NOTES

Thermal Decomposition of Ammonium Molybdoselenite and Its Iron Salt

the Late Sarju PRASAD and Virendra Nath GARG

Chemical Laboratories, Banaras Hindu University, Varanasi, India

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The previous work[1] on the preparation of unsaturated heteropoly salts of selenium and molybdenum has now been extended to a study of the solid-state decomposition reactions of ammonium molybdoselenite and its iron salt at high temperatures. In the present communication thermogravimetric analysis (T. G. A.) and differential thermal analysis (D. T. A.) are used in conjunction with infrared spectroscopy to study the nature of the decomposition of the compounds by observing (a) the loss of water molecules, (b) the loss of volatile material, and (c) the breakdown by pyrolysis as the temperature is increased.

Experimental

The ammonium molybdoselenite and its iron salt of the composition: $3(NH_4)_2O\cdot 2SeO_2\cdot 5MoO_3\cdot 30H_2O$ and $Fe_2O_3\cdot 2SeO_2\cdot 5MoO_3\cdot 24H_2O$ were prepared from seleneous acid and molybdic acid as has been described earlier.[1]

The T. G. A. studies were carried out by a Stanton Thermobalance (high-temperature model) with a 10-mg sensitivity. A heating rate of 3°C per min was employed, with a sample size ranging from 150—170 mesh. The loss in weight was within 2% of the theoretical values in all cases. The apparatus of differential thermal analysis employed in this work consists of an analytical furnace, a transformer, and recording equipment. The specimen holders, made of sintered alumina, have the dimensions $1'' \times 3/4'' \times 1/4''$. A heating rate[2] of 10°C per min was employed, with a sample size ranging from 100—120 mesh. For D. T. A. study the sample was well mixed with extra-pure alumina (E. Merck's) and tightly packed in one cell, whereas alumina alone as a reference material was placed in the other.

The infrared spectrum was recorded on a Perkin-Elmer Infracord apparatus in a potassium bromide medium by the disk method. The spectra are between 2—15 μ.

Results and Discussion

The T. G. A. curve of ammonium salt reveals that the compound loses 13 molecules of water at 120°C, and the rest in the temperature range from 230 to 320°C. The anhydrous ammonium salt thus obtained at 320°C is brown and gives the test for ammonia. It is insoluble in cold or strong acids and alkalies. Its insolubility shows that it is an interstitial solid solution in which selenium atoms are closely packed in the interstices of molybdenum atoms, this theory is supported by the D. T. A., in which an exothermic peak is obtained at 330°C which can be attributed to the lattice transition. The gradual cooling curve from high to low temperatures reveals no peak, thus indicating the irreversibility of the process.

After further heating the decomposition of the compound formed occurs mainly in the 330—420°C temperature range, with a loss of selenium dioxide and an oxidation of the ammonia released; this is confirmed by the strong exothermic peak at 390—420°C in the D. T. A. curve. The nitrogen atmosphere gives a normal endothermic peak, thereby showing that there is no oxidation of ammonia. It may be concluded that ammonia is either oxidized or decomposed at the surface of

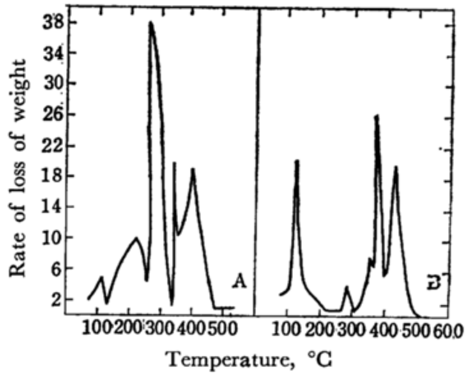

Fig. 1. Thermogravimetric analysis curves of ammonium selenitomolybdate (A) and ferric selenitomolybdate (B).

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[1] S. Prasad and V. N. Garg, This Bulletin, **38**, 1533 (1965).

