

Citation:

Ultee, A.J., On the action of hydrocyanic acid on ketones, in:
KNAW, Proceedings, 8 I, 1905, Amsterdam, 1905, pp. 141-144

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 ¹⁾, 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 ²⁾).

Three methods of formation of these substances are known:

1st. 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.

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

3rd. 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 ³⁾ 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

¹⁾ Bull. Soc. chim. [3] 31, 1322.

²⁾ Acetonecyanohydrin, obtained from Kahlbaum, seemed to contain much free hydrocyanic acid.

³⁾ Meeting 27 June 1896.

solutions possess hydroxyl ions; the presence of water greatly favours this catalysis.

If an attempt is made to isolate the evidently formed cyanohydrin by distillation under reduced pressure it is again resolved for the greater part into its components. If, however, the action of the potassium carbonate is stopped by means of a few drops of sulphuric acid, the mixture on being fractionated in vacuo first yields a distillate consisting of hydrocyanic acid and acetone and then the nitrile; by a second distillation this may be obtained in such a state of purity that silver nitrate with nitric acid no longer gives a precipitate of silver cyanide.

Traces of a base are, however, sufficient to again partially resolve the pure nitrile into its components, which in this case is, of course, accompanied by a fall in temperature.

Theory demands that the same equilibrium should be reached whether we start from one mol. of acetone plus one mol. of hydrogen cyanide or from pure cyanohydrin. In order to check this it is not necessary to determine the equilibrium both ways by analysis; the easiest plan is to measure some physical constant; for this I chose the refraction.

Found, starting from a mixture of acetone (1 mol.), hydrogen cyanide (1 mol.) and a trace of potassium hydroxide $n_D^{12} = 1,39721$.

Found, starting from the pure nitrile and a trace of potassium hydroxide $n_D^{12} = 1,39818$.

It having been thus ascertained that it makes no difference from what system we start, it became important to express the equilibrium in figures.

For practical reasons I always started from the nitriles; about one gram of the compound and 0,2 milligr. of potassium hydroxide (in a 10% solution) were introduced into a tube, which was then sealed and immersed in a beaker containing a solution of silver nitrate acidified with nitric acid, and the whole was then suspended in a thermostat for some hours.

If now the tube is broken the nitric acid at once neutralises the potassium hydroxide and the free hydrocyanic acid will be precipitated as silver cyanide. The liquid is decanted, the precipitate is dissolved in potassium cyanide and the silver deposited electrolytically in the usual manner. In this way it was found that one mol. of acetone and one mol. of hydrogen cyanide combine at 0° to the extent of 94,15%, at 25° to the extent of 88,60%.

For ethylmethylketone these values are, respectively 95,57% and 90,36%; for diethylketone 95,90% and 91,29%.

It is my intention to also determine this equilibrium in the case of other aliphatic and aromatic ketones and also aldehydes.

The investigation of URECH's diacetocyanohydrin and the products of the action of gaseous hydrochloric acid on oxynitriles quoted by PINNER¹⁾ but as far as I know not further studied, has already been taken in hand.

In the light of the above results I have examined the different modes of preparation of the oxynitriles more closely.

Method 1. Dry hydrocyanic acid mixed with dry acetone and kept for six months in a well-closed steamed flask is still completely unchanged. On mixing, a slight rise in temperature took place. That, however, no trace of the addition product has been formed may be proved by first determining the total percentage of hydrocyanic acid by means of the well-known titration with silver nitrate and then by ascertaining the amount of free hydrocyanic acid in the same way as was done in the determination of the equilibria. We will then find the same figures. After six months the mixture still showed the same refraction, which also proves that no change had yet taken place.

The reason why previous investigators obtained cyanohydrin all the same may be safely attributed to the fact that there were still present traces of moisture and that minute traces of alkalis from the glass vessel considerably accelerate the reaction.

It is now also obvious why the methods 2 and 3 should lead to a good result as the alkaline potassium cyanide is always present in excess. It need hardly be said that the formation of nascent hydrogen cyanide previously looked upon as the most important factor in method 2 has nothing to do with the real reaction.

Although former investigators²⁾ have not succeeded in preparing pure cyanohydrin by the second method, nothing is easier than the isolation of the pure nitrile by distillation under reduced pressure, if only care be taken to have a slight excess of hydrochloric acid present after the reaction has taken place.

The following are the chief properties of the nitriles, as yet investigated.

Dimethylketonecyanohydrin is a perfectly colourless liquid practically odourless. Sp. gr. at 18° 0,9342. Decomposes on distillation at the

¹⁾ B. B. 17, 2009.

²⁾ URECH, Ann. 164, 255.

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ordinary pressure, b.p. at 23 mm. 82° , m.p. $-19,5^\circ$, $n_D^{25} = 1,40526$.

Ethylmethylketonecyanohydrin, colourless liquid with a faint ketone-like odour. Sp. gr. at $18,5^\circ$ 0,9324. Boiling point at 20,5 m.m. 91° . Does not solidify in a paste of solid carbon dioxide and acetone. $n_D^{12,5} = 1,41775$.

Diethylketonecyanohydrin, colourless, a somewhat stronger odour than the former nitrile. Sp. gr. at $18,5^\circ$ 0,9300. Boiling point at 18,5 m.m. $97,5^\circ$, does not solidify in a paste of carbon dioxide and acetone. $n_D^{18} = 1,42585$.

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Chemistry. — “*The molecular rise of the lower critical temperature of a binary mixture of normal components.*” By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

1. In the “*Chemisch Weekblad*” of April 8th 1905 (II, N^o. 14) I derived an expression for the so-called molecular rise of the lower critical temperature, viz:

$$\frac{1}{T_1} \left(\frac{dT_x}{dx} \right)_0 = 2\sqrt{\theta\psi} - (1 + \psi),$$

in which θ represents the ratio of the two critical temperatures $\frac{T_2}{T_1}$ and ψ the ratio $\frac{b_2}{b_1}$.

In this I started from the approximate assumption, that the critical temperature of a binary mixture may be represented by the simple expression

$$fR T_x = \frac{a_x}{b_x}.$$

The formula found is at any rate more accurate than that of VAN 'T HOFF, according to which the molecular rise would be *constant* (*Chem. Weekbl.* of Nov. 21st 1903 (I, N^o. 8)), and I adduced a few examples to show that the expression found by me represents the experimental results of CENTNERSZWER¹⁾ very accurately — provided the molecular weight of the solvent SO_2 is *doubled*.

BÜCHNER in his thesis for the doctorate²⁾ came to pretty much the same result with regard to CO_2 as solvent. He, too, had to double the molecular weight of CO_2 in order to get sufficient concordance

¹⁾ Z. f. Ph. Ch. **46**, 427—501 (1903).

²⁾ June 1905, p. 125—130.