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Reactions of Aliphatic α-ω-Diamines in H^+-Pentasils

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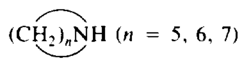
α-ω-Diamines [$H_2N(CH_2)_nNH_2$, $n = 2$–7] undergo surprisingly different reactions in the presence of steam, using a H^+-pentasil zeolite (Si/Al = 25–19,000) at 350°C, a LHSV ~0.8 hr^{-1}, atmospheric pressure in a plug flow reactor. Ethylenediamine and its linear and cyclic oligomers result in piperazine and 1,4-diazabicyclo(2.2.2)octane (TEDA), the latter in excellent efficiencies (~90%) and good rates (~30% conversion/pass) probably via the reaction of piperazine with protonated vinylamine. Minor by-products originate from a reductive cleavage reaction and alkyl pyrazine formation, 1,3-Propanediamine results in ~40% alkylpyridines, a small amount of allylamine and reductive cleavage products on balance. 1,4-Butanediamine was completely unreactive even at 400°C. The 1,5-, 1,6-, and 1,7-diamines form almost exclusively the cyclic secondary amines



$(CH_2)_nNH$ (n = 5, 6, 7).

This diverse chemistry has been rationalized based on differing reaction intermediates and transition states. The reductive cleavage reaction (yielding CH_3NH_2, $CH_3CH_2NH_2$, etc.) takes place only with n = 2 and 3 diamines. The pyrazines (n = 2) and pyridines (n = 3) generated are probably due to amine dehydrogenation, imine hydrolysis, followed by aldol and related condensation and dehydration/dehydrogenations of the intermediates to yield the aromatic products. The inactivity of the n = 4 may be due to high strain in the intramolecular cylization step which exists to lesser degree in the 1,5-, 1,6-, 1,7-diamines, as judged by their widely differing activities. © 1993 Academic Press, Inc.

INTRODUCTION

Zeolites (*1–3*) are employed in large quantities in the petroleum processing industry, principally in hydrocarbon cracking, isomerization, dewaxing, and related operations (*4*). In recent years, a considerable effort has been devoted to an exploration of the zeolite-catalyzed chemistries of polar organic molecules. The spectacular methanol-to-gasoline reaction (*5, 6*) was discovered over 2 decades ago in the Mobil laboratories. The mechanism of this reaction is still being disputed (*7, 8*). Many other polar organic molecules have been reacted, with the aid of a wide variety of zeolites. These efforts have been reviewed in recent publications (*9–11*). A wide variety of zeolite-catalyzed amine reactions have been reported. Of particular or commercial interest is the methanol–ammonia reaction leading to the methylamines. Here, by appropriate choice of a small pore (H^+-RHO) zeolite, surface treated with trimethyl phosphite (*12*), it was possible to prepare dimethylamine in preference to the thermodynamically favored trimethylamine by taking advantage of the shape selectivity (*13–15*) of the zeolite (*16, 17*). Much zeolite catalyzed chemistry has involved the synthesis of aziridines (*18*) from β-hydroxy alkyl amines, aldol condensations (*19, 20*), the transformation of O to N or S heterocyclics (*21*), the reaction of alcohols, especially ethanol with ammonia to give ethylamines (*22*), eth-

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[1] This is gratefully dedicated to a great teacher and friend, Dr. Harold Shechter, Newman Professor of Chemistry at The Ohio State University, on his 70th birthday.

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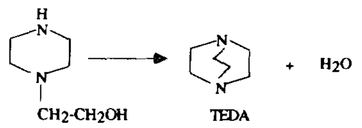
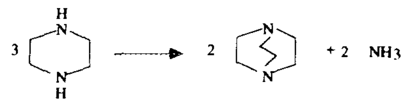
anolamine to ethylenediamines (*23*), and the reaction of 2-hydroxyethylpiperazine (*24–27*), or even piperazine itself (*28–30*) to give 1,4-diazabicyclo (2.2.2) octane (TEDA, a valuable polyurethane catalyst).

Advances in this TEDA synthesis are of particular interest. The early work (*24*) used 2-hydroxyethylpiperazine,



which was reacted over a variety of zeolites usually in poor yields and efficiencies. Other reports, published after the completion of this work, showed that the pentasil zeolite structure (*26, 27*) resulted in much improved efficiencies, and other patents disclosed that TEDA could be made from a lone piperazine (*28, 29*) in almost quantitative yield:



Similarly, pentasil zeolite catalyzed reactions of ethylenediamine and its various oligomers, were found to be useful starting materials for this synthesis (*29*). This showed that there could be a great deal of surprising and unexpected chemistry in amine reactions catalyzed by appropriate zeolites.

