Reactions of mixed dialkyl- and trialkylamines over Pd/γ-Al$_2$O$_3$

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Abstract

The reactions of the dialkylamines dipentylamine and N-methylhexylamine and the trialkylamines trihexylamine and N,N-dihexylmethylamine were studied over Pd/γ-Al$_2$O$_3$ at 300 °C and 3 MPa. Dipentylamine reacted by disproportionation to tripentylamine and pentylamine and by hydrogenolysis to pentylamine and pentane and pentene. Tripentylamine and N,N-dihexylmethylamine reacted by hydrogenolysis to dialkylamines and alkanes and alkenes. N-methylhexylamine reacted by disproportionation to the mixed trialkylamines N,N-dihexylmethylamine and N,N-dimethylhexylamine, as well as by hydrogenolysis to the alkylamines hexylamine and methylamine and the alkanes hexane and methane. The initial rates of formation of the mixed trialkylamines were almost equal. This indicates that not only the hexyl group, but also the methyl group can be transferred between two N-methylhexylamine molecules. In the reaction between dipentylamine and N,N-dihexylmethylamine, more N,N-dipentylmethylamine than N,N-dipentylhexylamine was formed. The comparable rates of transfer of methyl and other alkyl groups prove that enamines are not the only intermediates in the reactions of dialkyl- and trialkylamines.
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1. Introduction

Alkylamines are important industrial products produced from nitriles, aldehydes, and alcohols. Nitriles are industrially hydrogenated over metal catalysts to alkylamines, which are used in intermediate chemicals (e.g., fatty acids to nitriles to amines [1,2], 2-methylglutaronitrile to β-picoline to vitamin B [3]) and in monomers for polymer production (adiponitrile to hexamethylenediamine [2,4]). Metal catalysts are also used in the reductive amination of aldehydes and ketones [5], whereas acid catalysts are used in the production of methylamines from methanol and ammonia [4,6]. Alkylamines also play a role in the removal of nitrogen from heterocyclic molecules that are present in oil. In the industrial hydrotreating process, nitrogen removal occurs by hydrogenation of aromatic nitrogen-containing molecules and removal of the nitrogen atom from the resulting alkylamines in the form of ammonia [7].

In the present work, we address the mechanistic aspects of the reactions between alkylamines occurring over metal cata-

lysts. The basis for the understanding of these reactions was given by von Braun et al. [8], who proposed that in metal-catalyzed liquid-phase hydrogenation, nitriles are sequentially hydrogenated to amines with imines as intermediates,
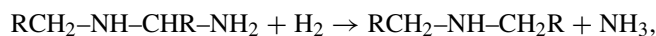
$$R–C\equiv N \rightarrow RCH=NH \rightarrow RCH_2NH_2.$$

The resulting amine can also add to the intermediate imine, forming a 1-aminodialkylamine (a geminal diamine) [8],

$$RCH_2NH_2 + RCH=NH \rightarrow RCH_2–NH–CHR–NH_2,$$
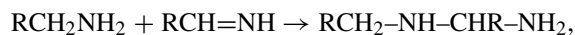
which can react to a dialkylamine and ammonia by ammonia elimination followed by hydrogenation,

$$RCH_2–NH–CHR–NH_2 \rightarrow RCH_2–N=CHR + NH_3,$$

$$RCH_2–N=CHR + H_2 \rightarrow RCH_2–NH–CH_2R.$$
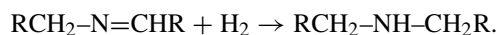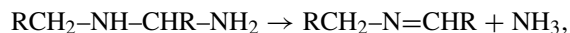
Other authors have proposed that direct hydrogenolysis,

$$RCH_2–NH–CHR–NH_2 + H_2 \rightarrow RCH_2–NH–CH_2R + NH_3,$$

is responsible for the formation of the dialkylamine from the 1-aminodialkylamine [9,10]. Kemball and Moss proposed a different mechanism without imine and 1-aminodialkylamino (gem diamine) intermediates. They explained the formation of

dimethylamine from methylamine on metal films by C–N bond scission of methylamine and reaction of the methyl group with adsorbed methylamine [11]. However, Anderson and Clark [12] showed with labeled methylamine that the disproportionation reaction is a bimolecular surface reaction between two adsorbed amine residues. One of these residues is generally assumed to be imine-like, validating the ideas of von Braun et al. [8]. These ideas have been verified in various studies [10,13,14].

The formation of trialkylamines from dialkylamines during the hydrogenation of nitriles and during reactions of alkylamines in general has been explained similarly as the formation of dialkylamines from alkylamines. First, dialkylamines are formed; these react with an imine to a 1-aminotrialkylamine,

$$(R^1CH_2)_2NH + R-CH=NH \rightarrow (R^1CH_2)_2N-CHR-NH_2.$$
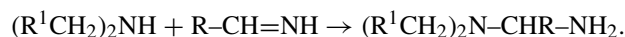
The 1-aminotrialkylamine cannot undergo ammonia elimination to an imine, because no hydrogen atom is available on the central N atom of a trialkylamine, whereas it is present in monoalkyl- and dialkylamines. However, an enamine can be formed from a trialkylamine if a β-H atom is available,

$$(R^1CH_2)_2N-CH(CH_2R)NH_2$$
$$\rightarrow (R^1CH_2)_2N-CH=CHR + NH_3.$$
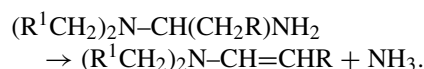
Hydrogenation of the enamine then gives the trialkylamine. Enamines are well-known intermediates in organic chemistry and have been proposed as intermediates in the reductive amination of aldehydes and ketones by dialkylamines to trialkylamines [10],

$$RCH_2CHO + R^1_2NH \rightarrow RCH_2CH(OH)NR^1_2$$
$$\rightarrow RCH=CHNR^1_2 \rightarrow RCH_2CH_2NR^1_2.$$
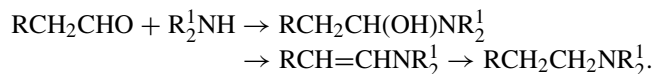
No tribenzylamine is formed in the hydrogenation of benzonitrile, and no diethylbenzylamine is formed in the hydrogenation of a mixture of benzonitrile and diethylamine [15]; however, diethylbutylamine is formed in the hydrogenation of a mixture of butyronitrile and diethylamine [14]. Volf and Pasek took these findings as proof that the formation of trialkylamines occurs by enamine intermediates, not by hydrogenolysis [14]. However, Gomez et al. found a small amount of tribenzylamine in the hydrogenation of benzonitrile [10], which means that hydrogenolysis plays some role in tribenzylamine formation.

To elucidate the mechanism of the reactions of alkylamines, we studied the reactions between C_5-NH-C_5 (dipentylamine) and C_1-NH-C_6 (*N*-methylhexylamine), between C_5-NH-C_5 and $C_1-N(C_6)_2$ (*N,N*-dihexylmethylamine), and between C_5-NH_2 (pentylamine) and C_1-NH-C_6. If 1-aminotrialkylamines can react to a trialkylamine only through an enamine intermediate, then the transfer of methyl groups between alkylamines is not possible. But if the alkylamine group can be removed by hydrogenolysis, then the formation of a dialkylmethylamine is also possible.

2. Experimental

Pd/γ-Al$_2$O$_3$ was prepared by the incipient wetness impregnation method [16]. Before impregnation, the γ-Al$_2$O$_3$ support (Condea pellets, milled and sieved to 35–60 mesh [400–250 µm

particle size], BET surface area of 223 m^2/g, and total pore volume of 0.6 mL/g) was dried in air at 120 °C for 4 h and calcined at 500 °C for 4 h. After the support was impregnated with a 5% aqueous solution of Pd(NH$_3$)$_4$(NO$_3$)$_2$, the catalyst was dried in air at room temperature for 3 h and then at 120 °C for 4 h, and was finally calcined at 500 °C for 4 h (at a heating rate of 5 °C/min). The Pd loading of the Pd/γ-Al$_2$O$_3$ catalyst was 5%, as determined by atomic absorption spectroscopy as well as by the inductively coupled plasma technique. An 0.05-g catalyst sample was mixed with 8 g of SiC and reduced in situ at 300 °C in flowing hydrogen (50 mL/min) at 0.5 MPa for 2 h before the reaction in a continuous-flow reactor. The reactions of C_1-NH-C_6 and $C_1-N(C_6)_2$, as well as the simultaneous reactions of C_5-NH-C_5 and $(C_6)_3N$ (trihexylamine), C_5-NH-C_5 and $C_1-N(C_6)_2$, and C_5-NH_2 and C_1-NH-C_6, were investigated at 300 °C and 3 MPa. The initial pressure of each amine was 5 kPa in all cases. The partial pressures of octane (solvent) and heptane (internal standard for gas chromatography [GC] analysis) were maintained at 185 and 20 kPa, respectively, with a hydrogen pressure of 2.79 MPa. In a typical experiment at 3 MPa, a 0.1 mL/min flow of the feed (C_1-NH-C_6 + heptane + octane) and 190 mL/min of H$_2$ through the reactor corresponds to a weight time of 5.5 g min/mol.

The reaction products were analyzed by off-line GC with a Varian 3800GC instrument containing a CP-Sil 8CB capillary column (50 m × 0.25 mm × 0.25 µm) and equipped with a flame ionization detector and a pulsed flame photometric detector. Gas chromatography–mass spectrometry (GC-MS) was also used for the identification of the reaction products using an Agilent GC-MS instrument with an HP-5MS capillary column (30 m × 0.25 mm × 0.25 µm) [17]. All products could be identified and quantified with the exception of CH$_3$NH$_2$ and CH$_4$. These C$_1$ products could not be quantified because it was not possible to close the mass balance between the off-line analysis results of the liquid samples of the amines and C$_5$ and C$_6$ hydrocarbons and the on-line gas analysis results of the C$_1$ products. After each series of experiments, the initial feed was re-entered to verify that the activity of the catalyst had remained constant. Before the initiation of a new experiment, the entire reactor was cleaned by purging with only the solvent (octane) and H$_2$ gas for 12 h at the reaction temperature. The samples were tested by GC-MS to ensure the absence of impurities in the reactor.

The conversion was determined from the remaining amount of reactant. Similar to Zhao et al. [17–19], we used the selectivities instead of the yields of the products in the reaction of the alkylamines as a function of weight or contact time, because using the selectivities makes it easier to distinguish between primary and secondary products. Even though the yields of the products were low at the initial weight time, and thus the uncertainty of the selectivities is quite high, distinguishing between an increase and a decrease in selectivity with time is easy. Although only the amines and C$_5$ and C$_6$ hydrocarbon products could be quantified, we were able to complete the mass balance of all reactions based on the C$_5$ or C$_6$ groups. Therefore, the selectivity S_i of a product P_i was defined as the number of molecules converted to that product divided by the number of all product molecules, multiplied by the number of carbon atoms

(N_i) in the C_5 or C_6 groups: $S_i(\%) = 100 N_i P_i / (\sum N_i P_i)$, in which the summation is over all product molecules "i" with C_5 or C_6 groups. With this definition, the mass balance of the carbon atoms is preserved. For instance, the C_6 selectivity of C_6–N(C_5)$_2$ is 33.3% in the reaction

$$C_5\text{–NH–}C_5 + (C_6)_3N \rightarrow C_6\text{–N}(C_5)_2 + C_6\text{–NH–}C_6,$$
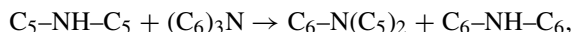
whereas the C_5 selectivity of C_6–N(C_5)$_2$ (N,N-dipentylhexyl-amine) is 100%.

