The Reactions of Amine, Polyamine and Amino Alcohol Corrosion Inhibitors in Water at High Temperature

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A stainless steel reactor has been used to investigate the reactions of mono-, di-, tri- and tetra-amines, amino alcohols and amino ethers in degassed aqueous solution at 240–300 °C. The predominant reactions involved nucleophilic substitutions, where the amino nitrogen acts as the nucleophile, and not solvolyses. With α,ω-diamines, cyclic and bicyclic amines were formed by inter- or intra-molecular processes. Amino alcohols react by displacement of the hydroxy rather than the amino group. The material balance deficit, however, was generally significant, and it is suggested that the missing materials are polyamines arising from polymerisation that competes with cyclisation. The major product from 1,2-diaminoethane and related polyaminoethanes and ethanolamines is diazobicyclo[2.2.2]octane.

The kinetics of some of the cyclisations were studied. Reactions of α,ω-diamines and 5-aminopentan-1-ol are first order in reactant. Conversion of 1,4-diaminobutane to pyrrolidine occurs with high selectivity at 240 °C; in contrast the reactions of the less reactive compounds were less selective, probably due to the formation of polymeric materials. The relative reactivity of the substrates is discussed in detail.

Steam–water cycling is used extensively in the chemical and power industries to transfer energy, for example, to drive turbines. In these systems it is crucial that the water used is of a high purity and free from dissolved oxygen and carbon dioxide to prevent potentially catastrophic corrosion of the mild steel equipment. The majority of the oxygen is removed by passing the water through a deaerator [1] and its concentration is reduced still further by the addition of a chemical scavenger such as hydrazine,[2] reaction (1). Acceptable oxygen levels for high

$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O \qquad (1)$$

pressure steam generators are typically < 5 ppb (5 μg dm^{-3}).[1b]

Volatile water-soluble amines are now frequently added to neutralise the carbonic acid [1b] formed from residual carbon dioxide and to provide a basic environment (pH ~ 9.0) thereby preventing acid corrosion by maintaining a passive magnetite oxide layer on the mild steel surfaces. Selection of suitable amine corrosion inhibitors depends on their distribution between the steam and water phases,[3] pK_a at operating conditions and thermal stability in water at the high temperatures now used in steam generation. The distribution coefficient should be such that the inhibitor is present in the vapour and liquid phases throughout the system. A number of amines have been used or proposed for use as corrosion inhibitors including ammonia,[4] morpholine,[4,5] 2-amino-2-methylpropan-1-ol (AMP),[4b,c,5c] cyclohexylamine,[4a,5c–f,6] piperidine,[4b,c,5d] *N,N*-diethylaminoethanol [5b,c] and 2-dimethylamino-2-methylpropan-1-ol.[5c] Ammonia is considered to be too weakly basic[4b,c] and it cannot be used in systems that contain copper surfaces owing to the formation of ammonia-containing complexes that provide a facile corrosion mechanism. Although morpholine and AMP are the most widely used, the former is not sufficiently basic for modern high temperature boiler systems and both are known to decompose under the vigorous operating conditions.[4c,7]

It is surprising that despite the technical importance of amine corrosion inhibitors, very little is known about their organic chemistry at high temperature in water. This, combined with the need to find new corrosion inhibitors, has led us to study the behaviour of a selection of amines, polyamines and amino alcohols at high temperature in aqueous solution. In this paper we report how the structure of the amine influences its chemical stability and the reactions that occur.

Results

Method.—Experimental methods for handling aqueous reaction mixtures at high temperatures and pressures were devised to reproduce the conditions typically found in a plant boiler system. The initial reactions were carried out in sealed stainless steel or glass tubes heated in a muffle furnace at 300 ± 20 °C. Although adequate for reactions in the presence of air, they could not be used reliably with deoxygenated solutions. Thus, the mixtures in stainless steel tubes, connected to a rotary oil pump *via* a valve, were degassed with four or five freeze–thaw cycles. However, neither a bellows valve (Nupro SS-4BG) nor a packed autoclave valve (Autoclave Engineering 10V-4071 TG) could withstand the repeated extremes of temperature (−196 to 300 °C) and pressure (10^{-2} mbar to 100 bar) and, as a result, deoxygenation with each failed after a few experiments, with valves leaking at either high or low temperatures. The freeze–thaw procedure also produced stress in glass tubes such that often they could not withstand the high pressures generated during the reaction at 300 °C. They could only be used safely at a maximum of 240 °C. A further problem arose from a white solid (probably silica) which was leached out of the glass during the reaction.

To overcome the difficulties described above a cylindrical, stainless steel, sampling reactor was designed and built (Fig. 1). This could be placed in a furnace and heated to the desired temperature ± 2 °C, or it could be connected to a vacuum line. The latter was used to remove air from the reactor and to introduce the degassed reaction mixture into the reactor. The pressure during reaction allowed samples to be removed *via* a thin coiled stainless steel tube and valve. The small internal volume of the sampling tube and valve ensured that the dead volume of material, which required flushing in taking sequential

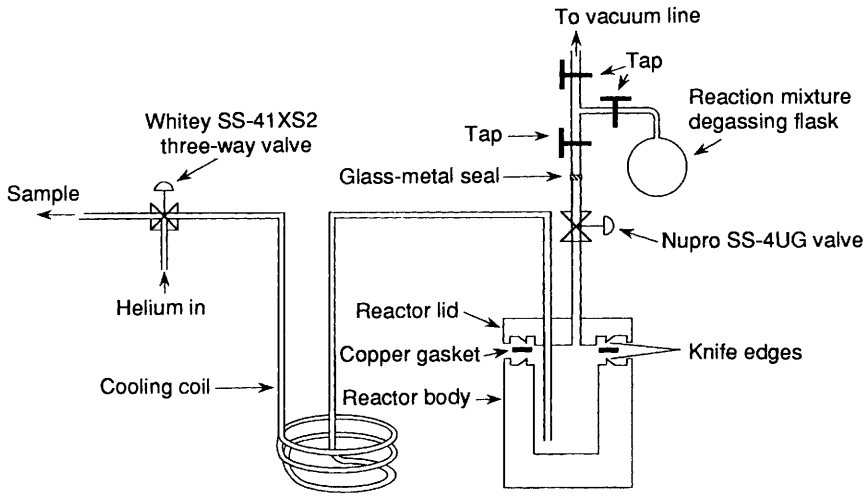


Fig. 1 Schematic cross-section through the sampling reactor

samples, was kept to a minimum. In reactions where no sampling was required the tube was replaced by a length of stainless steel rod.