These H^+-zeolite catalyzed amine reactions are essentially amine disproportionation reactions,

$$2RNH_2 \xrightarrow{H^+} R_2NH + NH_3, \quad \text{etc.},$$

which are carried out on a large scale in industry but are rarely mentioned in the numerous treatises on amine preparation (*30–33*). The reaction of aniline, using a small quantity of its hydrochloride salt as catalyst, on heating (300°C) leads cleanly to diphenylamine (*34*). The reaction of low boiling amines normally require pressure equipment, yet in zeolites, this reaction can be carried out at atmospheric pressure albeit at high temperatures (325°C) (*16*). The mechanisms of this reaction must involve the S_N2 displacement of the protonated amine function by an unprotonated amine (*35*):

This mechanism requires that the N–C–N atoms are arranged in a linear manner in the transition state.

The purpose of this investigation was to examine the chemistry of α-ω-aliphatic diamines and similar compounds as catalyzed by appropriate H^+-zeolites in order to delineate reaction paths and to determine the nature of the products.

EXPERIMENTAL

The reactions were carried out at atmospheric pressure in a plug flow, fixed bed, down-flow reactor which was 70 cm long and 1.91 cm in inner diameter. This was fed with a plunger pump. A separate heater in front of the reactor served as evaporator and preheater; a 3–5°C condenser collected the product(s). The catalyst bed (100 cm^3) was about 18 cm from the reactor entrance and was about 35 cm deep. Glass balls preceded and followed the catalyst bed. A 3-mm tube, inside of which was a sliding thermocouple, was used to obtain the axial temperature distribution. Heating was carried out with four independently controlled electrical heaters on the reactor and preheater. The reactions tended to be thermoneutral and excellent temperature control was maintained (±1–2°C).

Catalyst reactivations were carried out by steaming followed by the gradual addition of air to burn off the organic residues (at or less than 450°C). Normally, there was relatively little combustible material on the pentasil catalysts; several of the other zeolites appeared to coke badly. Reactivation invariably returned the catalysts to their initial activity.

The various amines, etc., were obtained from commercial sources (Aldrich and Fluka). The zeolite catalysts were obtained from UOP (Tarrytown, N.Y. Laboratories) usually as $\frac{1}{8}$-in broken strands. The bonding agents were either alumina or silica (Ludox). These zeolites were carefully acid washed three times with 5% hydrochloric acid (24 hr), ion exchanged with 5% aqueous ammonium nitrate, and heated at 450–550°C in air (shallow bed) for 18 hr.

Product analyses employed an HP-5890 gas chromatograph using flame ionization detection, helium as carrier gas, and a 30 × 0.25 mm SPB-5 capillary silica column. Gas chromatography–mass spectroscopy, electron impact, and chemical ionization techniques were used to identify the peaks. These were verified by spiking the reaction products with authentic compounds, almost all of which are commercially available. Area–wt% correlations, where desired, were established with mixtures of pure compounds; internal standards were used as needed; water was determined by Karl Fischer titration. This allowed accurate material balances, efficiencies, and conversions to be calculated for the piperazine to TEDA transformation(s). For the other reactions only area% was determined. On catalyst reactivation, by an oxidative burn-out, the exotherms were invariably small (5–10°C)—thus relatively light coking was observed (provided the reagents were fed as aqueous solutions).

RESULTS AND DISCUSSION

The majority of the work which involved the zeolite nature, etc., was carried out using the piperazine-to-TEDA reaction because of its apparent simplicity and high efficiency. The precise nature of the zeolite used has a profound effect on the course of this reaction (Table 1). The silica-bonded Silicalite (*43*) appeared to be the best of these catalysts with respect to both piperazine conversion as well as efficiency to TEDA. Many other zeolites were tested and found to be poor. Phosphating (*12*) does not seem to result in an improved catalyst; the use of alumina as bonding agent decreases both activity as well as selectivity. Pure, amorphous silica was completely inactive; yet, when this was doped with aluminum cation, a catalyst with poor activity/selectivity was obtained. The inactivity of the amorphous silica is also mirrored in the inactivity of a substantially Al-free Silicalite (*43*) (Si/Al ~23,000, Fig. 1). Framework aluminum (T_d) derived H^+ is definitely the catalytic agent for this amine transformation reaction.

The use of alumina as a bonding agent for the pentasil (Silicalite) resulted in a relatively poor catalyst, both with respect to activity and selectivity. Other investigators (*44*) have also observed that alumina-bonded, high silica zeolites have activities differing from silica-bonded catalysts. The reason for this may be due to the migration of aluminum from the binder into the zeolite structure during the heating period (~450–600°C) thereby changing the catalytic character of the zeolite. The inverse has also been observed (*45*). Alumina itself does not appear to be a good catalyst for the piperazine-to-TEDA reaction (*46*).

