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A cautionary note on “exothermic events” upon contact of carbodiimide coupling agents and the cellulose solvent *N*-methylmorpholine-*N*-oxide

Paul Jusner · Masaaki Aoki · Antje Potthast · Thomas Rosenau 

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Abstract The cellulose solvent *N*-methylmorpholine-*N*-oxide monohydrate (NMMO) reacts violently with carbodiimide coupling agents, such as the widely used DCC (dicyclohexylcarbodiimide) and EDC (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide), which can cause explosions, heavy smoke generation and complete charring of the reaction mixtures. For this reason it is clear that cellulose or other carbohydrates dissolved in NMMO (“Lyocell conditions”) cannot be safely esterified or amidified under DCC/EDC conditions. It is important to note that cellulosic material regenerated from NMMO solutions also poses a risk if it contains residual NMMO, which can then come into contact with DCC-type coupling agents in non-aqueous media, as recent accidents have unfortunately

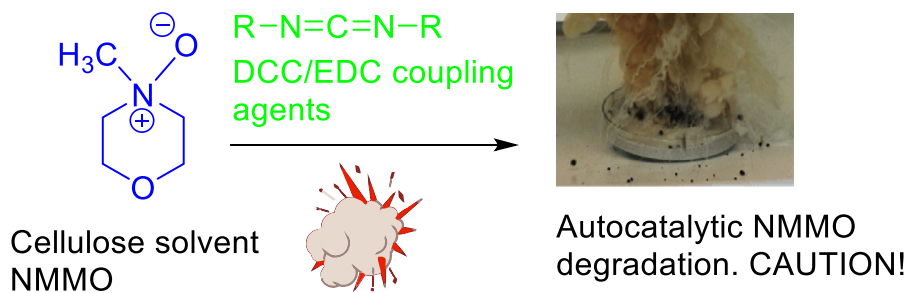
shown. Similarly, EDC/DCC traces in cellulose can have detrimental effects when trying to dissolve the material in NMMO. Working in aqueous systems generally reduces the risk of uncontrolled reactions, while alcohols or aprotic solvents are not very effective in this regard. Washing for NMMO removal or EDC/DCC removal should therefore always be carried out by aqueous media, if any possible, if there is a potential risk that the reagents might come into contact later. This warning describes the potential hazards of the reagent combination, highlights the underlying degradation mechanism and explains the precautions to be taken to avoid any “exothermic events”.

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Graphic abstract



Keywords Cellulose · Carbodiimide · Coupling agents · NMMO · Decomposition · Degradation · Exothermicity · Work safety

Introduction

The heterocyclic amine oxide NMMO (*N*-methylmorpholine *N*-oxide) is very well known as a cellulose solvent (Gränacher and Sallmann 1939). Used in the form of a monohydrate, NMMO is the basis of the lyocell process, an increasingly prominent alternative to the viscose process for manufacture of man-made cellulosic fibers. NMMO dissolves cellulose in quantities of up to approx. 15 wt% and forms a viscous solution at temperatures above 80 °C, which can be spun well (Fink et al. 2001; Sayyed et al. 2019). NMMO is also used as a reaction medium for cellulose modification and has been investigated as a treatment for fibers (Zhang et al. 2018; Öztürk et al. 2009; Manian et al. 2007) or swelling medium for biomass processing and utilization (Satari et al. 2019; Brodeur et al. 2016; Cai et al. 2016; Wikandari et al. 2016; Aslanzadeh et al. 2014).

In the last 6 months we received three inquiries about the chemistry of NMMO. In each case there had been an accident in chemical laboratories, in one case with two injured, in the other two cases only with material damages. We were contacted because in previous work we had dealt intensively with the chemistry of the solvent NMMO, possible side reactions and options for stabilizing NMMO systems (Rosenau et al. 2001, 2002). This ultimately led to the fact that industrial lyocell processes have become established and can now be conducted safely and chemical-efficiently on a large industrial scale.

However, it should not be forgotten that NMMO and NMMO monohydrate have inherent dangers that should not be neglected, but unfortunately are often forgotten. NMMO and its hydrate are solids that must be either melted ($T > 80\text{ °C}$) or used with cosolvents in order to dissolve cellulose. NMMO is also a strong oxidizing agent, which as such is used in synthesis chemistry (Cope et al. 1949; Rosenau et al. 2004; Pieterse 2013), but can of course also lead to unwanted oxidation (Adorjan et al. 2005; Rosenau et al. 2005a). In addition, NMMO tends to spontaneous decomposition reactions which can have catastrophic effects if larger quantities are involved as in industrial scale. But even on a small laboratory scale such “exothermic events” or “thermal runaway reactions” of NMMO, as they are euphemistically called, can be quite “spectacular” (see Fig. 1).

