**pH Effects in the acetaldehyde-ammonia reaction**

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The pH dependency of the reaction of acetaldehyde and ammonia to form the acetaldehyde-ammonia trimer has been studied in detail. Acetaldehyde-ammonia trimer is a molecule of interest in organic synthesis, since it can be used as substrate in many reactions involving acetaldehyde or ammonia. The trimer is well known in literature but no references are present so far to describe its formation from other ammonia sources than ammonium hydroxide. The focus of this study is on describing the course of reaction after addition of acetaldehyde to solutions of ammonia and various acids. Products have been analysed by means of \(^1\)H-NMR and IR spectroscopy and the complete range of pH values has been covered. Depending on pH, two reaction regimes can be distinguished: at high pH only trimer is formed. In contrast, at low pH only low quantities of trimer are produced and the nature of the applied acid has a distinct effect on the reaction outcome. Inorganic acids result in low trimer concentration and high quantity of unreacted ammonia. Polymer formation dominates with simple carboxylic acids. Complex organic acids, such as e.g. maleic or nicotinic acid, lead to comparable quantities of trimer and acetaldehyde. Based on our results, we propose some adjustments to the traditional reaction scheme developed for acetaldehyde-ammonia trimer formation at high pH.

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**Introduction**

Mixing of acetaldehyde, \(\text{CH}_3\text{CHO}\), and ammonia, \(\text{NH}_3\), results at room temperature and atmospheric pressure in the formation of a cyclic structure usually referred to as acetaldehyde-ammonia trimer (2,4,6-trimethyl-1,3,5-hexahydropyrazine) [1-3]. The reaction proceeds spontaneously and is highly exothermic. The trimer is in dry form a white solid that is only partially water-soluble [4]. The molecule is unstable at room temperature so that the product has to be maintained in organic solution. The acetaldehyde-ammonia trimer can be used to produce amines by hydrogenation [5, 6] or as building block in organic synthesis [7]. Other reported applications include its use as scavenger for sulfhydryl compounds (thanks to its analogy to amines [4]) or as precursor for ammonia production [8].

The mechanism of the formation of 2,4,6-trimethyl-1,3,5-hexahydropyrazine (\(\text{C}_6\text{H}_9\text{N}_3\)) has been widely studied, and possible steps of \(\text{RNH}_2\) addition to a carbonyl group were postulated [9-11]. Ogata et al. studied already in 1964 the first step of the reaction, the formation of 1-aminoethanol (\(\text{CH}_3\text{CH(OH)NH}_2\)), by means of spectrophotometry [12]. In this publication, equilibrium and kinetic data for the reaction at pH values ranging from 9 to 12 were reported. These authors came to the conclusion that the direct reaction to form 1-aminoethanol increases only slightly its rate with increasing pH of the solution. Furthermore, it was found that the reverse reaction is subject to acid catalysis. In 1973, Hull et al. proposed a complete scheme for the formation of acetaldehyde-ammonia trimer [13]. By means of NMR analysis, the reaction of acetaldehyde and ammonia was extensively investigated at pH values higher than 7. The intermediate species were only tentatively identified as a direct determination via NMR analysis is not possible. The following scheme was proposed [13] (see Figure 1): The imine (c) represents the monomer for the formation of trimer. The proposed values for the kinetic parameters are in good agreement with the earlier published calculations by Ogata et al. [12]. Recently, Vinogradoff et al. gave additional insight into the mechanism of acetaldehyde-ammonia trimer formation analysing its formation at low temperature in the presence of formic acid [14]. In this study, the intermediates proposed by Hull et al. were identified at low temperature using IR spectroscopy. Thanks to theoretical prediction of vibrational frequencies, the assignment of all bands to the respective species was possible and all necessary steps to produce the acetaldehyde-ammonia trimer were elucidated. In particular, under cryogenic conditions, the dehydration of 1-aminoethanol into ethanimine is possible in the presence of formic acid. Ethanimine is stabilized at low temperature and can react to trimer only at temperatures higher than 230 K. A theoretical study based on molecular modelling by Chen et al. has also investigated the reaction of formaldehyde, acetone and acetaldehyde with ammonia at low temperature [15].