3. Results

### 3.1. Simultaneous reaction of C_5–NH–C_5 and $(C_6)_3N$

To investigate whether not only longer alkyl groups, but also a methyl group, can be exchanged between alkylamine molecules, we studied the reaction of the mixed dialkylamine C_1–NH–C_6 and the reaction of a mixture of C_5–NH–C_5 and the mixed trialkylamine C_1–N(C_6)$_2$. Before presenting the results, we first present the results of the reactions of C_5–NH–C_5 and $(C_6)_3N$. Because each of these two amines has only one type of alkyl group, the analysis of the products and the elucidation of the reaction mechanisms was much more simple. Furthermore, for these molecules, a complete mass balance of the C_5 and C_6 groups could be performed.

The conversion of C_5–NH–C_5 in the simultaneous reaction of an equimolar mixture of 5 kPa C_5–NH–C_5 and 5 kPa $(C_6)_3N$ at 300 °C and 3 MPa was 27% at $\tau = 6$ g min/mol (Fig. 1), compared with 60% for $(C_6)_3N$ (Fig. 2). The reaction products were $(C_5)_3N$ (tripentylamine), C_5–NH$_2$, C_5 (pentane), $C_5^=$ (pentene), C_6–N(C_5)$_2$, C_5–NH–C_6 (N-pentylhexylamine), C_5–N(C_6)$_2$ (N,N-dihexylpentylamine), C_6–NH–C_6 (dihexyl-amine), C_6 (hexane), $C_6^=$ (hexene), and C_6–NH$_2$ (hexylamine). The selectivities of $(C_5)_3N$, C_5–NH$_2$, C_5, $C_5^=$, C_6–NH–C_6, C_6, $C_6^=$, and C_6–N(C_5)$_2$ were unequal to 0 at $\tau = 0$ (Figs. 1 and 2), indicating that these molecules are primary products. The selectivities of C_5, C_6–N(C_5)$_2$, and C_6 increased with increasing τ, indicating that they are secondary products as well. The selectivities of C_5–NH–C_6, C_5–N(C_6)$_2$, and C_6–NH$_2$ extrapolated to 0 at $\tau = 0$ and increased with increasing τ, indicating that these products are of secondary or higher origin.

Most products in the simultaneous reaction of C_5–NH–C_5 and $(C_6)_3N$ were produced by reactions of the pure amines, not by reactions between the two amines. Thus, the primary nature of the products $(C_5)_3N$ and C_5–NH$_2$ derives from the dispro-portionation reaction of two C_5–NH–C_5 molecules,

$$2C_5\text{–NH–}C_5 \rightarrow (C_5)_3N + C_5\text{–NH}_2, \tag{1}$$
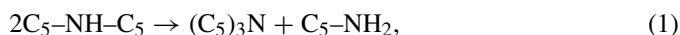
and the primary nature of C_5 and $C_5^=$ derives from dissociative chemisorption of C_5–NH–C_5 to surface-chemisorbed C_5–NH* and C_5^* groups,
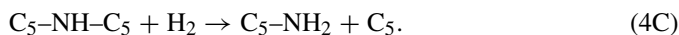
$$C_5\text{–NH–}C_5 \rightarrow C_5\text{–NH}^* + C_5^*. \tag{2}$$
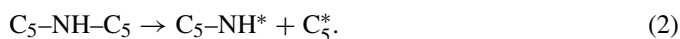
The C_5–NH* group reacted with a hydrogen atom at the metal surface to C_5–NH$_2$,
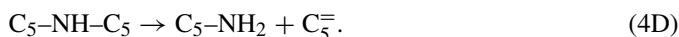
$$C_5\text{–NH}^* + H^* \rightarrow C_5\text{–NH}_2, \tag{3}$$

whereas the pentyl group reacted with a hydrogen atom to pen-tane [Eq. (4A)] or by hydride abstraction to pentene [Eq. (4B)],

$$C_5^* + H^* \rightarrow C_5, \tag{4A}$$

$$C_5^* \rightarrow C_5^= + H^*. \tag{4B}$$

Reactions (2), (3), and (4A), together with dissociative chemi-sorption of H_2, led to the hydrogenolysis reaction,

$$C_5\text{–NH–}C_5 + H_2 \rightarrow C_5\text{–NH}_2 + C_5. \tag{4C}$$

Reactions (2), (3), and (4B) led to the elimination reaction,

$$C_5\text{–NH–}C_5 \rightarrow C_5\text{–NH}_2 + C_5^=. \tag{4D}$$

Pentane can form by both hydrogenolysis and hydrogena-tion of pentene. Because noble metals are good hydrogenation catalysts, the formation of pentane from pentene occurs very rapidly. This explains the decreased pentene selectivity and in-creased pentane selectivity with increasing weight time (Fig. 1). Extrapolating the $(C_5)_3N$ and $C_5 + C_5^=$ selectivities to $\tau = 0$, we estimate that the initial rate of formation of $(C_5)_3N$ [Eq. (1)] was about 50% faster than the rate of dissociative chemisorp-tion [Eq. (2)].

Most C_6-containing products were formed by dissocia-tive chemisorption of $(C_6)_3N$, giving surface-chemisorbed $(C_6)_2$–N* and C_6^* groups,

$$(C_6)_3N \rightarrow (C_6)_2N^* + C_6^*. \tag{5A}$$

These groups led to the primary product C_6–NH–C_6 by hydro-genation of the $(C_6)_2$–N* group, to C_6 by hydrogenation of the C_6^* group, and to $C_6^=$ by hydride abstraction of the C_6^* group, similar to Eqs. (3), (4A), and (4B), respectively, but with C_6 instead of C_5 groups. The overall reactions were
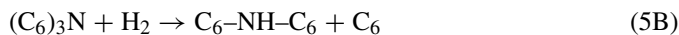
$$(C_6)_3N + H_2 \rightarrow C_6\text{–NH–}C_6 + C_6 \tag{5B}$$

and

$$(C_6)_3N \rightarrow C_6\text{–NH–}C_6 + C_6^=. \tag{5C}$$

The decreased hexene selectivity and increased hexane se-lectivity with increasing weight time (Fig. 2) are due to the hydrogenation of hexene to hexane. The hydrogenolysis rate of $(C_6)_3N$ [Eq. (5B)] was much higher than that of C_5–NH–C_5 [Eq. (4C)], although the initial concentrations of the two reac-tants were equal. This may be caused by a stronger adsorption of $(C_6)_3N$ compared with that of C_5–NH–C_5 (due to the greater number of alkyl chains and longer chain length in the former) and/or by a faster intrinsic reaction rate of the tertiary amine compared with the secondary amine.

C_6–N(C_5)$_2$ was the only primary product formed by reaction of both amine reactants,

$$C_5\text{–NH–}C_5 + (C_6)_3N \rightarrow C_6\text{–N}(C_5)_2 + C_6\text{–NH–}C_6. \tag{6}$$
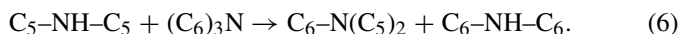
The initial reaction rate of Eq. (6) was about 7 times lower than that of Eq. (1) and 70 times lower than the formation of C_6–NH–C_6 from $(C_6)_3N$ [of which Eq. (5A) is the first step]. This might mean that both amine reactants adsorbed mainly in separate domains on the catalyst surface, so that in one domain only reactions between C_5–NH–C_5 molecules occurred and in the other domain only reactions between $(C_6)_3N$ molecules oc-curred.
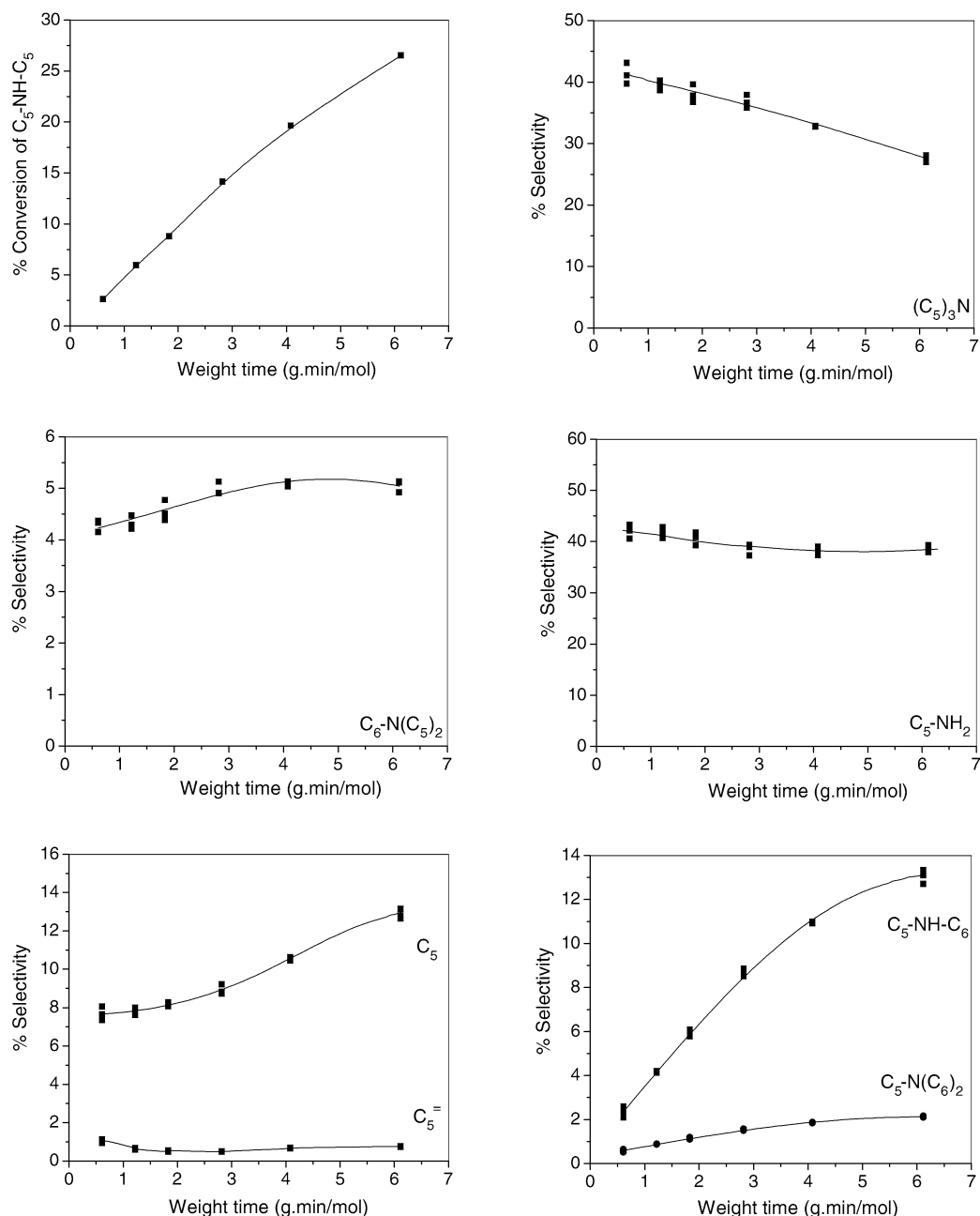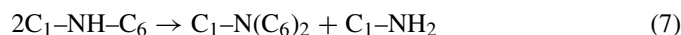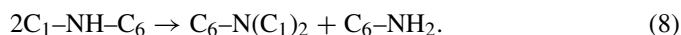
Fig. 1. Conversion of C_5–NH–C_5 and product selectivities (based on the C_5 mass balance) in the simultaneous reaction of C_5–NH–C_5 and $(C_6)_3$N.

