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Methoxycarbonylation of Aliphatic Diamines with Dimethyl Carbonate Promoted by *in situ* Generated Hydroxide Ion: A Mechanistic Consideration

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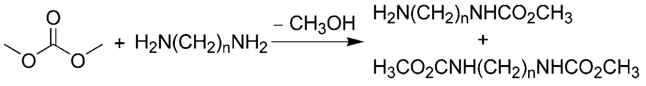
Abstract: The methoxycarbonylation reactions of aliphatic diamines with dimethyl carbonate are accelerated greatly in the presence of water. Theoretical investigations on the mechanistic aspects of the methoxycarbonylation of 1,6-hexanediamine strongly suggest that the hydroxide ion, generated *in situ* from the interaction of 1,6-hexanediamine with water, is an active catalytic species and plays a pivotal role in the rate-determining hydrogen abstraction step from the amino group.

Keywords: 1,6-di(methyl carbamate)hexane; dimethyl carbonate; isocyanates; methoxycarbonylation; non-phosgene process

Introduction

Non-phosgene processes for the synthesis of carbamates, precursors of isocyanates, have attracted increasing interest in recent years because of the environmental concern on the use of highly toxic phosgene.[1–9] Of the various non-phosgene processes so far reported, methoxycarbonylation of amines by dimethyl carbonate (DMC)[10–13] has been considered the most environmentally benign route to the carbamates because methoxycarbonylation reactions can be carried out under relatively mild conditions, producing methanol as the sole by-product as shown in Scheme 1.

Various substances including inorganic salts[5] and ionic liquids[6] were used as catalysts for the methoxycarbonylation of amines, but the processes using these catalysts need to be greatly improved in terms of catalytic activities and product purification for practical applications. In the patent literature, although it was stated that water was found to facilitate the methoxycarbonylation of aliphatic monoamines such as ammonia, ethylamine, and diethylamine in the presence of a solvent, the role of water was not discussed in detail.[14] Moreover, the methoxycarbonylation reactions of diamines using water as a promoter or a catalyst have never been attempted.



Scheme 1. Methoxycarbonylation of a diamine with DMC.

We report here the water-assisted methoxycarbonylation of 1,6-hexanediamine (HDA) with DMC as well as a theoretical investigation on the role of water. We focused on the methoxycarbonylation of HDA because the methoxycarbonylated product, 1,6-di(methyl carbamate)hexane (HDC), can be easily transformed into 1,6-hexanediisocyanate (HDI), one of the most important aliphatic diisocyanates.

Results and Discussion

Effect of Water on the Methoxycarbonylation of HDA

The methoxycarbonylation of HDA with DMC was significantly facilitated by the presence of water.

Table 1. Effect of water on the reaction of HDA with DMC.[a]

Run	Molar ratio (H_2O:HDA)	HDA conversion [%]	Yield [%]	
			HMC	HDC
1	0:1	8.2	8.1	0.1
2	0.25:1	41.8	39.6	2.1
3	0.5:1	66.1	55.1	10.6
4	1:1	75.1	56.0	19.0
5	2:1	89.6	51.0	38.5
6	3:1	95.5	40.2	55.3
7	4:1	99.8	37.2	62.5
8	5:1	99.6	34.7	64.6
9	6:1	99.8	34.7	65.0
10	8:1	99.4	34.6	64.6
11[b]	0:1	47.3	40.7	6.5

[a] The reaction was conducted for 4 h at 25 °C and at the molar ratio of DMC/HDA = 2 (HDA: 0.04 mol).

[b] The reaction was carried out in the presence of [BMim]OH at the molar ratio of [BMim]OH/HDA = 0.2.

Table 1 shows the results of the methoxycarbonylation of HDA with DMC carried out at 25 °C with and without the presence of water. The methoxycarbonylation of HDA proceeded very slowly in the absence water, producing HMC and HDC in yields of 8.1 and 0.1%, respectively. The yields of HMC and HDC, however, started to rise with the addition of water, implying that a new active catalytic species, presumably OH^-, is generated by the presence of water, possibly through the interaction between HDA and water. Both HDA conversion and HDC yield increased gradually with increasing molar ratio of H_2O/HDA up to 4 and then remained almost unchanged on further increases of the molar ratio.

