

The Mechanism of Pyridine Hydrogenolysis on Molybdenum-Containing Catalysts

IV. The Conversion of Piperidine

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The conversion of piperidine was investigated on a $\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$ catalysts as a function of the temperature, reaction time, initial piperidine partial pressure and the hydrogen pressure.

At 60 atm of hydrogen and conversions below 50% piperidine is selectively converted to ammonia and *N*-pentylpiperidine. This reaction appears to be a two-step process, ring-opening to pentylamine followed by a fast alkyl transfer from pentylamine to piperidine. The piperidine conversion is first order in piperidine as well as in hydrogen, and of -1 order in the total pressure of the nitrogen bases.

At higher conversions the rate of formation of pentane and ammonia are influenced by the rate of the (hydro)cracking steps, and also by the equilibrium constants of the alkyl transfer equilibria. The rate of a (hydro)cracking reaction is lower when a ring is present in the nitrogen base. The activation energies of these reactions were 160 kJ mol^{-1} , about 60 kJ mol^{-1} greater than those of alkyl transfer reactions.

At 1 atm of hydrogen the product composition was completely different from that observed at higher pressures of hydrogen.

The mechanism of the reactions is briefly discussed.

INTRODUCTION

Several authors have investigated the hydrodenitrogenation process by studying the conversion of nitrogen bases, like pyridine, piperidine and primary amines, on mostly sulfided molybdenum-containing catalysts (1-6). The deamination of primary amines is found to be fast compared with the denitrogenation of heterocyclic nitrogen bases (1-3). The rate determining step in the denitrogenation of these heterocyclic bases was reported to be the hydrogenation of the aromatic ring (2), or the rupture of this ring (1). In most of the hydrodenitrogenation studies (1, 4-6) the nitrogen bases are considered to be converted into ammonia and hydrocarbon according to one or a few reaction steps.

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However, Flinn, Larson and Beuther (2) showed that the reaction scheme is more complicated: they observed the presence of several unknown and unexpected intermediates.

We also reported the formation of intermediates in pyridine and pentylamine denitrogenation on an oxidic $\text{MoO}_3\text{-Al}_2\text{O}_3$ catalyst. *N-n*-Pentylpiperidine was observed in rather high amounts in the hydrogenolysis of pyridine (?); dipentylamine was formed by a fast disproportionation of pentylamine, as shown in Part III (8). The role of these intermediates in the denitrogenation of pyridine or of oil fractions is still unknown.

Not much information is present in the literature on the kinetics of piperidine hydrogenolysis. McIlvried (1) studied the piperidine conversion on a sulfided molybdena-alumina catalyst promoted with

nickel and cobalt. The degree of conversion was determined by Kjeldahl analysis of the nitrogen content of liquid reaction product. The rate of conversion could be described by a first order kinetics when the reaction time was varied and by about zero order when the initial piperidine partial pressure was changed. We reported the same type of kinetics for pyridine hydrogenation on CoO-MoO₃-Al₂O₃ (9).

The aim of the present study was to investigate the kinetics of the piperidine conversion, and the role of intermediate products, like *N*-pentylpiperidine, in the denitrogenation of organic nitrogen bases.

METHODS

Procedures

The high pressure equipment has been described elsewhere (7). The internal diameter of the reactor was 6 mm. The temperature of the catalyst was constant in time within 1°C; the temperature drop over the catalyst bed was 2°C at most. A thermostated saturator ($\pm 0.5^\circ\text{C}$) was used for the piperidine feed; *N*-pentylpiperidine was fed to the reactor by a capillary (7). The product compositions were determined by gas chromatographic analysis of samples taken directly after the throttle valve (10). Tubes and gas sampling valve were kept at 180°C to prevent condensation of the products. In some cases the product compositions were determined by analysis of liquid products which were obtained by means of a total condensation of reaction products in liquid nitrogen. The mass balances fitted within 10%.

A separate experiment showed no conversion of piperidine up to 350°C in the empty stainless steel reactor. At 60 atm hydrogen pressure little or no activity decline was observed at 300 and 325°C. The influence of internal and external diffusion on the rate of the reaction can be excluded as was shown by calculations.

The reaction time is defined as: $t = mP/\phi_t$ in which m = mass of catalyst (kg),

P = total pressure (N m⁻²) and ϕ_t = total moles fed to the reactor (mol sec⁻¹).

The computer simulations were carried out on a digital computer with a digital-analog converter (PDP-11).

Materials

Catalysts: γ -Al₂O₃ (AKZO, 213 m² g⁻¹), and 4% CoO-12% MoO₃-Al₂O₃ (Ketjenfine from AKZO, 235 m² g⁻¹). The particle diameter was 0.21-0.30 mm. Before use the catalysts were reduced with hydrogen at 450°C during at least 16 hr.

Piperidine was distilled under nitrogen on molecular sieves and brought into the saturator immediately after distillation.

N-Pentylpiperidine was prepared from piperidine and pentylbromide (11) and was 99.7% pure.

RESULTS

The piperidine conversion was investigated by varying the reaction temperature, the reaction time, the initial piperidine partial pressure and the hydrogen pressure. The conversion of *N*-pentylpiperidine was only studied as a function of temperature.