3.2. Reaction of C_1–NH–C_6

We studied C_1–NH–C_6 to see whether not only the hexyl group, but also the methyl group, can be exchanged in the disproportionation reaction. The conversion of 5 kPa C_1–NH–C_6 at 300 °C and 3 MPa was 65% at $\tau = 6$ g min/mol (Fig. 3). The products were C_1–N(C_6)$_2$, C_6–N(C_1)$_2$ (N,N-dimethylhexylamine), $(C_6)_3$N, C_6–NH–C_6, C_6–NH$_2$, hexenes, hexane, and C_1 products. The selectivities of C_1–N(C_6)$_2$, C_6–N(C_1)$_2$, and C_6–NH$_2$ increased continuously with decreasing weight time, indicating that these molecules are primary products. This can be explained by the two possible disproportionations of C_1–NH–C_6,

$$2C_1\text{–NH–}C_6 \rightarrow C_1\text{–N}(C_6)_2 + C_1\text{–NH}_2 \tag{7}$$

and

$$2C_1\text{–NH–}C_6 \rightarrow C_6\text{–N}(C_1)_2 + C_6\text{–NH}_2. \tag{8}$$

These reactions are equivalent to reaction (1). Extrapolation of the selectivities of C_1–N(C_6)$_2$ and C_6–N(C_1)$_2$ to $\tau = 0$ shows that the initial selectivity of C_1–N(C_6)$_2$ was 2.5 times higher than that of C_6–N(C_1)$_2$ (Fig. 3). Taking into account that the selectivities in Fig. 3 are based on the C_6 mass of the products, the initial rate of reaction (8) was about 20% less than that of reaction (7). In other words, the probability of transferring the C_1 group from one C_1–NH–C_6 molecule to another is only slightly smaller than that of transferring the C_6 group. The decreased selectivity of the mixed trialkylamines with increasing τ is due
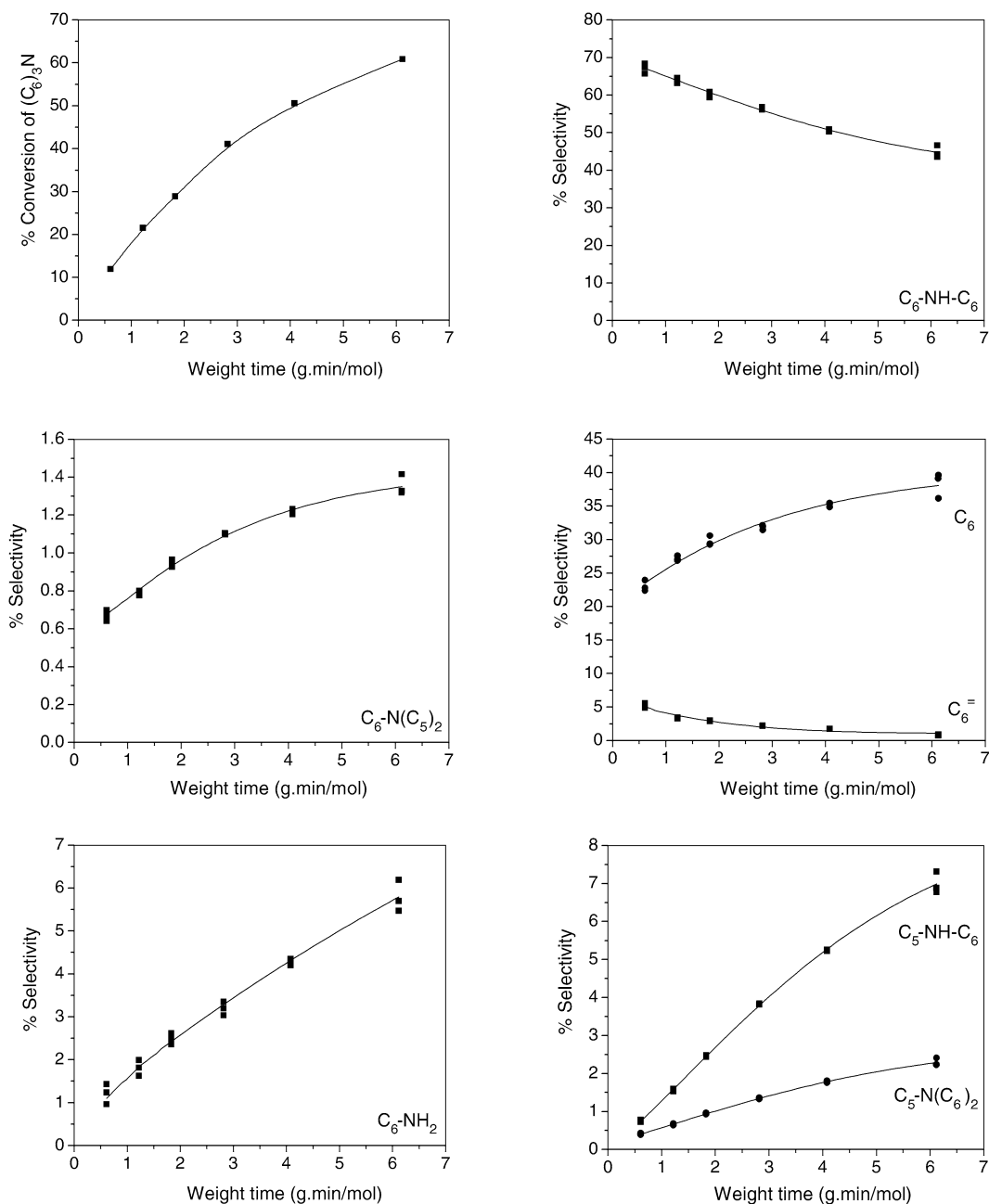
Fig. 2. Conversion of $(C_6)_3N$ and product selectivities (based on the C_6 mass balance) in the simultaneous reaction of $C_5–NH–C_5$ and $(C_6)_3N$.

to the dissociation reactions of $C_1–N(C_6)_2$ and $C_6–N(C_1)_2$, as discussed in Section 3.3.

The nonzero selectivities of hexane and hexene at $\tau = 0$ indicate that these molecules are of a primary nature. However, the selectivity of hexane increased with weight time, indicating that hexane is also formed as a secondary product. Hexane and hexene are primary products formed by dissociative chemisorption of $C_1–NH–C_6$ [Eq. (9A)], followed by hydrogenation or hydride abstraction of the hexyl group, similar to Eqs. (4A) and (4B),

$$C_1–NH–C_6 \rightarrow C_1–NH^* + C_6^*. \tag{9A}$$
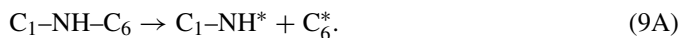
Hexane selectivity increased strongly with τ, indicating that hexane is produced in a secondary reaction as well. This

can occur by hydrogenation of hexene and by dissociation of $C_1–N(C_6)_2$ and $C_6–N(C_1)_2$ (Section 3.3). In addition to the dissociative chemisorption [Eq. (9A)], hydrogenolysis to $C_6–NH_2$ and methane is possible, initiated by the following dissociation:

$$C_1–NH–C_6 \rightarrow C_6–NH^* + C_1^*. \tag{9B}$$
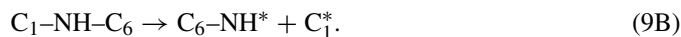
However, we could not study this reaction quantitatively, because although methane was detected, it could not be quantified.

