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Degradation of cellulosic materials by heating in DMAc/LiCl

Antje Potthast,[a] Thomas Rosenau,[a] Herbert Sixta[b] and Paul Kosma[a,*]

[a]*Christian-Doppler-Laboratory, University of Agricultural Sciences, Muthgasse 18, A-1190 Vienna, Austria*
[b]*R & D Department, Lenzing AG, A-4860 Lenzing, Austria*

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Abstract—*N*,*N*-Dimethylacetamide (DMAc, **1**)/lithium chloride is a frequently used solvent system for cellulosic materials. Heating or refluxing insoluble samples in DMAc/LiCl represents a common protocol for facilitating the subsequent dissolution. It is shown by kinetics using gel permeation chromatography (GPC) that the improved solubility is not caused by an alleged 'activation' of the pulp, but by progressing degradation of the cellulosic material. Ketene aminal **2** and *N*,*N*-dimethylketeniminium ions (**3**), the latter being known as reagent for cleavage of ethers and acetals, have been demonstrated to be present in DMAc and DMAc/LiCl at elevated temperatures by specific trapping of these intermediates in a Claisen rearrangement and in a thermal [2+2]-cycloaddition, respectively.

N,*N*-Dimethylacetamide (DMAc, **1**) containing lithium chloride is a very common solvent system in cellulose chemistry,[1,2] where it is frequently used for derivatization under homogeneous conditions.[3,4] Moreover, it has become the standard solvent for gel permeation chromatography (GPC) measurements of cellulosics.[5–7] To achieve dissolution in DMAc/LiCl, cellulosic pulps are subjected to so-called 'activation procedures', e.g. by treatment with liquid ammonia,[8,9] swelling in water followed by solvent exchange to DMAc,[5,10] or freeze-drying.[11] A very common protocol is also heating or refluxing the cellulose samples in DMAc, or in DMAc containing LiCl.[12,13] This treatment is thought to cause intra- and intercrystallite swelling, breaking of hydrogen bonds and increased accessibility. In the present work, two cellulose samples of different provenience (cf. Fig. 1) which are readily soluble in DMAc/LiCl have been employed to study the effects of the high temperature activation method in more detail.

As demonstrated by GPC measurements, heating in DMAc or DMAc/LiCl definitely causes cellulose degradation, which also explains the observed positive effect on dissolution (see Fig. 1). Already at temperatures as low as 85°C, a clear decrease in molecular weight was observed by GPC. The loss in DP (degree of polymerization) became more pronounced as temperature and LiCl content increased, and became rather severe at temperatures near the boiling point of DMAc (164°C). Cellulose degradation in the absence of LiCl is less pronounced than in its presence.

The cellulose degradation was observed for both pulps, the degradation rate being different. It appeared thus plausible to assume that a highly reactive, hitherto unidentified intermediate was present, which effected this cleavage, since merely a thermal decay could by no means account for the magnitude of the observed effects.

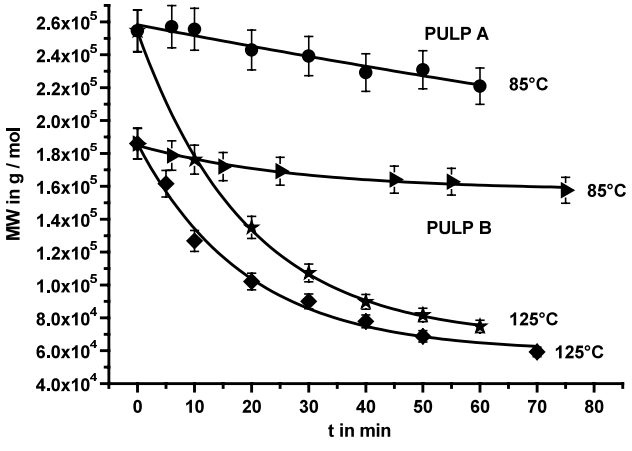

Figure 1. Degradation of two different pulps upon heating in DMAc/LiCl (9% w/v) at different temperatures. Pulp A: beech sulfite pulp; pulp B: eucalyptus prehydrolysis kraft pulp, error bars 5%.

Keywords: DMAc; LiCl; cellulose; degradation; keteniminium ions; trapping; cycloaddition; kinetics; gel permeation chromatography.

