UTILIZATION OF FURFURAL. II.

PREPARATION OF PYRROLYDINE FROM TETRAHYDROFURANE IN THE VAPOUR PHASE

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The optimum conditions of the ammonolysis of tetrahydrofurane, further the correlation between the yields of pyrrolidine and the applied physical and physicochemical parameters were established.

YUREV and co-workers [1], [2], [3], [6], [8] obtained pyrrolydine in 34% yield by passing a mixture of tetrahydrofurane vapours and ammonia through alumina catalyst. According to these authors, the following reaction takes place:

Although certain patent specifications [4], [5], [7] indicate the nature of catalysts applied, some of the essential data, as *e. g.* catalyst area, space velocity of tetrahydrofurane, required for the reproduction of the reaction are not given by the mentioned authors and other patent specifications, either. REPPE and co-workers [9] produced pyrrolidine in excellent yields without describing, however, the conditions of reaction in detail.

It appeared necessary, partly owing to the aforementioned facts, to subject the conversion of tetrahydrofurane into pyrrolidine to a systematic investigation. The correlation of conversion with temperature, with feed rates of tetrahydrofurane, with the ratio tetrahydrofurane: ammonia and with the material of the reactor tube were examined as functions of one and two variables as well.

In the figures disclosing the experimental results the following notations are applied:

Ko = conversion of pyrrolidine

$$Ko = 113{,}88 \frac{d}{a} \%,$$

where d is the quantity of obtained pyrrolidine in grams, a the applied amount of tetrahydrofurane in ml, v the feed rate of tetrahydrofurane in ml/hour, and c the mole ratio.

Fig. 1 proves that the conversion of pyrrolidine is independent of the nature of reactor tube (I: iron, II: stainless steel, III: aluminium). The three curves are not identical, differences existing in the shape and dimensions of reactors.

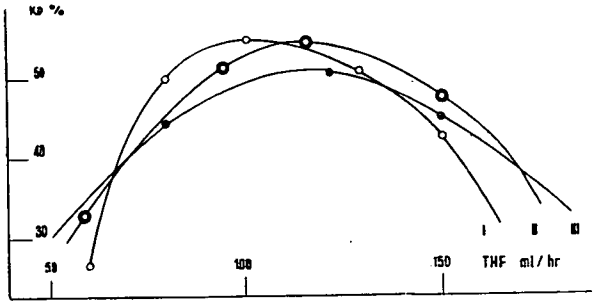


Fig. 1. 5 mole NH_3/1 mole THF
I. iron reactor
II. stainless steel reactor
III. aluminium reactor
(325° C)

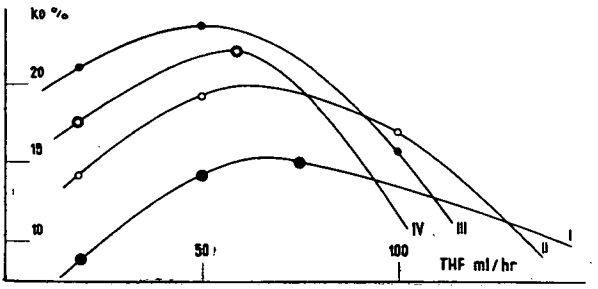


Fig. 2
I. 2 moles NH_3/1 mole tetrahydro-
II. 3,5 „ „ „ „ furane
III. 5 „ „ „ „
IV. 10 „ „ „ „
(275° C)

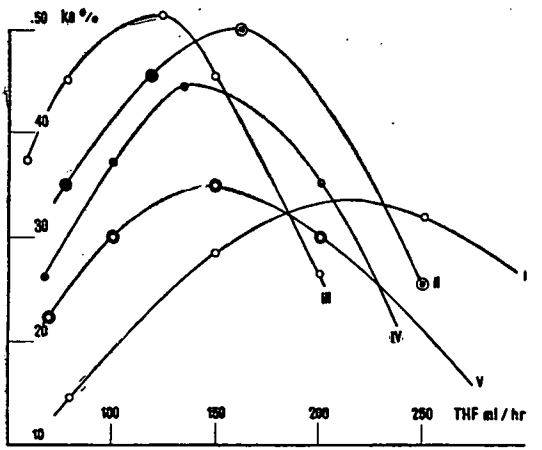


Fig. 3
I. 2 moles NH_3/1 mole tetrahydro-
II. 3,5 „ „ „ „ furane
III. 5 „ „ „ „
IV. 8 „ „ „ „
V. 10 „ „ „ „
(325° C)

Figures 2, 3, 4, 5 and 6 disclose the results of the series of experiments carried out in an aluminium tube reactor at various temperatures (275, 325, 350, 375 and 400° C). At various ratios of tetrahydrofurane to ammonia, conversion rates depend on the feed rates of tetrahydrofurane.