The clear superiority of the H^+ pentasil structure prompted an examination of the effect of its Si/Al ratio on this reaction; the results are illustrated in Fig. 1. The best activity was obtained at a Si/Al ratio of ~200 with a steep drop in activity on either side of this peak. If a pentasil with a Si/Al >800 or <50 had been tested, then a catalyst with only modest activity would have been found. Testing of zeolites for their catalytic properties must always be carried out over a wide range of Si/Al ratios in order to spot these maxima.

This finding is not novel. Theoretical work (*36, 37*) predicted a structure dependent catalytic activity varying with Si/Al ratio for reactions catalyzed by strong acid sites. Table 2 lists a number of such reactions, the Si/Al ratios of the activity maxi-

TABLE 1

Effect of the Zeolite Nature on the Piperazine-to-TEDA Reaction[a]

Catalyst nature	Si/Al (atom ratio)	Piperazine conversion[f] (%)	Efficiency to TEDA[f] (%)
H$^+$-Silicalite[b], SiO$_2$-bonded	87	20.5	93
H$^+$-Silicalite + 0.3% PO$_4$≡[c]-bonded	87	19.0	93
H$^+$-Silicalite + 0.5% PO$_4$≡[c]-bonded	87	14.7	88
H$^+$-Silicalite-Al$_2$O$_3$-bonded	87	16	83
SAPO-11 (Ref. (*3*))-Al$_2$O$_3$-bonded	—	3.4	~50
SAPO-41 (Ref. (*3*))-Al$_2$O$_3$-bonded	—	9.2	84
Faujasite Al$_2$O$_3$-bonded	—	<10	~40
Amorphous SiO$_2$[d]		0	—
Amorphous SiO$_2$[d] + 0.8% Al[e]		8.2	80

[a] Reaction conditions: 35 wt% aqueous piperazine feed, 350°C, ~80 g/hr, 100 cm^3 catalyst.

[b] High Si/Al H$^+$-pentasil zeolite (43).

[c] Impregnated with varying amounts of aqueous $(NH_4)_2HPO_4$ and heated to 450°C. ^{31}P-ss-NMR shows the phosphorus to be present as amorphous AlPO$_4$.

[d] Fuji-Davison Cariact-10; $\frac{1}{8}$-in spheres, ~250 m^2/g surface area, 200-Å pores amorphous SiO$_2$, <100 ppm Al.

[e] The above (see footnote *d*) was impregnated with aqueous Al(NO$_3$)$_3$ and heated at 450°C. ^{27}Al-ss-NMR shows only octahedral aluminum.

[f] From area–wt% correlations.

mum and the H$^+$-zeolite structure. The hexane cracking reaction appears to be an exception; the activities increased continuously with decrease in Si/Al ratio. It is not clear whether this Si/Al phenomenon is dependent on the zeolite structure, or on the specific reaction or on a combination of these variables and possibly some others.

The concentration of the water, co-fed with the piperazine, has a remarkable effect on the rate of conversion to TEDA. Figure 2 is a plot of the first-order rate constant of this reaction vs the piperazine concentration in the aqueous feed. The rate constant drops dramatically with increase of the piperazine concentration and appears to extrapolate

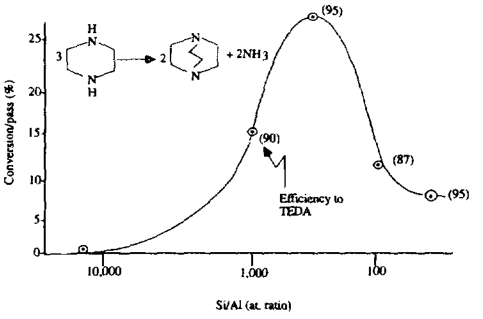


FIG. 1. Piperazine conversion/pass (%) vs. Si/Al (at. ratio; pentasil zeolite). Reaction conditions were the same as in Table 1.

TABLE 2

Dependence of Reacion Rate Maxima on Si/Al Ratios of Various H$^+$-Zeolites

Reaction	H$^+$-zeolite structure[a]	Si/Al ratio at maximum rate	Reference
Hydrolysis of ethyl acetate	MOR, MFI	20	(*40*)
Hydration of butene-2	MOR	8	(*38*)
Isomerization of *o*-dichlorobenzene	MOR	9	(*41*)
Isomerization of *o*-dichlorobenzene	BETA	~9	(*42*)
Hexane cracking	MOR, Y, MFI	All >10	(*39*)
Piperazine to TEDA	MFI	~200	This investigation

[a] For structural details, see (3).

