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The Mechanism of Pyridine Hydrogenolysis on Molybdenum-Containing Catalysts

III. Cracking, Hydrocracking, Dehydrogenation and Disproportionation of Pentylamine

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The conversion of pentylamine on a MoO_3–Al_2O_3 catalyst was studied between 250 and 350°C, at various hydrogen pressures. The reactions observed were cracking to pentene and ammonia, hydrocracking to pentane and ammonia, dehydrogenation to pentanimine and butylcarbonitrile, and disproportionation to ammonia and dipentylamine.

The equilibrium between pentylamine, dipentylamine and ammonia appeared to be established under most of the experimental conditions. The equilibrium constant is about 9 at 250°C and about 5 at 320°C. The disproportionation reaction is zero order in hydrogen and of -1 order in the initial pentylamine pressure.

Dehydrogenation was observed at low hydrogen pressures, and especially at higher temperatures; the reaction is first order in pentylamine.

Both cracking and hydrocracking take place, mainly above 300°C. Hydrocracking appears to be half order in hydrogen; the rate of cracking is almost independent of the hydrogen pressure. The hydrocarbon formation is of zero order in pentylamine or dipentylamine.

The same type of reactions (except hydrocracking) take place on alumina, but with a far lower reaction rate.

INTRODUCTION

One of the intermediates formed in the hydrogenolysis of pyridine is pentylamine (*1*). Knowledge of the kinetics of the conversion of this compound is necessary to distinguish whether deamination of pentylamine is rate determining in the hydrogenolysis of pyridine into pentane and ammonia. Moreover, this knowledge may increase the information about the mechanism of dehydrogenation, disproportionation and (hydro)cracking of nitrogen bases on molybdenum-containing catalysts.

Several authors have investigated the rate of conversion of primary amines on, mostly sulfided, molybdenum-containing catalysts at hydrogen pressures of about 60 atm (*2–4*). They reported a high rate of ammonia formation from the primary amines compared with heterocyclic nitrogen compounds; for instance, the rate of denitrogenation of hexylamine and piperidine differed by a factor of 15 (*2*). The conversion of amines into ammonia and hydrocarbons is generally considered to be a one step reaction. However, investigations at low pressures of hydrogen, mostly performed on alumina, showed the formation of several intermediates. Brey and Cobbledick (*5*) studied the conversion of butylamine on alumina at 380–430°C; besides butene and ammonia, the products dibutylamine and propylcarbonitrile were formed. Ebeid and Pašek (*6*) reported a fast disproportionation of ethylamine to

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ammonia and diethylamine on alumina above 300°C.

The kinetics of the conversion of amines on molybdenum-containing catalysts is not well known. At high pressures of hydrogen a first order process was found (3). Deviation of the first order kinetics was observed above 95% conversion. The results obtained *on alumina* at low pressures of hydrogen (mostly zero) are partly conflicting. The reaction order for the disproportionation and that for the cracking reaction were found to be one and zero, respectively, by Ebeid and Pašek (*6*). However, Catry and Jungers (*7*) concluded that the reaction orders are two and one, respectively.

The aim of our study was to investigate whether the types of reactions reported for the amine conversion on alumina also take place on the reduced MoO_3–Al_2O_3 catalyst and to examine the kinetics of the several reaction types.

METHODS

Procedures

Detailed information about the equipment has been given elsewhere (*1*). In the *high pressure equiment* a stainless steel reactor with an internal diameter of 6 mm has been used. The mean temperature of the catalyst bed was constant within 1°C during the experiment. The temperature of the largest part of the catalyst bed was constant within 5°C; however, in the last 15% of the catalyst bed the temperature dropped by about 15°C. This may give a systematic error in the reaction rate constant of up to 10%. The pentylamine was fed with a thermostated (±0.5°C) saturator. For the determination of the product composition gas samples were taken directly after the throttle valve and analyzed by gas chromatography (*8*). Tubes and gas sampling valve were heated at a temperature of at least 140°C to prevent condensation of the reaction products.

In the *low pressure equipment* a glass reactor with an internal diameter of 9 mm has been used; the diameter was 3 mm when less than 1 g catalyst was taken. The temperature of the whole catalyst bed was constant within 1°C. The organic compounds were supplied with the aid of two saturators in series; the second one was thermostated within ±0.1°C (separate systems were used when two compounds were supplied together). The composition of feed and product has been determined by gas chromatography; gas samples were taken using gas sampling valves thermostated at 60 and 140°C, respectively. Defects in the mass balances were less than 10%. These are partly due to the formation of high boiling compounds, like tripentylamine small amounts of which were often observed in the products.

Separate experiments demonstrated that no pentylamine conversion and pentene hydrogenation took place when the wall temperature of the reactors, for both the low and high pressure equipment, was below 350°C and when the injection ports of the gas chromatographs and the tubes were below 150°C. The influence of internal and external diffusion on the rate of the reaction can be excluded as was shown by calculations.

Some activity decline was observed for the disproportionation and the (hydro)-cracking reaction and found to be 30% in the first 20 hr and again 30% in the next 80 hr (the total amount of pentanimine and butylcarbonitrile remained constant). Therefore the measurements were mostly started 16 hr after feeding the pentylamine. The experimental points have been taken in arbitrary sequence to avoid the interference of the slight activity decline on the shape of the curve. The reaction time is defined as $t = mP/\phi_t$, in which m = mass of catalyst (kg), P = total pressure (N m^{-2}), ϕ_t = total moles fed (mol sec^{-1}).