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Experimental

In our study ammonia was applied as a 25-30 % vol./vol. solution from Sigma Aldrich. For comparison purposes, ammonia solution in methanol was also prepared by condensing ammonia at -20 °C from a gas cylinder to form a solution of 25-30 % vol./vol. in a sealed reactor. Acetaldehyde was applied in its liquid form with 99% purity as purchased from Sigma Aldrich. Acetic acid, sulfuric acid, and formic acid were applied as commercially supplied (96-99 %, Sigma Aldrich). Hydrochloric acid has been used in form of a 33 % solution in water (Sigma Aldrich). Oxalic acid, maleic acid, and nicotinic acid (Sigma Aldrich) are solids and were applied in form of their respective saturated solutions in water. The applied ammonium salts were also commercial samples from Sigma Aldrich. The reference acetaldehyde-ammonia trimer was purchased in its hydrated form in 96 % purity from Sigma Aldrich.

All reactions were carried out in a flask that was placed in an ice bath to avoid temperature increase due to the reaction exothermicity. For the reactions with salts, solutions of 10 M were prepared. Acetaldehyde was slowly added in stoichiometric amount to the nominal ammonia content. Solutions of ammonia and acid at different pH were prepared as follows: 50 mL of the commercial solution of ammonia were dosed into the flask. Subsequently, the desired acid was added dropwise while checking the pH using an electronic pH sensor. When the desired pH was reached, it was double checked using an universal indicator. All obtained solutions were cooled in the ice bath prior to acetaldehyde being added dropwise in stoichiometric amount to the nominal ammonia quantity. Acetaldehyde was always kept in the ice bath to prevent evaporation.

The obtained samples were analysed by means of 1H-NMR spectroscopy (Bruker, 400 MHz). All samples were prepared for NMR analysis in d6-DMSO and benzyl benzoate was applied as internal standard for quantitative evaluation. Benzyl benzoate does not interact with acetaldehyde-ammonia trimer and its characteristic peaks are well distinguishable from the product. Samples were analysed immediately after preparation to avoid product decomposition. In addition, control experiments were also carried out comparing commercial trimer samples with the ones obtained in our experiments using IR spectroscopy.

Results and discussion

Thermodynamics

No experimental thermodynamic data are available in the literature regarding acetaldehyde-ammonia trimer formation. In order to obtain a preliminary estimation of thermodynamic properties, theoretical predictions following theoretical prediction methodologies from the groups of Joback [17] and Gani [18, 19] were carried out. The respective results are presented in Tables 1 and 2.
The acetaldehyde-ammonia trimer is characterised by the presence of nitrogen and carbon in a 6-member ring together with three terminal methyl groups. The two prediction methods agree in the fact that the value of \( \Delta H^\circ \) is negative and the value of \( \Delta G^\circ \) is positive. The Joback method results in higher values for both quantities. This in turn has a direct influence on the calculation of reaction enthalpy and Gibbs free energy: the results from the Gani method suggest a stronger exothermic reaction with significantly higher thermodynamic driving force compared to the results obtained from the method of Joback. The origin of the difference between the two methods is the presence of a second order group contribution in the Gani method (absent in the Joback method) referring to ring effects that decreases the predicted enthalpy and Gibbs free energy. For the cyclic acetaldehyde-ammonia trimer, this feature should make the Gani method more suitable for the prediction of thermodynamic properties.

Note that the calculated results using the Gani method are in good agreement with our qualitative experimental observations. Acetaldehyde addition to ammonia results in a strongly exothermic reaction. A point of special interest is the calculation of the Gibbs free energy. The method of Joback predicts a \( \Delta G^\circ \) close to 0. The value predicted by the Gani method is instead much stronger negative. The equilibrium constant is predicted as \( 2.8 \times 10^9 \), very close to the experimental value given in [13]. For this reason, we consider for this study the values predicted using the Gani method since this method results in an obviously more appropriate representation of the system under investigation. The results of thermodynamic calculations for decreasing pH values show a decrease in the equilibrium constant value, due to the reaction of ammonia and acids. This results in a decrease in \( \Delta G^\circ \) and \( \Delta H^\circ \), as experimentally observed by a decreasing heat release during reaction at lower pH. Nevertheless, even at low pH the formation of acetaldehyde-ammonia trimer is thermodynamically clearly favoured.