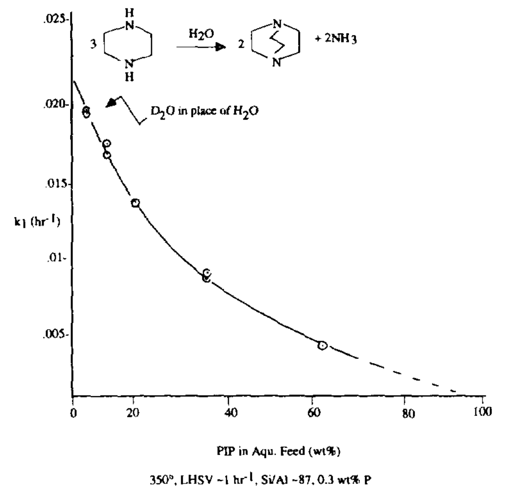


FIG. 2. Effect of water concentration in piperazine feed on reaction rate constant.

smoothly to zero at 100% piperazine. There appears to be no substantial deuterium effect upon replacement of the H_2O with D_2O.

Table 3 summarizes the results which were obtained when aqueous solutions of ethylenediamine or its oligomers were used as feeds. Under the particular conditions used here, piperazine (35 wt% aqueous) resulted in about 16 area% TEDA with 82% piperazine unconverted and very minor amounts of by-products. Ethylenediamine gave a 37% conversion to TEDA, 50% to piperazine with only 3.5% unconverted starting material. This molecule reacts much faster, to its cyclic products, than does piperazine; a mixture of ethylenediamine and piperazine (1 : 1 mole ratio) showed similar characteristics. Diethylenediamine is faster than piperazine yielding 36% piperazine, 25% TEDA, and 16% ethylenetriamine; 96% of the feed was converted to products. The diethylenetriamine cleaved and reassembled, to form *N*-(2-aminoethyl)piperazine (~15%). The use of the linear trimer of ethylenediamine also resulted in a product spectrum similar to that of the diethylenetriamine: ~18% ethylenediamine, ~17% piperazine, 15% TEDA, and 15% of the *N*-(2-aminoethyl)-piperazine at an approximately 92% conversion. The use of tris(2-aminoethyl)-amine gave mostly piperazine (75%), almost no ethylenediamine and a poor yield of TEDA (~14%). *N*-(2-aminoethyl)piperazine, contrary to expectations, resulted in little piperazine (14%), no ethylenediamine, 24% TEDA, and 58% of the starting material was recovered. In all cases, small quantities of ethylamine (0–5%) and pyrazine (.5—2%) were formed as well as *N*-ethylpiperazine (~1%). The use of an aqueous TEDA feed, with or without co-fed ammonia, resulted in a quantitative recovery of the starting material; TEDA is a stable product under these reaction conditions.

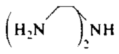
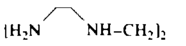
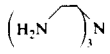
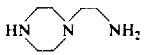
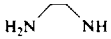
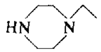
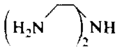
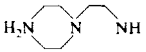
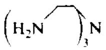
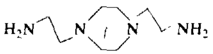
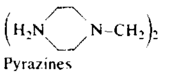
Figure 3 illustrates these results: the linear ethylenediamine oligomers are in rapid equilibrium with each other (excepting the *N*-(2-aminoethyl)piperazine) and are converted rapidly to piperazine. The latter reacted irreversibly to form mostly TEDA (the thermodynamic sink), small quantities of pyrazines and alkylated pyrazines, as well as the reductive cleavage product(s) ethylamine and ammonia, and small amounts of methylamine, while nominally consuming hydrogen. The deliberate addition of hydrogen to the feed did not increase the amount of cleavage products, nor decrease the pyrazine(s) formation. Hence, these products probably do not involve the generation or consumption of molecular hydrogen. The formation of cleaved products, pyrazines, piperazine, and TEDA from ethylenediamine and its oligomers was observed previously in alumina catalyzed reactions (*46*) and a European patent application was published after the completion of this work (*29*).

Table 4 summarizes in greater detail the reaction products of aqueous piperazine over the Si/Al-87 H^+-pentasil zeolite. These products result from a number of general reactions:

- The reductive cleavage of C–C and C–N single bonds yields methyl and ethylamine, as well as the *N*-ethyl and *N*-methylpiperazines.

