

---

This is an electronic reprint of the original article.  
This reprint may differ from the original in pagination and typographic detail.

Pääkkönen, Timo; Bertinetto, Carlo; Pönni, Raili; Tummala, Gopi Krishna; Nuopponen, Markus; Vuorinen, Tapani

**Rate-limiting steps in bromide-free TEMPO-mediated oxidation of cellulose-Quantification of the N-Oxoammonium cation by iodometric titration and UV-vis spectroscopy**

*Published in:*  
APPLIED CATALYSIS A-GENERAL

*DOI:*  
[10.1016/j.apcata.2015.07.024](https://doi.org/10.1016/j.apcata.2015.07.024)

Published: 01/01/2015

*Document Version*  
Peer reviewed version

*Please cite the original version:*

Pääkkönen, T., Bertinetto, C., Pönni, R., Tummala, G. K., Nuopponen, M., & Vuorinen, T. (2015). Rate-limiting steps in bromide-free TEMPO-mediated oxidation of cellulose-Quantification of the N-Oxoammonium cation by iodometric titration and UV-vis spectroscopy. *APPLIED CATALYSIS A-GENERAL*, 505(September 25), 532-538. <https://doi.org/10.1016/j.apcata.2015.07.024>

---

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.

1 **Rate-limiting Steps in Bromide-free TEMPO-mediated Oxidation of**  
2 **Cellulose – Quantification of the N-Oxoammonium Cation by Iodometric**  
3 **Titration and UV-Vis Spectroscopy**  
4

5 Timo Pääkkönen<sup>a,\*</sup>, Carlo Bertinetto<sup>a</sup>, Raili Pönni<sup>a</sup>, Gopi Krishna Tummala<sup>a</sup>, Markus Nuopponen<sup>b</sup>  
6 and Tapani Vuorinen<sup>a</sup>  
7

8 <sup>a</sup> Aalto University, School of Chemical Technology, Department of Forest Products Technology, P.O.  
9 Box 16300, 00076 Espoo, Finland  
10 timo.paakkonen@aalto.fi  
11 carlo.bertinetto@aalto.fi  
12 raili.ponni@aalto.fi  
13 tapani.vuorinen@aalto.fi  
14

15 Present address of Gopi Krishna Tummala:  
16 Uppsala University, Division of Nanotechnology and Functional Materials, Department of  
17 Engineering Sciences, Box 534, 75121 Uppsala, Sweden  
18 gopi.tummala@angstrom.uu.se  
19

20 <sup>b</sup> UPM, Tekniikantie 2 C, 02150 Espoo, Finland  
21 markus.nuopponen@upm.com  
22

23 \*corresponding author: Timo Pääkkönen  
24 Address: Aalto University, School of Chemical Technology, Department of Forest Products  
25 Technology, P.O. Box 16300, 00076 Aalto, Finland  
26 email: timo.paakkonen@aalto.fi  
27 phone: +358503440749  
28 fax: +35898554276  
29

30 *ABSTRACT*  
31

32 A iodometric titration method was introduced to study the conversion of 2,2,6,6-tetramethyl-1-  
33 piperidinyloxy (TEMPO) to the corresponding N-oxoammonium cation (TEMPO<sup>+</sup>) by hypochlorite in  
34 the absence and presence of bromide ion. The validity of the titration was verified with UV-Vis  
35 spectroscopy combined with a multivariate curve resolution (MCR) algorithm to calculate the  
36 concentrations and spectral signatures of the pure components (i.e. TEMPO, Cl(+1) and TEMPO<sup>+</sup>).

37 The formation of the oxoammonium cation was successfully followed during the activation of  
38 TEMPO by HOCl and HOBr. It was found that HOBr is a more effective activator for TEMPO than  
39 HOCl is. Moreover, the importance of a separate activation step for TEMPO with bromide-free  
40 TEMPO oxidations could be identified with this titration method. The content of TEMPO<sup>+</sup> was also  
41 monitored during the TEMPO-mediated oxidation of a cellulosic pulp by hypochlorite in the absence  
42 and presence of bromide. It was found that the oxidation of the alcoholic groups by TEMPO<sup>+</sup> was  
43 generally the rate-determining step and much slower than the regeneration of TEMPO<sup>+</sup> through  
44 oxidation of the hydroxylamine by HOCl and HOBr. However, at high pH the latter reaction became  
45 rate-limiting.

46

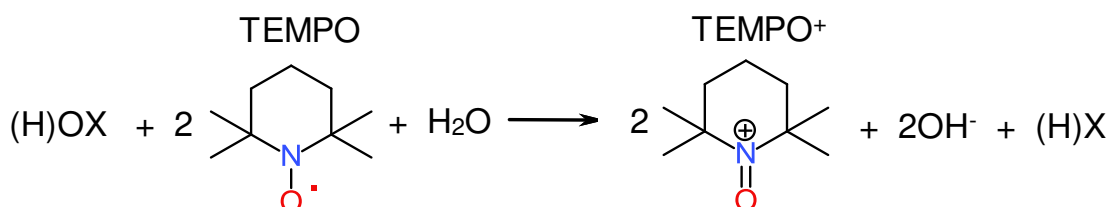
47 **Keywords:** birch pulp, iodometric titration, multivariate curve resolution, oxoammonium cation,  
48 TEMPO-mediated oxidation, UV-Vis spectrometry

## 49 1. Introduction

50 The chemistry of catalytic oxidation of alcohols with oxoammonium ion in aqueous media was  
51 reported decades ago [1-4]. The fast and selective oxidation of primary alcohols to carboxylates via  
52 aldehydes by oxoammonium ion was introduced later [5]. More recently, this method was applied  
53 to the oxidation of cellulose [6] and to the preparation of nanofibrillated cellulose (NFC) [7, 8].  
54 Altogether, this oxidation has gained a vast research interest [9-21]. The TEMPO-mediated oxidation  
55 reduces drastically the energy consumption during the pulp disintegration to NFC, which is a  
56 transparent gel consisting of individual cellulose microfibrils and microfibril bundles. The energy  
57 consumption of the nanocellulose production via a TEMPO-mediated oxidation can be reduced from  
58 700-1400 MJ kg<sup>-1</sup> (microfibrillated cellulose (MFC) process with a high pressure homogenizer  
59 treatment) to less than 7 MJ kg<sup>-1</sup> (TEMPO-oxidized NFC) [22]. NFC can be utilized, for example, as a  
60 reinforcing agent in composites [22, 23]. Other applications of NCF include gas-barrier films,  
61 electronics, cosmetics, and flame-resistant materials [22].

62 The most widely studied TEMPO-oxidation process is based on the use of the NaBr/TEMPO/NaOCl  
63 system. The pH level during this oxidation is typically 10 or higher [10, 12, 13, 19, 22]. The amount  
64 of bromide is commonly higher than the amount of TEMPO (mass ratio 10:1) during the oxidation  
65 [7]. Moreover, some TEMPO-oxidation methods without the application of bromide have been  
66 reported in the literature [20, 24]. For example, acid-neutral conditions (pH 3.5-6.8) have been  
67 applied to oxidize regenerated cellulose applying a TEMPO/NaOCl/NaClO<sub>2</sub> procedure without the  
68 use of bromide [24] With this low pH range, high carboxylate contents for the oxidized pulps (4  
69 mmol COOH / g) have been reported after an extended reaction time of almost 80 h. In addition, an  
70 electro-mediated oxidation has been used to oxidize the primary hydroxyl groups of cellulose to  
71 carboxylates without the addition of either NaOCl or NaBr. In this oxidation, TEMPO or a TEMPO

72 derivative is used with an amperometric system for the oxidation of the pulp. However, achieving a  
 73 carboxylate content of 1 mmol g<sup>-1</sup> of pulp requires a 48 hours oxidation, which indicates an  
 74 extremely low reaction rate [20]. As a conclusion, the TEMPO-mediated oxidations without bromide  
 75 are slower compared to the ones that apply bromide. However, a process without bromide would  
 76 be of interest since its presence in the waste water streams is highly undesired [11].



