Preparation of Vanadium(v) Oxide Tribromide, Vanadium(iv) Oxide Dibromide, and their Reactions with Ammonia

By **Augustinos Anagnostopoulos, David Nicholls,*** and **Michael E. Pettifer,** Donnan Laboratories, The University, Liverpool L69 3BX

Vanadium(v) oxide tribromide can be prepared in good yield by the reaction between vanadium(v) oxide trichloride and hydrogen bromide at 0°. Vanadium(iv) oxide dibromide is obtained by thermal decomposition of vanadium(v) oxide tribromide. Both these halides are soluble in liquid ammonia; $VOBr_2$ gives the penta-ammoniate $[VO(NH_3)_5]Br_2$, while $VOBr_3$ undergoes ammonolysis and reduction.

THE little known vanadium(v) oxide tribromide has heretofore been prepared by the high temperature bromination of vanadium oxides under a variety of conditions;[1-3] all such methods give low yields of the thermally unstable oxide tribromide. The preparation of vanadium(IV) oxide dibromide has also presented difficulties being obtained, *e.g.*, from $VOBr_3$,[1-3] by the action of bromine and sulphur monobromide on V_2O_5 in the presence of sulphur[4] and by the reaction of $VOCl_3$

---

[1] H. E. Roscoe, *Phil. Trans.*, 1870, **160**, 316; *Proc. Roy. Soc.*, 1870, **18**, 316; *J. Chem. Soc.*, 1871, **24**, 23.

[2] A. G. Loomis and H. Schlundt, *J. Phys. Chem.*, 1915, **19**, 734.

[3] F. G. Nunez and E. Figuera, *Compt. rend.*, 1938, **206**, 437.

[4] O. Ruff and H. Lickfett, *Chem. Ber.*, 1911, **44**, 2534.

with boron tribromide.[5] We now report simple high yield preparations of both halides and on their reactions with liquid ammonia.

RESULTS AND DISCUSSION

When vanadium(V) oxide trichloride is saturated with dry hydrogen bromide at 0°, halogen exchange occurs and vanadium(V) oxide tribromide is formed. This may be purified by distillation *in vacuo*; if vanadium(IV) oxide dibromide is required, the oxide tribromide may be decomposed *in situ* by heating to 160° in a current of hydrogen bromide. The direct reaction between $VOCl_3$ and hydrogen bromide at 160° does not give pure $VOBr_2$, contamination from chloride ions occurring. This preparation of $VOBr_3$ is analogous to that of $TiBr_4$ from $TiCl_4$;[6] it is somewhat surprising however that there is insignificant reduction of vanadium(V) by hydrogen bromide at 0°.

Vanadium(IV) oxide dibromide gives a brown solution in liquid ammonia at −37°. Evaporation of this solution gives a grey-brown residue of $[VO(NH_3)_5]Br_2$. The i.r. spectrum of this product confirms the absence of ammonium bromide and the magnetic moment confirms that no reduction has occurred. The reflectance spectrum of this compound shows two bands in the visible region, *i.e.* at 14 600 and 18 500 cm^{-1}, typical of oxovanadium(IV) complexes.[7] Since the two lowest energy bands in $[VO(H_2O)_5]^{2+}$ are at 13 060 and 16 000 cm^{-1}, our formulation of the penta-ammoniate as containing the $[VO(NH_3)_5]^{2+}$ ion is in accord with the relative positions of water and ammonia in the spectrochemical series.

Thermal decomposition of the penta-ammine at 120° *in vacuo* yields the grey $VOBr_2(NH_3)_2$. The i.r. spectrum of this compound shows ν(V–O) at 871 cm^{-1} and ν(V–Br) at 300 cm^{-1}. This is compatible with a six-co-ordinate polymeric structure with V–O–V bridges. Established five-co-ordinate complexes of the $VOBr_2L_2$ type[8] have their highest ν(V–Br) above 320 cm^{-1} and ν(V–O) in the region 940—1012 cm^{-1}. The electronic spectrum (diffuse reflectance) of $VOBr_2(NH_3)_2$ is identical in band shape to that of $[VO(NH_3)_5]^{2+}$ but with the two lowest energy *d–d* bands shifted to 10 600 and 15 100 cm^{-1} as expected for bromide co-ordination.

