

GUIDELINES FOR OPTIMAL DOSING STRATEGIES FOR REACTIONS OF ALDEHYDES AND AMMONIA

Emanuele Moioli^{*1,2}, Leo Schmid², Peter Wasserscheid¹, Hannsjörg Freund¹
¹Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Erlangen, Germany
²Lonza AG, Visp, Switzerland

Abstract

This paper explores the opportunity to change the process scheme for reactions of aldehydes with ammonia. In the proposed alternative process route, at first intermediate species are formed at low temperature, which then decompose with the addition of the other raw materials required to yield the final product at higher temperature. This allows defining an alternative process in terms of heat management and reactant dosing strategy. The second step of the reaction, conducted at high temperature, does not involve water formation, but ammonia production from the decomposition of the aldehyde–ammonia compound previously synthesized. Experimental results are provided to define the first process step and to compare the behavior of aliphatic aldehydes in the presence of ammonia or ammonium salts, respectively.

Keywords

Aldehydes, Ammonia, Dosing Strategy, Pre-mixer, Urotropine, Aldehyde-Ammonias.

Introduction

The condensation of aldehydes and ammonia at high temperature is a well-known reaction in organic synthesis, which allows preparing nitrogen containing carbon chains. The reaction of aldehydes and ammonia also takes place at low temperature, spontaneously forming molecules usually referred to as aldehyde-ammonias. The study of the relationship between the two reactions, formation of aldehyde-ammonias and condensation to final products, can open the way to the design of improved reactor schemes with improved management of reaction exothermicity and separation of products. The scope of this paper is to define general rules that should be taken into account in the design of a dosing strategy for aldehyde-ammonia reactions.

Thermodynamics

Condensation of aldehydes and ammonia is an exothermal reaction, resulting in the elimination of water by substitution of the C=O bond with a new C–C bond (Figure 1, scheme 1). The synthesis via aldehyde-ammonias inserts a new step, transforming the C=O bond into a C–N bond (scheme 2). The first step, involving water condensation, proceeds at room temperature. The second step towards the product is characterized only by ammonia condensation. This requires a different management of the reaction heat and leads to the

possibility of separating water to perform the second step in an anhydrous environment.

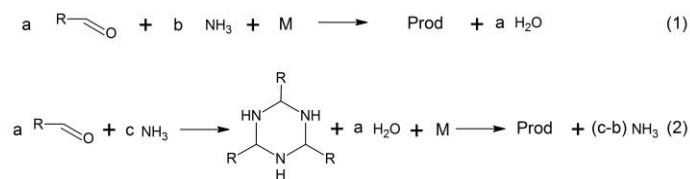


Figure 1. Two alternative process schemes in reactions of acetaldehyde and ammonia

The difference in reaction enthalpy for the second step from scheme 1 to scheme 2 is quantified as: $a \times (-285.83) - (c - b) \times (-80.29)$ [kJ/mole].

Experimental

The focus of this study is on aliphatic aldehydes. The low temperature products of aldehydes and ammonia were identified and quantified. Aldehydes were slowly added to an aqueous 25 Mol-% ammonia solution in a cooled and stirred reactor. Many tests were carried out changing the aldehyde-ammonia relative ratio or using ammonium salts, respectively.

*To whom all correspondence should be addressed

Results

For aldehydes from C₂ to C₄ a common trend is found. Their common characteristic is the presence of a threshold level of ammonia excess to reach 100 % yield in the trimer product (Figure 2).