### Table 2. Calculated thermodynamic properties for the reaction of trimer formation

<table>
<thead>
<tr>
<th>Method</th>
<th>( \Delta H^\circ [kJ/mol] )</th>
<th>( \Delta G^\circ [kJ/mol] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Joback</td>
<td>-123.6</td>
<td>-9.6</td>
</tr>
<tr>
<td>Gani</td>
<td>-157.5</td>
<td>-53.9</td>
</tr>
</tbody>
</table>

### Table 3. \( pH \) of the solutions of ammonium salts

<table>
<thead>
<tr>
<th>Anion</th>
<th>( pH )</th>
<th>( CO_2^- )</th>
<th>( HCO_3^- )</th>
<th>( Ac^- )</th>
<th>( CHOO )</th>
<th>( CHOO^- )</th>
<th>( SO_4^{2-} )</th>
<th>( NO_3^- )</th>
<th>( HSO_4^- )</th>
<th>( Cl^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>9</td>
<td>8</td>
<td>7</td>
<td>6.5</td>
<td>6</td>
<td>5.5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

The results reported here were measured few minutes after preparation of the solutions. Repeated measurements over several hours verified the stability of the mixture. With regard to trimer yield the results are quite disperse and do not show any clear trend. In

The acetaldehyde-ammonia trimer is experimentally accessible. The molar fractions of acetaldehyde and acetaldehyde-ammonia trimer were determined after mixing for few minutes by NMR analysis. The results are displayed in Figure 2, where the salts are listed in the order of decreasing \( pH \) of their aqueous solutions. The initial \( pH \) of the solutions prepared are reported in Table 3. Acetaldehyde ammonia-trimer and unreacted acetaldehyde are the only species determined by NMR. The remaining products are undefined polymeric structures, which - if present in high concentration – lead to a brownish colour of the reaction solution. The polymer formed was characterised by MS analysis. The results of these analyses show the presence of species with molecular weight higher than acetaldehyde-ammonia trimer. The analysis of the distribution of molecular weights suggests that these species are produced from aldol condensation of acetaldehyde in the presence of ammonia. This side reaction shows irreversible character, in contrast to the reversible behaviour of the acetaldehyde-ammonia reaction system.

### Figure 2. Molar fraction of acetaldehyde and acetaldehyde ammonia trimer in various ammonium salts (\( CH_2CHO_2=5 \) M)
contrast, the influence of the pH value of the salt solution on acetaldehyde conversion is much clearer. The quantity of unreacted acetaldehyde is considerable for salts of strong inorganic acids (about 40-50 %), while full acetaldehyde conversion is reached with the salts of carboxylic acids and with carbonates.

Interestingly, the results of Figure 2 can be classified into three different groups of acids showing very similar results: salts of inorganic acids, salts of organic acids and carbonates. The use of ammonium salts of inorganic acids results in a low production of undesired species, but also a large quantity of unreacted acetaldehyde (i.e., low acetaldehyde conversion) is observed. The sum of these two factors limits trimer formation to a yield of about 50 %. The NMR spectra indicate the formation of acetaldehyde in its hydrate form under these conditions. Under the low pH conditions, acetaldehyde is more likely to react with water producing acetaldehyde hydrate rather than to react with the ammonium ion to form the amino-alcohol which is the initial step for trimer formation. In this acidic environment, the acetaldehyde hydrate shows only a limited reactivity towards aldol condensation. This is the reason for the observed low polymer formation. Oxalic acid is at the border of this group as it allows a much higher production of trimer linked to a significantly larger acetaldehyde conversion.

The results of the second group, composed of salts of carboxylic acids, are completely different. When applying these salts, no signals of acetaldehyde and trimer are found in the NMR spectra. The solutions are clear when prepared but they become dark within a few minutes. It was therefore impossible to reveal whether the obvious production of tar was the result of trimer decomposition or of direct aldol condensation of acetaldehyde. To shed more light on the relevant reaction processes, the reaction with ammonium acetate was repeated adding a buffer to the solution. In this way, the production of tar was greatly slowed down and it was possible to analyse the actual reaction products. Under these modified conditions also NMR signals for the acetaldehyde-ammonia trimer could be detected. Therefore, we expect that the reaction mechanism still involves initial trimer formation followed by acid catalysed trimer decomposition.