* Corresponding author. Tel.: +43-1-36006 6071; fax: +43-1-36006 6059; e-mail: pkosma@edv2.boku.ac.at

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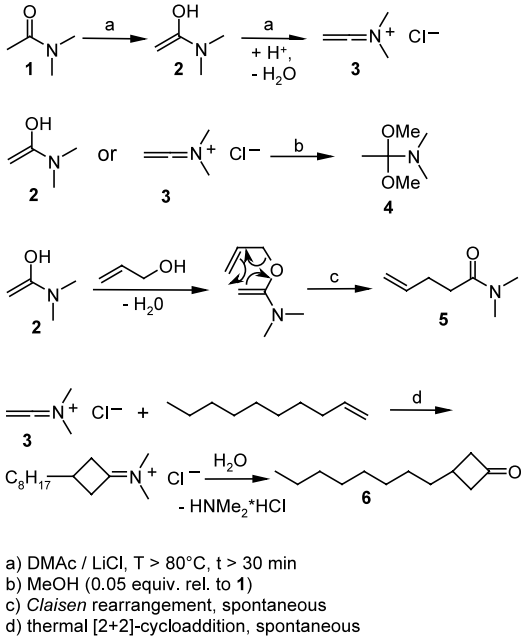
Addition of methanol to heated DMAc/LiCl produced small amounts of 1-dimethylamino-ethane-1,1-diol (**4**), which was indicative of the intermediacy of *N*,*N*-dimethylketene semiaminal (**2**)—the enol form of DMAc—and/or *N*,*N*-dimethylketeniminium ions (**3**). The occurrence of both intermediates in DMAc/LiCl at temperatures above 85°C was finally confirmed by trapping (see Scheme 1). For intermediate **2**, the reaction with allyl alcohol to an ketene aminal, which undergoes immediate Claisen-type rearrangement to 4-pentenoic acid *N*,*N*-dimethylamide (**5**),[14] was employed. To trap **3**, 1-decene was used, which reacted in a thermal, suprafacial–antarafacial [2+2]-cycloaddition to produce a cyclobutaniminium salt, finally giving 3-octyl-cyclobutanone (**6**)[15] upon hydrolysis. Trapping products **5** and **6** were found in heated DMAc and in heated DMAc/LiCl independent of the presence of dissolved or suspended pulp, lower amounts of trapping product being obtained in the presence of cellulose.

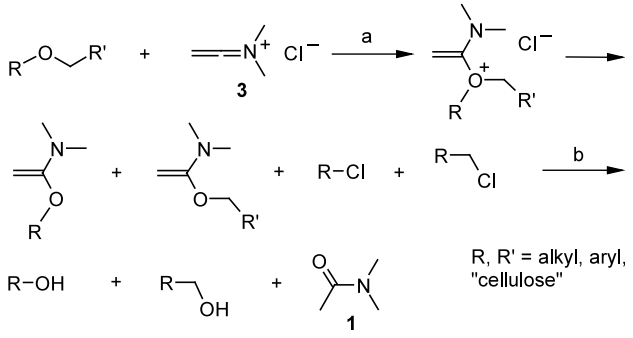
N,*N*-Dimethylketeniminium cations (**3**) are formed from DMAc via enol **2** in a thermal elimination. The water thereupon released is incorporated into the Li^+ ligand shell, which prevents the immediate reverse reaction. The chloride anions act as counterions to the keteniminium cation. Thus, a dynamic equilibrium between **3**, lithium cations, hydroxyl anions and chloride anions is established. The equilibrium concentration of **2** is determined by the endothermicity of the elimination process and the sum of strong ionic interactions in the solution; it is usually very low.[16,17] However, if keteniminium ions are removed from the reaction system, e.g. by trapping or by a competitive reaction with cellulose, they are continuously regenerated. The thermal formation of keteniminium salts from secondary amides in polar aprotic solutions in the presence of several salts has been reported,[18,19] but has never been described to occur in DMAc/LiCl mixtures. Keteniminium salts are known as reagents to affect cleavage of ethers, acetals and ketals.[20–22] In organic solutions containing electrolytes, hydroxyl groups and amino groups do not interfere with the reaction, as they are surrounded by a solvent shell and are thus shielded from attack by the strongly electrophilic keteniminium reagent.



