if it is assumed that the heat of sublimation of VCl_2Br is intermediate to those of VCl_3 and VBr_3, then a value for the heat of reaction 13

$$VCl_2Br(g) + Br(g) = VCl_2Br_2(g) \qquad (13)$$

very close to the value for (10) would be obtained.

In conclusion, it appears that mixed halides of vanadium(IV) are formed in the vapor produced by reaction of bromine with VCl_3 or $VCl_{3-x}Br_x$, but the relative abundance of the individual species must await further investigation.

Transport of VCl_2 and VBr_2 in Iodine Vapor.—The reaction of iodine vapor with VCl_2 in a sealed tube under a controlled temperature gradient, where iodine was maintained at 130 to 180° and VCl_2 at 350 to 400°, resulted in the vaporization of VCl_2 and the growth of large green platelets approximately 4 mm. square in a region of the tube at *ca.* 275°. X-Ray patterns of the deposited material showed that the crystals were pure VCl_2, a result also readily apparent from the characteristic color and shape of the crystals. That a mixed, higher halide of vanadium was formed in the reaction, and was responsible for the transport of the $VCl_2(s)$, is certain. The vapor pressure[3b] of VCl_2 at 400° is estimated to be only *ca.* 1×10^{-6} mm. and thus sublimation could not account for the observed transport of material. Because the vanadium(III) halides also have relatively low vapor pressures in the experimental temperature range it does not seem likely that vanadium(III) halide vapors could account for the observed transport. The most likely explanation lies in the formation of a mixed halide of vanadium(IV) in the reaction, possibly $VCl_2I_2(g)$. Such a species should only be stable in the gaseous phase and may account for the fact that only VCl_2 was recovered from the reaction.

In a similar reaction of $CrCl_2$ with iodine Handy and Gregory[12] obtained the mixed halide $CrCl_2I$ as the stable solid phase. In view of the otherwise close analogy between the mixed halides of vanadium(III) obtained in this work and those of chromium(III) the formation of VCl_2I was expected. If the compound VCl_2I exists its dissociation pressure of iodine must be greater than 1 atm. at *ca.* 275°. A more detailed study of the reaction between VCl_2 and iodine has been undertaken in order to identify the important vapor species.

Under conditions identical with those used for VCl_2 the reaction of VBr_2 with iodine proceeded to give a deposit of the mixed halide VBr_2I. The structure of VBr_2I has been discussed above and the lattice constants are given in Table I. The argument for the formation of $VBr_2I_2(g)$ in order to account for the transport and formation of $VBr_2I(s)$ is similar to that given for the formation of $VCl_2I_2(g)$.

CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND
DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA

Vaporization Reactions of Vanadium(III) Bromide. Dissociation and Disproportionation Equilibria, and the Formation of Vanadium(IV) Bromide[1a]

BY ROBERT E. MCCARLEY AND JAMES W. RODDY[1b]

Received May 13, 1963

The equilibria $VBr_3(s) = VBr_2(s) + {}^1/_2Br_2(g)$ (1) and $2VBr_3(s) = VBr_2(s) + VBr_4(g)$ (2) were studied over the range 644 to 805°K. by transpiration in helium. For (1) $\Delta H° = 23.1 \pm 0.9$ kcal./mole and $\Delta S° = 10.6 \pm 0.4$ e.u., while for (2) $\Delta H° = 37.7 \pm 1.3$ kcal./mole and $\Delta S° = 34.7 \pm 1.2$ e.u. Both transpiration in bromine vapor and static pressure measurements using a glass diaphragm gage showed that $VBr_3(s)$ vaporized as $VBr_4(g)$ in the presence of bromine according to $VBr_3(s) + {}^1/_2Br_2(g) = VBr_4(g)$ (3). The transpiration measurements gave for (3) $\Delta F° = 15.80 \times 10^3 - 23.9T$ for $T =$ 515–585°K. Solid VBr_4 was isolated by condensation of the vapor at −78° and was found to be stable at −45°. At higher temperatures the solid decomposed to $VBr_3(s)$ and bromine.

Introduction

During a study of the vaporization of vanadium(III) bromide by the effusion method[2] it was noticed that a volatile vanadium bromide was formed by decomposition of the sample. After escaping from the effusion cell a portion of the vanadium halide vapors was condensed in a trap at −196° along with small amounts of bromine. It thus appeared that in addition to the

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[1] (a) Contribution No. 1213. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission; (b) a portion of a thesis submitted by J. W. Roddy to the Iowa State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] R. E. McCarley and J. W. Roddy, *Inorg. Chem.*, **3**, 60 (1964).