3.3. Reaction of $C_1–N(C_6)_2$

To better understand the reactions of $C_1–N(C_6)_2$ in a mixture of $C_5–NH–C_5$ and $C_1–N(C_6)_2$ (Section 3.4) and the secondary reactions of $C_1–NH–C_6$ that we encountered in Section 3.2,
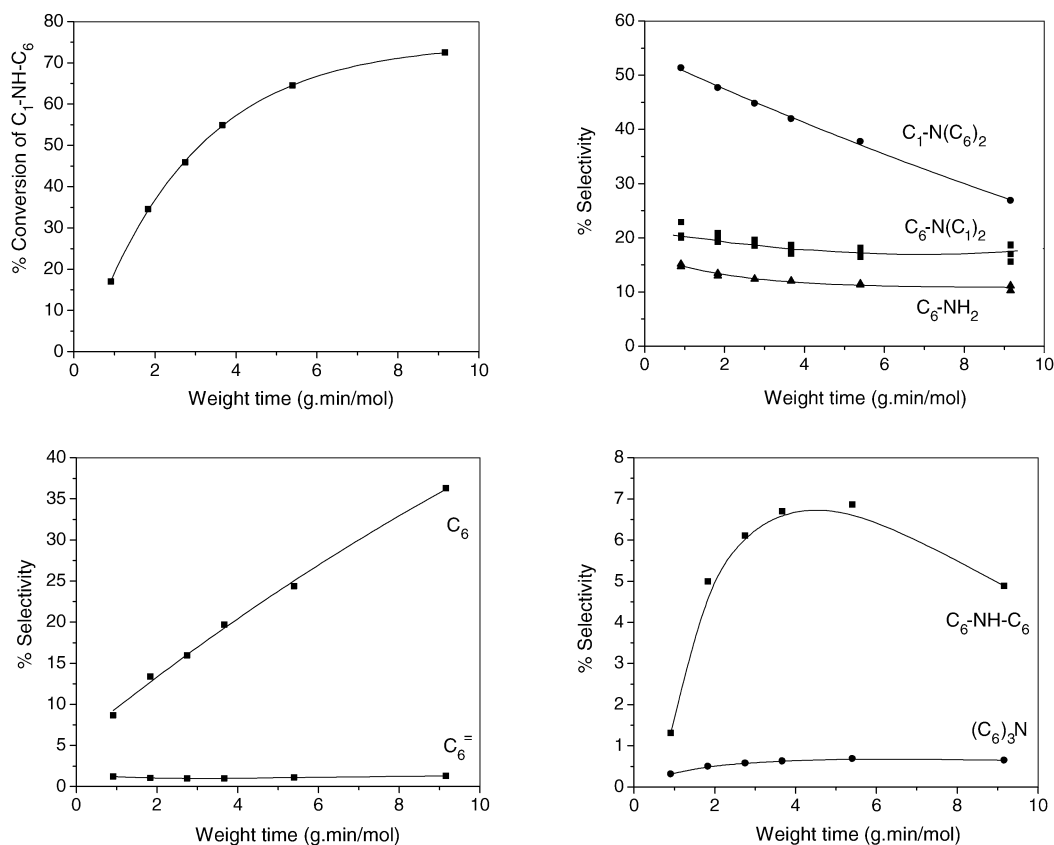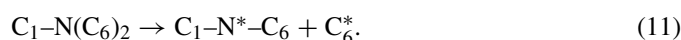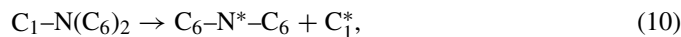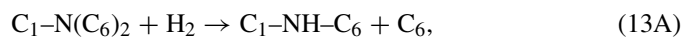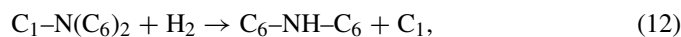
Fig. 3. Conversion and product selectivities (based on the C_6 mass balance) in the reaction of C_1–NH–C_6.
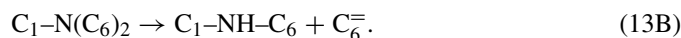
we studied the reactions of pure C_1–N(C_6)$_2$. The conversion of 5 kPa C_1–N(C_6)$_2$ at 300 °C and 3 MPa was 48% at $\tau = 6$ g min/mol (Fig. 4). The reaction products were C_1–NH–C_6, C_6–NH–C_6, C_6–N(C_1)$_2$, (C_6)$_3$N, C_6–NH$_2$, hexenes, hexane, and C_1 products. The selectivities of C_1–NH–C_6, C_6–NH–C_6, hexane, and hexenes extrapolated to nonzero values at $\tau = 0$, indicating that these molecules are primary products. These molecules could be formed by direct dissociative chemisorption of a C–N bond of C_1–N(C_6)$_2$ on the Pd catalyst surface,

$$C_1\text{–N}(C_6)_2 \rightarrow C_6\text{–N*–}C_6 + C_1^*, \tag{10}$$

$$C_1\text{–N}(C_6)_2 \rightarrow C_1\text{–N*–}C_6 + C_6^*. \tag{11}$$

These reactions are equivalent to reaction (5) for the trialkylamine (C_6)$_3$N with three uniform alkyl groups. The resulting chemisorbed dialkylamine groups are hydrogenated to dialkylamines. The methyl group reacts to CH$_4$, and the hexyl group can react by hydrogenation to hexane as well as by elimination to hexene [cf. Eqs. (4A) and (4B)]. This leads to the overall reactions

$$C_1\text{–N}(C_6)_2 + H_2 \rightarrow C_6\text{–NH–}C_6 + C_1, \tag{12}$$

$$C_1\text{–N}(C_6)_2 + H_2 \rightarrow C_1\text{–NH–}C_6 + C_6, \tag{13A}$$

and

$$C_1\text{–N}(C_6)_2 \rightarrow C_1\text{–NH–}C_6 + C_6^=. \tag{13B}$$

Extrapolation of the selectivities of C_1–NH–C_6 and C_6–NH–C_6 indicates that the initial rate of Eq. (12) is about 12 times slower

than the sum of the rates of Eqs. (13A) and (13B). (Note that the selectivities in Fig. 4 are based on the C_6 mass of the products.) In view of the twofold-greater abundance of the C_6 group in C_1–N(C_6)$_2$, this means that scission of the N–C_6 bond occurs about six times faster than that of the N–C_1 bond. In the trialkylamine C_1–N(C_6)$_2$, the C_1–N bond may be stronger than the C_6–N bond, and the C_6–N bond may be more susceptible to hydrogenolysis.

Hexane can form both by dissociation of the reactant molecule, followed by hydrogenation of the hexyl group, and by hydrogenation of the other primary product, hexene. This property explains the decreased hexene selectivity and increased hexane selectivity with increasing τ (Fig. 4).

The conversion of C_1–NH–C_6 (Section 3.2) was greater than that of C_1–N(C_6)$_2$, due to the fact that C_1–NH–C_6 can react not only by dissociation, but also by disproportionation, which trialkylamines cannot do. Sinfelt and co-workers [20,21] reported that alkylamines indeed react very rapidly by hydrogenolysis over noble metal catalysts.

3.4. Simultaneous reaction of C_5–NH–C_5 and C_1–N(C_6)$_2$

The reaction of an equimolar mixture of C_5–NH–C_5 and C_1–N(C_6)$_2$ was studied to see if not only the hexyl group, but also the methyl group, could be exchanged between the two amines. The conversions of 5 kPa C_5–NH–C_5 and 5 kPa C_1–N(C_6)$_2$ in their simultaneous reaction were almost equal—36% (Fig. 5) and 35% (Fig. 6) at $\tau = 6$ g min/mol, respectively.
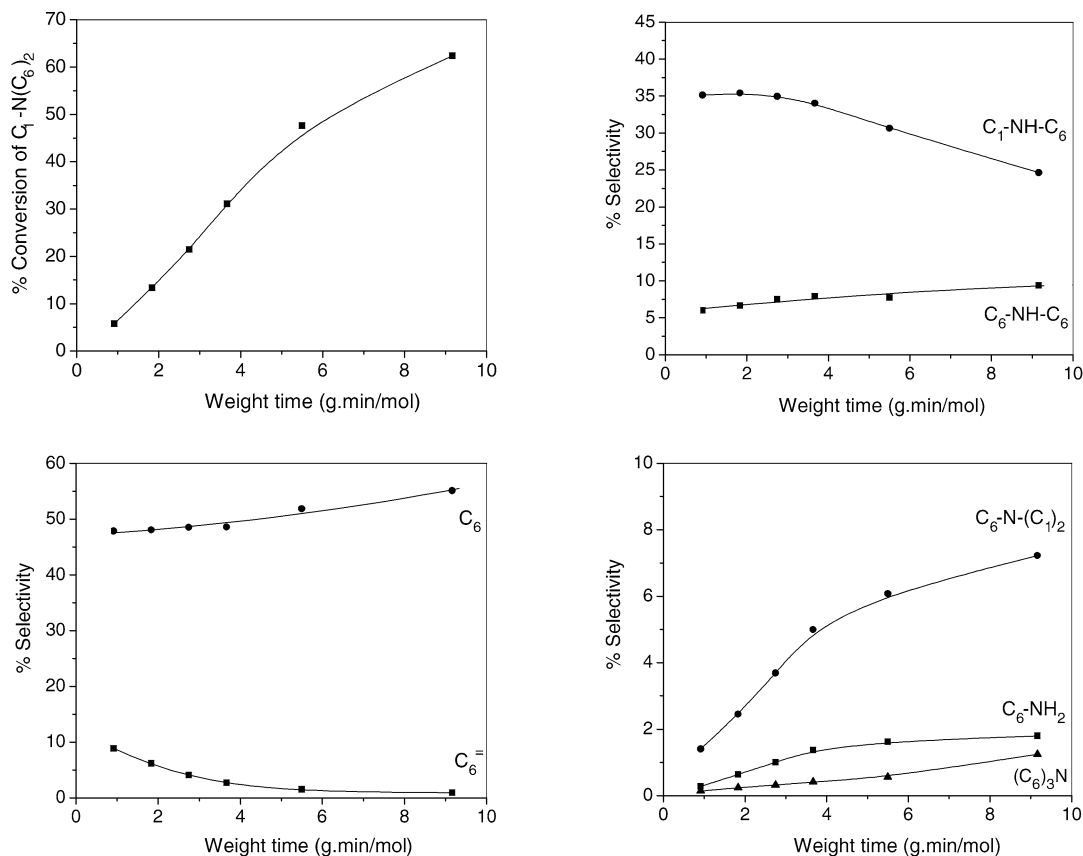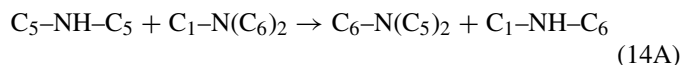
Fig. 4. Conversion and product selectivities (based on the C_6 mass balance) in the reaction of $C_1-N(C_6)_2$.

The conversion of trialkylamine decreased due to the presence of 5 kPa C_5-NH-C_5 (cf. Figs. 4 and 5), which is an indication of negative order. The products of the simultaneous reaction were $C_6-N(C_5)_2$, $(C_5)_3N$, $C_1-N(C_5)_2$ (N,N-dipentylmethylamine), $C_6-N(C_1)_2$, $C_5-N(C_6)_2$, $C_1-N(C_5)C_6$ (N-hexyl-N-pentylmethylamine), $(C_6)_3N$, C_1-NH-C_6, C_6-NH-C_6, C_5-NH-C_6, C_1-NH-C_5 (N-methylpentylamine), C_6-NH_2, C_5-NH_2, hexenes, hexane, pentenes, pentane, and C_1 products. The selectivities of all of the products were calculated based on the C_5 (Fig. 5) and C_6 (Fig. 6) groups separately. The nonzero selectivities for $(C_5)_3N$, $C_1-N(C_5)_2$, $C_6-N(C_5)_2$, C_5-NH_2, C_1-NH-C_6, C_6-NH-C_6, $C_6^=$, C_6, $C_5^=$, and C_5 at $\tau = 0$ means that all of these molecules are primary products. The selectivities of $C_6-N(C_5)_2$, C_5, C_6-NH-C_6, and C_6 increased with increasing weight time, indicating that these are secondary products as well. The selectivities of the trialkylamines $C_5-N(C_6)_2$, $C_1-N(C_5)C_6$, $C_6-N(C_1)_2$, and $(C_6)_3N$; of the dialkylamines C_1-NH-C_5 and C_5-NH-C_6; and of the alkylamine C_6-NH_2 were low and reached zero values at $\tau = 0$, demonstrating that these molecules are secondary in nature.
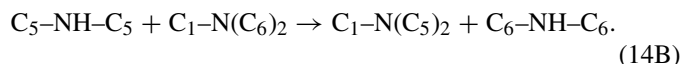
Analogous to the simultaneous reaction of C_5-NH-C_5 and $(C_6)_3N$, most products came from the reactions of the pure amines, not from the cross-reaction between the two amines. $(C_5)_3N$, C_5-NH_2, C_5, and $C_5^=$ were formed as primary products by disproportionation and dissociation of the reactants [Eqs. (1)–(4)]. From the initial selectivities, we estimate the disproportionation reaction to be about two times faster than the dissociation reaction.

