XXXIV.—*Note on Perchloric Ether.*

BY HENRY ENFIELD ROSCOE.

A BODY supposed to be perchloric ether, was obtained in the year 1840, by Messrs. Hare and Boyle,* by distilling perchlorate of barium with sulphovinate of the same metal. These observers state that, in explosive violence, this body is not surpassed by any

* Phil. Mag. 37, xix., 370.

substance known in chemistry, the explosions being produced by heat, friction, or percussion, and often taking place without any apparent cause.

I have examined the mode of production of this body, analysed it, and determined its approximate boiling point, and have thereby had frequent opportunity of verifying the statement concerning its extremely explosive nature.

Perchloric ether cannot be obtained by the action of iodide of ethyl upon an alcoholic solution of perchlorate of silver, even at a temperature of -10°C .; iodide of silver is precipitated, but the perchloric ether yields, with alcohol, perchloric acid and common ether. On bringing perchloric acid (ClO_4H) in contact with alcohol or ether, a violent explosion frequently ensues, probably owing to the formation of perchloric ether, but I was unable to prepare any quantity of the ether in this way, even when the mixture was effected at -20°C . —

Small quantities of perchloric ether may be obtained by distilling perchlorate of potassium with sulphovinate of calcium; but by far the best mode of preparing the substance is that proposed by Hare and Boyle, viz., by distilling the barium-salts of perchloric and sulphovinic acids in nearly equivalent proportions.

An intimate mixture of 10 grms. of crystallized sulphovinate of barium and 10 grms. of perchlorate of barium was, for this purpose, placed in a small retort, the neck of which had been bent downwards; the retort was immersed in an oil bath, and this was slowly heated, a large test-tube containing a small quantity of water, but not otherwise cooled, being used as a receiver. Between 140° and 160°C . tolerably large quantities of a colourless oily liquid heavier than water distilled over; and when the temperature rose to 170° , white fumes of hydrated perchloric acid coming over, the distillation was stopped. About two cubic centimeters of the oil was thus obtained in each operation. After carefully removing the receiver with the distillate, the water, which had a strongly acid re-action, was nearly all drawn off with a pipette, and the oil washed several times with water until the acid re-action was scarcely perceptible. The washed ether was then removed from the superincumbent water by means of a small pipette, care being taken that no water entered the pipette, and the ether immediately brought on to a small dry filter placed upon a wire triangle. After passing through a second filter, the ether dropped into a small glass containing a weighed quantity of alcohol, and as soon as about 20

drops of the ether had fallen into the alcohol, the glass was closed and re-weighed. To the alcoholic solution of the ether, an excess of alcoholic potash was added; this completely decomposed the ether, and after standing for some time, the insoluble perchlorate of potassium was thrown on a weighed filter, washed with alcohol acidified with acetic acid, dried and weighed. The filtrate and wash-alcohol was evaporated to dryness with excess of acetic acid, the residue ignited with peroxide of iron, and the chlorine estimated as silver-salt.

Treated in this way, 0.905 grm. perchloric ether yielded 0.9383 grm. perchlorate of potassium, and 0.0205 grm. chloride of silver.

Hence :—

			Calculated.	Found.
C_2H_5	..	29	22.57	
O_4	..	64	49.80	
Cl	..	35.5	27.63	27.13
		<hr/>	<hr/>	<hr/>
		128.5	100.00	

The oxygen, potassium, and chlorine contained in the perchlorate of potassium were severally estimated. Analysis gave the following numbers—

			Calculated.	Found.
Cl	..	35.5	25.63	25.36
O_4	..	64.0	46.21	46.65
K	..	39.0	28.16	27.52
		<hr/>	<hr/>	<hr/>
		138.5	100.00	99.53

Dry perchloric ether undergoes an explosive decomposition when poured from one vessel to another, or when its particles are in any way slightly shaken. The violence of these explosions is extreme; about 0.2 grm. of the ether contained in a very thin test-tube exploded with such force as to bore a hole 15mm. in diameter and 5mm. deep in a filter-stand of hard wood, and all the glass vessels near were shattered. The greatest care must be taken in working with this body; gloves and glass screens are absolutely necessary. In contact with water, the ether is much more stable, and may then be shaken, or even distilled, without any explosion occurring. Heated under a thin stratum of water, it was found to boil at 74°C. when the barometer stood at 755mm.