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On the Thermal Decomposition of *Trans*-Dibromotetraaquovanadium(III) Bromide, $[VBr_2(H_2O)_4]Br\cdot 2H_2O$*

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The thermal decomposition of $[VBr_2(H_2O)_4]Br\cdot 2H_2O$, I, *in an argon atmosphere proceeds mainly toward producing* V_2O_3*; a small fraction of V(III), less than 5%, disproportionates into* $VOBr_2$ *and a V(II) intermediate which is oxidized* in situ *with the corresponding evolution of hydrogen. The decomposition of* I *in steam proceeds similarly to that in argon up to about 500 °C. At higher temperatures additional hydrogen is evolved and mixtures of* V_4O_7 *and* V_5O_9 *are the final products.*

Our interest in the chemistry of vanadium bromides stemmed from the possibility of using these compounds as intermediates in a thermochemical subcycle for decomposing HBr. Such a process would be of considerable value in the development of thermochemical cycles for the production of hydrogen from water. At present, one of the leading candidate cycles being developed consists of three reactions: one that generates H_2SO_4 and HBr from SO_2, Br_2 and H_2O; another that decomposes H_2SO_4 thermally, and the third that decomposes HBr electrolytically [1]. Since the energy efficiency of electrolytic decomposition reactions are affected by the inherent relatively low-efficiency of conversion of heat to electricity, the replacement of an electrolytic step by a purely thermal one offers the possibility of increasing the overall efficiency of the hydrogen producing cycle. Preliminary calculations with available thermochemical data [2] suggested that, under certain conditions, the following reactions would take place:

$$2VBr_3 \xrightarrow{\geqslant 800^\circ C} 2VBr_2 + Br_2 \qquad (1)$$

$$2VBr_2 + 3H_2O \xrightarrow{\geqslant 400^\circ C} V_2O_3 + 4HBr + H_2 \qquad (2)$$

$$V_2O_3 + 6HBr \xrightarrow{100-150^\circ C} 2VBr_3 + 3H_2O \qquad (3)$$

The sum of reactions (1)–(3) is $2HBr \rightarrow H_2 + Br_2$. Reactions (1) and (2) reportedly have been experimentally demonstrated [3], although other workers have shown that, parallel to reaction (1), VBr_3 disproportionates into VBr_2 and VBr_4, the latter being thermally unstable [4, 5]. For reaction (3) we calculated that 80% and 43% of HBr, respectively, would react at 100 °C and 150 °C for a system at equilibrium at a total pressure of 10^5 Pa. Because reaction (3) had not been demonstrated, it was chosen for testing. Various experimental configurations and various mixtures of HBr(g) with N_2 or Ar at various temperatures up to 980 °C were initially used. Except for the sublimation of traces of vanadium bromides or oxybromides [very likely present as V(IV) or V(V) on the surface of the starting material, V_2O_3], no reaction occurred. A likely explanation for this behavior, typical for this type of reaction, is that it is kinetically limited.

Because it was known that V_2O_3 dissolves in HBr(aq) yielding $[VBr_2(H_2O)_4]Br\cdot 2H_2O$, *I*, generally written as $VBr_3\cdot 6H_2O$ [3], we decided to prepare *I* and to study its thermal behavior because data available on this and similar compounds was very confusing. Amirova *et al.* [3] reported that the two waters of hydration can be removed by heating in argon at temperatures up to 170 °C, while at higher temperatures, *e.g.*, 380 °C, hydrolysis occurs as evidenced by evolution of HBr (83% of the expected for complete hydrolysis). The compounds formed during the hydrolysis were not unequivocally identified although the authors concluded from IR spectra that $VOBr_2$ was present at temperatures up to 385 °C. They further concluded, by analogy with the reported behavior of $VOCl_2$, that $VOBr_2$ disproportionates at 490 °C into $VOBr_3$ and VOBr. However, Nicholls and Wilkinson [6] report that heating $VBr_3\cdot 6H_2O$ for 12 h at 212 °C in vacuo led to pure VOBr. Additional available information reveals that the thermal behavior, structures and IR spectra of the various vanadium oxybromides are not well known. It has also been reported that $VOBr_3$ decomposes to $VOBr_2$ and Br_2 at 160 °C in a current of HBr(g) [7], and that it decomposes slowly at room temperature and instantaneously at 180 °C in the absence of HBr [8].