Reaction Conditions.—The reactions were carried out with 1% (w/v) solutions of amine substrates in water. Although *ca.* 400 times more concentrated than amine solutions typically used in steam–water cycles, the higher concentration was chosen to facilitate product identification and quantification. All reaction mixtures were degassed and analysed, after 15 h, by gas chromatography and GC-MS, unless otherwise stated.

Reactions of α,ω-Diamino Alkanes.—Diamines of the general structure $H_2N(CH_2)_nNH_2$ (n = 2–7) gave the products and yields shown in Table 1. Two methylated analogues, *N,N'*-dimethyl-1,6-diaminohexane and 2,5-diamino-2,5-dimethylhexane were also investigated. In all the reactions, except those of 1,2-diaminoethane, 1,3-diaminopropane and 1,7-diaminoheptane, an intramolecular cyclisation to give an alicyclic monoamine was observed. With the short chain diamines, neither aziridine or azetidine was detected and instead six-membered cyclic amines involving at least two molecules of substrate were formed. 1,7-Diaminoheptane was consumed under the reaction conditions but no products were detected. 2,5-Diamino-2,5-dimethylhexane gave two major products, 2,2,5,5-tetramethylpyrrolidine and an aminoalkene, assigned the structure 5-amino-2,5-dimethylhex-2-ene, in approximately equal amounts.

Reactions of Polyamines and of an α,ω-Diamino Ether.—The products from the reactions of the polyamines and 2,2'-oxybis(ethylamine), carried out under the same conditions as the α,ω-diaminoalkanes are shown in Table 2. The diamino ether, the homomorph of 1,5-diaminopentane, gave the expected cyclised compound, morpholine together with other unidentified minor products. Monitoring the reaction at various times showed that morpholine was the only detectable product in the initial stages, and that other compounds only appeared later in the reaction. By contrast the nitrogen analogue did not give detectable amounts of the expected piperazine, but rather the major product was diazobicyclo[2.2.2]octane (DABCO). DABCO was also the major product from tris(2-aminoethyl)amine and 1-(2-aminoethyl)piperazine. The unsymmetrical triazine *N*-(3-aminopropyl)-1,4-diaminobutane (spermidine) gave a complex mixture of products containing mainly pyrrolidine and *N*-methylpyrrolidine with small amounts of other compounds.

Reactions of Amino Alcohols.—5-Aminopentan-1-ol when heated in degassed water gave only piperidine (Table 3); no tetrahydropyran was detected. The analogue, pentane-1,5-diol, when heated under the same conditions was unreactive. However, in air the diol gave tetrahydro-2*H*-pyran-2-one (δ-valerolactone) as the major product whereas the amino alcohol gave piperidine and not piperidin-2-one (δ-valerolactam). The major product from reacting ethanolamine or diethanolamine in degassed aqueous solution was DABCO and the minor products were largely piperazines, although diethanolamine also gave a small yield of ethane-1,2-diol and 4-(1-hydroxyethyl)morpholine (Table 3). Ethanolamine did not give diethanolamine or any morpholine derivatives.

2-Amino-2-methylpropan-1-ol was subject to extensive degradation when heated in degassed water at 300 °C, for apart from 2-methylpropanal, 2-methylpropionic acid and 2-methylpropionamide, methanoic acid and three unidentified major products were obtained.

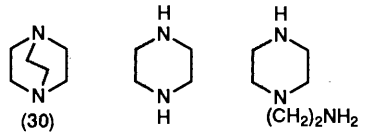
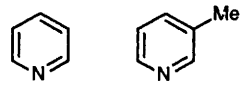
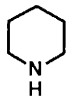
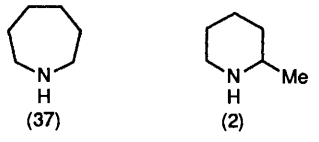
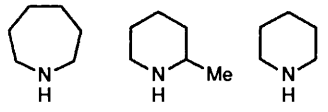
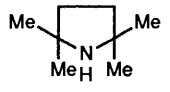
Reactions of Monoamines.—Five alicyclic secondary monoamines were heated in degassed water at 300 °C for 48 h (Table 4). Although mass balances for these reactions were not 100%, only hexamethyleneimine and morpholine gave any detectable products. The former rearranged to 2-methylpiperidine and the latter was extensively degraded to give at least fourteen products including 4-methyl-, 4-ethyl- and 4-acetyl-morpholine.

Three primary amines, 1-aminohexane, cyclohexylamine and 2-amino-2-methylbutane, were also subjected to the reaction conditions for 48 h. No products were obtained from the *n*-alkylamine although hex-1-ene, a possible product, would have been detected. Cyclohexylamine gave traces of cyclohexanol and cyclohexanone but no cyclohexene, and 2-amino-2-methylbutane gave a trace of a volatile product that could have been 2-methylbut-2-ene.

Material Balance Deficit.—Although some 'missing material' might arise from sample manipulation and errors inherent in the analytical techniques, the results in Tables 1–4 show that material balance deficit was commonly 40% or more. Duplicate reactions showed these losses to be repeatable. The loss of materials by adsorption on the reactor surfaces was shown to be unlikely. Thus, when the reaction of hexamethyleneimine (48 h) was followed by heating water in the same reactor, without cleaning of the metal surfaces between the two experiments, no significant quantity of organic material was detected in the water after heating for 15 h.