The effect of the temperature on piperidine conversion on the commercial CoO-MoO₃-Al₂O₃ catalyst is given in Fig. 1. Below 325°C piperidine is selectively converted into *N*-pentylpiperidine and ammonia. At increasing temperatures increasing amounts of ammonia and pentane are formed, together with small amounts of pentylamine and pyridine. Pentene was present in very small amounts (5-10% of the amount of pentane). The values given for pentane in this paper are the total amounts of pentane and pentene.

The effect of the reaction time was studied at 300 and 325°C (Figs. 2 and 3). These figures also show the selective formation of *N*-pentylpiperidine and ammonia. Pentane appears to be a consecutive product (Fig. 2). Pentylamine was observed in the products in small amounts which appeared to be independent of the reaction time (Figs. 2 and 3).

The effect of the initial piperidine partial pressure is demonstrated in Table 1. The

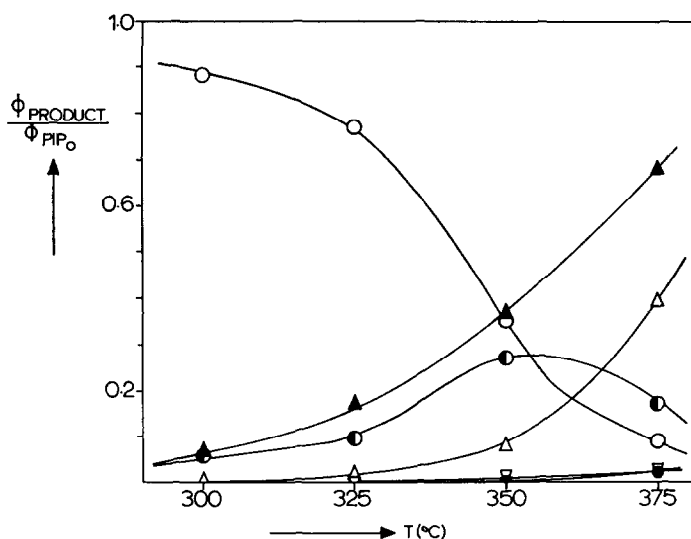


FIG. 1. The conversion of piperidine as a function of the temperature (0.77 g CoO-MoO₃-Al₂O₃; $P_{\text{H}_2} = 60 \times 10^6 \text{ N m}^{-2}$; $P_{\text{PIP}_0} = 0.33 \times 10^6 \text{ N m}^{-2}$; $t = 0.65 \times 10^7 \text{ kg N sec m}^{-2} \text{ mol}^{-1}$; (●) pyridine; (○) piperidine; (▲) ammonia; (△) pentane + pentenes; (●) *N*-pentylpiperidine; (▽) pentylamine).

total amount of nitrogen bases formed appeared to be only slightly dependent on the initial piperidine partial pressure; this points to a low order in piperidine. The change in the product distribution is remarkable: the amounts of pentylamine and decane increased nearly linearly with the piperidine pressure, whereas the forma-

tion of pentane decreased at increasing partial pressure of piperidine.

The effect of the hydrogen pressure has been studied at 325°C. The results were somewhat less accurate due to some condensation of the reaction products in the tubes and the gas sampling valve. The product distribution is given in Table 2.

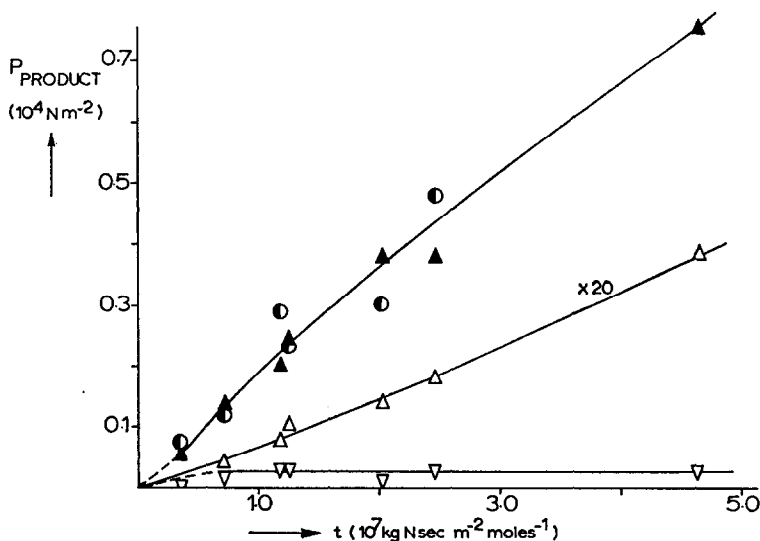


FIG. 2. The conversion of piperidine as a function of the reaction time at 300°C (0.70 g CoO-MoO₃-Al₂O₃; $P_{\text{H}_2} = 60 \times 10^6 \text{ N m}^{-2}$; $P_{\text{PIP}_0} = 0.41 \times 10^6 \text{ N m}^{-2}$; for the symbols see Fig. 1; the amount of pentane given is 20 times the amount analyzed).