In general, the decomposition processes and side reactions of NMMO can be divided into homolytic (radical) and heterolytic (ionic) decomposition

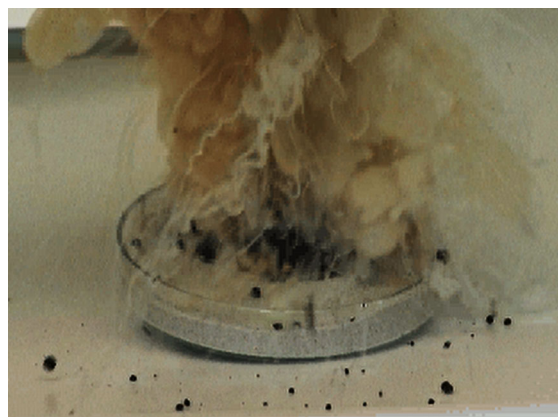


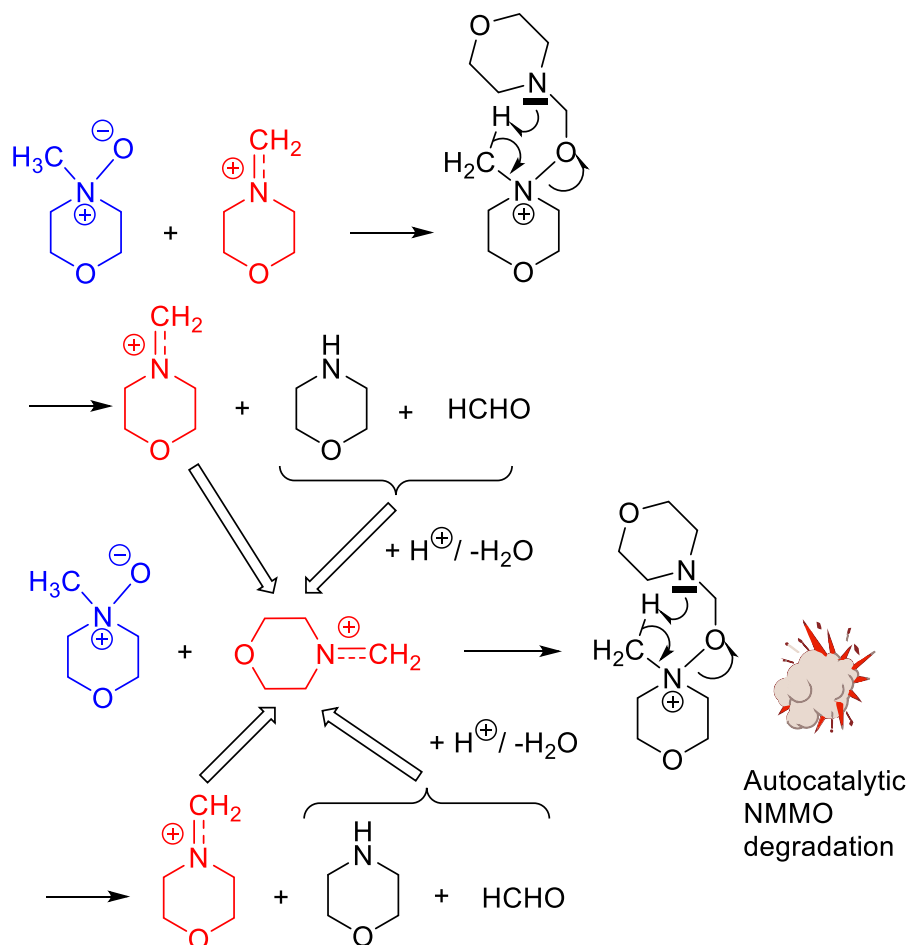
Fig. 1 Degradation of solid *N*-methylmorpholine-*N*-oxide monohydrate by a few drops of DCC solution in chloroform, picture taken after about 10–12 s