It can be seen that 275° is the lowest temperature at which the reaction can take place, although solely when tetrahydrofurane is dosed at a low feed rate. Conversion rates plotted against temperature yield a maximum curve, with a peak at 350°. It can be stated as well that the maximum con-

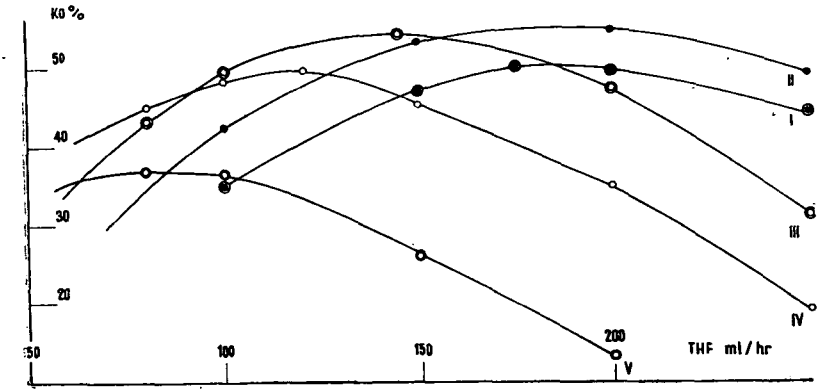


Fig. 4. I. 2 moles NH_3/1 mole tetrahydrofurane
II. 3,5 „ „ „ „
III. 6,5 „ „ „ „
IV. 10 „ „ „ „
V. 20 „ „ „ „
(350° C)

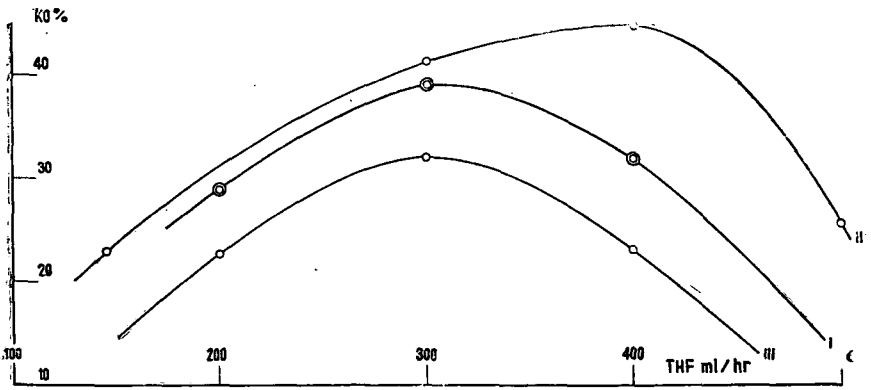


Fig. 5. I. 2,5 moles NH_3/1 mole tetrahydrofurane
II. 3,5 „ „ „ „
III. 10 „ „ „ „
(375° C)

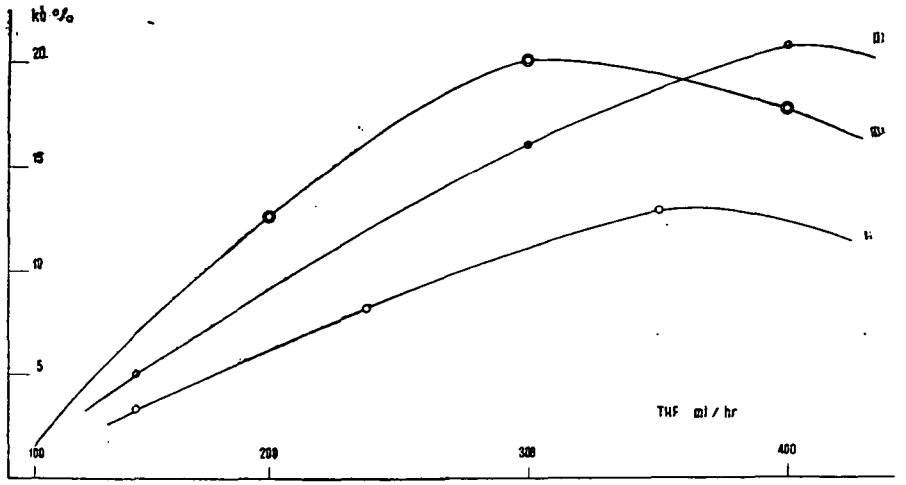
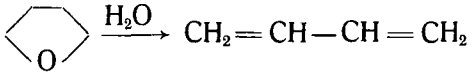


Fig. 6. I. 6 moles NH_3/1 mole tetrahydrofurane
II. 10 „ „ „ „
III. 20 „ „ „ „
(350° C)

version shifts with rising concentrations of ammonia to lower feed rates of tetrahydrofurane. Over 350° conversion rates again decrease.