It is noteworthy that for the reaction of 1,4-diaminobutane

Table 1 Products from the reactions of diamines in degassed aqueous solution at 300 °C after 15 h

Substrate	Products (yield, %)[a]	Material balance deficit (%)[b]
$H_2N(CH_2)_2NH_2$	 (30) + minor products	<70
$H_2N(CH_2)_3NH_2$		nd[c]
$H_2N(CH_2)_4NH_2$	(62)	38
$H_2N(CH_2)_5NH_2$	 (86)	14
$H_2N(CH_2)_6NH_2$	 (37) (2) $H_2N(CH_2)_6OH$	13
$H_2N(CH_2)_7NH_2$	none detected	nd[c]
$MeNH(CH_2)_6NHMe$	 $MeNH_2$	39
$Me_2C(CH_2)_2CMe_2$ (NH$_2$, NH$_2$)	 nd[c,d] $Me_2CCH_2CH{=}CMe_2$ (NH$_2$) nd[c,d]	nd[c]

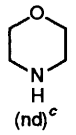
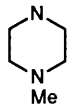
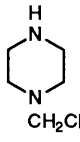
[a] Products formed in trace amounts where yields not indicated. [b] Initial amount of substrate used minus the sum of the yields of products and recovered substrate as a percentage. [c] Not determined. [d] GC peak areas suggest these products were formed in approximately equal quantities.

material balance deficit is temperature dependent. Thus, when an aqueous solution of this diamine was heated for 6 h at 240 °C conversion to pyrrolidine was almost complete. By contrast, heating at 300 °C for 15 h resulted in complete loss of substrate with only 62% yield of pyrrolidine. Furthermore, heating pyrrolidine for 48 h at 300 °C also leads to loss of material (32%) without the formation of GC-detectable products. The missing material is presumed to be mainly polyamine polymers.

Kinetics of Cyclisation of α,ω-Diaminoalkanes and 5-Aminopentan-1-ol.—The kinetic studies were potentially complicated by the distribution of the substrate and product between the liquid and vapour phases in the reactor. Removal of aliquots of the liquid for analysis leads to an increase in volume of the gaseous phase and a consequent redistribution of the amines between the phases. Thus, even without reaction, removal of liquid samples from the reactor will lead to changes in the concentration of substrate in the aqueous phase. Since the distribution coefficients (K_V) of the amines (where $K_V = [\text{amine}]_{\text{vapour}}/[\text{amine}]_{\text{liquid}}$) are neither known nor trivial to measure, we calculated the magnitude of their influence on the results using K_V values between 0 and 2.0. This shows that the problem can, to a first approximation, be ignored. Thus, for a reactor volume of 50 cm^3 removing 10 g of liquid phase from an initial aqueous solution of 3×10^{-3} mol amine in 30 g water, after re-equilibration between liquid and vapour phases, results in <4% change in the amine concentration in the liquid phase.

The change in concentration of substrate and the cyclised product with time was monitored for the reactions of 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane, *N,N'*-dimethyl-1,6-diaminohexane and 5-aminopentan-1-ol. There were large differences in their rates of cyclisation and the reactions of 1,4-diaminobutane and 1,5-diaminopentane were too fast at 300 °C to obtain sufficient data for kinetic analyses. The reaction of the former diamine was complete within 1 h at 300 °C. These two substrates were reacted at lower temperatures, 240 and 260 °C, respectively. Only in the reaction of 1,4-diaminobutane did the sum of the concentrations of substrate and product remain constant throughout the reaction; this cyclisation followed first-order kinetics for both substrate loss and product formation with a rate constant of $1.80 \pm 0.12 \times 10^{-4}\ s^{-1}$ at 240 °C. With the other amines, the material balance deficit increased as the reactions progressed, although excellent first-order rate plots were generally obtained for loss of the substrate amine over 90% of reaction. Only for 1,6-diaminohexane did the plot of ln [amine substrate] *vs.* time deviate from linearity (increasing rate) towards the end of the reaction (after ~1.6 half-lives). Two typical rate plots are shown in Fig. 2. Derived first-order rate constants for four α,ω-diamines and that for 5-aminopentan-1-ol are given in Table 5. Very preliminary temperature coefficient data for the reaction of 1,4-diaminobutane suggests that this, and probably also the other reactions, are entropically controlled in the sense that the entropy of activation is large and negative.

Table 2 Products from the reactions of polyamines and bis(2-aminoethyl)ether in degassed aqueous solution at 300 °C after 15 h

Substrate	Products (yield, %)[a]		Material balance deficit (%)[b]
$O(CH_2CH_2NH_2)_2$	 (nd)[c]	+ minor products	nd[c]
$HN(CH_2CH_2NH_2)_2$	(47)	 $HOCH_2CH_2OH$ $HOCH_2CH_2NH_2$	<53
$N(CH_2CH_2NH_2)_3$	(67)	+ minor products	<33
	(nd)[c]	+ minor products	nd[c]
$H_2N(CH_2)_3NH(CH_2)_4NH_2$		+ minor products	nd[c]

[a] Products formed in trace amounts where yields not indicated. [b] Initial amount of substrate used minus the sum of the yields of products and recovered substrate as a percentage. [c] Not determined.