Materials

Catalyst: γ-Al_2O_3 (AKZO, 213 m^2 g^{-1}) and 22% MoO_3–Al_2O_3 (195 m^2 g^{-1}). The latter catalyst has a high surface area of molybdenum oxide, spread out in a monomolecular layer over the alumina surface (*9*). The particle diameter was 0.3–0.6 mm (0.21–0.30 mm in cases where less than 1 g

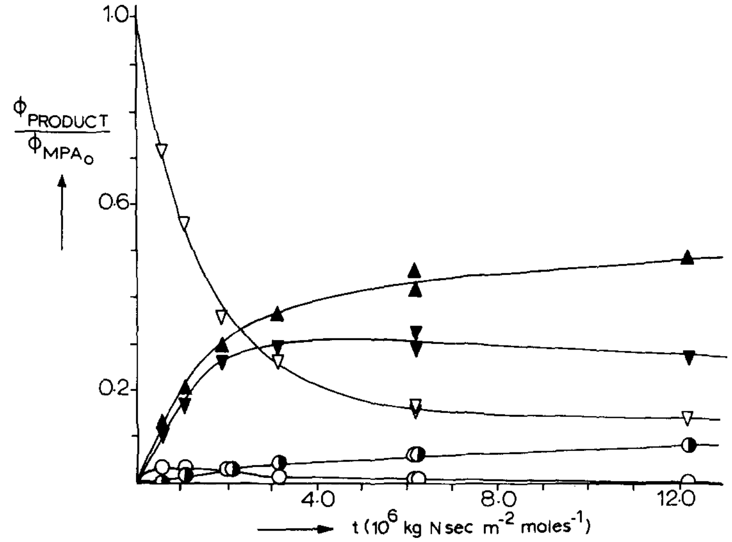


FIG. 1. The conversion of pentylamine at 250°C. (2.52 g MoO_3-Al_2O_3; $P_{H_2} = 1.0 \times 10^5$ N m^{-2}; $P_{MPA_0} = 1.05 \times 10^3$ N m^{-2}); (▽) pentylamine; (▼) dipentylamine; (▲) ammonia; (◑) butylcarbonitrile; (○) pentanimine.

catalyst was used). Before use all the catalysts were reduced in hydrogen at 450°C for at least 16 hr.

RESULTS

The conversion of *n*-pentylamine was studied by varying the temperature, the reaction time, the partial pressure of the amine and the hydrogen pressure. The effect of other nitrogen bases on the rate of the amine conversion was also investigated. Most experiments were performed on the MoO_3–Al_2O_3 catalyst and only a few on alumina.

Effect of the Temperature and the Reaction Time

The conversion of *n*-pentylamine (MPA) on a MoO_3–Al_2O_3 catalyst at a *hydrogen pressure of 1 atm* was studied at 250, 320, 340 and 360°C. The result at 250°C is given in Fig. 1. This figure shows that at low conversions equimolar amounts of ammonia and dipentylamine are rather selectively formed by the following disproportionation or alkyl transfer reaction:

2-Pentylamine → ammonia + dipentylamine (DPA).

Other products were pentanimine (PI) and butylcarbonitrile (BCN). (Both have been identified by mass spectroscopy and infrared spectroscopy after gas chromatographic separation). These products might be formed by a direct dehydrogenation of the monopentylamine. Pentane and pentene were only observed in small amounts in the products. The amount increased linearly with the reaction time up to 2.6% at $t = 12.2 \times 10^6$ (kg N sec m^{-2} mol^{-1}). This result shows that the cracking rate of monopentylamine or dipentylamine must be small at 250°C.

Figure 2 gives the product distribution at 320°C. Pentane is taken as the total amount of pentane + pentenes. Isopentane was only present in very small amounts in the products; next to pentene-1 a large amount of pentene-2 was observed, indicating a rather high rate of double bond isomerization.

Figures 1 and 2 show that at increasing temperatures the cracking and dehydrogenation products are formed in larger amounts than dipentylamine. The relative amounts of ammonia formed decreased at higher temperatures (50% at 250°C and 30% at 320°C). At 360°C the conversion to ammonia was only 10% at total conversion of pentylamine; in this case even a

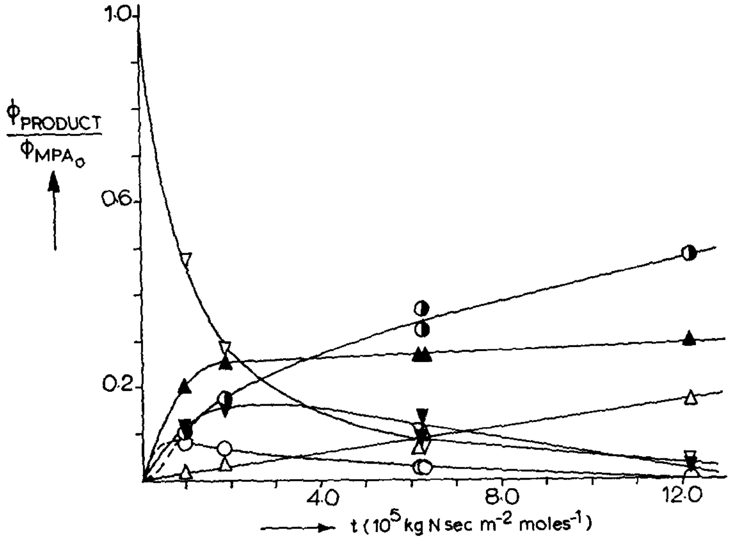


FIG. 2. The conversion of pentylamine at 320°C. (0.26 g MoO_3-Al_2O_3; $P_{H_2} = 1.0 \times 10^5$ N m^{-2}; $P_{MPA_0} = 0.88 \times 10^3$ N m^{-2}); for the symbols see Fig. 1; (△) pentane + pentenes.

maximum was found for the partial pressure of ammonia as a function of the reaction time.

The ratio pentenes–pentane was about 1 at 320°C; an increase of this ratio at increasing temperatures and reaction times was observed within a factor of 2 over the range of temperatures and the reaction times studied.

Effect of the Initial Pentylamine Pressure

The influence of the initial pentylamine pressure on the pentylamine conversion was studied at low conversions to determine the reaction order in the amine for the dehydrogenation and for the disproportionation reaction. The results are given in Table 1.