To test the possible hydrolysis of HDC to HMC and HDA, HDC was reacted with a large excess of water (molar ratio of water/HDC = 20) at 25 °C, but GC and ^{1}H NMR analysis did not reveal the formation of HMC and HDA. This finding is a clear indication that the hydrolysis of HDC hardly takes place under the experimental conditions.

Effect of DMC/HDA Molar Ratio

The effect of the molar ratio of DMC/HDA was also investigated at 25 °C at the molar ratio of H_2O/HDA = 6 and the results are listed in Table 2. The conversion of HDA was almost quantitative in the DMC/HDA molar range 2–6. However, as was predicted, the formation of HMC prevails at the molar ratio of DMC/HDA = 1, indicating that HDA is methoxycarbonylated to HMC more readily than HMC to HDC. The HDC yield increased to about 4-fold when the molar ratio was raised from 1 to 2, while the HMC yield fell from 62.5% to 34.7%. The HDC yield remained almost constant on further increases of the molar ratio.

Table 2. Effect of molar ratio of DMC/HAD.[a]

Run	Molar ratio (DMC: HDA)	HDA conversion [%]	Yield [%]	
			HMC	HDC
1	1:1	79.8	62.5	17.2
2	2:1	99.8	34.7	65.0
3	3:1	100	34.2	65.8
4	4:1	99.6	33.2	66.3
5	5:1	99.1	34.1	64.8
6	6:1	98.6	34.2	64.2

[a] The reaction was conducted for 4 h at 25 °C and at the molar ratio of H_2O/HDA = 6 (HDA: 0.04 mol).

The methylated side products, $H_2N(CH_2)_6NHMe$ and $MeNH(CH_2)_6NHCO_2Me$, were also produced, but in yields of around 0.2% only at higher molar ratios of DMC/HDA.

Effect of Reaction Time

The change of product composition with time is shown in Figure 1. The HDC yield and the HDA conversion rose gradually with time up to 6 h and then remained almost constant thereafter at around 66% and 100%, respectively. However, the HMC yield reached a maximum at 0.5 h and then started to fall to about 33%, implying that HMC is an intermediate on the way to HDC. The HDC yield, however, never exceeded 67%, clearly indicating that an equlibrium exists among HDC, HMC, and HDA, possibly because of the presence of the co-produced CH_3OH.

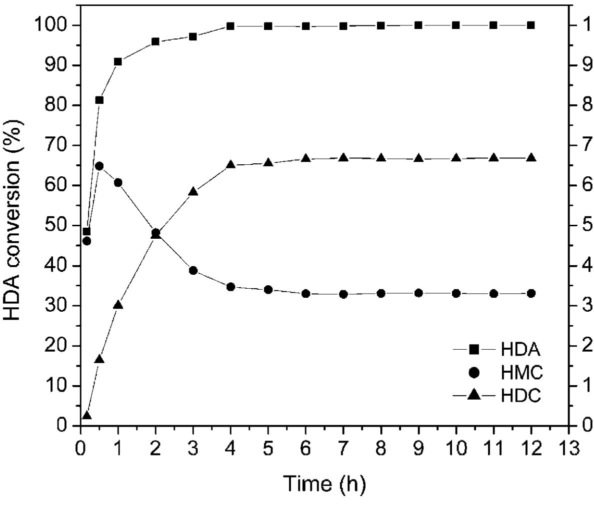


Figure 1. Change of product composition with time.

To confirm that HMC is an intermediate of HDC, HMC was methoxycarbonylated at the molar ratio of HMC/DMC/H_2O = 1/2/6 at 25 °C. Contrary to our prediction, the methoxycarbonylation of HMC was extremely slow, resulting in conversion of less than 2% HMC to HDC over 4 h. This was a rather unexpected result because HDC was produced in a yield of 65% from the methoxycarbonylation of HDA conducted at 25 °C for 4 h at the molar ratio of HDA/DMC/H_2O = 1/2/6. One possible explanation for this is that the methoxycarbonylation of HMC occurs at a reasonable rate only in the presence of HDA as a hydroxide ion (OH^-) supplier or proceeds at a much higher temperature. The activation of HMC by OH^- and the subsequent hydrogen abstraction from the NH_2 group seem to require a much higher energy than that required for HDA, possibly due to the presence of an electron-withdrawing carbamate group in HMC (see Section on Computational Calculations). In fact, the conversion of HMC to HDC increased significantly to 23% when the methoxycarboylation of HMC was carried out in the presence of small amounts of HDA at the molar ratio of HMC/DMC/H_2O/HDA = 1/2/6/0.1.

