

November 25, 1858.

W. R. GROVE, Esq., V.P., in the Chair.

In accordance with the Statutes, notice was given of the ensuing Anniversary Meeting, and the list of Officers and Council proposed for election was read, as follows :—

President.—Sir Benjamin Collins Brodie, Bart.

Treasurer.—Major-General Sabine, R.A.

Secretaries.— $\left\{ \begin{array}{l} \text{William Sharpey, M.D.} \\ \text{George Gabriel Stokes, Esq., M.A.} \end{array} \right.$

Foreign Secretary.—William Hallows Miller, Esq., M.A.

Other Members of the Council.—Henry Wentworth Dyke Acland, M.D. ; Rear-Admiral Sir George Back, D.C.L. ; The Rev. John Barlow, M.A. ; Thomas Bell, Esq., Pres. L.S. ; His Grace the Duke of Devonshire, M.A. ; Edward Frankland, Ph.D. ; John Peter Gassiot, Esq. ; Philip Hardwick, Esq., R.A. ; Arthur Henfrey, Esq. ; Lieut.-Colonel Henry James, R.E. ; Sir Roderick Impey Murchison, M.A., D.C.L. ; John Percy, M.D. ; Archibald Smith, Esq., M.A. ; The Rev. William Whewell, D.D. ; Charles Wheatstone, Esq. ; The Lord Wrottesley, M.A.

Captain Boxer, R.A., was admitted into the Society.

Robert W. Bunsen, Louis Poinsot, and Carl Theodor von Siebold, having been severally balloted for, were elected Foreign Members of the Society.

The following communications were read :—

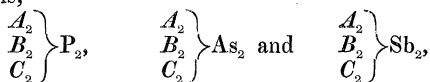
- I. "Researches on the Phosphorus-Bases."—No. III. Phophoretted Ureas. By A. W. Hofmann, Ph.D., F.R.S.
Received November 18, 1858.

The existence in the nitrogen-series of a well-defined group of diamines of the formula

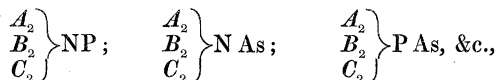


rendered it probable that the continued study of the phosphorus-,

arsenic-, and antimony-bases would lead to the discovery of the corresponding terms,



which might be designated as diphosphines, diarsines, and distibines; and the further prosecution of this line of thought very naturally suggested the idea of searching for a group of intermediate compounds containing simultaneously nitrogen and phosphorus, nitrogen and arsenic, phosphorus and arsenic, &c., compounds expressed by the formulæ



which might be termed phosphamines, arsamines, phospharsines, &c.

Among the several processes likely to furnish this result, none appeared more promising than the reaction between a monamine and a monophosphine of opposite chemical characters.

In the conception of this idea, I have studied the deportment of cyanic acid and some of its derivatives with phosphoretted hydrogen and its homologues, in the hope of producing combinations similar in constitution to the ureas, but differing from these substances by containing phosphorus in the place of one equivalent of nitrogen.

The action of cyanate and sulphocyanide of phenyl, an account of which I have lately* submitted to the Royal Society, upon triethylphosphine, seemed to include the conditions for the realization of such compounds.

On bringing cyanate of phenyl in contact with triethylphosphine, a most lively reaction ensues; the mixture begins to boil, and the phosphorus-base is apt to be inflamed. On cooling, the liquid solidifies into a crystalline mass, which is insoluble in water, soluble in alcohol and ether, and crystallizes from the latter solvent in beautiful little square tables, tasteless, inodorous, and infusible at 100° C. On submitting this compound to analysis, I was surprised to find that it contained no phosphorus, and that it exhibited the composition of the original cyanate of phenyl, from which it differs so essentially in its properties. This substance is the *cyanurate of phenyl*, generated from the cyanate by simple transposition of the elements. The

* Proceedings, vol. ix. p. 274.

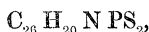
triethylphosphine participates only indirectly in the reaction; in giving rise to the transformation of the cyanate, the phosphorous body plays the part of a ferment, a comparison which is moreover suggested by the large proportion of cyanate over which the influence of a minute quantity of phosphorus-base extends. A glass rod moistened with triethylphosphine solidifies, almost instantaneously, a considerable quantity of the cyanate. The transformation of the cyanate under the influence of triethylphosphine, into cyanurate, although the principal phase of the reaction, is attended by other changes which I intend to examine more minutely by and by.