[2] S. Prasad and V. N. Garg, *Indian J. Chem. (communicated)*.

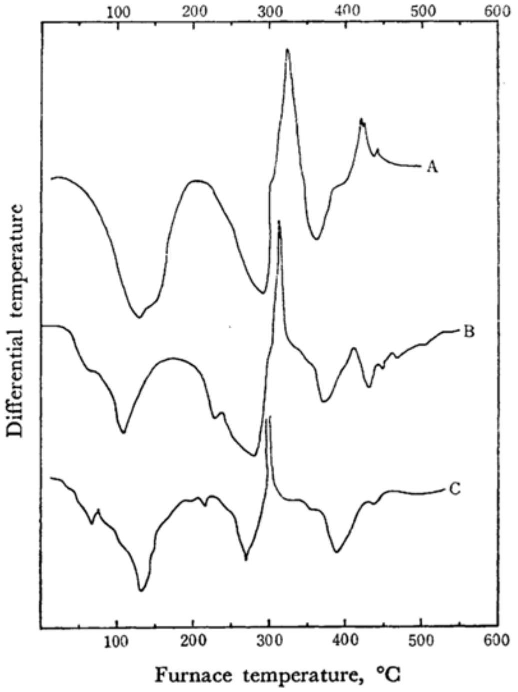

Fig. 2. Differential thermal analysis curves of Ammonium molybdoselenite in air (A) and in atmosphere of nitrogen (B) and ferric molybdoselenite in air (C).

molybdenum oxide through its catalytic action.[3]

In the case of iron molybdoselenite the T. G. A. curve shows a distinct region at 140°C where loss occurs due to 17 water molecules. Afterwards a flat plateau, corresponding to the iron salt with 7 water molecules, is obtained; these molecules are lost in the temperature range of 270—290°C. The two endothermic peaks, with maxima around 135°C and 280°C respectively, correspond to the dehydration of the compound. The exothermic peak at 310°C is interesting because no significant weight losses were noted in the T. G. A. curve in this temperature range; it can be attributed to the lattice transition, as in the ammonium salt. One endotherm, that at 360°C, may be due to the escape of selenium dioxide.

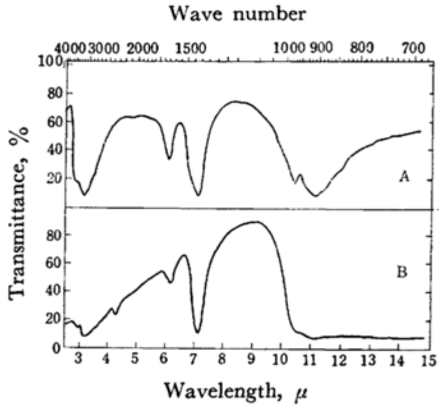

Fig. 3. Infrared spectra of ammonium molybdoselenite (A) and heated ammonium molybdoselenite (B).

In the infrared spectra one peak is observed in the 3 μ region (3450—3400 cm^{-1}); this peak is due to the O–H stretching vibration of water. In the 6 μ region a weak absorption band appears at 1640—1620 cm^{-1} which corresponds to the bending mode of water. It has been found that on dehydration, these bands are fully or partially eliminated and that the overall spectrum is considerably altered. The introduction of water molecules into the lattice usually results in a rearrangement of the packing and in the adoption of a different crystalline form. The water molecules may form hydrogen bonding with some part of the anions and, consequently, their vibrational frequencies, may be affected. The regions of the absorption of Se–O and Mo–O[4] linkages are so close that, in the compounds, the absorption bands of the two overlap to a considerable extent to form a broad band about 900 cm^{-1}. In the case of ammonium salt, the absorbances at 3100 cm^{-1} and 1400 cm^{-1} are characteristic of the ammonium ion.

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

[4] Landolt - Börnstein, " Physikalisch - Chemische Tabellen," 2 Teil (1951).