To find out the reason for the significantly lower reactivity of HMC than that of HDA toward the methoxycarbonylation, the interactions of OH^- with HDA and HMC were compared by means of computational calculations (*vide infra*).

Effect of Reaction Temperature

As shown in Figure 2, the HDA conversion did not change much with the temperature increases, but the HMC yield increased by about 14% with the rise of temperature from 40 to 60 °C at the expense of the HDC yield. This finding implies that the equilibrium between HMC and HDC is shifted slightly towards the formation of HMC at elevated temperatures.

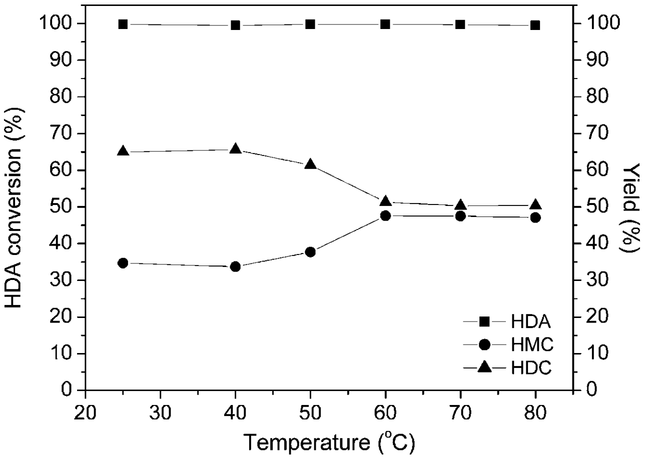


Figure 2. Change of product composition with temperature.

Equilibrium Considerations

To shift the equilibrium of HDA methoxycarbonylation toward the formation of HDC, the reaction was carried out using a Dean–Stark apparatus in the presence of excess quantities of DMC (DMC/HDA = 10). CH_3OH was continuously withdrawn from the reaction system as an azeotropic mixture with DMC as soon as it formed. To reduce the formation of methylated products at elevated temperatures, the reaction was performed at 25 °C for 2 h then at a reflux temperature for an additional 2 h. The reaction, carried out in the presence of water, produced HDC in a yield of over 98% along with a small amount of methylated side product, $H_2N(CH_2)_6NHMe$. On the contrary, the reaction performed in the absence of water produced HDC, HMC, and a series of methylated products [$H_2N(CH_2)_6NHMe$, $MeHN(CH_2)_6NHMe$, and $MeHN(CH_2)_6NHCO_2Me$] in yields of 41, 39, and 13%, respectively. From these results, it is obvious that the presence of water suppresses the formation of methylated side products while increasing the yield and selectivity of HDC. The presence of water seems to provide an unfavourable environment for DMC to function as a methylating agent.

Interestingly, the formation of methylated side products was negligible when the HMC was methoxycarbonylated instead of HDA at reflux for 4 h at the molar ratio of HMC/DMC/water = 1/10/3. The presence of an electron-withdrawing carbamate group at the other end of HMC seems to greatly restrict the methylation of the HMC amino group. For this reason, to avoid the formation of methylated side products, HDA should be methoxycarbonylated first at a low temperature just enough to convert all HDA to HMC and HDC, and then at reflux to convert HMC to HDC while simultaneously removing CH_3OH.