processes (Rosenau et al. 2001). The homolytic reactions are mainly induced by the presence of redox-active transition metal ions, the ionic ones by acylation or alkylation reagents. In each case, an interaction with the exocyclic oxygen atom takes place, which weakens the high-energy N–O bond and—upon its cleavage—releases considerable amounts of energy. Particularly critical here is the autocatalytic decomposition of NMMO by carbenium–iminium ions (Rosenau et al. 1999; Potthast et al. 2000). These are formed as a central intermediate product of decomposition, which itself accelerates further decomposition. The mechanism of this process is shown in Scheme 1. Once started, such a thermal decomposition reaction cannot be stopped. NMMO decomposition on a larger scale can lead to complete destruction of the plant, explosions, flash fires and fires. From an industrial perspective, however, less dramatic aspects of NMMO decomposition reactions

are also important because they involve loss of solvent and the need to use stabilizers to prevent these decomposition reactions (Rosenau et al. 2002, 2005b). The problem of NMMO stability or NMMO loss concerns both technological aspects and, evidently, economic aspects.

But even on a smaller laboratory scale, the spontaneous decomposition of NMMO must be taken seriously—accidents have happened and continue to happen, as the above-mentioned incidents show. In all these cases, attempts have been made here to carry out esterifications or amidations of polysaccharidic substrates—cellulose as polyalcohol or chitin as polyamine—with low-molecular acids, using the coupling reagents dicyclohexylcarbodiimide (DCC) or 1-ethyl-3-(3-aminopropyl)carbodiimide (EDC) in NMMO solution or NMMO-containing solvent systems. Here—known from previous work—a pronounced instability of NMMO was to be expected. We have

Scheme 1 Schematic of the mechanism of the autocatalytic decomposition of NMMO induced by carbenium–iminium ions (Mannich intermediates). Once induced, the reaction becomes uncontrollable within seconds



taken these accidents as an occasion to investigate the interaction of the cellulose solvent NMMO with common coupling reagents in a small-scale study in more detail and thus to point out once again the possible dangers of careless handling of NMMO.

Materials and methods

General

All chemicals were commercially available and of the highest purity available. Thin layer chromatography (TLC) was performed on silica gel 60 plates (5 × 10 cm, 0.25 mm) with fluorescence detection under UV light at 254 nm. *N*-Methylmorpholine-*N*-oxide was recrystallized from dioxane, *N*-methylmorpholine-*N*-oxide monohydrate from acetone.

The pulps used for this project were a beech (*Fagus sylvatica*) sulfite pulp supplied by Lenzing AG, Austria, and an eucalypt (*Eucalyptus globulus*) Kraft pulp obtained from ENCE Group, Spain. The pulp parameters are summarized in Table 1.

Preparation of stock solutions

Chloroform was freshly filtered over basic aluminum oxide (Brockmann grade 2) and was used to prepare a solution of dicyclohexylcarbodiimide (0.1 M). 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide was dissolved in 2-propanol (0.1 M). Solutions of *N*-methylmorpholine-*N*-oxide of different concentrations in different solvents (acetone, water) were prepared (see Table 2).

A solution of DCC-activated benzoic acid in chloroform (0.1 M) was prepared by mixing a 0.2 M solution of benzoic acid in chloroform (50 mL) with a 0.2 M solution of DCC in chloroform (50 mL), followed by stirring at r.t. under exclusion of moisture and air for 30 min. Solutions of lower concentration were prepared by dilution with chloroform.

A solution of EDC-activated benzoic acid in 2-propanol/water (v/v = 1:1, 0.1 M) was prepared by dropwise mixing a 0.2 M solution of gluconic acid in water (50 mL) with a 0.2 M solution of EDC in 2-propanol (50 mL) at approx. 5 °C (ice bath) so that no precipitate was formed, followed by stirring under exclusion of air for 1 h. Solutions of lower concentration were prepared by dilution with 2-propanol/water (v/v = 1:1).

Table 1 Parameters of the cellulosic pulps used

	Beech sulfite pulp	Eucalyptus Kraft pulp
Brightness (%ISO)	88.5	86
Kappa number	0.79	0.6
Intrinsic viscosity (mL/g) ^a	546	843
R18 (%)	93	92
Monosaccharide composition (%) ^b	Glucose 94.07 ± 0.08 ^c	Glucose 77.55 ± 0.12
	Xylose 3.38 ± 0.01	Xylose 18.45 ± 0.06
	Mannose 0.77 ± 0.003	Mannose 0.11 ± 0.004
	Arabinose 0.00	Arabinose 0.03 ± 0.002
	Galactose 0.01 ± 0.001	Galactose 0.31 ± 0.001
	Rhamnose 0.00	Rhamnose 0.00
Crystallinity index ^d	0.56	0.48
Mw (kg/mol) ^e	280	460