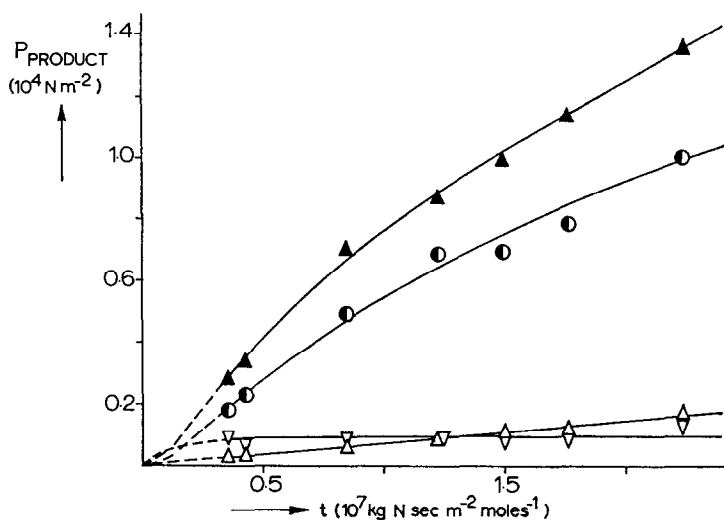


FIG. 3. The conversion of piperidine as a function of the reaction time at 325°C (0.77 g CoO–NoO₃–Al₂O₃; $P_{H_2} = 60 \times 10^5 \text{ N m}^{-2}$; $P_{PIP_0} = 0.33 \times 10^6 \text{ N m}^{-2}$ for the symbols see Fig. 1).

Experiments at 1 atm of hydrogen have also been performed on both the CoO–MoO₃–Al₂O₃ catalyst and on alumina (Figs. 4 and 5, respectively). The temperature was increased stepwise in these experiments. Decreasing the temperature at the end of the experiment showed a decline in the catalytic activity, the piperidine conversion for the CoO–MoO–Al₂O₃ catalyst falling from 0.3 to 0.1 (325°C) and for alumina from 0.4 to 0.3 (360°C). Figure 5 clearly shows the lower activity of alumina not only for dehydrogenation, as could be expected, but also for the conversion of piperidine into ammonia.

The formation of the compound C₁₀H₁₆ is remarkable. Separation of the products

by preparative gas chromatography, followed by mass spectrometry of the samples obtained, revealed that this hydrocarbon does not contain CH₃-groups and probably no ring structure. It may be the compound 1,5,9-decatriene.

In contrast to the experiments at high pressures of hydrogen, pentane, pentene, and *N*-pentylpiperidine were only observed in very small amounts in the products of the low pressure experiments.

The conversion of *N*-pentylpiperidine was only investigated as a function of temperature (Fig. 6). Cleavage of the C–N bond in the ring as well as the C–N bond between this ring and the pentyl group, do occur in the main reactions.

TABLE 1
THE EFFECT OF THE INITIAL PIPERIDINE PARTIAL PRESSURE ON THE PIPERIDINE CONVERSION^a

P_{PIP_0} (10 ⁵ N m ⁻²)	Product composition (pressures in 10 ⁵ N m ⁻²)					Total of nitrogen bases
	Pentane	Ammonia	<i>N</i> -Pentyl- piperidine	Pentylamine	Decane	
7.5	1.35	3.3	2.0	0.1	0.01	5.4
15.7	0.92	5.0 ₅	2.9	0.2	0.02	8.1
32.7	0.47	5.1 ₅	3.4 ₅	0.3	0.04	8.9
34.3	0.56	4.9 ₅	4.3	0.5	0.05	9.7
50.7	0.36	5.8	3.8 ₅	0.6	0.07	10.2
86.5	0.26	5.8	4.3	0.8	0.11	10.9

^a 0.77 g CoO–MoO₃–Al₂O₃; $T = 325^\circ\text{C}$; $P_{H_2} = 60 \times 10^5 \text{ N m}^{-2}$; $t = 0.65 \times 10^7 \text{ kg N sec m}^{-2} \text{ mol}^{-1}$.

TABLE 2
THE EFFECT OF THE HYDROGEN PRESSURE ON THE PIPERIDINE CONVERSION^a

Hydrogen pressure (10^5 N m^{-2})	Product composition (10^3 N m^{-2}) ^b			
	Pentylamine	<i>N</i> -Pentylpiperidine	Ammonia	Pentane
30	0.2	1.0	1.7	0.06
60	0.6	2.2	3.3	0.30
80	0.8	3.6	3.5	0.58

^a 0.77 g CoO-MoO₃-Al₂O₃; $T = 325^\circ\text{C}$; $P_{\text{PIP}_0} = 0.33 \times 10^5 \text{ N m}^{-2}$; $t = 0.42 \times 10^7 \text{ kg N sec m}^{-2} \text{ mol}^{-1}$.

^b Pyridine was observed only in a small amount, in particular in the experiments at 60 and $80 \times 10^5 \text{ N m}^{-2}$ hydrogen pressure.

DISCUSSION

The Reaction Scheme

The following conclusions can be drawn from our results:

i. Piperidine is converted into ammonia, pentane and pyridine; *N*-pentylpiperidine is an intermediate in the ammonia formation (Fig. 1).

ii. *N*-Pentylpiperidine is converted into ammonia and pentane; piperidine, dipentylamine and pentylamine are intermediate products (Fig. 6).

These conclusions and the formation of dipentylamine and ammonia from pentylamine by a fast alkyl transfer reaction (8) point to a reaction scheme such as that given in Fig. 7. As shown in the scheme piperidine may be formed back from its products by alkyl transfer reaction.

