14. *Some Yttrium-group Oxalates.*

By Joseph K. Marsh.

Yttrium oxalate forms 6-, 10-, and 17-hydrates, but the 9-hydrate commonly cited is found to be a complex ammonium salt. Ytterbium oxalate hexahydrate has been prepared.

In the cerium group of rare earths the oxalate most commonly formed on precipitation is the decahydrate, though a number of others, particularly the 9- and the 11-hydrates, are known. In the yttrium group the results recorded are more diverse, and particulars of conditions of precipitation are usually lacking. A thorough investigation of these entities would involve prolonged phase-rule studies, but it is now found that precipitation of the oxalates under the conditions usual in practice frequently affords definite pure hydrates.

The 6- and 10-*hydrates* of yttrium oxalate have not hitherto been reported, and the 17-hydrate appears to be peculiar to yttrium. 6-, 9-, 10-, 12-, and 14-Hydrates of erbium oxalate have been recorded. The hexa- and the deca-hydrate, which are paralleled by other neighbouring earths, can be accepted with certainty, but owing to the great difficulty of obtaining erbium material free from yttrium, the existence of the higher hydrates is doubtful: they probably result from admixture of the 17-hydrate with the lower hydrates.

The ytterbium oxalate decahydrate described by Nilson (*Ber.*, 1880, **13**, 1430) and by Rimbach and Schubert (*Z. physikal. Chem.*, 1909, **67**, 196) was not obtained. The heptahydrate has been described by Bodlaender (Diss., Berlin, 1915, 14), but the ***hexahydrate***, which appears to be the most stable oxalate, is new.

It would seem that all the rare earths in serial order from lanthanum to erbium or ytterbium yield oxalate decahydrates, and all the earths from yttrium or erbium to lutecium probably yield oxalate hexahydrates.

In precipitating the yttrium earth oxalates the formation of the dense hexahydrate at the boiling point should be aimed at in order to facilitate subsequent ignition to oxide.

Experimental.

A nitrate solution of the earth was mixed with 2N-nitric acid to give a N/2-solution of the earth for experiments at low temperatures, or a N-solution for those at high temperatures. To these mixtures 10% oxalic acid was added very slowly

(1 hour) but in excess, so that precipitation of oxalate was avoided as far as possible, and a slow crystal growth occurred. This was allowed to proceed for 4 hours. Sometimes there was an initial precipitation of oxalate, followed by crystal growth. After the separation of the hydrates from hot solution another small, well-crystallised crop of oxalate was obtained by allowing the mother-liquor to cool overnight. The weighed oxalates were dried at 130° and then ignited in a gas crucible furnace to constant weight of oxide. The oxalate radicals were estimated by titration of weighed samples of the salts with N/10-potassium permanganate.

The yttrium used contained a small quantity of erbium, which was estimated by comparison of the absorption spectrum with a standard erbium solution. The amount found (0·25%) was calculated to raise the effective atomic weight of yttrium to 89·1, and this value has been used in calculating the theoretical composition of the yttrium salts. The erbium material available contained considerable yttrium. Samples of oxalate precipitated at 0° gave Er_2O_3, 44·57; C_2O_4, 33·35%. The formula $Er_2(C_2O_4)_3$ being assumed, the effective atomic weight of erbium is found to be 152·5. This value has been used in computations. The erbium oxalate hydrates must be deduced solely from ignition data. Most of the oxalate determinations were not made till 2 years after those of the oxides.

Dysprosium Oxalate.—The precipitate at 100° was the known decahydrate (Found: Dy_2O_3, 48·74, 48·78; C_2O_4, 34·43. Calc.: Dy_2O_3, 48·50; C_2O_4, 34·34%). This also separated on cooling from 90° to 15°, but the precipitate at 15° appeared to be a hydrate with $11H_2O$, but it lost water on storing [Found: Dy_2O_3, 47·63, 47·58. Calc. for $Dy_2(C_2O_4)_3,11H_2O$: Dy_2O_3, 47·40%].

Yttrium Oxalate.—The precipitate at 100° was a *hexahydrate.* It formed a dense, hard cake of prismatic crystals [Found: Y_2O_3, 40·05; C_2O_4, 47·83. $Y_2(C_2O_4)_3,6H_2O$ requires Y_2O_3, 40·11; C_2O_4, 47·97%]. The precipitate between 90° and 15° was well crystallised and proved to be the *decahydrate.* It resembled the decahydrates of dysprosium and gadolinium oxalates [Found: Y_2O_3, 36·40; C_2O_4, 42·45. $Y_2(C_2O_4)_3,10H_2O$ requires Y_2O_3, 36·35; C_2O_4, 42·43%]. The precipitate at 15° was the 17-hydrate described by Brauner (J., 1898, **73**, 951) (Found: Y_2O_3, 29·99, 30·16; C_2O_4, 35·30. Calc.: Y_2O_3, 30·24; C_2O_4, 35·29%). At 0° there was obtained a precipitate corresponding to a 12·4-hydrate, but this was probably not homogeneous.

The nonahydrate has been regarded as the most usual hydrate of yttrium oxalate. In its preparation, Bahr and Bunsen (*Annalen*, 1866, **137**, 1) and Rimbach and Schubert (*Z. physikal. Chem.*, 1909, **67**, 196) used ammonium oxalate as precipitant, but with this reagent the author obtained a precipitate which on ignition yielded an oxide residue corresponding to $Y_2(C_2O_4)_3,8·75H_2O$. Washed four times with boiling water, the precipitate continued to give a strong Nessler reaction, and on ignition it liberated a distinct odour of ammonia. It is not therefore a simple yttrium oxalate.

Erbium Oxalate.—The hexahydrate was prepared by precipitation at 100° with oxalic acid. It was similar in appearance to the corresponding yttrium salt [Found: Er_2O_3, 52·10. Calc.: 52·14%]. A small precipitate obtained on cooling (90—15°) resembled the decahydrates of other rare earths, but was not analysed.

Ytterbium Oxalate.—The *hexahydrate* was precipitated at 100° [Found: Yb_2O_3, 55·00, 54·87; C_2O_4 36·51. $Yb_2(C_2O_4)_3,6H_2O$ requires Yb_2O_3, 54·87; C_2O_4, 36·77%]. The heptahydrate was precipitated at 15° (Found: Yb_2O_3, 53·65, 53·67. Calc.: Yb_2O_3, 53·60%); on keeping it formed the hexahydrate.

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