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THERMAL DECOMPOSITIONS OF $(NH_4)_2WSe_4$ AND $(NH_4)_3VS_4$ UNDER NORMAL AND REDUCED NITROGEN PRESSURES

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The thermal decomposition of ammonium tetraselenotungstate and ammonium tetrathiovanadate was studied by simultaneous TG, DTG and DTA and by dissociation pressure measurements. The tetraseleno compound shows different modes of decomposition under reduced and normal nitrogen pressures. The tetrathiovanadate decomposes to V_2S_5, ammonia and hydrogen sulphide both under normal and reduced nitrogen pressures. The approximate enthalpies of decomposition are also reported.

In previous communications [1, 2] results were reported on the thermal decompositions of some ammonium salts of thiomolybdates and thiotungstates. The thermochemical data presented in these papers were obtained by means of a Derivatograph [1] and dissociation pressure measurements [2]. In the present communication we report results on the thermal decompositions of ammonium tetraselenotungstate, $(NH_4)_2WSe_4$, and ammonium tetrathiovanadate, $(NH_4)_3VS_4$, obtained by the two methods mentioned above. The thermal results were obtained under reduced and normal nitrogen pressures, the dissociation pressures were measured under high vacuum (10^{-4} torr).

Experimental

Ammonium tetraselenotungstate and ammonium tetrathiovanadate were prepared according to Lenher and Fruehan [3] and Krüss and Ohnmias [4], respectively. Measurements were made using a Mettler Thermal Analyser in the temperature range ambient to 800°, using a heating rate of 10° per minute. Dissociation pressure measurements were made with an apparatus described previously [2].

Results and discussion

Thermal decomposition of $(NH_4)_2WSe_4$: The thermal decomposition of the tetraselenotungstate is very complex. The compound exhibits different modes of decomposition under normal and reduced nitrogen pressures. Decomposition under

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reduced nitrogen pressure (11 mm Hg) follows the same course as that under high vacuum [5]:

$$(NH_4)_2WSe_4(s) = 2NH_3(g) + H_2Se(g) + WSe_3(s) \quad (1)$$

$$WSe_3(s) = WSe_2(s) + Se(g) \quad (2)$$

$$WSe_2(s) = W(s) + 2Se(g) \quad (3)$$

The temperatures characterizing different events in the decomposition process vary with the conditions prevailing in the furnace, of course.

The thermal decomposition data for the decomposition under reduced nitrogen pressure are given in Table 1. The calculated and observed weight losses for the

Table 1

Thermal data on decomposition of ammonium tetraselenotungstate under reduced nitrogen pressure

No.	Event	Temperature, °C
1.	Stability of the compound	ambient to 150°
2a.	Decomposition to WSe_3, H_2Se and ammonia	150°
b.	DTG peak	202°
c.	DTA peak (endothermic)	200°
d.	Completion of decomposition	ca. 230°
3a.	Stability of the intermediate (WSe_3)	ca. 230—305°
b.	Decomposition of WSe_3 to WSe_2 and Se	ca. 305°
c.	Completion of decomposition	ca. 470°

Table 2

Weight loss data for thermal decomposition of ammonium tetraselenotungstate under reduced nitrogen pressure

Wt. loss for first step		Wt. loss for second step	
Calcd., %	Obs., %	Calcd., %	Obs., %
21.4	21.5	14.8	15.8

first step agree with reaction 1 (Table 2). The calculated and observed weight losses for the second step corresponding to reaction 2 also agree well.

Decomposition under normal nitrogen pressure follows a different course. The thermal decomposition data are recorded in Table 3 and the weight loss data in Table 4. As can be seen from these Tables, the decomposition under normal nitrogen pressure follows a different course. The calculated and observed weight losses for the first and second steps do not agree, whereas the calculated and observed weight losses for the two steps combined agree satisfactorily.

Table 3

Thermal data on decomposition of ammonium tetraselenotungstate under normal nitrogen pressure

No.	Event	Temperature, °C
1.	Stability of the compound	ambient to 180°
2a.	Decomposition of the compound to WSe_3, etc.	180°
b.	DTG peak	245°
c.	DTA peak (endothermic)	250°
d.	Completion of decomposition	ca. 260°
3a.	Stability of the intermediate (WSe_3 + Se)	260–380°
b.	Decomposition of the intermediate	ca. 380°
c.	Completion of decomposition	ca. 560°

This anomalous behavior under normal nitrogen pressure may be accounted for if the probable decomposition of the hydrogen selenide formed in the first step is considered. Under these conditions, selenium is deposited in the range 180–260°, giving a low value for the weight loss for the first step, in accordance with observations. The selenium thus deposited volatilizes at higher temperatures, leading to a higher weight loss for the second step, also in agreement with observations. Thus, even though the theoretical and observed weight losses do not agree

Table 4

Weight loss data for thermal decomposition of ammonium tetraselenotungstate under normal nitrogen pressure

Wt. loss for first step		Wt. loss for second step	
Calcd., %	Obs., %	Calcd., %	Obs., %
21.4	14.0	14.8	21.0
Wt. loss for the two steps combined:		Calcd. % 36.2	Obs. % 35.0

separately for the first and second steps, they do agree for the two steps combined. The probable reaction scheme for the decomposition under normal nitrogen pressure may therefore be written as follows:

