Analysis of total nitrogen according to Kjeldahl-Gunning, and for urea nitrogen by the Benedict and Gephart and the P. T. methods were carried out in each mixture. Besides these the total nitrogen in the filtrate from the phosphotungstic acid precipitation was determined. The Benedict and Gephart method was modified insofar as 10 per cent. sulphuric acid was substituted for hydrochloric acid in the hydrolysis.

The results obtained indicate that the accuracy of the urea estimation is not impaired by the addition of phosphotungstic acid. Uric acid and creatinine are practically completely precipitated by phosphotungstic acid, and that which remains in solution is not sufficient to appreciably affect the urea values.

In Tables II and III are recorded figures on a mixed sample of human urines to which varying amounts of uric acid and urea had been added. To make the results comparative the urine was diluted one-half with water previous to its analysis and the mixtures with urea and uric acid diluted in the same proportion. It is evident that if the addition of uric acid does not affect the method then the values of urea nitrogen for the mixtures should coincide with the figure obtained on the urine diluted one-half with water. The calculated values in the last column are such as would be expected, considering that the increase of total nitrogen is due entirely to added urea when such was added.

The influence of added ammonium chloride is shown in the figures of Table IV. The same urine was used for this experiment as in the previous series reported in Table III. It is evident from the figures that there is no reason to believe that under these conditions ammonia is not completely precipitated by phosphotungstic acid.

Finally the comparative results of urea estimation on one sample of mixed human urine as obtained by the Folin, the Benedict and Gephart and by the P. T. methods are compiled in Table V. We desire to emphasize the fact that the figures of urea by the P. T. method are duplicates of six distinct analyses of the same urine and not six duplicates of one filtrate.

[Contributions from the Havemeyer Laboratories of Columbia University, No. 166.]

THE CONDENSATION OF ACETONE BY MEANS OF CALCIUM OXIDE.

By Alfred Hoffman.[1]

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The formation of mesityl oxide from two, and of isophorone and the xylitones from three and four molecules of acetone under the influence of calcium oxide has been studied and the constitution of the products

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[1] Read at the General Meeting of the Am. Chem. Soc., Baltimore, Dec. 1908.

established by a number of investigators.[1] The present research deals with the mechanism of the reaction. The questions considered were the following: Does acetone condense to form all of the above products simultaneously, or are the simpler ones formed first, and then the more complex? Are there any other products formed?

To decide the first question, an apparatus was used which prevented the first products formed from again coming into contact with the reagent. This consists of an ordinary Soxhlet extraction apparatus in which the acetone is placed in the flask and the reagent, lime, in the extraction cup. On heating on the water-bath, the acetone is volatilized, condenses on the lime and siphons off in the usual manner. As the reaction is quite slow, only a small part of the acetone in contact with the lime is condensed each time. The high boiling point, 130°, of even the simplest product, mesityl-oxide, prevents its volatilization with the acetone.

After heating several days on the water-bath, the condensation product had accumulated to such an extent that the mixture ceased to boil. It was then fractioned and found to consist, with the exception of unchanged acetone, almost entirely of mesityl oxide. The high-boiling products, such as isophorone and the xylitones, were present only in traces. It is therefore evident that they are secondary products formed by the condensation of mesityl oxide with acetone or with itself.

On careful fractionation of a large amount of condensation product, a small quantity of a substance was isolated which was identified as diacetone, $(CH_3)_2C(OH)CH_2COCH_3$. This substance has been described in the literature as the result of the action of alkalies on acetone and has also been considered a hypothetical step in the condensation of acetone to mesityl oxide.[2] Of the latter fact, no proof has apparently been offered up to the present time excepting the easy conversion of diacetone to mesityl oxide by dehydrating agents. In the present case, it seemed probable that the calcium hydroxide formed from the oxide had caused the formation of the diacetone. In order to prove this, the experiment was repeated as above, substituting dry calcium hydroxide for the oxide. Again a condensation product was obtained, consisting entirely of diacetone. It is interesting to note that although, according to the investigations of Koelichen,[3] the conversion of acetone to diacetone by an alkali is a reversible reaction and at the temperature of the water-bath only a few per cent. of the diacetone are in equilibrium with the acetone, it is possible by the above arrangement to prepare very concentrated solutions of the former.

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[1] Voelkel, *Ann.*, **82**, 63 (1852). Fittig, *Ann.*, **110**, 32 (1859). Knoevenagel, *Ann.*, **207**, 185 (1897). Also several others.

[2] Cohen, *Organic Chemistry*, **1907**, p. 273.

[3] *Zeit. phys. Chem.*, **33**, 171 (1900).

It remains to be shown that the mesityl oxide formed in the first experiment was actually formed by the dehydration of diacetone. Absolutely dry acetone and purest calcium oxide were heated together in a sealed tube at 105–10° for several hours and the acetone recovered entirely unchanged. When, however, a trace of calcium hydroxide was added, the product was a thick sirup of the higher condensation products. Hydroxide and acetone alone gave only acetone with a small quantity of diacetone. Hence, a definite proof has been obtained that the reaction proceeds in two stages as has been formerly shown in the case of aldehydes.

In the same way it was shown that dry mesityl oxide and acetone, or mesityl oxide alone do not react with pure calcium oxide, but do if hydroxide is present. The intermediate products in this case are still under investigation, as are the products formed in the case of the homologous ketones, as well as the product formed by the ketone with the alkali preliminary to the aldol condensation.

HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY,
NEW YORK, April 27, 1909.

NOTE.

A Useful Oil Bath.—A mixture of ten parts of refined cotton-seed oil and one part of beeswax makes a very satisfactory oil bath. It emits very little fume below 250° C. and can be used safely almost throughout the range of the ordinary mercury thermometer, having a flash point above 300° C. when heated in an open cup. A sample of hard paraffin under the same conditions flashed at 215° C.

The mixture has the advantage of the paraffin bath that it solidifies on cooling, so that there is not the liability of the oil spilling out when not in use, and it has the added advantage that it melts quickly and can be used almost immediately after heat is applied, as there is no hard cake that must first be melted as with paraffin. LOUIS W. BOSART, JR.

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