77

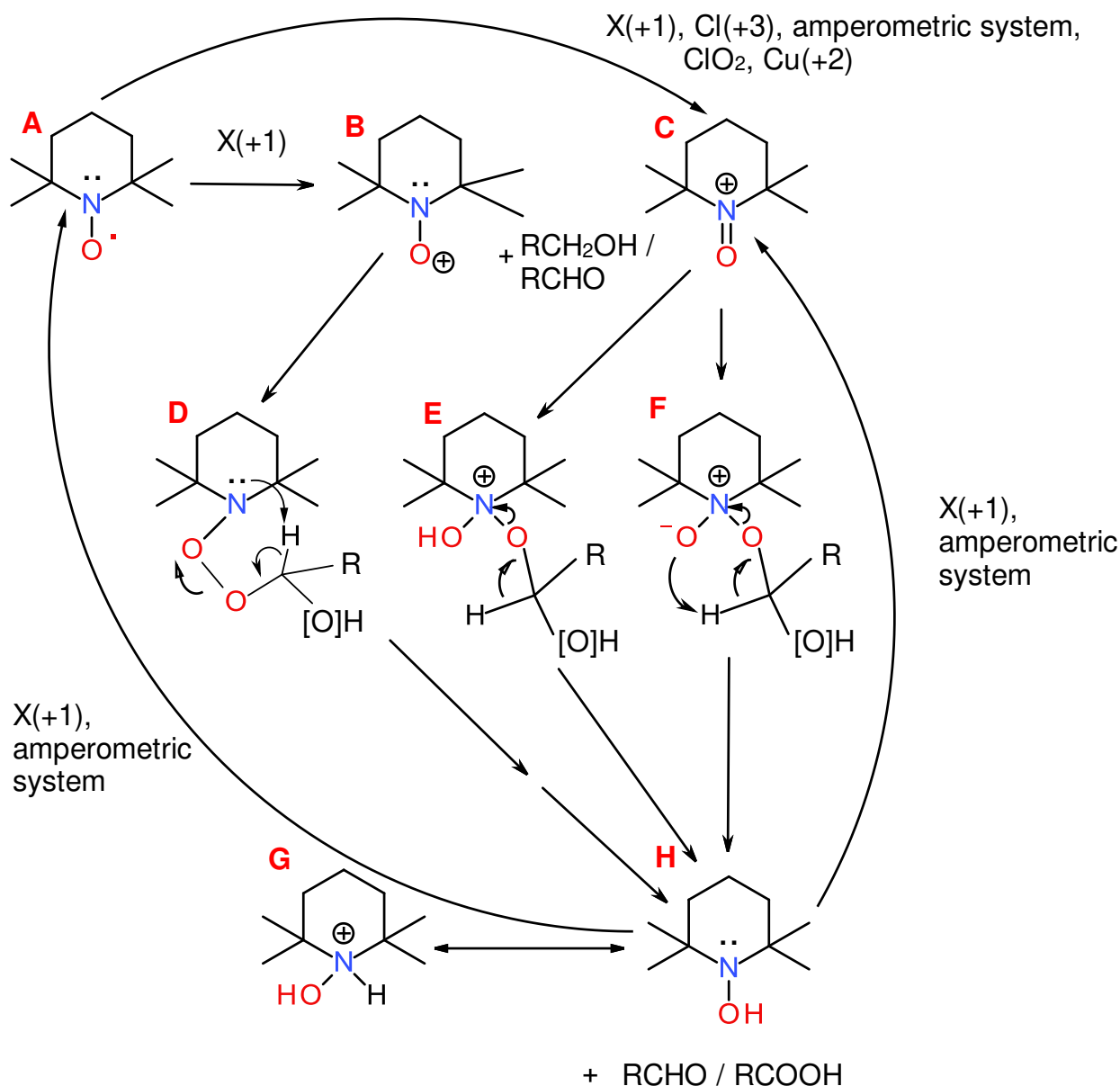
78 **Scheme 1.** Modified activation mechanism of TEMPO radical by HOX [11].

79 The role of bromide as a radical TEMPO activator has not yet been clearly elaborated. The lack of an  
 80 analysis method for TEMPO<sup>+</sup> impedes the study of the catalytic cycle of the TEMPO-mediated  
 81 oxidation. On one hand, it has been proposed that the primary oxidant, e.g. NaOBr when NaOCl is  
 82 present (Scheme 1), oxidizes the hydroxyl amine to oxidized TEMPO via a radical intermediate [12,  
 83 25]. On the other hand, NaOCl has been proposed to activate TEMPO at pH 10 prior to the  
 84 NaOBr/TEMPO oxidation without a radical TEMPO intermediate [22]. Both NaClO<sub>2</sub> and NaOCl have  
 85 been proposed as TEMPO activators during the TEMPO oxidation under the low pH conditions (pH  
 86 3.5-6.8) [21, 24, 26]. HOBr has been proposed to be the activator for TEMPO during the  
 87 NaBr/TEMPO/NaOCl oxidation at pH 10.8 where the formation of HOBr in the presence of ClO<sup>-</sup> and  
 88 Br<sup>-</sup> promotes the conversion of TEMPO to TEMPO<sup>+</sup> in a reaction which is similar to the one shown  
 89 in Scheme 1 [14]. A similar reaction was proposed earlier by de Nooy et al. [9].

90 The pKa values of HOCl (7.5) and HOBr (8.7) define the applicable pH level during the TEMPO  
 91 activation. At pH > pKa the hypohalous acids exist increasingly as hypohalites that are inactive in the  
 92 catalytic oxidation. Accordingly, the NaBr/TEMPO/NaOCl oxidations take place under higher pH  
 93 level than the NaOCl/TEMPO oxidations [11]. The complexity of the system and the number of the  
 94 reactions involved are substantial when both HOCl and HOBr are present in the solution [27].  
 95 Interestingly, the NaBr/TEMPO/NaOCl (pH 10) oxidation of starch without a separate TEMPO  
 96 activation step is reported to be three times faster than the NaOCl/TEMPO oxidation [11]. However,  
 97 the reaction rates of the initial conversion of TEMPO to TEMPO<sup>+</sup> and its catalytic reaction with starch  
 98 were not studied separately [11].

99 Several reaction paths have been proposed for the TEMPO-mediated oxidation of the primary and  
 100 secondary hydroxyl groups. However, some of the elementary reactions, e.g. the conversion of the  
 101 hydroxylamine (TEMPOH) to TEMPO<sup>+</sup> and the initial conversion of TEMPO to TEMPO<sup>+</sup>, are lacking  
 102 plausible reaction mechanisms. Scheme 2 summarizes the most commonly proposed reaction  
 103 routes and mechanisms published so far. The conversion of TEMPO to TEMPO<sup>+</sup> (A→C) has been  
 104 quite often left without explanation in the early studies [4, 5]. Nevertheless, some routes for this  
 105 conversion have been proposed, even though the reaction mechanisms have not been addressed.

106 TEMPO<sup>+</sup> has been proposed to form during a reaction between CuCl<sub>2</sub> and TEMPO [3]. Similarly, the  
 107 formation of TEMPO<sup>+</sup> during a reaction between Br(+1) and TEMPO [14, 18, 25, 28] as well as  
 108 between Cl(+1) and TEMPO [11, 16, 24, 26, 29] or Cl<sub>2</sub> and TEMPO [30] have been reported in  
 109 numerous studies. In addition, the conversion of TEMPO to TEMPO<sup>+</sup> has been proposed to take  
 110 place during a reaction with NaClO<sub>2</sub> under neutral and acidic conditions [26] and during a reaction  
 111 between ClO<sub>2</sub> and TEMPO via a transition complex intermediate [31, 32]. Despite the vast research  
 112 interest on the TEMPO-mediated oxidation, the reaction mechanisms for the formation of TEMPO<sup>+</sup>  
 113 still remain unrevealed.



114

115 **Scheme 2.** Proposed reaction routes for TEMPO-mediated oxidation of primary and secondary  
 116 alcohols.

117 The TEMPO-mediated oxidation of alcoholic groups has been suggested to proceed via an  
 118 A→C→F→H route under alkaline conditions and via an A→C→E→H route under acidic conditions,

119 where the formation of a reactive complex (E, F) is generated by a nucleophilic attack of an  
120 alcoholate anion on the nitrogen atom of TEMPO<sup>+</sup> [5, 10, 12, 22, 33, 34]. Additionally, an  
121 A→B→D→H route has been proposed to occur under alkaline conditions, where the formation of  
122 a reactive complex (D) is generated by a nucleophilic attack of an alcoholate anion on the oxygen  
123 atom of TEMPO [34]. Moreover, hydroxylamine has been proposed to shift to the protonated  
124 hydroxylamine H→G under low pH [12, 35]. Furthermore, the conversion of TEMPOH to TEMPO<sup>+</sup>  
125 (H→C) is proposed to take place under alkaline conditions with [7, 12, 36] and without [11, 22, 26,  
126 29, 37-39] the radical intermediate by a reaction with X(+1) or by applying an amperometric system.

127 For the present, only few elementary reaction rate constants for the TEMPO-mediated oxidation  
128 process have been determined. Some kinetic studies have been published with primary and  
129 secondary alcohols. The equilibrium constant (K) for the formation of a complex (F) with MeO<sup>-</sup> and  
130 TEMPO<sup>+</sup> ( $1.3 \times 10^{13} \text{ M}^{-1}$ ) is reported to be  $10^6$  times larger than that for the formation of the  
131 corresponding *i*-PrO<sup>-</sup> complex ( $1.1 \times 10^7 \text{ M}^{-1}$ ) [34]. In addition, the rate constants for the reactions  
132 between aldehydes / alcohols and TEMPO<sup>+</sup> under alkaline conditions have been studied [9]. Those  
133 reactions were followed by monitoring the consumption of hypochlorite [9]. However, measuring  
134 hypochlorite consumption does not allow differentiating between the reaction of TEMPO<sup>+</sup> with the  
135 alcohol and the conversion of TEMPOH to TEMPO<sup>+</sup>. Thus specific quantification of TEMPO<sup>+</sup> would  
136 be useful for the determination of the rate constants for the individual reactions in the catalytic  
137 cycle. In addition, it is obvious that the mechanism of the conversion of TEMPO or TEMPOH to  
138 TEMPO<sup>+</sup> is not clearly defined due to the rival reaction routes which have been proposed in the  
139 earlier studies. Therefore, a method for the determination of TEMPO<sup>+</sup> would be a useful tool within  
140 this field of research.