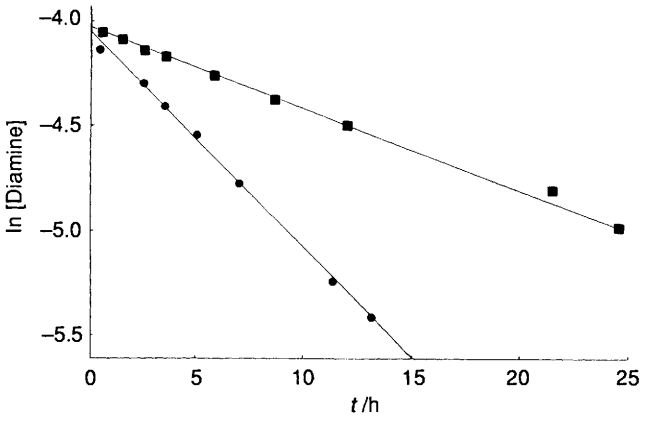


Fig. 2 Typical first-order plots for high temperature reaction of diamines in water: ■ 1,5-diaminopentane (260 °C); ● *N,N'*-dimethyl-1,6-diaminohexane (300 °C)

Discussion

It is interesting that the dominant reaction of dilute aqueous solutions of amines at 300 °C is not solvolysis. Despite the high concentration of water relative to substrate, the inter- or intra-molecular displacement of one amino group by another is the preferred mode of reaction. Thus 1,6-diaminohexane is the only diamine studied that gives any amino alcohol and this is only formed in trace quantities. Similarly, only minor yields of ethane-1,2-diol and ethanolamine were formed from bis(2-aminoethyl)amine and of ethane-1,2-diol from diethanolamine.

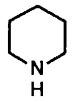
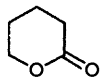
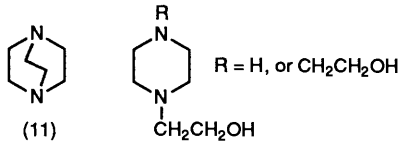
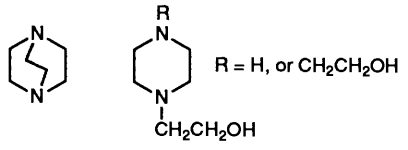
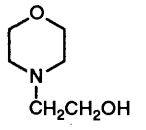
A common feature of the reactions of almost all the di- and tri-amines and amino alcohols studied is ring formation by either intra- or inter-molecular cyclisation. Just which reaction is favoured is governed by enthalpy and entropy considerations. Thus although intramolecular substitutions of $H_2N(CH_2)_nNH_2$ (n = 2–7) to give cyclic secondary amines are allowed *n-exo-tet* processes,[8] the three-, four- and eight-membered ring compounds were not detected. Entropy changes on intramolecular cyclisations would be expected to disfavour the formation of larger rings[9] although this effect could be moderated by changes in the entropy of solvation.[10] By contrast, enthalpy changes during cyclisation, which are thought to reflect the strain energies of the rings to be formed (Table 6),[11] will disfavour the smallest rings. Thus, both entropy and enthalpy factors control whether intramolecular cyclisation or competing intermolecular processes predominate.

With 1,6-diaminohexane and its *N,N'*-dimethyl derivative hexamethyleneimines were the major products detected with significant yields of 2-methylpiperidines also being formed. Since heating aqueous solutions of hexamethyleneimine leads to 2-methylpiperidine and the former compound is the only detectable product in the early stages of the reaction of 1,6-diaminohexane, it is probable that the piperidines arise from a ring contraction of the initially-formed seven membered ring amine rather than from a direct cyclisation of 1,6-diaminohexane. The precise mechanism of this rearrangement remains unclear, although it is possible that it might involve elimination to give 6-aminohex-1-ene followed by recyclisation to the piperidine (see below).

The cyclisation of α,ω-diamines has been achieved previously by irradiation (>300 nm) in the presence of a TiO_2/Pt catalyst,[12] or by heating in diphenyl ether in the presence of $RuCl_2(PPh_3)_2$.[13] It also occurs in the gas phase in chemical ionisation mass spectrometry.[14] However, we are not aware of any reports of these reactions in solution in the absence of a catalyst.

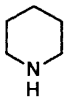
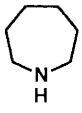
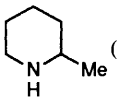
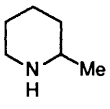
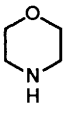
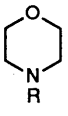
By analogy with the reactions of α,ω-diamines two possible

Table 3 Products from the reactions of aminoalcohols and pentane-1,5-diol in degassed aqueous solution at 300 °C after 15 h

Substrate	Products (yield, %)[a]	Material balance deficit (%)[b]
$H_2N(CH_2)_5OH$[c]	 (75)	18
$HO(CH_2)_5OH$[d]		
$H_2NCH_2CH_2OH$	 (11) R = H, or CH_2CH_2OH	<89
$HN(CH_2CH_2OH)_2$	 R = H, or CH_2CH_2OH	
	 $HOCH_2CH_2OH$	
$H_2NCMe_2CH_2OH$	Me_2CHCHO Me_2CHCO_2H $Me_2CHCONH_2$ (nd)[e]	(nd)[e]
	HCO_2H + three unidentified products	

[a] Products formed in trace amounts where yields not indicated. [b] Initial amount of substrate minus the sum of the yields of products and recovered substrate as a percentage. [c] Reaction in air gives the same product. [d] Reaction in air. No product detected in absence of air. [e] Not determined.

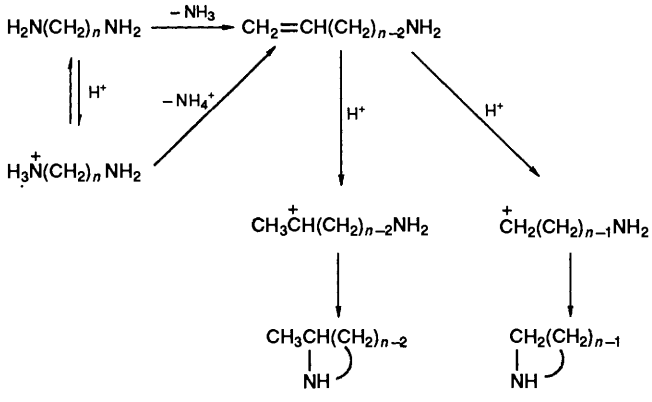
Table 4 Products from the reactions of cyclic secondary amines in degassed aqueous solution at 300 °C for 48 h

Substrate	Products (yield, %)[a]	Material balance deficit (%)[b]
	—	32
	—	32
	 (13)	62
	—	9
	 + other products	nd[c]
	R = Me, Et, Ac	

[a] Yields of major components of reaction mixture only measured. [b] Initial amount of substrate minus the sum of yields of product and recovered substrate as a percentage. [c] Not determined.

products might be expected from 5-aminopentan-1-ol, namely piperidine or tetrahydropyran. However, in agreement with earlier work where this amino alcohol was heated in the presence of $RuH_2(PPh_3)_4$[15] or copper on alumina,[16] cyclodehydration is the only significant reaction.

