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A note on the chemical fate of the DABCO catalyst in amine-catalyzed hypochlorite bleaching of cellulosic pulps

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Abstract Hypochlorous acid bleaching under amine catalysis (H_{cat} bleaching stage) is an optimized bleaching stage variant that is characterized by working at weakly acidic, near-neutral pH, having high bleaching efficiency, and discharging only very small amounts of chloro-organics. This study addressed the chemical fate of the used 1,4-diazabicyclo[2.2.2]octane (DABCO) catalyst. While literature proposed either homolytic or heterolytic breakage of one ethylene bridge and subsequent release of the resulting fragments as two molecules of formaldehyde, we demonstrated the degradation to proceed by ionic elimination of one ethylene

bridge starting from mono-*N*-chlorinated DABCO. The resulting *N*-vinyl (enamine) derivative adds water under the release of acetaldehyde and formation of piperazine. The generation of acetaldehyde was experimentally confirmed by 2,4-dinitrophenylhydrazine trapping, directly from the processing liquid. The experimental findings agreed superbly with computations which showed the “acetaldehyde mechanism” to be much favored over the previously proposed pathways under C–C bond cleavage and release of formaldehyde. The results of this study add to a better understanding of the novel H_{cat} bleaching system.

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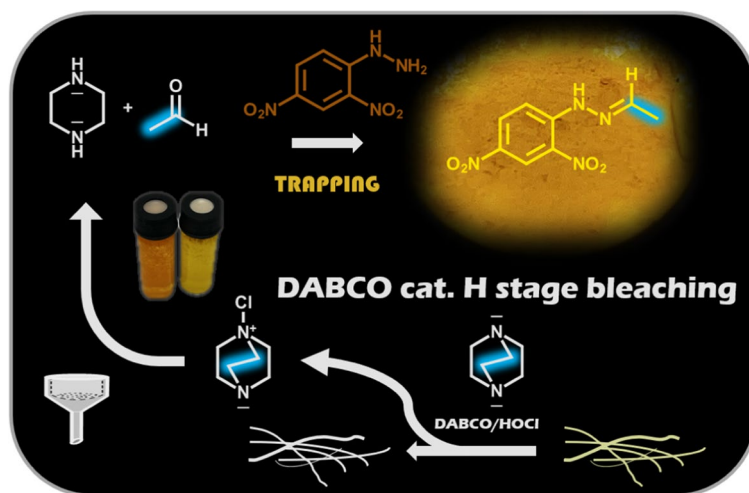
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Graphical abstract



Keywords Bleaching · Cellulose · Chloramines · DABCO · Elimination reaction · H stage · Hypochlorous acid · Pulp

Introduction

Bleaching is an essential step in the production of cellulosic pulps for paper, fibers and cellulose derivatives. It aims at removing residual lignin and residual color from pulp, ensuring compliance with the different quality standards for the various cellulose applications. As well-known from bleaching chemistry and technology, traditional bleaching processes involve multiple stages (Suess 2010). The more conventional setups utilized chlorine-based agents while more modern variants built on chlorine-free processes and oxygen-based active agents to achieve effective delignification while preserving the cellulose structure. Despite significant advancements in sustainable bleaching methods, challenges persist in finding a balance between effective, sufficient delignification and discoloration on the one side and preservation of the integrity of cellulose (and in some cases hemicellulose in addition) on the other side (Suess 2010).

Classical hypochlorite bleaching, the so-called “H stage”, works under alkaline conditions. It is known to be effective with regard to chromophore removal, yet still inflicted with environmental