The third group of ammonium salts applied comprises ammonium carbonate and bicarbonate salts. The reaction outcome in this group is characterised by total conversion of acetaldehyde and high selectivity to acetaldehyde ammonia trimer. This is in good agreement to the common assumption in literature [12] that the trimer is easier formed under basic conditions. It is still surprising that such high trimer yields can be obtained using an ammonium salt.

Another special aspect related to the use of carbonates salts is the incipient CO₂ formation during acetaldehyde addition. This is most probably due to the decomposition of carbonic acid that goes hand in hand with the trimer formation reaction. CO₂ is released by the reaction of acetaldehyde and carbonates (e.g. 3 CH₃CHO + 3 NH₄HCO₃ ↔ trimer + H₂O + CO₂), and its presence in the solution should influence the stability of the produced trimer.

Detailed study of the effect of ammonium carbonate addition

In order to further investigate the effect of CO₂ formation on trimer stability, two identical solutions of acetaldehyde in ammonium carbonate were prepared and then stored under different conditions: the first at atmospheric pressure and the second in a sealed container under 7 bar of nitrogen atmosphere. At regular intervals, samples were collected from both solutions in order to assess by NMR analysis the content of acetaldehyde and trimer. The results over a time of 24 hours are reported in Figure 3. The solution stored at atmospheric pressure was free to develop gaseous CO₂ until the content of CO₂ in the liquid reached the equilibrium (after approx. eight hours). The solution stored under pressure showed a much slower CO₂ depletion. At ambient pressure, the decomposition of trimer was fast and after eight hours a negligible quantity of trimer was detectable. The acetaldehyde in the solution increased from zero (since it was not present at preparation time) to an equilibrium value of about 15 %, which then remained unchanged until the end of the experiment. The result of the experiment under pressure is quite different. The decomposition of trimer was much slower, and at the end of the experimental run, the concentration of this component was still considerable. In this case, acetaldehyde showed a trend similar to the previous one, reaching a compatible equilibrium value after eight hours. These results must be interpreted in the light of the relative instability of trimer. At equilibrium, acetaldehyde ammonia trimer is not favoured compared to its decomposition products. The role of CO₂ lies in an inhibiting effect to trimer decomposition, enhancing its stability over time. The sealed solution is buffered in comparison to the solution stored at atmospheric pressure. Therefore, this solution features more suitable pH for the storage of trimer avoiding decomposition. In this sense, the role of CO₂ is to maintain the correct pH to suppress polymer formation.

To sum up the effects of ammonium carbonate addition, it is fair to state that its addition leads to a pH range of 9-10 which is favourable for trimer formation. However, this does not prevent trimer decomposition over time.
Quantitative pH range screening

Comparison of hydrochloric acid, acetic acid and oxalic acid effects

In this section we compare the results of acetaldehyde addition to solutions of ammonia and, respectively, hydrochloric acid, acetic acid and oxalic acid. These three acids will be used throughout the discussion as reference for acetaldehyde reactivity. The reference points used for the comparison are at pH 2, 5, 7, 8, 9 and 10. Results for the three compounds are shown in Figure 4. The results of the addition of acetaldehyde to hydrochloric acid can be explained with the following considerations: When low quantities of hydrochloric acid are added to ammonia, all the acetaldehyde is converted and reacts to trimer. No side products are formed. The decrease of pH results in a slight decrease of trimer formation, up to a yield of 90 % at pH 8. Up to this quantity of hydrochloric acid, the reaction is practically not influenced by the presence of the acid. A further decrease of pH causes a drop in trimer concentration. This change is due to approaching conditions in which ammonia is completely protonated to ammonium chloride. This point is also characterized by a relative high molar fraction of acetaldehyde in the product solution (~ 60%). The results do not sensibly change when reducing the pH, meaning that an increase in hydrochloric acid content does not change the reactivity compared to the ammonium chloride case.

The pH influence on the reaction in the presence of acetic acid is quite different. At high pH (low quantities of acetic acid added), acetaldehyde ammonia trimer is the main product, even though it does not reach the full yield observed with hydrochloric acid. A drop in trimer molar yield due to protonation of ammonia is observable at relatively high pH. The range of pH with largest polymer formation is particularly large for acetic acid (between pH 7 and 9). In the same pH range, unreacted acetaldehyde is not observed, in full agreement with the previous observations for the ammonium acetate case. Further decrease of pH following the addition of more acetic acid to ammonia solution does allow the formation of acetaldehyde ammonia trimer. At pH 4, a maximum in acetaldehyde concentration is found. This means that the quantity of acetic acid present in this solution favours trimer decomposition, but also the aldehyde form compared to the imine form.