Effect of the Hydrogen Pressure

To investigate the effect of the hydrogen pressure, experiments were performed in helium as well as at hydrogen pressures up to 60 atm. In the high pressure experiments temperature, reaction time and initial pentylamine pressure were also varied

TABLE 1

THE EFFECT OF THE INITIAL PENTYLAMINE PRESSURE ON THE PENTYLAMINE CONVERSION[a]

Sequence of expts	Initial pentylamine pressure (10^2 N m^{-2})	Partial pressures of products: Disproportionation products $P_{NH_3} + P_{DPA}$ (10^2 N m^{-2})	Partial pressures of products: Dehydrogenation products $P_{PI} + P_{BCN}$ (10^2 N m^{-2})	$\frac{P_{PI} + P_{BCN}}{P_{MPA_0}}$ (%)
3	3.3	0.6_5	0.13	3.9
5	6.0	0.6	0.22	3.7
7	9.2	0.5	0.32	3.5
1	9.3	0.9	0.34	3.7
2	15.0	0.8_5	0.46	3.1
4	20.5	0.8	0.59	2.9
6	23.9	0.5_5	0.58	2.4

[a] $T = 250$°C; $P_{H_2} = 1.1 \times 10^5$ N m^{-2}; 0.27 g MoO_3-Al_2O_3; $t = 2.1 \times 10^5$ kg N sec m^{-2} mol^{-1}.

TABLE 2
THE EFFECT OF TEMPERATURE ON THE CONVERSION OF PENTYLAMINE AT A HIGH PRESSURE OF HYDROGEN[a]

Temp (°C)	Pentylamine (mol%)	Dipentylamine (mol%)	Ammonia (mol%)	Pentane (mol%)	Pentenes (mol%)
250	15	46	40	0.5	0.3
320	13	29	58	28	3.5
350	1	1	98	80	0.5

[a] $P_{H_2} = 29 \times 10^5$ N m^{-2}; $P_{MPA_0} = 6 \times 10^3$ N m^{-2}; 1.43 g MoO_3-Al_2O_3; $t = 5.7 \times 10^6$ kg N sec m^{-2} mol^{-1}. The values are given as moles product/initial moles of pentylamine; pentanimine and butylcarbonitrile were not found in the products. Decane was found in small amounts (2% at 350°C).

to investigate whether there were similar results at low and at high hydrogen pressures.

The *influence of the temperature* on the product composition for the pentylamine conversion at a hydrogen pressure of 29 × 10^5 N m^{-2} is given in Table. 2. Pentanimine and butylcarbonitrile could not be detected. At low temperatures only disproportionation into ammonia and diamine takes place. (Hydro)cracking of the amines is observed above 300°C.

A few experiments were made at 250°C and 60 atm of hydrogen to investigate the *effect of the hydrogen pressure* on the rate of the disproportionation reaction (Table 3). The order in hydrogen of the (hydro)-cracking reaction was studied by varying the hydrogen pressure at reaction conditions in which the disproportionation equilibruim was established. The results of the experiments performed at two different initial pentylamine pressures are given in Table 4.

A few experiments have been carried out to determine the conversion of pentylamine as a function of *the reaction time* and of *the initial pentylamine pressure* (t = 320°C, $P_{H_2} = 29 \times 10^5$ N m^{-2}). In accordance with the results at a lower hydrogen pressure (Fig. 2) we observed:

A linear decrease of the dipentylamine pressure as a function of the reaction time (after its maximum), together with a linear increase of the partial pressure of pentane + pentenes.

A total amount of pentane + pentenes, which was independent of the initial pentylamine pressure (see also Table 4); the ratio pentane—pentenes appeared to decrease with increasing initial pressure of the amine.

Apart from the experiments performed at hydrogen pressures from 1 to 60 × 10^5 N m^{-2} some were carried out in helium. (In this case a small but increasing partial pressure of hydrogen over the catalyst bed

TABLE 3
THE INFLUENCE OF THE HYDROGEN PRESSURE ON THE DISPROPORTIONATION REACTION (MoO_3-Al_2O_3 CATALYST, T = 250°C)

Reaction conditions			Products	Rate constants (10^{-3} mol kg^{-1} sec^{-1})	
P_{H_2} (10^5 N m^{-2})	P_{MPA_0} (10^3 N m^{-2})	t (10^5 kg N sec m^2 mol^{-1})	$P_{NH_3} + P_{DPA}$ (10^3 N m^{-2})	k_1[a]	k_2[a]
0.01	1.05	3.7	0.10	0.3	0.3
1.1	1.05	3.5	0.15	0.5	0.5
60	40	31	3.4	1.2	1.2
60	13	133	10.4	1.6	3.9

[a] Two different rate equations were used: $r = k_1(P_{MPA}/P_{MPA_0})$ and $r = k_2(P_{MPA}/P_{MPA_0})^2$.

TABLE 4

INFLUENCE OF THE PARTIAL PRESSURES OF HYDROGEN AND PENTYLAMINE ON THE (HYDRO)CRACKING OF PENTYLAMINE[a]

P_{H_2} (10^5 N m^{-2})	$P_{MPA_0} = 6.3 \times 10^3$ (N m^{-2})		$P_{MPA_0} = 30 \times 10^3$ (N m^{-2})		Pentane + pentenes; mean value (10^3 N m^{-2})
	Pentane (10^3 N m^{-2})	Pentenes (10^3 N m^{-2})	Pentane (10^3 N m^{-2})	Pentenes (10^3 N m^{-2})	
20	1.2	0.2	1.1	0.3	1.4
29	1.5_5	0.1_5	1.3	0.3	1.6_5
58	2.5	0.1	1.8	0.2	2.3

[a] 1.43 g MoO_3-Al_2O_3; $T = 320°C$; $t = 5.7 \times 10^6$ kg N sec m^{-2} mol^{-1}.

can be expected). The product composition as a function of the reaction time at 320°C is given in Fig. 3. Comparison with Fig. 2 shows a more selective conversion to butylcarbonitrile. A similar experiment was made at 250°C. Comparison of the results with those of the experiment at the hydrogen pressure of 1.0×10^5 N m^{-2} showed that the rate of disproportionation was 40% lower (Table 3) and that the rate of dehydrogenation was about three times higher. In helium the decrease of the rate of nitrile formation at longer reaction times was not as striking as shown in Fig. 1.

