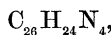


Further, from a short notice published some years ago by Mr. Perkin*, safranine appears to be a by-product in the preparation of mauveine.

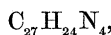
Relations such as suggested by the above formulæ must, however, be received with great caution. The violet colouring-matter derived from safranine by phenylation has not as yet been further characterized. No great stress can be laid on the similar colour-reactions with acids exhibited by both bases, since the methylated rosanilines, on treatment with acids, also become first blue and then green. Moreover it is doubtful whether the base obtained by Mr. Perkin as a secondary product in the manufacture of mauveine really is the same safranine which we have investigated, inasmuch as some preliminary analyses have led him to a very different composition, which appears to be expressed by the formula



Finally, the composition of mauveine itself cannot be looked upon as established above all question; at least Mr. Perkin† seems still to hesitate between the formula



which appears to result from more recent experiments, and the formula

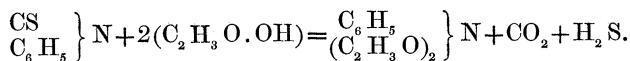


previously announced by him.

The relations here pointed out are, however, well worthy of a thorough experimental investigation. As we intend to continue this inquiry, an opportunity may present itself for their further elucidation.

IV. "New Method for producing Amides and Nitriles." By E. A. LETTS, Berlin University Laboratory. Communicated by A. W. HOFMANN, F.R.S. Received August 15, 1872.

Some time since Professor Hofmann‡ showed that phenyl mustard-oil, when acted on by acetic acid under pressure, is converted into phenyl-diacetamide, carbonic anhydride and sulphuretted hydrogen being separated.



Bearing this reaction in mind, the question arose as to how the metallic sulphocyanates would behave under similar circumstances; at Professor Hofmann's suggestion I have submitted this question to an experimental investigation.

Action of Acetic Acid on Potassium Sulphocyanate.

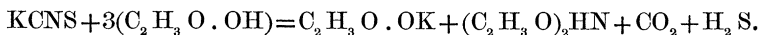
Supposing the potassium salt of sulphocyanic acid to undergo a change

* Perkin, Proc. R. Inst. of Great Britain, vol. v. p. 572.

† Perkin, *loc. cit.*

‡ Hofmann, Berichte d. Deutsch. Chem. Gesell. 1870.

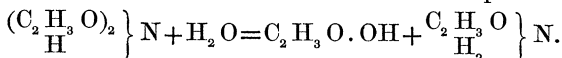
analogous to that observed with the phenyl mustard-oil, it was to be expected that 1 molecule of this body would react with 3 molecules of acetic acid to produce 1 molecule of potassium acetate and 1 molecule of diacetamide, carbonic anhydride and sulphuretted hydrogen being evolved.



The reaction, however, takes a different course.

In my first experiments the acetic acid was allowed to react on the sulphocyanate under pressure; but it soon became evident that this was unnecessary, simple digestion of the two bodies in a flask provided with an upright condenser being amply sufficient.

The powdered salt dissolves readily in the boiling acid, and an immediate and copious disengagement of gas ensues, in which carbonic anhydride and sulphuretted hydrogen may be readily recognized. Considerable time, however, elapses before the sulphocyanate is completely decomposed, some three or four days being required for a mixture of 100 grms. of potassium sulphocyanate and 180 grms. of acetic acid. At the end of this time the products of the reaction were submitted to distillation and commenced boiling at 170° – 180° ; the thermometer, however, rose rapidly to 216° ; and between this temperature and 220° the distillate solidified in the receiver to a radiating crystalline mass, which analysis showed to be pure *acetamide**. Above 220° nothing further distilled, the residue in the retort consisting wholly of potassium acetate. In what manner had acetamide been formed, instead of diacetamide expected in the reaction? It appeared not unlikely that the acetic acid employed contained some water, and that the diacetamide produced in the first instance was thus converted into the monocompound—



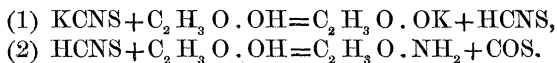
To remove any water which might possibly have been present, the acetic acid was treated with phosphoric anhydride, and the experiment with the sulphocyanate repeated; but even now acetamide was exclusively obtained.

On submitting, however, the gases evolved during the reaction to a closer examination, the formation of acetamide became at once intelligible. It was found that a large proportion of these consisted of carbonic oxysulphide (COS). To prove the presence of this compound, it was only necessary to pass the evolved gases through a bottle containing a slightly acid solution of lead, by which the sulphuretted hydrogen was retained: thus purified, they produced no further precipitate when passed through a second bottle containing the same solution; but precipitation at once took place if this were rendered alkaline by soda or ammonia.