141 In this study, we introduce a iodometric titration method to quantitatively monitor TEMPO<sup>+</sup> during  
142 TEMPO-mediated oxidation of alcohols. The validity of the iodometric titration method is verified  
143 with UV-Vis absorption spectroscopy by fitting with the spectra of the pure components, i.e. TEMPO,  
144 Cl(+1) and TEMPO<sup>+</sup>, as calculated by a multivariate curve resolution algorithm (MCR). Moreover, the  
145 method with UV-Vis spectroscopy and MCR algorithm can be applied separately to quantify both  
146 TEMPO<sup>+</sup> and TEMPO. The iodometric titration method [1, 2, 30, 40] is applied to study a separate  
147 activation step of TEMPO prior to the TEMPO-mediated oxidation. Moreover, the role of HOX (e.g.  
148 HOCl and HOBr) as an activator of TEMPO is studied by the titration method. Finally, the TEMPO-  
149 mediated oxidation with a separate activation step of TEMPO and the titration method to determine  
150 TEMPO<sup>+</sup> are applied during an oxidation of a cellulosic pulp, a process commonly applied for the  
151 preparation of NFC.

## 152 **2. Experimental**

### 153 **2.1. Materials**

154 Industrially dried fully-bleached birch kraft pulp (Finland), fully-bleached eucalyptus kraft pulp  
155 (Brazil) and eucalyptus prehydrolysis kraft pulp (Brazil) were used as the raw materials for the  
156 TEMPO-mediated oxidation of cellulose. Xylitol (Sigma Aldrich (St Louis)) was used as the raw  
157 material for the TEMPO-mediated oxidation of alcohol. TEMPO (Sigma Aldrich (St Louis)) was used  
158 as a catalyst. A 13 % NaOCl solution (Merck (Darmstadt, Germany)) was the primary oxidant in the  
159 TEMPO-oxidations. 22 g of ortho-boric acid (VWR (Leuven, Belgium)) and 1.8 g of NaOH pellets (VWR  
160 (Leuven, Belgium)) were diluted to 2000 ml of distilled water to prepare a borate buffer (pH 8.3) in  
161 situ. 1 M NaOH (Merck (Darmstadt, Germany)), 1 M HCl (Merck (Darmstadt, Germany)), Büchi  
162 reactor (volume 1.6 dm<sup>3</sup>), and Metrohm 718 Stat Titrino titrator with pH adjustment were applied  
163 during the pulp oxidations. UV-Vis absorption spectra were measured with a Shimadzu UV-2550  
164 spectrophotometer (Shimadzu Corporation (Kyoto, Japan)). Ion-exchanged water was used in pulp  
165 washings.

## 166 2.2. Activation of TEMPO by NaOCl

167 NaOCl and TEMPO were mixed in a buffer solution (pH 8.3) at room temperature. The consumption  
168 of Cl(+1) and the formation of TEMPO<sup>+</sup> were monitored by iodometric titration. In parallel  
169 experiments absorption spectra of the samples withdrawn were measured in the UV-visible region  
170 with a Shimadzu UV-2550 spectrophotometer. Reference spectra of the buffer, 2 mM TEMPO in the  
171 buffer and 4 mM NaOCl were also measured. All solutions were diluted with the buffer solution in  
172 a 1:5 ratio prior to the measurements. The concentrations of Cl(+1), TEMPO and TEMPO<sup>+</sup> were  
173 obtained through mathematical analysis of the spectra.

174

175

## 176 2.3. Oxidations of the cellulose pulps and xylitol

177 All oxidations were carried out in a Büchi glass reactor (1.6 dm<sup>3</sup>) at 25 °C. The chemical dosages and  
178 the consistency of the pulp suspension were varied while its volume was 1.2 dm<sup>3</sup> in all experiments.  
179 Radical TEMPO was mixed with a stoichiometric excess of NaOCl in water. The pH level of the  
180 solution was adjusted to 7.5 with sulfuric acid. The solution was mixed in a closed vessel until TEMPO  
181 was completely dissolved and converted to TEMPO<sup>+</sup> by HOCl. The pulp and the activated TEMPO  
182 solution were mixed and NaOCl was added to the closed reactor by a pump. After the addition of  
183 NaOCl, pH was kept constant at the target level by adding 1 M NaOH with an automatic titrator. The  
184 oxidation rate was followed by iodometric titration until all oxidant was consumed.

185 Xylitol was oxidized correspondingly excluding the adjustment of oxidation solution pH with borate  
186 buffer to 8.3. Automatic titrator was not used for pH adjustment after NaOCl addition due to  
187 buffered conditions.

## 188 2.4. Conversion of residual aldehydes to carboxylates with chlorous acid

189 TEMPO-oxidized pulp suspension was acidified to pH 3 with HCl and NaClO<sub>2</sub> Was added (10 mM  
190 initial concentration). The suspension was mixed in the Büchi reactor for 2h at 50 °C. Finally, the  
191 pulp was washed with pure water. CED-viscosity of the pulp was analyzed according to the standard  
192 method SCAN-CM 15.99 prior to the calculation of DP [41].

### 193 2.5. Analyzing of carboxylate and aldehyde contents of pulps

194 The carboxylate content of the pulps were determined by conductometric titration (SCAN-CM  
195 65:02) using Methrohm 751 GPD Titrino automatic titrator and Tiamo 1.2.1. software. The aldehyde  
196 contents of the pulps were calculated as the difference in their carboxylate contents after and  
197 before the post-oxidation with HClO<sub>2</sub>.

198

### 199 2.6. Iodometric titration of Cl(+1), Br(+1)) and TEMPO<sup>+</sup>

200 The applied titration sequence is based on the method of Wartiovaara [42] excluding the analysis  
201 of TEMPO<sup>+</sup>. Wartiovaara describes a three point titration of ClO<sub>2</sub> and hypochlorite at pH 8.3, further  
202 titration of chlorite at pH below 2, and finally, the titration of chlorate at pH below 1. Only the  
203 alkaline (pH 8.3) titrations to determine the formed TEMPO<sup>+</sup> and Cl(+1) were conducted. The  
204 liberated iodine was titrated against Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> using starch as an indicator. The titration of iodine with  
205 sodium thiosulfate is based on the following reaction (Eq 1):



207 First, 25 ml of a borate buffer (pH 8.3) was added to two sample containers. Then, 0.5 ml of DMSO,  
208 which can be used as a masking agent for HOCl and HOBr, was added to one of the sample  
209 containers [43-47]. A known amount of the sample solutions together with an excess amount of KI  
210 was added to both of the sample containers. When bromine was present, the solution required  
211 stabilization for a few minutes prior to the addition of KI, since HOBr is trapped by DMSO more  
212 slowly than HOCl. All samples were titrated against Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> using starch as an indicator. The  
213 following reactions (Eq. 2 and Eq. 3) occur in the mildly alkaline medium:



216 The DMSO containing sample includes only the reaction product (iodine) with TEMPO<sup>+</sup>, since HOCl  
217 (or HOBr) is trapped with DMSO. Iodide reduces TEMPO<sup>+</sup> to TEMPO radical [1, 2, 30, 40]. Thus the  
218 thiosulphate consumption corresponds stoichiometrically to the amount of TEMPO<sup>+</sup> in the sample  
219 (Eq. 1 and Eq. 3).

### 220 2.8. UV-Vis absorption spectroscopy of TEMPO/NaOCl/buffer solutions



221 NaOCl/TEMPO mixtures in a buffer solution (pH 8.3) were prepared and measured with a Shimadzu  
222 UV-2550 spectrophotometer correspondingly to the ones which were applied in the titrations. 2  
223 mM TEMPO and 4 mM NaOCl solutions in the buffer media and the buffer solution without any  
224 added chemicals were measured as reference samples. All solutions were diluted with a ratio of  
225 1/5 by the buffer solution prior to the measurements.