It was found that maximum quantities of pyrrolidine can be obtained at temperatures between 325 and 350° at feed rate of 150—200 ml of tetrahydrofurane/hour, applying a mole ratio 3—5:1 of ammonia to tetrahydrofurane and a contact time of 12—20 sec. It was proved in the course of experiments that also a gaseous substance forms in varying quantities, mainly consisting of butadiene [8].



Subsequent to completing the reactions, the products were processed and a great number of by-products were isolated. Of these, pyrrole (I), 1-butene (3)-yl-pyrrolidine (II) and carbasole (III) were identified on the basis of their physical constants of the melting points of the end picrates, respectively. These by-products were earlier isolated by YUREV [8] and REPPE [9] as well. Their formation is interpreted as follows.

Besides, also a crystalline substance of m. p. 164,5° was isolated, possessing, according to the data of elementary analysis, the overall formula $C_{12}H_{18}$.

The quantity and quality of the by-products proved to be linear functions of temperature. However, they also depend apparently on the space velocity (the amount of by-products ranged 30% at 400°-at a space velocity of 300—400 ml tetrahydrofurane/hour, rising to 90% at 100 ml/hr. affording in the latter case a solid product).

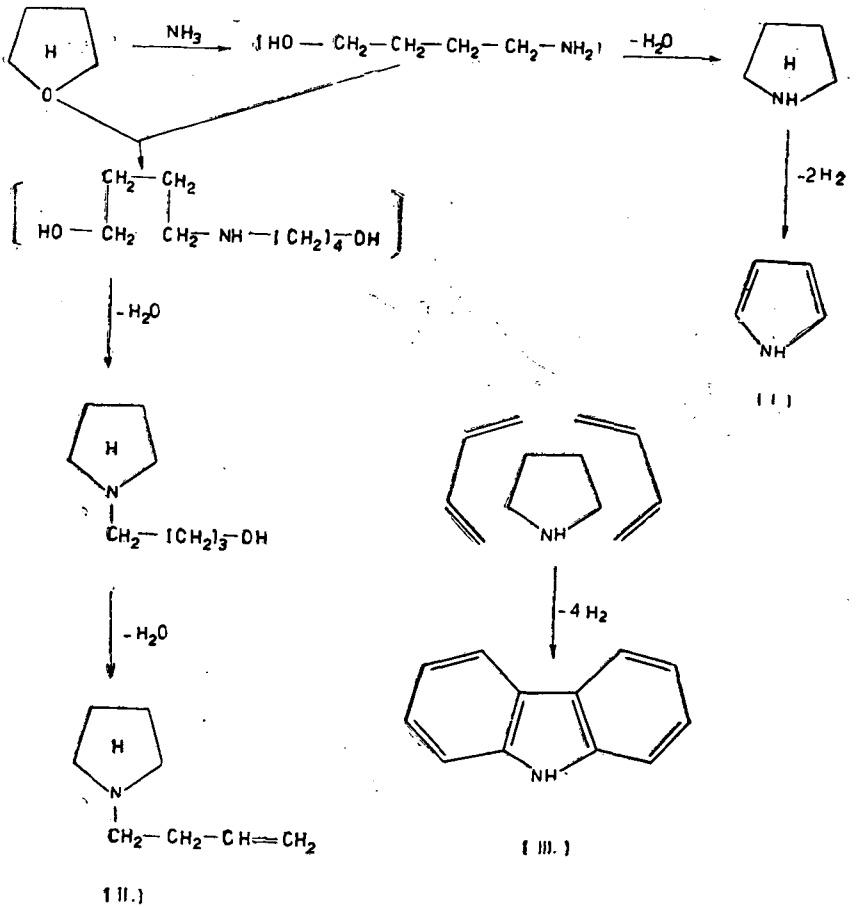


Fig. 7

Experimental

Substances applied

Tetrahydrofurane: b. p. 64—65°; sp. gr. 0,87; n_D^{21}: 1,40762.

Gaseous ammonia, technical grade.

Catalyst: γ-alumina. Catalyst of type RB-13 prepared by the Research Institute of Organic Chemical Industry, Budapest, was applied in the present experiments. On applying optimum conditions, the activity of catalyst did not decrease during use. When, however, experiments were carried out under conditions other than optimum, the surface of catalyst became contaminated by by-products of higher boiling points, and thus repeated activations were necessary.

Description of the apparatus

(The connecting tube (17) is needed only when preparing pyrrole, due to the low b. p. of furane).