$C_1-N(C_6)_2$ reacted by dissociation to C_6-NH-C_6, C_1-NH-C_6, C_6, and $C_6^=$ as primary products [Eqs. (10)–(13)]. Considering the statistical factor of 2 between C_6 and C_1 in $C_1-N(C_6)_2$, the likelihood of removing the C_6 group is about 5 times higher than that of removing the C_1 group. The C_1-N bond of the trialkylamine $C_1-N(C_6)_2$ is most likely stronger than the C_6-N bond, and thus the C_6-N bond is more susceptible to hydrogenolysis. Furthermore, hexane can form from the hydrogenation of hexene in addition to the hydrogenolysis of the reactant molecule [Eq. (13A)].

The trialkylamines $C_6-N(C_5)_2$ and $C_1-N(C_5)_2$ were formed as primary products by cross-disproportionation of the reactants,

$$C_5-NH-C_5 + C_1-N(C_6)_2 \rightarrow C_6-N(C_5)_2 + C_1-NH-C_6 \tag{14A}$$

and

$$C_5-NH-C_5 + C_1-N(C_6)_2 \rightarrow C_1-N(C_5)_2 + C_6-NH-C_6. \tag{14B}$$

Considering the statistical factor of 2 between the C_6 and C_1 groups in $C_1-N(C_6)_2$, C_5-NH-C_5 is 10 times more likely to react with the C_1 group of $C_1-N(C_6)_2$ than with the C_6 group. This may be due to higher steric hindrance of the bulky hexyl group than the methyl group in $C_1-N(C_6)_2$ during interaction with the bulky C_5-NH-C_5.
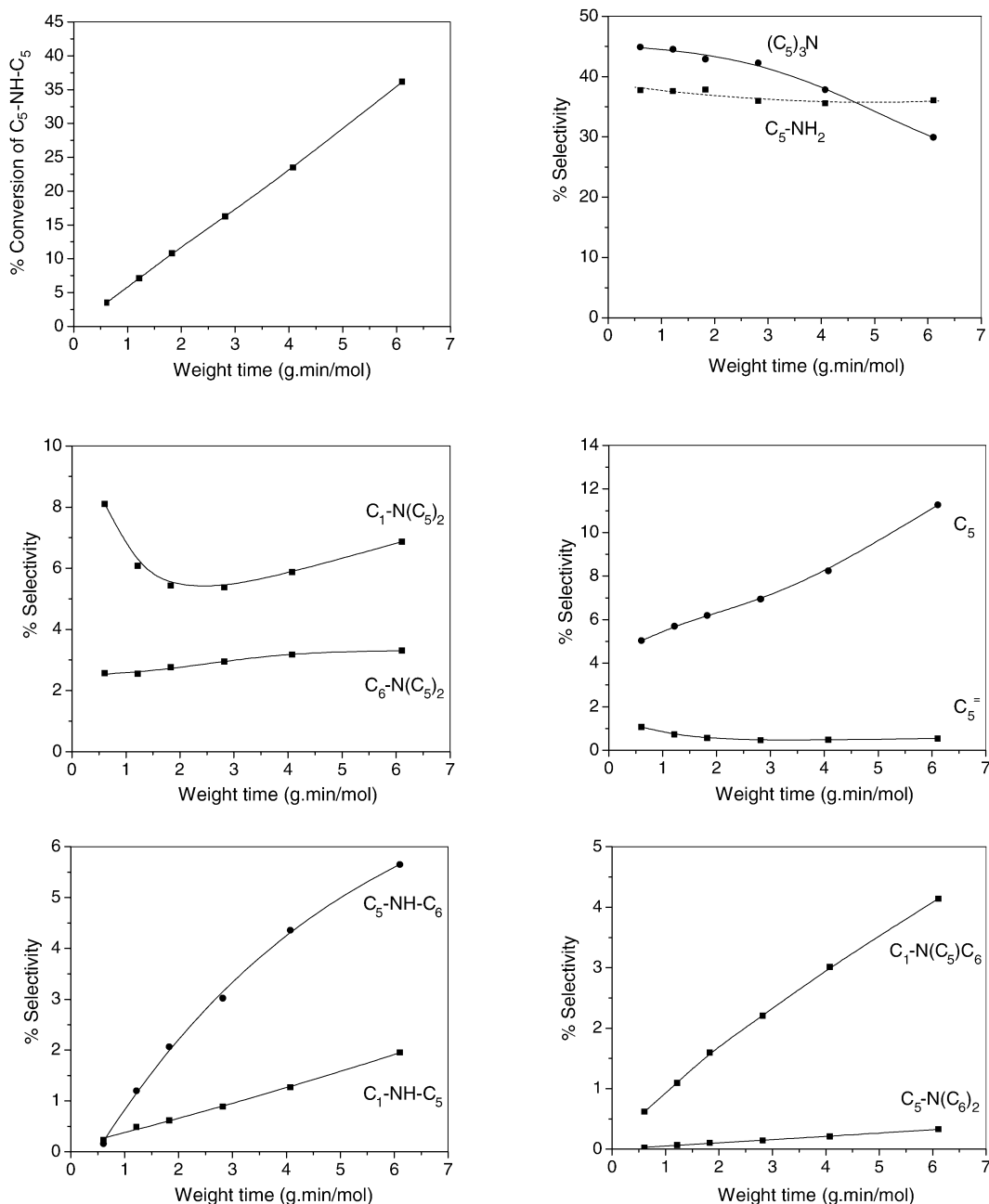
Fig. 5. Conversion of C_5–NH–C_5 and product selectivities (based on the C_5 mass balance) in the simultaneous reaction of C_5–NH–C_5 and C_1–N(C_6)$_2$.

3.5. Simultaneous reaction of C_5–NH$_2$ and C_1–NH–C_6

As discussed in the Introduction, the reaction between a monoalkylamine and a dialkylamine can occur in one of two ways: (1) An exchange reaction to another monoalkylamine and dialkylamine can occur via an imine intermediate, or (2) a disproportionation reaction to a trialkylamine and ammonia can occur via an enamine intermediate. The first reaction should always be possible, because imine intermediates are possible in both mono- and dialkylamines, whereas the second reaction by an enamine intermediate can occur only for alkyl groups with ethyl groups or larger, but not for methyl groups. Consequently, we studied the reaction of 5 kPa C_5–NH$_2$ and 5 kPa C_1–NH–C_6.

The conversion of C_5–NH$_2$ was 42% at $\tau = 6$ g min/mol (Fig. 7). The conversion of C_1–NH–C_6 was reduced from 65% in the absence of C_5–NH$_2$ (Fig. 3) to 47% in the presence of 5 kPa C_5–NH$_2$ (Fig. 8) at $\tau = 6$ g min/mol, indicating negative order. The products of the simultaneous reaction were C_6–N(C_1)$_2$, C_1–N(C_6)$_2$, C_1–N(C_5)C_6, C_6–N(C_5)$_2$, C_5–N(C_6)$_2$, C_1–N(C_5)$_2$, (C_6)$_3$N, (C_5)$_3$N, C_5–NH–C_5, C_6–NH–C_6, C_5–NH–C_6, C_1–NH–C_5, C_6–NH$_2$, hexenes, hexane, pentenes, pentane, and C_1 products (Table 1). As before, the selectivities shown in Figs. 7 and 8 are based on C_5 and C_6 mass balances. C_6–N(C_1)$_2$, C_1–N(C_6)$_2$, C_1–N(C_5)C_6, C_5–NH–C_5, C_5–NH–C_6, C_1–NH–C_5, C_6–NH$_2$, $C_6^=$, C_6, $C_5^=$, and C_5 are primary products, as deduced from their nonzero selectivities at $\tau = 0$. The selectivities of C_6–N(C_5)$_2$, C_5–N(C_6)$_2$,
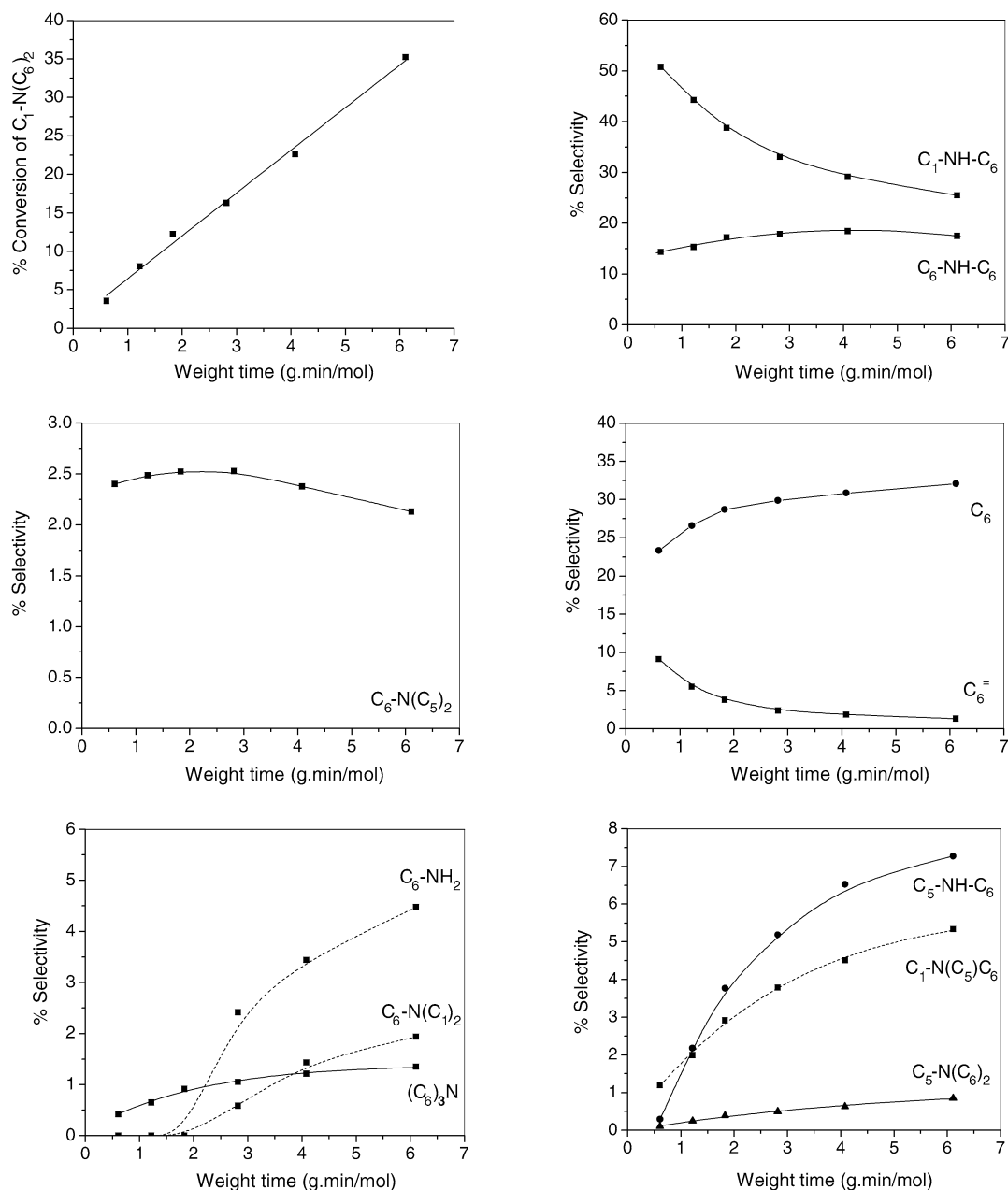
Fig. 6. Conversion of $C_1–N(C_6)_2$ and product selectivities (based on the C_6 mass balance) in the simultaneous reaction of $C_5–NH–C_5$ and $C_1–N(C_6)_2$.