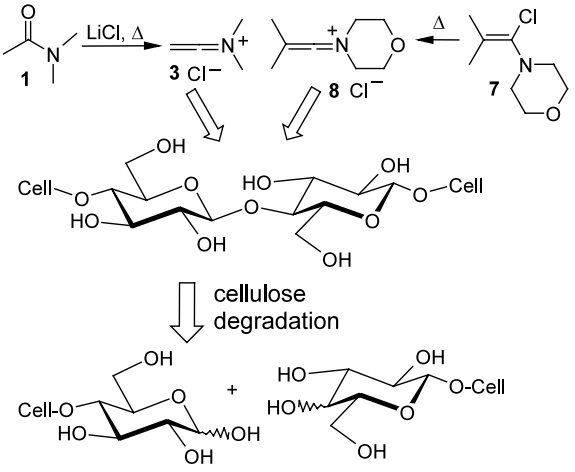
Scheme 1. Formation of intermediates **2** and **3** from DMAc (**1**) and proof of their intermediacy by specific trapping reactions.

The same general mechanism as in Scheme 2 must be assumed also for the cleavage of glycosidic bonds in cellulosics. The electrophilic transient species **3** attacks the glycosidic oxygen, followed by cleavage of the glycosidic bond and secondary hydrolytic reactions.

The detrimental effect of keteniminium ions on the integrity of cellulosic pulps was confirmed by addition of an external degrading agent of the keteniminium type (Scheme 3): when 4-(1-chloro-2-methylpropenyl) morpholine **7** (0.1% relative to pulp), which immediately releases keteniminium ion **8** upon thermal treatment, was added to a solution of pulp in DMAc/LiCl (9%, w/v) heated to 85°C, the cellulose was completely degraded to oligomers within 30 min.



Scheme 2. General mechanism of the cleavage of ether and acetal bonds by *N*,*N*-dimethylketeniminium ions (**3**).



Scheme 3. Degradation of cellulosics by cleavage of glycosidic bonds induced by keteniminium ions (**3** or **8**).

In summary, DMAc/LiCl at temperatures above 85°C contains **3** as highly reactive intermediate, which is able to cleave glycosidic bonds. Heating or refluxing cellulosics in DMAc or DMAc/LiCl should no longer be used as an 'activation procedure': it causes pulp degradation, and it thus influences the molecular weight distribution of the material, so that subsequent GPC analysis will not report the data of the original sample.