TABLE 3

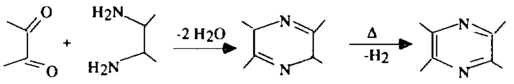
Reaction of Various Ethylenediamine Oligomers over Si/Al-87 H^+-Pentasil[a]

Reagent	Piperazine	Ethylenediamine	PIP + ED[b] (1 : 1 mole)				
Feed (wt%)							
Reagent	35	32	23.6 PIP 16.4 ED	40	33	35	40
Water	65	68	60	60	67	65	60
Rate (g/hr)	70	64	75	81	84	80	65
Product (area%)							
CH_3CH_2NH	.15	1.3	.9	1.1	.6	5.3	.22
	.18	3.5	5.8	16.3	17.8	1.3	.0
Piperazine	81.8	50.2	66.0	36.2	16.8	75.3	13.6
	.92	.86	1.0	1.1	.85	1.4	
TEDA	15.9	37.3	23.6	25.3	15.3	13.6	24.0
				3.4			
	.17		1.7	15.3	15.3	.1	58.2
						.1	
					4.6		
					8.3		
Pyrazines	.63	2.08	.83	2.2	.6	.96	.54

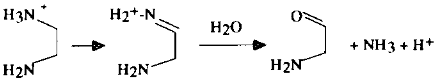
[a] 350°C, 100 ml catalyst containing 0.3% P; when aqueous or NH_4OH containing TEDA was fed, then there was a 100% recovery, therefore, no reaction.

[b] PIP = Piperazine, ED = ethylenediamine.

- The piperazine and traces of ethylenediamine oligomers are due to the acid catalyzed amine disproportionation reactions (*33*).
- The pyrazines are mostly the alkylated (*R* = Me, Et) materials, very little pyrazine itself is observed. The precise origin of these heterocyclics is not clear. The classic method(s) for pyrazine synthesis involve the reaction of diketones or aldehydes with appropriate diamines, which give the diazines:



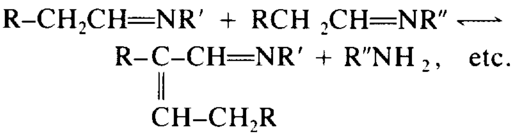
The latter are readily oxidized (by air (*47*)) to the pyrazines. In this case, it is proposed that ethylenediamine, or its oligomers dehydrogenate to an imine (ethanol has been shown to dehydrogenate to acetaldehyde over a Si/Al ~400°C pentasil (*48*)),



which hydrolyzes to the aldehyde-amine and this, in turn, condenses with itself to form the diazine, etc. The azines can also undergo amine-H$^+$ disproportionation reactions,

$$RCH = NH + R'NH_2 \rightarrow RCH = NR' + NH_3, \quad \text{etc.},$$

or they can C-alkylate (*49*),

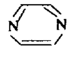
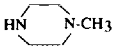
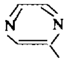
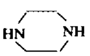
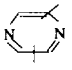
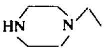
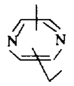
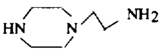


$$R{-}CH_2CH{=}NR' + RCH_2CH{=}NR'' \longleftrightarrow \underset{\substack{\| \\ CH-CH_2R}}{R{-}C}{-}CH{=}NR' + R''NH_2, \quad \text{etc.}$$

It is not clear why so many multiply alkylated pyrazines make their appearance. Obviously, some of the methyl and ethyl groups could originate from alkylation and the reductive cleavage reaction chemistry.

TABLE 4

Typical Reaction Product Composition

Product	%
CH_3NH_2	.09
$CH_3CH_2NH_2$	.28
$H_2NCH_2CH_2NH_2$	.16
	.07
	.09
	.05
	76.4
	~.2
	~.8
	~.1
	20.6
	~.06

Note. Si/Al = 87, 0.3 wt% P, 35% aq. PIP, 350°, LHSV ~0.8 hr^{-1}

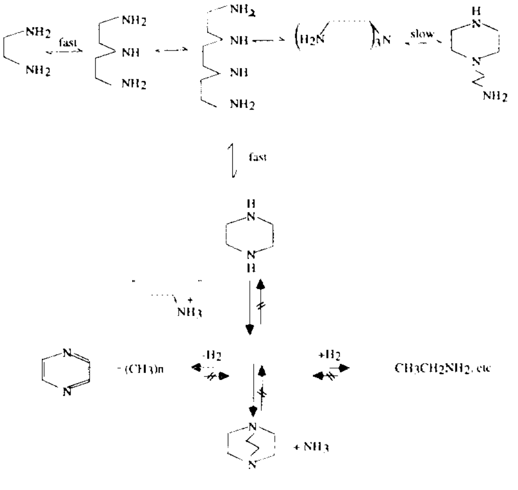


FIG. 3. Reaction paths of the conversion of ethylenediamine and its oligomers to TEDA.