The mechanism of the intramolecular cyclisations of the diamines is likely to be a heterolytic process involving either elimination–addition (Scheme 1) or nucleophilic substitution



Scheme 1

(Scheme 2). The pH of the aqueous solutions at 300 °C is difficult to measure, but some of the diamine will be protonated under the reaction conditions which would facilitate both elimination (Scheme 1) and substitution (Scheme 2). However, products from reactions of some of the unhindered α,ω-diamines

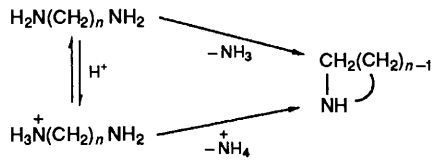
Table 5 First-order rate constants for the reaction of diamines and aminoalcohols in degassed aqueous solution[a]

Substrate	T/° C	$k_{obs}/10^{-5}$ s^{-1}
$H_2N(CH_2)_4NH_2$	240	18.0
$H_2N(CH_2)_5NH_2$	260	2.49
$H_2N(CH_2)_5OH$	260	0.77
$MeNH(CH_2)_6NHMe$	300	6.34
$H_2N(CH_2)_6NH_2$	300	1.10[b]

[a] First-order plots were linear for >2.8 half-lives. [b] After 1.6 half-lives the rate constant increases with time.

Table 6 Strain energies of cyclic hydrocarbons, ethers and amines[11]

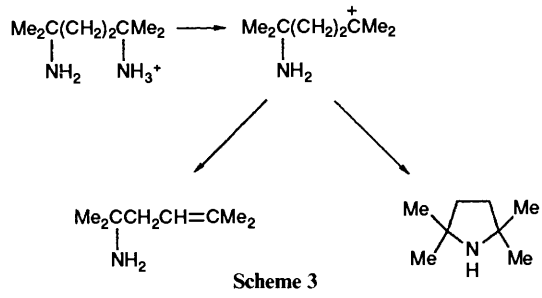
Compound	Ring size	Strain energy/kJ mol^{-1}
Cyclopropane	3	115.5
Oxirane	3	115.5
Aziridine	3	115.9
Cyclobutane	4	109.6
Oxetane	4	110.5
Azetidine	4	109.6
Cyclopentane	5	26.4
Tetrahydrofuran	5	28.0
Pyrrolidine	5	28.5
Cyclohexane	6	0
Tetrahydropyran	6	9.2
Piperidine	6	4.2
Cycloheptane	7	26.8



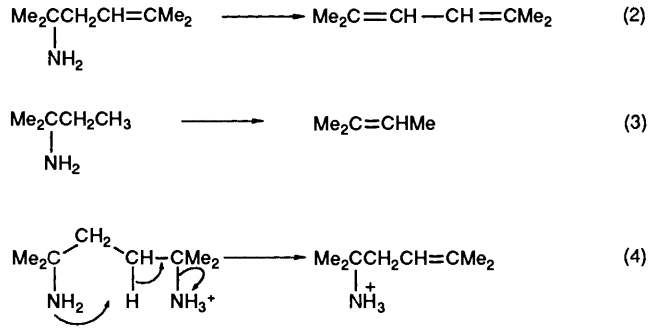
Scheme 2

are not compatible with the elimination–additon pathway. For example, this mechanism would predict the formation of 2-methylpiperidine and not hexamethyleneimine from 1,6-diaminohexane, since the piperidine formation is *via* the more stable carbocation and leads to the less strained six-membered ring. However, hexamethyleneimine and not 2-methylpiperidine is the first formed and predominant product. An intramolecular S_N2 reaction accounts for this product and also for the absence of 2-methylpyrrolidine in the reaction of 1,5-diaminopentane, although the latter result might be explained in an elimination–addition mechanism by the greater stability of the piperidine over the isomeric pyrrolidine. We conclude that the cyclisations of 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane and *N,N'*-dimethyl-1,6-diaminohexane are all likely to be intramolecular S_N2 processes. However, this would be unfavourable for the hindered 2,5-diamino-2,5-dimethylhexane and it is noteworthy that with this substrate both elimination, to give 5-amino-2,5-dimethylhex-2-ene, and intramolecular substitution are the major reaction pathways. Although it is possible that steric and electronic effects could lead to a change in mechanism with the formation of a carbocation which could subsequently undergo cyclisation or elimination (S_N1/E1) (Scheme 3), such a mechanism does not explain the absence of 2,5-dimethylhexa-2,5-diene, reaction (2), nor does it account for the stability of the tertiary alkylamine, 2-amino-2-methylbutane, towards deamination, reaction (3). An alternative mechanism for elimination of NH_3 from the hindered 2,5-diamino-2,5-dimethylhexane, which is not possible with the monoamines involves an internal elimination, reaction (4). This would then be followed by cyclisation to give the pyrrolidine.