^aDetermined as cuen viscosity (measured in cupri-ethylenediamine) according to Ahn et al. (2019)

^bDetermined by total acid hydrolysis and subsequent analysis of the monosaccharides with anion-exchange chromatography

^cStandard deviation as means from three independent measurements

^dDetermined by ¹³C solid-state NMR according to Zuckerstätter et al. (2009)

^eDetermined by GPC according to Potthast et al. (2015)

Table 2 Decomposition of NMMO (solid or solution) by solutions of either coupling reagents (DCC/EDC) or DCC/EDC-activated carboxylic acids

NMMO (wt%)	Coupling agent	t_{onset} (s)	Observation
Solid (2 g)	1 drop 5 wt% DCC in CHCl_3	< 3	Violent reaction, smoke generation, charring
Solid monohydrate (2 g)	1 drop 5 wt% DCC in CHCl_3	< 3	Violent reaction, smoke generation, charring
1 M in acetone (50 mL)	5 wt% EDC in 2-propanol (5 mL)	< 3	Sudden, strong boiling, solution shot out of the vessel in a jet
0.1 M in acetone (50 mL)	5 wt% EDC in 2-propanol (5 mL)	10	Sudden boiling, brownish discoloration
50 wt% in water (50 mL)	5 wt% EDC in 2-propanol (5 mL)	10	Sudden boiling, solution splashed out of the vessel
10 wt% in water (50 mL)	5 wt% EDC in 2-propanol (5 mL)	30	Boiling, solution turns dark yellow
Solid (2 g)	1 drop 5 wt% PhCOOH/DCC in CHCl_3	45	Violent reaction, smoke generation, charring
Solid (2 g)	2 mL 5 wt% PhCOOH/DCC in acetone	< 3	Violent reaction, smoke generation, charring
Solid monohydrate (2 g)	2 mL 5 wt% PhCOOH/DCC in acetone	< 3	Violent reaction, smoke generation, charring
50 wt% in acetone (50 mL)	0.1 M PhCOOH/EDC in 2-propanol (5 mL)	< 3	Sudden strong boiling, solution shot out of the vessel
10 wt% in acetone (50 mL)	0.1 M PhCOOH/EDC in 2-propanol (5 mL)	10	Sudden strong boiling
1 wt% in acetone (50 mL)	1 mM PhCOOH/EDC in 2-propanol (5 mL)	25	Mild, short boiling
10 wt% in acetone (50 mL)	10 mM PhCOOH/EDC in 2-propanol (5 mL)	10	Sudden, strong boiling, solution splashed out of the vessel
10 wt% in acetone (50 mL)	1 mM PhCOOH/EDC in 2-propanol (5 mL)	10	Sudden, strong boiling, solution splashed out of the vessel
10 wt% in acetone (50 mL)	0.1 mM PhCOOH/EDC in 2-propanol (5 mL)	> 180	Boiling of the mixture, no violent course
50 wt% in water (50 mL)	0.1 M PhCOOH/EDC in 2-propanol (5 mL)	45	Boiling, solution splashed out of the vessel
50 wt% in water (50 mL)	0.1 M GlcA/EDC in 5 mL water/2-propanol (v/v = 1:1)	55	Boiling, solution splashed, dark discoloration
10 wt% in water (50 mL)	0.1 M EDC in 2-propanol (10 mL)	80	Warming to 90 °C, solution turned dark yellow
10 wt% in water (50 mL)	0.1 M GlcA/EDC in 5 mL water/2-propanol (v/v = 1:1)	60	Warming to 82 °C, solution turned almost black
1 wt% in water (50 mL)	0.1 M EDC in 2-propanol (10 mL)	200	No apparent degradation or warming
1 wt% in water (50 mL)	0.1 M GlcA/EDC in 5 mL water/2-propanol (v/v = 1:1)	215	No apparent degradation or warming

t_{onset} : Time in s until the start of the decomposition reaction, perceptible by charring and smoke development (solid) or sudden temperature increase (solution)

Cold caustic extraction

Cellulosic pulp (air-dried, 10 g) was disintegrated for 20 s with a kitchen blender in deionized water

(250 mL). Excess water was removed by filtration through a Büchner funnel under reduced pressure. The disintegrated pulp was placed in high-density polyethylene bottles (500 mL) together with a 2 M

aqueous NaOH solution (80 g/L, 200 mL). The bottles were closed and put on a laboratory shaker for 0.5 h at 21 °C. Subsequently, the pulp was filtered through a glass frit and rinsed, first, with 0.5 L of fresh 2 M aqueous NaOH solution, followed by a second washing step with deionized water until the filtrate featured a neutral pH value (measured with pH indicator paper).

