Investigations into the mechanism of the liquid-phase hydrogenation of nitriles over Raney-Co catalysts

Peter Schärringer, Thomas E. Müller *, Johannes A. Lercher

Lehrstuhl II für Technische Chemie, Department Chemie, Technische Universität München, Lichtenbergstr. 4, 85747 Garching, Germany

Abstract

The co-hydrogenation of acetonitrile and butyronitrile over Raney-Co was investigated in order to obtain insight into the mechanism underlying the formation of secondary amines. Acetonitrile was reduced much faster to the corresponding primary amine due to stronger adsorption on the catalyst surface. In parallel, dialkylimines were formed and subsequently converted to secondary amines. It is suggested that the dialkylimines are formed by reaction of partially hydrogenated intermediate species on the cobalt surface with amines. In this respect, *n*-butylamine was found to react much faster than ethylamine. The stronger inductive effect of the butyl chain is thought to facilitate nucleophilic attack of the amine at the α-C-atom of the surface species. By comparing the C_2 and C_4 balance for dialkylimines and dialkylamines, it was found that direct hydrogenation of the dialkylimine cannot be the only way of dialkylamine formation. Instead, it is suggested that alkyl group transfer occurs by reaction of a monoalkylamine with a dialkylimine and cross-transfer between two dialkylimines.
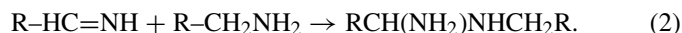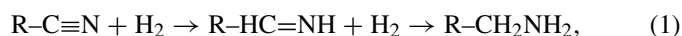© 2007 Elsevier Inc. All rights reserved.

1. Introduction

The production of amines by hydrogenation of nitriles is a common industrial process [1]. Important examples include the hydrogenation of 1,4-dicyanobutane to 1,6-diaminohexane used for the production of nylon-6,6 [2,3] and the conversion of fatty nitriles to fatty amines, which are used, e.g., as feedstock for surface active substances, like fabric softeners and detergents. In general, products formed during hydrogenation of nitriles are primary, secondary, and tertiary amines. The product distribution depends on the catalyst applied [4,5]. For the selective hydrogenation of nitriles to primary amines, skeletal metal catalysts based on Co and Ni are often used as they provide the lowest cost per unit mass of catalyst [6] combined with a high activity [4].

Frequently, the formation of secondary and tertiary amines is undesired. The mechanism of the condensation reaction leading to higher amines has therefore been analyzed by numerous authors. The discussions have mostly been based on a mechanism suggested by von Braun et al. [7] and were summarized in several publications [8–10]. The main findings are summarized below as basis for a detailed analysis of the mechanistic aspects. Von Braun proposed that an aldimine, which occurs as intermediate in the sequential nitrile hydrogenation [11], reacts with amine to a 1-amino-dialkylamine,

$$R–C\equiv N + H_2 \rightarrow R–HC=NH + H_2 \rightarrow R–CH_2NH_2, \quad (1)$$

$$R–HC=NH + R–CH_2NH_2 \rightarrow RCH(NH_2)NHCH_2R. \quad (2)$$

The 1-amino-dialkylamine can undergo ammonia elimination resulting in a dialkylimine,

$$RCH(NH_2)NHCH_2R \rightarrow R–HC=NCH_2R + NH_3. \quad (3)$$
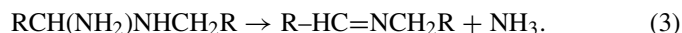
The dialkylimine is further hydrogenated to the secondary amine,

$$R–HC=NCH_2R + H_2 \rightarrow RCH_2NHCH_2R. \quad (4)$$

* Corresponding author. Present address: Zentrum für Katalyseforschung, Institut für Technische und Makromolekulare Chemie, RWTH-Aachen, Worringerweg 1, 52074 Aachen, Germany. Fax: +49 241 80 22177.
E-mail address: thomas.mueller@catalyticcenter.rwth-aachen.de (T.E. Müller).

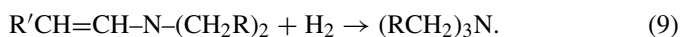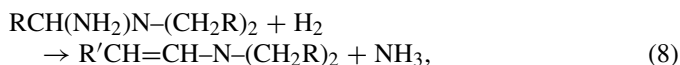Alternatively, direct hydrogenolysis of the 1-amino-dialkyl-amine may occur,

$$RCH(NH_2)NHCH_2R + H_2 \rightarrow RCH_2NHCH_2R + NH_3. \quad (5)$$
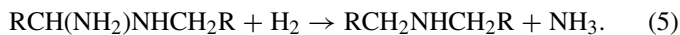
For the formation of tertiary amines, starting from addition of a secondary amine to an imine resulting in 1-amino-trialkylamine [12],

$$(RCH_2)_2NH + R–HC=NH \rightarrow RCH(NH_2)N–(CH_2R)_2, \quad (6)$$
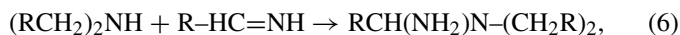
two different subsequent reaction steps were proposed. One is the direct hydrogenolysis of 1-amino-trialkylamine,

$$RCH(NH_2)N–(CH_2R)_2 + H_2 \rightarrow (RCH_2)_3N + NH_3. \quad (7)$$
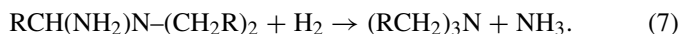
As an alternative reaction path, NH_3 elimination resulting in an enamine followed by hydrogenation to a tertiary amine was proposed [13],

$$RCH(NH_2)N–(CH_2R)_2 + H_2$$
$$\rightarrow R'CH=CH–N–(CH_2R)_2 + NH_3, \quad (8)$$

$$R'CH=CH–N–(CH_2R)_2 + H_2 \rightarrow (RCH_2)_3N. \quad (9)$$

The aldimine intermediate has not been confirmed by direct observation, which is attributed to its high reactivity [8]. High reactivity also holds for enamines, but they have been identified by GC-MS as reaction intermediates [8]. Other studies based on indirect observations suggested that the enamine mechanism prevails [4,14]. However, in the reductive amination of benzaldehyde a considerable amount of tribenzylamine was detected [9]. As enamine formation requires a β-H-atom, which is not available with benzaldehyde, hydrogenolysis is considered as the mechanistic pathway responsible for the formation of a tertiary amine in this reaction.

Recently, Sivasankar and Prins [10] found in their study on reactions of mixed di- and trialkylamines over Pd/γ-Al$_2$O$_3$ that methyl-groups can be transferred between alkylamines. This was taken as a proof that a 1-amino-trialkylamine, formed by reaction of a dialkylamine with a dialkylimine, does not have to achieve alkylamine elimination through an enamine intermediate, but can do so by direct hydrogenolysis. An imine radical was proposed as possible intermediate in the transfer of the alkyl group.

During the deuteration of CH_3CN, Huang and Sachtler [15] observed a surprising discrepancy between the number of D-atoms found in the products and that predicted by the straight-forward stoichiometry of nitrile hydrogenation. The D-atoms were added preferentially to the C-atom of the C≡N group, while H-atoms were added to the N-atom. These results were explained by a concerted reaction mechanism, as is presented exemplarily for Ru in Fig. 1. The secondary amine is formed by reaction of an alkyl group with the N=Ru bonded intermediate. Addition of another alkyl group to the Ru-bound secondary amide provides the tertiary amine.

The aim of the present study was to obtain detailed mechanistic information on the surface reactions leading on the one hand to primary amines and on the other hand to the formation of secondary or tertiary amines. As model reaction, the liquid phase hydrogenation of acetonitrile and butyronitrile over a Raney-Co catalyst was explored. To elucidate the role of
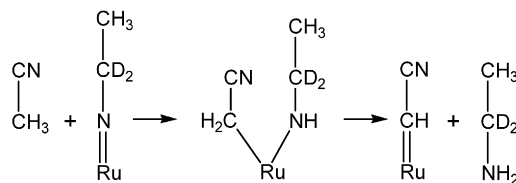

Fig. 1. Concerted reaction mechanism proposed for the deuteration of acetonitrile [15].

alkyl group transfer, acetonitrile and butyronitrile were hydrogenated in the presence of *n*-butylamine and ethylamine, respectively. Further, CD_3CN was hydrogenated to explore, if the methyl-group is involved in hydrogenation or condensation reactions.

2. Experimental

2.1. Materials

Raney-Co 2700 catalyst (Grace Davison division of W.R. Grace and Co., lot #7865) was received as an aqueous suspension. The chemical composition was 1.85 wt% Al, 97.51 wt% Co, 0.3 wt% Fe, and 0.34 wt% Ni. Due to its sensitivity to oxygen, the catalyst was stored and handled under inert atmosphere throughout all preparation steps. It was washed with de-ionized water until the pH of the washing water was neutral. The remaining water was removed by drying in partial vacuum ($p < 1$ kPa) for 30 h at 323 K. After outgassing at 473 K for 6 h the BET area was 22.4 m^2 g$_{Cat}^{-1}$ and the number of accessible metal atoms was 0.36 mmol g$_{Cat}^{-1}$.

The other chemicals were used as received from commercial suppliers (acetonitrile-d$_3$, ⩾99.5%, Deutero GmbH; acetonitrile, ⩾99.5% GC-assay, Fluka; ethylamine, ⩾99.5% GC-assay, Fluka; diethylamine, ⩾99.5% GC-assay, Fluka; butyronitrile, ⩾99% GC-assay, Fluka; mono- and di-*n*-butylamine, >99% GC-assay, Aldrich; *N*-ethylbutylamine, ⩾98.0%, Aldrich; 1-octanol, ⩾99.5% GC-assay, Fluka; *n*-hexane, ⩾99.0% GC-assay, Roth; H$_2$, 99.999 vol%, Air Liquide).