Tetrahydrofurane is transferred with the use of the Diesel pump 14 operated by an electromotor, from burette 15 through pressure pipe 16, drop counter 18 and condenser 8, into evaporator 2 of the shape of a large test-tube, located in the tube reactor. Condenser 8 serves to prevent the flow of heat from the tube reactor of 350° to the drop counter. Namely, the drop counter made from glass can be connected to the metal tubes by rubber stoppers only in this way. Gaseous ammonia flows from flask 19 through

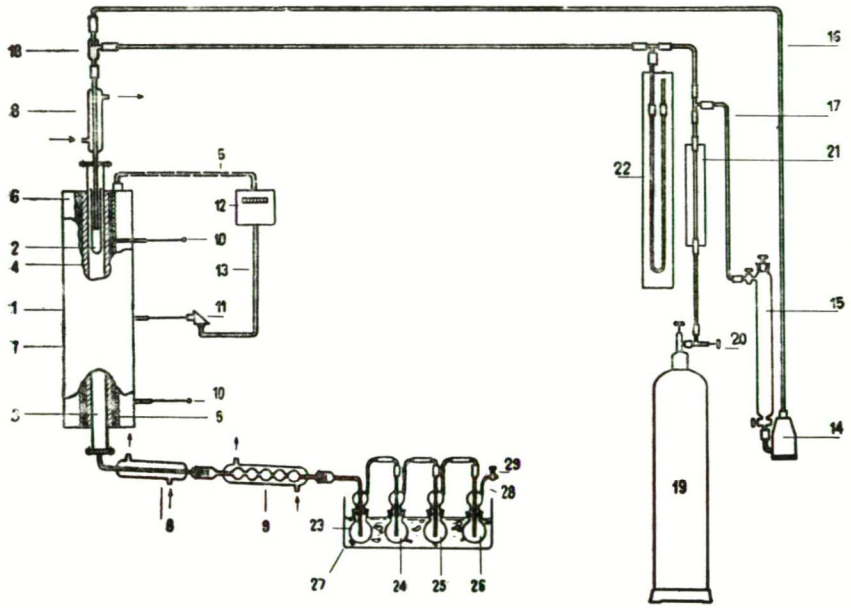


Fig. 8

needle valve 20 and rotameter 21 to meet tetrahydrofurane in the drop counter 18 where a part of tetrahydrofurane evaporates. The residual portion of tetrahydrofurane evaporates in evaporator 2 and the vapours are mixed with ammonia in the thin cylindrical area between the walls of evaporator and reactor tube, further in the area filled with chamotte beads in the upper portion of the catalyst space. The reaction takes place on the surface of alumina. Tube reactor is coated by aluminium cover 4 of 4 cm thickness, securing the steady heating of catalyst space 3. The aluminium cover reaches to the iron tube which served as a container of molten metal when the aluminium was cast. The iron tube is heated by three coils of cekas wire of 10 m length and 0,5 mm diameter 5 insulated by chamotte beads. The output of the heating coils ranges 700 watt. The coils are wound parallel to each other

around the metal block. On starting the experiment, all three coils are switched on. The operating temperature is attained by this way within 1,5 hour. Then, it is satisfactory to switch on one of the coils only, connected with temperature control 12, in order to maintain the desired temperature. The temperature of the apparatus is measured by thermoelement 11 and controlled by mercury thermometers 10. The mean thickness of heat insulation 6 is 15 cm. The main quantity of crude pyrrolidine accumulates in collector 23 inserted after ball condenser 9. It is attempted to condense further amounts of crude pyrrolidine or unchanged tetrahydrofurane in collector flasks 24,25 and 26. Tube 28 should be connected to a ventilating pipe, under a slight suction.

Reactor	Diameter cm of reactor tube	Length cm	Volume of catalyst cu. cm	Length/diameter
Iron	5.1	120	2460	23,5
Stainless steel	5,3	100	2200	18,86
Aluminium	6,8	87	3160	12,8

In order to establish the optimum conditions of the production of pyrrolidine, experiments were carried out with the aluminium reactor. The distribution of temperature along the reactor was as follows.

Length, cm	11,7	23	34,5	46,25	57,3	69,2
t, °C	265	310	320	320	297	275

The given values of length were measured from the bottom of reactor tube.

Isolation of reaction products

The colour of reaction products varied from light brown to black, depending on the conditions of reaction. On distilling the products under atmospheric pressure until the temperature of distillate attained 110°, the distillate was saturated with potassium hydroxide, crude pyrrolidine separated, dried over potassium hydroxide and fractionated by a 40 cm Widmer column. The combined distillation residues were fractionated. By this way, some pyrrolidine (86—91°), then pyrrole (125—131°) and 1-butenyl pyrrolidine (152—160°) could be separated, whilst carbasol could be isolated from the residue.

* * *

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