Preparation of cellulosic pulps containing traces of coupling agents

Cellulosic pulp (air-dried, 1 g) was disintegrated for 20 s with a kitchen blender in chloroform (or 2-propanol/water, v/v = 1:1). Excess solvent was removed by filtration through a Büchner funnel under reduced pressure. To the filter cake, a 0.1 M solution of DCC in chloroform (or 0.1 M EDC in 2-propanol/water, v/v = 1:1) was added so that the amount added coupling agent in the solution was 1% of the air-dried pulp. Alternatively, 0.1 M solutions of the DCC/EDC-activated carboxylic acids were used. From the pulp suspensions the solvents were removed in vacuo at r.t. and pulps were kept vacuum-sealed in plastic bags and kept at 5 °C in the dark.

Degradation of solid NMMO by solutions of DCC/EDC

N-Methylmorpholine-*N*-oxide (2 g) or *N*-methylmorpholine-*N*-oxide monohydrate (2 g) was placed in cone-shaped form in a magnesia dish. A drop of DCC (EDC) solution or of DCC(EDC)-activated carboxylic acids was added to the top of the solid *N*-oxide. CAUTION! There is a violent, explosive reaction under splashing, strong smoke evolution, complete charring, and possibly fire. Perform ONLY in a well-functioning fume hood, observing all necessary precautionary measures (safety shield, safety goggles)!

Degradation of NMMO solutions by solutions of DCC/EDC

In an open 3-neck Pyrex reactor, equipped with mechanical stirrer and a thermocouple, a solution of DCC (EDC) was added to a solution of *N*-methylmorpholine-*N*-oxide under stirring at room temperature under ambient atmosphere. The stirring was continued and the course of temperature as well as

visual observations were recorded. For the concentrations and volumes used, please, refer to Table 2. CAUTION! There might be a violent reaction under sudden boiling and splashing. Perform ONLY in a well-functioning fume hood, observing all necessary precautionary measures (safety shield, safety goggles)!

Degradation of lyocell dopes and NMMO/cosolvent mixtures by cellulosic pulps

Following previous work (Rosenau et al. 2001, 2002; Böhmendorfer et al. 2017), a computer-monitored IKA C-6000 bomb calorimeter with efficient stirrer and efficient heating (50°/min) was used to prepare solutions of cellulosic pulps and to follow the uncontrolled degradation of NMMO and NMMO mixtures. Melts of *N*-methylmorpholine-*N*-oxide monohydrate at 90 °C or NMMO/cosolvent mixtures at 80 °C were prepared. In some cases, stabilizing agents (0.1 wt%) were added, see Table 3. Under efficient stirring, the cellulosic pulp (5 wt%) containing traces of DCC, EDC or EDC-activated carboxylic acids (1% rel. to pulp) was added to the NMMO phase. The vessel was closed immediately and time and pressure were recorded. Xylan was used in analogy to the pulp. The time to the onset of the spontaneous degradation (“ t_{onset} ”), seen in a sudden increase in temperature and pressure, was taken as a measure of the (in)stability of the mixture. For the co-solvents in the binary NMMO mixtures, stabilizing agents and concentrations see Table 3.

Results and discussion

Irrespective of whether NMMO is present as a solid substance or in organic solution, contact with the coupling reagents DCC or EDC leads to almost immediate, spontaneous decomposition of the amine oxide. If NMMO monohydrate and 1 wt% DCC are mixed with a spatula, an explosion-like reaction takes place within a few seconds with complete decomposition, strong smoke development and sometimes inflammation (Fig. 1). The same effect is achieved by adding a drop of DCC solution in chloroform to solid NMMO monohydrate (see Table 2). The behavior of EDC is completely analogous. It should be noted

Table 3 Decomposition of NMMO monohydrate (pure substance or component in a binary solvent mixture) by pulps (5 wt% rel. to solvent) containing residual concentrations (1 wt% rel. to pulp) of either coupling reagents (DCC/EDC) or DCC/EDC-activated carboxylic acids

