CCCCXLVIII.—*Potassium Rheni-iodide.*

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ENK (*Ber.*, 1931, **64**, 791) has described the preparation of potassium rhenichloride by heating together appropriate amounts of potassium per-rhenate, hydrochloric acid, and potassium iodide, and subsequently evaporating the solution so produced to crystallisation. The same compound has also been independently described by Briscoe, Robinson, and Stoddart (this vol., p. 2263), who obtained it by melting a mixture of potassium chloride and metallic rhenium in dry chlorine, extracting the residue with cold water, and evaporating the solution at the ordinary temperature in a desiccator. Investigation of these rheni-compounds has been extended by the preparation of the analogous bromine (Krauss and Steinfeld, *Ber.*, 1931, **64**, 2552) compounds in a manner similar to that employed by Enk (*loc. cit.*). Krauss and Steinfeld also claim to have obtained compounds of the composition represented by the formulæ K_3ReCl_6 and $K_4Re_2Cl_{11}$, together with the corresponding thallium salts.

The present paper concerns the preparation and properties of *potassium rheni-iodide,* a salt which has not hitherto been described. It is produced by heating potassium per-rhenate with excess of potassium iodide and aqueous hydrogen iodide at the b. p. of the latter, and can be separated from the dark-coloured solution as crystals, shining black by reflected, and dark chocolate-brown by transmitted light. Some idea of the stability of the compound may be gained from the fact that it can be heated to 200° without decomposition. At about 210° there is slight decrepitation, but marked liberation of iodine is not evident below about 300°. With a limited quantity of water, a dark violet-black solution results, which, on dilution, changes to dark brown or black and is evidently colloidal in character. Boiling this liquid leads to flocculation and the separation of a black precipitate which, as was anticipated, proved to be hydrated rhenium dioxide. In alcohol, or ether, either hot or cold, the crystals are only slightly soluble, but they readily dissolve in acetone, from which potassium rheni-iodide may be recrystallised with acetone of crystallisation. On heating in oxygen, iodine is evolved and a black residue is left, whilst in nitrogen the decomposition takes place quantitatively to potassium iodide, metallic rhenium, and iodine.

Potassium osmi-iodide (K_2OsI_6) is stable in the presence of hydriodic acid but hydrolysed by water, and the dark violet crystals of the compound are stable in hydrogen below about 300° but evolve hydrogen iodide at higher temperatures (Wintribert, *Ann. Chim. Phys.*, 1903, **28**, 15), leaving presumably potassium iodide and metallic osmium.

EXPERIMENTAL.

About 1 g. of potassium per-rhenate was added to excess of potassium iodide and aqueous hydrogen iodide (*d* 1·7) and heated to the boiling point of the liquid; the relative amounts of reactants appear to be immaterial provided the hydriodic acid be in excess. On cooling, crystals separated. Evaporation of the resulting mother-liquor produced a second crop of equally pure crystals, but the third batch resulting from a further concentration was always contaminated with potassium iodide. Crystals from the earlier crops were separated and dried, first on a porous plate at the ordinary temperature and subsequently by heating on a water-bath at approximately 100°. Certain batches were recrystallised from acetone. The analysis of the material was carried out by treating a weighed amount (0·09—0·39 g.) with about 50 c.c. of distilled water and boiling it; the rhenium separated as a flocculent precipitate of hydrated rhenium dioxide. After standing for about an hour, this was collected on a tared Gooch crucible, dried at 110°, and finally weighed as rhenium dioxide. The filtrate was then heated to boiling, one or two drops of dilute nitric acid were added, and the iodine content was estimated by precipitation as silver iodide, which, after being washed, was dried and weighed in a manner similar to the rhenium dioxide. The following results prove the material to be *potassium rheni-iodide* (K_2ReI_6 requires K, 7·68; Re, 18·14; I, 74·18%).

	Re, %.	I, %.	K (by diff.), %.	Remarks.
	18·94	73·50	7·56	Dried on porous plate at the ordinary temp.
	18·85	73·70	7·45	
	19·95	73·77	6·28	Dried at 100°.
	18·86	74·59	6·55	
	17·85	72·93	9·22	
	18·21	73·43	8·36	
Mean	18·77	73·65	7·57	

About 0·2 g. of potassium rheni-iodide was heated in a stream of dry nitrogen to dull redness, and the loss of weight determined. The operation effected a complete removal of the iodine, which began to be evolved at about 300°, and the weight of the residue indicated that this took place according to the equation

$$K_2ReI_6 \longrightarrow 2KI + Re + 4I$$

(Found: loss, 49·44. Calc. for loss of 4I: 49·52%).

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