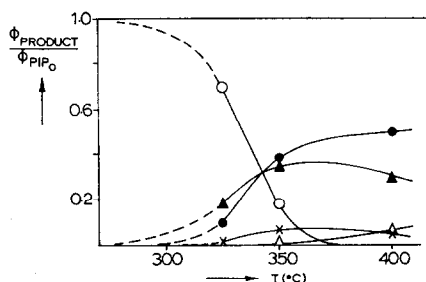


FIG. 4. The conversion of piperidine at $1 \times 10^5 \text{ N m}^{-2}$ hydrogen on the CoO-MoO₃-Al₂O₃ catalyst as a function of the temperature [1.7 g CoO-MoO₃-Al₂O₃; $P_{\text{PIP}} = 2.1 \times 10^3 \text{ N m}^{-2}$; $t = 4.6 \times 10^6 \text{ kg N sec m}^{-2} \text{ mol}^{-1}$; for the symbols see Fig. 1; (X) C₁₀H₁₆].

Establishment of Equilibria

Pyridine-piperidine hydrogenation reaction. The pyridine-piperidine equilibrium is completely on the pyridine side at 1 atm H₂ and temperatures above 300°C. Hence, this equilibrium is not established in our experiments at low hydrogen pressures. Calculations showed that this equilibrium was also not established in the experiments at hydrogen pressures up to 60 atm; the amounts of pyridine formed in these experiments were low (<0.5%).

(Hydro)cracking reactions. Both cracking and hydrocracking reactions can be considered as irreversible reactions, due to the high value of their equilibrium constants [$>10^7 \text{ N m}^{-2}$ and 10^6 , respectively, over the temperature range studied; see Fig. 5 in Ref. (7)]. This fact excludes the formation of *N*-pentylpiperidine from pentene and piperidine [see also Ref. (7)].

Alkyl transfer reactions. Figure 7 shows

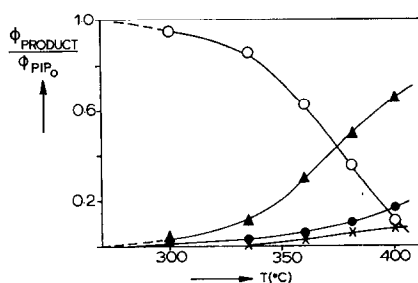


FIG. 5. The conversion of piperidine at $1 \times 10^5 \text{ N m}^{-2}$ hydrogen on alumina as a function of the temperature [2.2 g Al₂O₃; $P_{\text{PIP}_0} = 1.4 \times 10^3 \text{ N m}^{-2}$; $t = 5.5 \times 10^6 \text{ kg N sec m}^{-2} \text{ mol}^{-1}$; for the symbols see Fig. 1; (X) C₁₀H₁₆].

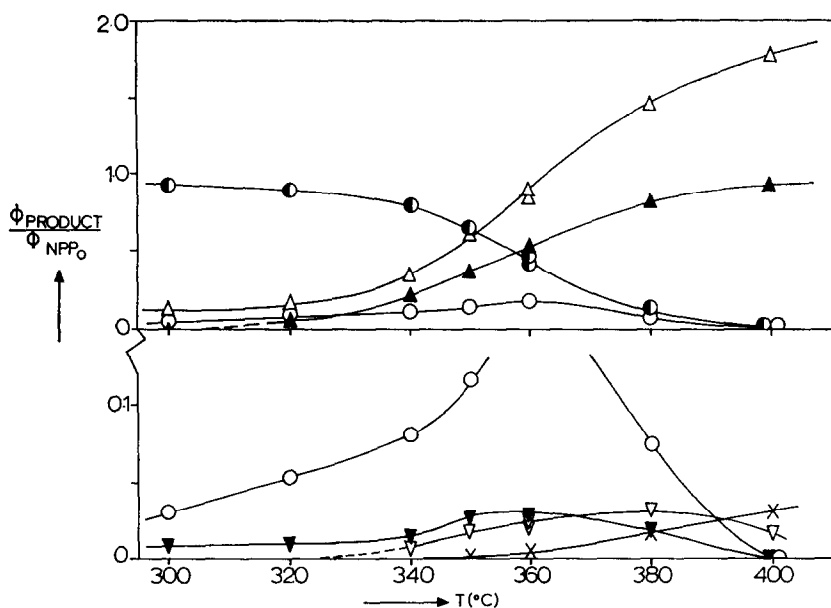


FIG. 6. The conversion of *N*-pentylpiperidine as a function of the temperature [0.7 g CoO-MoO₃-Al₂O₃; $P_{H_2} = 60 \times 10^6$ N m⁻²; $P_{NPP_0} = 0.13 \times 10^6$ N m⁻²; $t = 1.5 \times 10^7$ kg N sec m⁻² mol⁻¹; for the symbols see Fig. 1; (▼) dipentylamine⁷, (×) C₁₀H₂₂].

that *N*-pentylpiperidine (NPP) and ammonia may be formed by alkyl transfer from pentylamine to piperidine (PIP). The preceding paper (8) shows that the equilibrium of another alkyl transfer reaction, the disproportionation of two pentylamine (MPA) molecules into dipentylamine (DPA) and ammonia, is already established at relative short reaction times ($t = 0.5 \times 10^7$ kg N sec m⁻² mol⁻¹, $T = 325^\circ\text{C}$). The equilibrium constant, $K = P_{DPA} P_{NH_3} / P_{MPA}^2$, was found to be 5 at 325°C .

