Catalysis of Isocyanate–Alcohol and Blocked-Isocyanate–Alcohol Reactions by Amidines

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Synopsis

The catalytic activity of completely substituted amidines in the reactions of isocyanates and blocked isocyanates with polyols was investigated. A bicyclic amidine was an effective catalyst for these reactions, whereas the monocyclic caprolactam type amidines were found to be ineffective.

INTRODUCTION

Bifunctional catalysis is a term used when two catalytic groups present within the same molecule act on a substrate.[1] Concerted bifunctional catalysis, involving simultaneous proton transfers has been proposed by Swain and Brown[2] for the mutarotation of 2,3,4,6-tetramethyl-D-glucose in the presence of 2-hydroxypyridine (Scheme 1). 2-Hydroxypyridine with both acidic and basic sites functions as the bifunctional catalyst. This proposal followed from the observed 50-fold rate enhancement by the 2-hydroxypyridine relative to pyridine and phenol, and first order rate dependence on both phenol and pyridine with mixtures.

Reduction in the number of species comprising the transition-state complex and elimination of high-energy intermediates from the reaction mechanism can be two major advantages for this type of catalyst.

Essentially all of the reactions used in thermosetting coatings involve a proton transfer. This can be seen (1) in the transetherification reaction of an alkoxy methyl melamine,[3] (2) in the ring opening reactions of epoxides,[4] and (3) in isocyanate–alcohol reactions[5] (Scheme 2). Amidines containing at least one proton ($-N=\overset{|}{C}-NH-$) are of interest as catalysts for such reactions, since it is possible for them to undergo concerted proton transfer reactions.[6]

Completely substituted amidines that cannot undergo concerted proton transfer ($-N=\overset{|}{C}-NR-$) have been used as catalysts for the reaction of aliphatic and aromatic isocyanates with polyols.[7,8] Films with good properties were obtained at moderate temperatures. A German patent to Bayer[9] describes their use as catalysts for the reaction between multifunctional phenol-blocked isocyanates and amines.

Evidence for bifunctional catalysis by amides and ureas has been reported for the reaction of phenylisocyanates and amines.[10] These reports prompted us

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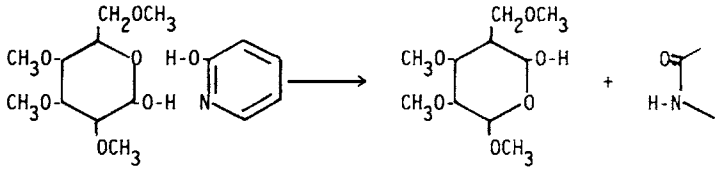
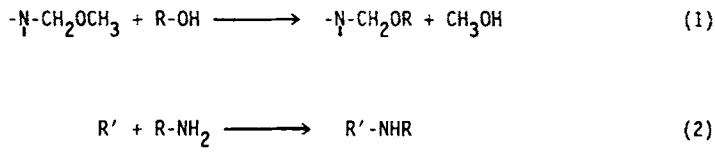
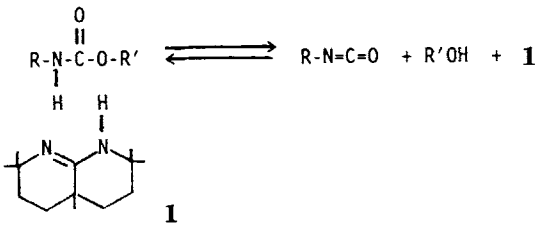


Scheme 1.



Scheme 2.

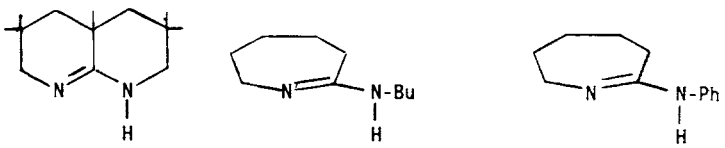


Scheme 3.

to investigate the role of amidines that can undergo concerted proton transfer in the catalysis of isocyanate–alcohol and blocked-isocyanate–alcohol reactions.