problems due to the formation and release of small amounts of chloro-organics (Kolar et al. 1983; Gallard and von Gunten 2002; Lehtimaa et al. 2010). Recent work has brought a renaissance of hypochlorite – or more correctly: hypochlorous acid (HOCl) – as the active bleaching agent. An optimized approach works under neutral or weakly acidic, near-neutral conditions (pH 5–7) under which non-dissociated hypochlorous acid dominates rather than the hypochlorite anion. It was recognized for its efficacy in delignification and at the same time the extremely low chloro-organics discharge, compared to the conventional D stage or H stage counterparts (Afsahi et al. 2015, 2019a, b; Chenna et al. 2013, 2016). In this context, the incorporation of tertiary amine catalysts, especially 1,4-diazabicyclo[2.2.2]octane (DABCO) and some of its derivatives (1-carboxymethyl-1-azonia-4-azabicyclo[2.2.2]octane chloride (CM-DABCO) and 1-carboethoxymethyl-1-azonia-4-aza-bicyclo[2.2.2]octane chloride (CEM-DABCO)), offered additional improvements of hypochlorous acid bleaching by positively influencing efficiency (rate of chromophore removal), selectivity (less cellulose damage) and chemical charges. DABCO exhibited interesting activity in promoting hypochlorous acid reactions, with the mechanism involving the formation of *N*-chloramines as bleaching-active agents (Prütz 1998; Afsahi et al. 2019c; Isaza Ferro 2023) and

was also especially active against highly resonance-stabilized cellulosic key chromophores (Korntner et al. 2015; Rosenau et al. 2007).

Recent work of the Vuorinen group has explored in great detail the catalytic role of DABCO and other tertiary amines in enhancing the selectivity of hypochlorous acid towards lignin and has significantly contributed to the understanding of amine-catalyzed hypochlorous acid bleaching mechanisms and kinetics (Isaza Ferro 2023; Isaza Ferro et al. 2021a, b, 2022). Due to the small amount added (typically 0.1 wt%), the catalyst was not intended for recovery or recycling, but instead was assumed to be slowly degraded according to a previously proposed mechanism (Dennis et al. 1967; Brenneisein et al. 1965; Rosenblatt et al. 1972; Hull et al. 1967) and eventually washed out. However, general mechanistic considerations raised some doubts about the DABCO degradation as proposed in the literature. This study describes our attempts to elucidate the further fate of DABCO under conditions of hypochlorous acid bleaching and to establish – or possibly correct – the corresponding mechanisms. To this end, we used a combination of trapping reactions, NMR spectroscopy and computational chemistry.

Materials and methods

General

Commercial chemicals from Sigma-Aldrich (Schnellendorf, Germany) were of the highest grade available and were used without further purification. Distilled water was used for all aqueous solutions. Solvents were purchased in synthesis grade from Carl Roth, Sigma-Aldrich and VWR and were used as received.

DABCO-catalyzed hypochlorous acid bleaching

The H_{cat} bleaching stage was performed as described in Afsahi et al. (2019b), working at RT with 1% active chlorine (initial pH=4.5) and 0.1 wt% of DABCO at a pulp consistency of 3%. The pulp slurry (200 mL) was washed with the same volume of distilled water, and the washings were used directly for the trapping experiments.

Preparation of Brady's reagent

An acidic solution of 2,4-dinitrophenylhydrazine in EtOH was prepared following two different published protocols implementing minor modifications.

Method A (RSC Education 2018): To H_3PO_4 conc. (12.5 mL, 85 wt% in H_2O) was added 2,4-DNPH (0.750 g wet [contains 0.5 g H_2O /1.5 g] $\hat{=}$ 1.0 g pure 2,4-DNPH, 2.524 mmol) and stirred at RT until dissolution. Absolute EtOH was added up to a volume of 25 mL yielding a dark orange solution (BR I; $c(2,4\text{-DNPH})=0.101$ M; $c(H_3PO_4)=7.40$ M).

Method B (Ruekberg and Rossoni 2005): A suspension of 2,4-DNPH (3.00 g, wet [contains 0.5 g H_2O /1.5 g] $\hat{=}$ 2.0 g pure 2,4-DNPH, 10.09 mmol) in absolute EtOH (75 mL) was cooled to 0 °C in an ice/water bath before conc. H_2SO_4 (17 mL) was carefully added under stirring. After complete addition, the suspension was warmed until the solid had fully dissolved. After cooling to RT, deionized H_2O was added up to a volume of 100 mL yielding a dark orange solution (BR II; $c(2,4\text{-DNPH})=0.101$ M; $c(H_2SO_4)=3.06$ M).