2.2. Catalysis

The hydrogenation reactions were conducted in a batch reactor (160 cm^3; Parr Instrument) at constant hydrogen pressure. Raney-Co catalyst was suspended under inert atmosphere in the reaction mixture (for composition see Table 1). Hexane was used both as solvent and as internal standard for GC chromatography. The autoclave was charged with the reaction mixture under a flow of nitrogen. After closing, the reactor was pressurized and depressurized with nitrogen several times to remove residual oxygen. The reaction mixture was then heated to the reaction temperature (383 K). The reaction was started by rapidly pressurizing the reactor with hydrogen to 45 bar and subsequently starting the stirrer (1500 rpm). Samples for off-line GC, GC-MS and NMR analysis were periodically withdrawn through a dip-tube with filter for solids.

GC analysis was carried out on an HP Gas Chromatograph 5890 equipped with a cross-linked 5% diphenyl–95%
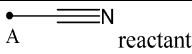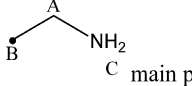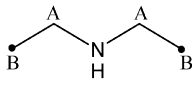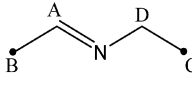
Table 1
Concentration and amount of reactants and catalyst used in the hydrogenation reactions

Reactant(s)[a]	Concentration [mol dm^{-3}]	Hexane [cm^3]	Amount of catalyst [g]	C_1–C≡N [cm^3]	C_3–C≡N [cm^3]	C_4–NH_2 [cm^3]	C_2–NH_2 [cm^3]
C_1–C≡N	9.52	40.0	1.05	40.0	–	–	–
C_1–C≡N	4.08	50.0	0.95	13.6	–	–	–
CD_3CN	9.52	40.0	1.06	40.0	–	–	–
C_3–C≡N	7.12	40.0	1.00	–	66.1	–	–
C_3–C≡N	4.08	40.0	1.01	–	22.1	–	–
C_1–C≡N + C_3–C≡N	4.08[b]	40.0	1.01	20.0	33.4	–	–
C_1–C≡N + C_4–NH_2	4.08[b]	36.0	1.00	20.0	–	37.5	–
C_3–C≡N + C_2–NH_2	4.08[b]	16.5	0.48	–	15.9	–	12.1

[a] For each of the two starting materials.
[b] For compound names refer to Table 3.

Table 2
Assignment of the ^{1}H NMR signals of the final product mixture of CD_3CN hydrogenation [16,17]

Molecule	Group	Chemical shift [ppm]	Assignment
C_1–C≡N	A	1.98	A ≡≡N reactant
C_2–NH_2	A	2.74	A NH$_2$ C main product
	B	1.10 t	
	C	(0.5–4.0)[a]	
C_2–NH–C_2	A	2.64	A A N H B B
	B	1.10	
C_2–NH–C_2	A	3.35	A D N B C
	B	1.80	
	C	1.20	
	D	ca. 2.7[b]	

Note that the position of the signals in ^{2}D NMR is the same. t = triplet, • = CD_3 partially substituted with H.
[a] Position variable.
[b] Not identified due to overlap with other signals.

Table 3
Abbreviations for the reagents, intermediates, and products discussed in this work

Compound	Formula
Acetonitrile	C_1–C≡N
Acetonitrile-d$_3$	CD_3CN
Butyronitrile	C_3–C≡N
Ethylamine	C_2–NH_2
n-Butylamine	C_4–NH_2
N-ethylidene-ethylamine	C_1–HC=N–C_2
N-butylidene-butylamine	C_3–HC=N–C_4
N-ethylidene-butylamine	C_1–HC=N–C_4
N-butylidene-ethylamine	C_3–HC=N–C_2
Diethylamine	C_2–NH–C_2
Di-*n*-butylamine	C_4–NH–C_4
N-ethyl-butylamine	C_2–NH–C_4

dimethylpolysiloxane column (Rtx-5 amine, 30 m, Restek GmbH). GC-MS analysis was performed on a Shimadzu GCMS-QP20105 equipped with a cross-linked (5%-phenyl)-methylpolysiloxane column (HP-5, 32 m, Agilent). ^{1}H NMR and ^{2}D NMR measurements were conducted on a Bruker DPX-400 (400 MHz) instrument with CD_3Cl as solvent containing 1 vol% tetramethylsilane as standard. The assignment of the NMR signals is given in Table 2. The reaction rate was calculated from the decrease in acetonitrile and butyronitrile concentration in the linear range of the concentration curves (in general in the range 0–80% conversion). The selectivity was calculated by dividing the molar amount of the respective product by the amount of acetonitrile or butyronitrile converted. At full conversion, the selectivity is thus obtained from $S = (n_k|\upsilon_i|)/(n_{i,0}|\upsilon_k|)$ with $n_{i,0}$ = initial amount of acetonitrile or butyronitrile, n_k = amount of ethylamine or butylamine at full conversion of the respective reactant, υ_i, υ_k = stoichiometric coefficient of the reactant and product, respectively. Prior to the experiments, a test on mass transfer limitations at a stirring speed of 1500 rpm was performed by varying the amount of catalyst in the range of 0–2.0 g. The rate of reaction was proportional to the amount of cata-lyst, showing that external mass transfer limitations were absent.

3. Results

3.1. Hydrogenation of C_1–C≡N and CD_3CN

To investigate the mechanistic aspects of the formation of secondary amines during the hydrogenation of nitriles, the hydrogenation of single nitriles, mixtures of nitriles as well as mixtures of nitriles and amines was explored. The presence of alkyl groups with different chain length, thereby, served as a molecular marker to follow the transfer of alkyl groups from one molecule to another.

As a reference experiment, the hydrogenation of C_1–C≡N was studied first (for abbreviations see Table 3). The profile for a starting concentration $c_{0,AN} = 9.52$ mol dm^{-3} is shown in Fig. 2. The concentration of C_1–C≡N decreased almost linearly with time. It was converted at a rate of 4.50×10^{-3} mol min^{-1} g$_{Cat}^{-1}$. With a selectivity of 89%, the main product was C_2–NH_2. The only by-product was C_2–NH–C_2 (11%). C_1–HC=N–C_2 was observed as a reaction intermediate. The formation of C_1–HC=N–C_2 and C_2–NH_2 started immediately after the start of the reaction, showing that both were primary products. The concentration of C_2–NH–C_2 increased with a time delay, suggesting that it is a secondary product. After 80–90% of C_1–C≡N had been converted, the concentration
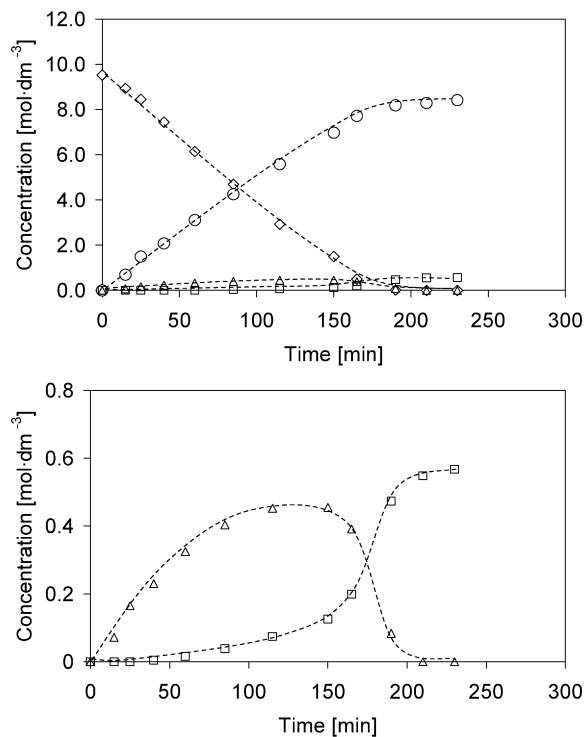
Fig. 2. Concentration profile for the hydrogenation of C_1–$C\equiv N$ over Raney-Co at 383 K, $p = 45$ bar, $c_{0,AN} = 9.52$ mol dm^{-3}. Part of the diagram was magnified to clarify the formation of the by-product C_2–NH–C_2 (lower graph). ($\diamondsuit$) C_1–$C\equiv N$, ($\bigcirc$) C_2–NH_2, ($\triangle$) C_1–HC=N–C_2, ($\square$) C_2–NH–C_2.
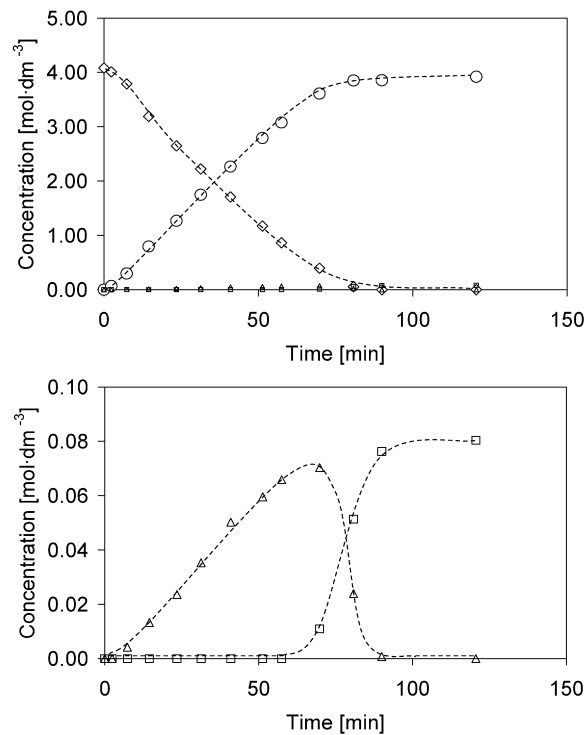

Fig. 3. Concentration profile for the hydrogenation of C_1–$C\equiv N$ over Raney-Co at 383 K, $p = 45$ bar, $c_{0,AN} = 4.08$ mol dm^{-3}. ($\diamondsuit$) C_1–$C\equiv N$, ($\bigcirc$) C_2–NH_2, ($\triangle$) C_1–HC=N–C_2, ($\square$) C_2–NH–C_2.

of C_1–HC=N–C_2 decreased rapidly, while C_2–NH–C_2 was formed in parallel. This sequence is indicative of weaker adsorption of C_1–HC=N–C_2 on the catalyst surface compared to C_1–$C\equiv N$.