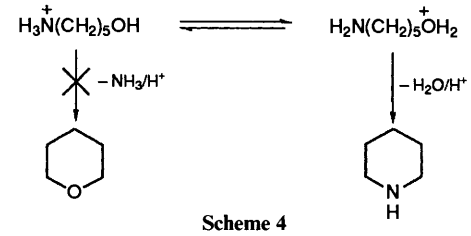
By analogy with the cyclisation of the α,ω-diamines, 5-



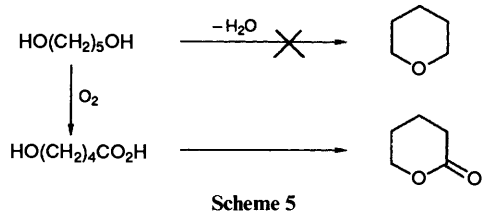
Scheme 3



aminopentan-1-ol undergoes the nucleophilic displacement of the hydroxy by the amino group rather than *vice versa*. Presumably such factors as the greater nucleophilicity of the amino group, the smaller strain energy of the piperidine (Table 6) and the more favourable entropy of solvation of the water-soluble piperidine, discourage the formation of the tetrahydropyran (Scheme 4). In agreement with these conclusions, with pentane-1,5-diol cyclisation is not observed although interestingly if the reaction is conducted in air, autoxidation to 5-hydroxypentanoic acid provides a favourable cyclisation to the δ-lactone (Scheme 5). With 5-aminopentan-1-ol in air



Scheme 4

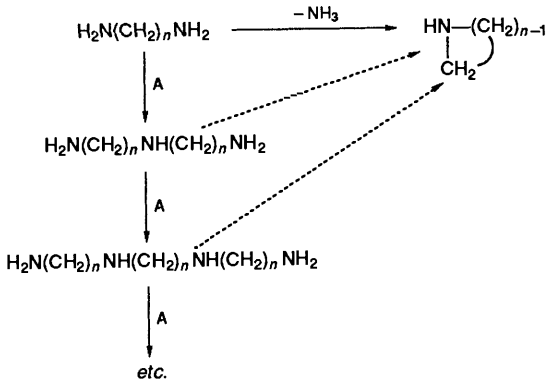


Scheme 5

cyclisation presumably occurs faster than alcohol oxidation since no δ-lactam was detected.

It was expected that the kinetic studies would show that the cyclisations of the α,ω-diamines and of 5-aminopentan-1-ol follow first-order kinetics. This was observed with 1,4-diaminobutane, 1,5-diaminopentane, 5-aminopentan-1-ol and *N,N'*-dimethyl-1,6-diaminohexane but the reaction of 1,6-diaminohexane deviated from first-order behaviour after *ca.* 1.6 half-lives with the rate constant increasing with time. The 1,4-diamine was the only substrate where the material balance deficit remained approximately zero throughout the reaction, with the others the sum of the concentrations of substrate and product decreased as the reaction progressed. The missing material is likely to arise from intermolecular reactions, leading to polyamines, which compete with the intramolecular

cyclisation. The compounds so formed would not have been readily detected by the GC analysis. Only with the fastest cyclisation (that of 1,4-diaminobutane) is the competing polyamine formation insignificant (Scheme 6).



A = $H_2N(CH_2)_nNH_2/-NH_3^+$

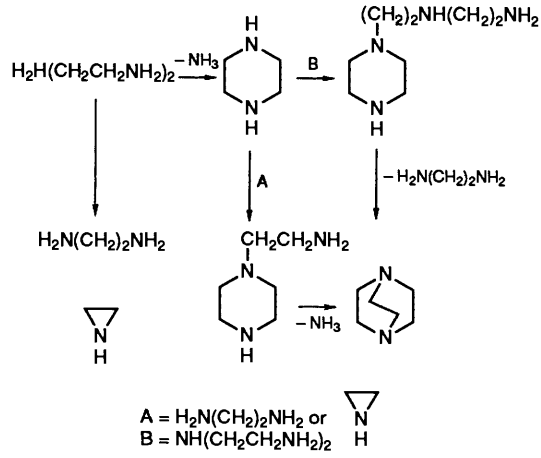
Scheme 6

Comparison of the rates of reaction of the α,ω-diaminoalkanes gives the order of reactivity $C_4 > C_5 > C_6$. The observed order of rates of ring formation, 5 > 6 > 7, was expected from the results of a previous study on the intramolecular S_N2 reactions of 1-amino-ω-bromoalkanes in water[17] and can be accounted for as described above. The greater reactivity of *N,N'*-dimethyl-1,6-diaminohexane than 1,6-diaminohexane probably reflects the influence of *N*-methylation on the nucleophilicity and leaving group properties of the amino group.[18] Interestingly, replacing an amino by an hydroxy group in 1,5-diaminopentane has only a relatively small effect on the rate of cyclisation (a statistical correction for the presence of only one amino group in the aminoalcohol is necessary).

With 1,3-diaminopropane intramolecular cyclisation to give azetidine is energetically unfavourable, as is intermolecular reaction to 1,5-diazocyclooctane. The fact that heating an aqueous solution of 1,7-diaminoheptane did not lead to 1-azacyclooctane is consistent with the latter conclusion. Since the simple cyclisations do not readily occur with the 1,3-diamine it reacts *via* alternative pathways (Table 1). These reactions were not investigated further.