## 226 2.9. Mathematical reconstruction of pure spectral components from UV-Vis data

227 First, the range of linear response in the UV-Vis measurements was identified by looking at the  
228 singularities in their loading factors from Principal Component Analysis (PCA) [48]; the range  
229 46assumed to be TEMPO, TEMPO<sup>+</sup>, HOCl/OCl mixture (which is referred to as Cl(+1)) and a constant  
230 background consisting of a baseline and absorption by the buffer. A number of varying components  
231 equal to three was also confirmed by PCA: the first three factors explain over 99% of data variance  
232 (for data at 200-400 nm). The background, derived from the spectrum of a buffer-only solution, was  
233 subtracted from all spectra. The millimolar spectra of pure TEMPO and Cl(+1) were taken from  
234 spectra of the respective substance in buffer, after subtracting the background and dividing for the  
235 concentration. The spectrum of TEMPO<sup>+</sup> was reconstructed by an algorithm, inspired by the  
236 Multivariate Curve Resolution-Alternate Least Squares method [49], which recursively alternates  
237 least-squares fitting of the bilinear model  $\mathbf{D} = \mathbf{CS} + \mathbf{E}$  and the application of constraints to the  
238 obtained solution.  $\mathbf{D}$  is the  $n \times w$  matrix of UV-Vis measurements ( $n$  = number of measurements,  $w$   
239 = number of wavechannels),  $\mathbf{C}$  is the  $n \times p$  matrix of concentrations in mmol/l ( $p$  = number of  
240 independent components, here equal to 3),  $\mathbf{S}$  is the  $p \times w$  matrix of spectra of pure components and  
241  $\mathbf{E}$  accounts for noise. The constraints included non-negativity of absorbances and concentrations,  
242 stoichiometric balances and monotonic decrease of reactants; they were applied by substituting any  
243 absorption or concentration that violated these constraints with the closest admissible value. The  
244 initial estimate for the spectrum of 1 mM TEMPO<sup>+</sup> was taken as the spectrum from the latest point  
245 (332 minutes) in the reaction mixture, subtracted by the background, divided by 1.8 (i.e. 90% of the  
246 initial 1 mM TEMPO) and again subtracted by the spectrum of 1 mM Cl(+1). The algorithm was  
247 iterated until convergence and the final spectra were used to obtain the concentrations of the  
248 corresponding substances by linear least-squares fit. All calculations were performed using  
249 MATLAB<sup>®</sup> version 8.2 R2014a (The Mathworks (USA)).

## 250 3. Results and discussion

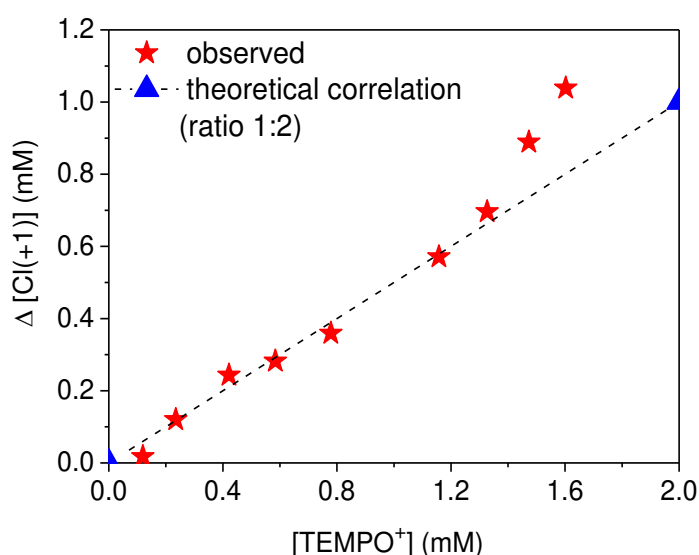
### 251 3.1. Iodometric titration of TEMPO<sup>+</sup> and Cl(+1)

252 The reaction of TEMPO and NaOCl was studied in a pH 8.3 buffer solution because at this pH the  
253 content of the undissociated HOCl (pKa 7.5), that is the reactive species, is still relatively high (~14  
254 %). The reaction was monitored as a function of time by iodometric titrations with and without  
255 DMSO, which is used as a masking agent for HOCl [43-46] (S1). The formation of a reaction product  
256 was detected when DMSO was applied. This compound disappeared when an aliphatic alcohol, n-

257 propanol, was added in the reaction mixture of TEMPO and NaOCl. The slow formation under the  
258 low reactant concentrations and the disappearance with the added alcohol promotes an  
259 assumption that the component is the oxidized form of TEMPO, namely TEMPO<sup>+</sup> which is reported  
260 to react stoichiometrically with iodine as described by Eq. 3 [1, 2, 30, 40]. TEMPO<sup>+</sup> is converted to  
261 its reduced form, a hydroxylamine (TEMPOH), during the reaction with alcohols (Scheme 2). Primary  
262 aliphatic alcohols can be oxidized with TEMPO to the corresponding aldehydes in few minutes [5].  
263 The oxidation of the alcohols with TEMPO is clearly faster with added NaBr [11]. The co-catalysis by  
264 bromide could be due to the faster activation of TEMPO to its oxidized form.

265 The thiosulphate consumption with the added DMSO was converted to the concentration of  
266 TEMPO<sup>+</sup> according to Eqs. 1 and 3 (Fig. 3). The concentration of Cl(+1) was obtained from the  
267 difference in the thiosulphate consumption with and without the added DMSO by applying Eqs. 1  
268 and 2. TEMPO<sup>+</sup> was clearly formed in parallel with the consumption of Cl(+1).

269



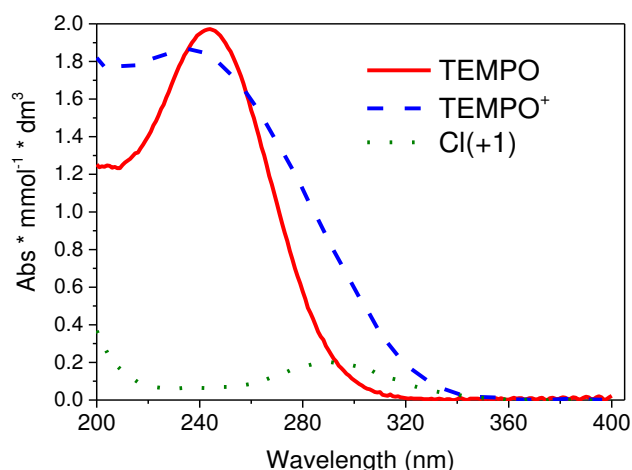
270

271 **Fig. 1.** The correlation between the consumed Cl(+1) and the formed TEMPO<sup>+</sup> in a reaction of 2 mM  
272 TEMPO and 4 mM NaOCl in a borate buffer (pH 8.3) at room temperature. The concentrations of  
273 TEMPO<sup>+</sup> formed and Cl(+1) consumed were obtained by iodometric titration. Corresponding  
274 correlation with reaction times added is shown in supplementary material.

275 The correlation between the consumed Cl(+1) and the TEMPO<sup>+</sup> formed is further illustrated in Fig.  
276 1. The stoichiometry of the activation reaction with HOCl and TEMPO is proposed to be 1:2 [11].  
277 The observed results correlate with the 1:2 stoichiometry except for the longest reaction times. This  
278 deviation could be explained with the formation of ClO<sub>3</sub><sup>-</sup> which was detected after several hours of  
279 reaction time. The chlorate formation correlates with the self-decomposition of HOCl [27], which is  
280 more pronounced at long reaction times and especially at high Cl(+1) concentrations.

281 3.2. UV-Vis absorption spectroscopy of TEMPO, TEMPO<sup>+</sup> and Cl(+1)

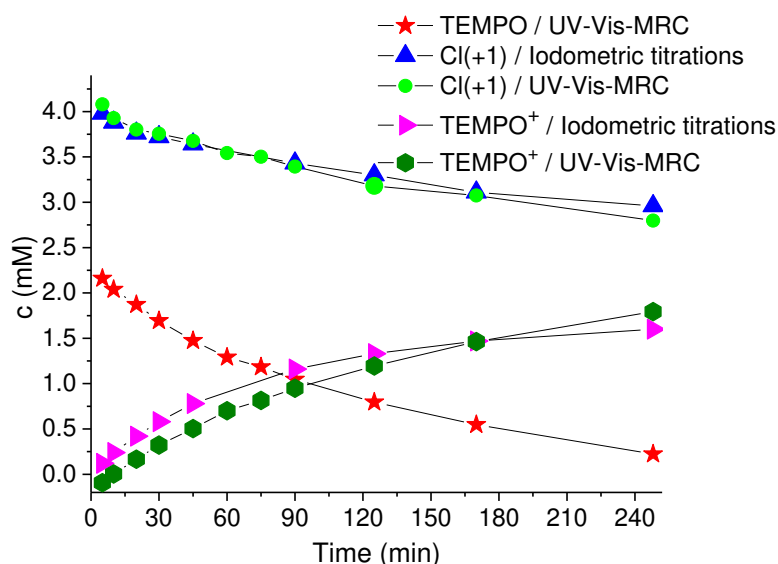
282 The conversion of TEMPO and Cl(+1) and the formation of TEMPO<sup>+</sup> were monitored also by UV-Vis  
283 absorption spectroscopy (Fig. 3). The spectra of the reaction solutions and the corresponding  
284 spectra of Cl(+1) in the borate buffer are shown in the supplementary material. Mathematical fitting  
285 was used instead of direct observation of the absorption maxima shifting due to the overlapping of  
286 the spectra of TEMPO, TEMPO<sup>+</sup>, and the Cl(+1). The mathematically reconstructed spectra of  
287 TEMPO, TEMPO<sup>+</sup>, and Cl(+1), shown in Fig. 2, are based on the measurements illustrated in the  
288 supplementary material.