Computational Calculations

To elucidate the role of water, the interactions between HDA and DMC with and without the presence of water were theoretically investigated at the B3LYP/6-31+G* level of the theory using the *Gaussian 03* program.[15] Four cases were calculated: (i) in the absence of water, (ii) in the presence of water, (iii) in the presence of OH^-, and (iv) in the co-presence of both water and OH^-. For each case, as in Figure 3, the methoxycarbonylation was seen to proceed through a tetrahedral intermediate (I*). In the absence of water and OH^-, the free energy of activation ($\Delta G^{\neq}$) for the first transition state (TS1) and the free energy of formation for the tetrahedral intermediate (ΔG_i) were calculated as 38.1 and 20.7 kcal mol^{-1}, respectively (Figure 3a). $\Delta G^{\neq}$ and ΔG_i were

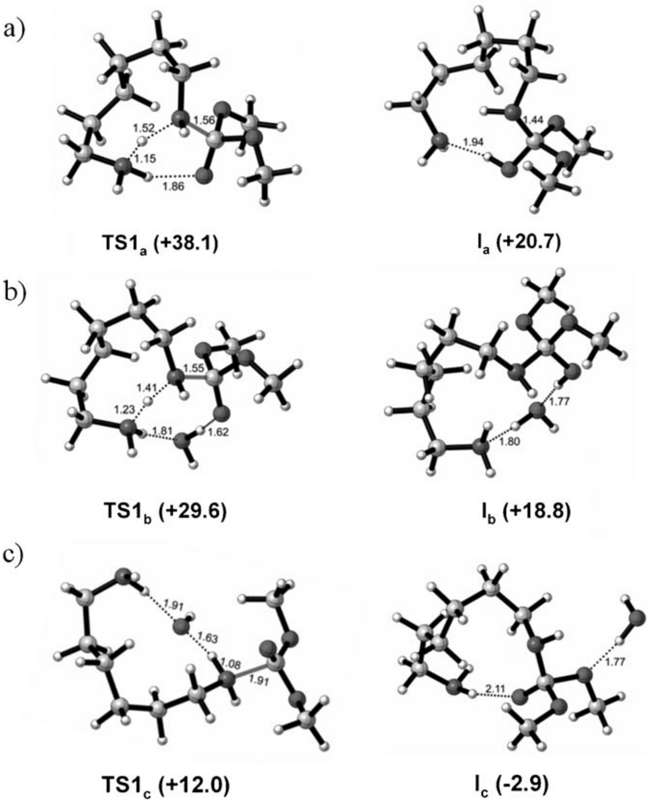


Figure 3. Optimized geometries of the first transition states (TS1) and tetrahedral intermediates (I*) for the methoxycarbonylation of HDA with DMC: a) in the absence of water and OH^-, b) in the presence of water, c) in the presence of OH^-. The numbers in parentheses refer to activation energy or free energy of formation in kcal mol^{-1}.

reduced to 29.6 and 18.8 kcal mol^{-1}, respectively when a water molecule was intentionally included in the calculation (Figure 3 b). However, these values are still too high to explain the experimental results obtained in the presence of water. Surprisingly, $\Delta G^{\neq}$ and ΔG_i were greatly reduced to 12 and -2.9 kcal mol^{-1}, respectively, when the water molecule was replaced by OH^-, clearly implying that OH^- is an active species in the methoxycarbonylation of HDA (Figure 3 c). This is a reasonable deduction because amine is easily transformed into ammonium hydroxide on contact with water. The involvement of an additional water molecule in the transition state was not helpful in reducing the activation energy further (see Supporting Information). Details of the calculation results of the mechanisms for four different cases are provided in the Supporting Information.

Based on the computational and experimental results, it is concluded that OH^-, *in situ* generated by the interaction of HDA with water, is involved in the rate-determining hydrogen abstraction step in which hydrogen is abstracted from the amino group. Activation of the nucleophile through the cleavage of an N–H bond by OH^- and the stabilization of the resulting negative charge on the electrophile (DMC) by water molecules may be achieved in a cooperative network of hydrogen bonds. With such strong interactions, both the cleavage of the C–O bond and the formation of C–N bond seem to be accelerated to form carbamates.