The reaction profile for a lower starting concentration of C_1–$C\equiv N$ ($c_{0,AN} = 4.08$ mol dm^{-3}) is shown in Fig. 3. The rate of C_1–$C\equiv N$ conversion was slightly lower (4.06×10^{-3} mol min^{-1} g$_{Cat}^{-1}$), whereas enhanced selectivity to C_2–NH_2 (96%) was noteworthy. C_1–HC=N–C_2 was also formed and further converted to C_2–NH–C_2 (4%). Closer inspection of the profile reveals significant differences compared to the experiment with higher starting concentration (Fig. 2). The secondary amine C_2–NH–C_2 was formed only when more than 90% of C_1–$C\equiv N$ had been hydrogenated. Then, a sudden decrease of C_1–HC=N–C_2 concentration occurred, accompanied by the formation of C_2–NH–C_2. This indicates that in the initial phase of the reaction the surface is fully saturated with nitrile molecules.

To obtain insight into the role of the methyl H-atoms of C_1–$C\equiv N$, CD_3CN was hydrogenated (Fig. 4). The concentration profile was very similar to that of the hydrogenation of C_1–$C\equiv N$ at the same starting concentration ($c_{0,AN} = 9.52$ mol dm^{-3}) except that the time of constant reaction rate was shorter. The hydrogenation proceeded at a rate of 4.09×10^{-3} mol min^{-1} g$_{Cat}^{-1}$, which is a factor of 9% lower than with non-deuterated C_1–$C\equiv N$. The selectivity to C_2–NH_2 was slightly higher (90%) and C_2–NH–C_2 was the only by-product formed with a selectivity of 10%.
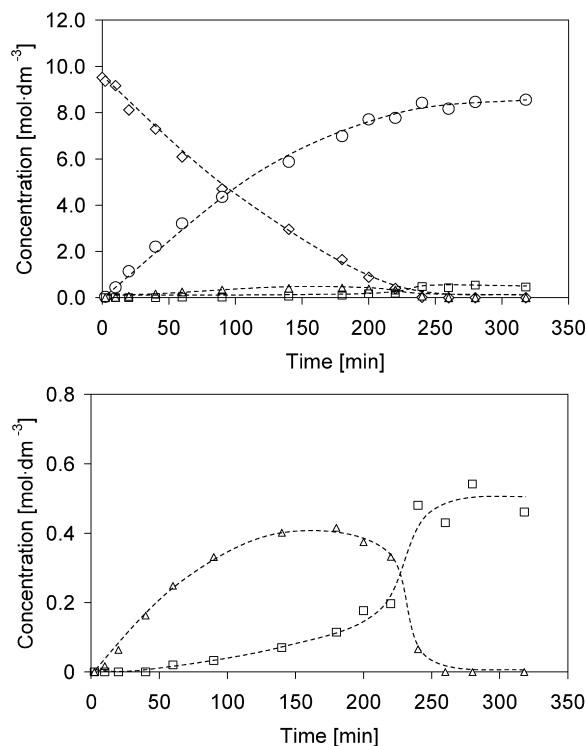

Fig. 4. Concentration profile for the hydrogenation of CD_3CN over Raney-Co at 383 K, $p = 45$ bar, $c_{0,AN-d3} = 9.52$ mol dm^{-3}. ($\diamondsuit$) CD_3CN, ($\bigcirc$) C_2–NH_2, ($\triangle$) C_1–HC=N–C_2, ($\square$) C_2–NH–C_2.
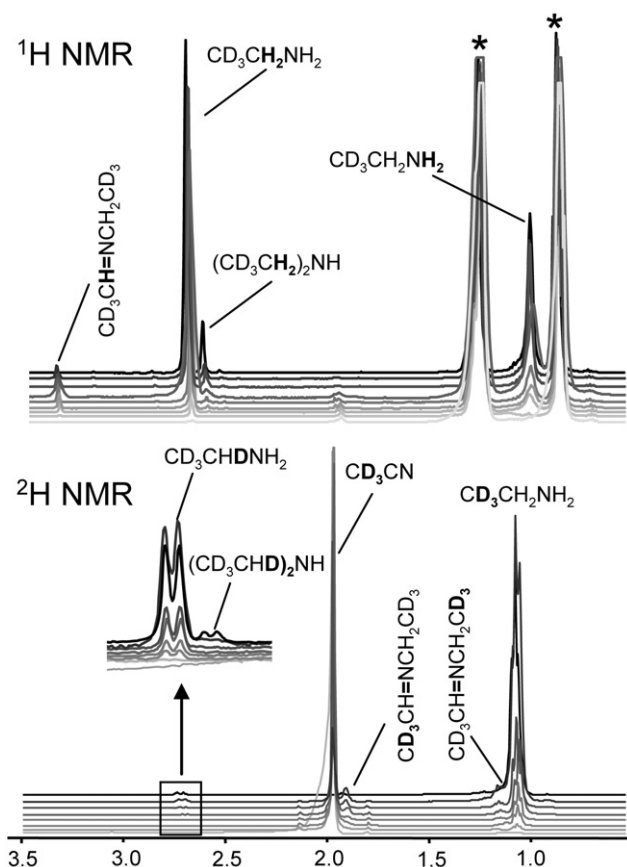
Fig. 5. Time resolved ^{1}H NMR and ^{2}D NMR results obtained during the hydrogenation of CD$_3$CN. Spectra were recorded after 2.3, 10, 20, 40, 60, 90, 120, 200, and 318 min. * Solvent peaks (*n*-hexane).

Information about H/D exchange during the reaction was obtained by following the reaction with ^{1}H and ^{2}D NMR spectroscopy (Fig. 5). The time resolved area of the peaks (normalized to area of TMS or CDCl$_3$) is plotted in Figs. 6 and 7, respectively. The decrease of the CD$_3$CN and the increase of the CD$_3$CH$_2$NH$_2$ concentration corresponded well with the reaction profiles obtained from the GC data. C$_1$–C≡N, which is found in trace amounts in CD$_3$CN, is hydrogenated after an induction period of ~60 min. Additional deuterium was found in 0.8% of the C$_2$–NH$_2$ molecules formed (CD$_3$CHDNH$_2$) and to a very low extent (0.15%) in partially deuterated secondary amine (CD$_3$CHD)$_2$NH. The two peaks at 1.80 and 1.20 ppm, which first increased and then decreased in intensity, were assigned to the methyl and ethyl CD$_3$ group in CD$_3$CH=NCH$_2$CD$_3$, respectively. In ^{1}H NMR, the imine H-atom was observed at 3.35 ppm. In the ^{2}D NMR spectra, the signal at 3.35 ppm was not observed, which suggests that CD$_3$CD=NCH$_2$CD$_3$ was either not formed or its concentration was below the detection limit. These observations clearly show that little H/D exchange occurred during the reaction.

To study the influence of the length of the alkyl chain on the rate of reaction, C$_3$–C≡N was hydrogenated. A typical concentration profile for the hydrogenation of C$_3$–C≡N at 383 K and $c_{0,BN} = 4.08$ mol dm^{-3} is shown in Fig. 8. The course of the reaction was very similar to that for the hydrogenation of

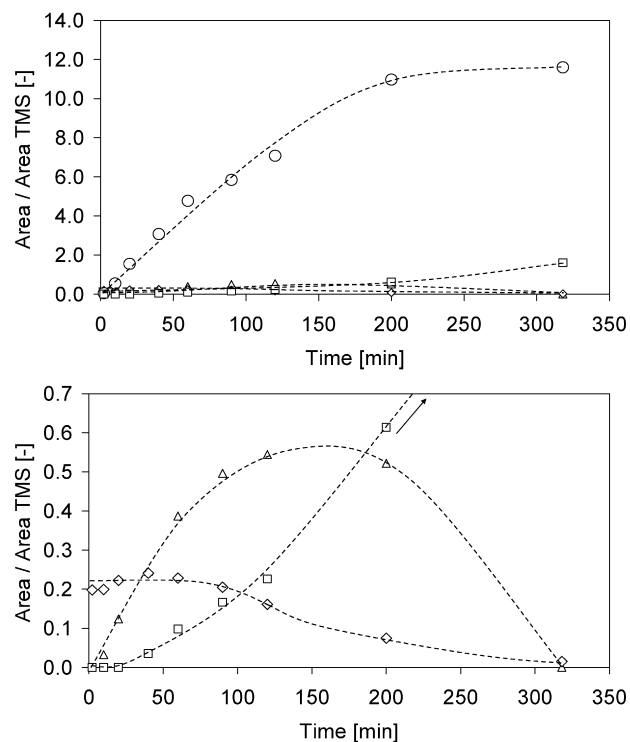Fig. 6. Profile for the hydrogenation of CD$_3$CN over Raney-Co at 383 K, $p = 45$ bar generated from ^{1}H NMR measurements. (◇) CH$_3$CN, (○) CD$_3$CH$_2$NH$_2$, (△) CD$_3$CH=NCH$_2$CD$_3$, (□) (CD$_3$CH$_2$)$_2$NH.
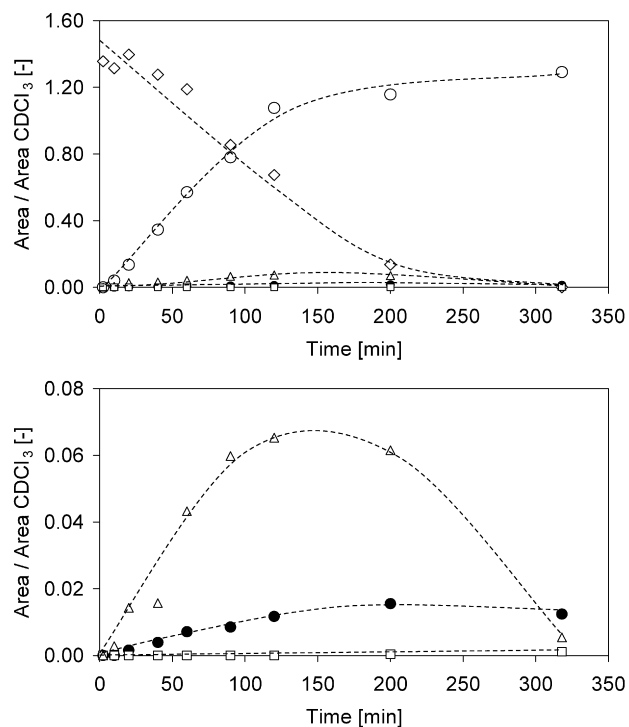