289

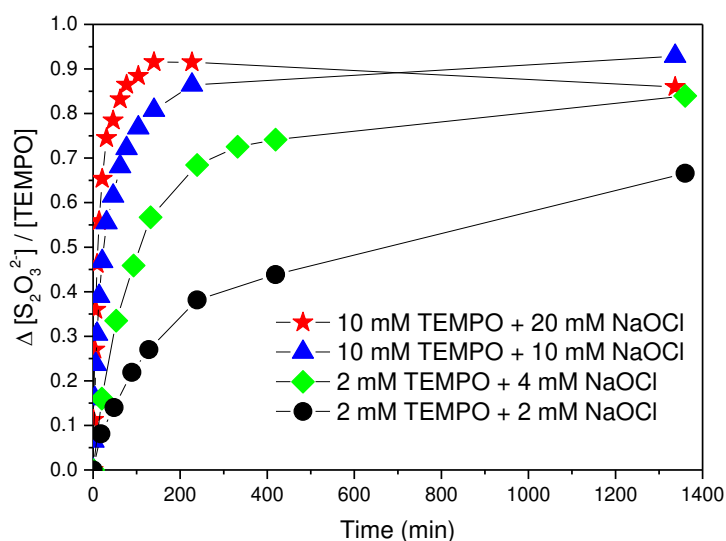
290 **Fig. 2.** Mathematically reconstructed spectra of TEMPO, TEMPO<sup>+</sup>, and Cl(+1) from monitoring the  
291 reaction of 2 mM TEMPO and 4 mM NaOCl in a borate buffer (pH 8.3) by UV-Vis spectroscopy at  
292 room temperature.

293 The formation rate of TEMPO<sup>+</sup> in 2 mM TEMPO solution, which is typically applied in the TEMPO-  
294 mediated oxidation, and the formation rate in a more concentrated TEMPO solution are compared  
295 in Fig. 4. The concentration ratio of NaOCl and TEMPO and the concentration of NaOCl clearly  
296 influence on how fast TEMPO<sup>+</sup> is formed. In the plateau point of TEMPO<sup>+</sup> formation the consumption  
297 of thiosulfate (iodometric titration in the presence of DMSO) is almost equal to the amount of  
298 TEMPO added. The results demonstrate the benefit of a separate activation step of TEMPO prior to  
299 its application as a bromide-free oxidation catalyst e.g. for the oxidation of cellulosic pulps. A  
300 separate activation of TEMPO by NaOCl at pH 7-8 can be accomplished within an half of hour when  
301 20-40 mM TEMPO and excess of NaOCl are used (results not shown).



302

303 **Fig. 3** Disappearance of Cl(+1) and TEMPO and formation of TEMPO<sup>+</sup> in a reaction mixture of 2 mM  
 304 TEMPO and 4 mM NaOCl in a borate buffer (pH 8.3) at room temperature. The graph compares the  
 305 results obtained by iodometric titration and UV-Vis spectroscopy combined with MCR.



306

307 **Fig. 4.** Effect of the concentrations of TEMPO and NaOCl on the conversion to TEMPO<sup>+</sup> in a borate  
 308 buffer (pH 8.3) as a function of time, analyzed by iodometric titration.

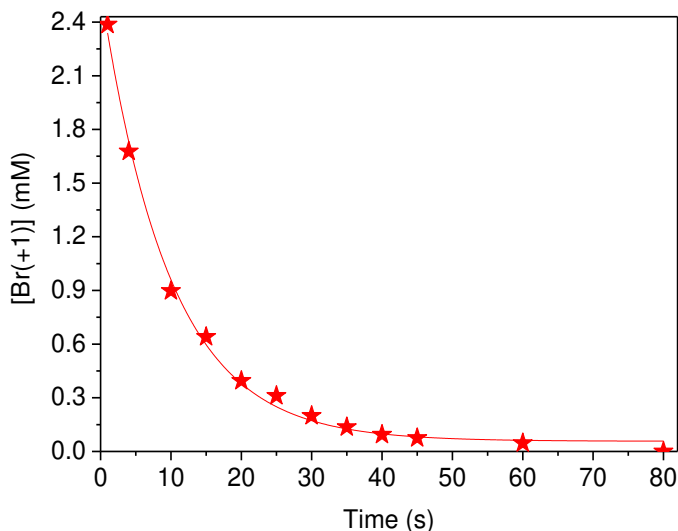
309 3.3. Iodometric titration of TEMPO<sup>+</sup> in the presence of added NaBr

310 The use of DMSO as a masking agent for HOCl has been reported widely [43-46]. DMSO can be  
 311 applied as a masking agent for HOBr correspondingly [47]. However, the reaction rate between  
 312 HOBr and DMSO is slower than the reaction rate between HOCl and DMSO. The required time for  
 313 removing all HOBr in the mixture of NaBr and NaOCl by DMSO was determined by varying the  
 314 incubation time prior to the addition of KI and starch (Fig. 5). The trapping of HOBr by DMSO

315 appeared to follow the first order exponential decay, thus, the following equation was fitted to the  
316 titration data:

$$317 \quad [\text{HOBr}] = [\text{HOBr}]_0 \cdot \exp(-kt) \quad (\text{Eq. 4})$$

318 where the rate constant  $k$  is  $0.10 \text{ s}^{-1}$ . Thus a delay of 2 min between the addition of DMSO and the  
319 addition of KI was considered appropriate to enable the titration of  $\text{TEMPO}^+$  regardless of the  
320 amount of  $\text{Br}(+1)$  present in the sample solution.

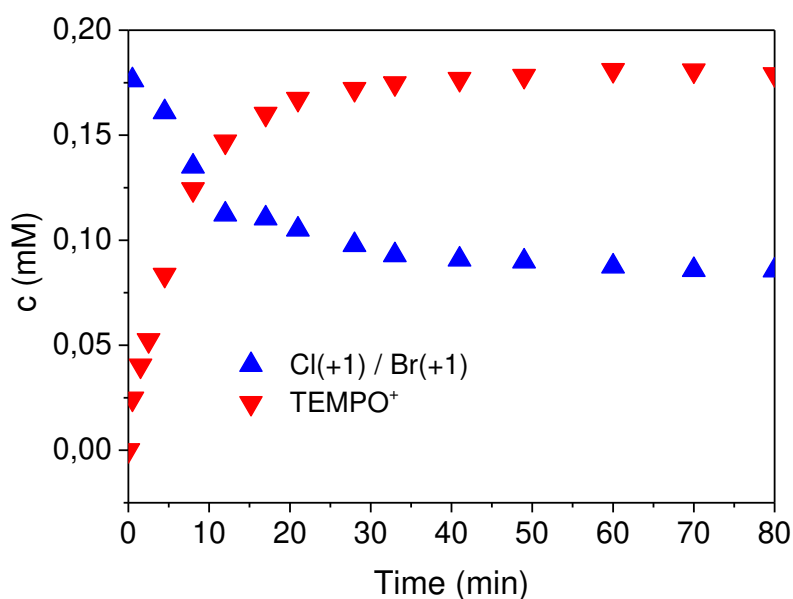


321

322 **Fig. 5.** The decomposition of HOBr, formed in 4 mM NaBr and 4 mM NaOCl in a borate buffer (pH  
323 8.3) at RT, by DMSO as monitored by iodometric titration.

324 The iodometric titration with and without added DMSO was applied for monitoring the  
325 NaBr/TEMPO/NaOCl reaction system similarly as presented in supplementary data (S1) for the  
326 TEMPO/NaOCl system (S2). The formation rate of  $\text{TEMPO}^+$  was high despite the 10 times lower  
327 concentration level compared to the bromide-free system (S1 and Fig. 3). The use of bromide as an  
328 accelerating compound of TEMPO-mediated oxidation is well known and reported [10, 12]. Our  
329 experiments verify one of the important effects of bromide as a co-catalyst is the faster conversion  
330 of TEMPO to  $\text{TEMPO}^+$ .

331 The correlation between the consumption of  $\text{Cl}(+1)/\text{Br}(+1)$  and formation of  $\text{TEMPO}^+$  (Fig. 6) was  
332 similar to the one detected with the TEMPO/NaOCl system (S1 and Fig. 3). In both cases the  
333 hypohalous acids were consumed and  $\text{TEMPO}^+$  formed in the theoretical 1:2 ratio.

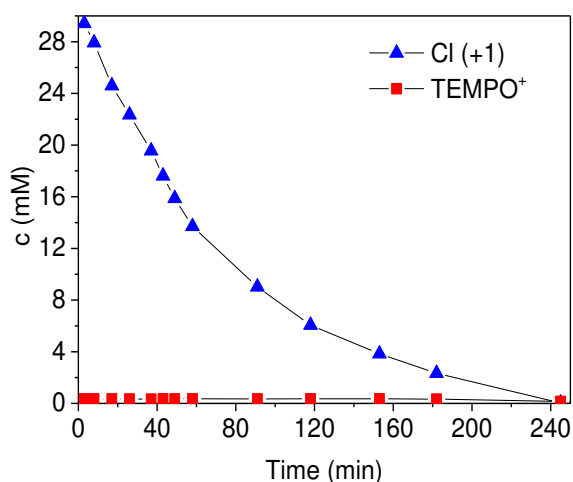


334

335 **Fig. 6.** Disappearance of Cl(+1)/Br(+1) and formation of TEMPO<sup>+</sup> in a reaction mixture of 0.2 mM  
 336 TEMPO, 0.2 mM NaBr, and 0.2 mM NaOCl in a borate buffer (pH 8.3) at room temperature.

