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Studies of Some Telluro-Vanadomolybdates

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Ammonium telluro-vanadomolybdate, $6(NH_4)_2O\cdot TeO_3\cdot 3V_2O_5\cdot 4MoO_3\cdot 15H_2O$, has been synthesized, its properties studied, and its composition determined by analytical methods. Copper, silver, calcium, strontium, barium and lead salts have then been prepared from the ammonium salt. D. T. A. of ammonium and strontium salts have been carried out to investigate the thermal changes. The infrared spectra of the ammonium salt and its dehydrated product have been recorded, and the characteristic frequencies assigned.

A large number of condensation products of molybdenum and vanadium have been reported.[1] Gibbs[2] prepared two heterotriammonium phosphovanadomolybdates, $8(NH_4)_2O\cdot P_2O_5\cdot 8V_2O_5\cdot 14MoO_3+50H_2O$ and $7(NH_4)_2O\cdot 2P_2O_5\cdot V_2O_5\cdot 48MoO_3+30H_2O$, by boiling ammonium phosphomolybdate with an ammonium vanadate solution. Later Blum[3] confirmed Gibbs by showing the possibility of the condensation of vanadium, molybdenum and phosphorus and by isolating $5(NH_4)_2O\cdot P_2O_5\cdot 11V_2O_5\cdot 11MoO_3\cdot 50H_2O$.

Telluric acid has been condensed to form heteropoly salts with molybdic acid,[4-6] and a series of vanadotellurites have been reported by Jena.[7]

The formation of heteropoly salts of tellurium with molybdic acid[8] and vanadium pentoxide[9] to form various salts has been studied in this laboratory. A heterotritellurovanadotungstate series[10] has also been investigated. This work is now extended to a study of the heterotrisalt formation of tellurium, vanadium and molybdenum. This paper will report the preparation of ammonium telluro-vanadomolybdate and its salts with copper, silver, calcium, strontium, barium and lead. The differential thermal analysis technique has been applied to a study of the thermal changes in the case of ammonium and strontium salts and the infrared spectra of the ammonium salt and its dehydrated product (the compound heated above 300°C) recorded in the KBr phase.

Experimental and Results

Ammonium Telluro-vanadomolybdate. — A mixture of telluric acid and 18.72 g. of ammonium metavanadate was refluxed in an ammoniacal medium for four hours. Twenty-six grams of molybdic acid dissolved in a sufficient quantity of aqueous ammonium was then added to the above solution, and the mixture was refluxed for another 8 hr. The solution was then evaporated to a small bulk and kept in a refrigerator for crystallization. The crystalline ammonium telluro-vanadomolybdate which was obtained was recrystallized and analyzed. Found: $(NH_4)_2O$, 15.98; TeO_3, 9.63; V_2O_5, 28.45; MoO_3, 31.08; H_2O, 14.86. Calcd. for $6(NH_4)_2O\cdot TeO_3\cdot 3V_2O_5\cdot 4MoO_3\cdot 15H_2O$: $(NH_4)_2O$, 16.61; TeO_3, 9.346; V_2O_5, 29.06; MoO_3, 30.65; H_2O, 14.37%.

A yellow crystalline substance highly soluble in water, the compound is decomposed by acids and alkalies.

Copper Salt.—A greenish-yellow compound was precipitated when a dilute solution of copper sulfate was added to the ammonium salt solution. Found: CuO, 24.82; TeO_3, 9.53; V_2O_5, 28.62; MoO_3, 31.08; H_2O, 5.95. Calcd. for $6CuO\cdot TeO_3\cdot 3V_2O_5\cdot 4MoO_3\cdot 6H_2O$: CuO, 25.36,; TeO_3, 9.33; V_2O_5, 29.01; MoO_3, 30.60; H_2O, 5.738%.

Silver Salt.—This is an orange yellow compound obtained by adding a dilute silver nitrate solution to the ammonium salt solution. The salt is blackened when exposed to light. Found: Ag_2O, 49.08; TeO_3, 6.62; V_2O_5, 18.92; MoO_3, 21.48; H_2O, 3.90. Calcd. for $6Ag_2O\cdot TeO_3\cdot 3V_2O_5\cdot 4MoO_3\cdot 5H_2O$: Ag_2O, 50.02; TeO_3, 6.32; V_2O_5, 19.65; MoO_3, 20.72; H_2O, 3.239%.