TABLE 5

Effect of Co-fed Oxygen on the Piperazine-to-TEDA Reaction[a]

Co-fed oxygen (mole O_2/mole Piperazine)	0.0	0.37	0.86
Products (area%)			
CH_3NH_2	.12	1.8	3.1
$CH_3CH_2NH_2$	.15	0.12	1.1
Ethylenediamine	.12	1.9	9.3
Pyrazines	0.47	17.1[b]	18.5[b]
Piperazine	78.7	59.3	50.5
TEDA	19.1	8.7	0.2

[a] 350°C, 35% aqueous piperazine, ~70 g/hr, H^+-Pentasil Si/Al ~87, 0.3% P.

[b] Pyrazine was about 40% of this mixture.

Aldol reactions of the aldehyde(s), etc., could also contribute, as well as alkylation of the presumed azine intermediates. It is exceptionally difficult to examine this chemistry in detail due to the labile nature of the intermediates and the difficulty of examining reaction mechanisms which proceed inside a 5.5-Å catalyst pore.

A remarkable change takes place when oxygen is co-fed with the aqueous piperazine (Table 5). Under conditions where, in the absence of oxygen, 19% TEDA is formed, virtually no TEDA makes its appearance when 0.86 mole O_2 is added (per mole of piperazine). The reductive cleavage reaction increases from about 0.3% methyl- and ethylamines to 4.2% and the formation of ethylenediamine rises from 0.1 to 9.3%. The consumption of piperazine also increases considerably. Pyrazine and alkylated pyrazines are now the major part of the product stream. This unexpected change may well be due to an oxygen driven shift in the equilibrium,

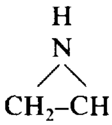
$$-CH_2NH_2 \xrightarrow[-H_2]{H^+} -CH{=}NH \xrightarrow{H_2O} -\overset{\overset{\displaystyle O}{\|}}{C}H, \quad \text{etc.,}$$

which simply reroutes the usually very efficient piperazine to TEDA reaction into the pyrazine(s) direction. The reason for the relatively large amounts of methyl- and ethylamines and especially ethylenediamine are unknown.

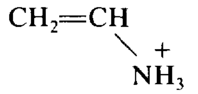
The H^+-pentasil catalyzed reactions of light paraffins to aromatics is also strongly affected by co-feeding oxygen (*50*). The formation of aromatic products (BTX), when oxygen and propane were reacted, is strongly enhanced, presumably due to the scavenging of hydrogen.

Proposed Piperazine-to-TEDA Reaction Mechanism

Figure 3 is an overall flow sheet of the ethylenediamine–piperazine–TEDA, etc., reaction course. Subsequent to the ethylenediamine oligomerization(s), the irreversible formation of TEDA, the reductive cleavage products and the various pyrazines takes place. Clearly, this is not a simple set of reactions. An attempt was made to gain a better understanding of the piperazine to TEDA reaction. In order for this reaction to proceed, piperazine must cleave into the elements of "C_2H_2" (not acetylene) and ammonia, and the "C_2H_2" is reattached to another piperazine molecule to yield TEDA. Acetylene is an unlikely intermediate since its co-feeding with aqueous piperazine resulted in no material changes in the reaction products. It is suggested that either aziridine (*51*),

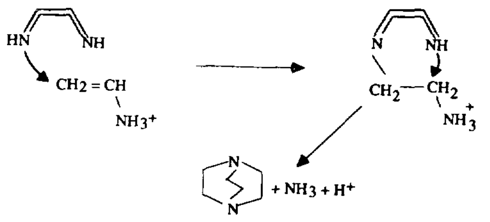


or, more likely, the protonated vinyl amine (*52*),



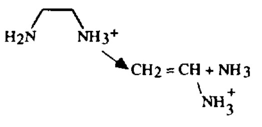
$$CH_2{=}CH\overset{+}{N}H_3$$

is the unstable cleavage product of piperazine which subsequently reacts with more piperazine to yield TEDA and ammonia. The reaction is visualized as a Michael-type addition across an activated carbon–carbon double bond (*53*):



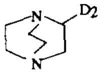
The evidence, while not compelling, is reasonable:

- The increase in the reaction rate constant (Fig. 2) with increased dilution in water is suggestive of solvation of a very polar transition state, e.g., the piperazine-protonated vinylamine. Solvation of such a system should greatly aid the reaction rate.
- Ethylenediamine reacts much more rapidly to form piperazine and eventually TEDA than does piperazine itself (Table 3). This may be due to the greater ease of ammonia loss in the case of ethylenediamine, than the break-up of the stable piperazine ring to form this intermediate,

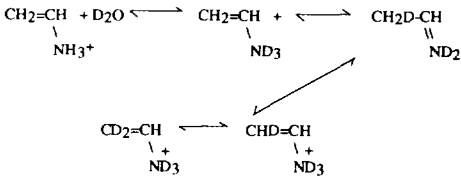


than the break-up of the stable piperazine ring to form this intermediate.