When $VOBr_3$ reacts with liquid ammonia at −37°, a dark brown solution is formed and nitrogen is slowly evolved. Removal of the excess of ammonia at the end of the reaction gives a grey-brown residue of composition $VOBr_3,6{\cdot}5NH_3$ at −37° which becomes $VOBr_3,6{\cdot}0NH_3$ at 0° and approximately $VOBr_3,5{\cdot}9NH_3$ at 20°. This room temperature composition varied somewhat from experiment to experiment, becoming closer to $VOBr_3,5{\cdot}7NH_3$ when the mixture was evacuated at 20° for many hours. The i.r. spectrum of this residue is quite different to that of $VOBr_2(NH_3)_5$ and indicates the presence of ammonium bromide. Vapour pressure–composition (NH_3/V) isotherms for the systems $VOBr_3$–NH_3 and ' $VOBr_3,6NH_3$ '–NH_3 at −37° both show univariant portions 3·0 mole ratios long at the vapour pressures corresponding to each of the dissociations:[9]

$$NH_4Br,3NH_3 \rightleftharpoons NH_4Br,1{\cdot}5NH_3 + 1{\cdot}5NH_3$$
$$NH_4Br,1{\cdot}5NH_3 \rightleftharpoons NH_4Br + 1{\cdot}5NH_3.$$

It is evident therefore that ' $VOBr_3,6NH_3$ ' contains $2NH_4Br$. The magnetic moment and electronic spectrum of this mixture confirms that the vanadium has been reduced to the +4 oxidation state. The two lowest energy (*d–d*) transitions in the reflectance spectrum are at 13 400 and 16 800 cm^{-1}; by comparison with the band positions for $[VO(NH_3)_5]^{2+}$ and $VOBr_2(NH_3)_2$ these figures indicate some bromide ion co-ordination to vanadium in the mixture. Accordingly, we formulate $VOBr_3,6NH_3$ as $VO(NH_2)Br(NH_3)_3 + 2NH_4Br$. The vanadium species is evidently not a stable phase at room temperature, some decomposition to a lower ammoniate occurring.

Since $VOBr_2$ is not ammonolysed in liquid ammonia the ammonolytic product of $VOBr_2$ must arise by virtue of the initial ammonolysis of $VOBr_3$ occurring prior to reduction. A simplified reaction scheme (neglecting co-ordinated ammonia molecules) is

$$VOBr_3 + 2NH_3 \xrightarrow{\text{fast}} VOBr_2(NH_2) + NH_4Br$$

$$VOBr_2(NH_2) + 4/3NH_3 \xrightarrow{\text{slow}} VOBr(NH_2) + 1/6N_2 + NH_4Br$$

Thus two moles of ammonium bromide are produced per vanadium, one of these comes from ammonolysis and the other arises from reduction of the vanadium. This reduction can be visualised as electron transfer from a co-ordinated bromide ion to vanadium, the bromine produced reacting with ammonia to give nitrogen and ammonium bromide. Whilst this reduction is expected ($VOBr_3$ is reduced by neutral donor molecules as well as by bromide ions[8,10]) the ammonolysis reaction differs from that reported[11] for $VOCl_3$. This latter halide reacts with ammonia at −10° according to

$$3VOCl_3 + 19NH_3 \xrightarrow{\text{fast}} 3VOCl_2(NH_3)_5 + 3NH_4Cl + 1/2N_2$$

cf. our reaction with $VOBr_3$:

$$3VOBr_3 + 19NH_3 \xrightarrow{\text{slow}} 3VOBr(NH_2)(NH_3)_3 + 6NH_4Br + 1/2N_2$$

Upon washing with liquid ammonia, the $VOCl_2(NH_3)_5$ is reported to undergo partial ammonolysis and some reduction to the +3 oxidation state.

Thermal decomposition of the mixture of composition $VOBr_3,6NH_3$ results in the evolution of three moles of

---

[5] P. M. Druce and M. F. Lappert, *J. Chem. Soc.* (*A*), 1971, 3595.

[6] R. B. Johannesen and C. L. Gordon, *Inorg. Synth.*, 1967, **9**, 46.

[7] J. Selbin, *Co-ordination Chem. Rev.*, 1966, **1**, 293.

[8] D. Nicholls and K. R. Seddon, *J.C.S. Dalton*, **1973**, 2751.

[9] E. Bannister and G. W. A. Fowles, *J. Chem. Soc.*, 1958, 4374.

[10] D. Nicholls and K. R. Seddon, *J.C.S. Dalton*, **1973**, 2747.

[11] N. I. Vorob'ev, L. V. Kobets, S. S. Gusev, and Yu. A. Raikov, *Russian J. Inorg. Chem.*, 1970, **15**, 117.

ammonia by 210°. However, although ammonium bromide sublimes out of the hot zone, pure $VOBr(NH_2)$ could not be isolated as the residue because of some reaction with ammonium bromide above 150° (which resulted in some volatilisation of vanadium).