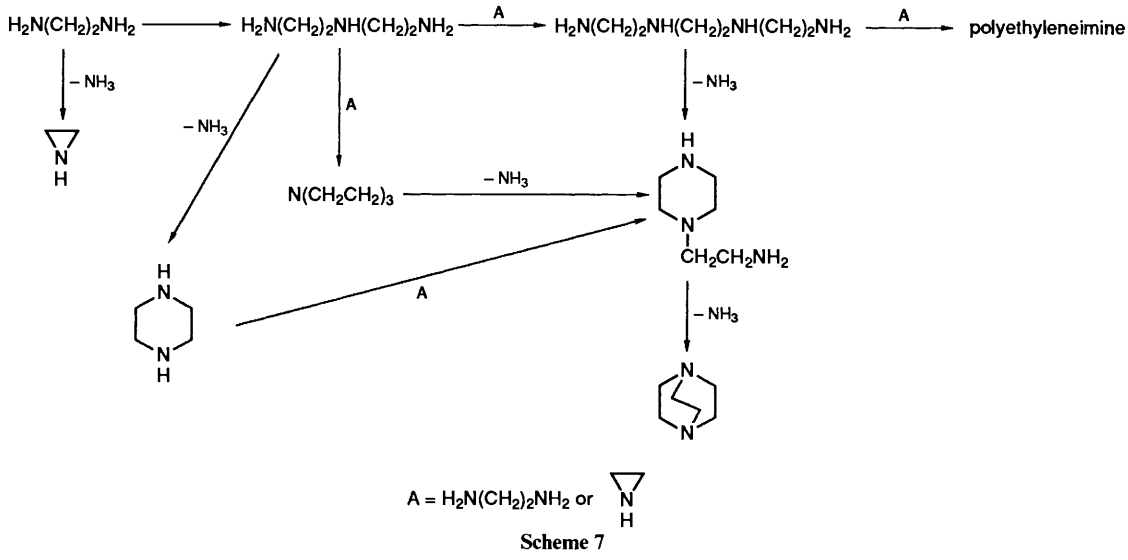
The major product detected from 1,2-diaminoethane was DABCO although most of the substrate remained unaccounted for. Several possible pathways can be written for the formation of the bicyclo diamine; indeed, it is likely that two or more of these are operating simultaneously under the reaction conditions. 1,2-Diaminoethane could undergo a series of self-reactions to give bis(2-aminoethyl)amine, tris(2-aminoethyl)-amine, *N,N'*-bis(2-aminoethyl)-1,2-diaminoethane and larger molecular weight polyethyleneimines either by sequential intermolecular nucleophilic substitutions or *via* the formation of aziridine. Subsequent cyclisations of these materials would then give piperazine, 1-(2-aminoethyl)piperazine and DABCO (Scheme 7). In agreement with these mechanisms tris(2-aminoethyl)amine and 1-(2-aminoethyl)piperazine each react to give DABCO. The absence of aziridine in the reaction products would be explained by its low stability under the reaction conditions so that, in effect, at 300 °C it is only present as a reactive intermediate.

Interestingly, the reaction of bis(2-aminoethyl)amine differs from its carbon and oxygen analogues, 1,5-diaminopentane and bis(2-aminoethyl)ether. Whereas the latter two compounds give piperidine and morpholine, respectively, no piperazine was detected with the triamine. Instead DABCO was the major product. Possible routes to the bicyclic diamine are shown in Scheme 8.



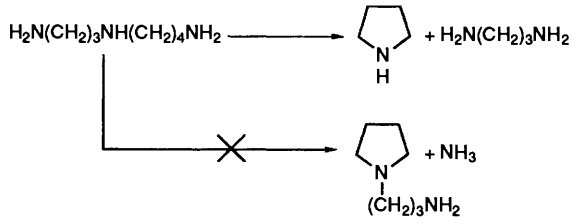
Scheme 8

Evidence for fragmentations in the reactions of the polyamines, such as the conversion of bis(2-aminoethyl)amine into 1,2-diaminoethane and aziridine (Scheme 8), was obtained from the reaction of *N*-(3-aminopropyl)-1,4-diaminobutane (spermidine) which gave pyrrolidine as a major product. The absence of 1-(3-aminopropyl)pyrrolidine suggests that for this substrate fragmentation is favoured over the nucleophilic



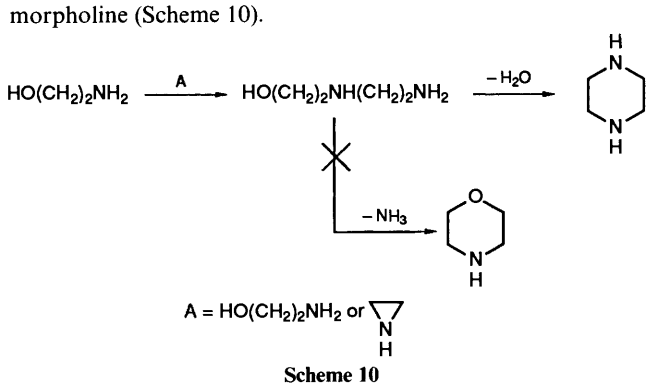
Scheme 7

displacement of NH_3 (Scheme 9). It is noteworthy that in the chemical ionisation mass spectrum of spermidine the most abundant ion is $[MHH_2N(CH_2)_2NH_2]^+$ obtained by fragmentation of pyrrolidine from the parent ion.[14] Scheme 9 opens up a further possibility that larger polyamine oligomers, under the reaction conditions, could also break down to simpler cyclic amines.



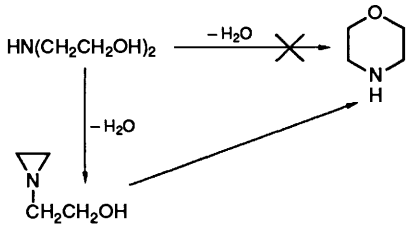
Scheme 9

The products from ethanolamine are similar to those from 1,2-diaminoethane and it is likely that the amino alcohol reacts by an analogous mechanism to the diamine. It is noteworthy that neither diethanolamine nor any morpholine derivatives were detected. The absence of these compounds suggests that the initial combination of two ethanolamines leads to *N*-(2-aminoethyl)ethanolamine, rather than diethanolamine or bis(2-aminoethyl)ether, and that this, like 5-aminopentan-1-ol, reacts to give a cyclic diamine, piperazine rather than an amino ether, morpholine (Scheme 10).



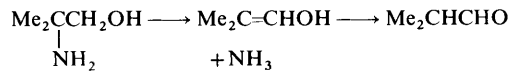
Scheme 10

Perhaps not surprisingly the product mixture from diethanolamine resembles that from ethanolamine, although the former interestingly includes a morpholine derivative, 4-(2-hydroxyethyl)morpholine. Since neither 5-aminopentan-1-ol nor pentane-1,5-diol react to give tetrahydropyran, it is unlikely that the morpholine ring is formed directly by cyclodehydration of the substrate. An alternative mechanism which is not possible with α,ω-pentane derivatives involves the initial formation of 1-(2-hydroxyethyl)aziridine. This might then provide sufficient driving force for the subsequent intramolecular rearrangement shown in Scheme 11.