To check whether an equilibrium is es-

tablished for reaction 4 of the scheme in Fig. 7, we calculated the values of a pressure function defined as $F(P_i) = P_{NPP} P_{NH_3} / P_{MPA} P_{PIP}$ for the piperidine conversion as a function of the reaction time (Fig. 3). Steadily increasing values were obtained up to 10.7 at $t = 2.24 \times 10^7$ kg N sec m⁻² mol⁻¹. Hence, the equilibrium was not established under these conditions. The value of the equilibrium constant K_4 was estimated by means of the method of Van Krevelen and Chermin (13); this constant was about 100 between 250 and 400°C .

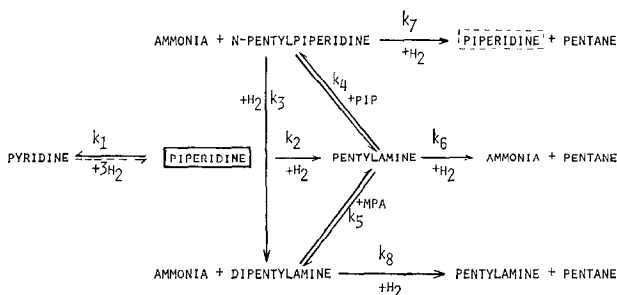


FIG. 7. Reaction scheme for the piperidine conversion on a catalyst containing molybdenum oxide.

Relative Importance of the Various Reaction Steps

Further arguments for the reaction scheme given in Fig. 7 and the relative importance of the various reactions are now discussed.

Figures 2 and 3 show a selective conversion of piperidine to *N*-pentylpiperidine and ammonia. The formation of *N*-pentylpiperidine direct from two piperidine molecules is unlikely because this formation is found to be first order in piperidine and, moreover, it can hardly be understood from a mechanistic consideration.

Experimental evidence for the formation of *N*-pentylpiperidine by alkyl transfer from pentylamine to piperidine was found in the increase of the *N*-pentylpiperidine formation when pentylamine was added to the piperidine feed. Moreover, this reaction offers an explanation for the constant pentylamine pressure as a function of the reaction time, as shown in Figs. 2 and 3 (and discussed below). The conclusion can be drawn that *N*-pentylpiperidine and ammonia are formed by ring-opening of piperidine followed by a rather fast alkyl transfer from pentylamine to piperidine (the reactions 2 and 4).

The hydrocracking of *N*-pentylpiperidine is a rather slow process as can be concluded by comparing the rate of conversion of *N*-pentylpiperidine with that of piperidine. The conversion of *N*-pentylpiperidine at 325°C and $t = 1.5 \times 10^7$ kg N sec m⁻² mol⁻¹ is about 7% (Fig. 6). Under approximately the same conditions the piperidine conversion is 60% (Fig. 3). This shows that $k_7 < k_2$; the formation of piperidine from its product *N*-pentylpiperidine can be neglected when the rate of the piperidine conversion is interpreted.

The Kinetics of the Piperidine (Hydro)cracking into Pentylamine

As stated before the piperidine conversion can be described by a rather slow reaction 2 followed by a fast reaction 4 (Fig. 7). Hence, at not too high conversions the rate determining step in the *N*-pentylpiperidine and ammonia formation is the

(hydro)cracking of piperidine to pentylamine. This reaction appears to be first order as can be calculated from the data in Figs. 2 and 3 (the shape of the curves for ammonia, pentylamine and *N*-pentylpiperidine are based on computer simulations in which reaction 2 was taken as being of first order and reaction 4 of second order).

A nearly zero order in piperidine of the piperidine (hydro)cracking was found when the initial piperidine partial pressure was varied (Table 1). In Fig. 8 $t/\ln(P_{PIP_0}/P_{PIP})$ is plotted as a function of the initial piperidine pressure. The straight line through the origin shows that piperidine (hydro)cracking can be described with the following kinetic equation:

$$-\frac{dP_{PIP}}{dt} = 2k_2 \frac{P_{PIP}}{P_{PIP_0}} P_{H_2}^n \quad (1)$$

(the factor 2 takes into account that nearly every pentylamine molecule formed reacts very fast with piperidine according to reaction 4). This type of kinetics, which may be called a poisoned zero order type, is in agreement with those reported for the conversion of other nitrogen bases on the molybdenum-containing catalysts (1, 8, 9). It is essential in these kinetics that the catalyst surface is totally covered with the nitrogen bases, and that the surface concentrations are proportional to the partial pressures of the bases.

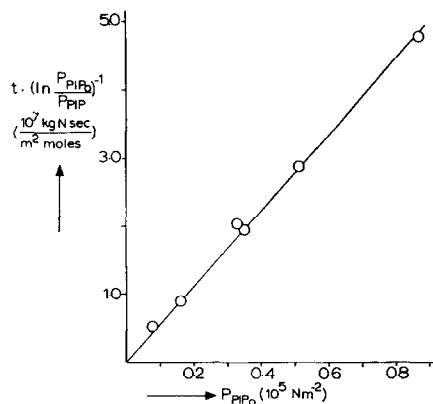


FIG. 8. Plot to verify Eq. (1) for the piperidine conversion (results of Table 1).

