Degradation of the cellulosic key chromophore 2,5-dihydroxy-[1,4]-benzoquinone (DHBQ) under conditions of chlorine dioxide pulp bleaching: formation of rhodizonate as secondary chromophore—a combined experimental and theoretical study

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Received: 24 November 2019 / Accepted: 20 January 2020 © The Author(s) 2020

Abstract 2,5-Dihydroxy-[1,4]-benzoquinone (DHBQ, 1) is the most prominent representative of cellulosic key chromophores, which occur almost ubiquitously in all types of aged cellulosics. The degradation of DHBQ by chlorine dioxide under conditions of industrial pulp bleaching (“D stage”) was studied, i.e. in moderately acidic medium (pH 3) at temperatures between 50 and 90 °C. The degradation in the presence of excess ClO₂ generates rhodizonic acid (RhA, 5,6-dihydroxycyclohex-5-ene-1,2,3,4-tetron, 2) as a secondary chromophore which is even more stable and more potent as a chromophore than the starting DHBQ, especially in the form of its salts. At least a threefold ClO₂ excess is needed for complete DHBQ consumption. The reaction from DHBQ to RhA involves pentahydroxybenzene (PHB, 1) as an intermediate which is either readily further oxidized to RhA by excess ClO₂ or slowly reconverted to DHBQ in the absence of ClO₂. The RhA yield after 30 min reaction time had a maximum of 83% at a DHBQ/ClO₂ molar ratio of 1:5, and decreased with increasing ClO₂ charge, reaching 38% at a DHBQ/ClO₂ ratio of

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Published online: 10 February 2020
Degradation of DHBQ by ClO$_2$ is 42 times faster than that of RhA (50 °C, pH 3). RhA is present in aqueous medium in the form of its dihydrate, 2,3,5,6-hexahydroxycyclohex-2-ene-1,4-dione, which contains two pairs of geminal diols at C-5 and C-6. At pH 5 and above it forms an aromatic C$_6$O$_6$$^{2-}$ dianion, so that the RhA salts are very stable. These salts are intensively colored, not only the ones with transition metal cations, but also those with monovalent (Na$^+$, K$^+$) and especially divalent (Ca$^{2+}$, Mg$^{2+}$) main group metals, and usually have very low solubility so that they precipitate on the pulp fibers. It was demonstrated that the inferior ClO$_2$-bleachability of some pulps is due to the conversion of DHBQ into colored RhA and its respective salts.

**Keywords** Aging · Bleaching · Brightness reversion · Cellulose · Chlorine dioxide · Chromophores · Computational chemistry · Density functional theory (DFT) · 2,5-Dihydroxy-[1,4]-benzoquinone · Pulp bleaching · Rhodizonate · Rhodizonic acid · Yellowing

**Introduction**

In recent years, there have been several reports of lowered bleachability of cellulosic pulps upon chlorine dioxide bleaching (so-called “D stage”) in the final bleaching stage, which was associated with an increased content of transition metal ions. Manganese, copper and iron are the “best-known” and most relevant transition metals in pulp production, and therefore also those that are regularly monitored in pulp. The content of (transition) metals varies depending on the wood species and also shows strong seasonal fluctuations for a particular wood species. Our model pulp studies in this regard were rather inconclusive: in some cases, the bleachability correlated clearly with the metal content, in other cases not at all. It seemed logical to attribute the brightness reversion behavior to transition metal-induced radical processes and oxidative pulp damage. But then it remained completely unclear why the supposed chromophores formed during these processes should not be immediately destroyed—quasi “in situ”—in the D-stage, and, in particular, why calcium and magnesium, which as main group metal ions are innocent with regard to inducing redox chemistry and radical reactions, showed in some cases just as negative effects as the transition metals did.

Because it was known that the three cellulosic key chromophores (Kortntner et al. 2015) can develop directly from oxidatively damaged cellulose (Roseau et al. 2005, 2017), several pulp samples with poor bleachability were tested for the content of key chromophores according to the CRI method (Roseau et al. 2004a, 2011). This technique has been developed for the analysis of aromatic and quinoid traces of chromophores in cellulosic matrices, which are otherwise inaccessible due to their extremely low concentrations. CRI thus is the only approach available to date that allows cellulosic chromophores to be isolated and their structures to be identified, covering up to 75% of the total mass of chromophores isolated. It should be recalled that the CRI method works with
highly bleached pulps and addresses chromophores with “carbohydrate history”, i.e. generated from cellulosics and hemicellulosics, thus excluding pulps with higher lignin contents and lignin-based chromophores that would overrun this analytical method.