EXPERIMENTAL

Preparation of Vanadium(V) *Oxide Tribromide*.—Hydrogen bromide was dried by passage through concentrated sulphuric acid (traces of Br_2 and SO_2 do not interfere) and passed through $VOCl_3$ (30 g) in a flask cooled in ice–water. The mixture darkened and ultimately assumed the dark red-brown colour and high specific gravity of $VOBr_3$ (1—2 h are necessary to ensure complete halogen exchange). The flask was transferred to a vacuum line under a dry nitrogen atmosphere and the more volatile contents (bromine and any unreacted $VOCl_3$) removed *in vacuo* at 20°. The remaining $VOBr_3$ was then distilled from traces of $VOBr_2$ by warming to 60—80°, the first fraction (10%) being discarded (yield 25—40 g, 47—75%). The $VOBr_3$ was stored at $-78°$ and redistilled immediately prior to use (Found: Br, 77·6; V, 16·7; Cl (by trace analysis), 0·0; Br_3OV requires Br, 78·18; V, 16·62%).

Preparation of Vanadium(IV) *Oxide Dibromide*.—$VOCl_3$ was saturated as above with hydrogen bromide except that room temperature was conveniently used without detrimental effect. With hydrogen bromide still passing through the apparatus the temperature of the flask was raised to 160° when rapid decomposition of $VOBr_3$ occurred. When the liberation of bromine ceased, the flask and contents were allowed to cool and dry nitrogen flushed through the apparatus to displace hydrogen bromide. The cold flask was then transferred to the vacuum line and any volatile materials removed *in vacuo* at room temperature. The $VOBr_2$ left in the flask was an olive-brown powder but sometimes appeared black especially when the sample had been in direct contact with the glass surface (Found: Br, 70·2; V, 22·3; Cl (by trace analysis), 0·0; Br_2OV requires Br, 70·47; V, 22·47%).

Reaction of Vanadium(V) *Oxide Tribromide with Ammonia*.—Liquid ammonia (50 ml) was distilled on to $VOBr_3$ (5 g) and the resulting dark brown solution kept at $-37°$ until no further non-condensible gas was evolved (4—5 days). Evaporation of the ammonia at $-33°$ followed by evacuation of the residue at room temperature for 2 h gave a grey-brown solid (Found: Br, 58·8; V, 12·3; NH_3, 24·0; μ_{eff}(20°) 1·6 B.M.; $VOBr_3(NH_3)_6$ requires Br, 58·65; V, 12·49; NH_3, 24·98%). When this solid was thermally decomposed stepwise *in vacuo* (to 210°), ammonia was steadily evolved and NH_4Br sublimed at 155°; no intermediate stable phases were observed, the residue and sublimate at 210° having the composition '$VOBr_3$,3·0NH_3'.

Reaction with Vanadium(IV) *Oxide Dibromide with Ammonia*.—$VOBr_2$ (2 g) was dissolved in liquid ammonia (150 ml) (it was considerably less soluble than $VOBr_3$) and the excess of ammonia removed *in vacuo* at $-33°$ and finally at room temperature. A grey-brown solid remained (Found: Br, 51·0; V, 16·5; NH_3, 26·9%; μ_{eff}(20°) 1·7 B.M.; $VOBr_2(NH_3)_5$ requires Br, 51·25; V, 16·34; NH_3, 27·28%). When this solid (2·733 g) was heated *in vacuo*, negligible decomposition occurred up to 70°; thereafter ammonia was evolved, the decomposition being fast at 120° and leaving a grey residue (2·300 g) (Found: Br, 61·0; V, 19·9; NH_3, 12·9; weight loss 15·84%, μ_{eff}(20°) 1·6 B.M.; $VOBr_2(NH_3)_2$ requires Br, 61·30; V, 19·54; NH_3, 13·05; weight loss 16·36%. This residue was stable up to 200°.

Instrumental and Analytical Methods.—These were carried out as described previously;[9,12] chlorine trace analysis was performed by the Alfred Bernhardt Mikroanalytisches Laboratorium.

One of us (A. A.) thanks the National Hellenic Research Foundation for leave of absence and the Royal Society for financial assistance.

[3/2032 *Received*, 3*rd October*, 1973]

---

[12] I. M. Griffiths, D. Nicholls, and K. R. Seddon, *J. Chem. Soc.* (*A*), 1971, 2513.