XIII.—*On a Crystallised Hydrate of Phenylc Alcohol.*

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I OBSERVED some time since that when four parts of carbolic acid were well agitated with one part of water, and the whole exposed to a temperature of 4°C ., the sides of the containing vessel became lined with fine large crystals, which proved, on more careful examination, to be six-sided prisms of the rhombic system. This new substance was found to be soluble in water, alcohol, and ether, and to melt at a temperature of 16°C . To ascertain its composition some of the crystals were taken and carefully dried between folds of blotting paper, and then submitted to analysis, when the following results were obtained:—

0·435 of substance gave 0·260 of water, or 6·67 of hydrogen, and 1·112 of carbonic acid, or 69·65 of carbon.

In a second analysis, 0·488 of substance gave 0·301 of water, or 6·85 hydrogen, and 1·243 of carbonic acid, or 69·5 of carbon.

These results correspond in composition to a bihydrate of phenyl, or to the ordinary hydrate of phenyl + 1 eq. water, as seen by the following formulæ:—

	$\text{C}_{12}\text{H}_5\text{O}.\text{HO}$	$\text{C}_{12}\text{H}_5\text{O}.\text{2HO}$	$\text{C}_{12}\text{H}_5\text{O}.\text{3HO}$	Found.
Carbon.....	76·59	69·90	64·29	69·13
Hydrogen	6·38	6·80	7·14	6·72
Oxygen	17·03	23·30	28·57	24·15
	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00

The above figures show that the substance analysed is ordinary phenylc alcohol, which has taken an equivalent of water to form a new crystalline compound, and what further substantiates this opinion is that when it has been liquified by a temperature above 16°C ., and heat is applied, it gradually loses water, and the boiling point of the liquid rises until it reaches 187°C ., the boiling point of phenylc alcohol.

This is, I believe, the first instance of an alcohol uniting with one equivalent of water to form a crystallized hydrate. The only apparent exception with which I am acquainted is the hydrate of propyl-alcohol discovered by Erlenmeyer. I say apparent,

because, from the short extracts I have been able to read of his paper, it does not appear that he has separated the water which forms the hydrate of the alcohol obtained by him; in fact, the product appears to distil without decomposition.

The neutrality of bihydrate of phenyl on litmus paper, as well as that of the ordinary hydrate, led me to enquire if the ordinary hydrate should be considered an acid, as stated in most of our text-books (as carboic or phenic acid), or as an alcohol, or as a body having some similar properties to glycerin.

To decide this point I made the following series of experiments: I took 100 cub. cent. of solutions of caustic potash, having the following specific gravities—1·02, 1·03, 1·04, 1·06, and added successively to each of them 25 cub. cent. of the ordinary hydrate of phenyl, perfectly pure, and having a melting point of 34° C.

The following table gives the results observed:—

Specific gravity of caustic potash.	25 c. c.		On adding 25 c. c. of the ordinary hydrate of phenyl to 100 c. c. of solution caustic potash of the above strength, the mixture separated into two layers—the upper layer consisting of 104 c. c., a solution of carboic acid in alkali, and the lower layer of 21. c. c. carboic acid, which has taken up a certain amount of water.			
	1·02					
1·03	25 c. c.	25 c. c.	25 c. c.	On adding, as before, hydrate of phenyl to solution of caustic potash of the above strength, it was not until the addition of the 3rd measure of 25 c. c. that the mixture separated into two layers; the upper layer = 45 c. c., and the lower one = 130 c. c.		
	No suspension.	No suspension.	No suspension.			
1·04	25 c. c.	25 c. c.	25 c. c.	25 c. c.	In this instance it required 100 c. c. carboic acid before separation took place, when the following results were obtained:—Higher layer = 13 c. c. of alkaline solution, and lower layer = 187 c. c. of acid solution.	
	No suspension.	No suspension.	No suspension.	No suspension.		
1·06	25 c. c.	25 c. c.	25 c. c.	25 c. c.	25 c. c.	25 c. c.
						In this instance, even after the addition of 175 c. c. of carboic acid, no separation took place.

The above experiments clearly show that the solubility of phenic acid in the alkaline solution is not due to a combination of the acid with the alkali, for in that case the quantity of phenylic acid which would have entered into solution would have increased in ratio to the quantity of potash in solution, whilst no such ratio exists, and therefore no combination.

