

It has also been shown that tephrosin is a hydroxydeguelin and that the hydroxyl group in tephrosin occupies the position of one of the hydrogen atoms attached to either carbon atom 7 or 8 in the deguelin formula.

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NOTES

The Decomposition of *n*-Valerolactone

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Proof has already been presented¹ in support of the statement that *n*-valerolactone will not withstand distillation at atmospheric pressure—reports to the contrary notwithstanding—since it undergoes partial decomposition as it approaches its boiling point. The nature of this decomposition has now been traced to the formation, in the main, of a polymerization product, and an explanation has been found for the discrepancies in the vapor pressure curves of this compound when obtained by two different methods of procedure, a dynamic² and a static.³ How the former conclusion has been arrived at is summarized in this communication.

In order to fix a point of departure in the study of this problem, the assumption was made that the decomposition in question is accompanied by the evolution of carbon dioxide and the formation of a butene (2:3 or 1:2). The set-up in which the decomposition studies were carried out closely simulated the conditions which obtain in the determination of pressure-temperature relationships. To that end the lactone was heated under thermostatically controlled conditions in a 2.5-cc. bulbous glass decomposition chamber to which had been sealed an 8-mm. delivery tube provided with a short upright side arm which was later to serve the dual purpose of introducing or removing samples and as an aid in sweeping out the air from the apparatus with nitrogen. At a distance of about 25 mm. from this side arm, the tube was bent at an angle of 45°; beyond that, as a precautionary measure against loss of material during heating, it took the form of a spiral condenser. A delivery tube leading from the latter to an inverted, mercury-filled buret completed the system.

That the reaction herein involved is not wholly due to a decarboxylation with the formation of a butene was shown by the fact that a 3.16-g. sample yielded only about 1 cc. of gas on heating for 530 hours at 202 ± 0.5°, which is four degrees below the alleged boiling point of this compound at atmospheric pressure. Although this gas was found to contain some carbon dioxide, yet no evidence could be secured that ethylenic hydrocarbons had been formed in the decomposition. A repetition of the

¹ Schuette and Thomas, *THIS JOURNAL*, **52**, 2028 (1930).

² Ramsay and Young, *J. Chem. Soc.*, **47**, 42 (1885).

³ Smith and Menzies, *THIS JOURNAL*, **32**, 1412 (1910).

experiment during the course of which, at three time intervals, samples were removed for ultimate analysis showed that the residue, except for change in color, had altered only slightly during a 773-hour heating, having changed from $C = 59.58$ and $H = 8.17$ to $C = 59.32$ and $H = 7.74$. For these reasons it appears quite probable that the main course of the reaction is such as to favor the formation of a polymerization product. Further support for this conclusion may be found in the fact that the observed vapor pressures¹ when measured by a dynamic method² were lower than the calculated at any given temperature above that at which this compound begins to decompose. This is to be expected were a polymerization takes place.

The static method³ of measuring pressure-temperature relationships which was employed is very susceptible to the influence of gaseous decomposition products even though their quantity may be small. An immediate effect of this characteristic is to be found in the higher values which were obtained by this method of measurement. The foregoing observations account, it seems, for the discrepancies which were previously noted in vapor pressure measurements by two different methods of approach.

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Preparation and Properties of the Normal Barium Salt of *l*-Cystine.¹

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Several normal metallic salts of cystine have already been described. In 1900, Embden² prepared the normal copper salt and employed it in the isolation of the amino acid. A little later, Neuberg and Mayer³ prepared the corresponding salts of silver, mercury, lead and cadmium as well as of copper. Recently, Toennies and Lavine⁴ have succeeded in obtaining the lithium, sodium and potassium salts of cystine in crystalline form.

In the course of a study of the alkaline decomposition of cystine, which will be presented in a separate paper, it was observed while adding crystalline barium hydrate to a hot aqueous suspension of *l*-cystine that most of the cystine went into solution at a certain stage and that immediately thereafter a pale yellow precipitate separated out. By filtering off this pre-

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² Embden, *Z. physiol. Chem.*, **32**, 94 (1901).

³ Neuberg and Mayer, *ibid.*, **44**, 498 (1905).

⁴ Toennies and Lavine, *J. Biol. Chem.*, **90**, 203 (1931).