Derivatization and isolation of acetaldehyde

To the aqueous bleaching washing solution (5.0 mL), five drops of BR I or BR II were added at RT while stirring, whereupon a yellow solid precipitated. The vial was tightly closed and the suspension stirred for 30 min before the fluffy yellow precipitate was isolated by vacuum filtration. The filter cake was washed with a mixture of EtOH: H_2O (2.0 mL, 1:1 v/v). Prior to NMR analysis, the product was dried *in vacuo*. As a positive control experiment, an aqueous solution of acetaldehyde (5.0 mL, $c=0.0908$ mM) was treated identically.

NMR analysis

Solution-state NMR spectra were recorded using a Bruker Avance II 400 spectrometer equipped with a cryogenically-cooled broadband observing (BBO) 5 mm probe-head (CryoProbe™ Prodigy, N_2 -cooled). The NMR experiments were performed with z-gradients at RT at resonance frequencies of 400.13 MHz for 1H , 100.61 MHz for ^{13}C , and 40.54 MHz for ^{15}N using standard Bruker pulse programs. Chemical shifts are given in parts per million (ppm) and

were referenced to the respective solvent as internal reference (DMSO- d_6 ; 2.50 ppm for ^1H , 39.52 ppm for ^{13}C). ^1H NMR spectra were recorded with 32 k complex data points and apodized using a Gaussian window function ($l_b = -0.30$ Hz and $g_b = 0.30$ Hz) prior to *Fourier* transformation. ^{13}C NMR *J*-modulated spectra using WALTZ16 ^1H decoupling (Bruker pulse program “*jmod*”) were recorded with 65 k complex data points. S/N was enhanced utilizing an exponential window function ($l_b = 1.0$ Hz) before *Fourier* transformation. ^1H - ^1H COSY using gradient pulse for selection (Bruker pulse program “*cosygpqf*”) was used to determine homonuclear shift correlation and acquired with 2048×256 data points. The multiplicity-edited HSQC experiment (Bruker pulse program “*hsqcedetgpsp.3*”) was performed using adiabatic pulses for inversion of ^{13}C and GARP-sequence for broadband ^{13}C -decoupling, optimized for $^1J(\text{CH}) = 145$ Hz and acquired with 1024×256 data points. For determination of long-range ^1H - ^{13}C couplings, an HMBC experiment using gradient pulses and a low-pass filter without decoupling (Bruker pulse program “*hmbcgpplndqf*”) was performed and acquired with 1024×256 data points. The relative spatial arrangement of protons was elucidated using a selective 1D NOESY experiment implementing an excitation sculpting technique with simple pulsed field gradients (PFG, Bruker pulse program “*selnogp*”) and acquired with 16 k complex data points. To determine ^1H - ^{15}N couplings, a ^1H - ^{15}N HMBC experiment (Bruker pulse program “*hmbcgpplndqf*”) was performed acquiring 1048×128 data points; ^{15}N shifts were extracted from the obtained 2D spectra. All NMR data was acquired and processed using Bruker TopSpin 4.3.0 and/or 3.2.7 software.

NMR data of standards and identification of compounds

1,4-Diazabicyclo[2.2.2]octane (DABCO, **1**). ^1H NMR (DMSO- d_6): δ 2.60 ppm (s, 12H, $6 \times \text{CH}_2$); ^{13}C NMR (DMSO- d_6): δ 46.97 ppm.

1,4-Diazacyclohexane (pyridazine, **2**). ^1H NMR (DMSO- d_6): δ 2.58 (s, 8H, $4 \times \text{CH}_2$), 1.98 ppm (s, b, 2H, NH); ^{13}C NMR (DMSO- d_6): δ 46.94 ppm; ^{15}N NMR (DMSO- d_6): δ -246.16 ppm.

