

*Citation:*

Romburgh, P. van, On the action of ammonia and amines on allyl formate, in:  
KNAW, Proceedings, 8 I, 1905, Amsterdam, 1905, pp. 138-141

**Chemistry.** — “*On the action of ammonia and amines on allyl formate*”. By Prof. P. VAN ROMBURGH.

The great ease with which allyl formate is saponified by alkalis induced me to try whether ammonia, which, as is well-known, acts upon esters of fatty acids but slowly at the ordinary temperature, would not react equally readily on this ester. The result surpassed my expectation.

If gaseous ammonia is passed into allyl formate still containing a little allyl alcohol, it is rapidly absorbed whilst the liquid gradually becomes so hot, that it is necessary to connect the flask with a reflux apparatus in order to prevent loss of ester. If the contents are heated to 120°, when the increase in weight slightly exceeds 1 mol. of ammonia to one mol. of ester, the excess of ammonia passes off with the allyl alcohol and if now the residue is distilled in vacuo, a fine yield of formamide is obtained (b.p.<sub>10</sub> 113°), which, after a single freezing, melts at 2°.4<sup>1</sup>).

If, however, dry ammonia is passed into *pure* allyl formate, hardly any action is noticed in the first hour. The ammonia is but slowly dissolved so that the concentration is only very small, but gradually as the reaction proceeds the gas is more eagerly absorbed and the temperature rises increasingly.

If, therefore, we wish to prepare in a short time large quantities of formamide by means of this method it is advisable to add to the allyl formate a few percents of allyl alcohol, although this may cause a slight diminution in the limit value<sup>2</sup>), as happens, generally, in the formation of amides from esters.

I showed many years ago that allyl formate may be readily prepared by heating the diformine<sup>3</sup>) of glycerol, obtained from glycerol and oxalic acid. As we can now obtain commercial formic acid of great concentration (99—100 %) at a very low price, large quan-

<sup>1</sup>) FRANCHIMONT (Rec. XVI, 137) found the melting point at 3°; other observers state a lower figure.

Pure formamide may be distilled by rapid heating without perceptible decomposition (b.p. 219°); at least with such a preparation I did not succeed in demonstrating the formation of ammonia and carbon monoxide, which are readily obtained from an impure product.

<sup>2</sup>) BONZ, Zeitschr. phys. Chem. II, 865.

<sup>3</sup>) I think it is not superfluous to point out that the theory recently defended by NEF (Ann. 335, 230) that the formation of allyl alcohol from glycerol and oxalic acid must be explained by a dissociation of diformine into formic acid and propargyl alcohol is based on an error. The main product of diformine on heating is allyl formate.

ties of allyl formate may be prepared in a still more convenient manner by heating equal parts by weight of glycerol and formic acid. The temperature is kept for some time at 125°, during which dilute formic acid distills over. Gradually it is raised to 240° and, with a quiet evolution of CO<sub>2</sub>, containing a little CO, a mixture passes over consisting of allyl formate, allyl alcohol and a very little formic acid. This is again submitted to distillation, the portion boiling up to 100° being collected. After treatment with dry potassium carbonate, the liquid is again distilled and the portion boiling below 85°, which mainly consists of allyl formate, is collected separately.

This ester may also be procured by distilling allyl alcohol with twice its weight of formic acid and collecting the portion passing over below 85°. The product is then treated with dry potassium carbonate and once more rectified.

After it had been ascertained that ammonia acts so very readily with allyl formate it was decided to try the action of amines also.

The investigation showed that amines of the fatty series, primary as well as secondary ones, readily react with the same. Benzylamine, phenylhydrazine and piperidine also seemed to react but no reaction could be observed with aniline.

If we mix one of these amines with allyl formate, in the majority of cases a rise in temperature does not necessarily take place immediately.

This rise rather varies in the different cases; whilst its maximum is sometimes reached fairly quickly, sometimes only after a lapse of about 20 minutes.

The reaction appears to be of such a nature that when working at a constant temperature we can ascertain its progress by means of a quantitative determination of the absorbed amine.

I intend making a series of experiments with different amines. The following contains a brief description of some qualitative experiments.

If methyl- or ethylamine is passed into allyl formate these substances are absorbed with great evolution of heat and the amides formed are left behind after distilling off the allyl alcohol.

5 grams of propylamine being mixed with 10 grams of allyl formate the temperature rapidly rose from 19° to 60° and propylformamide (b.p. 219°—220°) was formed.

5 grams of isopropylamine being mixed with 10 grams of the ester the temperature slowly rose to 50°, whilst a good yield of isopropylformamide was obtained (b.p. 203°—204°).