337 3.4. Monitoring of the TEMPO-mediated oxidation of xylitol

338 The iodometric titration of Cl(+1) and TEMPO<sup>+</sup> was applied to study the catalytic oxidation of xylitol  
 339 with preactivated TEMPO (2 mM) at pH 8.3 in buffered conditions [Fig. 7]. Interestingly, 30 mM  
 340 NaOCl was consumed during reaction with 7.5 mM xylitol. The observed 4:1 stoichiometry  
 341 corresponds to the expected conversion of xylitol into xylaric acid. The concentration of TEMPO<sup>+</sup>  
 342 remained at a constant level until all hypochlorite was consumed after which also TEMPO<sup>+</sup>  
 343 disappeared.



344

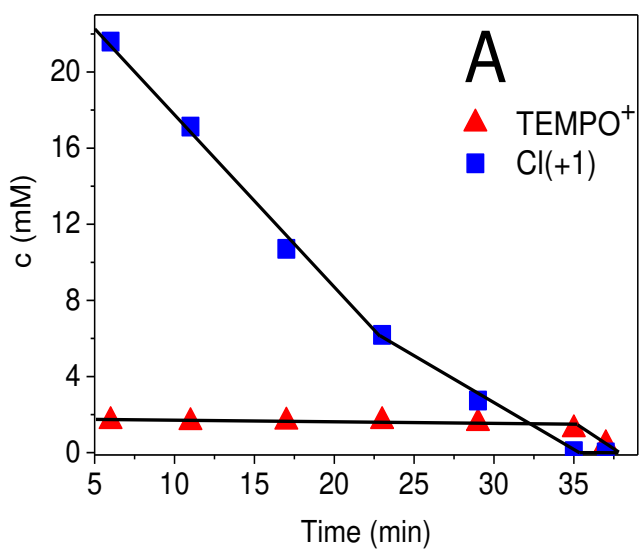
345 **Fig.7.** Disappearance of Cl(+1) and TEMPO<sup>+</sup> during TEMPO (0.4 mM) catalyzed oxidation of a 7.5 mM  
 346 xylitol with 30 mM NaOCl at room temperature. pH was buffered with borate buffer to 8.3.

347 3.5. Monitoring of the TEMPO-mediated oxidation of bleached pulps by iodometric titration

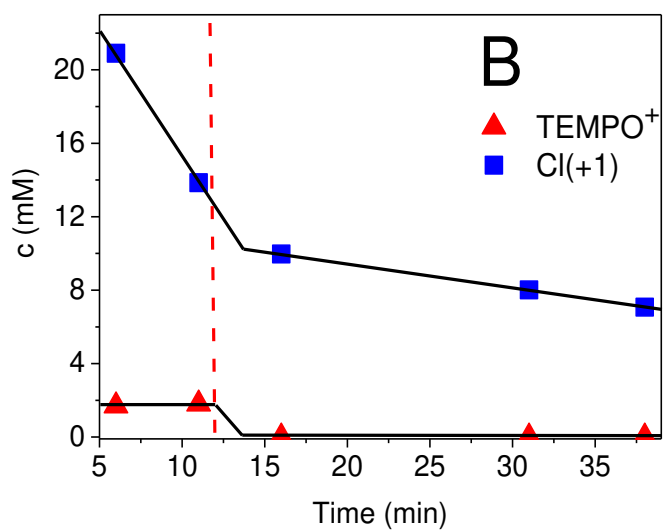
348 The iodometric titration of Cl(+1) and TEMPO<sup>+</sup> was applied to study the catalytic oxidation of a  
349 bleached birch kraft pulp with preactivated TEMPO (2 mM) at pH 9 that has been reported to be the  
350 optimum pH for the bromide-free oxidation [11] (Fig. 8 A). During the course of the oxidation TEMPO  
351 existed mostly in the form of TEMPO<sup>+</sup>, the concentration of which stayed at a constant level (1.7  
352 mM) until all Cl(+1) was consumed (Fig. 8 A). Similar observations were made with bleached  
353 eucalyptus kraft and eucalyptus prehydrolysis kraft pulps (supplementary material). Then TEMPO<sup>+</sup>  
354 disappeared at a rate equal to the final rate of conversion of Cl(+1). These observations indicate that  
355 the oxidation of TEMPOH to TEMPO<sup>+</sup> is much faster than its oxidative reaction with the primary  
356 alcohol groups in cellulose. A similar conclusion was reported earlier by Bragd et al. [11] who found  
357 that the rate of TEMPO catalyzed oxidation of methyl  $\alpha$ -D-glucopyranoside was unaffected by the  
358 concentration of Cl(+1). However, when pH of the reaction mixture was adjusted from 9 to 10.5 (Fig.  
359 8 B) during the reaction, TEMPO<sup>+</sup> almost disappeared (< 0.2 mM TEMPO<sup>+</sup>) after which the reaction  
360 continued with a much lower rate. Thus, at the high pH reoxidation of TEMPOH became the rate-  
361 limiting reaction, probably due to the low content of HOCl at the high alkalinity.

362 Under identical conditions more carboxylate and aldehyde groups (0.92 and 0.21 mmol/g,  
363 respectively) were formed in the eucalyptus prehydrolysis kraft pulp in comparison with the normal  
364 eucalyptus kraft pulp (0.75 and 0.13 mmol/g, respectively) (supplementary material). The enhanced  
365 oxidation of the prehydrolysis kraft pulp can be explained by its lower xylan content. Similar effect  
366 of the xylan content on the oxidation of cellulosic pulps has been reported earlier [29].

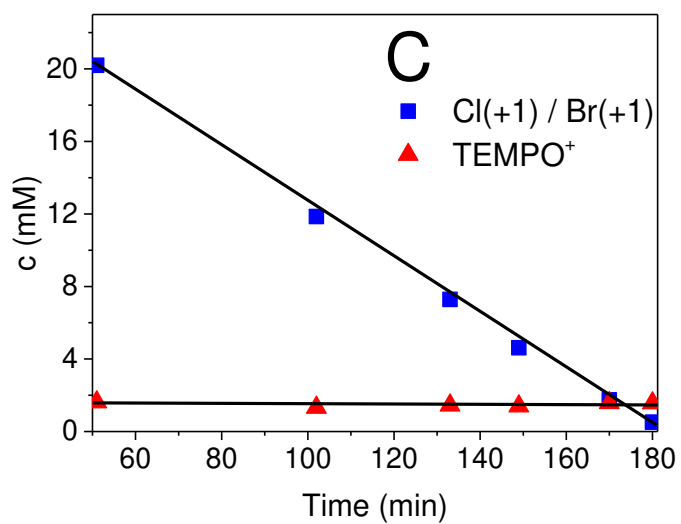
367 When a small amount of NaBr was used as a co-catalyst, the concentration of TEMPO<sup>+</sup> stayed close  
368 to the concentration of the added TEMPO even though the oxidation was carried out at pH 10 (Fig.  
369 8 C). The bromide-assisted oxidation has been reported to be fastest at pH 10 [11]. Our results verify  
370 that the NaBr addition that leads to formation of HOBr, promotes the reoxidation of TEMPOH at  
371 least at high pH levels. In part, this can be understood by the lower degree of dissociation of HOBr  
372 (pKa 8.7) in comparison with HOCl (pKa 7.5). These examples demonstrate the utility of the  
373 iodometric titration in unravelling the rate-determining steps in the TEMPO catalyzed oxidation of  
374 cellulosic pulps.



375



376



377



379 **Fig. 8.** Disappearance of Cl(+1) and TEMPO<sup>+</sup> during TEMPO (2 mM) catalyzed oxidation of a bleached  
380 birch kraft pulp (4 % consistency) with NaOCl at room temperature. [A] oxidation with preactivated  
381 TEMPO and 57 mM NaOCl at pH 9, [B] repetition of A oxidation except pH adjustment ( 9 → 10.5)  
382 with NaOH after 12 minutes reaction time (dash line). [C] Disappearance of Cl(+1)/Br(+1) and  
383 TEMPO<sup>+</sup> during TEMPO (2 mM) and NaBr (0.4 mM) catalyzed oxidation of a bleached birch kraft pulp  
384 (3.3 % consistency) with NaOCl (97 mM) at pH 10 at room temperature. TEMPO was preactivated  
385 prior to the oxidation.

## 386 4. Conclusions

387 The quantification of TEMPO<sup>+</sup> by iodometric titration is a useful tool for studying the chemistry of  
388 the TEMPO-mediated oxidation of primary alcohols. Similar and complementary information can be  
389 obtained by UV-Vis spectroscopy combined with multivariate curve resolution, which can be applied  
390 for simultaneous quantification of Cl(+1)/Br(+1), TEMPO<sup>+</sup> and TEMPO. In general, conversion of  
391 TEMPO to TEMPO<sup>+</sup> is the slowest step in bromide-free oxidation of the alcohols by Cl(+1). The use  
392 of bromide accelerates this conversion that can also be accomplished through a separate  
393 pretreatment of TEMPO with an excess of Cl(+1) in neutral conditions. The rate of the preactivation  
394 depends on the concentrations of TEMPO and Cl(+1) and is high enough to be applied in potential  
395 industrial processes such as catalytic oxidation of cellulosic pulps. TEMPO<sup>+</sup> was the dominant form  
396 of TEMPO in the catalytic oxidation of a birch kraft pulp under optimal conditions which confirms  
397 the earlier observation on the oxidation of the hydroxymethyl groups being the rate-determining  
398 step in the catalytic process.