The involvement of *in situ* generated OH^- is indirectly supported by a separate experiment using 3-butyl-1-methylimidazolium hydroxide ([BMim]OH) as the catalyst. The conversion of HDA surged to 47.3% from 8.2% when the methoxycarbonylation was performed in the presence of [BMim]OH at 25 °C and at the molar ratio of [BMim]OH/HDA = 0.2, implying that OH^- catalyzed the methoxycarbonylation of HDA (see Table 1, runs 1 and 13).

To identify the reason for the different reactivities of HDA and HMC to methoxycarbonylation, the interactions of OH^- with HDA and HMC were compared based on theoretical calculations. As can be seen from the optimized structure of HDA (HDA-OH^-) in Figure 4 a, the distances between bonds in the oxygen atom of OH^- and the hydrogen atoms of two NH_2 were calculated as 1.84 and 1.87 Å, respectively, indicating that OH^- interacts strongly with two amino groups of HDA. Such a strong interaction as this would facilitate the rate-determining hydrogen abstraction from NH_2.

Interestingly, two optimized structures, keto (HMC$_k$-OH^-) and enol (HMC$_e$-OH^-) forms, are obtained from the interaction of OH^- with HMC as shown in Figure 4 b and c. Caculations of free energy of formation (ΔG) show that HMC$_e$-OH^- is more stable than HMC$_k$-OH^- and HDA-OH^- by 1 and 17 kcal mol^{-1}, respectively. For the activation of HMC, OH^- should interact with the amino group

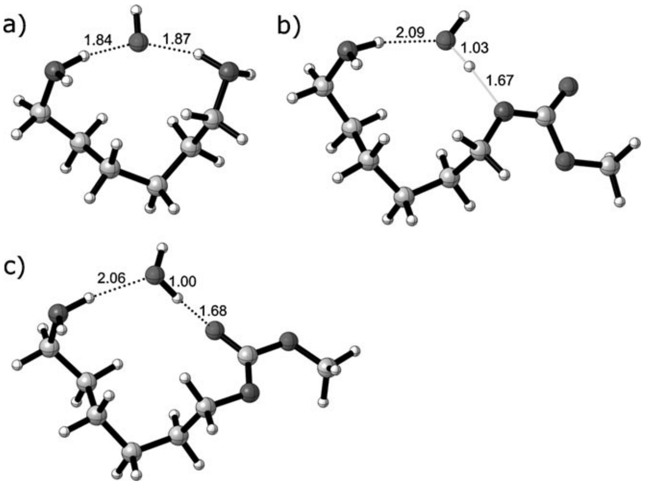


Figure 4. Optimized structures showing the interactions of HDA and HMC with OH^-: a) HDA-OH^-, b) HMC$_k$-OH^-, c) HMC$_e$-OH^-.

rather than with the carbamate group, but the comparison of the bond distances in the optimized structure of HMC-OH$^-$ clearly reveals that OH$^-$ favours the interaction with the hydrogen atom of the more acidic carbamate group over the amino group. For HMC$_e$-OH$^-$, the bond distance between the oxygen atom of OH$^-$ and the hydrogen atom of enol OH is calculated as 1.00 Å, which is shorter than that between the oxygen atom of OH$^-$ and the hydrogen atom of NH$_2$ (1.06 Å). From these computational results, it is believed that the lower activity of HMC than that of HDA toward the methoxycarbonylation can be largely ascribed to the lengthening of the bond distance between OH$^-$ and NH$_2$ from 1.84 Å in HDA-OH$^-$ to 2.06 Å in HMC$_e$-OH$^-$. Consequently, the rate of hydrogen abstraction from the NH$_2$ group of HMC would be much slower.

Effect of Solvent

The effect of solvents on the methoxycarbonylation was also studied at 25 °C with the molar ratio of HDA/DMC/solvent at 1/2/6. As noted in Table 3, the reaction did not proceed at all in aprotic non-polar solvents such as tetrahydrofuran (THF) or dioxane in the absence of water. In aprotic solvents, the generation of an active anionic species like OH$^-$ and the subsequent activation of HDA do not seem to take place. THF and dioxane do not contain acidic hydrogen(s) that could interact with the negative charge developing on the carbonyl oxygen of the DMC and therefore fail to stabilize the tetrahedral intermediate. Alternatively, the oxygen atom of THF or dioxane seems to interact strongly with the H atoms of the amino groups of HDA through hydrogen bonds, thereby diminishing the ability of amino groups to interact with the tetrahedral intermediate. This absence of a stabilizing interaction might completely quench the reaction.