The order in *hydrogen* of the piperidine (hydro)cracking to pentylamine is about one as can be concluded from the amounts of ammonia and *N*-pentylpiperidine formed at various hydrogen pressures (Table 2). A similar experiment at 300°C confirmed this conclusion. (From the pyridine conversion a zero order in hydrogen was estimated for this reaction (9); this conclusion may be incorrect due to the neglect of the rather complex conversion of piperidine.)

The measurements at 1 atm H₂ show that the selectivity of the piperidine conversion totally changes going to low hydrogen pressures (Fig. 7). Pentane and *N*-pentylpiperidine were not observed in the products and C₁₀H₁₆ was found in rather high amounts. The activity decline predominantly observed at 1 atm H₂ will probably be due to the formation of this compound.

The activation energy of the piperidine (hydro)cracking is about 170 kJ mol⁻¹, as could be estimated from the rate of piperidine conversion at 300 and 325°C. From the results given in Fig. 1, a somewhat lower value for the activation energy (150 kJ mol⁻¹) was obtained, probably due to the effect of the equilibrium 4 and reaction 7 on the rate of piperidine conversion.

Some information can be given about the activation energy of the piperidine hydrogenation. The change in selectivity in the pyridine and ammonia formation, shown in Figs. 1 and 4, points to a higher activation energy for the dehydrogenation reaction than for the (hydro)cracking reaction.

Kinetics of the (Hydro)cracking Reactions 3, 6 and 7

The piperidine conversions at 300 and 325°C show constant amounts of pentylamine as a function of the reaction time (Figs. 2 and 3). This indicates that the stationary state approximation can be applied for the pentylamine, at least at low conversions; hence, for the piperidine conversion the following equations can be derived (if a second order for the reaction 4 is assumed):

$$P_{\text{MPA}} = \frac{k_2}{k_6 + k_4 P_{\text{PIP}}/P_{\text{PIP}_0}} P_{\text{PIP}} = \frac{k_2}{k_4} P_{\text{PIP}_0}; \quad (2)$$

k_6 is small compared with $k_4 P_{\text{PIP}}/P_{\text{PIP}_0}$ because the *N*-pentylpiperidine formation is much faster than the pentane formation.

$$\frac{dP_{\text{PA}}}{dt} = k_6 \frac{P_{\text{MPA}}}{P_{\text{PIP}_0}} = k_6 \frac{k_2}{k_4} \quad (3)$$

$$\frac{dP_{\text{NPP}}}{dt} = k_4 \frac{P_{\text{PIP}} P_{\text{MPA}}}{(P_{\text{PIP}_0})^2} = k_2 \frac{P_{\text{PIP}}}{P_{\text{PIP}_0}} \quad (4)$$

Equation (3) is only correct if the rate of (hydro)cracking of *N*-pentylpiperidine is low compared with that of pentylamine.

Several experimental observations can be explained with these equations. It has already been shown that Eq. (4) describes very well the *N*-pentylpiperidine formation. The increasing pentylamine pressure in Table 1 can be explained with Eq. (2). The zero order pentane formation is in accordance with the results given in Figs. 2 and 3. The linear increase of the amount of pentane shows that reaction 7 contributes only slightly to the pentane formation at low conversions.

Deviation from this zero order pentane formation has been found when the initial partial pressure of piperidine was varied; increasing amounts of pentane were observed at decreasing partial pressures of piperidine (Table 1). This indicates that Eq. (3) does not apply for this case due to the rather high conversions in these experiments. (At high conversions reaction 7 contributes to the pentane formation.)

Equation (3) shows that the order in hydrogen of the pentane formation depends on the kinetics of the reactions 2, 4 and 6. The pentane formation may have an overall order in hydrogen of about 2 as can be concluded from Table 2. A first order in hydrogen was found for reaction 2 (see above). Hence, reaction 6 may be first order in hydrogen and reaction 4 zero order in hydrogen. The amounts of pentylamine formed at different hydrogen pressures also point to a zero order in hydrogen for reaction 4 as can be shown from Eq.

(2). In a former publication (8) half order in hydrogen has been concluded for reaction 6 and zero order in hydrogen for an alkyl transfer reaction (reaction 5 in Fig. 7).

Not much information is available on the kinetics of *N*-pentylpiperidine (hydro)-cracking. The apparent activation energy was estimated from the results given in Fig. 6 and found to be 150 kJ mol⁻¹. Although the Arrhenius plot shows a straight line, the value of the activation energy can only be an estimate due to the influence of various reactions on the *N*-pentylpiperidine conversion.

Comparing this activation energy with those of other hydrocracking reactions shows that a somewhat higher value was obtained for the piperidine (hydro)cracking (see above) and an identical value for the pentylamine (hydro)cracking (8). Hence, the activation energies of (hydro)-cracking reactions may be about 160 kJ mol⁻¹. The activation energy for alkyl transfer reactions may be lower, namely about 100 kJ mol⁻¹ (8). The lower pentylamine amounts in the piperidine conversion at 300°C (Figs. 2 and 3) supports the last conclusion.