Type of NMMO	Pulp with small amounts of coupling agent	t_{onset} (s) ^a	Observation
Monohydrate	BS, 1 wt% ECC	45	Violent reaction, heat and smoke generation, charring
Monohydrate	BS, 1 wt% DCC	50	Violent reaction, heat and smoke generation, charring
Monohydrate	EK, 1 wt% ECC	45	Violent reaction, heat and smoke generation, charring
Monohydrate	EK, 1 wt% DCC	55	Violent reaction, heat and smoke generation, charring
Monohydrate	BS, 1 wt% PhCOOH/EDC	75	Violent reaction, heat and smoke generation, charring
Monohydrate	BS, 1 wt% GlcA/EDC	90	Violent reaction, heat and smoke generation, charring
Monohydrate/DMSO (25 wt%)	BS, 1 wt% ECC	30	Violent reaction, strong heat generation, dark brown discoloration, T > 150 °C
Monohydrate/DMSO (50 wt%)	BS, 1 wt% ECC	65	Violent reaction, heat generation, brown discoloration
Monohydrate/DMSO (75 wt%)	BS, 1 wt% ECC	95	Heat generation, T ~ 120 °C, brown discoloration
Monohydrate/DMSO (75 wt%)	EK, 1 wt% ECC	95	Heat generation, T ~ 120 °C, brown discoloration
Monohydrate/DMSO (75 wt%)	BS, xylan extracted, 1 wt% ECC	70	Heat generation, T ~ 120 °C, brown discoloration
Monohydrate/DMSO (75 wt%)	EK, xylan extracted, 1 wt% ECC	75	Heat generation, T ~ 120 °C, brown discoloration
Monohydrate/DMSO (75 wt%)	Beech xylan, 1 wt% ECC	180	Slower heat generation, T ~ 75 °C, brown discoloration
Monohydrate/H ₂ O (50 wt%)	BS, 1 wt% ECC	80	Heat generation, boiling, brownish color
Monohydrate/2-propanol (50 wt%)	BS, 1 wt% ECC	65	Heat generation, vigorous boiling, brownish precipitate
Monohydrate/pyridine (50 wt%)	BS, 1 wt% ECC	220	Slower heat generation, yellow discoloration
Monohydrate, 0.1 wt% NaOH (2 M aq. soln.)	BS, 1 wt% ECC	235	Violent reaction, heat and smoke generation, charring
Monohydrate, 0.1 wt% morpholine	BS, 1 wt% DCC	–	No apparent side reaction, faint yellow discoloration
Monohydrate, 0.1 wt% morpholine	BS, 1 wt% PhCOOH/EDC	–	No apparent side reaction, yellow discoloration
Monohydrate, 0.1 wt% piperidine	BS, 1 wt% ECC	–	No apparent side reaction, no discoloration

t_{onset} : Time in s until the start of the decomposition reaction, perceptible by sudden temperature increase. BS: beech sulfite pulp, EK: Eucalyptus kraft pulp

^aAverage of 3 runs, difference between measurements < 10 s

that stoichiometric amounts of DCC/EDC are not required. As soon as minute quantities of carbenium–iminium ions (Scheme 1) are formed, which under the concentrated conditions find no other reaction partner than further NMMO, the autocatalytic degradation cycle is initiated and can no longer be stopped. This leads to complete—and strongly exothermic—decomposition of the NMMO.

In solutions of NMMO the reaction proceeds analogously, but the effect is less drastic than in solid

NMMO due to dilution and better heat dissipation through the solvent. In the case of a 10 wt% (0.85 M) solution of NMMO in acetone at room temperature, the addition of a 5 wt% EDC solution leads to such strong heating that the solution shoots out of the flask in a jet. When mixing 0.1 M solutions of NMMO in chloroform with a few drops of 1% DCC solution in the same solvent, there is still spontaneous heating of the solution which brings the solution to a boil and causes a brown coloration. These effects are of course