Conversion of Pentylamine on Alumina

Some experiments have been performed on γ-alumina to investigate whether the free alumina surface contributes to the total activity of a commercial CoO–MoO_3–Al_2O_3 catalyst. The product composition as a function of the reaction time at 320°C has been given in Fig. 4. The effect of the initial pentylamine pressure on the amounts of products formed is demonstrated in Table 5.

The Influence of Nitrogen-Bases on the Pentylamine Conversion and the Pentene Hydrogenation on MoO_3-Al_2O_3

The pentylamine conversion on the MoO_3–Al_2O_3 catalyst at 250°C has been determined both with and without addition of about an equivalent amount of piperidine and pyridine. The conversion decreased due to the addition of nitrogen

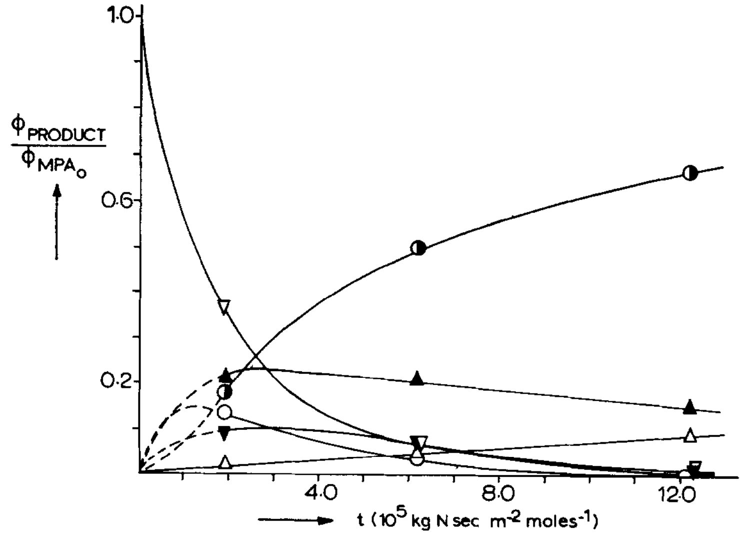


FIG. 3. The conversion of pentylamine at very low hydrogen pressures. (0.26 g MoO_3–Al_2O_3; $T = 320°C$; $P_{He} = 1.0 \times 10^5$ N m^{-2}; $P_{MPA} = 0.88 \times 10^3$ N m^{-2}); for the symbols see Fig. 1; (△) pentane + pentenes.

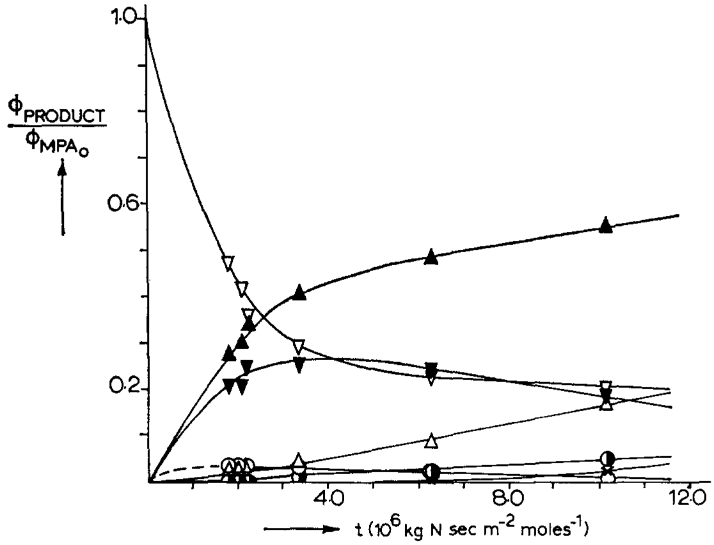


FIG. 4. The conversion of pentylamine on alumina at 320°C. (1.00 g catalyst, $P_{H_2} = 1.0 \times 10^5$ N m^{-2}; $P_{MPA_0} = 0.9 \times 10^3$ N m^{-2}); for the symbols see Fig. 1; (△) pentane + pentenes; (×) decane or decene.

bases from 0.20 to 0.15. The effect of these bases on the dehydrogenation appeared to be less.

The influence of ammonia on the pentylamine conversion is given in Table 6. Similar experiments at 250 and 360°C in 1 atm of hydrogen also showed a decrease of the dipentylamine and imine partial pressure and an increase of the formation of butylcarbonitrile.

To investigate whether the cracking of pentylamine into pentane and ammonia is a one step process (hydrocracking) or a two step process (cracking and hydrogenation of pentene), the following experiments were performed:

A MoO_3–Al_2O_3 catalyst was fed successively with pentene, pentylamine with pentene and pentylamine alone. In the absence of pentylamine a complete conversion of pentene into pentane was found (Table 7). Addition of pentylamine to the feed showed a decrease in the pentane formation to the same level as observed in the amine conversion alone. Hence, pentylamine poisoned the hydrogenation of pentene from a conversion of 100% to a value below 2% (detection level). The isomerization of pentene-1 to pentene-2 was only partly poisoned. These results have been confirmed by a duplicate experiment in which also a slow recovery of the pentene hydrogenation was demonstrated when the pentylamine feed was stopped; the conversion was 90% after 1 hr of purging with hydrogen with 1 ml sec^{-1}.

Experiments with the pulse technique, not reported in this paper, showed that the

TABLE 5

EFFECT OF THE INITIAL PENTYLAMINE PRESSURE ON THE PENTYLAMINE CONVERSION ON ALUMINA[a]

Initial pentylamine pressure (10^2 N m^{-2})	Partial pressures of the products (10^2 N m^{-2})					
	Pentylamine	Dipentylamine	Ammonia	Pentene	Pentanimine	Butylcarbonitrile
5.6	1.9	1.4	2.0	0.22	0.19	0.07
11.1	5.1	2.4	3.2	0.21	0.35	0.05
19.2	13.3	2.6	2.9	0.13	0.36	0.03

[a] 1.0 g Al_2O_3; $T = 320$°C; $P_{H_2} = 1.0 \times 10^5$ N m^{-2}; $t = 1.7 \times 10^6$ kg N sec m^{-2} mol^{-1}.