Very different results were obtained by substituting for the cyanate the sulphocyanide of phenyl. The reaction between this body and triethylphosphine is very violent, and frequently gives rise to the inflammation of the phosphorus-base. The mixture assumes a deep yellow colour, and often deposits splendid yellow needles on cooling; frequently, however, it remains liquid for hours and even for days, but suddenly solidifies, when touched with a glass rod, into a hard, yellow, crystalline mass. This substance is insoluble in water; it dissolves with the greatest facility in alcohol, hot or cold, likewise in warm, less so in cold ether. Recrystallization from boiling ether affords, in fact, the best means of procuring the new body in a state of purity. This end is likewise considerably facilitated, by allowing the sulphocyanide of phenyl to act upon the triethylphosphine in the presence of a considerable quantity of ether.

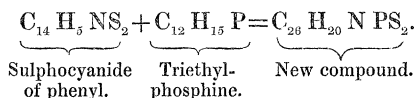
In the pure state the new compound presents itself in the form of well-defined prisms of uranium-yellow colour, which fuse at 61° C. They cannot be heated much beyond their fusing-point without being altered; at 100° C. they are entirely decomposed, evolving a most peculiar odour, which is also observed on evaporating the ethereal mother-liquor.

The new compound possesses the characters of a well-defined base. Quite insoluble in water, it dissolves in the most dilute acids, forming with some of them, such as hydrochloric and hydrobromic acid, beautifully crystallized saline compounds. From these salts the base may be separated again by cautiously adding either potassa or ammonia. The hydrochloric solution of the base yields with dichloride of platinum a yellow crystalline precipitate, sparingly soluble in water, insoluble in alcohol and ether.

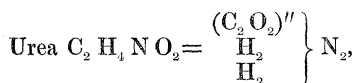
Analysis of the yellow crystals, dried over sulphuric acid, led to the formula



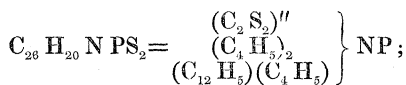
which shows that they are formed by the simple union of the two substances placed in contact :



If we consider urea as a diamine derived from diammonia by the substitution of the diatomic molecule carbonyl ($\text{C}_2 \text{O}_2$)'' for 2 equivs. of hydrogen,



—the simplest perhaps of the many views brought forward regarding the constitution of urea,—the new substance, which formation as well as chemical deportment essentially characterize as an analogue of urea, may be represented by the following formula :—



that is, urea, the oxygen of which is replaced by sulphur, the hydrogen by ethyl and phenyl, and lastly, half the nitrogen by phosphorus.

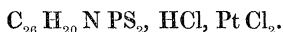
The formation of this compound presents considerable interest, not only as an illustration of the remarkable persistence of the type urea, but also as furnishing the first unequivocal instance of the formation of ureas containing no longer any unreplaced hydrogen, the existence of which had as yet remained doubtful.

The new urea forms, as I have stated, a series of well-defined beautifully crystallized salts. Its solution in warm hydrochloric acid solidifies, on cooling, into a crystalline mass, which, when recrystallized from warm water, is obtained in splendid needles of a bright cadmium-yellow colour, often several inches in length. They are decomposed at 100°C ., and must therefore be dried over sulphuric acid *in vacuo*. Analysis proved them to contain



The solution of this salt yields with dichloride of platinum a bright yellow precipitate, which under the microscope is found to consist of

small lily-shaped crystals. Dried over sulphuric acid *in vacuo* it contains

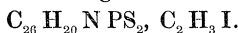


The hydrochlorate yields also a precipitate with trichloride of gold ; the salt is, however, rapidly blackened.

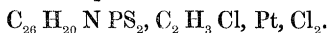
The hydrobromate, both in preparation and properties, resembles the hydrochlorate. Its composition is



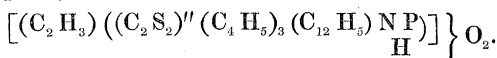
The urea readily combines with iodide of methyl and ethyl. The methyl-compound immediately separates in the crystalline form on mixing an ethereal solution of the urea with iodide of methyl ; it is soluble in water, and crystallizes from a boiling solution in beautiful golden-yellow needles, containing



The iodide, by the action of chloride of silver, may be converted into the chloride ; this yields with dichloride of platinum a fine needle-formed salt, which may be recrystallized without decomposition. The formula of this platinum-salt is



When treated with oxide of silver, the iodide furnishes a powerfully alkaline liquid, probably the corresponding base



Scarcely separated, however, this substance decomposes with liberation of sulphocyanide of phenyl, the oxide of methyl-triethylphosphonium remaining in solution. This salt is sufficiently characterized by the readily crystallizable octahedral platinum-salt.

I have not been able to obtain either the sulphate or the nitrate of the urea, probably on account of the great instability of the new substance.