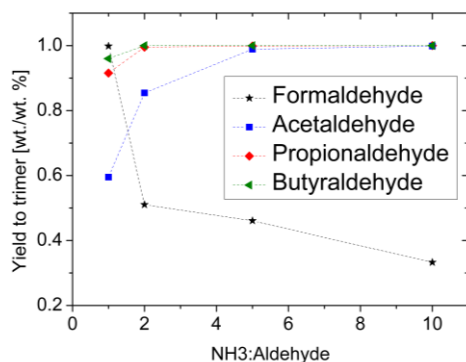


Figure 2. Effect of molar ratio on trimer yield

This threshold value decreases upon increasing the carbon content of aldehydes. The aldehyde not converted to trimer is lost in long chain polymers, which are not available for further reactions. For the case of formaldehyde, a different behavior is observed. This molecule forms a different structure, called urotropine (hexamethylenetetramine, C₆H₁₂N₄). The yield of urotropine is 100 % at a CH₂O:NH₃ molar ratio equal to 1, but tends to decrease sharply with an excess of ammonia. This represents a reversed trend as compared to the higher aldehydes. As a direct consequence, it is necessary to apply a different mixing strategy if formaldehyde is required by the reaction scheme for the desired product. When formaldehyde is used as synthetic building block together with higher aldehydes (e.g. acetaldehyde), the order of addition of raw materials added to the reaction mixture is crucial; a conceptual mismanagement in this reaction phase can already cause the loss of large quantities of the carbon chain precursor in the pre-mixer. In some applications, a basic pH can be undesirable because of the particular properties of co-reactants or products. For this reason, the use of ammonium salts instead of ammonium hydroxide is an interesting option. According to our previous experimental studies, the effect of ammonium salts on acetaldehyde ammonia trimer formation can be schematized using three different salts: a) ammonium chloride, b) ammonium acetate, c) ammonium oxalate. These salts are tested with the aldehydes used in the study. Results are shown in Figure 3a.

As observed before, formaldehyde shows a different reactivity than the higher aldehydes. Formaldehyde forms urotropine with about 100 % yield with all the three salts considered. Higher aldehydes form trimers only in limited amounts, with a minimum quantity when using ammonium acetate. The increase in the carbon atom number in the aldehydes appears to reduce the specific effect of the salt type on the reaction. This is due to the increase in the aliphatic character of the molecules, and the consequent

decrease of the influence of the C=O bond on the entire molecule.

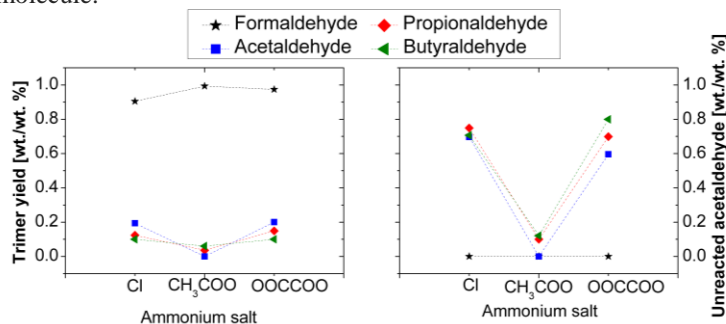


Figure 3. Products (a) and unreacted aldehydes (b) of the reaction of aldehydes and ammonium salts

A special feature of higher aldehydes is the presence of large quantities of unreacted aldehydes in the case of ammonium chloride and oxalate. Ammonium acetate, in contrast, is a catalyst for the polymerization of aldehydes, causing their irreversible loss (Figure 3b).

Conclusions

The low temperature mixing of aldehydes and ammonia leads to the formation of aldehyde-ammonia trimers with aldehydes of the fraction C₂-C₄, while a different product is formed by reaction of formaldehyde and ammonia. For this reason, two different trends of reaction yield upon increasing the aldehyde to ammonia ratio are identified. Formaldehyde is quantitatively converted to urotropine if not being in excess of ammonia. C₂-C₄ aldehydes form 100 % trimer only with an excess of ammonia. These results are important to determine the minimum amount of ammonia to be used in a pre-mixer to avoid aldehyde loss. At the same time, these general rules allow for deriving the best dosing strategy to be applied when different aldehydes are to be used in the reaction scheme. General rules are also provided when using ammonium salts instead of aqueous ammonia. In this case, apart from formaldehyde which quantitatively forms urotropine, it is impossible to obtain large quantities of trimer because most of the aldehyde fed does not react with ammonium chloride and oxalate. The case of ammonium acetate is different because the reaction of C₂-C₄ aldehydes with the latter results in an irreversible formation of polymerization products.

References

- W. Hull et al., *J. Org. Chem.*, Vol. 38, No. 17 (1973)
- A. Nielsen et al., *J. Org. Chem.*, Vol. 38, No. 19 (1973)
- A. Nielsen et al., *J. Org. Chem.*, Vol. 44, No. 10 (1979)

Acknowledgments

This project has received funding from the European Union's Seventh Framework Program for research, technological development and demonstration under grant agreement no. 607114.