$C_1–N(C_5)_2$, $(C_6)_3N$, $(C_5)_3N$, and $C_6–NH–C_6$ approached zero values at $\tau = 0$, indicating that they are secondary or even tertiary products.

Similar to the simultaneous reactions of $C_5–NH–C_5$ and $(C_6)_3N$ and of $C_5–NH–C_5$ and $C_1–N(C_6)_2$, the major products of the simultaneous reaction of $C_5–NH_2$ and $C_1–NH–C_6$ came from the reaction of the pure amines, not from the cross-reaction between the two amines. Dipentylamine was initially formed by the disproportionation of pentylamine,

$$2C_5–NH_2 \rightarrow C_5–NH–C_5 + NH_3. \qquad (15)$$

In addition to disproportionation, pentylamine reacted by hydrogenolysis to pentane and pentenes as primary products. Similarly, $C_1–NH–C_6$ reacted by disproportionation to $C_1–N(C_6)_2$, $C_6–N(C_1)_2$, and $C_6–NH_2$ as primary products

[Eqs. (7) and (8)]. $C_1–NH–C_6$ can undergo both self-disproportionation and dissociation, yielding hexane and hexenes as primary products [Eq. (9A)]. In addition, dissociation of hexylamine contributes to the secondary formation of hexane and hexenes.

The mixed $C_1–N(C_5)C_6$ amine is a primary product formed by the cross-disproportionation of the two reactant amines with the liberation of ammonia,

$$C_5–NH_2 + C_1–NH–C_6 \rightarrow C_1–N(C_5)C_6 + NH_3. \qquad (16)$$
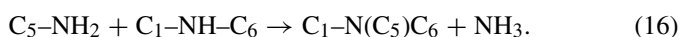
Similarly, the mixed dialkylamines $C_5–NH–C_6$ and $C_1–NH–C_5$ were formed by exchange reactions between the reactants with the formation of a primary amine,
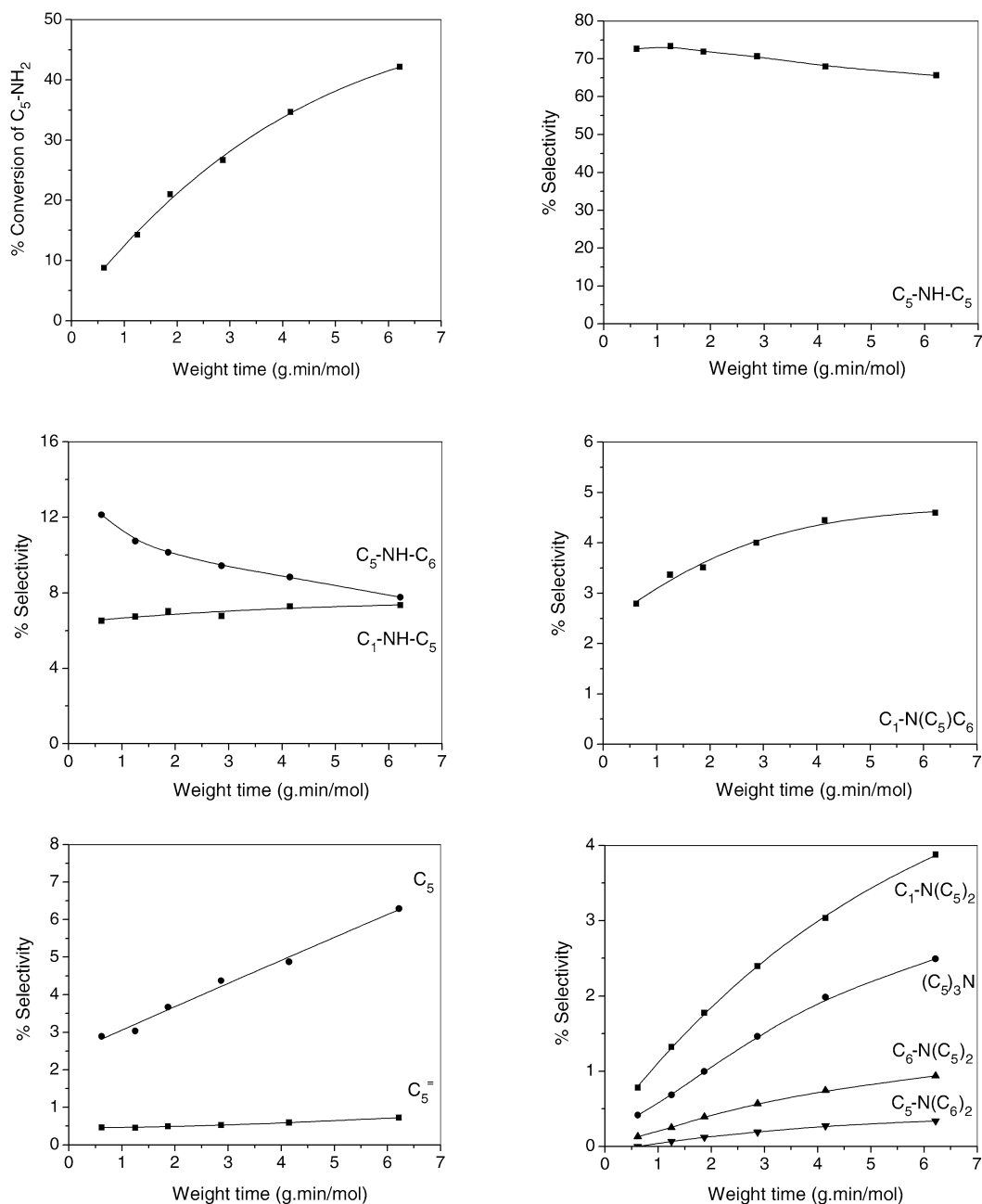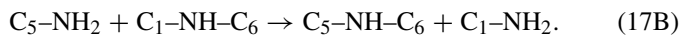
$$C_5–NH_2 + C_1–NH–C_6 \rightarrow C_1–NH–C_5 + C_6–NH_2 \qquad (17A)$$
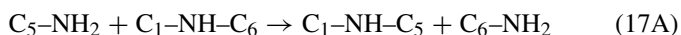
Fig. 7. Conversion of C_5–NH_2 and product selectivities (based on the C_5 mass balance) in the simultaneous reaction of C_5–NH_2 and C_1–NH–C_6.

and

$$C_5\text{–}NH_2 + C_1\text{–}NH\text{–}C_6 \rightarrow C_5\text{–}NH\text{–}C_6 + C_1\text{–}NH_2. \qquad (17B)$$

The three primary products of the reaction of C_5–NH_2 with C_1–NH–C_6 [C_1–$N(C_5)C_6$, C_1–NH–C_5, and C_6–NH–C_5] were formed at a ratio of 2.3:6.5:14.5 (Fig. 7).

3.6. Reaction of N,N,N',N'-tetramethyldiaminomethane

If alkylamines can react only through imine and enamine intermediates, then the 1-aminotrialkylamine (gem diamine) is a crucial intermediate. Only when one of the three alkyl groups contains a β-H atom can an enamine be formed from this gem-diamine intermediate. To verify that indeed a gem diamine

cannot react if it does not contain β-H atoms, we studied the reaction of 5 kPa N,N,N',N'-tetramethyldiaminomethane. This molecule was reacted under the same conditions as the reactions of the alkylamines, at 3 MPa, and complete conversion to trimethylamine, dimethylamine, and a trace of methylamine was already observed at the low temperature of 150 °C. To check whether the support was responsible for this reaction, we also ran the reaction over pure alumina, but observed a small conversion.

4. Discussion

When we assume that only imines and enamines can act as intermediates in the reactions between alkylamines, we can
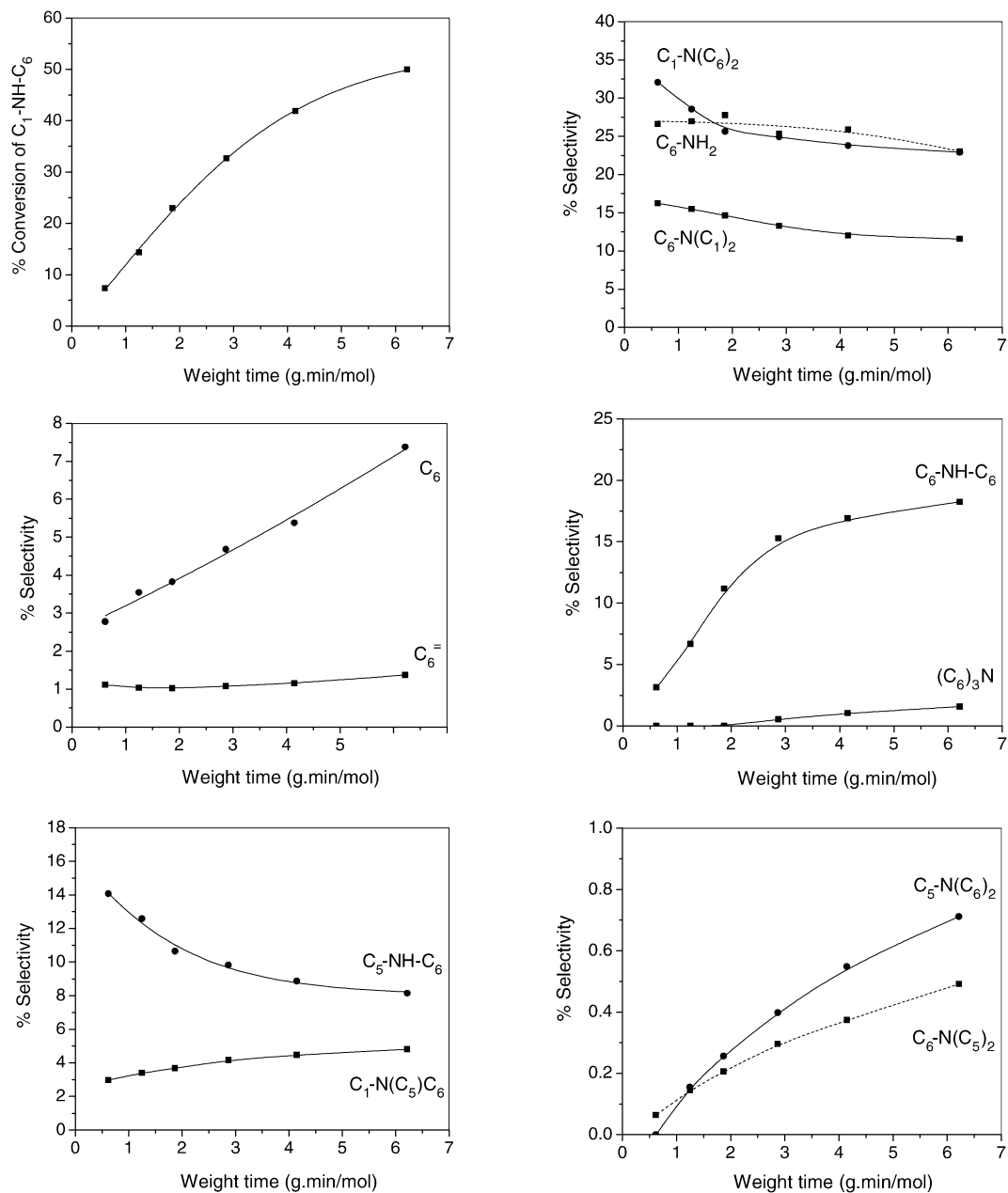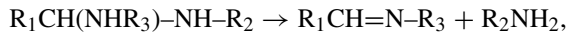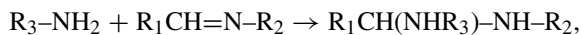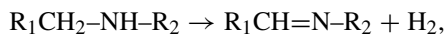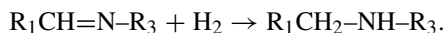
Fig. 8. Conversion of C_1–NH–C_6 and product selectivities (based on the C_6 mass balance) in the simultaneous reaction of C_5–NH$_2$ and C_1–NH–C_6.

