

LXIII.—*On the Synthetical Production of Urea from Benzene, Ammonia, and Air, by the Action of Heated Platinum.*

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IN conducting some experiments with a coil of platinum wire, heated to a bright redness, it was observed that on placing this coil in a flask containing a small quantity of benzene and ammonia solution, the flask in a short time became coated with a white deposit.

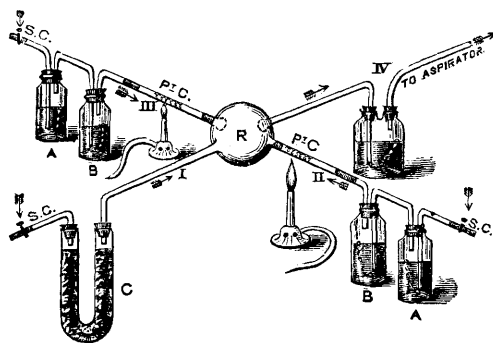
As, however, the quantity of substance produced by this means was too small for the purposes of analysis, the following alteration in the mode of its formation was made:—

Air was drawn, by means of an aspirator, through washing bottles containing (1) ammonia and (2) benzene, the glass tubes conveying the air dipping below the surface of the liquid in both bottles, then through a tube containing a helix of platinum wire, heated to dull redness by a Bunsen burner, and finally through water, contained in potash bulbs, to absorb the products of the action.

On analysis the water, at the end of the experiment, was found to contain ammonium carbonate, nitrite, and nitrate; but it was also observed that a solid crystalline substance had collected in the tube containing the platinum, depositing not far from the heated wire. On analysing this substance qualitatively it appeared to be ammonium cyanate, giving the following reactions:—When treated with dilute sulphuric or hydrochloric acid it evolved cyanic acid, recognised by its odour; its solution gave with silver nitrate a white precipitate, soluble in dilute nitric acid, and converted by hydrochloric acid into silver chloride, with evolution of cyanic acid. After boiling its aqueous solution and evaporating to a small bulk, it gave with strong nitric acid a crystalline precipitate, soluble in potash solution, and evolving ammonia when boiled with it, indicating its conversion into urea.

In order to obtain as large a quantity of the substance as possible, I adopted the form of apparatus shown in the diagram, in which two tubes containing heated platinum are used, and the product formed is allowed to collect in a bulb (diagram).

APPARATUS FOR THE SYNTHETICAL PRODUCTION OF UREA.



Air enters the globular receiver *R*, by the tubes *II* and *III* impregnated with ammonia and benzene vapour by bubbling through the bottles *AA* and *BB*, containing strong ammonia-solution and benzene respectively; the proportion of air that is admitted is regulated by the screw-clips *S.C.* *S.C.* Before entering *R* the air, ammonia, and benzene-vapour pass through the coils of platinum wire *PtC* *PtC*, which are heated by the Bunsen burners.

The tube *I* delivers air, dried by passing through the tube *C*, containing dried calcium chloride. This dry air removes the excess of ammonia and most of the ammonium carbonate and water.

When this form of apparatus is employed, the ammonium cyanate first produced is entirely converted into urea. The maximum product is obtained when a slow current of air is passed through the ammonia

and benzene, because if much air is used, the benzene appears to be entirely converted into carbon dioxide and water.

The urea thus formed was found not to be pure, but mixed with ammonium carbonate and sulphate (derived from carbon disulphide in the benzene), and with an organic impurity apparently of a resinous nature, the presence of which, it is curious to observe, prevented the precipitation of urea by oxalic acid. This impurity is soluble in ether. To purify the urea, the solution which collects in the bulb was evaporated to dryness, the residue extracted with absolute alcohol, filtered, evaporated to a small bulk, and the urea precipitated by excess of ether. It was found necessary to repeat this process, or to recrystallise from alcohol several times in order to obtain the urea sufficiently pure for organic analysis. In performing the analysis of the substance, the carbon and hydrogen were determined in the usual way by combustion with oxide of copper.

The nitrogen was determined by conversion into ammonia by heating with soda-lime, the ammonia being absorbed by hydrochloric acid, and precipitated by excess of platinic chloride, and the precipitate was washed, dried, ignited, and weighed as metallic platinum.

The following table gives the results of the carbon and hydrogen determinations:—

Amount of substance taken.	Weight of CO ₂ found.	Percentage of carbon.	Weight of H ₂ O found.	Percentage of hydrogen.
1. 0·1746 gram	0·133 gram	20·73	0·109 gram	6·93
2. 0·185 „	0·142 „	20·9	0·115 „	6·86
3. 0·292 „	0·2155 „	20·14	0·18 „	6·84

The determination 3 was obtained from a sample of urea which was quite white, while the two determinations 1 and 2 were obtained from samples which were coloured yellow by the resinous impurity before mentioned; and since urea contains less carbon than almost any common organic bodies, the presence of a small amount of foreign organic matter would account for the high percentages of the two first determinations.

The following table gives the results of the nitrogen determinations:—

Weight of substance taken.	Weight of Pt obtained.	Corresponding percentage of N.
0·1568 gram	0·514 gram	46·5
0·298 „	0·976 „	46·51
0·192 „	0·630 „	46·6
0·171 „	0·564 „	46·83
0·203 „	0·6645 „	46·48

The following numbers give the mean of the whole results:—

	Mean. Found.	Calculated.
Carbon.....	20·88 per cent.	20·00 per cent.
Hydrogen	6·87 „	6·66 „
Nitrogen.....	46·584 „	46·66 „
Oxygen (by diff.) ..	25·666 „	26·66 „
Total	100·00 „	99·98 „

The substance produced answers all the characteristic tests for urea, that is (1), on boiling with potash it gave ammonia. (2) On treating it with nitric acid, crystals of urea nitrate separated. (3) Oxalic acid produced crystals of urea oxalate after the resinous impurity had been removed by washing with ether. This fact, together with the determinations above given, leaves no doubt as to its identity. The numbers obtained by the analysis of the perfectly colourless sample give the following percentage composition:—

	Found.	Required.
Carbon	20·14	20·00
Hydrogen	6·84	6·66
Nitrogen.....	46·60	46·66
Oxygen	26·42	26·66

As it seemed probable that other substances besides the heated platinum wire might yield larger quantities of the substance, the following experiments were tried:—

Heated spongy platinum and platinised asbestos were tried as substitutes for the platinum wire, but they apparently produced too much oxidation, forming more ammonium carbonate and less urea, than in the case of the wire.

Platinised charcoal produced small quantities of urea, but it acts slowly and requires a high temperature, probably owing to the reducing action of the charcoal.

Olefiant gas was also employed in some experiments instead of benzene, when it was found that large quantities of ammonium carbonate were produced, but no urea.

From the relationship existing between them it was determined to substitute acetylene for benzene, and it was found that in this case a considerable amount of urea was produced, the acetylene behaving in a manner very similar to the benzene vapour.

Further experiments with regard to this last mode of formation of the urea are now in progress.