Scheme 11

The amino alcohol AMP was extensively degraded at 300 °C giving a mixture of compounds which were not all identified although the major product was 2-methylpropanal. In a related study using this amino alcohol in a chemical plant boiler system (270–280 °C) the only organic product observed was this aldehyde together with ammonia.[19] Furthermore, quantitation of the ammonia formed revealed that it was equivalent to the AMP consumed. These results suggest that the initial reaction with this substrate may be elimination of ammonia to give the aldehyde (Scheme 12) which reacts further to give the other products.



Scheme 12

In conclusion, aqueous solutions of cyclic and acyclic monoamines are markedly more stable at 300 °C than those of analogous diamines, amino alcohols or amino ethers. This implies that the reactivity of the substrate is increased by a nearby heteroatom in the same molecule. The precise nature of this neighbouring group effect, however, was not investigated further.

Experimental

Materials.—All materials were commercially available and purified by distillation or recrystallisation if GC analysis showed the purity to be <99%. Distilled water was used in all the reactions.

Instrumentation.—GC used a Pye-Unicam PU 4500 chromatograph equipped with a flame ionisation detector. The results were analysed using a Trivector Scientific Ltd Trilab 2000 chromatography data collection system. The majority of the analyses used glass columns packed with either PEG 1500, 5% w/w, on Gas ChromQ (which had been treated with KOH, 2.5% w/w), Tenax GC or Apiezon L, 10% w/w, on Celite (treated with KOH, 5% w/w). Capillary analyses used an on-column injector and an SGE QC3/BP-1 column. Some capillary analyses were carried out with a split/splitless injector using a Perkin Elmer 8320 gas chromatograph fitted with a flame ionisation detector.

GC–MS with packed columns used a Pye 104 chromatograph coupled to a Kratos MS 3074 mass spectrometer. Capillary GC–MS used either a Finnegan 9500 chromatograph attached to a Finnegan mass spectrometer or a Finnegan 4000 GC-MS system.

The gauge used to measure the pressure obtained in the vacuum line when degassing samples was an Edwards 505 Penning gauge.

Reactor Design and Sample Collection.—The cylindrical reactor (Fig. 1) was made of stainless steel and had an internal volume of 57 cm^3. The lid was sealed to the reaction vessel using an annealed copper gasket. Calculations showed the unit was capable of withstanding >12 000 psi (816 bar).

The reactor was connected to a vacuum line *via* a stainless steel tube (6.3 mm outer diameter and 3.1 mm internal diameter), a Nupro SS-4UG critical service valve and a flexible glass to metal seal. For kinetic studies the reaction pressure was used to force liquid samples out of the reactor *via* a thin stainless steel tube (1 m length, 1.6 mm outer diameter and 0.55 mm internal diameter) which was coiled and cooled in a cold water bath. The sample volume (typically 0.5 cm^3) was controlled with a Whitey SS-41XS2 three-way ball valve attached to the end of the sampling coil. Samples were collected in pre-weighed tubes. Repeat sampling required the dead volume in the cooling coil (0.23 cm^3) to be flushed before the next sample was collected. In non-kinetic studies the sample coil in the reactor was replaced by a stainless steel rod (1.6 mm outer diameter).

Product Identification and Quantification.—The products and recovered starting materials were separated and quantified by gas chromatography. All products, except those from the reaction of 2,5-diamino-2,5-dimethylhexane, were identified by comparison of retention times and mass spectra with those of authentic commercially available compounds.

The only significant products from 2,5-diamino-2,5-dimethylhexane, detected by gas chromatograhy, were shown by mass spectrometry to be isomers. They had m/z 127 (M^+, 2%), 112 (100), 95 (56), 84 (18), 70 (10), 67 (18), 58 (40), 55 (21) and 42 (97) and m/z 127 (M^+, <0.1%), 112 (1), 95 (5), 70 (11), 59 (21), 58 (100, $Me_2CNH_2^+$), 43 (16) and 42 (33). The former was assigned to 2,2,5,5-tetramethylpyrrolidine, since it had an analogous fragmentation pattern to its commercially available homologue 2,2,6,6-tetramethylpiperidine; m/z 141 (M^+, 2%), 126 (100), 109 (12), 98 (9), 70 (66), 69 (38), 58 (68), 56 (12), 41 (42) and 42 (43). The mass spectrum of the other product has a dominant fragment ion at m/z 58, assigned to $Me_2CNH_2^+$, as would be expected in the mass spectrum of 5-amino-2,5-dimethylhex-2-ene.

Sample and Reactor Deoxygenation.—The air in the reactor and reaction mixture was removed using the vacuum line (Fig. 1). The reactor was first evacuated with a rotary pump and purged with pure helium (*via* the Whitey valve and sampling coil) several times. The reaction mixture (typically 30 cm^3) was degassed in a separate glass vessel with several freeze–thaw cycles to a pressure of $<6 \times 10^{-5}$ mbar when frozen. With the Nupro valve to the reactor open the pressure was $\leq 10^{-4}$ mbar. The degassed aqueous sample was distilled into the cooled (liquid N_2) reactor before the Nupro valve was closed and the reactor removed from the vacuum line.

Reactor Heating.—The reactor was placed in a pre-heated furnace equipped with a Sirect proportional temperature controller (CNS Instruments Ltd., London) and a platinum–rhodium thermocouple (± 2 °C). Measurement of the temperature of the water inside the reactor, with a thermocouple, showed that this stabilised at 300 °C in <50 min.

Cleaning the Stainless Steel Reactor.—The cylindrical reactor vessel was cleaned by filling it with a mixture of orthophosphoric acid, sulfuric acid and water (3:1:1, v/v). After several hours the acid was removed and the reactor washed with a large volume of distilled water. The lid was cleaned by rubbing with Scotch Brite and washing extensively with distilled water. The tubes and valves were carefully washed with a large volume of distilled water.

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