XXIV.—*On the Combination of Carbonic Oxide with Potassium.*

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It is now some years since Liebig made the curious observation that carbonic oxide is absorbed by and combines with potassium. This distinguished chemist did not make any exact experiment on the amount of this absorption, and simply put forward a conjecture upon the subject founded upon the inadequate data in his possession. From that time to the present, the reaction has not been further investigated. It appeared to me that, viewed in connection with recent experiments, this question assumed a new interest, and that it was probable that the reaction was of a much simpler character than Liebig had surmised. In the more close examination of this experiment, I have discovered some remarkable points in it, which have not hitherto been observed.

The carbonic oxide used in the following experiments was prepared by the process of Fownes, the decomposition of ferrocyanide of potassium, by concentrated sulphuric acid; the gas was carefully dried and purified, any traces of oxygen from air accidentally present being separated by the passage of the gas through a Liebig's apparatus containing pyrogallate of potash. The potassium also was, as far as possible, freed from adhering impurities by filtration through wash-leather immediately before the experiment. This purification of the potassium, so that it shall present a perfectly clean surface to the action of the gas, is an essential condition of success. The potassium was rapidly wiped from naphtha by blotting paper and introduced into a bulb tube, or, when large quantities were operated on, into a Florence flask, which had previously been filled with carbonic oxide and weighed. The vessel containing the potassium was heated in an air bath in such a manner that the progress of the experiment could be observed. A gage-tube dipping into mercury was attached to the apparatus, which was rendered air tight. The absorption commences considerably under $100^{\circ}\text{C}.$, and at about $80^{\circ}\text{C}.$ a change in the potassium is indicated by the appearance of the most beautiful arborescence, the potassium shooting out into crystals resembling

frosted silver in appearance, and at the same time spreading itself over the surface of the glass. This change continues until the whole of the potassium has become similar in appearance, and converted into these crystals of a dead grey colour. The metallic appearance which the crystals at first present is most probably due to the spreading out of the metal over the surface. During this change, the gauge-tube indicates a slow and moderate absorption, the mercury standing at the level of about half an inch in the tube, while the passage of the gas is regulated with extreme slowness. If pressure is put on the gas so as to accelerate its passage, it bubbles through the apparatus. The formation of this substance is the first stage in the action. On its completion, a further change is indicated by the formation of dark spots on the surface of the crystals, which, when their formation has once commenced, spread over the surface with great rapidity, the carbonic oxide being simultaneously absorbed. This absorption is as rapid as the absorption of carbonic acid by potash, and if the gas be not allowed sufficiently free access to the substance, the mercury will indicate in the gauge tube a pressure of from 20 to 30 inches. It is attended with great evolution of heat. This absorption takes place with the greatest rapidity at comparatively low temperatures. With the aim of preserving the substance in this stage, I have frequently allowed the temperature to fall before the formation of the dark spots indicated the further alteration. At a certain stage however in the cooling, when the temperature has perhaps fallen as low as 40°C ., the second action almost invariably commences nor have my efforts to procure this body in a pure condition by means of other devices been more successful. The final product of the experiment is of a dark red colour and retains the crystalline form of the body from which it is produced. During the progress of the experiment, spots of blue and green appear on the substance indicating the partial formation of other bodies. The constitution of the substance is determined by the following experiments:—

Potassium taken.	Increase in weight.	Increase in weight on 100 parts.
6.40 grms.	4.57 grms.	71.4
5.461 „	3.967 „	72.4
0.674 „	0.475 „	70.48
4.858 „	3.469 „	71.4
5.6886 „	4.086 „	71.8
4.669 „	3.362 „	72.07

In these six experiments, which I have selected at random from a larger number giving equally concordant results, the mean increase in weight on 100 parts of the substance is 71.59 parts, and 100 parts of the substance formed are thus constituted.

Potassium	.	.	.	58.27
Carbonic oxide	.	.	,	41.73
				<hr/>
				100.00

On the assumption that one atom of potassium weighing 39.2 absorbs 1 atom of carbonic oxide weighing 28, 100 parts of potassium would absorb 71.2 parts of carbonic oxide, and the constitution of the substance formed would be—

K	.	.	.	39.2	58.33
CO	.	.	.	28.0	41.67
				<hr/>	<hr/>
				67.2	100.00

The experiments of Berthelot have shewn that carbonic oxide combines with hydrate of potash to form formiate of potash, formic acid that is, in which one atom of hydrogen is replaced by one of potassium. Now the result of this experiment, the body COK (or rather $C_2O_2K_2$) has the constitution of the radicle of formic acid, $C_2O_2H_2$, in which the whole of the hydrogen is replaced by potassium. It is not improbable that the intermediate substance may be the body COK_2 , or the hydride of formyle, in which a similar replacement is effected.

Experiments which I have made with the view of replacing the potassium in this substance by organic groups have been without result. Neither iodide of ethyl nor even chloride of benzoyl act upon it. There is every reason to believe that it consists of two bodies, anhydrous potash, and rhodizionate of potash. Brought in contact with water, it decomposes with terrific violence, and even the dry substance, under circumstances which are not well ascertained, occasionally explodes. It may be preserved under naphtha. When pure and anhydrous alcohol is poured upon it, a great elevation of temperature ensues but the decomposition is far less violent than with water. Even this experiment, however, must be made with the greatest caution. No gas is given off, but a

portion of ethylate of potash remains in solution, and the rhodizionate appears as a red insoluble powder. I endeavoured to ascertain the nature of this decomposition. Alcohol was repeatedly digested with, and poured off from the residue; and the potash was precipitated from it by carbonic acid, and determined as sulphate.

Two experiments gave the following results.—

I. 100 parts of potassium absorbed 72·4 parts of carbonic oxide, and 38·4 parts of potassium were extracted by the alcohol.

II. 100 parts of potassium absorbed 71·8 parts of carbonic oxide and 41·77 parts of potassium were extracted by the alcohol.

We may assume therefore that of 5 parts of the potassium taken, 2 are extracted by the alcohol and 3 remain in the residue as rhodizionate, which would give for its constitution $C_{10}O_8K_6$

I do not pretend that the constitution of the rhodizionate can be thus determined with certainty, but its formula has never yet been ascertained by any adequate and reliable experiments. Such efforts as I have made to ascertain it have been defeated by the extreme facility with which it is oxidized with formation of croconate. Rhodizionate of potash if perfectly pure, dissolves in dilute acetic acid with a pale pink colour, and the solution gives with acetate of baryta a brilliant red precipitate; but this precipitate alters in colour during the process of washing, and the solution of the potash-salt speedily becomes alkaline and yellow from the formation of croconate. I have never seen the oxalate of potash which others have observed in the decompositions of this class of bodies; and I may observe that this decomposition, with the formation of croconate of potash and hydrate of potash, can readily be accounted for on the hypothesis I have given, simply by the action of air and moisture.