Calcium Salt.—When a dilute solution of calcium acetate is added to the ammonium salt solution, a yellow compound is separated. It is

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1) "Gmelins Handbuch der Anorganischen Chemie," 8 Auflage System-Nummer **53**, Verlag Chemie, Berlin (1935), p. 376.

2) W. Gibbs, *Am. Chem. J.*, **5**, 391 (1883).

3) W. Blum, *J. Am. Chem. Soc.*, **30**, 1858 (1908).

4) A. Miolati, *Z. Physik. Chem.*, **70**, 330 (1910).

5) V. W. Meloche and W. Woodstock *J. Am. Chem. Soc.*, **51**, 171 (1929).

6) S. R. Wood and A. Carlson, ibid., **61**, 1810 (1939).

7) C. Jena, "Uber Verbindungen Welche Vanadisaure und Tellurigesaure enthalten Giessen," (1907) (J. W. Mellor, "A Comprehensive Treatise on Theoretical and Inorganic Chemistry," Vol. 11, Longman Green & Co. (1931), p. 81).

8) S. Prasad and K. C. Pathak, *J. Indian Chem. Soc.*, **42**, 373 (1965).

9) S. Prasad and K. C. Pathak, to be published.

10) S. Prasad and K. C. Pathak, to be published.

decomposed by acids. Found: CaO, 18.48; TeO_3, 9.64; V_2O_5, 31.08; MoO_3, 32.96; H_2O, 7.84. Calcd. for $6CaO \cdot TeO_3 \cdot 3V_2O_5 \cdot 4MoO_3 \cdot 8H_2O$: CaO, 18.93; TeO_3, 9.88; V_2O_5, 30.73; MoO_3, 32.41; H_2O, 8.104%.

Strontium Salt.—This a yellow compound obtained by adding a dilute solution of strontium acetate to the ammonium salt solution. The compound was filtered after some time and analyzed. Found: SrO, 30.86; TeO_3, 8.28; V_2O_5, 26.22; MoO_3, 28.86; H_2O, 5.78. Calcd. for $6SrO \cdot TeO_3 \cdot 3V_2O_5 \cdot 4MoO_3 \cdot 7H_2O$: SrO, 30.40; TeO_3, 8.586; V_2O_5, 26.70; MoO_3, 28.16; H_2O, 6.162%.

Barium Salt.—When a dilute solution of barium chloride was added to the ammonium salt solution, a yellow compound began to separate. It was kept for few hours to settle, and then filtered, dried and analyzed. The compound is decomposed by acids. Found: BaO, 38.34; TeO_3, 7.12; V_2O_5, 23.53; MoO_3, 24.62; H_2O, 6.39. Calcd. for $6BaO \cdot TeO_3 \cdot 3V_2O_5 \cdot 4MoO_3 \cdot 8H_2O$: BaO, 38.95; TeO_3, 7.437; V_2O_5, 23.13; MoO_3, 24.39; H_2O, 6.099%.

Lead Salt.—A heavy yellow precipitate was obtained by adding a solution of lead nitrate to the ammonium salt solution. Found: PbO, 50.02; TeO_3, 6.12; V_2O_5, 19.48; MoO_3, 21.47; H_2O, 2.91. Calcd. for $6PbO \cdot TeO_3 \cdot 3V_2O_5 \cdot 4MoO_3 \cdot 5H_2O$: PbO, 49.12; TeO_3, 6.442; V_2O_5, 20.03; MoO_3, 21.13; H_2O, 3.301%.

Estimations. — Tellurium was estimated as metallic tellurium[11]; ammonia, as has been described earlier[8]; molybdenum, by precipitating it as molybdenum sulfide and igniting to molybdenum(VI) oxide, and vanadium, by titrating it against a standard potassium permanganate solution at 70°C in a dilute sulfuric acid medium. The other metals were estimated by standard methods. The water content was determined by difference as not all the water molecules were removed at 120°C.