As expected, the methoxycarbonylation proceeded by the use of water coupled with THF, but the HDC yield was considerably lower than that obtained in the presence of water only. In contrast to aprotic solvents, protic solvents such as methanol and D$_2$O promoted the methoxycarbonylation reaction although the effect was not as pronounced as that with H$_2$O. It is likely that the deprotonation of D$_2$O by an amino group to generate an active species like OD$^-$ is slower than that of H$_2$O. The difference in the promoting effect between H$_2$O and D$_2$O on the methoxycarbonylation could also be rationalized by the deuterium effect.

Table 3. Effect of solvent on the methoxycarbonylation of HDA with DMC.[a]

Run	Solvent	HDA conversion [%]	HDC yield [%]
1	THF	0	0
2	dioxane	0	0
3	MeOH	42.1	3.1
4	D$_2$O	75.2	42.4
5[b]	THF/H$_2$O	52.5	5.0

[a] The reaction was conducted for 4 h at 25 °C and at the molar ratio of HDA/DMC/solvent = 1/2/6 (HDA: 0.04 mol).

[b] Molar ratio of HDA/DMC/THF/H$_2$O = 1/2/3/3.

Plausible Mechanism for the Methoxycarbonylation of HDA

Based on these theoretical and experimental results, a plausible mechanism for the methoxycarbonylation of HDA is suggested. As shown in Figure 5, HDA is likely to be activated first by OH$^-$, generated *in situ* from the interaction of HDA and H$_2$O, through hydrogen bonds (see also Supporting Information, c). Subsequent abstraction of hydrogen from one of the amino groups would result in the generation of amido anion, **A** with the concomitant loss of H$_2$O. Nucleophilic attack of the anion on the carbon atom of DMC produces an intermediate species, **B**, which in turn transforms into HMC on interaction with H$_2$O, simultaneously with the loss of CH$_3$OH and the regeneration of OH$^-$. Further methoxycarbonylation of HMC to produce HDC would proceed in a similar manner to that of HDA.

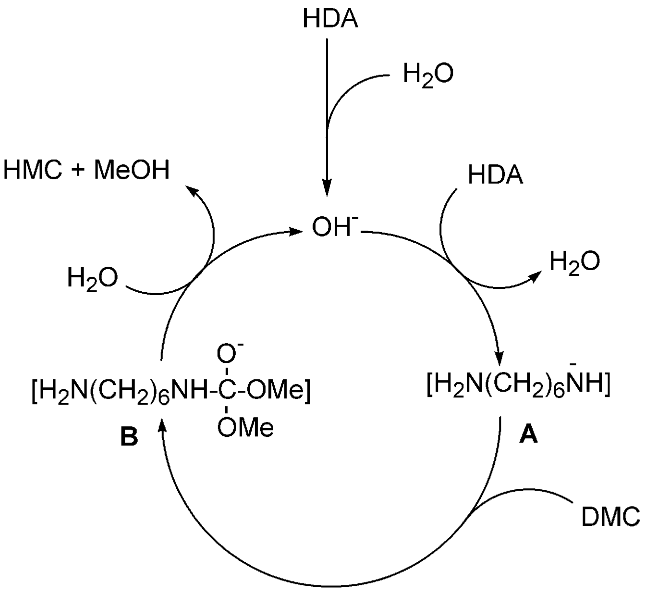


Figure 5. Plausible mechanism for the hydroxide ion-catalyzed methoxycarbonylation of HDA. Cation (HDAH$^+$) was omitted for clarity.

Table 4. Effect of water on the methoxycarbonylation of various diamines.[a]

Run	Diamine	Molar ratio (H_2O:Diamine)	Diamine conversion [%]	Carbamate yield (%) Mono	Di
1	EDA	0:1	51.6	43.4	8.1
2	EDA	6:1	100	38.4	61.5
3	BDA	0:1	43.1	40.0	3.0
4	BDA	6:1	98.8	38.1	60.6
5	HDA	0:1	8.2	8.1	0.1
6	HDA	6:1	99.8	34.5	65.0
7	ODA	0:1	1.5	1.5	0
8	ODA	6:1	91.0	47.0	43.7

[a] The reaction was conducted for 4 h at 25 °C and at the molar ratio of DMC/diamine = 2.