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The solid $VOBr_2$ has been reported to sublime at 320 °C and start to decompose into VOBr and Br_2 at 350 °C under vacuum [9]; to start decomposing at temperatures slightly above room temperature and probably faster at about 260 °C [10]; and, as mentioned above, to disproportionate into $VOBr_3$ and VOBr at 490 °C [3].

VOBr has been reported to decompose to V_2O_3 and VBr_3 under reduced pressure at 480 °C [9] or at 350 °C under vacuum [11], and has been reported to decompose to VO and Br_2 in the temperature range 315–495 °C while going through an intermediate $VOBr_{0.5}$ [10].

The data available on IR spectra of VO^{2+} also reflect to some extent that oxodihalides of vanadium have not been sufficiently identified. The V–O stretching vibration of such compounds, with and without various ligands (including some VO^{3+} compounds), falls in the range of 870–1035 cm^{-1} (7 and 12 a–f).

The above inconsistent results, and especially the reported observation [3] that compound *I* converts to $VOBr_2$ which suggests that hydrogen may be evolved, led us to study the thermal decomposition of *I* emphasizing the search for the hydrogen evolved in the reaction.

Experimental

Compound *I* was synthesized by refluxing typically 16.4 g of 99.7% vanadium powder (325 mesh, Cotronics), with 120 ml 48% HBr(aq) (Mallinckrodt) at 100 °C for 4 h [13]. This and all subsequent steps were carried out in the presence of a continuously flowing stream of argon. The resulting green solution was filtered and then concentrated to about half of its original volume by distillation. Large green crystals formed when the system was cooled slowly to 0 °C. This product was collected by filtration and stored in a vacuum desiccator over $Mg(ClO_4)_2$. Because of the compound's facile oxidation by traces of air, we used the once-crystallized product for subsequent experiments without further purification. *Anal.* Calc. for $VBr_3H_{12}O_6$: V, 12.78; Br, 60.12%. Found: V, 12.68; V(III), 12.68; Br, 61.6%.

The thermal decomposition of *I* in the presence of flowing gases (Ar, and mixtures of Ar-steam) was studied in the following manner: Samples of *I* (1–2 g) were weighed into Pt boats which were quickly inserted into fused quartz reaction tubes and purged with dry Ar (flow rate 100 ml min^{-1}). Each reaction tube was fitted with a quartz thermocouple well and with Teflon gas inlet and exit lines. Steam was supplied at 100 °C and heated to ~250 °C in a nickel container where it was mixed with Ar prior to entering into the reaction tube. The Ar carrier gas transported reaction products and unreacted $H_2O_{(g)}$ through (a) a water-cooled condenser, (b) a trap containing aqueous NaOH (2–12 *N*), and (c) a $CaSO_4$ drying column. Evolution of acidic gases was monitored by titration of the condensed steam and/or samples taken from the NaOH trap. The gases then passed through a Beckman 741 Oxygen Analyzer (for ascertaining the absence of air), a Gow-Mac 20–150 thermal conductivity cell calibrated for H_2 in Ar, and finally through a Wet Test flow meter. A horizontal tube furnace equipped with a pre-programmed thermal controller heated the samples at a uniform rate, usually 2–5 °C min^{-1}.

Vacuum experiments were conducted in glass or quartz tubes at pressures less than 0.2 Pa. A sand-filled box furnace was used to heat the samples. Samples of the evolved gases were collected in Urrey-tubes by freezing with liquid nitrogen and these gases were analyzed by F.T. IR.