A possible mechanism for the unblocking of an isocyanate catalyzed by an amidine is shown in Scheme 3. In this mechanism, the amidine **1** removes the proton from nitrogen (of the urethane) and delivers a proton to oxygen to produce the alcohol. The amidine is regenerated. The reaction of an isocyanate with an alcohol (the reverse reaction) can be catalyzed accordingly (principle of microscopic reversibility).

Herein, we report on the catalytic activity of amidines **1, 2,** and **3,** shown in Figure 1, as well as of the tertiary amines, shown in Figure 2, in the reactions of isocyanates and oxime-blocked isocyanates with polyols.



1 2 3

Fig. 1. Amidines used in our studies.

EXPERIMENTAL

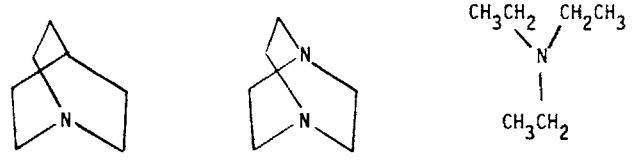
Materials

Amidine **1,** 3,3,6,9,9-pentamethyl-2,10-diazabicyclo [4.4.0] dec-1-ene was commercially available from Fluka. It was handled under nitrogen atmosphere since it reacts with carbon dioxide. Dabco, Aldrich 97%, was sublimed before use. Quinuclidine from Aldrich and triethylamine from Baker were used as received. Hexamethylene diisocyanate isocyanurate trimer (Desmodur KL5-2444, av eq wt 210, % NCO 20), polymethylene polyphenyl isocyanate (Mondur XP-744, av eq wt 179, % NCO 23.5) and a polyester polyol (Desmophen 651A-65, av eq wt 325, % OH 5.2) were obtained from Mobay. Isophorone diisocyanate isocyanurate trimer (IPDI-T 1890S, av eq wt 365, % NCO 12) was obtained from Huls. Cellosolve acetate, Aldrich 99%, was distilled and dried over molecular sieves before use. 2-Butanone oxime from Alfa, was distilled.

Amidine **2,** 2-butylamino-1-aza-1-cycloheptene, was synthesized according to a known procedure.[11] Butylamine (7.4 g, 1×10^{-1} mol) was added dropwise at 29°C to a solution of *o*-methylcaprolactam (8 g, 6.3×10^{-2} mol) in 50 mL of methanol. After 2 days the mixture was distilled to give 7 g (68% yield) of the product, mp 73–75°C NMR ($CDCl_3$) (ppm) 0.9 (3H, CH_3, t), 1.5 (10H, m), 2.3 (2H, CH_2—C, d), 3.1 (2H, CH_2—N, t), 3.35 (2H, CH_2—N, d), 4.8 (1H, NH, br).

Amidine **3,** 2-anilino-1-aza-1-cyloheptene, was synthesized as follows. Aniline (9.6 g, 0.1 mol) and *o*-methylcaprolactam (12.7 g, 0.1 mol) were heated at 147°C for 3 h, while methanol was distilled off simultaneously. A crude solid precipitated at room temperature and was recrystallized from heptane to yield 9.4 g (50%) of **3,** mp 104–105°C; lit[12] mp 102–104°C.

Hexamethylene diisocyanate isocyanurate trimer (HDI-T) and polymethylene polyphenyl isocyanate (MDI) were blocked with 2-butanone oxime by



Quinuclidine DABCO Et_3N

Fig. 2. Tertiary amines used in our studies.

reacting equivalent amounts of the isocyanate resin and the oxime in cellosolve acetate. The reaction was run at 70°C under nitrogen for 3 days. An IR spectrum confirmed the disappearance of free isocyanate. The blocked isocyanates were used in subsequent studies without further purification.

Instrumental

H^1-NMR spectra were obtained on a Varian EM390 spectrometer. IR spectra were obtained on a Perkin-Elmer 137 NaCl spectrophotometer.

Gel Time Studies

Appropriate amounts of reactants were introduced into test tubes. The catalysts were added as solutions in an appropriate solvent, generally cellosolve acetate. The tubes were capped with corks, shaken for a few seconds in order for the reactants to mix and placed in a constant temperature oil bath. At regular intervals, the tubes were removed from the oil bath to observe whether the solution had gelled. The time at which no flow of the solution was observed was taken as the gel time.