### 399 *Acknowledgements*

400 This study was supported by UPM Nanocenter and the Finnish Funding Agency for Innovation  
401 (TEKES). We thank Mrs Mirja Reinikainen for excellent laboratory work.

### 402 *References*

- 403 [1] V.D. Sen', V.A. Golubev and T.M. Kosheleva, Russ. Chem. B+ 26 (1977) 678-683.
- 404 [2] V. Golubev, V. Sen', E.G. Rozantsev, Russ. Chem. B+ 28 (1979) 1927-1931.
- 405 [3] M.F. Semmelhack, C.R. Schmid, D.A. Cortes and C.S. Chou, J. Am. Chem. Soc. 106 (1984) 3374-  
406 3376.
- 407 [4] M.F. Semmelhack, C.S. Chou and D.A. Cortes, J. Am. Chem. Soc. 105 (1983) 4492-4494.
- 408 [5] P.L. Anelli, C. Biffi, F. Montanari, S. Quici, J. Org. Chem. 52 (1987) 2559-2562.

- 409 [6] A. Isogai, Y. Kato, *Cellulose* 5 (1998) 153-164.
- 410 [7] T. Saito, Y. Okita, T. Nge, J. Sugiyama, A. Isogai, *Carbohydr. Polym.* 65 (2006) 435-440.
- 411 [8] T. Saito, Y. Nishiyama, J. Putaux, M. Vignon, A. Isogai, *Biomacromolecules* 7 (2006) 1687-1691.
- 412 [9] A.E.J. de Nooy, A.C. Besemer and H. van Bakkum, *Tetrahedron* 51 (1995) 8023-8032.
- 413 [10] A.E.J. de Nooy, A.C. Besemer and H. van Bakkum, *Carbohydr. Res.* 269 (1995) 89-98.
- 414 [11] P.L. Bragd, A.C. Besemer, H. van Bakkum, *Carbohydr. Res.* 328 (2000) 355-363.
- 415 [12] P.L. Bragd, H. van Bakkum and A.C. Besemer, *Top. Catal.* 27 (2004) 49-66.
- 416 [13] T. Saito and A. Isogai, *Biomacromolecules* 5 (2004) 1983-1989.
- 417 [14] B. Sun, C. Gu, J. Ma, B. Liang, *Cellulose* 12 (2005) 59-66.
- 418 [15] T. Saito, Y. Nishiyama, J. Putaux, M. Vignon, A. Isogai, *Biomacromolecules* 7 (2006) 1687-1691.
- 419 [16] T. Saito, M. Hirota, N. Tamura, S. Kimura, H. Fukuzumi, L. Heux, A. Isogai, *Biomacromolecules*  
420 10 (2009) 1992-1996.
- 421 [17] Y. Okita, T. Saito, A. Isogai, *Holzforschung* 63 (2009) 529-535.
- 422 [18] S. Iwamoto, W. Kai, T. Isogai, T. Saito, A. Isogai and T. Iwata, *Polym. Degrad. Stab.* 95 (2010)  
423 1394-1398.
- 424 [19] A. Isogai and T. Saito, US 2010/0233481 A1 (2010).
- 425 [20] T. Isogai, T. Saito, A. Isogai, *Cellulose* 18 (2011) 421-431.
- 426 [21] R. Tanaka, T. Saito, A. Isogai, *Int. J. Biol. Macromol.* 51 (2012) 228-234.
- 427 [22] A. Isogai, T. Saito, H. Fukuzumi, *Nanoscale* 3 (2011) 71-85.
- 428 [23] M. Bulota, S. Tanpichai, M. Hughes, S.J. Eichhorn, *ACS Appl. Mater. Interfaces* 4 (2011) 331-  
429 337.
- 430 [24] M. Hirota, N. Tamura, T. Saito and A. Isogai, *Carbohydr. Polym.* 78 (2009) 330-335.
- 431 [25] T. Kitaoka, A. Isogai and F. Onabe, *Nord. Pulp. Pap. Res. J.* 14 (1999) 279-284.
- 432 [26] T. Saito, M. Hirota, N. Tamura and A. Isogai, *J. Wood Sci.* 56 (2010) 227-232.

- 433 [27] M. Lewin, M. Avrahami, *J. Am. Chem. Soc.* 77 (1955) 4491-4498.
- 434 [28] T. Saito, Y. Okita, T.T. Nge, J. Sugiyama, A. Isogai, *Carbohydr. Polym.* 65 (2006) 435-440.
- 435 [29] R. Pönni, T. Pääkkönen, M. Nuopponen, J. Pere, T. Vuorinen, *Cellulose*. 21 (2014) 2859-2869.
- 436 [30] V.A. Golubev, E.G. Rozantsev, M.B. Neiman, Institute of Chemical Physics, Academy of  
437 Sciences USSR (1965) 1927-1936.
- 438 [31] I.M. Ganiev, Q.K. Timerghazin, A.F. Khalizov, V.V. Shereshovets, A.I. Grigor'ev, G.A. Tolstikov, J.  
439 *Phys. Org. Chem.* 14 (2001) 38-42.
- 440 [32] I.M. Ganiev, Q.K. Timerghazin, A.F. Khalizov, N.M. Andriyashina, V.V. Shereshovets, L.B.  
441 Volodarsky, G.A. Tolstokov, *Tetrahedron Lett.* 40 (1999) 4737-4740.
- 442 [33] A.E.J. de Nooy, A.C. Besemer, H. van Bekkum, *Tetrahedron* 51 (1995) 8023-8032.
- 443 [34] W.F. Bailey, J.M. Bobbitt, K.B. Wiberg, *J. Org. Chem.* 72 (2007) 4504-4509.
- 444 [35] A. Israeli, M. Patt, M. Oron, A. Samuni, R. Kohen, S. Goldstein, *Free Radical Biol. Med.* 38  
445 (2005) 317-324.
- 446 [36] J.T. Hill-Cousins, J. Kuleshova, R.A. Green, P.R. Birkin, D. Pletcher, T.J. Underwood, S.G. Leach,  
447 R.C.D. Brown, *ChemSusChem* 5 (2012) 326-331.
- 448 [37] D. Liaigre, T. Breton and E.M. Belgsir, *Electrochem. Commun.* 7 (2005) 312-316.
- 449 [38] T. Isogai, T. Saito, A. Isogai, *Biomacromolecules* 11 (2010) 1593-1599.
- 450 [39] J. Peyre, T. Pääkkönen, M. Reza, E. Kontturi, *Green. Chem.* (2015).
- 451 [40] E.G. Rozantsev, V.D. Sholle, *Synthesis* (1971) 401-414.
- 452 [41] D. da Silva Perez and A.R.P. van Heiningen, *Proceedings of Seventh European Workshop on*  
453 *Lignocellulosics and Pulp* (2002) 393-396.
- 454 [42] I. Wartiovaara, *Paperi ja Puu* 64 (1982) 534-545.
- 455 [43] N. Imaizumi, T. Kanayama, K. Oikawa, *Analyst* 120 (1995) 1983-1987.
- 456 [44] T. Lehtimaa, V. Tarvo, G. Mortha, S. Kuitunen, T. Vuorinen, *Ind. Eng. Chem. Res.* 47 (2008)  
457 5284-5290.

458 [45] V. Tarvo, T. Lehtimaa, S. Kuitunen, V. Alopaeus, T. Vuorinen, J. Aittamaa, *Ind. Eng. Chem. Res.*  
459 48 (2009) 6280-6286.

460 [46] B.H. Yoon, L. Wang, *J. Pulp. Pap. Sci.* 28 (2002) 274-279.

461 [47] J. Viroopakshappa, V. Jagannadham, *J. Chem. Sci.* 114 (2002) 149-154.

462 [48] H. Abdi, L.J. Williams, *Wiley Interdisciplinary Reviews: Computational Statistics* 2 (2010) 433-  
463 459.

464 [49] J. Jaumot, R. Gargallo, A. de Juan, R. Tauler, *Chemometrics Intellig. Lab. Syst.* 76 (2005) 101-  
465 110.