Acknowledgements

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References

1. Dawsey, T. R.; McCormick, C. L. *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.* **1990**, *C30*, 405–440.
2. Morgenstern, B.; Kammer, H. W. *TRIP* **1996**, *4*, 87–92.
3. Heinze, T. *Prog. Polym. Sci.* **2001**, *26*, 1689–1762.
4. Rahn, K.; Diamantaglou, M.; Klemm, D.; Berghmans, H.; Heinze, T. *Angew. Makromol. Chem.* **1996**, *238*, 143–163.
5. Kennedy, J. F.; Rivera, Z. S.; White, C. A.; Lloyd, L. L.; Warner, F. P. *Cellulose Chem. Technol.* **1990**, *24*, 319–325.
6. Striegel, A. M. *Carb. Polym.* **1997**, *34*, 267–274.
7. Schelosky, N.; Röder, T.; Baldinger, T. *Das Papier* **1999**, *53*, 728–738.
8. Morgenstern, B.; Berger, W. *Acta Polymerica* **1993**, *44*, 100.
9. Röder, T.; Morgenstern, B.; Schelosky, N.; Glatter, O. *Polymer* **2002**, *42*, 6765–6773.
10. Kvernheim, A. L.; Lystad, E. *Acta Chem. Scand.* **1989**, *43*, 209–211.
11. Röhrling, J.; Potthast, A.; Rosenau, T.; Lange, T.; Ebner, G.; Sixta, H.; Kosma, P. *Biomacromolecules* **2000**, *3*, 969–975.
12. Klemm, D.; Philipp, B.; Heinze, T.; Heinze, U.; Wagenknecht, W. *Comprehensive Cellulose Chemistry*; Wiley-VCH: Weinheim, 1998; Vol. 2, p. 331.
13. Tosh, B.; Saikia, C. N.; Dass, N. N. *Carb. Res.* **2000**, *327*, 345–352.
14. 4-Pentenoic acid *N*,*N*-dimethylamide (**5**). ^{1}H NMR ($CDCl_3$): δ 2.36 (m, 4H, C$\underline{H}_2$-C$\underline{H}_2$), 2.95 (s, 3H, N-C$\underline{H}_3$), 3.01 (s, 3H, N-C$\underline{H}_3$), 4.99 (dd, 1H, CH=C$\underline{H}_2$, ^{3}J=10.0 Hz, ^{3}J=1.5 Hz), 5.06 (dd, 1H, CH=C$\underline{H}_2$, ^{3}J=17.5 Hz, ^{2}J=1.5 Hz), 5.88 (m, 1H, C$\underline{H}$=CH$_2$). ^{13}C NMR ($CDCl_3$): δ 29.1 (^{3}CH$_2$), 32.5 (^{2}CH$_2$), 35.3 (N-CH$_3$), 37.1 (N-CH$_3$), 115.0 (=^{5}CH$_2$), 137.6 (^{4}CH=), 172.2 (^{1}CO). The two *N*-methyl groups are not magnetically equivalent due to the hindered rotation around the C-N amide bond.
15. Characterized as 3-octylcyclobutanone-2,4-dinitrophenylhydrazone: yellow crystals; mp=144–146°C. ^{1}H NMR ($CDCl_3$): δ 0.89 (t, 3H, $^{8'}$CH$_3$-), 1.28 (m, 10H, $^{2'}$CH$_2$, $^{3'}$CH$_2$, $^{4'}$CH$_2$, $^{5'}$CH$_2$, $^{6'}$CH$_2$), 1.54 (m, 4H, $^{1'}$CH$_2$, $^{7'}$CH$_2$), 2.56 (m, 1H, ^{3}CH), 2.65 (m, 2H, ^{2}CH^{A}, ^{4}CH^{A}), 3.14 (m, 2H, ^{2}CH^{B}, ^{4}CH^{B}), 7.86 (d, 1H, $^{6''}$CH), 8.28 (dd, 1H, $^{5''}$CH), 9.11 (s, 1H, 3''CH), 10.72 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 14.1 ($^{8'}$CH$_3$), 22.6 ($^{7'}$CH$_2$); 27.4 ($^{2'}$CH$_2$); 28.0 (^{3}CH); 29.2; 29.4; 29.5 ($^{3'}$CH$_2$, $^{4'}$CH$_2$, $^{5'}$CH$_2$); 31.8; ($^{6'}$CH$_2$), 36.2 ($^{1'}$CH$_2$), 37.1 (^{2}CH$_2$), 39.5 (^{4}CH$_2$), 116.0 ($^{6''}$CH$_2$); 123.5 ($^{3''}$CH$_2$); 128.7 ($^{4''}$CH$_2$); 129.9 ($^{5''}$CH$_2$); 137.5 ($^{2''}$CH$_2$); 144.8 ($^{1''}$CH$_2$); 160.0 (^{1}CO). As *cis*/*trans*-isomerism occurs at the C=N double bond of the hydrazone, C-2 (*cis*) and C-4 (*trans*) of the cyclobutane lose their magnetic equivalence.
16. Barthel, J.; Krienke, H.; Kunz, W. *Physical Chemistry of Electrolyte Solutions*; Steinkopff: Darmstadt, 1998.
17. Varela, L. M.; Rega, C.; Sarmiento, F. *J. Chem. Phys.* **1999**, *110*, 4483.
18. Stewart, R. *The Proton*: *Applications to Organic Chemistry*; Academic Press: New York, 1985.
19. Zhang, W. M.; Collins, R.; Mahmood, K.; Dowd, P. *Tetrahedron Lett.* **1995**, *36*, 2729–2732.
20. Böhme, J.; Viehe, H. J. *Iminium Salts in Organic Chemistry Part I*; Wiley: New York, 1976.
21. Arcelli, A.; Cecchi, R.; Porzi, G.; Rinaldi, S.; Sandri, S. *Tetrahedron* **2001**, *57*, 6843–6846.
22. Penn, J. H.; Deng, D. L. *Tetrahedron* **1992**, *48*, 4823–4830.