This phenomenon is not present at lower pH, where no acetaldehyde is recovered. The role of acetic acid in catalysing the various steps of acetaldehyde ammonia formation is complex and strongly varies with the relative amounts of acetic acid and ammonia present.

Trimer preparation tests give also different results when the acid used to vary the pH is oxalic acid. Once again, at pH 10 trimer is formed quantitatively. The decrease of pH lowers the trimer formation slower than in the case of hydrochloric and acetic acid. In fact, at pH 9, still 80 % trimer molar fraction is observed, while at pH 8 the solution contains 20 % trimer. It is important to underline in this case that the reaction system at certain pH values obtained by using oxalic acid is not completely comparable with the two previous cases because of the solubility limit of oxalic acid in water. For this reason, solutions prepared with oxalic acid are more diluted so that a higher quantity of acid is necessary to achieve the same pH in the solution. A particular trend of solutions containing oxalic acid is found in trimer concentration at low pH. Compared to the...
experiment at pH 8, the yield of trimer tends to increase and is stabilizing at pH lower than 5 at a value of around 30%. The trend of acetaldehyde is quite similar to that previously observed for hydrochloric acid. A maximum for acetaldehyde is found at pH 8, corresponding to a minimum in trimer. At lower pH, the molar fraction of acetaldehyde decreases and is stabilizing at a value of around 50%. It is important to note that in the case of oxalic acid also at low pH values less than 20% of the acetaldehyde fed is lost in polymerization products.

For all the three acids considered in this section, it is important to distinguish the pure effects of pH and the effects of acid concentration. Owing to the differing strength of the applied acids, the concentration of acid needed to adjust a certain pH is different. At high and neutral pH, the most important effect of the added acid is due to the protonation of the reactant. At low pH, the effect of concentration is more relevant, as high amounts of acid are required to lower the pH. In this case, all reactants are fully protonated and further side reactions are influenced by the nature and quantity of free acid present in the solution.

To summarize this first quantitative analysis, we have observed that at high pH all acids under investigation allow almost quantitative trimer production. This is an indication that a small quantity of acid does not affect the capability of ammonia to react with acetaldehyde to form the respective imine, and consequently acetaldehyde ammonia trimer. The increase of acid concentration in solution results in the decrease of trimer yield. The differences found among the three different acids used are mainly the result of the different quantity of acid necessary to achieve the same pH in the solution. The most important differences appear when the threshold of complete ammonia transformation into the ammonium salt is reached. As already observed in the previous section, the use of ammonium salts gives results that depend on the nature of the salt used.

For pH values lower than the value identified for the corresponding ammonium acid, acidity has a catalytic effect on the trimer decomposition reaction. This is also confirmed by dissolution tests of commercial acetaldehyde ammonia trimer in 0.1 M hydrochloric acid. The unstable imine groups formed by trimer decomposition undergo a further reaction depending on the nature of the applied acid. A schematic and simplified representation of the reaction is depicted in Figure 5. The difference between the different acids causes either complete reverse reaction to acetaldehyde (or acetaldehyde does not react) or favours aldol condensation to polymerization products. For acetic acid, a catalyst for both named reactions, it is impossible to stabilize the trimer in presence of free acid. The final product of the reaction network is determined by the quantity of free acetic acid present: at low and intermediate pH (regions < 4 and 6-9) only polymer is formed. In the pH range between 4 and 6, acetaldehyde is found in the reaction mixture.

The case for the other two considered acids is less complex: there is no special effect of pH in acidic conditions on the course of reaction. The relative quantity of acetaldehyde and trimer is practically constant for pH < 7.