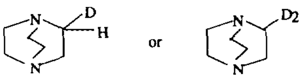
- The use of D_2O in place of H_2O (Fig. 2) results in deuterated TEDA, but not more than two deuterium atoms per TEDA molecule and both are on the same carbon atom:



The total deuterium incorporation is small, about 20–30 times the natural deuterium background concentration. This can be rationalized by H–D exchange of the protonated vinylamine (probably a slow reaction),

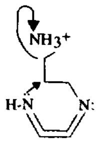


which reacts with piperazine to give mono- or dideuterated TEDA:



This H–D exchange of the vinylamine is similar to enol hydrogen exchange in ketones or aldehydes (*54*).

A most logical alternate path would be the reaction of *N*-(2-aminoethyl)-piperazine to ring close to TEDA with loss of ammonia:



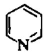
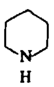
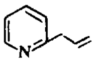
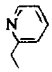
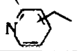
At first glance, this appears to be a very interesting alternative, except that (Table 3) this molecule reacts much slower than even ethylenediamine to form TEDA and molecular modeling shows that the proposed transition state would involve an assembly of about 7–8 Å in diameter, while the pentasil pores are only 5.4 Å. Geometrically, this is therefore an unlikely event and probably rules out this reaction path.

Reaction Paths of Other α-ω-Diamines

Table 6 summarizes the results which were obtained when the higher α-ω-diamines ($H_2N(CH_2)_nNH_2$, n = 3–7) were reacted, as aqueous solutions, over the Si/Al ~87 H^+-pentasil zeolite. The 1,3-propanediamine proved to be very reactive. At 350°C and LHSV ~0.8, there was a 98%

TABLE 6

Reaction Products from α-ω-Diamines $H_2N(CH_2)nNH_2$ (n = 3–6)[a]

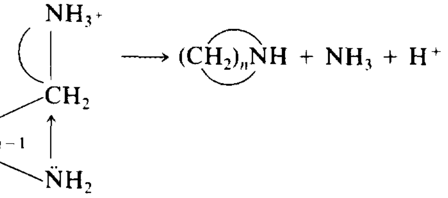
Feed	35% Aqueous $H_2N(CH_2)_3NH_2$	35% Aqueous $H_2N(CH_2)_4NH_2$		35% Aqueous $H_2N(CH_2)_5NH_2$		35% Aqueous $H_2N(CH_2)_6NH_2$		35% Aqueous $H_2N(CH_2)_7NH_2$	
Feed Rate (g/hr)[a]	80	80		80		78		77	
Reaction Temp. (°C)	350	400		275		375		350	
Product Analyses (Area %, Organics Only)									
CH_3NH_2	11.6			CH_3NH_2	.02	CH_3NH_2	.03	CH_3NH_2	.15
$CH_3CH_2NH_2$	32.5	$CH_3CH_2NH_2$	.08	$CH_3CH_2NH_2$	.07	$CH_3CH_2NH_2$	.09	$(CH_2)_7NH$	1.63
$CH_3CH_2CH_2NH_2$	trace					$(CH_2)_6NH$	22.1	$H_2N(CH_2)_7NH_2$	96.2
								Unknown	1.4
$CH_2{=}CHCH_2NH_2$	4.19	$H_2N(CH_2)_4NH_2$	98.2						
	8.01				13.9	$H_2N(CH_2)_6NH_2$	74.0		
	1.21			$H_2N(CH_2)_5NH_2$	82.9				
	1.60		1.23						
	15.7								
	5.3								
	.42								
	4.22								

[a] Using Si/Al = 87 H^+ Pentasil + 35% aqueous solution.

conversion to form products which were due to two reactions previously encountered: C–N and C–C reductive cleavage products as well as aromatic compounds (pyridine and variously alkylated pyridines). About half of the reaction products were methyl- and ethylamine with a trace of n-propylamine. The other half was pyridine (8%) and various methyl- and ethylpyridines. The origin of these pyridines is probably the result of the same chemistry which generated the pyrazines: dehydrogenation to imines, hydrolysis to the aldehyde, aldol condensations, etc. The large amounts of only alkyl substituted pyridines and C–C, C–N cleavage products (no $-CH_2NH_2$ substituted pyridines were observed) again show how important the reductive cleavage reaction is in this chemistry. Some allylamine was observed (4.2%) which can arise only from ammonia elimination.