Fig. 7. Profile for the hydrogenation of CD$_3$CN over Raney-Co at 383 K, $p = 45$ bar generated from ^{2}D NMR measurements. (◇) CD$_3$CN, (○) CD$_3$CH$_2$NH$_2$, (●) CD$_3$CHDNH$_2$, (□) (CD$_3$CHD)$_2$NH, (△) CD$_3$CH=NCH$_2$CD$_3$, mean values of the areas at 1.20 and 1.80 ppm. Hydrogenation of C$_3$–C≡N.
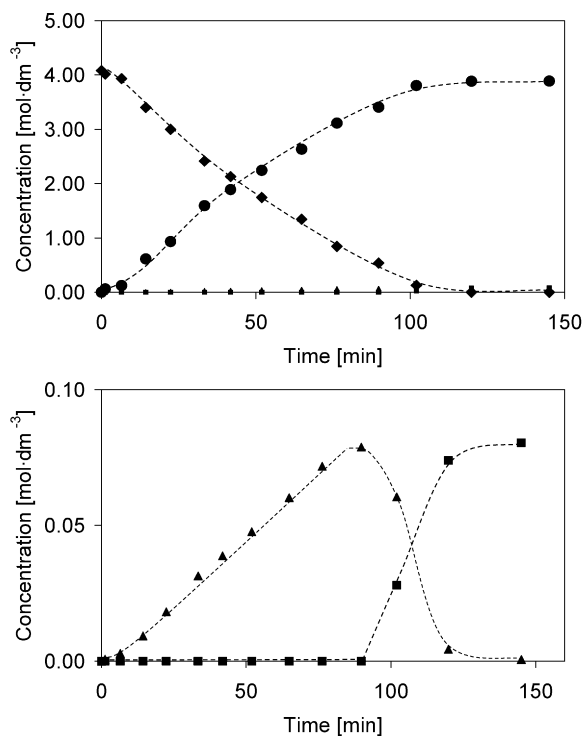
Fig. 8. Concentration profile for the hydrogenation of C_3–C≡N over Raney-Co at 383 K, $p = 45$ bar, $c_{0,BN} = 4.08$ mol dm^{-3}. (◆) C_3–C≡N, (●) C_4–NH$_2$, (▲) C_3–HC=N–C_4, (■) C_4–NH–C_4.

C_1–C≡N. After a short induction period (<2 min) the reaction started at a rate of 3.44×10^{-3} mol min^{-1} g$_{Cat}^{-1}$. At full conversion, the only by-product was C_4–NH–C_4 (4%). In agreement with a previous paper [18], C_4–NH$_2$ and C_3–HC=N–C_4 were observed right after the start of the reaction suggesting that both were primary products. After ~30 min, the rate of C_3–HC=N–C_4 formation increased compared to the rate at the start of the reaction. The formation of C_4–NH–C_4 was observed only after more than 90% of C_3–C≡N had been converted. The increase in concentration of C_4–NH–C_4 correlated with the rapid decrease in C_3–HC=N–C_4 concentration. It is, thus, assumed that C_4–NH–C_4 is a sequential product of the hydrogenation of C_3–HC=N–C_4. As with C_1–C≡N, the hydrogenation was also carried out at a higher starting concentration ($c_{0,BN} = 7.12$ mol dm^{-3}). As the reaction profile strongly resembled that at lower concentration, also with respect to the formation of the only by-product C_4–NH–C_4, the graph not shown here. The rate increased only slightly to 3.48×10^{-3} mol min^{-1} g$_{Cat}^{-1}$, but the selectivity to C_4–NH$_2$ decreased significantly (88%, see Table 8).

3.2. Co-hydrogenation of C_1–C≡N and C_3–C≡N

The results of the co-hydrogenation of C_1–C≡N and C_3–C≡N are shown in Fig. 9. The reaction conditions were equal to those in the hydrogenation of the single compounds (383 K, $c_{0,AN}$ and $c_{0,BN} = 4.08$ mol dm^{-3}). Both nitriles were hydrogenated immediately after the start of the reaction. The profiles of C_1–C≡N depletion and C_2–NH$_2$ formation were similar to that of hydrogenation of pure C_1–C≡N, whereas the
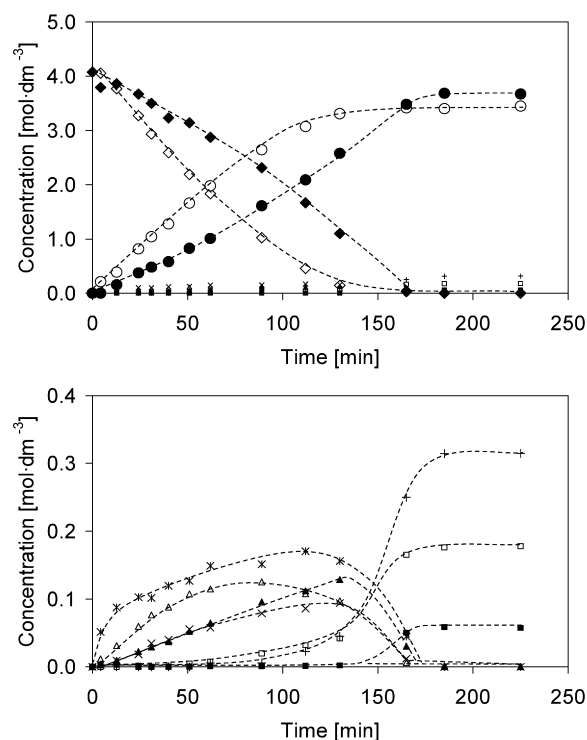

Fig. 9. Concentration profile for the co-hydrogenation of C_1–C≡N and C_3–C≡N over Raney-Co at 383 K, $p = 45$ bar, $c_{0,AN}$ and $c_{0,BN} = 4.08$ mol dm^{-3}. (◇) C_1–C≡N, (○) C_2–NH$_2$, (△) C_1–HC=N–C_2, (□) C_2–NH–C_2, (◆) C_3–C≡N, (●) C_4–NH$_2$, (▲) C_3–HC=N–C_4, (■) C_4–NH–C_4, (×) C_3–HC=N–C_2, (∗) C_1–HC=N–C_4, (+) C_2–NH–C_4.

rate of C_3–C≡N hydrogenation was significantly reduced by the presence of C_1–C≡N. The nitriles C_1–C≡N and C_3–C≡N were converted at an initial rate of 3.67×10^3 mol min^{-1} g$_{Cat}^{-1}$ and 1.87×10^3 mol min^{-1} g$_{Cat}^{-1}$, respectively. The selectivity is qualitatively compared to the hydrogenation of the single nitriles at higher starting concentration, as the added concentration of the two compounds was 8.16 mol dm^{-3}. The selectivity to C_2–NH$_2$ was reduced to 84%, while for C_4–NH$_2$ it was slightly increased to 89%. As by-products, the symmetric secondary amines C_2–NH–C_2 and C_4–NH–C_4 were formed with a selectivity of 9 and 3%, respectively. The unsymmetric secondary amine C_2–NH–C_4 was formed with 8% selectivity. An overview of the intermediates and final products is provided in Table 4. Four different imines were formed as primary products. The unsymmetric imines C_3–HC=N–C_2 and C_1–HC=N–C_4 and the symmetric imines C_3–HC=N–C_4 and C_1–HC=N–C_2 were identified. C_1–HC=N–C_4 was formed at the highest rate of all intermediates followed by C_1–HC=N–C_2. The dialkylimines C_3–HC=N–C_2 and C_3–HC=N–C_4 were formed with the same albeit lower rate. The secondary amines started forming with a time delay of 50 min in the case of C_2–NH–C_2 and C_2–NH–C_4 and 130 min in the case of C_4–NH–C_4.