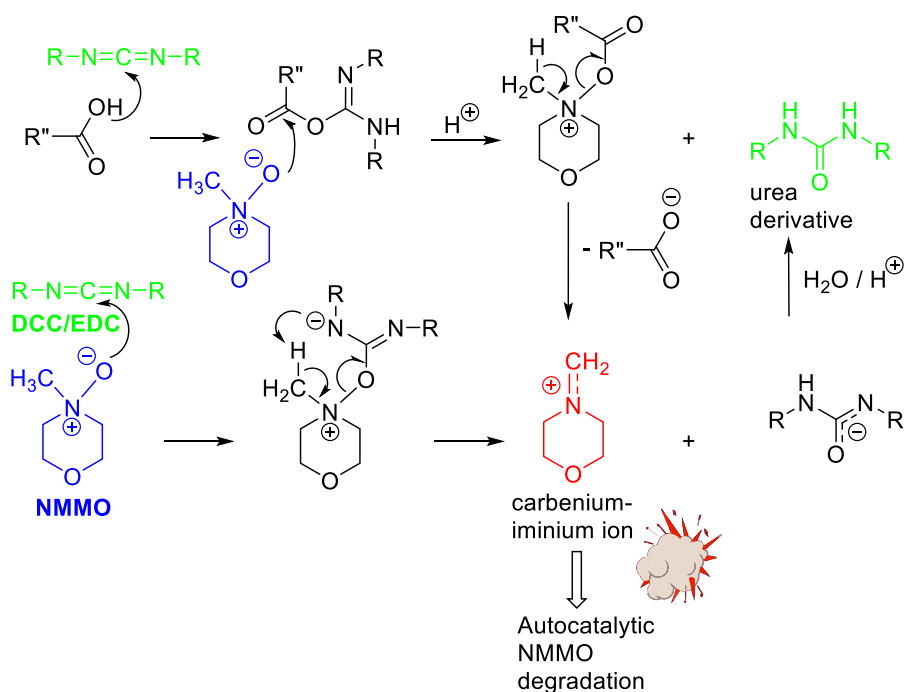
mainly dependent on the concentration of NMMO, but also on the type (heat capacity) of the solvent and the effectiveness of possible cooling.

The mechanism of the decomposition reaction is shown in Scheme 2. Similar to acylating agents or strong alkylating agents, DCC/EDC react as strong electrophilic compounds with the exocyclic oxygen atom of NMMO, which leads to N-O bond breakage and ultimately to the formation of a carbenium-iminium ion. This then initiates the autocatalytic NMMO decomposition according to the known mechanism (Scheme 1). In general, there is no difference whether NMMO is used in anhydrous form (as often used in organic synthesis) or as NMMO monohydrate, such as the common cellulose solvent. DCC/EDC react much faster with the much more nucleophilic NMMO oxygen than with (hydrate) water. EDC was even developed for use in aqueous solvent systems and therefore shows only low reactivity towards water.

Also after activation of acids by DCC/EDC the decomposing effect on NMMO/NMMO monohydrate persists. The intermediate *O*-acyl-isoureas formed in

this process have been “prepared” for further reaction with alcohols (to form esters) or amines (to form amides) by conversion with the coupling reagent, so to speak, and accordingly represent “activated carboxylic acids”. They are strong acylating agents and react not only with alcohols to form esters and with amines to form amides, but also with NMMO under attack and acylation at the exocyclic oxygen, which finally leads to complete decomposition of the amine oxide, completely analogous to the reaction of the coupling reagents DCC/EDC themselves, i.e. in the absence of carboxylic acids to be activated (Scheme 2).

The decomposition reaction is of course also here dependent on concentration and dilution effects (Table 1). Again, the concentration of NMMO is decisive, whereas the concentration of coupling reagent or activated acid has only a minor effect. Even low concentrations of DCC/EDC or DCC/EDC-carboxylic acid mixtures, down to 1 mM, start the complete decomposition of organic NMMO solutions, but the further course of NMMO decomposition is determined by the autocatalytic NMMO



Scheme 2 Degradation of NMMO (as solid or in solution) either by coupling reagents of the carbodiimide type itself or by carbodiimide-activated carboxylic acids. R = cyclohexyl, 1-ethyl-3-(3-aminopropyl); R''COOH = any carboxylic acid.

For better understanding NMMO is shown in blue, the coupling reagents in green and the autocatalytically active *N*-(methylene)iminium (carbenium-iminium) ion in red

decomposition, for which the concentration of the initiator is irrelevant. Also in water the effect can be observed down to a NMMO concentration of about 0.5 M (approx. 5 wt%). While in organic solvents the limit of instability is 1 wt% NMMO, it is about five to ten times higher in water.

The summary of the results in Table 2 clearly shows that solutions that may contain traces or even higher concentrations of DCC/EDC coupling reagents or of DCC/EDC-activated carboxylic acids should never be brought into contact with NMMO solutions, let alone with NMMO melts, cellulose solutions in NMMO monohydrate or lyocell spinning dopes in general. There is a high probability that spontaneous decomposition reactions will occur as a result, and there is a realistic health hazard and danger in terms of occupational health and safety!

The influence of cellulose dissolved in NMMO on the reaction is minimal. NMMO is only insignificantly stabilized by dissolved cellulose, if at all (Table 3). For the experiments in Table 3, a 5% solution of cellulosic pulps in NMMO monohydrate was used (see experimental section).