Computer Simulations

Computer simulations were performed for the piperidine and *N*-pentylpiperidine conversion on the basis of the reaction scheme of Fig. 7. The kinetics of the hydrocracking steps and the alkyl transfer reactions were taken as follows:

$$\text{hydrocracking} = k \frac{P_i}{P_{N_0}}$$

and

$$\text{alkyl transfer} = k \frac{P_i P_j}{P_{N_0}^2}$$

(P_{N_0} = total pressure of the nitrogen bases).

Simulation of Fig. 3 and the product distribution at 325°C in Fig. 6 yielded the following rate constants:

$$\left. \begin{aligned} k_2 &= 0.9 \times 10^{-3} \text{ mol kg}^{-1} \text{ sec}^{-1} \\ k_3 &= 0.06 \times 10^{-3} \text{ mol kg}^{-1} \text{ sec}^{-1} \\ k_6 &= 2.5 \times 10^{-3} \text{ mol kg}^{-1} \text{ sec}^{-1} \\ k_7 &= 0.06 \times 10^{-3} \text{ mol kg}^{-1} \text{ sec}^{-1} \\ k_8 &= 6 \times 10^{-3} \text{ mol kg}^{-1} \text{ sec}^{-1} \end{aligned} \right\} \text{(hydro)-} \\ \text{cracking} \\ \text{reactions}$$

$$\left. \begin{aligned} k_4 &= 30 \times 10^{-3} \text{ mol kg}^{-1} \text{ sec}^{-1} \\ k_5 &= 10 \times 10^{-3} \text{ mol kg}^{-1} \text{ sec}^{-1} \\ k_{-5} &= 2 \times 10^{-3} \text{ mol kg}^{-1} \text{ sec}^{-1} \end{aligned} \right\} \text{alkyl} \\ \text{transfer} \\ \text{reactions}$$

The values of k_5 and k_{-5} were estimated from our pentylamine studies (8). The value of k_4 can be calculated from k_4 and the value of the equilibrium constant K_4 . This constant was estimated from the values of the pressure function $F(P_i) = P_{NH_3} P_{NPP}/P_{PIP} P_{MPA}$ at high conversions. This indicates an equilibrium constant of about 50, which is in the neighborhood of that estimated by means of the method of Van Krevelen and Chermin. From this value we calculated:

$$k_{-4} = 0.6 \times 10^{-3} \text{ mol kg}^{-1} \text{ sec}^{-1}.$$

The values of the rate constants showed that:

i. The pentane formation via reaction 7 can only be important when the *N*-pentylpiperidine partial pressure is much higher than that of pentylamine.

ii. The formation of piperidine from *N*-pentylpiperidine is slow. *N*-pentylpiperidine mainly converts via the reverse reaction 4.

iii. The assumption $k_4 P_{PIP}/P_{PIP_0} \gg k_6$ made in the derivation of Eq. (2) is allowed at not too high conversions.

Rate Influencing Steps in the Conversion of Piperidine and Pyridine

With all the rate constants given above the piperidine conversion was simulated at higher reaction times than experimentally applied at 325°C. The result is given in dimensionless parameters in Fig. 9. This figure shows a sharp increase of the amount of ammonia at short reaction times. Above about 50% conversion the rate of ammonia formation decreases considerably. In Table 3 the reaction steps are given, which mainly

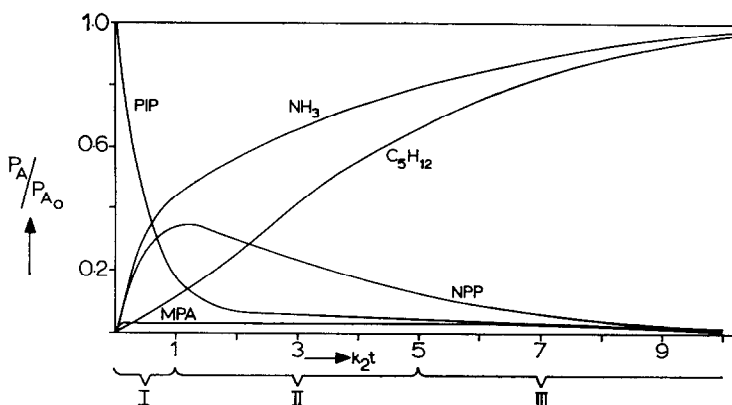


FIG. 9. Piperidine conversion obtained by computer simulation (for the reaction rate constants used, see the discussion; PIP₂ = piperidine, MPA = pentylamine, NPP = *N*-pentylpiperidine).

influence the rate of ammonia formation and pentane formation at the different conversion levels. At higher temperatures the region II in Fig. 9 will diminish due to the lower activation energies of the reactions 4 and 5 compared with the reactions 2 and 6. Table 3 shows that above 40% conversion into ammonia the rates of the reactions 4 and 5 only have a small influence on the gross reaction rate, due to the approach of the establishment of alkyl transfer equilibria. Under mild conditions (low conversions) the rate of ammonia formation is mainly influenced by the cracking of piperidine into pentylamine, and under more severe conditions by the rate of hydrocracking of the bases, especially of piperidine, *N*-pentylpiperidine and pentylamine. In the latter case the rate is influenced by the value of the equilibrium constants of the alkyl transfer reactions.