TABLE 6
INFLUENCE OF AMMONIA ON THE PENTYLAMINE CONVERSION[a]

Partial pressure of ammonia in the feed (10^2 N m^{-2})	Partial pressures of the products (10^2 N m^{-2})							$F_1(P_i)$ for the disproportionation
	Pentylamine	Dipentylamine	Ammonia	Pentane	Pentenes	Pentanimine	Butylcarbonitrile	
0	0.66	0.67	2.1	0.28	0.18	0.39	4.80	3.2
7.2	1.39	0.39	8.2	0.17	0.09	0.16	5.45	1.64

[a] 250 mg MoO_3-Al_2O_3; $T = 320°C$; $P_{He} = 1.0 \times 10^5$ N m^{-2}; $P_{MPA_0} = 9.6 \times 10^2$ N m^{-2}; $t = 6.2 \times 10^6$ kg N sec m^{-2} mol^{-1}.

hydrogenation of pentane was already poisoned by small amounts of nitrogen bases.

DISCUSSION

The results obtained suggest the reaction scheme given in Fig. 5. This figure shows disproportionation, dehydrogenation, cracking and hydrocracking reactions. The system is very analogous to the conversion of alcohols; alcohols disproportionate selectively into water and ether at low temperatures and dehydrate at higher temperatures (>200°C for alumina). Dehydrogenation of alcohols is observed on several catalysts.

We shall discuss below the kinetics of each of the various types of reaction and the influence of other amines on the kinetics. We shall also give some suggestions about the mechanisms of the reactions, discuss the results on alumina and the rate determining step in the pentylamine decomposition.

Disproportionation

At low temperatures disproportionation appears to be very selective at low and at high pressures of hydrogen (Fig. 1, Table 2). The more or less constant ammonia and dipentylamine pressures at long reaction times (Fig. 1) suggest the establishment of an equilibrium.

To investigate whether the disproportionation equilibrium is established, we calculated the values of the following pressure function:

$$F_1(P_i) = \frac{P_{DPA}P_{NH_3}}{P_{MPA}^2}.$$

Establishment of equilibrium demands that this function should have a constant value at increasing reaction times, and $F_1(P_i)$ then equals the equilibrium constant. Values of $F_1(P_i)$ given in Table 8 show that the disproportionation is near equilibrium at 250 and 320°C. These values, as well as those obtained in other experiments suggest that the equilibrium constant may be 8–10 at 250°C and 4–6 at 320°C. This is in accordance with the values of 10 at 250°C and 5 at 320°C, estimated for the equilibrium constant by the method of Van Krevelen and Chermin *(10)* and the value of 3 reported by Catry

TABLE 7
INFLUENCE OF PENTYLAMINE ON THE PENTENE HYDROGENATION[a]

Feed (10^2 N m^{-2})		Partial pressures of the products (10^2 N m^{-2})[b]					
Pentene-1	Pentylamine	Ammonia	Pentane	Pentene-1	Pentene-2	Decane	Butylcarbonitrile
0.8	—	—	0.8	<0.01	<0.01	Not analyzed	—
0.8	2.7	1.0	0.42	0.17	0.95	0.1	1.65
—	2.7	1.0	0.42	0.07	0.30	0.1	1.65

[a] 250 mg MoO_3-Al_2O_3; $T = 320°C$; $P_{H_2} = 1.1 \times 10^5$ N m^{-2}; $t = 5.8 \times 10^5$ kg N sec m^{-2} mol^{-1}.

[b] Pentylamine and dipentylamine were not observed in the products.

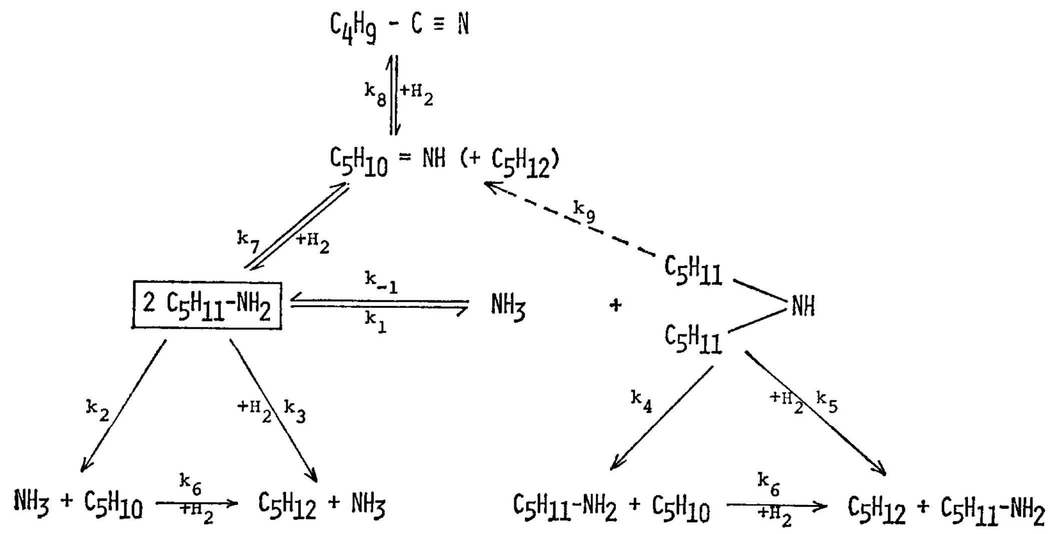


FIG. 5. Reaction scheme for the conversion of pentylamine on a molybdenum oxide-containing catalyst.

and Jungers (*7*) for the equilibrium constant of the butylamine disproportionation at 350°C.