Methoxycarbonylation of Other Diamines

As illustrated in Table 4, the effect of water was also investigated for the methoxycarbonylation of diamines other than HDA, including 1,2-ethanediamine (EDA), 1,4-butanediamine (BDA), and 1,8-octanediamine (ODA). As in the methoxycarbonylation of HDA, the presence of water also greatly accelerated the methoxycarbonylation reactions of EDA, BDA, and ODA, resulting in much higher conversions of diamines and yields of dicarbamates compared with those from the reactions carried out in the absence of water. In general, the diamine conversions and the dicarbamate yields decrease with the increasing number of CH_2 groups between the two amino moieties. The significantly reduced reactivities of HDA and ODA with a longer alkylene chain in the absence of water could be largely attributed to their low solubility in DMC.

It is worth mentioning here that in the methoxycarbonylation of diamines, the process using water would be more economical than those employing metal salts[5,16] and oxides[17] in terms of catalyst and product recovery.

Conclusions

In conclusion, the presence of water greatly accelerates the methoxycarbonylation reactions of diamines, including EDA, BDA, HDA, and ODA while suppressing the formation of methylated side products

Theoretical calculations of the optimized transition and intermediate structures reveal that the OH^-, presumably generated from the interaction between HDA and water, is an active species for the methoxycarbonylation of HDA and plays a pivotal role in the rate-determining hydrogen abstraction step from the amino group.

We hope that our findings on the methoxycarbonylation of diamines will be of great help in the development of benign and economical non-phosgene commercial processes for manufacturing isocyanates.

Experimental Section

Chemicals

Unless otherwise stated, all reagents were purchased from Aldrich Chemical Co. and used as received.

Catalysis

A typical methoxycarbonylation reaction was performed as follows: HDA (40 mmol, 4.65 g), DMC (80 mmol, 7.20 g), and water (240 mmol, 4.32 g) were loaded into a 50-mL two-necked flask equipped with a condenser and a magnetic stir bar. The flask was then heated to a specified temperature with vigorous stirring. After the reaction was completed, the product mixture was dissolved in methanol and analyzed using an Agilent 6890 gas chromatograph equipped with a thermal conductivity detector and a DB-5 capillary column (30 m × 0.32 mm × 0.25 μm). Products were characterized using a Bruker 400 NMR spectrometer and an Agilent 6890–5973 MSD GC-mass spectrometer equipped with an HP-5MS capillary column (30 m × 0.32 mm × 0.25 μm).

^1H NMR data of HDC and methyl-6-aminohexane-1-carbamate (HMC) obtained are listed below.

HDC: ^1H NMR (400 MHz, CD_3OD, 25 °C): $\delta = 3.6$ (s, 6H, CH_3), 3.1 (t, 4H, CH_2), 1.5 (m, 4H, CH_2), 1.4 (m, 4H, CH_2).

HMC: ^1H NMR (400 MHz, CD_3OD, 25 °C): $\delta = 3.6$ (s, 3H, CH_3), 3.1 (t, 2H, CH_2), 2.8 (t, 2H, CH_2), 1.6 (m, 2H, CH_2), 1.5 (m, 2H, CH_2), 1.4 (m, 4H, CH_2).

Calculated elemental analysis (%) for $C_8H_{18}N_2O_2$: C 55.2, H 10.4, O 18.4; found: C 56.3, H 9.9, O 18.7.

To enhance the yield of HDC, the methoxycarbonylation of HDA was also carried out using a Dean–Stark apparatus in the presence of excess of DMC (HDA/DMC/H_2O = 1/10/6 or 1/10/0). The reaction was performed at 25 °C for 2 h and then at a reflux temperature for an additional 2 h with a continuous withdrawal of the co-product CH_3OH as an azeotrope with DMC from the reaction system.

Acknowledgements

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