Simultaneous thermogravimetry/differential thermal analyses (TGA/DTA) were run on a Mettler Thermoanalyzer 1 instrument. Samples of *I* (100 mg) were heated in a Pt-10% Rh crucible under a stream of dry, purified Ar (flow rate 5.72 l min^{-1}). The DTA reference material was finely ground alumina. In various runs, constant heating rates ranged from 0.2 to 10 °C min^{-1}. All solid reaction products were transferred into a dry box where samples were prepared for elemental analysis and for characterization by IR and powder X-ray diffraction. The KBr pellets containing the various solids prepared for IR spectroscopy under an inert atmosphere changed color very rapidly on exposure to air in the instrument indicating probable hydrolysis and/or oxidation. Thus, the results were considered invalid and will not be reported.

Results and Discussion

In general, our TGA/DTA results agree with those of Amirova *et al.*, [3], although our interpretation is necessarily different. Between 50 and 94 °C, samples of *I* typically lost 9.76–9.79% of their original weight in an endothermic reaction. This corresponds to the weight of 2.18 mol H_2O per mol vanadium. At 94 to 160 °C, both H_2O and HBr are evolved endothermically, with about 80% of the observed 33.91% weight loss occurring at a rate of 1.5–2.2 mg °C^{-1} between 135 and 155 °C. This observation agrees well with the 33.58% calculated for the loss of $3H_2O$ and 1 HBr. If this interpretation were correct, the remaining solid should have the composition $VBr_2(OH)(H_2O)$; subsequent tube furnace experiments confirmed that the Br/V ratio in samples heated to 180 °C is about 2.2. Between 160 and 410 °C, weight loss is very slow (less than 0.17 mg °C^{-1}); the observed 36.16% decrease is less than the 40.26% calculated for removal of 4HBr. Upon cooling from 425 °C to room temperature, the samples typically lost an additional 0.6 to 0.9%, giving an overall weight loss of 80.7%. According to X-ray analysis, the product was essentially pure V_2O_3. For conversion of $[VBr_2(H_2O)_4Br\cdot 2.18H_2O$ into V_2O_3, the expected weight loss is 81.36%. These results, together with analysis of the gases collected in vacuum experiments leads us to propose the following reactions for the bulk of thermal decomposition of $[VBr_2(H_2O)_4Br\cdot 2H_2O$:

$$[VBr_2(H_2O)_4]Br\cdot 2H_2O \xrightarrow[-2H_2O]{\text{up to } 94\,^\circ C} [VBr_2(H_2O)_4]Br + 2H_2O \tag{4}$$

$$[VBr_2(H_2O)_4]Br \xrightarrow[-2H_2O,HBr]{120-190\,^\circ C} [V(OH)(H_2O)Br_2] + 2H_2O + HBr \tag{5}$$

$$[V(OH)(H_2O)Br_2] \xrightarrow[-2HBr]{190-420\,^\circ C} [VO(OH)] + 2HBr \tag{6}$$

$$[VO(OH)] \xrightarrow{420-1000\,^\circ C} VO_{1.5} + 1/2H_2O \tag{7}$$

The product of reaction 6 could also be formulated '$V_2O_3\cdot H_2O$'. (H_2 found: 1.4 wt.%, expected 1.2 wt.%).

The main overall decomposition reaction for *I* can be represented thus by the sum of eqns. (4) to (7):

$$[VBr_2(H_2O)_4]Br\cdot 2H_2O \rightarrow 1/2V_2O_3 + 3HBr + 9/2H_2O \tag{8}$$

The experiments performed in the tube furnace which involved the continuous measurement of the hydrogen evolved indicated that indeed small amounts of $H_{2(g)}$ [2–4% of that expected for complete conversion of V(III) to V(IV)] were evolved between 380 and 540 °C. At the same time, traces of a brown solid (probably $VOBr_2$) condensed in the cooler portion of the quartz reaction tube. We believe that both the $VOBr_2$ and the H_2 are the products of a disproportionation reaction in which the V(II) formed is oxidized by coordinated -OH or -OH_2 groups. We may speculate that the disproportionation stems from reaction (6) proceeding in two steps, the first being