Some information about the kinetics of the disproportionation in pentylamine may be obtained from Fig. 1. The shape of the curves for ammonia and dipentylamine is similar to that of a first order reaction; the same reaction order is reported for the disproportionation of amines on alumina (*6*, *11*, *12*). A reaction order of 2 is expected when the reaction is of the Langmuir–Hinshelwood type. However, we were unable to discriminate between a first and second order, because a possible stronger adsorption of pentylamine than dipentylamine and ammonia, as well as the formation of tripentylamine, might influence the interpretation of the results.

The order of this disproportionation reaction with respect to the initial pressure of pentylamine proves to be zero (Table 1); (the difference in the values for the partial pressures of ammonia and dipentylamine can be explained by a slight activity decline of the catalyst; see the sequence of the experiments). Different orders of reaction by varying the reaction

TABLE 8

VALUES OF THE PRESSURE FUNCTIONS $F(P_i)$ FOR THE DISPROPORTIONATION REACTION AND DEHYDROGENATION REACTION AS A FUNCTION OF THE REACTION TIME AT 250 AND 320°C (FIGS. 1 AND 2)

t (10^6 kg N sec m^{-2} mol^{-1})	T (°C)	$F_1(P_i)$ disproportionation	$F_2(P_i)$ (10^{10} N^2 m^{-4}) dehydrogenation
1.08	250	0.1_5	0.04
1.88	250	0.6_5	0.09
3.08	250	1.1	0.16
6.17	250	5.0	0.38
12.2	250	6.6	0.60
0.10	320	0.2	0.2_5
0.19	320	0.7	0.7
0.62	320	3.6	3.8
1.22	320	5.0	14

time and the initial partial pressure were also found for the conversion of other nitrogen bases on molybdenum-containing catalysts (*2, 13*).

The order in hydrogen of the alkyl transfer reaction is low, as can be concluded from Table 3. An increase of the hydrogen pressure by a factor of 60, together with an increase in the initial pentylamine pressure by a factor of 30, only gives an increase in the rate of the disproportionation by a factor of about 3 (the rather fast rate of establishment of the disproportionation equilibrium of the experiment described in Table 2 gives evidence for a somewhat higher value). The larger rate of disproportionation at high pressures of hydrogen may be due to a smaller activity decline at these higher hydrogen pressures or to an additional conversion on other active sites on which pentylamine is less strongly adsorbed.

Cracking and Hydrocracking

The equilibrium constants of the cracking and hydrocracking reactions are very large ($>10^8$ N m^{-2} and $>10^7$, respectively, in the temperature range studied). These equilibria are not established in our experiments. The same applies to the hydrogenation of pentene to pentane ($K_{eq} > 10^{-1}$ m^2 N^{-1}).

The kinetics for the total formation of pentane and pentenes are discussed first. Figures 2 and 3, as well as the experiment at 250°C, show a linear relationship between this total amount and the reaction time. Evidence for an identical result at 29 atm of hydrogen and 350°C was also obtained. This proves an overall zero order for the cracking or hydrocracking reaction.

The dependence of the rate of (hydro)-cracking on the initial pentylamine pressure also appeared to be zero order, as can be concluded from the results given in Table 4. This table also demonstrates the effect of the hydrogen pressure on the rate of (hydro)cracking. The order in hydrogen proves to be about 0.5.

Discrimination between the several formation reactions of pentenes or pentane is difficult, because these products are involved in so many reactions (Fig. 5). A first question is whether the (hydro)cracking rates of monopentylamine or dipentylamine differ. Only a few results are available on the dipentylamine conversion. The products formed from dipentylamine at 250 and 320°C were pentane, pentenes, ammonia, tripentylamine and small amounts of monopentylamine and butylcarbonitrile. At 250°C the amount of pentane + pentenes appeared to be a factor of three higher than the amount formed from monopentylamine at the same reaction time. Hence, the (hydro)cracking rates of both amines are about the same, when calculated per alkyl group.

A second question is whether cracking or hydrocracking takes place. From Table 7 the conclusion was drawn that at 320°C and 1 atm of hydrogen the hydrogenation of pentene is completely poisoned by pentylamine. Hence, under those circumstances reaction 6 may be excluded from the scheme of Fig. 5. This result, together with the formation of pentene as well as pentane from pentylamine, suggest that both cracking and hydrocracking of the amines occur. The rates of cracking and hydrocracking are about the same at a hydrogen pressure of 1.0×10^5 N m^{-2}, as can be concluded from the amounts of pentane and pentene formed. These conclusions are only correct if reaction 9 in the scheme in Fig. 5 may be neglected. Support for this is found in the small amounts of pentanimine and butylcarbonitrile formed when converting dipentylamine at 250 and 320°C and 1.0×10^5 N m^{-2} hydrogen pressure.

The (hydro)cracking reactions were found to have an overall order in hydrogen of about 0.5 at hydrogen pressures above 29×10^5 N m^{-2} (Table 4). Extrapolation to a hydrogen pressure of 1.0×10^5 N m^{-2} gives a rate constant of 0.54×10^{-3} mol kg^{-1} sec^{-1} (the rate equation used for the calculation of the rate constant k is $r = k = k' \, p_{H_2}{}^{1/2}$). The rate constant calculated from Fig. 2 is 1.5×10^{-3} mol kg^{-1} sec^{-1}. This difference, and the rather high amounts of pentane + pentenes in the experiment in helium (Fig. 3), suggest a lower order in hydrogen of the (hydro)cracking below 29 atm of hydrogen. This points to a cracking reaction which is zero order in hydrogen and a hydrocracking reaction which is half order in hydrogen.

Dehydrogenation

Dehydrogenation of pentylamine into pentanimine and butylcarbonitrile was only observed at low pressures of hydrogen. Pentanimine is an intermediate product in the dehydrogenation reaction, as is shown in Figs. 1 and 2.