The same conclusion applies for the rate determining steps in the denitrogenation of

pyridine. In this case the influence of the alkyl transfer reactions on the ammonia formation is somewhat less, because these reactions are of the second order (pyridine will decrease the surface coverage of piperidine and pentylamine, which will have a larger effect on the rate of the alkyl transfer reaction from pentylamine to piperidine than on the rate of the first order (hydro)cracking of pentylamine). As reported earlier (9) the hydrogenation of pyridine also influences the rate of denitrogenation at low temperatures; above 400°C only the value of the equilibrium constant will have an influence on this rate.

A general conclusion from these results is that the reaction time necessary for practically complete deamination of pyridine and of piperidine mainly depends on the rate of (hydro)cracking reactions. The position of the hydrogenation and disproportionation equilibria also influence the rate of denitrogenation. Whether the same

TABLE 3
REACTION STEPS, WHOSE RATES INFLUENCE THE RATES OF AMMONIA AND PENTANE FORMATION FROM PIPERIDINE AT DIFFERENT CONVERSION LEVELS; SEE FIG. 9

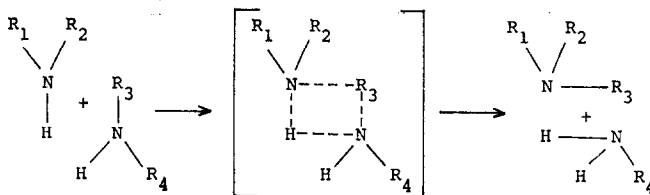
Conversion level:	I	II	III
The rate of NH ₃ formation is mainly influenced by	2	2, 3, 6 and 7, also 8	2 and 6
The rate of C ₅ formation is mainly influenced by	2 and 6	2, 3, 6 and 7, also 8	2 and 6

conclusion applies for the denitrogenation of oil fractions depends on the influence of H_2S (14) and the partial pressures of the hydrocarbons compared with those of nitrogen bases.

Mechanisms of Some Reactions

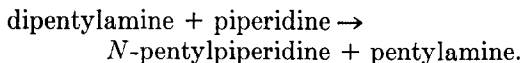
This subject has been discussed more extensively in Part III (8).

Alkyl transfer reactions. The mechanism of an alkyl transfer reaction may be (8):



(R_1 and R_2 , e.g., are pentyl groups or form a ring structure). The nitrogen may be adsorbed on molybdenum sites; the hydrogen atom and the alkyl group may interact with the oxygen ions.

Two alkyl transfer reactions were taken into account so far. However, also other transfer reactions may occur, e.g.,

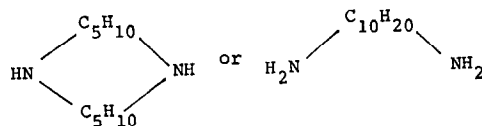


This reaction will have a low reaction rate due to the low partial pressure of dipentylamine ($0.4 \times 10^2 \text{ N m}^{-2}$ for the experiment given in Fig. 3).

Alkyl transfer reactions occur by cleavage of C-N bonds and the transfer of a *n*-pentyl group. The absence of isomers of *N-n*-pentylpiperidine exclude other reactions, such as the formation of (*N*-1-methylbutyl)piperidine.

(Hydro)cracking reactions. In Part III (8) we reported that both cracking and hydrocracking of C-N bonds occur on the $MoO_3-Al_2O_3$ catalyst. The first order in hydrogen and the formation of $C_{10}H_{16}$ at 1 atm H_2 show that cracking may occur predominantly at low H_2 pressures and hydrocracking at high H_2 pressures. Cracking may also occur to a slight extent at higher pressures (60 atm) because this reaction can explain the values given for

decane (Table 1); the dependence of the amounts of decane and pentane on increasing piperidine pressure indicate that decane is not formed from pentane or pentene, but may be formed directly from two piperidine molecules. Possible intermediates in this formation are:



We were not able to detect these compounds analytically.

The rates of the (hydro)cracking reactions at $325^\circ C$ show that this rate decreases in the order: dipentylamine > pentylamine > piperidine > *N*-pentylpiperidine. The equal values of k_3 and k_7 show that the rupture of a ring is not essential for the level of the reaction rate. This does not correspond with the order in which alcohols are dehydrated in Al_2O_3 , i.e., tertiary > secondary > primary; alcohols with a ring structure, e.g., cyclohexanol, do not form an exception to this rule. The lower reaction rates of nitrogen bases with a ring structure may be due to the strong adsorption of the nitrogen atom to molybdenum, which may interfere with the interaction of a hydrogen atom (of the β -C-atom) with the catalyst surface.

CONCLUSIONS

1. The piperidine hydrogenolysis proceeds via a ring opening to pentylamine, followed by alkyl transfer from pentylamine to piperidine (*N*-pentylpiperidine and ammonia are formed). Hydrocracking of these bases form pentane and also ammonia.

2. The rate of the denitrogenation of piperidine is influenced by the rates of the (hydro)cracking reactions and by the equi-

librium constants of the alkyl transfer reactions.

3. The rate equation for the (hydro)-cracking reactions is $r = k(P_n/P_{N_0})P_{H_2}$.

4. The rate equation for the alkyl transfer reactions is $r = k(P_n P_m/P_{N_0})^2 P_{H_2}^0$.

5. The activation energies of the (hydro)-cracking reactions are about 160 kJ mol⁻¹; the alkyl transfer reactions have smaller activation energies (about 100 kJ mol⁻¹).

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