

Citation:

Romburgh, P. van, Action of methylethylketone on 2.3.4.6. Tetranitrophenyl methylnitramine, in: KNAW, Proceedings, 18 I, 1915, Amsterdam, 1915, pp. 98-100

17. From these tables it is evident that the velocity of melting at the same temperature is *cef. par.* greater with β -sodium than with α -sodium. Consequently the quantity of heat wanted to transform 1 gram of solid β -sodium into the molten state is less than that which must be added for that purpose to the same quantity of α -sodium. From this we may conclude that the transformation β -sodium \rightarrow α -sodium is accompanied by an *evolution* of heat. The fact that this heat of transformation is positive, proves that *if* there exists a transition point it is to be looked for in the direction of higher temperatures¹⁾. The facts described in § 14, prove that such a transition point does not exist and consequently sodium is monotropic.

18. Finally it may be pointed out that HAGEN²⁾, who determined the coefficient of dilation of sodium (between 0° C. and its melting point) by dilatometric measurements, was not able to observe these phenomena as the quantity of metal used by him (40 grams) has been too small.

The value of this physical constant determined by this author is consequently *fortuitous* and must be redetermined with the pure α - and β -modifications.

We express our best thanks to Dr. H. R. KRUYT to whom we are indebted for many valuable remarks.

Utrecht, April 1915.

VAN 'T HOFF-Laboratory.

Chemistry. — “Action of methylethylketone on 2. 3. 4. 6. tetranitrophenylmethylnitramine”. By Prof. P. VAN ROMBURGH.

(Communicated in the meeting of April 23, 1915).

As stated by me previously³⁾, this nitramine reacts readily with alcohols and amines. Water also acts on it with formation of nitrous acid and of 2. 4. 6. trinitromethylnitraminophenol. Whereas at the ordinary temperature this action proceeds very slowly it takes place fairly rapidly at boiling temperature.

In order to get to know more accurately the progressive change of the reaction some previous investigations were made a few years ago by me conjointly with Dr. SINNIGER, which gave the result

¹⁾ BAKHUIS ROOZEBOOM, Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre. 1, 178; Braunschweig 1901.

²⁾ Wied. Ann. 19, 436 (1883)

³⁾ Rec 8, 275 (1889).

that the nitramine, when dissolved in acetone, reacts very rapidly with water even at the ordinary temperature, so that the preparation of the phenol in this manner is a very simple one.

Now it did not seem devoid of importance to know something more as to the rôle played here by the acetone and, therefore, I have studied this reaction more closely. It appeared, however, that great difficulties are experienced in the separation and identification of the products generated in addition to hydrocyanic acid, which forms abundantly, so that I thought it desirable to try whether satisfactory results can be obtained more readily by using another ketone, which then perhaps may serve to also elucidate the reaction with acetone.

It now appeared that methylethylketone lends itself very well for that purpose.

If, at the ordinary temperature, we dissolve the nitramine in so much moist ketone that a concentrated solution is obtained, we notice that the original pale yellow colour of the solution rapidly begins to darken and soon after, a yellow product crystallizes, which proved to be the 2.4.6. trinitromethylnitroaminophenol. In my experiments I generally used 11 grams of nitramine, which I dissolved in 16 c.c. of ketone to which 0.8 c.c. of water was added. At first, I took more nitramine (33 grams = $\frac{1}{10}$ gram mol.) but then towards the end of the operations explosions frequently took place.

If we decant the ketone solution from the crystals and subject the same to a distillation (in the water-bath) an intensively yellow coloured liquid with a peculiar odour passes over. It contains hydrogen cyanide which was identified by the Prussian blue test. The yellow colour, also the odour pointed to the presence of diacetyl.

If to the liquid we add a solution of silver nitrate to precipitate the hydrogen cyanide and subsequently to the filtrate an *excess* of ammonia a white voluminous precipitate is obtained which according to FITTIG, DAIMLER, and KELLER¹⁾ is characteristic of diacetyl. The detection of the diacetyl by means of hydroxylamine presented, owing to the excess of methylethylketone, a little difficulty.

Still, by using a liberal quantity of hydroxylamine I succeeded in obtaining crystals of dimethylglyoxime, which gave with a nickel salt and ammonia the characteristic red nickel compound.

In order to detect any volatile products eventually formed, the flask which had been heated in the waterbath at 100° was evacuated and placed in an oilbath heated at 120°. A substance began to

¹⁾ Ann. 249, 205 (1888).

distill which deposited in a crystalline form in the exit tube, when the flask exploded with a loud report.

In subsequent experiments the heating was therefore solely conducted in vacuo at 100° in a waterbath and in this way I also succeeded in obtaining small quantities of crystals, which after being pressed between paper melted at 76° and gave no depression of the melting point with *α*-*iso*-nitrosomethylethylketone. In addition there distilled a little of a liquid acid, which, after neutralisation with sodium carbonate solution gave with silver nitrate a white precipitate, which on heating with water turned black.

If the nitramine is heated with moist methylethylketone a rather violent action sets in, but otherwise the reaction proceeds as described above. If we take ketone that has been dried over calcium chloride we also get a yellow, diacetyl containing distillate.

If, however, we take nitramine that has been standing for some days in a desiccator over sulphuric acid and ketone that has been dried with phosphoric anhydride, no reaction takes place at the ordinary temperature even after two days. On heating in the waterbath the ketone passes over entirely colourless. If the distillation is interrupted, the nitramine in the flask crystallizes unchanged. On long continued heating in the waterbath the distillate first shows traces of hydrogen cyanide and gradually also a faint yellow coloration, which need cause no surprise because, on heating at 100°, the nitramine itself yields traces of nitrous vapours. So much, however, is pretty certain that in the experiment with moist ketone the formation of the reaction products found will have to be attributed largely to the action on the ketone of the nitrous acid generated by the water, when the strongly acid phenol will also have exerted its influence.

The fact that the reaction takes place so rapidly in the ketone solution even at the ordinary temperature may be caused by the great concentration, but there also exists the possibility that the presence of the acetone accelerates the reaction. Experiments to make sure about this and also to study the influence of the water on the nitramine in other indifferent solvents are in progress. In water-saturated ether a conversion of nitramine into phenol also takes place fairly rapidly.

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