3.3. Hydrogenation of C_1–C≡N in the presence of C_4–NH$_2$

The hydrogenation of C_1–C≡N in the presence of an equimolar amount of C_4–NH$_2$ was carried out at 383 K

Table 4
General reaction sequence for the co-hydrogenation of C_1–C≡N and C_3–C≡N

Reactants	Primary products	Secondary products
C_1–C≡N	C_1–NH_2	C_2–NH–C_2
C_3–C≡N	C_4–NH_2	C_2–NH–C_4
	C_1–HC=N–C_4	C_4–NH–C_4
	C_1–HC=N–C_2	
	C_3–HC=N–C_4	
	C_3–HC=N–C_1	

Table 5
General reaction sequence for the hydrogenation of C_1–C≡N in the presence of C_4–NH_2

Reactants	Primary products	Secondary products	Final products
C_1–C≡N	C_2–NH_2	C_1–HC=N–C_2	C_2–NH–C_4
C_4–NH_2	C_1–HC=N–C_4	C_3–HC=N–C_4	C_2–NH–C_2
	(C_3–HC=N–C_4)[a]		C_4–NH–C_4

[a] Primary product due to conversion of C_4–NH_2 prior to the addition of hydrogen.

Fig. 10. Concentration profile for the hydrogenation of C_1–C≡N in the presence of C_4–NH_2 over Raney-Co at 383 K, $p = 45$ bar, $c_{0,AN} = 4.08$ mol dm^{-3}. (◇) C_1–C≡N, (○) C_2–NH_2, (●) C_4–NH_2, (△) C_1–HC=N–C_2, (□) C_2–NH–C_2, (▲) C_3–HC=N–C_4, (◆) C_4–NH–C_4, (×) C_3–HC=N–C_2, (∗) C_1–HC=N–C_4, (+) C_2–NH–C_4.
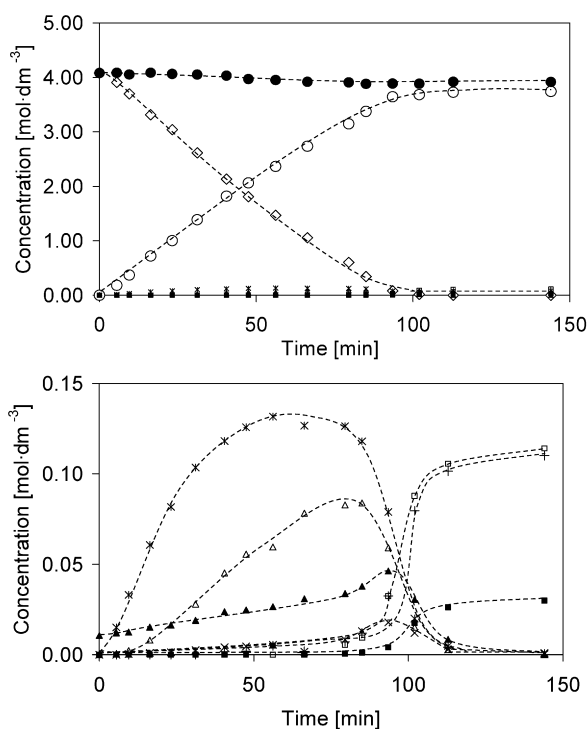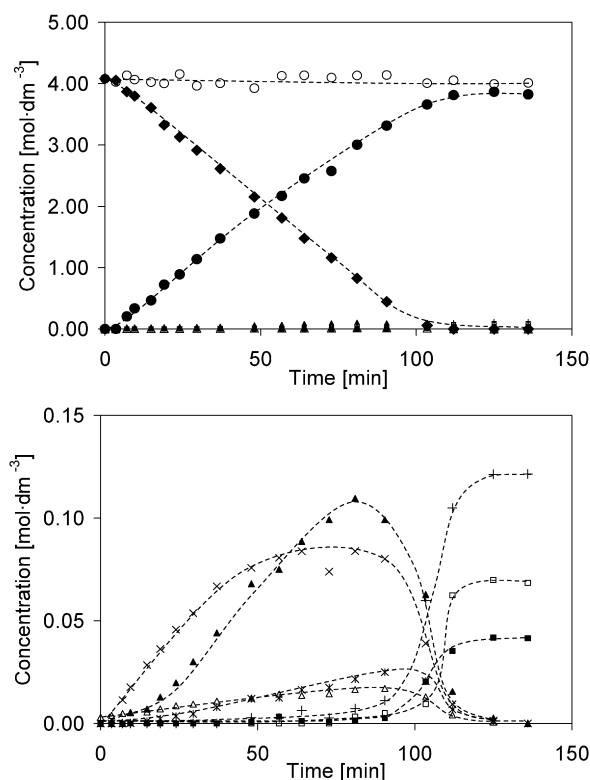

Fig. 11. Concentration profile for the hydrogenation of C_3–C≡N in the presence of C_2–NH_2 over Raney-Co at 383 K, $p = 45$ bar, $c_{0,BN} = 4.08$ mol dm^{-3}. (◇) C_2–NH_2, (△) C_1–HC=N–C_2, (□) C_2–NH–C_2, (◆) C_3–C≡N, (●) C_4–NH_2, (▲) C_3–HC=N–C_4, (■) C_4–NH–C_4, (×) C_3–HC=N–C_2, (∗) C_1–HC=N–C_4, (+) C_2–NH–C_4.

and $c_{0,AN} = 4.08$ mol dm^{-3}. Fig. 10 shows the concentration profiles of the reaction. Compared to the hydrogenation of C_1–C≡N, the rate of reaction unexpectedly increased by 10% (4.46×10^3 mol min^{-1} g$_{Cat}^{-1}$). The selectivity to C_2–NH_2 was 92% and thus 4% lower than in the absence of C_4–NH_2. As by-products, C_2–NH–C_2 and C_2–NH–C_4 were formed with a selectivity of 6 and 3%, respectively. With respect to the starting concentration of C_4–NH_2, the selectivity to C_4–NH–C_4 was 2%. The reaction intermediates and products are summarized in Table 5. In a sample taken before the addition of hydrogen ($t = 0$ min), a considerable amount of C_3–HC=N–C_4 was found. In the further course of the reaction, this intermediate was formed with the second lowest rate (Table 7). Right after the addition of hydrogen, C_1–HC=N–C_4 was formed with the highest rate. C_1–HC=N–C_2 started developing after an induction period of 10 min with the second highest rate. After a further delay C_3–HC=N–C_2 was formed. After most of the acetonitrile (~80%) had been hydrogenated, the fast forma-

tion of the secondary amines coincided with a rapid depletion of the imine intermediates. Between 66 and 80 min the final product C_2–NH–C_4 developed shortly before C_2–NH–C_2; both were then formed in parallel, while the concentration of the imine intermediates decreased. In the final part of the reaction, the concentration of both amines increased at approximately the same rate. A significant amount of C_4–NH–C_4 was formed only after the maximum concentration of C_3–HC=N–C_4 had been reached.

3.4. Hydrogenation of C_3–C≡N in the presence of C_2–NH_2

C_3–C≡N was hydrogenated in the presence of an equimolar amount of C_2–NH_2 at 383 K and $c_{0,BN} = 4.08$ mol dm^{-3}. The concentration profile of the reaction is depicted in Fig. 11. In comparison to the reaction without C_2–NH_2, the rate of re-

action increased by 15% (3.94×10^3 mol min^{-1} g$_{Cat}^{-1}$). With 95%, the selectivity to C_4–NH_2 was 1% lower than in the absence of C_2–NH_2. C_4–NH–C_4 and C_2–NH–C_4 were observed as by-products with a selectivity of 2 and 3%, respectively. Additionally, with respect to the starting concentration of C_2–NH_2, 3% of C_2–NH–C_2 was found. To clarify the course of the reaction, Table 6 summarizes the nature of the reaction products. C_1–HC=N–C_2 occurred as a primary product before the addition of hydrogen and was then formed at a relatively low rate. Another primary product was the imine C_3–HC=N–C_2, which developed at approximately the same rate as C_3–HC=N–C_4 (after a time delay of 10 min). Only after 80% of C_3–C≡N had been hydrogenated considerable increase in the concentration of secondary amines was observed coinciding with rapid conversion of the imine intermediates.

4. Discussion

4.1. H/D exchange and kinetic isotope effect in the hydrogenation of CD₃CN

For a better overview in the following discussion, reaction rates and selectivities are summarized in Tables 7 and 8, respectively. As mentioned before, the H/D exchange in the deuteration of CH_3CN over Ru catalysts indicated participation of the nitrile methyl-group in the formation of ethylamine (see Fig. 1) [15]. The very small degree of H/D exchange observed in this study for the hydrogenation of CD_3CN suggests that on Raney-Co the methyl group hardly interacts with other molecules adsorbed on the catalyst surface. Thus, a mechanism, in which transfer of D from the CD_3 group to either C or N of the CN triple bond occurs, can be excluded. However, the kinetic isotope effect of $k_{CH_3CN}/k_{CD_3CN} = 1.10$ suggests that nitrile participates in the rate-determining step of the reaction. The isotope effect was close to the inverse ratio of the molar masses ($CD_3CN/CH_3CN = 1.07$) indicating that lower diffusivity of CD_3CN due to its higher mass plays a key role. The rate of dialkylimine formation was higher with CH_3CN than with CD_3CN (factor 1.4) resulting in a lower selectivity to ethylamine. This is an indication that deuterated compounds also participate in the rate-determining step of the bimolecular reaction leading to by-products.

Table 6
General reaction sequence for the hydrogenation of C_3–C≡N in the presence of C_2–NH_2

Reactant	Primary products	Secondary products	Final products
C_3–C≡N	C_4–NH_2	C_3–HC=N–C_4	C_2–NH–C_4
C_2–NH_2	C_3–HC=N–C_2	C_1–HC=N–C_4	C_2–NH–C_2
	(C_1–HC=N–C_2)[a]		C_4–NH–C_4

[a] Primary product due to reaction of C_2–NH_2 prior to the addition of hydrogen.