An equilibrium between butylcarbonitrile and pentylamine was not yet established under our reaction conditions as can be concluded from the increasing values of a pressure function, defined as $F_2(P_i) = P_{BCN} P_{H_2}{}^2/P_{MPA}$, as a function of the reaction time (Table 8). The equilibrium will be established at somewhat longer reaction times; from the ratio of the rate constants of the conversion of pentylamine and butylcarbonitrile, respectively, the equilibrium constant was estimated to be 2.7 at 250°C (this value is higher than that calculated for the butylamine–propylcarbonitrile equilibrium (*14*), i.e., 0.2 at 250°C and 7 at 320°C).

Pentanimine and butylcarbonitrile were only observed in the experiments at low hydrogen pressures. The absence of these products at a hydrogen pressure of 29 atm is due to the shift of the dehydrogenation equilibrium to pentylamine at increasing hydrogen pressures.

Regarding the kinetics of the dehydrogenation reaction the conclusions are as follows: as a function of reaction time the dehydrogenation is first order in pentylamine, as was indicated by computer simulations of Figs. 1 and 2. Table 1 also shows a first order process by varying the initial amine pressure, at least below 10^3 N m^{-2}. The order of the reaction in hydrogen is not well known. Figures 2 and 3 only suggest a small effect, if any, of the hydrogen pressure on the dehydrogenation.

Summary of the Kinetics Results

The results of the kinetics of the four types of reactions are summarized in Table 9.

The zero order behavior found for the disproportionation and (hydro)cracking reactions by varying the initial pentylamine pressure can be explained by assuming a strong adsorption of the nitrogen bases with identical adsorption constants of the bases. Assuming the surface reaction as rate determining and a Langmuir type adsorption as an approximation of the adsorption behavior, the following rate equation can be derived:

$$r = k\theta_A{}^n = k\left\{\frac{b_A P_A}{1 + b_A P_A + \Sigma_i b_i P_i}\right\}^n$$

where b_i, P_i are the adsorption constant and partial pressure of product i. Because $P_A + \Sigma P_i = P_{A_0}$, $b_i = b_A$ and $b_A P_{A_0} \gg 1$, the rate equation can be simplified into:

$$r = k(b_A P_A/b_A P_{A_0})^n = k(P_A/P_{A_0})^n$$

The supposition $b_A P_{A_0} \gg 1$ is confirmed by former investigations (*13*).

The reaction whose rate can be described with the equation above will show the

TABLE 9

SUMMARY OF THE KINETICS OF THE PENTYLAMINE (MPA) CONVERSION ON A MoO_3–Al_2O_3 CATALYST

	Reaction order in Pentylamine by varying the			
Type of reaction	Reaction time	P_{MPA_0}	Reaction order in hydrogen	Activation energies[a] (kJ mol^{-1})
Disproportionation		0	0	100
(Hydro)cracking	0	0	0.5[a]	150
Dehydrogenation	1	1	Low	150

[a] The hydrocracking is about half order in hydrogen; the cracking reaction may be of zero order.

order n by varying the reaction time and the zero order by varying the initial partial pressures of the nitrogen bases (at not too high conversions).

The results of our poisoning experiments are also in accordance with this type of kinetics. Table 6 shows that ammonia addition to the feed decreased both the rate of disproportionation and that of the (hydro)cracking (the higher value obtained for butylcarbonitrile is due to the higher pentylamine pressure in the reactor when ammonia is added to the feed).

Corresponding experiments at 250°C with addition of pyridine and piperidine to the pentylamine feed showed that their poisoning influence was about half that of ammonia. With the rate equation given above (P_{A_0} = total pressure of the nitrogen bases) the ratio b_{MPA}/b_{NH_3} is found to be about 1 and the ratio b_{MPA}/b_{PYR} and b_{MPA}/b_{PIP} about 2 or 4 depending on the order of the disproportionation reaction. For a general description of the kinetics the assumption of the same order of magnitude of the adsorption constants may be useful.

The activation energies given in Table 9, and those reported for the disproportionation and cracking of both amines and alcohols on alumina (*6, 12, 15, 16*) show that cracking reactions may have higher activation energies than disproportionation reactions and that for similar reactions the activation energies for the nitrogen bases may be higher than those for alcohols.

Mechanistic Interpretation of the Results

The main kinetic results obtained on the MoO_3–Al_2O_3 catalyst may be well explained by the following model:

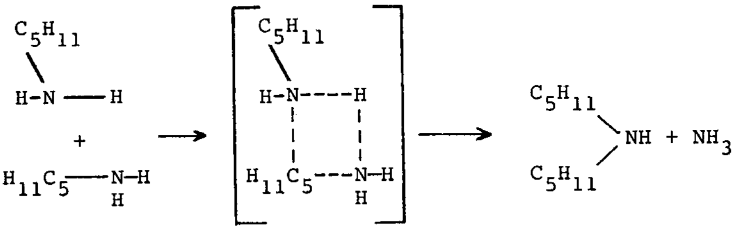
The surface is almost completely covered with nitrogen bases (*13*).

The nitrogen bases have equal adsorption constants. The results of the poisoning experiments, in which the pentylamine conversion was poisoned by other nitrogen bases, showed that this may be true only in rough approximation.

The (hydro)cracking rate of dipentylamine is twice that of pentylamine.

The zero order disproportionation (Table 1) is expected on this model, because increase of the pentylamine pressure [above 1×10^3 N m^{-2} (*13*)] does not increase the surface coverage of pentylamine. This zero order excludes an Eley–Rideal mechanism. As a function of the reaction time a *second* order of reaction seems more probable when the rate determining step is a surface reaction. As stated before discrimination between a first or a second order from the experimental results was impossible.