5 grams of isobutylamine being mixed with 7 grams of allyl formate the temperature rose to 75°. The — not as yet described — isobutylformamide boiled at 229°.

5 grams of allylamine being mixed with 10 grams of the ester the temperature rose to 65° and the allyl alcohol being removed by distillation, allylformamide was obtained (b.p. 220°.5).

With benzylamine (5 grams) and allyl formate (5 grams) the temperature rose from 19° to 55°. The alcohol being distilled off and allowed to cool to the ordinary temperature, there remained in the flask a solid mass, m. p. 62°. The melting point was not altered after recrystallisation the compound from petroleum ether, which is very suitable for this purpose.

Benzylformamide was first obtained by HOLLEMAN<sup>1)</sup>, who described it as a substance melting at 49°. This statement is probably due to a clerical error, at least, a specimen prepared by Prof. HOLLEMAN and kindly presented to me by Dr. VERMEULEN of the Groningen Laboratory did not begin to soften until 59°. Boiling petroleum ether extracted a substance melting at 62°, which on being mixed with my own product did not alter its melting point.

Phenylhydrazine gives no rise of temperature with allyl formate, but on being kept for a day, an abundant quantity of formylphenylhydrazine forms, m. p. 145°.

With secondary aliphatic amines there is less heat evolved in the action on allyl formate.

Dimethylamine readily forms dimethylformamide. The action of 7 grams diethylamine on 10 grams of allyl formate causes (in about 20 minutes) a slow rise to 33°. Diaethylformamide was readily obtainable in a pure condition. Dipropylamine (5 grams) mixed in a WEINHOLD flask with 5 grams of the ester caused a slow rise to 35°.5. The dipropylformamide obtained boiled at 211° (corr.).

Judging from a preliminary experiment, diisopropylamine seems to react less readily; 3 grams of both compounds being mixed, only a slight elevation of temperature was noticed. This reaction deserves in particular a closer study.

With diisobutylamine the evolution of heat is also trifling; only 3° rise 10 grams of each substance being mixed. All the same, a good yield of diisobutylformamide was obtained, which boils at 227°—228° (corr.) and which, to my knowledge, has not yet been described.

Methylbenzylformamide (5 grams) with allyl formate (5 grams) gives a rise to 55°. The product formed has not yet been solidified.

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<sup>1)</sup> Rec. 13. 415.

Piperidine (10 grams) with allyl formate (14 grams) gives a rise from 10° to 83°, and a very good yield of the formyl derivative, b. p. 220°.

The boiling points of the substituted formamides exhibit peculiar regularities to which I hope to refer later on.

The dialkylformamides and formylpiperidine have acquired some importance owing to the interesting researches of BOUVEAULT <sup>1)</sup>, who used them as a starting point in the preparation of aldehydes; the above described simple methods of preparation may perhaps prove to be of service.

**Chemistry.** — “*On the action of hydrocyanic acid on ketones*”.

By A. J. ULTEE. (Communicated by Prof. P. VAN ROMBURGH).

Although it is stated in every textbook on organic chemistry that ketones may combine with hydrocyanic acid, the conditions under which this addition takes place have up to the present not been studied, and only those few cyanohydrins which are solid and may consequently be readily purified by recrystallisation have been isolated in a pure condition <sup>2)</sup>).

Three methods of formation of these substances are known:

1<sup>st</sup>. Action of dilute or anhydrous hydrocyanic acid on ketones, either by heating the mixture for some hours in sealed tubes at 100° or by simply leaving the two components in contact with each other at the ordinary temperature for several months.

2<sup>nd</sup>. Action of nascent hydrogen cyanide on ketones, for instance by very slowly dropping fuming hydrochloric acid on potassium cyanide covered with acetone.

3<sup>rd</sup>. By double decomposition of the so-called bisulphite compounds of the ketones with a solution of potassium cyanide.

A closer study of the nitriles of the oxy-acids was made in consequence of an observation made by Prof. VAN ROMBURGH <sup>3)</sup> as to the action of solid potassium carbonate on a mixture of dry acetone and hydrocyanic acid; a small quantity of this salt caused the mass to boil and the temperature to rise to 70°.

The same phenomenon is caused by potassium hydroxide, potassium cyanide, ammonia, amines, in fact by all substances whose aqueous

<sup>1)</sup> Bull. Soc. chim. [3] 31, 1322.

<sup>2)</sup> Acetonecyanohydrin, obtained from Kahlbaum, seemed to contain much free hydrocyanic acid.

<sup>3)</sup> Meeting 27 June 1896.