The differential thermal analysis of ammonium and strontium salt was carried out by the method described in an earlier communication.[9] The infrared spectra of the ammonium salt and its dehydrated product (the compound heated at 300°C) was recorded between 2 and 15 μ on a Perkin-Elmer infracord in a potassium bromide medium by the disc-technique method.

Discussion

The composition of ammonium telluro-vanadomolybdate has been determined by analytical methods. Its anionic nature has been confirmed by passing a freshly-prepared solution of the ammonium salt through a cation exchange resin (Amberlite IR 120); in this case the tellurium, vanadium and molybdenum contents of the solution remained unchanged. In precipitated copper, silver, calcium, strontium, barium and lead salts, the anion has the same composition in all cases.

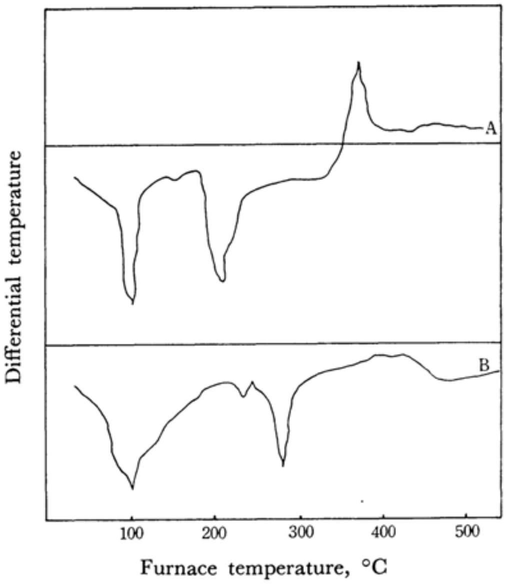

Fig. 1. Differential thermal analysis curves.
A. Ammonium telluro-vanadomolybdate
B. Strontium telluro-vanadomolybdate

The D. T. A. curve of the ammonium salt reveals two endotherms, at about 105 and 210°C, and a characteristic exotherm at about 370°C. The two endothermic peaks correspond to the dehydration of the compound; 6 water molecules are removed at 105°C, and the rest at about 210°C. The characteristic exothermic peak at 370°C is due either to the oxidation or to the decomposition of ammonia at the surface of molybdenum(VI) oxide or vanadium(V) oxide serving as a catalyst. The characteristic exotherm around this temperature has been observed while studying the D. T. A. of ammonium molybdate[12] and ammonium vanadate.[13] The oxidation of ammonia in the last stage of decomposition may be suggested as a possible source of exothermic heat.

In the case of strontium salt the water molecules are removed in two different temperature ranges, first at 105°C and the others at about 280°C, resulting in two endothermic peaks.

In the infrared spectrum of ammonium telluro-vanadomolybodate a broad band is observed in the region of 3400 cm^{-1} which is due to the intermixing of the N–H vibration of ammonium ions with the O–H stretching vibration of water. A sharp peak at 1650 cm^{-1} is observed; it represents

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[11] V. Lenher and A. W. Homberger, *J. Am. Chem. Soc.*, **30**, 387 (1908).

[12] E. Ma, This Bulletin, **37**, 171 (1964).

[13] M. Taniguchi and T. R. Ingraham, *Can. J. Chem.*, **1964**, 2467.

the bending mode of the O–H vibrations of water. The spectrum of the above salt was recorded after heating it to 300°C; it was thus observed that the above bands are eliminated and that the overall spectrum is considerably altered. A strong peak at 1400 cm^{-1} is due to the hydrogen bonding of the constitutional water molecules held in the interstices of the crystal lattice; this has also been confirmed by the D. T. A. curve. These water molecules are firmly bound, but they are released at quite a higher temperature, one which may be sufficient to break the bonds.

The broad band in the 840—900 cm^{-1} region indicates the predominant character of V–O valence vibrations in conjunction with Mo–O vibrations; this character has been confirmed by a study of the spectrum of the heated salt, in which the complexity arising from the different bond has vanished and two distinct peaks at 910 and 980 cm^{-1} are observed.

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