What further substantiates this view is, that if to 100 c. c. of alkaline solution of sp. gr. 1.03 is added successively 25 c. c. of carbolic acid, the first two enter into solution, but on a further addition of 25 cub. cent, not only do they remain undissolved, but they separate or carry down with them nearly their own bulk of acid, which had been previously held in solution. This novel fact of the separation of a substance already held in solution by the simple addition of a further quantity of the same compound, proves beyond all doubt that an alkaline solution acts only as a solvent for the hydrate of phenyl, and is therefore not a combination of carbolic acid with oxide of potassium.

The above table also illustrates another interesting fact, viz., that if to a solution of alkali of sp. gr. 1.06 is added successively 25 c. c. of pure carbolic acid, no separation takes place; for we were able to add 200 c. c. of hydrate of phenyl without any of it separating. This is due, probably, to the fact that the hydrate of phenyl takes up a certain amount of water, which reduces its specific gravity until it is almost identical with that of the alkaline solution.

Further. Two volumes of liquified hydrate of phenyl were mixed with one volume of concentrated caustic ley, and the mixture distilled in a retort, when 98 % of the original acid passed over into the receiver, whilst the 2 % left in the retort was decomposed into a resinous matter, due to the oxidizing action of the alkali upon the carbolic acid.

I may state that these experiments were repeated with the bihydrate of phenyl, when precisely similar results were obtained, if the quantity of water it contains is taken into account, leaving no doubt that they are identical bodies, with the exception that the new hydrate contains 1 eq. more water, not of composition, but simply of crystallization.

It is stated in our text-books that phenic acid is prepared by mixing the oils of tar, which distil between 150° C. and 200° C., with a highly concentrated solution of caustic potash, and that the whole, on cooling, forms a white crystalline mass. If we repeat

this process, substituting for the oil of tar pure hydrate of phenyl, a white solid mass is also obtained, which, on being pressed a great number of times between folds of blotting paper, so as to remove as near as possible the whole of the excess of alkali, a white crystalline mass is obtained, which proves, on examination, to be crystals of hydrate of phenyl contaminated with a little alkali.

Carbolic acid absorbs with great avidity dry ammoniacal gas, but no combination takes place, for if the mixture is heated the ammonia gas is expelled, not a trace remaining in combination with the acid.

It is barely necessary to add that if the ammoniacal carbolic acid is heated in a closed tube, water and aniline are produced.

Both the hydrates of phenyl, when heated with oxide of lead, dissolve it, and both form a solid compound. These, on being well washed with water to remove all excess of phenic acid, and dried, are found on analysis to have an identical composition, viz., $C_{12}H_6O_2 + 2PbO$.

This compound is slightly soluble in hot alcohol, and deposits on cooling.

As a solution of both the hydrates of phenyl give, with a solution of subacetate of lead, a white bulky precipitate (which contracts on drying in a remarkable manner, remaining as a white amorphous powder), I made the following series of experiments to ascertain if the precipitates which are produced under these circumstances have a constant composition. For this purpose I mixed 200 c. c. of a saturated solution of the ordinary hydrate with 10 c. c. of a solution of subacetate of lead, containing 1.614 of oxide of lead. The precipitate produced was collected, washed slightly, and dried at $110^{\circ}C$., when 1.090 grm. of it gave, on calcination, 0.698 grm. of oxide of lead, or 64 % PbO .

In another experiment I took the same quantity of carbolic acid solution, and added to it double the quantity of subacetate of lead. In this instance the quantity of oxide of lead in 100 parts of the precipitate was equal to 68.2 %, showing that in this precipitate there was 4 % more oxide of lead than in the preceding one, and therefore that there is no definite compound formed; in fact, there is so little affinity between hydrate of phenyl and oxide of lead that if one of the above precipitates is washed several times with boiling water, it loses a large proportion of the hydrate of phenyl. In one instance, for example, 0.470 grm. of the above

washed precipitate (dried again, of course, at 110 C.) gave, on calcination, 0.393 grm. of oxide of lead; consequently, the precipitate contained 83.6 % of oxide. There can, therefore, be no doubt that the hydrate of phenyl, like many other organic substances, does not give any well-defined compound with oxide of lead.

Lastly. Carbolic acid does not decompose alkaline carbonates even under the influence of heat. The small amount of carbonate which disappears is not decomposed, but merely enters into solution.

From the above facts I conclude that what has been called carbolic or phenic acid is a neutral compound, and must be regarded as the hydrate of an alcohol, and the new substance described by me is the bihydrate of the same radical.