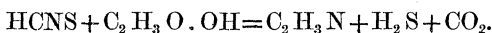
* The liquid products passing over before 216° yield considerable quantities of the amide on fractionation; the same remark applies to the other experiments with the *fatty acids* to be presently described.

This is the characteristic behaviour of carbonic oxysulphide, which was further identified by its odour, great density, and inflammability.

The principal reaction that takes place when acetic acid is treated with potassium sulphocyanate accordingly is as follows :—



The sulphuretted hydrogen and carbonic anhydride, produced simultaneously with the carbonic oxysulphide, are the complements of a second reaction, the principal product of which I have no doubt is *acetonitrile* :

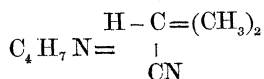


I must remark, however, that I have not actually proved the formation of this body by experiment. My investigations in the acetic series were completed before this phase of the reaction was thoroughly understood; and thus probably, owing to its low boiling-point (77°), the acetonitrile had been carried off with the stream of disengaged gases, and had escaped detection. I have not repeated the experiment, because in other series it has been easy to demonstrate the formation of the nitrile.

Action of Isobutyric Acid on Potassium Sulphocyanate.

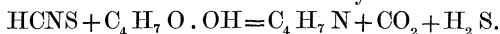
If potassium sulphocyanate be heated with isobutyric acid (which may now be readily obtained in a state of purity by oxidation of isobutylic alcohol separated from fusel-oil), the salt melts under the acid to an oily layer, from the surface of which bubbles of gas are plentifully disengaged, consisting, as in the preceding case, of carbonic oxysulphide, carbonic anhydride, and sulphuretted hydrogen. In consequence of the higher boiling-point of isobutyric acid (154°), the reaction proceeds more rapidly than with acetic acid. If the mixture be submitted to distillation when all disengagement of gas has ceased, it begins boiling a few degrees above 100°, the thermometer rapidly rising to 216°; during this time an aromatic liquid passes over, possessing the odour of butyric acid.

Between 216° and 220° the thermometer remains tolerably stationary, the distillate solidifying in the receiver to a white crystalline mass. On fractionating the liquid portion passing over before 200°, no product can be obtained showing a constant boiling-point; but on treating it with a solution of caustic soda, an oily aromatic liquid of characteristic odour floats on the surface, which, separated by a tap-funnel and dried over calcium chloride, boils constantly between 107° and 108°. Its composition and reactions characterize this substance as isobutyronitrile :



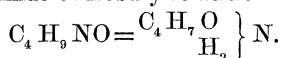
		Theory.	Experiment.
C ₄	48	69·56
H ₇	7	10·14
N	14	20·30
		<hr/>	<hr/>
		69	100·00

Boiled for some time with an alkali, this nitrile is converted into isobutyric acid and ammonia. The complementary products attending the production of this body are carbonic anhydride and sulphuretted hydrogen, the copious evolution of which has been already mentioned :



Isobutyronitrile has been prepared by Morkownikoff*. He obtained it by treating isopropyl iodide with cyanide of potassium ; but probably not in a state of purity, as he gives 80° as its boiling-point, whereas 107–108° (the number obtained by myself) approaches more closely that observed for the normal butyronitrile (114°).

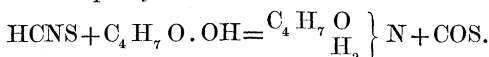
The crystalline substance before described as passing over between 216° and 220° is the amide of isobutyric acid :



The analysis gave :—

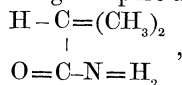
		Theory.	Experiment.
C ₄	48	55·17
H ₉	9	10·35
N	14	16·09
O	16	18·39
		<hr/>	<hr/>
		87	100·00

Isobutyramide forms a white crystalline mass of pleasant aromatic odour ; it fuses between 100° and 102°, and when heated somewhat above this temperature, but far short of its boiling-point, sublimes in beautiful iridescent laminae. It boils between 216° and 220°, and distils without the slightest decomposition. It dissolves readily in water and alcohol, and slightly in ether. Isobutyramide is the principal product of the action of isobutyric acid on potassium sulphocyanate :

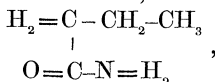


200 grms. of the acid yielded 60 grms. pure amide.

Isobutyramide,



is distinguished from the normal amide,

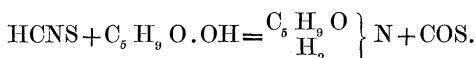
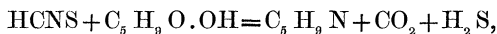


* Morkownikoff, Jahresb. xviii. 318.

by its lower melting-point. The isocompound fuses between 100° and 102° , whereas the normal butyramide melts at 115° . The boiling-point is much the same for both*.