1,4-butanediamine unexpectedly proved to be almost completely unreactive even at 400°C. The reductive cleavage reaction was virtually absent, no cyclization to tetrahydropyrrole was observed and about 1% of a pyridine compound appeared to be present.

The 1,5-, 1,6-, and 1,7-diamines had widely differing reactivities (C5 ≫ C6 > C7). The products were almost exclusively the cyclic secondary amines,



(n = 5, 6, 7),

with almost no reductive cleavage, ammonia elimination, or aromatic products present.

TABLE 7

Reaction Products of 1,3-Propane-diamine and 3-Amino-1-propanol[a]

	Reagent	
	$H_2N(CH_2)_3NH_2$	$H_2N(CH_2)_3OH$
Starting material reacted (%)	88	98
Products (area%)		
Reductive cleavage (CH_3NH_2, $CH_3CH_2NH_2$, $n\text{-}C_3H_7NH_2$)	38	45
Loss of NH_3 or H_2O (Allylamine or allylalcohol)	11.5	4
Aromatics (Pyridines)	29	35
Pyridine	11	8
3- or 4-Methylpyridines	14	16

[a] Si/Al ~87, 0.3 wt% P, ~35% aqueous feed solutions, LHSV ~0.8 hr^{-1}, 350°C. The gas chromatographic method could not separate 3- from 4-methylpyridine.

Table 7 compares the product spectrum of 1,3-propanediamine with that of 3-amino-1-propanol. In both cases, the reagents proved to be highly reactive forming products which were very similar: Reductive cleavage products leading to methyl, ethyl, and *n*-propylamines amounted to 38 and 45%; the loss of ammonia or water resulted in allylamine or allyl alcohol (11.5 and 4%, respectively), while the pyridines were 29 and 35%, respectively.

Table 8 summarizes the reactions of these α-ω-diamines by reaction class: reductive cleavage, aromatics, cyclization, elimination. The $n = 5,6,7$ have widely differing activities but by only one reaction path (intramolecular elimination to the cyclic secondary amine). The $n = 4$, oddly enough, proved to be totally unreactive even at 400°C. The $n = 2$ and 3 had roughly similar chemistry but widely differing product spectra.

Attempts were made using the Textronic CACHE system to apply molecular mechanics to the wide variety of chemistries uncovered here which proceed within the confines of a 5.4-Å MFI channel, or the slightly larger intersections. It could be demonstrated that the ring closure of the *N*-(2-aminoethyl)-piperazine to yield TEDA is unlikely and hence another geometrically less demanding route is required. The complete inactivity of the 1,4-butanediamine as contrasted to the relative ease of cyclization of the 1,5- → 1,7-diamines is a puzzle as are the C–C and C–N cleavage reaction(s) of the 1,2 and 1,3 systems.

TABLE 8

Comparison of the α-ω-Diamines by Reaction Products Class[a]

	$H_2N(CH_2)nNH_2$ (n =)					
	2	3	4	5	6	7
Reaction temp. (°C)	350	350	400	275	375	350
Activity (conversion of starting material, %)	97	88	~1	17	26	4
Reductive cleavage (to CH_3NH_2,$CH_3CH_2NH_2$, etc.)	1.3	38	0	.1	.1	0
Aromatics	2	29	0	0	0	0
Cyclization	87[b]	0	0	14[c]	22[c]	2[c]
Elimination ($-NH_3$, $-H_2O$)	—	12	0	0	0	0

[a] Using Si/Al ~87, as ~35% aqueous feed, LHSV ~0.8 hr^{-1}.

[b] To piperazine and TEDA.

[c] To $(CH_2)nNH$, n = 5, 6, 7.

SUMMARY

It has been shown that the α-ω diamines $H_2N(CH_2)_nNH_2$ (n = 2–7) at 350–400°C in the presence of excess steam, undergo surprisingly different reactions. When n is two (ethylene diamine) the stable, terminal product is TEDA in high efficiency (~90%), with small quantities of alkyl pyrazines and the cleavage products methyl and ethylamine as minor coproducts. Ethylenediamine oligomers and, principally, piperazine are the reactive, isolable intermediates. When oxygen is coinjected, the reaction products are almost exclusively the alkyl pyrazines. The silica bonded, H^+ – MFI structure appears to be optimum for the piperazine-to-TEDA reaction when the Si/Al is about 200. Other zeolite structures and particularly alumina bonded catalysts are not as useful.

When n is 3 (1,3-diaminopropane), about half of the products are alkyl pyridines and the balance the cleavage products methyl and ethylamine. When n is 4, even at 400°C, there is virtually no reaction. When n is 5, 6, or 7, only the cyclic, secondary amines and ammonia are the reaction products.

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