Acetaldehyde as the respective 2,4-dinitrophenylhydrazone derivative (1-(*E*)-ethylidene-2-(2,4-dinitrophenyl)

hydrazine, **5**). ^1H NMR (DMSO- d_6): δ 11.35 (s, 1H, NH), 8.83 (d, 1H, $J = 2.61$ Hz, 3- CH_{ar}), 8.33 (ddd, 1H, $J = 9.67 / 2.61 / 0.78$ Hz, 5- CH_{ar}), 8.01 (dq, 1H, $J = 5.38 / 0.57$ Hz, $-\text{CH}=\text{N}$), 7.86 (d, 1H, $J = 9.67$ Hz, 6- CH_{ar}), 2.01 ppm (d, 3H, $J = 5.38$ Hz, $-\text{CH}_3$); ^{13}C NMR (DMSO- d_6): δ 151.56 ($-\text{N}=\text{CH}$), 144.73 (1- C_{ar}), 136.54 (4- C_{ar}), 129.90 (5- CH_{ar}), 128.70 (2- C_{ar}), 123.20 (3- CH_{ar}), 116.33 (6- CH_{ar}), 18.70 ppm (CH_3); ^{15}N NMR (DMSO- d_6): δ -67.60 ($-\text{N}=\text{CHCH}_3$), -227.91 ppm (1- $\text{C}_{\text{ar}}\text{-NH}$ -).

Computations

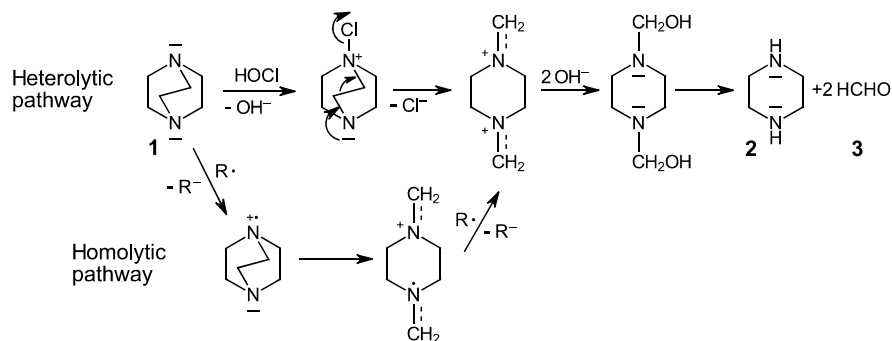
The GAUSSIAN09 software (Frisch et al. 2016) was employed in all calculations. The DFT(M06-2X) level of theory was applied for geometry optimization, frequency calculation, and energy evaluation throughout this study, with the 6-311G(d,p) basis sets for C, O, H, Cl and N, with diffuse functions being added to C, O, Cl and N. It was ascertained that each equilibrium geometry exhibited no imaginary frequency. Changes in enthalpy, entropy, and Gibbs energy were calculated for 298.15 K.

Results and discussion

Literature accounts propose degradation of DABCO by hypochlorite / hypochlorous acid to proceed via C–C cleavage of one of the ethylene bridges with the two remaining C_1 -units being eventually released as formaldehyde (Dennis et al. 1967; Rosenblatt et al. 1972; Hull et al. 1967). The bond cleavage is supposed to proceed heterolytically, starting from the *N*-monochloramine, which is fragmented under the release of chloride and the formation of a bis(*N*-methyleneiminium) dication. Alternatively, the DABCO-derived aminyl cation radical was proposed, which should undergo β -fragmentation and further one-electron oxidation to the same bis(*N*-methyleneiminium) dication. Subsequent addition of two equivalents of water would release two equivalents of formaldehyde and piperazine (Scheme 1).

Some general considerations and preliminary experiments shed some doubt on these literature mechanisms: the medium in H_{cat} bleaching consists of water and some dissolved or dissociated electrolytes. In such highly polar protic reaction media of high ionicity, generally, monomolecular reactions (substitutions/eliminations) would be favored

Scheme 1 Literature proposal (Dennis et al. 1967; Rosenblatt et al. 1972; Hull et al. 1967) for the heterolytic and homolytic degradation pathways of DABCO (1) in the presence of hypochlorite / hypochlorous acid, eventually leading to the formation of piperazine (2) and two equivalents of formaldehyde (3)



over bimolecular ones (*e.g.*, S_N1 over S_N2 reactions) because the high polarity stabilizes charged (ionic) transition states and intermediates. Polar covalent bonds, such as C-O or C-N, would be much more prone to cleavage than non-polarized C-C bonds; ionic fragmentation along a saturated aliphatic side chain – not involving C=C double bonds or hetero-analogous double bond structures (*e.g.*, C=O) – would be rather “exotic”. The suggested ionic fragmentation of an ethylene (-CH₂-CH₂-) moiety seemed thus somewhat questionable, and the same was true for a homolytic cleavage under the prevailing conditions.

