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This agreement makes it already very probable that the Rontgen rays also consist in transversal vibrations; these experiments however yield a firmer proof for this thesis. If namely we accept the supposition of Barkla as to the way of generation of secondary rays in bodies with a small atomic weight, then it may easily be shown, that the supposition of a longitudinal vibration of the primary Röntgen rays would, in the experiment discussed here, lead to a maximum action of the tertiary rays in a vertical plane and not in an horizontal plane, as was the case.

Groningen, Physical Laboratory of the University.

Chemistry. — "Triformin (Glyceryl triformate)". By Prof. P. VAN ROMBURGII.

Many years ago I was engaged in studying the action of oxalic acid on glycerol 1) and then showed that in the preparation of formic acid by Lorin's method difformin is produced as an intermediate product.

Even then I made efforts to prepare triformin, which seemed to me of some importance as it is the most simple representative of the fats, by heating the diformin with anhydrous oxalic acid, but I was not successful at the time. Afterwards Lorin's repeated these last experiments with very large quantities of anhydrous oxalic acid and stated that the formic acid content finally rises to  $75^{\circ}/_{\circ}$ , but he does not mention any successful efforts to isolate the triformin.

Since my first investigations, I have not ceased efforts to gain my object. I confirmed Lorin's statements that on using very large quantities of anhydrous oxalic acid, the formic acid content of the residue may be increased and I thought that the desired product might be obtained after all by a prolonged action.

Repeated efforts have not, however, had the desired result, although a formin with a high formic acid content was produced from which could be obtained, by fractional distillation in vacuo, a triformin still containing a few percent of the di-compound.

I will only mention a few series of experiments which I made at Buitenzorg, first with Dr. Nanninga and afterwards with Dr. Long. In the first, a product was obtained which had a sp.gr. 1.309 at 25°, and gave on titration 76.6°/<sub>0</sub> of formic acid, whilst pure triformin requires 78.4°/<sub>0</sub>. The deficiency points to the presence of fully 10°/<sub>0</sub> of diformin in the product obtained.

<sup>1)</sup> Compt. Rend. 93 (1881) 847.

<sup>2)</sup> Compt. Rend. 100 (1885) 282.

(110)

In the other, the diformin, was treated daily, during a month, with a large quantity of anhydrous oxalic acid, but even then the result was not more favourable.

The difficulty in preparing large quantities of perfectly anhydrous oxalic acid coupled with the fact that carbon monoxide is formed in the reaction, which necessitates a formation of water from the formic acid, satisfactorily explains the fact that the reaction does not proceed in the manner desired. A complete separation of di- and triformin cannot be effected in vacuo as the boiling points of the two compounds differ but little.

I, therefore, had recourse to the action of anhydrous formic acid on diformin. I prepared the anhydrous acid by distilling the strong acid with sulphuric acid in vacuo and subsequent treatment with anhydrous copper sulphate. Even now I did not succeed in preparing the triformin in a perfectly pure condition, for on titration it always gave values indicating the presence of some  $10^{\circ}/_{\circ}$  of diformin.

Afterwards, when  $100^{\circ}/_{\circ}$  formic acid had become a cheap commercial product, I repeated these experiments on the larger scale, but, although the percentage of diformin decreased, a pure triformin was not obtained.

I had also tried repeatedly to obtain a crystallised product by refrigeration but in vain until at last, by cooling a formin with high formic acid content in liquefied ammonia for a long time, I was fortunate enough to notice a small crystal being formed in the very viscous mass. By allowing the temperature to rise gradually and stirring all the while with a glass rod, I succeeded in almost completely solidifying the contents of the tube. If now the crystals are drained at 0° and pressed at low temperature between filter paper and if the said process is then repeated a few times, we obtain, finally, a perfectly colourless product melting at 18°, which on being titrated gave the amount of formic acid required by triformin.

The sp. gr. of the fused product at 18° is 1.320.

$$n_{18}^d = 1.4412.$$

MR. 35.22; calculated 35.32.

The pure product when once fused, solidifies on cooling with great difficulty unless it is inoculated with a trace of the crystallised substance. On rapid crystallisation needles are obtained, on slow crystallisation large compact crystals are formed.

In vacuo it may be distilled unaltered; the boiling point is 163° at 38<sup>mm</sup>. On distillation at the ordinary pressure it is but very slightly decomposed. The boiling point is then 266°. A product contaminated

with diformin, however, cannot be distilled under those circumstances, but is decomposed with evolution of carbon monoxide and dioxide and formation of allyl formate.

If triformin is heated slowly a decided evolution of gas is noticed at 210° but in order to prolong this, the temperature must rise gradually. The gas evolved consists of about equal volumes of carbon monoxide and dioxide. The distillate contains as chief product allyl formate, some formic acid, and further, small quantities of allyl alcohol. In the flask a little glycerol is left 1).

Triformin is but slowly saponified in the cold by water in which it is insoluble, but on warming saponification takes place rapidly.

Ammonia acts with formation of glycerol and formamide. With amines, substituted formamides are formed, which fact I communicated previously <sup>2</sup>).

The properties described show that triformin, the simplest fat, differs considerably in its properties from the triglycerol esters of the higher fatty acids.

Chemistry. — "On some derivatives of 1-3-5-hexatriene". By Prof. P. van Romburgh and Mr. W. van Dorssen.

In the meeting of Dec. 30 1905 it was communicated that, by heating the diformate of s-divinylglycol we had succeeded, in preparing a hydrocarbon of the composition  $C_{\mathfrak{g}}H_{\mathfrak{g}}$  to which we gave the formula:

$$CH_2 = CH - CH = CH - CH = CH_2$$
.

Since then, this hydrocarbon has been prepared in a somewhat larger quantity, and after repeated distillation over metallic sodium, 50 grams could be fractionated in a Ladenburg flask in an atmosphere of carbon dioxide.

The main portion now boiled between 77°—78°.5 (corr.; pressure 764.4 mm.).

Sp. gr.<sub>13.5</sub> 0.749  $n_{D|3.5}$  1.4884

Again, a small quantity of a product with a higher sp. gr. and a larger index of refraction could be isolated.

<sup>1)</sup> This decomposition of triformin has induced me to study the behaviour of the formates of different glycols and polyhydric alcohols on heating. Investigations have been in progress for some time in my laboratory.

<sup>2)</sup> Meeting 30 Sept. 1905.