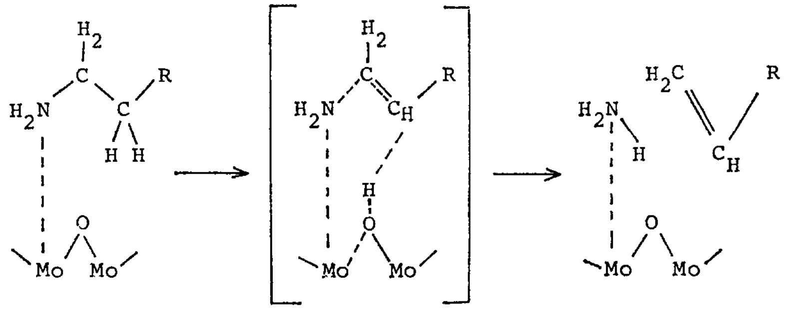
A possible mechanism of this disproportionation is an alkyl and hydrogen transfer between two neighboring pentylamine molecules:



The nitrogen atom may be bonded to the molybdenum and the hydrogen and pentyl group may have an interaction with the oxygen atoms of the molybdenum oxide.

The zero order kinetics found for *(hydro) cracking* are expected as a function of the initial pentylamine pressure and not too long reaction times, due to the more or less constant concentration of pentyl groups on the catalyst surface. A decrease in the (hydro)cracking rate should be observed at long reaction times, because ammonia will cover an important part of the surface (the same applies for the butylcarbonitrile, but this compound may have a lower adsorption constant). Table 6 shows that the (hydro)cracking rate indeed decreased by addition of ammonia to the feed, but we did not observe a decrease of the pentane (pentene) formation at longer reaction times (Fig. 2). Computer simulations showed that this may point to a stronger adsorption or a higher cracking rate of dipentylamine.

The cracking may take place as follows:



An analogous mechanism was proposed for the alcohol dehydration (*17*) and recently for the deamination of triethylamine on alumina (*18*).

A possible mechanism of the hydrocracking reaction is the donation of a hydrogen atom from an OH group of the molybdenum oxide to the nitrogen atom.

The *dehydrogenation* was found to be first order as a function of the reaction time, as well as a function of the initial pentylamine pressure; this is contrary to the disproportionation and cracking reactions. Another difference is that the conversion into imine + nitrile appeared to be hardly influenced by the observed initial activity decline of the catalyst. These phenomena point to the presence of separate catalytic sites for the dehydrogenation of pentylamine.

Evidence for the heterogeneity of surface sites on the molybdenum oxide on alumina was also obtained from the pulse experiments. Total poisoning of the hydrogenation was observed when the amount of poison injected corresponds with only about 25 mol% of the molybdenum oxide present on the catalyst (*19*). Because all this molybdenum oxide is exposed (*9*), we may conclude that either only a part of the molybdenum oxide forms active sites, or that more than one molybdenum site is involved in this hydrogenation step.

Conversion of Pentylamine on Alumina

Comparison between our data discussed so far and literature data is difficult because detailed kinetic information is only reported for the amine conversion on alumina. However, our investigations showed the same selectivity pattern for alumina and a MoO_3/Al_2O_3 catalyst; the most important difference found between the two catalysts is the far lower activity of the alumina for all types of reactions, especially for the dehydrogenation reaction (Figs. 2 and 4).

For alumina we also observed a zero order disproportionation and cracking reaction when the initial amine pressure was varied (Table 5). This is partly in conflict with kinetic data reported in the literature (*6*, *7*, *12*, *18*), but in good agreement with our adsorption studies which showed a high coverage of the alumina surface with nitrogen bases at low partial pressures of these bases (*13*). The difference between our results and the literature data may be due to a different pretreatment of the alumina.

An interesting point is the far higher activity of molybdena–alumina compared with alumina for the alkyl transfer and cracking reaction (a factor of about 25; the difference in the dehydrogenation rate is about a factor of 60). In the mechanisms of disproportionation and cracking given above, the transfer of hydrogen atoms on the surface of the catalyst is essential. This transfer may occur with a far higher rate on molybdena–alumina, due to the higher acidity of the MoO_3–Al_2O_3 catalyst (*20*), or to the interaction between hydrogen atoms and the oxygen of the molybdenum oxide in combination with a change in the valence state of the molybdenum ion.

Rate Determining Steps in the Pentylamine Decomposition

From the results obtained the following conclusions can be drawn:

At low conversions the rate of ammonia formation is mainly influenced by the disproportionation reaction.

At conversions above 60% (hydro)cracking of pentylamine or dipentylamine is rate determining in the ammonia formation.

The fast disproportionation reaction and the rather slow hydrocracking reactions may give a gross rate of ammonia formation which approximately corresponds to a first order reaction. First order denitrogenation of amines has been reported by Flinn, Larson and Beuther (3); the deviation from first order which they observed at high conversions may be due to the occurrence of disproportionation or alkyl transfer reactions.

According to several authors deamination of primary amines is not rate determining in hydrodenitrogenation of heterocyclic nitrogen bases, because under the same reaction conditions the rate of ammonia formation from amines is high compared with those from heterocyclic nitrogen bases. However, the conversion of amines turns out to be rather complex and this conclusion about the rate determining step in the denitrogenation may be incorrect, especially when other nitrogen bases are concerned in alkyl transfer reactions (*21*).

CONCLUSIONS

1. On both alumina and a MoO_3–Al_2O_3 catalyst a fast disproportionation of pentylamine to ammonia and dipentylamine is found. The rate equation for the disproportionation is: $r = k\ (P_{MPA}/P_{MPA_0})^n P_{H_2}{}^0$. The activation energy is about 100 kJ mol^{-1}.

2. A first order dehydrogenation of pentylamine to butylcarbonitrile was observed at hydrogen pressures of 1 atm and less. The selectivity of the pentylamine conversion in this compound increases at increasing temperatures.

3. Both cracking and hydrocracking of C–N bonds appear to take place. The cracking and hydrocracking are of about zero order in the amines; the order in hydrogen is 0.5 for the hydrocracking. The activation energy is about 150 kJ mol^{-1}.

4. Even at high pressures of hydrogen (up to 60 atm) and high temperatures (up to 350°C) the disproportionation reaction is fast compared with the cracking reaction. The equilibrium constant of the disproportionation is about 9 at 250°C and about 5 at 320°C.

5. A MoO_3–Al_2O_3 catalyst is considerably more active than alumina for all the types of reactions observed.

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