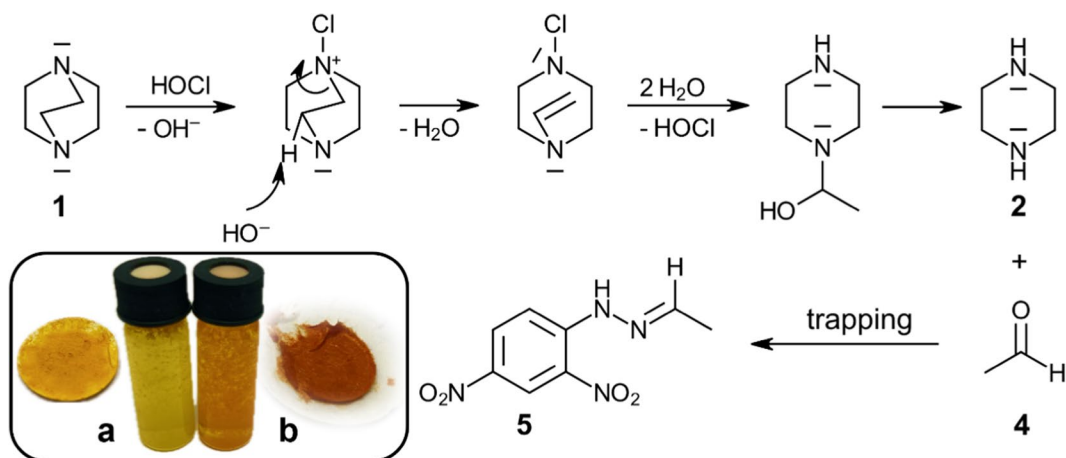
Spin trapping at pH 5 (with model compounds instead of pulp) and different traps, such as EMPO (Stolze et al. 2003), did not provide any indication of radical species being present. While this by no means meant a solid proof of their absence, the outcome was different at alkaline pH (pH=10) of a classical D or H stage: EPR spectra showed mixtures of EMPO-adducts with different *O*-centered and *C*-centered radicals.

Attempts to detect the possibly formed formaldehyde – which should be a final product of both the heterolytic and homolytic pathways – were unsuccessful. We used chromotropic acid for detection due to its quite high selectivity. While most alternative HCHO-scavengers (*e.g.*, dimedone, purpald, phenylhydrazone derivatives, or semicarbazones) have a high cross-reactivity towards other aliphatic aldehydes (including even monosaccharides), such interferences are hardly present in the reaction between HCHO and chromotropic acid (Poh et al. 1989), as the HCHO-condensation product has a characteristic UV-absorbance which can be readily separated from those of other aldehydes (Jendral et al. 2011).

Experimentally, the occurrence of acetaldehyde (CH₃-CHO, 4) – *i.e.*, the higher homolog of the postulated formaldehyde – directly in the reaction medium was proven by trapping with 2,4-dinitrophenyl hydrazine (Scheme 2 and Fig. 1). This trapping agent, called Brady’s reagent, was chosen for its ability to form well-precipitating solids that can be easily purified and analyzed, even in the case of very low aldehyde concentrations – in the present case the 2,4-dinitrophenylhydrazone of acetaldehyde (5). There were no HCHO or aldehydes other than acetaldehyde detected. We can thus safely state that the degradation of DABCO (1) under H_{cat} conditions proceeds under the formation of piperazine (2) and acetaldehyde (4), meaning that one of the catalyst’s ethylene bridges is lost in the form of acetaldehyde, with concomitant conversion of the bis-tertiary into a bis-secondary amine (see Scheme 2).