It is equally hazardous if NMMO is brought into contact with cellulose that still contains traces of coupling reagents or DCC/EDC-activated acids as remnants of modification reactions. This may be the case, for example, if the modified cellulosic material is to be swollen in NMMO systems or, after dissolution under lyocell conditions, formed into films, fibers or beads, etc. In the case of pure NMMO melts this also leads to complete decomposition within a few seconds, similar to that in Fig. 1. In binary solvent systems with NMMO as one component, the reaction is attenuated by the dilution effect and—depending on the NMMO concentration—the reaction mixture is again brought to boiling or at least heated up. But even here there is a potential danger (burns, splashing etc.).

Table 3 demonstrates the effect that different pulps containing 1 wt% of coupling reagent or DCC/EDC-activated carboxylic acids have on NMMO and NMMO mixtures as solvents/swelling agents. The concentration of pulp was constant at 5 wt% of the solvent mixture and the concentration of coupling reagent was 1 wt% relative to the pulp, i.e. 0.05 wt% relative to the solvent. Here, in analogy to earlier NMMO studies, work was carried out in a calorimetric bomb and the time from the first contact of the reactants to the start of the decomposition reaction,

which is noticeable by a sudden significant rise in temperature, was measured (“ t_{onset} ”). The shorter t_{onset} , the more unstable the mixture or the more reactive the DCC/EDC-containing pulp. Table 3 clearly shows that there are no significant differences between different pulps when it comes to contact with pure NMMO (monohydrate). In binary solvent systems with NMMO, the reactivity generally decreases with increasing content of the second solvent, so that reactivity nuances become more visible: while the type of pulp itself continued to have no influence, the pulp with higher hemicellulose content (xylan) appeared at least slightly more stable, so that immediate decomposition no longer occurred.

The protective effect of xylan can be explained by the fact that xylan—compared to cellulose—is oxidized much faster by NMMO at the reducing ends than cellulose (in addition, xylan contains significantly higher concentrations of reducing ends due to its lower molecular weight). These are oxidized to xyloic acid moieties with NMMO being reduced to NMM. NMM, in turn, is strongly basic and has thus a stabilizing effect on NMMO. Although this hypothesis on the mechanism of action has not been clearly proven, the fact that isolated xylan with 1 wt% DCC/EDC residual content in NMMO is significantly more stable than the same mass of pulp (Table 3) is an important indication of the validity of this theory.

While the addition of alcohols or water does not provide sufficient stabilization, secondary amines completely prevent the decomposition effect of DCC/EDC residues on NMMO if their concentration is in the order of (or above) the DCC/EDC concentration (see Table 3). This effect is easy to understand for two reasons: on the one hand, the secondary amines react quickly with the activated carboxylic acids, which are thus no longer able to initiate the decomposition of NMMO, thus forming amides; on the other hand, by trapping the carbenium–iminium ions, they interrupt the critical decomposition cycle of NMMO, forming stable formaminals (Rosenau et al. 2002). It is therefore recommended—as a conclusion—to add 1–2 mol% secondary amine (morpholine, piperidine) to NMMO or NMMO mixtures when processing cellulosic materials which may contain DCC/EDC residues, in order to stabilize the solution against NMMO degradation. This is much more effective than an aqueous alkaline solution of the same concentration (Table 3). The addition of secondary amines is in

many cases compatible with the intended reaction course. They can also be easily removed from the cellulose product by a slightly acidic wash.

Conclusions

In summary, DCC/EDC and similar coupling reagents are incompatible with NMMO. Contact can lead to dangerous, highly exothermic, uncontrollable decomposition reactions. Particularly treacherous are traces of DCC/EDC or DCC/EDC-activated carboxylic acids, which remained in cellulosic material that is brought into contact with NMMO in subsequent reaction steps. In general, NMMO solvent systems (preferably with lowest possible NMMO contents) are safer than pure NMMO as melt (lyocell conditions). Small amounts of secondary amine (in the order of magnitude of the concentration of the DCC/EDC traces) effectively stabilize the systems against the otherwise threatening decomposition reactions and exothermic reactions, so that such an addition is highly recommended whenever possible.

The present small study provides additional insights into the chemical mechanisms of the frequently used cellulose solvent and swelling agent NMMO, which has a potential for danger, but can be used completely harmlessly if handled properly, as the decades of use in large-scale cellulose fiber production proves. Above all, however, we hope that the warnings contained in this document will help to raise awareness of the inherent dangers of working with NMMO at elevated temperatures—especially if inexperienced in handling NMMO—so that in future all related accidents in the laboratories can be prevented.

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