Table 7
Summary of the initial reaction rates of nitrile conversion and the rates of dialkylimine formation in the different hydrogenation reactions

Reactant(s)	Concentr. [mol dm^{-3}]	Rate of conv. $\times 10^3$ [mol min^{-1} g$_{Cat}^{-1}$]		Rate of formation $\times 10^3$ [mol min^{-1} g$_{Cat}^{-1}$]			
		C_1–C≡N	C_3–C≡N	C_1–HC=N–C_2	C_3–HC=N–C_4	C_1–HC=N–C_4	C_3–HC=N–C_2
C_1–C≡N	9.52	4.50	–	0.42	–	–	–
C_1–C≡N	4.08	4.06	–	0.09	–	–	–
CD_3CN	9.52	4.09	–	0.30	–	–	–
C_3–C≡N	7.12	–	3.48	–	0.19	–	–
C_3–C≡N	4.08	–	3.44	–	0.05	–	–
C_1–C≡N + C_3–C≡N	4.08	3.67	1.87	0.20	0.10	0.46	0.09
C_1–C≡N + C_4–NH_2	4.08	4.46	–	0.13	0.03	0.32	0.01
C_3–C≡N + C_2–NH_2	4.08	–	3.94	0.04	0.17	0.03	0.18

Table 8
Summary of the selectivities in the final reaction mixtures

Reactant(s)	Concentration [mol dm^{-3}]	Selectivity [%]				
		C_2–NH_2	C_4–NH_2	C_2–NH–C_2	C_4–NH–C_4	C_2–NH–C_4
C_1–C≡N	9.52	99	–	11	–	–
C_1–C≡N	4.08	96	–	4	–	–
CD_3CN	9.52	90	–	10		
C_3–C≡N	7.12	–	88	–	12	–
C_3–C≡N	4.08	–	96	–	4	–
C_1–C≡N + C_3–C≡N	4.08	84	89	9	3[a]	8
C_1–C≡N + C_4–NH_2	4.08	92	–	6	2[a]	3
C_3–C≡N + C_2–NH_2	4.08	–	95	3	2	3

[a] Calculated based on the amount of amine present in the reaction mixture prior to the start of the reaction. Therefore, the overall selectivity was >100% in the two specific cases. All other selectivities were determined with respect to the nitriles applied.

4.2. Role of the strength of adsorption

In both, hydrogenation of the single nitriles and co-hydrogenation of C_1–C≡N and C_3–C≡N, the rate for C_1–C≡N consumption was higher than for C_3–C≡N. The difference may be caused by a stronger adsorption of C_1–C≡N and/or by a faster intrinsic reaction rate [10]. In the co-hydrogenation of the two compounds, the initial rate of C_3–C≡N consumption was reduced much more than that of C_1–C≡N, when compared to the reactions with only one nitrile as reactant. With decreasing amount of C_1–C≡N, the reaction rate of C_3–C≡N hydrogenation increased. Both observations indicate that C_1–C≡N adsorbs more strongly on the surface of Raney-Co. In consequence, the surface concentration of C_1–C≡N is higher than of C_3–C≡N during the initial phase of the reaction, when both nitriles are present in equal concentration in the liquid phase. When the reaction mixture becomes depleted of C_1–C≡N, the surface concentration of C_3–C≡N increases and C_3–C≡N hydrogenation becomes faster. Note that according to our experimental results, C_1–C≡N adsorbs more strongly on the surface than C_3–C≡N, whereas it is the other way around with the amines. Analysis of the proton affinity showed that butyronitrile is more basic than acetonitrile and butylamine more basic than ethylamine [24]. However, the higher steric demand of the propyl group might explain the weaker adsorption of butyronitrile on cobalt compared to acetonitrile.
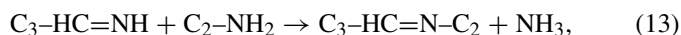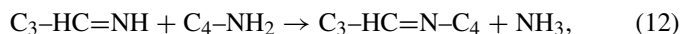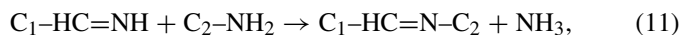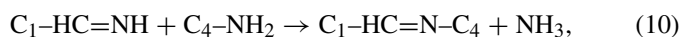
In parallel to the hydrogenation of the nitrile, dialkylimines are formed, which were shown to be primary reaction products. This strongly suggests that the condensation reactions occur on the catalyst surface, in agreement with other studies [8,19,20]. For both nitriles investigated, the selectivity to primary amines was lowered upon an increase of the starting concentration of the reactants. Thus, it is concluded that the surface concentration of precursors necessary for the formation of secondary amines increases with the concentration of nitrile. For example, in the hydrogenation of C_1–C≡N the rate of hydrogenation increased by a factor of 1.13, whereas the rate of formation of C_1–HC=N–C_2 was a factor of 4.7 higher, when raising the starting concentration from 4.08 to 9.52 $mol\,dm^{-3}$. While the hydrogenation was almost independent of the nitrile concentration, indicating an order close to zero due to full coverage of the sites participating in the hydrogenation, a positive order was observed for the formation of dialkylimines. Note that the factor of $4.7 \approx 2^2$ is indicative of a bimolecular reaction.

The different influence on the rate of hydrogenation and by-product formation indicates that the two processes take place on different sites. While the sites for hydrogenation were almost saturated at lower nitrile concentrations, those for condensation had remaining sorption capacity. It has been reported that addition of amines to the reaction mixture has no effect [19,21] indicating that amines are adsorbed either weakly or on other sites than those used for hydrogenation. Also a retarding effect on the rate of hydrogenation has been described [22] suggesting that amines are more strongly adsorbed on the metal than nitriles. In this study, in the presence of an equimolar amount of amine, the rate of hydrogenation was slightly increased for both nitriles, which is another indication for the dual site mechanism

proposed. In fact, the rate of nitrile conversion in the presence of amine was approximately equal to the sum of the rates of nitrile consumption in the absence of amine and the rate of formation of the unsymmetric dialkylimines. Hence, faster reaction of the nitrile is mostly due to enhanced by-product formation. This observation again suggests that the by-product formation takes place on other sites than the hydrogenation. Note that a hydrogenation step is involved in the formation of the precursor of the condensation product. Either, a partially hydrogenated intermediate migrates to the condensation sites as proposed by Verhaak et al. [20] or, which is considered less likely, hydrogenation also takes place on the condensation sites resulting in a surface intermediate more susceptible to condensation than to further hydrogenation.

4.3. Reaction steps during co-hydrogenation of two nitriles

In the co-hydrogenation of C_1–C≡N and C_3–C≡N, the development of by-products can roughly be divided into two periods. Formation of the imine intermediates occurred during the first period, while the further reaction of these intermediates giving rise to secondary amines constitutes the second period. The primary nature of all imine intermediates suggests that—at least in the initial phase of the reaction—they were formed in the same way. Formally, the formation of dialkylimine intermediates can be explained by the overall reactions,
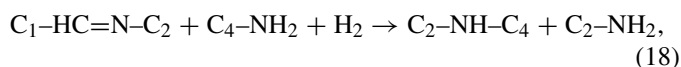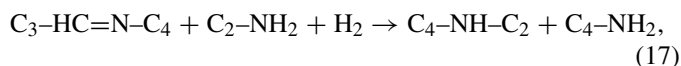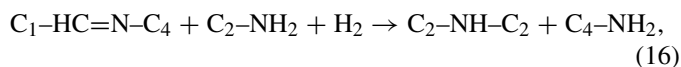
$$C_1\text{–}HC{=}NH + C_4\text{–}NH_2 \rightarrow C_1\text{–}HC{=}N\text{–}C_4 + NH_3, \qquad (10)$$

$$C_1\text{–}HC{=}NH + C_2\text{–}NH_2 \rightarrow C_1\text{–}HC{=}N\text{–}C_2 + NH_3, \qquad (11)$$

$$C_3\text{–}HC{=}NH + C_4\text{–}NH_2 \rightarrow C_3\text{–}HC{=}N\text{–}C_4 + NH_3, \qquad (12)$$

$$C_3\text{–}HC{=}NH + C_2\text{–}NH_2 \rightarrow C_3\text{–}HC{=}N\text{–}C_2 + NH_3, \qquad (13)$$

or by disproportionation of the respective amines as, e.g.,

$$2C_2\text{–}NH_2 \rightarrow C_1\text{–}HC{=}N\text{–}C_2 + NH_3 + H_2. \qquad (14)$$
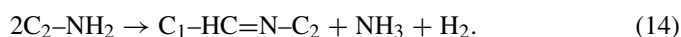
As a dehydrogenation step is involved, the later reaction (Eq. (14)) appears unlikely at high hydrogen pressures. The primary nature of the dialkylimines suggests that surface species were involved, which did not desorb from the surface before the condensation reaction occurred. In the second period of the reaction the dialkylimines were transformed to dialkylamines, which is possible by hydrogenation of the dialkylimines as, e.g.,

$$C_1\text{–}HC{=}N\text{–}C_4 + H_2 \rightarrow C_2\text{–}NH\text{–}C_4. \qquad (15)$$