1st step

$$(NH_4)_2WSe_4 = 2NH_3(g) + H_2Se(g) + WSe_3 \quad (4)$$

$$H_2Se(g) = H_2(g) + Se \text{ (partially)} \quad (5)$$

2nd step

$$WSe_3(s) = WSe_2(s) + Se(g) \quad (6)$$

$$Se(s) = Se(g) \quad (7)$$

The heat of decomposition of $(NH_4)_2WSe_4$ to WSe_3, NH_3 and H_2Se was calculated from the DTA peak obtained under reduced nitrogen pressure. A value of 47 kcal/mole of compound decomposed was obtained. The result is estimated to be accurate to $\pm(5-10)$ kcal/mole.

Dissociation pressures for decomposition of the tetraselenotungstate were measured in the range $80-102°$, each measurement being made after a minimum period of 48 hs. These values lie roughly in the range $80-210$ mm Hg.

Thermal decomposition of $(NH_4)_3VS_4$: The thermal decomposition of ammonium tetrathiovanadate follows the same course under either reduced or normal nitrogen pressure. The decomposition proceeds in two steps: first to V_2S_5, ammonia and hydrogen sulphide, and then the decomposition of V_2S_5 to V_2S_3 and gaseous sulphur. This is in agreement with the observations of Buisine and Tridot [6]; however, it is not clear from their publication whether their experiments were carried out under reduced or normal nitrogen pressure. The thermal decomposition data are given in Table 5. The calculated and observed weight losses agree well for both steps, irrespective of the nitrogen pressure (Table 6). The decomposition scheme under reduced or normal nitrogen pressure is as follows:

$$2(NH_4)_3VS_4 = 6NH_3 + 3H_2S + V_2S_5 \quad (8)$$

$$V_2S_5 = V_2S_3 + 2S \quad (9)$$

Table 5

Thermal data on decomposition of ammonium tetrathiovanadate under normal and reduced nitrogen pressures

No.	Event	Temperature, °C	
		Normal N_2 pressure	Reduced N_2 pressure
1.	Stability of the compound	amb. to 50°	amb. to 81°
2a.	Decomposition to V_2S_5, NH_3 and H_2S	ca. 50°	ca. 81°
b.	DTG peak	117°	144°
c.	DTA peak (endothermic)	118°	148°
d.	Completion of decomposition	ca. 190°	ca. 203°
3a.	Stability of V_2S_5	190–290°	203–368°
b.	Decomposition of V_2S_5 to V_2S_3 and S	ca. 290°	ca. 368°
c.	DTG peak	365°	425°
d.	DTA peak (endothermic)	372°	395–451°
e.	Completion of decomposition	ca. 400°	ca. 445°

The enthalpy change (heat of decomposition) was calculated to be 79 kcal per mole of tetrathiovanadate. This result is estimated to be accurate to $\pm(10-15)$ kcal/mole.

Table 6

Weight loss data for thermal decomposition of ammonium tetrathiovanadate under normal and reduced nitrogen pressures

Wt. loss for first step		Wt. loss for second step	
Calcd., %	Obs., %	Calcd., %	Obs., %
44.6	43.7	13.7	14.9

The dissociation pressures for decomposition of tetrathiovanadate were measured in the range 25–45°. Equilibrium pressures were measured after a period of 24 hr. These values lie roughly in the range 80–450 mm Hg.

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RÉSUMÉ — On a étudié la décomposition thermique du tétrasélénotungstate d'ammonium et du tétrathiovanadate d'ammonium à TG, TGD et ATD simultanées et par mesures des pressions de dissociation. Le tétrasélénotungstate se décompose différemment suivant que la pression d'azote est normale ou réduite. Au contraire, le tétrathiovanadate se décompose en V_2S_5, NH_3 et SH_2 à la fois sous pressions normale ou réduite d'azote. Les enthalpies approximatives de décomposition sont également données.

ZUSAMMENFASSUNG — Die thermische Zersetzung von Ammoniumtetraselenowolframat und Ammoniumtetrathiovanadat wurde simultan mit TG, DTG und DTA, und durch Dissoziationsdruckmessungen untersucht. Die Tetraselenoverbindung zeigt unterschiedliche Zersetzungen bei reduzierten und normalen Stickstoffdrucken. Das Tetrathiovanadat zerfällt sowohl bei normalen als auch bei reduzierten Stickstoffdrucken zu V_2S_5, Ammoniak und Schwefelwasserstoff. Die annähernden Enthalpien der Zersetzung werden angegeben.

Резюме — Термическое разложение тетраселеновольфрамата- и тетратиованадата аммиака было изучено с помощью TG, DTG, DTA одновременной техники и измерением давления диссоциации. Тетраселеновое соединение показывает различные типы разложения при пониженном и нормальном давлении азота. В тех же самых условиях тетратиованадат разлагается до V_2O_5, аммиака и сероводорода. Приведены также приближенные значения энтальпии разложения.