RESULTS

The catalytic activity of amidines **1**, **2**, and **3** in the reaction of isophorone diisocyanate isocyanurate trimer (IPDI-T) an aliphatic isocyanate, with triethylene glycol (TEG) and polymethylene polyphenyl isocyanate (MDI), an aromatic isocyanate, with a polyglycol triol (Dow 15-200) was studied by determining gel times. The results of the studies are shown in Table I. Results

TABLE I
Catalysis of Reaction of Aliphatic and Aromatic Isocyanates with Polyols by Amidines and Amines

	Gel times (min)[a]	
Catalyst[b]	Aliphatic[c] 90°C	Aromatic[d] 40°C
Bicyclic amidine **1**	6	86
Cyclic amidine **2**	> 300	> 1000
Cyclic amidine **3**	> 300	> 1000
Quinuclidine	23	18
DABCO	41	30
Et_3N	> 120	> 300
None	> 1000	> 2500

[a] Average of 2 determinations, range of experimental values ± 5%.

[b] Amidines (9–10 mg, 5×10^{-5} mol) in 1 mL of cellosolve acetate (CA); amines (10 mg, 9×10^{-5} mol) in 1 mL of CA.

[c] Isophorone diisocyanate isocyanurate trimer (IPDI-T 1890S) (1 g, 2.8 meq NCO); triethylene glycol (TEG) (0.2 g, 2.8 meq OH).

[d] Polymethylene polyphenyl isocyanate (MDI) (0.5 g, 2.8 meq NCO); polyglycol ether triol (Dow 15-200) (2.4 g, 2.8 meq OH); an additional 1 mL of CA was used.

with quinuclidine, 1,4-diazabicyclo [2.2.2] octane (DABCO) and triethylamine (Et_3N) are included for comparison.

The results of catalytic activity of amidine **1** compared to that of amines in the reaction of oxime-blocked hexamethylene diisocyanate isocyanurate trimer (HDI-T) (aliphatic isocyanate) and oxime-blocked MDI with a polyester polyol (Desmophen 651A-65) are provided in Table II.

The bicyclic amidine **1** was shown to be a more effective catalyst than quinuclidine and DABCO in an aliphatic isocyanate–polyol reaction and less effective with an aromatic isocyanate. This was observed for the reactions of both blocked and unblocked isocyanates (Tables I and II). The cyclic amidines **2** and **3** were found to be ineffective catalysts for the reactions of aliphatic and aromatic isocyanates with alcohols (Table I).

DISCUSSION

Catalysis of isocyanate–alcohol reaction by tertiary amines, such as DABCO, probably involves removal of a proton from the alcohol during addition to the isocyanate, as shown in eq. (4). This would facilitate reaction by lowering the energy of the intermediate relative to the uncatalyzed reaction [eq. (5)], since positively charged nitrogen is lower in energy than positively charged oxygen.

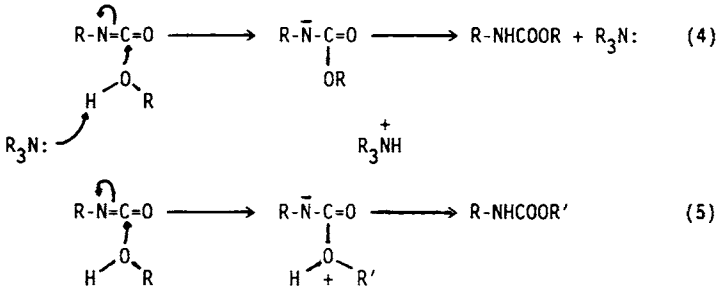


TABLE II
Catalysis of Reactions of Oxime-Blocked Aliphatic and Aromatic Isocyanates with a Polyol at 170°C

	Gel times (min)[a]	
Catalyst[b]	Aliphatic[c]	Aromatic[d]
Amidine **1**	60	13
Quinuclidine	80	5
DABCO	101	7
Et_3N	115	60
None	120	70

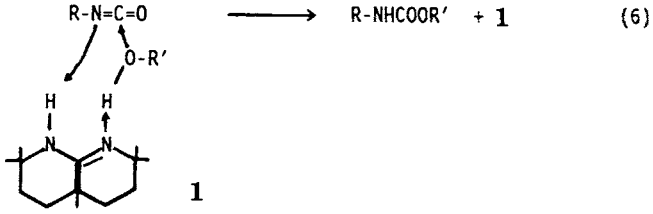
[a] Average of 2 determinations; range of experimental values ± 5%.