$$[V(OH)(H_2O)\cdot Br_2] \rightarrow [VO(H_2O)Br] + HBr \tag{6a}$$

(where the solid product can also be written $VOBr\cdot H_2O$). This compound then would disproportionate into $VOBr_2$ and VO and the latter reduce water to hydrogen. Such a reaction can be represented by

$$2[VO(H_2O)Br] \rightarrow VOBr_2 + 1/2V_2O_3 + 3/2H_2O + 1/2H_2 \tag{9}$$

Continued heating to 1000 °C yielded V_2O_3 as the only other solid reaction product. Thus, although we confirm qualitatively the results of Amirova *et al.* [3] that the thermal decomposition of *I* produces $VOBr_2$, we can state here, based on H_2 measurements, that the amount is less than 5% of the overall decomposition reaction which leads to the formation of V_2O_3.

In attempts to enhance the production of hydrogen and speculating that water could have been evolved too rapidly to oxidize the V(II) originated by disproportionation, several portions of *I* were heated in a flowing gaseous mixture of Ar and steam ($P_{H_2O} \simeq 10^5$ Pa). With steam, hydrogen evolution was observed to occur at 320 °C, with a maximum partial pressure at 420 °C; but, the total H_2 evolved up to 500 °C was again ≤5% of that expected for total conversion to V(IV). The presence of steam also produced another difference with respect to previous experiments: no colored vapors were released and additional evolution of significant amounts of H_2 started again at 530 ± 10 °C; this reached a maximum at about 800 °C. The total amount of H_2 measured agreed very well with the X-ray diffraction analysis of the solid residues: major and minor phases present, respectively, V_4O_7 and V_5O_9. The measured weight losses also agreed quite well with these results. Thus, the behavior of $[V(H_2O)_4Br_2]Br\cdot 2H_2O$ on heating in steam can be represented mainly by:

$$4[V(H_2O)_4Br_2]Br\cdot 2H_2O \xrightarrow{H_2O(g)} V_4O_7 + 17H_2O + 12HBr + H_2 \tag{10}$$

In order to elucidate reaction (10) we exposed V_2O_3 to Ar-steam mixtures similar to those for *I*. It was found that H_2 starts to evolve at 530 ± 10 °C and reaches a maximum in the temperature range 800–1000 °C. The total H_2 evolved again agreed with the identified products, in this case V_5O_9 (major phase) and V_4O_7 (minor phase). The reaction can thus be represented by

$$5/2V_2O_3 + 3/2H_2O \rightarrow V_5O_9 + 3/2H_2 \tag{11}$$

In attempts to still find a means for splitting HBr thermally, the products of reactions (10) and (11) were heated up to 1000 °C in a stream of HBr(g) ($P_{HBr} \approx 6.7 \times 10^4$ Pa). No reaction occurred as evidenced by the absence of bromine evolution, by the constancy of weight and by the X-ray diffraction patterns of the solids.

Conclusions

It can be concluded from the above results that the thermal decomposition of $[VBr_2(H_2O)_4]Br\cdot 2H_2O$, *I*, leads mainly (≥95%) to the formation of V_2O_3 with a concurrent small yield (≤5%) of $VOBr_2$ and hydrogen in contradiction to work reported in ref. 3.

Attempts to prepare pure VOBr by decomposition of *I* were unsuccessful under the experimental conditions given in ref. 6 (12 h at 212 °C); in an isolated instance we were able to identify the presence of VOBr by X-ray diffraction in samples heated at 500 °C for 3 h. The reaction of *I* with steam can be interpreted without difficulty: *I* decomposes essentially to V_2O_3 and this is then oxidized by the steam to higher oxides of vanadium and hydrogen. Based on our experience we are led to believe that the inconsistencies reported in the literature regarding the thermal behavior of the various vanadium oxybromides may be due to the presence in their sphere of coordination of different amounts of protonated species (OH^- and/or H_2O).

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