An alternative reaction is the reaction of an amine with a dialkylimine to 1-alkylamino-dialkylamine followed by either formation of an imine and subsequent hydrogenation or by direct hydrogenolysis resulting in another amine and dialkylamine as, e.g.,

$$C_1\text{–}HC{=}N\text{–}C_4 + C_2\text{–}NH_2 + H_2 \rightarrow C_2\text{–}NH\text{–}C_2 + C_4\text{–}NH_2, \qquad (16)$$

$$C_3\text{–}HC{=}N\text{–}C_4 + C_2\text{–}NH_2 + H_2 \rightarrow C_4\text{–}NH\text{–}C_2 + C_4\text{–}NH_2, \qquad (17)$$

$$C_1\text{–}HC{=}N\text{–}C_2 + C_4\text{–}NH_2 + H_2 \rightarrow C_2\text{–}NH\text{–}C_4 + C_2\text{–}NH_2, \qquad (18)$$

$$C_3-HC{=}N-C_2 + C_4-NH_4 + H_2 \rightarrow C_4-NH-C_4 + C_2-NH_2. \tag{19}$$
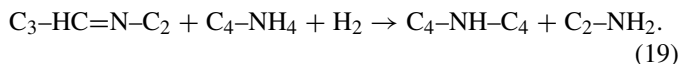
Cross-disproportionation of two dialkylimines followed by hydrogenation resulting in two dialkylamines may also occur resulting in the overall reaction,

$$C_3-HC{=}N-C_4 + C_1-HC{=}N-C_2 + 2H_2 \rightarrow 2C_2-NH-C_4. \tag{20}$$
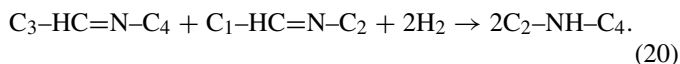
Note that, when comparing the mass balance of the dialkylimine intermediates with that of the final products (dialkylamines) only a slight deviation of $\sim$5% was observed. Taking into account experimental error, this suggests that all dialkylimine molecules reacted to dialkylamines. Thus, the hydrogenolysis of dialkylimines leading to a primary amine and an alkane as, e.g.,

$$C_3-HC{=}N-C_4 + 2H_2 \rightarrow C_4-NH_2 + C_4, \tag{21}$$

or the elimination reaction resulting in primary amine and an alkene,

$$C_3-HC{=}N-C_4 + H_2 \rightarrow C_4-NH_2 + C_4^=, \tag{22}$$

as recently described for reactions over Pd/γ-Al$_2$O$_3$ at higher temperature in the gas phase [10], did not occur to a significant extent.

To differentiate between the reactions in Eqs. (15)–(20), mass balances for C$_2$ and C$_4$ groups in the side products were calculated at selected times. If alkyl group transfer occurred, the mass balance for the respective group changes although the overall mass balance of this type of molecules is constant. For evaluation, the mass balance was calculated shortly before the rapid consumption of the dialkylimines started ($t = 130$ min) and at the end of the reaction ($t = 225$ min). The number of C$_2$ groups increased roughly by the same amount (0.12 mol dm^{-3}) as the number of C$_4$ groups decreased. This suggests that C$_4$ groups were replaced by C$_2$ groups originating most likely from C$_2$–NH$_2$ (Eqs. (16)–(18)). Hydrogenation of the dialkylimine occurred in parallel. Although cross-disproportionation cannot be excluded, it seems to play a minor role.

During the hydrogenation of C$_1$–C≡N in the presence of C$_4$–NH$_2$, two distinct periods with respect to formation of by-products could also be observed. The first period is the formation of dialkylimine intermediates, which is formally described by Eqs. (10)–(13). The mass balance shows that in the second period of the reaction, the hydrogenation of dialkylimines (Eq. (15)) was accompanied by reaction of a dialkylimine with a primary amine (Eqs. (16)–(19)) and/or cross-disproportionation of two dialkylimines (Eq. (20)). The occurrence of C$_3$–HC=N–C$_4$ before the start of the reaction can be explained by a disproportionation reaction analogous to Eq. (14),

$$2C_4-NH_2 \rightarrow C_3-HC{=}N-C_4 + NH_3 + H_2. \tag{23}$$
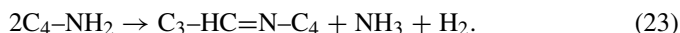
Between the time, where the amount of dialkylimines was approximately at maximum ($t = 80$ min) and the end of the reaction ($t = 145$ min), the number of C$_2$ groups in the side products increased by the same amount (0.033 mol dm^{-3}) as the number of C$_4$ groups decreased. This strongly suggests that the

C$_4$ group in C$_n$–HC=N–C$_4$ was replaced by C$_2$ stemming from C$_2$–NH$_2$. Note that in the time interval, in which dialkylimines were rapidly converted (between 85 and 112 min), a slight increase of the concentration of *n*-butylamine was observed. The increase (0.036 mol dm^{-3}) was approximately equal to the decrease of the C$_4$ groups in dialkylamine (0.033 mol dm^{-3}). Thus, cross-disproportionation (Eq. (20)) cannot be the only way of alkyl group transfer, as in this case the C$_2$ and C$_4$ mass balances should not change.

As for the hydrogenation of C$_1$–C≡N in the presence of C$_4$–NH$_2$, the side reactions in the hydrogenation of C$_3$–C≡N in the presence of C$_2$–NH$_2$ can roughly be subdivided in two regions. Dialkylimines are formed due to the formal reactions in Eqs. (10)–(13). These undergo further reaction to dialkylamines (Eqs. (15)–(20)). The occurrence of C$_1$–HC=N–C$_2$ before the start of the reaction can be explained by disproportionation of two C$_2$–NH$_2$ molecules (Eq. (14)). Note, that the mass balance for dialkylimines and dialkylamines is almost equal (maximum deviation 5%) suggesting that all dialkylimine molecules reacted to dialkylamines. Hence, hydrogenolysis of dialkylimines leading to a primary amine and an alkane (Eq. (21)) or the elimination reaction resulting in a primary amine and an alkene (Eq. (22)) appear unlikely. The number of C$_2$ groups increased by 0.09 mol dm^{-3} between $t = 90$ min (point with maximum concentration in dialkylimine) and $t = 140$ min (final concentration of dialkylamines). In the same time interval, the number of C$_4$ groups decreased by the same amount. Hence, a considerable amount of C$_4$ groups was exchanged by C$_2$ groups. The source is concluded to be C$_2$–NH$_2$.

4.4. Mechanistic aspects of dialkylimine formation

The formation of secondary amines occurred in two discrete steps. In parallel to the formation of primary amines, dialkylimines were formed first, which at least partly left the catalyst surface. The dialkylimines re-adsorbed on the surface after most of the nitrile had been depleted and were hydrogenated to dialkylamines. Note that the first step governs the selectivity to secondary amines. As mentioned above, the formation of secondary dialkylimines can be explained formally by von Braun's mechanism (Eqs. (1)–(5)) [7]. However, aldimines have not been observed directly [8] and other pathways therefore have to be taken into account (shown together with the aldimine path in Fig. 12) [5,18,23]. The two most likely paths involve transfer of the first two H-atoms either to the nitrile N- or C-atom resulting in a carbene or nitrene, respectively (see also [25]). In the following discussion, the different reactivity of the surface structures will be considered.

First, the relative rates of dialkylimine formation will be discussed. In the co-hydrogenation of C$_1$–C≡N and C$_3$–C≡N, all possible dialkylimines were primary products. Interestingly, C$_1$–HC=N–C$_4$ the formal condensation product of C$_4$–NH$_2$ and C$_1$–HC=NH showed the highest rate of formation, though C$_2$–NH$_2$ was formed at a much higher rate than C$_4$–NH$_2$ and very little C$_4$–NH$_2$ was detected in the liquid phase. The second highest rate was observed for C$_1$–HC=N–C$_2$, which would have been expected considering the relative concentrations of
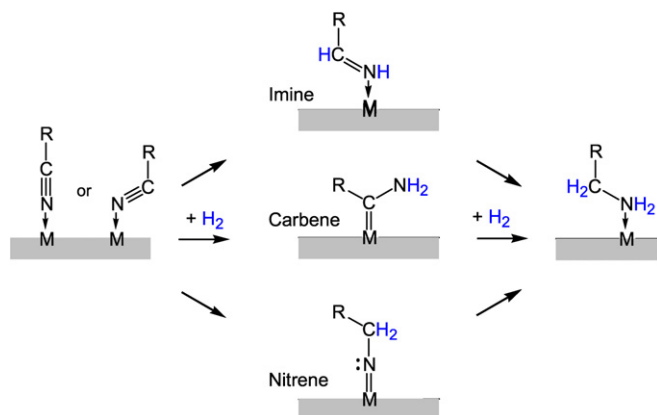
Fig. 12. Surface reactions suggested for the hydrogenation of nitriles.

C_2–NH_2 and C_4–NH_2. Similar results were obtained for the reactions of the respective nitriles in the presence of amine. In both cases, the highest rate was observed for the unsymmetric dialkylimine, which is the result of the formal condensation of C_1–HC=NH with C_4–NH_2 and of C_3–HC=NH with C_2–NH_2. However, the rate in the case of the reaction with C_4–NH_2 was almost twice as high as with C_2–NH_2. Thus, the nature of the amine seems to play an important role. In this respect, Volf and Pasek [4] related nitriles with varying chain length with the Tafts constant σ^*, which is a measure for the inductive effect of the alkyl chain on the N-atom. They found in nitrile hydrogenation that the selectivity to the primary amine decreased with increasing chain length. In consequence of the increasing inductive effect, C_4–NH_2 ($\sigma^* = -0.130$) would attack the electrophilic C-atom in C_1–HC=NH more readily than C_2–NH_2 ($\sigma^* = -0.100$). Similar argumentation holds for the carbene route.
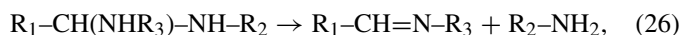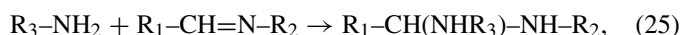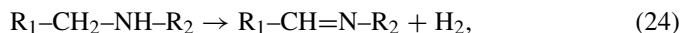
In the hydrogenation of the single nitriles in the presence of an amine (C_4–NH_2 and C_2–NH_2), only the product of amine disproportionation (C_3–HC=N–C_4 and C_1–HC=N–C_2, respectively) and the respective unsymmetric dialkylimine (C_1–HC=N–C_4 and C_3–HC=N–C_2, respectively) were observed as primary by-products. This is in marked contrast to the co-hydrogenation of C_1–C≡N and C_3–C≡N. It is speculated that the amine added to the reaction mixture blocks sites, on which the reaction leading to dialkylimines occurs.