On dissolving the base, even in dilute nitric acid, it is immediately decomposed with separation of sulphocyanide of phenyl, the triethylphosphine being oxidized. The same change is observed when one of the more stable salts, such as the hydrochlorate, is dissolved in a large quantity of water ; the liquid soon becomes turbid from the elimination of oily globules of sulphocyanide of phenyl, and now contains the hydrochlorate of the phosphorus-base.

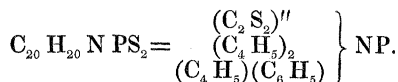
On adding ammonia to a salt of the urea, similar phenomena are

observed. From a concentrated solution, the base is separated without change; but when dilute and hot solutions are employed, the turbidity at first produced disappears, and after a few minutes beautiful crystals of phenyl-sulphocarbamide ($C_{14}H_8N_2S_2$)* make their appearance; at the same time the odour of triethylphosphine becomes perceptible.

With potassa the deportment is perfectly analogous, but the crystals formed after some time are diphenyl-sulphocarbamide (sulphocarbamilide, $C_{26}H_{12}N_2S_2$) instead of phenyl-sulphocarbamide.

On adding to an ethereal solution of the urea a few drops of bisulphide of carbon, the liquid, when gently heated, assumes a deep crimson colour, and deposits, on cooling, the beautiful compound $(C_4H_5)_3P, C_2S_4$, which I have described some time ago†. The mother-liquor yields on evaporation oily drops of sulphocyanide of phenyl.

The deportment of triethylphosphine with sulphocyanide of phenyl induced me to investigate the action of this body upon several other sulphocyanides. The substance which at once suggested itself for examination was sulphocyanide of allyl, mustard-oil. This compound reacts most powerfully with the phosphorus-base. On mixing the two bodies, a powerful evolution of heat takes place, and the mixture assumes a deep brown colour, but does not solidify either on cooling or on agitation. After several days' standing, however, very large well-defined crystals are deposited which unfortunately are contaminated with the brown colouring matter of the solution. I have not yet succeeded in getting them perfectly white, and have therefore not analysed them. Their formation, however, and their general characters leave no doubt that they are the corresponding allyl-compound,



Triethylphosphine has remained in contact with sulphocyanide of ethyl for more than a month without depositing any crystals. *A priori*, however, the formation of an urea under these circumstances was doubtful, since sulphocyanide of ethyl differs from the corresponding phenyl- and allyl-compounds, even in its deportment with ammonia and the monamines.

* Proceedings of the Royal Society, vol. ix. p. 276.

† Ibid. p. 290.

In conclusion, it deserves to be mentioned that there appears to exist a similar series of arsenetted ureas. Triethylarsine, when left for some weeks in contact with sulphocyanide of phenyl, deposits small crystals of a body which I believe to be the arsenic-compound corresponding to the phosphorus-urea described in this paper. This body requires a more minute examination.

- II. "On the Deflection of the Plumb-line in India caused by the Attraction of the Himalaya Mountains and the elevated regions beyond, and its modification by the compensating effect of a Deficiency of Matter below the Mountain Mass." By the Venerable Archdeacon PRATT. Communicated by Mr. STOKES, Sec. R.S. Received October 25, 1858.

(Abstract.)

The author begins by referring to his former paper, published in the 'Transactions' for 1855, in which he calculated the deflections caused by the mountain mass on the north of Hindostan, at three principal stations of the Great Arc, in the plane of the meridian, viz. Kaliana (lat. $29^{\circ} 30' 48''$), Kalianpur ($24^{\circ} 7' 11''$), and Damargida ($18^{\circ} 3' 15''$). He made them $27''\cdot853$, $11''\cdot968$, and $6''\cdot909$ (or more correctly, as revised in the present Paper, $27''\cdot978$, $12''\cdot047$, and $6''\cdot790$); and showed that the comparison of these two portions of the arc—which, if it *be* elliptical, and if the amplitudes are accurately known, ought to give the exact ellipticity of the arc in question—gives an ellipticity of $\frac{1}{426}$, instead of the mean $\frac{1}{300}$.

2. He next states that the Astronomer Royal, in a subsequent communication (in 1855), suggests that there is most probably a deficiency of matter immediately below the mountains which will cause a *negative* deflection, and so compensate for the mountain attraction. Three objections are urged against this hypothesis, as stated by Mr. Airy. It requires (1) that the solid crust should be only about ten miles thick; (2) that the crust should be lighter than the lava on which it rests; (3) that wherever there is a protuberance upwards in mountain masses and table-lands, there must be a corresponding projection of the crust downwards into the fluid, which it is difficult to conceive, as the same reason which is used to show it would prove also that, where there are hollows above as in deep