466

467

468

469

470

471

472

473

474

475

476

477

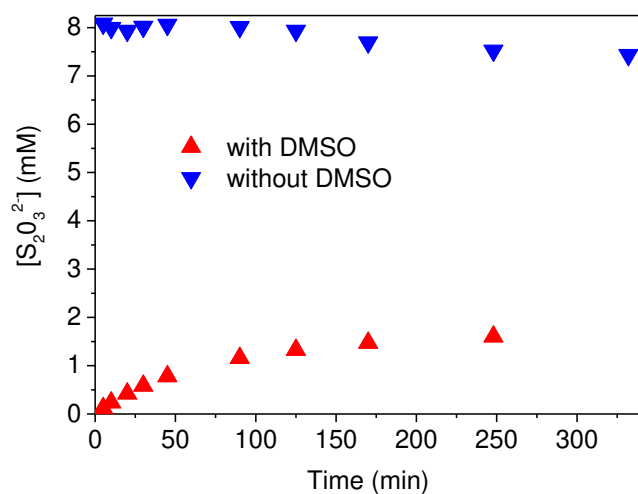
478

479

480

481

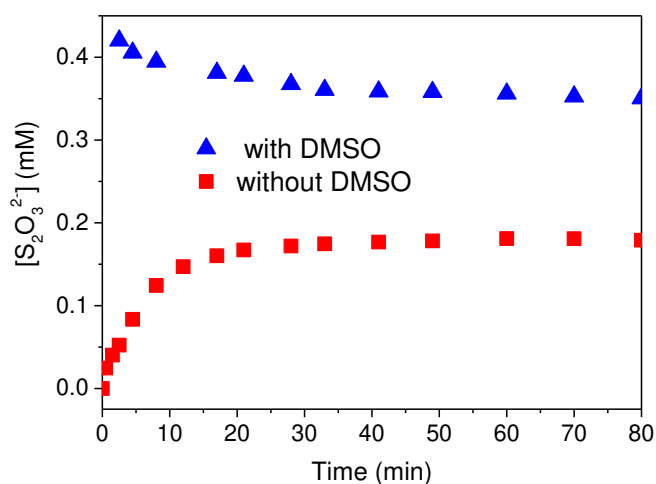
482 **Supplementary data**



483

484 **Fig. S1.** Iodometric titration of a reaction mixture of 2 mM TEMPO and 4 mM NaOCl in a borate buffer (pH  
485 8.3) at room temperature. A product, which was not trapped by DMSO, was formed as a function of reaction  
486 time.

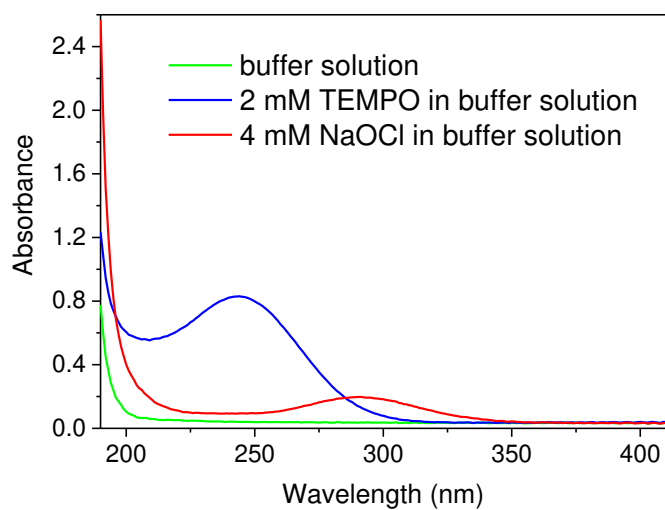
487



488

489 **Fig. S2.** Iodometric titration of a reaction mixture of 0.2 mM TEMPO, 0.2 mM NaBr and 0.2 mM NaOCl in a  
490 borate buffer (pH 8.3) at room temperature. A 2 min delay was applied between the additions of DMSO and  
491 KI to remove HOBr before the TEMPO<sup>+</sup> titration.

492



493

494 **Fig. S3.** UV-Vis spectra of borate buffer solution (pH 8.3), 2 mM TEMPO in buffer solution and 4 mM NaOCl  
 495 in buffer solution. TEMPO and NaOCl solutions were diluted (1/5) with buffer solution just before UV-Vis  
 496 measurement.

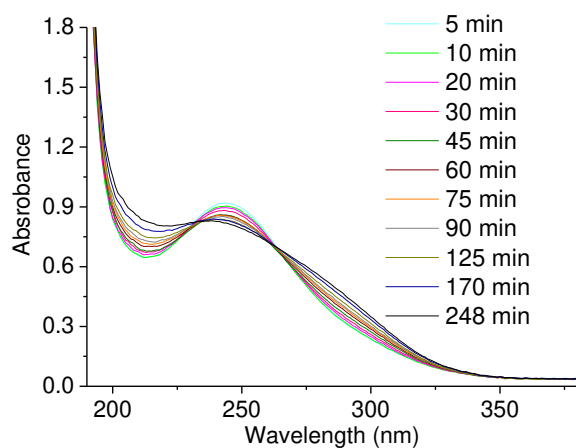
497

498

499

500

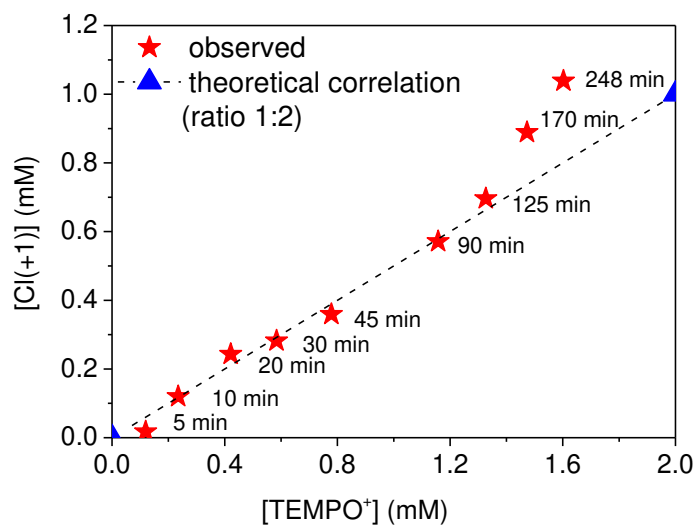
501



502

503 **Fig. S4.** UV-Vis spectra of mixtures (2 mM TEMPO and 4 mM NaOCl) in borate buffer solution (pH 8.3) as a  
 504 function of time. TEMPO/NaOCl solutions were diluted (1/5) with buffer solution just before UV-Vis  
 505 measurement.

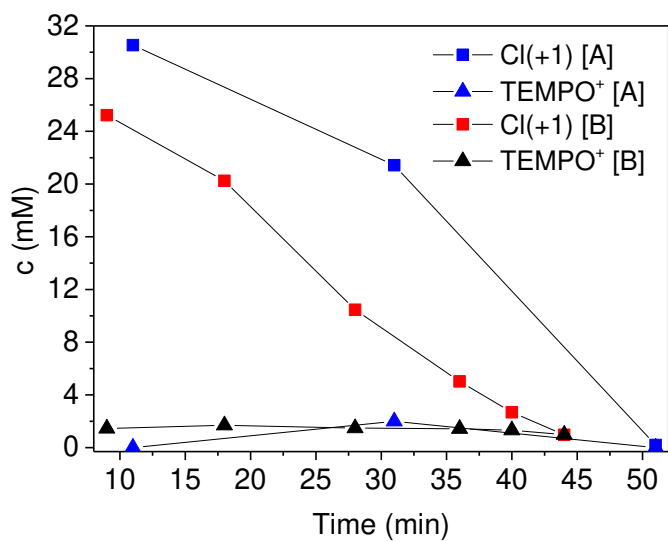
506



507

508 **Fig. S5.** The correlation between the consumed Cl(+1) and the formed TEMPO<sup>+</sup> including the reaction times.  
 509 2 mM TEMPO and 4 mM NaOCl were diluted with a borate buffer (pH 8.3) at room temperature. The  
 510 measured TEMPO<sup>+</sup> and the consumed Cl(+1) are based on the iodometric titrations.

511



512

513 **Fig. S6.** Disappearance of Cl(+1) and TEMPO<sup>+</sup> during TEMPO (2 mM) catalyzed oxidation of [A] a fully bleached  
 514 eucalyptus kraft pulp with preactivated TEMPO, 98 mM NaOCl, 4 % pulp consistency at room temperature.  
 515 A eucalyptus prehydrolysis kraft pulp [B] was oxidized under similar conditions.

516

517

518

519

520 **Table S1.** TEMPO-mediated oxidation of bleached birch kraft pulp (8A-C), bleached eucalyptus kraft pulp (S6  
 521 A) and bleached eucalyptus prehydrolysis kraft pulp (S6B). Catalyst addition was 2 mM and oxidations were  
 522 applied at room temperature.

523	Oxidation	Fig. 8 A and B	Fig. 8 C	Fig. S6 A	Fig. S6 B
524	Catalyst	TEMPO	TEMPO	TEMPO	TEMPO
525	Preactivation	HOCl	-	HOCl	HOCl
526	Primary oxidant	HOCl	HOBr	HOCl	HOCl
527	Oxidation pH	9	10	9	9
528	Pulp consistency (%)	4	3.3	4	4
529	Reaction time, min	37	180	51	50
530	NaClO addition	1.4	3.0	2.4	2.4
531	(mmol NaClO / g pulp)				
532	Carboxylate content	0.57	0.99	0.75	0.92
533	(mmol COOH / g pulp)				
534	Aldehyde content	0.09	0.02	0.13	0.21
535	(mmol COOH / g pulp)				
536	DP after residual aldehyde	1860	1450	936	612
537	conversion to carboxylates				