predict which alkylamine reactions can occur. Comparing the predictions with the experimental results then allows us to verify the assumption of imine and enamine intermediates. The reaction between a monoalkylamine and a dialkylamine can be considered to take place in the following steps:

$$R_1CH_2–NH–R_2 \rightarrow R_1CH=N–R_2 + H_2,$$

$$R_3–NH_2 + R_1CH=N–R_2 \rightarrow R_1CH(NHR_3)–NH–R_2,$$

$$R_1CH(NHR_3)–NH–R_2 \rightarrow R_1CH=N–R_3 + R_2NH_2,$$

and

$$R_1CH=N–R_3 + H_2 \rightarrow R_1CH_2–NH–R_3.$$

The overall reaction is then an exchange reaction between an alkylamine and a dialkylamine, giving another alkylamine and dialkylamine,

$$R_3–NH_2 + R_1CH_2–NH–R_2 \rightarrow R_1CH_2–NH–R_3 + R_2NH_2. \tag{18}$$
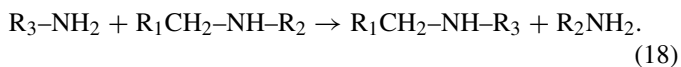
In the analogous reaction between two dialkylamines, a 1-alkylaminotrialkylamine $R_3CH(NR_1R_2)–NH–R_4$ is formed,

$$R_3–NH–R_4 + R_1CH=N–R_2 \rightarrow R_1CH(NR_3R_4)–NH–R_2.$$
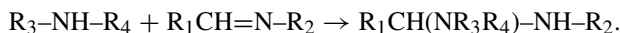
This diamine can undergo elimination only via an enamine; however, in that case a β-H atom must be present,

$$R_1^1CH_2CH(NR_3R_4)–NH–R_2$$
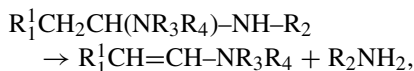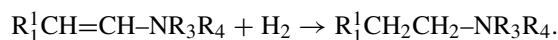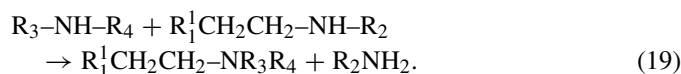$$\rightarrow R_1^1CH=CH–NR_3R_4 + R_2NH_2,$$

Table 1
General classification of the products observed for the reaction of C_5-NH_2, C_1-NH-C_6, as well as the simultaneous reaction of C_5-NH_2 and C_1-NH-C_6 over Pd/Al$_2$O$_3$

Reactant	Primary products	Secondary or tertiary products
C_5-NH_2	C_5-NH-C_5	$(C_5)_3N$
	$C_5^=$, C_5	
C_1-NH-C_6	$C_6-N(C_1)_2$	$(C_6)_3N$
	$C_1-N(C_6)_2$	C_6-NH-C_6
	C_6-NH_2	
	$C_6^=$, C_6	
C_5-NH_2	C_5-NH-C_5	$(C_5)_3N$
+	$C_5^=$, C_5	
C_1-NH-C_6	$C_6-N(C_1)_2$	$(C_6)_3N$
	$C_1-N(C_6)_2$	C_6-NH-C_6
	C_6-NH_2	
	$C_6^=$, C_6	
	$C_1-N(C_5)C_6$	$C_6-N(C_5)_2$
	C_5-NH-C_6	$C_5-N(C_6)_2$
	C_1-NH-C_5	$C_1-N(C_5)_2$

$R_1^|CH=CH-NR_3R_4 + H_2 \rightarrow R_1^|CH_2CH_2-NR_3R_4.$

The overall reaction is a disproportionation reaction,

$$R_3-NH-R_4 + R_1^|CH_2CH_2-NH-R_2$$
$$\rightarrow R_1^|CH_2CH_2-NR_3R_4 + R_2NH_2. \qquad (19)$$
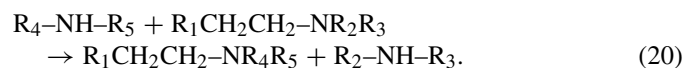
Therefore, exchange of an alkyl group between a dialkylamine and a monoalkylamine under formation of a new dialkylamine is always possible via an imine intermediate [Eq. (18)]. The same holds for the disproportionation reaction of two monoalkylamines to a dialkylamine and ammonia [Eq. (18) with $R_2 = H$]. The disproportionation of two dialkylamines to

a trialkylamine and a monoalkylamine [Eq. (19)] and of a dialkylamine and a monoalkylamine [Eq. (19) with $R_2 = H$] to a trialkylamine and ammonia can occur only if an enamine can be formed as intermediate (Scheme 1). This requires that the R_1 group contains a β-H atom and thus at least two carbon atoms. The same is true for the reaction between a dialkyl- and a trialkylamine,

$$R_1CH_2CH_2-NR_2R_3 \rightarrow R_1CH=CH-NR_2R_3,$$

$$R_4-NH-R_5 + R_1CH=CH-NR_2R_3$$
$$\rightarrow R_1CH_2CH(NR_4R_5)-NR_2R_3,$$

$$R_1CH_2CH(NR_4R_5)-NR_2R_3$$
$$\rightarrow R_1CH=CH-NR_4R_5 + R_2-NH-R_3,$$

$$R_1CH=CH-NR_4R_5 + H_2 \rightarrow R_1CH_2CH_2-NR_4R_5.$$

The overall reaction is

$$R_4-NH-R_5 + R_1CH_2CH_2-NR_2R_3$$
$$\rightarrow R_1CH_2CH_2-NR_4R_5 + R_2-NH-R_3. \qquad (20)$$
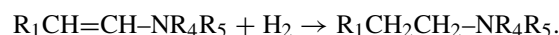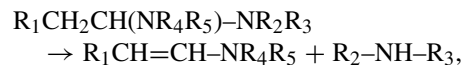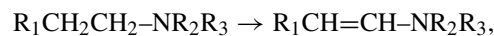
To test whether enamines are important for reactions between alkylamines, we thus should investigate whether the disproportionation reaction between two dialkylamines (Scheme 2) and between a monoalkylamine and a dialkylamine, as well as the exchange reaction of a dialkylamine and a trialkylamine (Scheme 3), occur preferentially via exchange of the alkyl groups with more than one carbon atom. Therefore, we tested the reaction of C_1-NH-C_6 and the reaction of C_5-NH-C_5 with $C_1-N(C_6)_2$. C_1-NH-C_6 reacted by disproportionation to $C_1-N(C_6)_2$ as well as $C_6-N(C_1)_2$, and the likelihood of transferring the C_1 group was only 20% less than that of transferring the C_6 group. In the exchange between C_5-NH-C_5 and $C_1-N(C_6)_2$, the trialkylamines $C_1-N(C_5)_2$ and $C_6-N(C_5)_2$
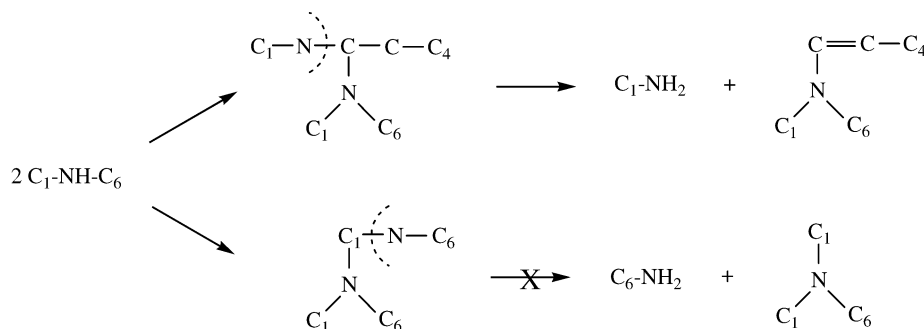
Scheme 1. Formation of a mixed trialkylamine from a dialkylamine via an enamine intermediate.
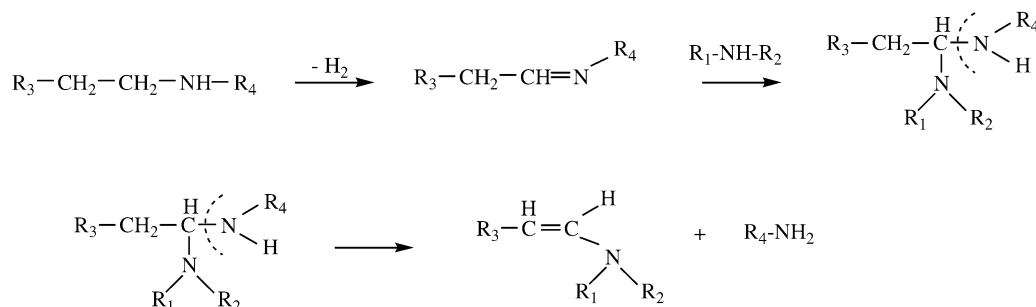
Scheme 2. Transformation of dialkylamines to trialkylamines through an imine intermediate.
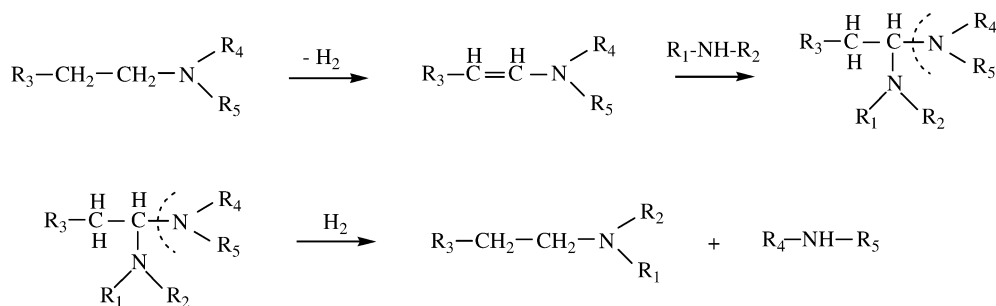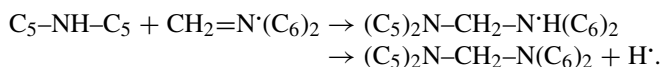
Scheme 3. Disproportionation of a dialkylamine and a trialkylamine via an enamine intermediate.