The mechanism of the process would start from *N*-chloro-DABCO which can be conceived as having a quaternized nitrogen. Elimination, involving one of the β-hydrogens, produces an *N*-vinyl intermediate (enamine), which adds a hydroxide anion to form an acetaldehyde hemiaminal and subsequently free acetaldehyde. The removed ethylene bridge – by contrast to literature postulates – does not undergo C-C bond cleavage and is released as an intact C₂ unit (acetaldehyde) rather than two C₁ equivalents (formaldehyde).

Quaternization (cationization) of the nitrogen generally weakens the C-N bonds and favors the elimination of alkyl groups from this nitrogen. This is a well-known process in organic chemistry, often termed *Hofmann* elimination (Hofmann 1851), which has been widely used in synthesis applications. In fact, the exhaustive methylation/alkylation of amines followed by elimination was used in the early days of chemistry to diagnose the position of nitrogen



Scheme 2 Revised degradation pathways of DABCO (**1**) in the presence of hypochlorous acid, leading to the formation of piperazine (**2**) and acetaldehyde (**4**), which was experimentally confirmed by trapping as respective 2,4-dinitrophenylhydra-

zone derivative (**5**); bottom left: bright yellow precipitate of 1-(*E*)-ethylidene-2-(2,4-dinitrophenyl)hydrazine (**5**) isolated from the washing solution (**a**) and orange precipitate of the 2,4-DNPH reagent in the blank sample (**b**)

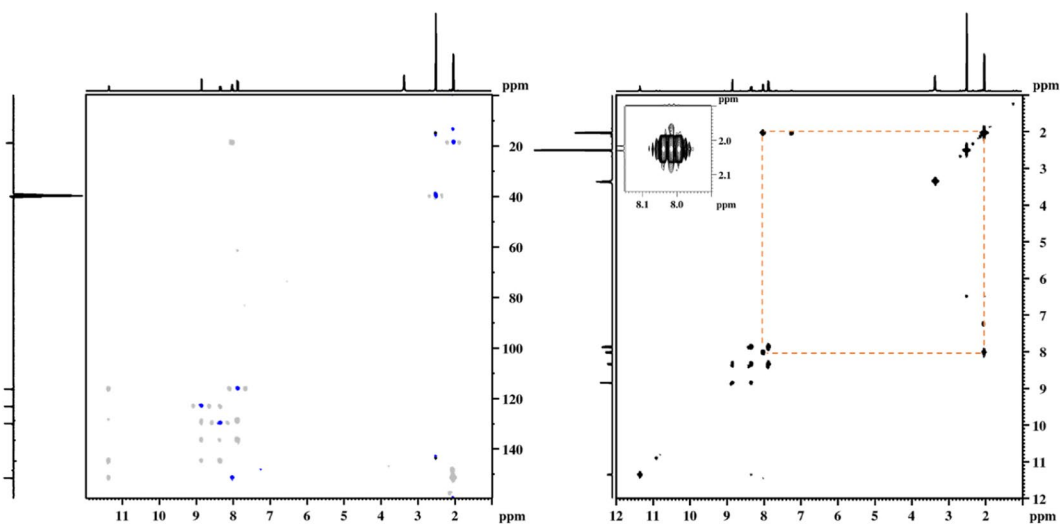


Fig. 1 Left: Multiplicity-edited ^1H - ^{13}C HSQC NMR spectrum (CH_3/CH shown in blue, CH_2 would appear in red) stacked with ^1H - ^{13}C HMBC NMR spectrum (grey) of the iso-

lated acetaldehyde trapping product **5**. Right: ^1H - ^1H COSY spectrum of **5**, CH_3 - CH correlation of the C_2 -fragment originating from acetaldehyde highlighted in orange

in an unknown molecule (DePuy and King 1960). Similar elimination processes are known for tertiary amine *N*-oxides, in which the oxygen is the fourth *N*-substituent that facilitates the elimination of an *N*-alkyl group (Cope elimination) (Cope et al 1949; Cope and Trumbull 1960). Further, tight complexation with metal ions through the nitrogen's electron lone pair has a quaternizing effect and can induce

the elimination of substituents (Potthast et al. 2002). The present case, an *N*-chloro substituent, would be another variant of *C*-elimination from a temporarily quaternized nitrogen.