[b] Amidine (7 mg, 3×10^{-5} mol) in 1 mL of CA; amines (7 mg, 6×10^{-5} mol) in 1 mL of CA.

[c] 2-Butanone oxime-blocked HDI-T (0.73 g, 2.4 meq NCO); polyol polyester (Desmophen 651A-65) (0.75 g, 2.4 meq OH).

[d] 2-Butanone oxime-blocked MDI (0.73 g, 2.8 meq NCO); Desmophen 651A-65 (0.93 g, 2.8 meq OH); an additional 1 mL of CA was used.

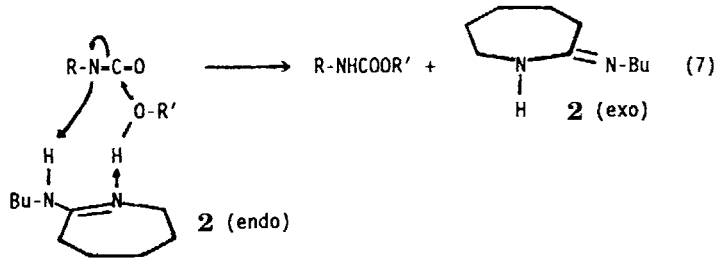
The order of reactivity found for the amines was, quinuclidine > DABCO > Et_3N. Since quinuclidine is more basic than DABCO (by about 2 pK units) and less sterically hindered than triethylamine, the results indicate that both steric accessibility and basicity contribute toward catalytic effectiveness of tertiary amines. The greater catalytic activity of bicyclic amidine **1** with aliphatic isocyanates and blocked aliphatic isocyanates, may be attributed to concurrent proton removal from the alcohol, and proton addition to the isocyanate, as shown in eq. (6). The concerted mechanism obviates formation of the anionic intermediate.



It is important to note that this mechanism seems to deliver a proton to the less stabilized nitrogen of an aliphatic intermediate anion ($R-\bar{N}-COOR$) more efficiently, relative to the more stabilized nitrogen of the aromatic anion ($Ar-\bar{N}-COOR$).

It is also seen in Table I that the gel times obtained with amidines **2** and **3** are much longer than the ones for amidine **1**, in both aliphatic and aromatic isocyanate–polyol reactions. The essential lack of catalytic activity of cyclic amidines **2** and **3** may result from electronic and/or steric factors.

In contrast to amidine **1**, which remains unchanged in the catalysis, amidines **2** and **3** must cycle between proton tautomers with exo and endo carbon–nitrogen double bonds, as shown in eq. (7) for amidine **2**. It is possible that the exocyclic (or endocyclic) double bond tautomer is less stable than the endocyclic (or exocyclic) tautomer.



A second possibility is that, the N—H group of amidines **2** and **3** may be more sterically hindered by the butyl and phenyl groups, respectively, compared with the N—H group of amidine **1**, making H-abstraction more difficult.

A third possibility is that the preferred N—H and nitrogen lone pair conformations of amidines **2** and **3** are not favorable for concerted proton transfer, as illustrated for amidine **2** in Figure 3. In contrast, N—H group and nitrogen lone pair are fixed in favorable conformations for amidine **1**.

Fig. 3. Unfavorable conformations for concerted proton transfer.

CONCLUSIONS

For reactions of isocyanates and oxime-blocked isocyanates with polyols, amidine **1**, which is commercially available, was found to be catalytically more effective than quinuclidine and triethylenediamine (DABCO) with aliphatic isocyanates, but less effective with aromatic isocyanates. Concerted bifunctional catalysis may be the reason for the observed effectiveness of amidine **1**.

The readily prepared cyclic amidines **2** and **3** (from caprolactam), however, were essentially ineffective as catalysts in these reactions, probably due to electronic and/or steric factors.

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