were both formed. The likelihood of transferring the C_1 group was 10-fold greater than that of transferring the C_6 group. These reactions demonstrate that methyl groups can be transferred between amines at least as readily as larger alkyl groups. In agreement with these results, Kemball and Moss [11] and Anderson and Clark [12] reported that trimethylamine is formed from methylamine as well as from dimethylamine over metal films.

The transfer of a methyl group cannot be explained by an enamine intermediate. Thus, enamines cannot be responsible for the elimination of the alkylamine group from the 1-alkylaminotrialkylamine (gem-diamine) intermediate with a methylene unit between the two nitrogen atoms. Nevertheless, this reaction does occur, as confirmed by the reaction of N,N,N',N'-tetramethyldiaminomethane. This gem-diamine molecule, with a methylene group between the two nitrogen atoms, is already cleaved at 150 °C, a much lower temperature than the 300 °C used in the reactions of the alkylamines. C–N bond hydrogenolysis seems to be the only possible explanation of the cleavage of gem-diamines, which lack β-H atoms in the alkyl groups. That hydrogenolysis of a geminal diamine occurs is, of course, not unexpected, because dissociative hydrogenolysis occurred in all reactions of the alkylamines. Moreover, the fact that it occurs at low temperature also should not be a surprise, because the attachment of another electron-donating group (e.g., an amine group) to the same carbon atom weakens the C–N bond substantially. From our results, it is not possible to determine whether hydrogenolysis is also responsible for the C–N bond cleavage in cases where an enamine can be formed. Hydrogenolysis requires simultaneous bonding of the neighboring C and N atoms on the metal surface, which may be sterically difficult in some cases. This might explain why tribenzylamine is formed only at low concentrations in the hydrogenation of benzonitrile [10,14], due to the difficult adsorption of the 1-aminotribenzylamine intermediate on a flat metal surface.

Although hydrogenolysis explains the dissociation of a gem-diamine formed by reaction of an alkylamine with an alkylimine, it does not explain how exchange occurs between a dialkylamine and a trialkylamine. This exchange cannot occur through an attack by the trialkylamine on the dialkylimine formed from the dialkylamine, because of the formation of a quaternary nitrogen atom. The reverse reaction (of the dialkylamine with the enamine of the trialkylamine) is possible and would explain the formation of C_6–$N(C_5)_2$ in the reaction of C_5–NH–C_5 with $(C_6)_3$N [Eq. (20)]. However, it cannot

explain the formation of C_1–$N(C_5)_2$ in the reaction between C_5–NH–C_5 and C_1–$N(C_6)_2$, because C_1–$N(C_6)_2$ cannot form a $CH_2=N(C_6)_2$ imine, and the formation of a charged iminium cation $CH_2=N^+(C_6)_2$ intermediate on a metal surface does not seem likely. An alternative explanation would be that hydrogen abstraction of the methyl group of the methyldihexylamine forms the imine radical $CH_2=N^·(C_6)_2$, which then reacts with dipentylamine to a geminal diamine that eventually gives C_1–$N(C_5)_2$,

$$C_5\text{–NH–}C_5 + CH_2=N^·(C_6)_2 \rightarrow (C_5)_2N\text{–}CH_2\text{–}N^·H(C_6)_2$$
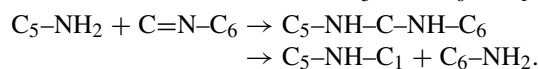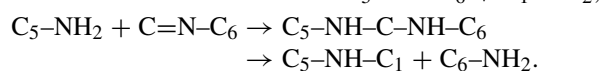$$\rightarrow (C_5)_2N\text{–}CH_2\text{–}N(C_6)_2 + H^·.$$

The imine radical intermediate is closely related to the iminium cation, which is a well-known reaction intermediate in organic reactions. Although an iminium cation can be formed from an amine by abstraction of a proton and two electrons (or of a hydrogen atom and an electron), the imine radical is formed by abstraction of a proton and an electron or of a hydrogen atom. Another possible explanation for the formation of C_1–$N(C_5)_2$ in the reaction between C_5–NH–C_5 and C_1–$N(C_6)_2$ is that the reaction occurs by dissociation of C_1–$N(C_6)_2$,

$$C_1\text{–}N(C_6)_2 \rightarrow C_6\text{–}N^·\text{–}C_6 + C_1^·,$$

$$C_1\text{–}N(C_6)_2 \rightarrow C_1\text{–}N^·\text{–}C_6 + C_6^·,$$
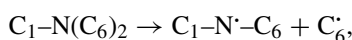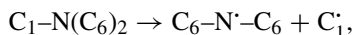
and that the resulting alkyl groups react with C_5–NH–C_5. The experiments with C_1–$N(C_6)_2$ showed that scission of the C_6 group was 6 times faster than that of the C_1 group; thus we should expect a 12-fold higher concentration of $C_6^·$ radicals than of $C_1^·$ radicals. However, C_6–$N(C_5)_2$ formation is 5 times slower than C_1–$N(C_5)_2$ formation, which could mean that the C_1 group diffuses 60 times faster than the C_6 group to meet the C_5–NH–C_5 reactant (Scheme 2), but it seems more likely that dissociative hydrogenolysis is not responsible for the reaction of C_5–NH–C_5 with C_1–$N(C_6)_2$. In their study of the reactions of methylamines over several metal films, Anderson and Clark already argued against hydrogenolysis as a reaction step in the total pathway. They found no nitrogen exchange in the reaction of CH_3NH_2 in the presence of $^{15}NH_3$, and in the reaction of a mixture of $^{13}CH_3NH_2$ and $CH_3{}^{15}NH_2$ observed the double-labeled exchange product $^{13}CH_3{}^{15}NH_2$ only as a secondary reaction product formed from dimethylamine [12]. These results proved that the reaction of CH_3^* with NH_3 does not occur; the authors considered the results also as evidence that the reaction between CH_3^* and CH_3NH_2 does not occur. Later work by Migone et al. questioned this conclusion, however [22]. We

believe that the imine radical $CH_2=N^{\cdot}(C_6)_2$ is a sound possible explanation for the exchange of a methyl group between $C_5–NH–C_5$ and $C_1–N(C_6)_2$.

The reaction rates seem to follow the order of the imine stabilities, which may be due to the fact that the stability order of imine radicals is similar to that of the corresponding imines. Thus, the three primary products $C_6–NH–C_5$, $C_1–NH–C_5$, and $C_1–N(C_5)C_6$ are formed at a ratio of 14.5:6.5:2.3 in the reaction of $C_5–NH_2$ with $C_1–NH–C_6$ (Fig. 7). The first two molecules may be formed by reaction of $C_5–NH_2$ with the imines formed from $C_1–NH–C_6$. First a 1-alkylaminodialkylamine is formed, then the alkylamine group is eliminated under formation of an imine, and this imine is hydrogenated to the final dialkylamine,

$$C_5–NH_2 + C_5–CH=N–C_1 \rightarrow C_5–NH–C(C_5)(NH–C_1)$$
$$\rightarrow C_5–NH–C_6 + C_1–NH_2,$$
$$C_5–NH_2 + C=N–C_6 \rightarrow C_5–NH–C–NH–C_6$$
$$\rightarrow C_5–NH–C_1 + C_6–NH_2.$$

The trialkylamine $C_1–N(C_5)C_6$ is formed by reaction of $C_1–NH–C_6$ with the imine of $C_5–NH_2$, elimination of ammonia from the intermediate 1-aminodialkylamine, and hydrogenation of the formed enamine,

$$C_1–NH–C_6 + C_4–C=NH \rightarrow C_1–N(C_6)–C(C_4)–NH_2$$
$$\rightarrow C_1–N(C_6)–C=C–C_3$$
$$\rightarrow C_1–N(C_6)C_5.$$
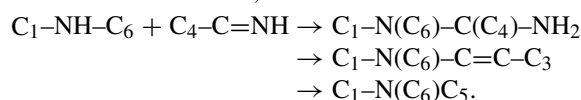
The rates of formation follow the order $C_6–NH–C_5 > C_1–NH–C_5 > C_1–N(C_5)C_6$, which is the same as that of the stabilities of the imine intermediates, $C_5–C=N–C_1 > C=N–C_6 > C_4–C=NH$.

In the reaction of $C_1–NH–C_6$, the likelihood of transferring the C_1 group from one $C_1–NH–C_6$ molecule to another is only slightly less than that of transferring the C_6 group. Enamine formation can stabilize the imine intermediate in the C_6 group but not in the C_1 group of $C_1–NH–C_6$, and the stability of the imine intermediates follows the order $CH_2=N–C_6 < CH_3–N=CH–C_5$. Therefore, an attack of the second $C_1–NH–C_6$ molecule is slightly more likely on the $CH_3–N=CH–C_5$ imine than on the $CH_2=N–C_6$ imine, and, consequently, more $C_1–N(C_6)_2$ than $C_6–N(C_1)_2$ will be formed.

5. Conclusion

Our disproportionation experiments on dialkyl- and trialkylamines demonstrate that methyl groups are transferred between alkylamines at a rate similar to that for higher alkyl groups. This means that the cleavage of an aminotrialkylamine, which is formed by reaction of a dialkylamine with a dialkylimine, does not have to achieve alkylamine elimination through an enamine intermediate, but can also do so by direct hydrogenolysis. This was confirmed by the experiments on N,N,N',N'-tetramethyldiaminomethane showing that this molecule could be cleaved already at low temperature. Imines and enamines may function as intermediates in the reaction of alkylamines, but this cannot explain the transfer of the methyl group from methyldihexylamine to dipentylamine; an imine radical is proposed as intermediate in this reaction.

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