At present, we are unable to decide about the detailed mechanism with regard to being either an E2 (bimolecular) or E1 (monomolecular) process – while the ionic medium would favor E1, the

relatively low temperature and the fact that the nitrogen is primary (with regard to the C-chain) both seem to speak in favor of E2. A distinction could be provided by using deuterated DABCO: in the case of an E2 mechanism, there should be a clear kinetic deuterium isotope effect, while an E1 process would not be influenced by isotopic labeling. However, the question of an E1 vs. E2 mechanism is rather academic as both processes give the same product. Finally, it should be noted that the amount of acetaldehyde captured is smaller than the amount of piperazine formed (approx. 45 mol%), although stoichiometry would formally require equivalence. This is understandable because of the possible incompleteness of the trapping reaction, an easy evaporative loss of acetaldehyde, which has a boiling point of 20.2 °C (!), or further oxidation to acetic acid by the chlorine-based oxidants present. Also, acetaldehyde can reversibly react with cellulosic pulp by the formation of hemiacetal links with the cellulose's hydroxy groups (Simon et al. 2023; Hosoya et al. 2018). We cannot exclude the possibility that small amounts of formaldehyde were also formed in parallel. Blank experiments with formaldehyde and acetaldehyde added in equivalent amounts showed that both were consumed at quite comparable rates, by excess oxidation (and perhaps additional volatilization). Therefore, if HCHO had indeed been formed in parallel as DABCO degradation product, its concentration was at least one order of magnitude lower than that of acetaldehyde, because HCHO was not (or no longer) detectable under the pertaining conditions.

Computational results on the DFT(M06-2X) level of theory, with a polarizable continuum model (PCM) in water, confirmed the preference of the ionic cleavage as a C₂ unit over the previously proposed mechanisms with two C₁ units. Apparently, the only reaction path for a C–C bond cleavage is the formation of a triplet diradical (N=CH₂, N-CH₂• and Cl•) while the direct homolytic and heterolytic C–C cleavage can be excluded because of unreasonably high energy barriers. The Gibbs energy of this triplet process is 37.7 kcal/mol, which is at the same time the minimum for the Gibbs activation energy. With a value of 29.2 kcal/mol, the $\Delta G^{\circ\ddagger}$ for the experimentally observed elimination process (N–CH=CH₂) was significantly smaller (proton abstraction in β -position by HO[−] as the base, in a cluster of water molecules).

Conclusions

This study addressed the chemical fate of the 1,4-diazabicyclo[2.2.2]octane (DABCO) catalyst in the context of amine-catalyzed hypochlorous acid bleaching of cellulosic pulps (H_{cat} bleaching). Contrary to the previously proposed degradation pathways involving either homolytic or heterolytic breakage of one ethylene bridge with the release of formaldehyde, this research presented evidence supporting an alternative mechanism. The degradation of DABCO under H_{cat} conditions was shown to proceed through the ionic elimination of one ethylene bridge, originating from mono-*N*-chlorinated DABCO. This results in the formation of an *N*-vinyl (enamine) derivative and eventually the release of acetaldehyde and piperazine.

As demonstrated by Afsahi et al. (2019b, c), the use of DABCO derivatives that exhibit higher stability under the prevailing conditions (CM-DABCO and CEM-DABCO) is recommended and seems to be a logical way out of the observed instability of DABCO. While explaining the experimental formation of acetaldehyde, the proposed mechanism is not able to account for the higher stability of *N*-alkylated DABCO derivatives. Nevertheless, the experimental findings and mechanistic insights offer a more nuanced understanding of the chemical transformations occurring in the H_{cat} bleaching system and correct the corresponding literature data.

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Authors' contributions All authors contributed to the study's conception and design. Material preparation, data collection and analysis were performed by all authors. The first draft of the manuscript was written by T.R. All authors commented on previous versions and read and approved the final manuscript.

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Data availability No datasets were generated or analysed during the current study.

Code availability Not applicable.

Declarations

Ethics approval Not applicable.

Consent to participate Not applicable.

Consent for publication All authors agreed to the publication in the submitted form.

Competing interests The authors declare no competing interests.

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