Action of Valeric Acid on Potassium Sulphocyanate.

In this instance, too, the reaction proceeds according to the two equations—

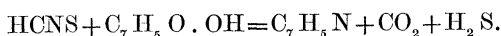


The separation and purification of the valeronitrile and valeramide are similar in all respects to those employed for the corresponding compounds in the butyric series. Valeronitrile, already investigated by other chemists, boils between 125° and 128° . By treatment with fuming nitric acid, it is converted into a crystalline substance (perhaps $\text{C}_5 \text{H}_8 (\text{NO}_2)_2 \text{N}$), which I have not as yet been able to examine further.

Valeramide closely resembles isobutyramide. It is a white crystalline body of pleasant aromatic odour, recalling that of valerian-root: it is soluble in water, alcohol, and ether; in the last-mentioned liquid much more so than isobutyramide. From hot water it crystallizes in large right-angled but very thin plates. Valeramide fuses between 125° and 128° , and sublimes, in the same manner as isobutyramide, below its boiling-point, which lies between 230° and 232° . It distils without decomposition.

Action of Benzoic Acid on Potassium Sulphocyanate.

The aromatic acids of the $\text{C}_n \text{H}_{(2n-8)} \text{O}_2$ series act in an analogous manner on potassium sulphocyanate, with the difference, however, that here nearly exclusively the nitrile is formed. The production of amide is so insignificant as to be scarcely recognizable. The reaction with *benzoic acid* takes place with particular facility, according to the equation



2 mols. benzoic acid and 1 mol. potassium sulphocyanate (both in a perfectly dry condition) are placed in a retort, to the mouth of which a long wide tube is attached to serve as condenser. The apparatus thus arranged is placed vertically, and heated either in a paraffin-bath or over the naked flame. Both bodies melt, forming two layers, of which benzoic acid is the lower one. At 190° the reaction commences, carbonic anhydride and sulphuretted hydrogen being evolved. At a higher temperature the mixture enters into ebullition, and in about half an hour is converted into a solid mass. The retort is now reversed, and the contents

* It is remarkable that acetamide, butyramide, and isobutyramide all have nearly the same boiling-point, namely 216° – 220° .

strongly heated; they melt, boil, and yield a semisolid distillate. The distillation is carried on as far as possible without charring the residue, which consists of potassium benzoate (from which half the benzoic acid employed may be recovered). By addition of ammonia to the semisolid distillate any benzoic acid that has passed over is retained, whilst the nitrile distils with the water, from which it is afterwards separated, dried, and redistilled. A roughly carried out experiment yielded 50 per cent. of the theoretical quantity of nitrile in a perfectly pure condition; the loss owing to secondary reactions is amply compensated by the ease and rapidity of the operation.

Action of Cuminic Acid on Potassium Sulphocyanate.

An experiment with cuminic acid yielded very satisfactory results: cumonitrile was obtained in about the same proportions as the benzonitrile. The temperature at which the reaction commenced was here about 210° ; the nitrile was purified as in the preceding case.

Finally, an experiment was made with cinnamic acid; but although sulphuretted hydrogen was evolved, and the reaction appeared to proceed exactly as in the foregoing cases, no cinnamonitrile was obtained in the liquid distillate. The cinnamic acid seemed to be decomposed into carbonic anhydride and cinnamol before being acted upon by the sulphocyanic acid.

The ease with which nitriles and amides are obtained in this manner, both in the aromatic and fatty series, induces me to hope that the new method may be of use in many cases, and perhaps, by its application to other series, give rise to bodies hitherto uninvestigated.

The tediousness of preparing the acid chloride and subsequent treatment with ammonia (for the amide), or of the amide with phosphoric anhydride (for the nitrile), in the ordinary method for producing these nitrogen compounds, is here replaced by simple digestion of the acid with sulphocyanate of potassium, bodies generally readily procurable.

- V. "Investigation of the Attraction of a Galvanic Coil on a small Magnetic Mass." By JAMES STUART, M.A., Fellow of Trinity College, Cambridge. Communicated by the President. Received July 26, 1872.

From investigations given by Ampère, we can deduce an expression for the potential U at an external point Q of a closed circular galvanic current carried by a wire of indefinitely small section. Let a be the radius of the circle; let the distance of Q from C , the centre of the circle, be r ; and let the line CQ make an angle θ with the normal to the plane of the circle. Then it can be shown that when r is less than a ,