From the results described, the different routes shown in Fig. 12 cannot be clearly discriminated. Nucleophilic attack of the nitrogen electron lone pair seems to be an important factor. In principle, it can occur at the C-atom of the carbene or the imine, which—after proton transfer—provides 1-amino-dialkylamine. Elimination of ammonia yields the dialkylimine. Direct hydrogenolysis of the 1-amino-dialkylamine (Eq. (5)) can be excluded due to the appearance of dialkylimines in the bulk liquid phase. With the nitrene route, an attack of the electron lone pair of the nitrene N-atom at the α-C-atom of an amine adsorbed in vicinity appears possible. The nucleophilic substitution at the saturated α-carbon is followed by subsequent proton transfer from the dialkylamide to the surface NH_2 group providing the dialkylimine.

The higher rate for the reaction of C_4–NH_2 compared to C_2–NH_2 is consistent with a higher reactivity during the nucleophilic attack (carbene and imine route). Considering the nitrene route, stronger adsorption of C_4–NH_2 than C_2–NH_2 might lead to more positive polarization of the α-C-atom facilitating alkyl group transfer to the nitrene. However, this route to dialkylimine appears less likely.

4.5. Mechanistic aspects of dialkylimine hydrogenation

In the second step of the formation of secondary amines, the dialkylimines are hydrogenated to dialkylamines. Unexpectedly, this rather straightforward reaction is accompanied by considerable exchange of alkyl groups. In all reactions, in which alkyl group exchange was observed, the number of C_2 groups increased and the number of C_4 groups decreased in the dialkylamines relative to the dialkylimines. The results strongly suggest that C_2–NH_2 is the source of the C_2 groups. Sivasankar and Prins [10] proposed that the reaction of a monoalkylamine and a dialkylamine can take place in the following steps:

$$R_1\text{–}CH_2\text{–}NH\text{–}R_2 \rightarrow R_1\text{–}CH=N\text{–}R_2 + H_2, \tag{24}$$

$$R_3\text{–}NH_2 + R_1\text{–}CH=N\text{–}R_2 \rightarrow R_1\text{–}CH(NHR_3)\text{–}NH\text{–}R_2, \tag{25}$$

$$R_1\text{–}CH(NHR_3)\text{–}NH\text{–}R_2 \rightarrow R_1\text{–}CH=N\text{–}R_3 + R_2\text{–}NH_2, \tag{26}$$

$$R_1\text{–}CH=N\text{–}R_3 + H_2 \rightarrow R_1\text{–}CH_2\text{–}NH\text{–}R_3. \tag{27}$$

The overall exchange reaction starting from a monoalkylamine and a dialkylamine provides another alkylamine and dialkylamine,

$$R_3\text{–}NH_2 + R_1\text{–}CH_2\text{–}NH\text{–}R_2 \rightarrow R_1\text{–}CH_2\text{–}NH\text{–}R_3 + R_2\text{–}NH_2. \tag{28}$$
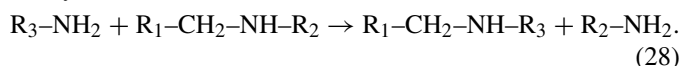
Starting with a dialkylimine, Eqs. (25)–(27) can explain the reaction sequence observed in this study (compare, e.g., Eq. (16)). The 1-alkylamino-dialkylamine (product in Eq. (25)) may also undergo direct hydrogenolysis to give a dialkylamine and an alkylamine. As mentioned above, it is quite certain that hydrogenation (or hydrogenolysis) and alkyl group transfer take place on the catalyst surface, making re-adsorption of dialkylimine necessary. Hence, the exchange of the alkyl groups can only occur in the final phase of the reaction (see above).

The probability of C_2–NH_2 replacing C_4–NH_2 in the dialkylimines is considerably higher than the other way round. Among the dialkylimines, C_3–CH=N–C_4 was converted to the respective dialkylamine to the lowest extent. It is suggested that the alkyl group transfer takes place on the catalyst surface via the formation of 1-alkylamino-dialkylamine (Fig. 13). To demonstrate the reaction network, the reactions of the dialkylimines with C_2–NH_2 and C_4–NH_2 are shown in Fig. 13. The reaction of dialkylimine and monoalkylamine may occur either with both reactants adsorbed on the surface (Langmuir–Hinshelwood mechanism) or through nucleophilic attack of an amine on the adsorbed imine (Eley–Rideal mechanism). The resulting 1-alkylamino-dialkylamine can either split off C_2–NH_2 or C_4–NH_2 by direct hydrogenolysis or form another dialkylimine, which is further hydrogenated to dialkylamine. It is proposed that the product distribution depends on the relative thermodynamic stability
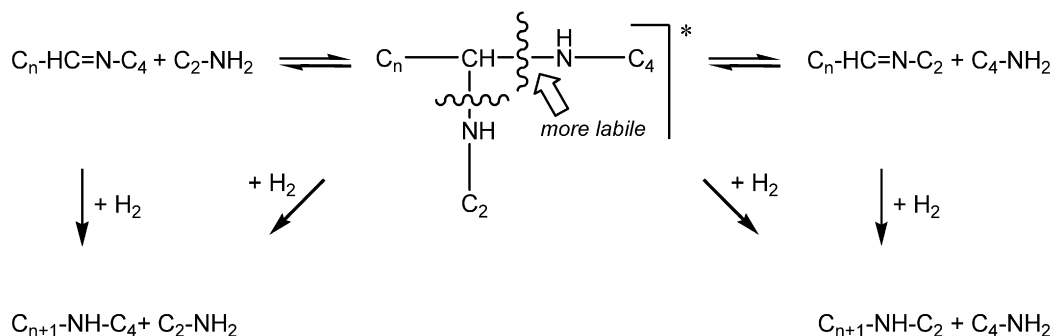
Fig. 13. Alkyl group transfer between a dialkylimine and a monoalkylamine ($n = 1, 3$). * Adsorbed on surface.
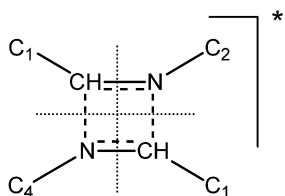

Fig. 14. Cross-transfer of alkyl groups between two dialkylimine molecules. * Adsorbed on surface.

of the dialkylimines formed. As the stabilities follow the order $C_1–CH=N–C_2 > C_1–CH=N–C_4 \approx C_3–CH=N–C_2 > C_3–CH=N–C_4$, the amount of $C_n–CH=N–C_2$ is expected to increase relative to the amount of $C_n–CH=N–C_4$ ($n = 1, 3$).

However, the reactions shown cannot be the only way of alkyl group transfer. For instance, in the reaction of $C_3–C\equiv N$ in the presence of $C_2–NH_2$, the intermediates $C_1–CH=N–C_2$ and $C_1–CH=N–C_4$ only account for 70% of $C_2–NH–C_2$ and $C_2–NH–C_4$ formed. Thus, it is concluded that other reactions occur, which are accountable for the alkyl group transfer. The recently proposed decomposition of dialkylamines and surface-chemisorbed amino and alkyl groups [10] can be excluded in our case, as the mass balance in the liquid phase was closed. Instead, cross-transfer of alkyl groups between two dialkylimines is considered a possible explanation for the change of the distribution of C_2 and C_4 during the reaction of dialkylimines to dialkylamines (Fig. 14). Note that this reaction can only occur on the catalyst surface, as $2 + 2$ cycloadditions are orbital forbidden under thermal conditions.

5. Conclusions

In the co-hydrogenation of the two nitriles, acetonitrile was hydrogenated at a significantly higher rate, which indicates that acetonitrile is more strongly adsorbed on the active sites. The experiments with mixed nitrile and amine reactants suggest that the rate of dialkylimine formation strongly depended on the amine (n-butylamine, ethylamine) participating in the condensation reaction. The reaction of the partially hydrogenated surface intermediate with n-butylamine occurred at a higher rate, which is attributed mostly to the stronger inductive effect of the butyl group and/or stronger adsorption of n-butylamine compared to ethylamine. In the presence of amines in the initial reaction mixture, the rate of hydrogenation remained approxi-

mately the same as in the absence of amines and only a slight decrease in selectivity to the primary amine was observed. This suggests that condensation reactions occurred on different sites than nitrile hydrogenation.

After most of the nitrile has been hydrogenated, the dialkylimines are re-adsorbed, and reduced to the corresponding dialkylamines. During this reaction, the number of C_2 groups increased, while the number of C_4 groups decreased in parallel, which is indicative of alkyl group transfer between monoalkylamines and dialkylimines. The exchange might proceed through a surface bound 1-alkylamino-dialkylamine with subsequent cleavage of the C–N bond. The parallel occurring exchange of C_2 and C_4 groups between different dialkylimines is attributed to a surface bound intermediate formed by $2 + 2$ cycloaddition of two dialkylimines.

In summary, close investigation of the reaction pathways involved during formation and consumption of the dialkylimine intermediates provided insight into the reaction pathways, which lead to the formation of condensation products during the hydrogenation of nitriles. This provides the basis for fine-tuning the catalysts with respect to activity and selectivity.

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