Comparison of HCl and H₂SO₄ addition

In a next step we compared the results of hydrochloric and sulfuric acid addition. The molar fraction of acetaldehyde and trimer as a function of pH is shown for these two acids in Figure 6. The similarity in terms of trimer production is evident. The only meaningful difference is found at pH 8. Here, the different values in trimer molar fraction can be explained by a stoichiometric effect caused by the difference in strength of the two acids. A major difference between sulfuric acid and hydrochloric acid is found at low pH. While with sulfuric acid all acetaldehyde is lost into irreversible polymerization, a certain amount of trimer and a relative high quantity of acetaldehyde is recovered with hydrochloric acid. The different results for these two acids at low pH are due to the different catalytic activity in the aldol condensation reaction. Since acetaldehyde cannot react to acetaldehyde-ammonia trimer under these conditions, the extent of side reactions (mainly aldol condensation) is determined by the nature and catalytic activity of the acid.

Comparison of acetic acid and formic acid addition

Formic acid addition to the reaction system was compared to acetic acid addition. Both acids are very similar except for their different strength, as stated by the pKa value of 3.74 (formic acid) and 4.74 (acetic acid). The results of this comparison are depicted in Figure 7. The molar fraction of acetaldehyde ammonia trimer produced in formic acid is completely superimposable to that obtained with acetic acid at the same conditions. At pH 10, a small difference can be observed; the molar fraction of trimer is slightly lower for the formic acid case. This difference is mainly due to variation in acid strength, which makes formic acid less suitable as additive for trimer formation. Formic acid shows the same drop in trimer molar fraction lowering the pH at 8 and it does not allow trimer formation at any lower pH. The main difference between the two acids is found in
unreacted acetaldehyde at low pH. As discussed above, acetic acid is capable to stabilize acetaldehyde at pH 4, creating an evident maximum in acetaldehyde. This effect is not present for the formic acid case, as formic acid does not allow for the conservation of acetaldehyde under acidic conditions. The loss of acetaldehyde should suggest that the conditions used in the experiments with formic acid are more beneficial for aldol condensation, both starting from acetaldehyde or from the corresponding imine. Very interesting is the observation that in formic acid the entire pH spectrum is characterised by low acetaldehyde molar fraction. This is a clear proof of the fact that formic acid is a strong catalyst for the decomposition of acetaldehyde.

Figure 6 Comparison hydrochloric acid and sulfuric acid (CH$_3$CHO=5 M)

Figure 7 Comparison formic acid and acetic acid (CH$_3$CHO=5 M)

Comparison of the addition of three complex organic acids

To further support the results obtained with oxalic acid addition, the addition of maleic acid and nicotinic acid was also tested. Maleic acid is of interest as a dicarboxylic acid with longer alkyl chain and a double bond. Nicotinic acid brings the additional feature of a pyridine ring to the reaction. The obtained results are shown in Figure 8. The similarity of all three acid additions at pH values below 8 is evident. In contrast, a significant difference between the three acids is noticed at high pH. While oxalic acid and nicotinic acid show under these conditions the expected very high trimer yield, maleic acid addition results in large portion of unreacted acetaldehyde, a unique observation in this entire study. This is most probably caused by an inhibiting effect of the double bond of maleic acid on the acetaldehyde or ammonia reactivity. Another point of interest is the observation that the quantity of trimer produced is almost equal at very low and high pH for maleic acid addition. Low amounts of polymerization product are observed with this acid throughout the whole pH spectrum.
Summary and conclusions
A detailed study of the reaction of acetaldehyde and ammonia at various pH conditions using different acids was carried out in order to understand the effect of acid addition on trimer formation. The acid additions under investigation included inorganic and organic acids. At high pH, the acetaldehyde ammonia trimer is the main product which is obtained in yields close to 100%. When lowering the pH value by acid addition, the trimer formation decreases. Minimum trimer formation is observed at the pH value that corresponds to the one of the corresponding ammonium salt solution. This pH value is characteristic for the applied acid additive. At low pH, the reaction outcome differs significantly for the different types of acids applied. Inorganic acid additions lead at low pH to an inhibition of the reaction with large quantity of unreacted acetaldehyde and a small quantity of trimer found in the reaction mixture. Carboxylic acid additions lead at low pH values to aldol condensation that converts acetaldehyde into polymer.

Our results show the importance of pH control in the acetaldehyde-ammonia reaction. The least favourable pH-range for trimer formation is around neutral pH as all ammonium salts catalyse effectively polymer formation. High trimer formation is observed at high pH (with only small quantities of the respective acid addition acid) or at low pH with inorganic acids. An exception is maleic acid addition at high pH that results in incomplete conversion and significant amounts of unreacted acetaldehyde.

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