In all pulps with deficient final D-stage bleachability, coming from different mills in three continents, we found high contents, between 3 and 6 ppm, of the key chromophore 2,5-dihydroxy-[1,4]-benzoquinone (DHBQ, 1) (Hosoya et al. 2013a), whereas the content of DHBQ in a highly bleached pulp is usually in the low ppb range. DHBQ is known to be formed from oxidative damage (carbonyl groups) along the cellulose chains (Rosenau et al. 2005). Also, effects of metal ions in the chemistry of DHBQ have been observed (Hosoya et al. 2015). The content of the two other key chromophores, 2,5-dihydroxy-[1,4]-naphthoquinone (DHNQ) and 2,6-dihydroxyacetophenone (DHAP), in the difficult-to-bleach pulps was not increased beyond normal levels (< 10 ppb).

DHBQ (1) is a nearly ubiquitous cellulosic chromophore because it is both a prime survivor of bleaching treatments and a regeneration product from condensation of low-molecular weight fragments upon cellulose aging (Rosenau et al. 2007, 2008). Even a seemingly negligible oxidative modification, such as a single hydroxyl group oxidized to a carbonyl group, can lead to the formation of a DHBQ moiety along the cellulose chain (Rosenau et al. 2008, 2017). The high stability of DHBQ and its dianion towards bleaching treatments is attributed to exceptional resonance stabilization (Hosoya and Rosenau 2013b, c). The double bonds in the peculiar system of DHBQ have much greater stability towards bleaching agents (under both acidic and alkaline conditions) than conventional double bonds conjugated with each other or with carbonyl groups. In acidic media and in solid state, the two hydroxyl protons are equidistant to the two respective neighboring oxygen atoms (see Scheme 1). In alkaline media, DHBQ is deprotonated to form an exceptionally stable dianion. The stability of the DHBQ dianion accounts for the easy release of the hydroxyl protons, i.e. the high acidity of the compound, with the pKₐ being 2.71. DHBQ is thus significantly more acidic than, for example, acetic acid (pKₐ = 4.76). The delocalized double bonds explain why most bleaching agents react so sluggishly with DHBQ, which survives bleaching treatments much longer than other chromophores: since bleaching agents attack localized double bonds in their usual mode of action, they have a hard time with DHBQ which lacks such “proper” double bonds due to its resonance delocalization. Fast and reliable methods to detect and quantify DHBQ, even at the very low concentrations in cellulosic pulps, have become available (Potthast et al. 2018), which is a prerequisite for monitoring both bleaching sequences and model compound studies.

Several previous accounts have addressed the chemistry of DHBQ, which has recently been reviewed (Hosoya et al. 2013a). The strong resonance stabilization of the corresponding dianion and prominent keto-enol interconversions are typical features of this compound. Its preferred reaction paths are electrophilic substitutions, mainly at C-3 and C-6 (Bras- sard and L’Ecuyer, 1958; Jimenez-Alonso et al. 2007; Misiolek et al. 2009), while the oxygens are rather resistant (Keegstra et al. 1996a). Such processes occur for instance with S-ylides (Rosenau et al. 2004b) or iodonium species (Papoutsis et al. 1994). Typical examples for nucleophilic reactions, which occur at either C-1, C-2, C-4 and C-5 with little regioselectivity, are reactions with amines (Manthey et al. 1989; Zhang and Jin 2003), and the follow-up chemistry to N-heterocycles (Placin et al. 2000; Seillan et al. 2008; Tang et al. 2009). As the compound is prone to both nucleophilic and electrophilic attack, there is a wide range of options for chemical modifications of the structure. Reduction to the hydroquinone form proceeds easily, but requires stabilization of the product in the form of alkyl or acyl derivatives (Schlote et al. 1994; Keegstra et al. 1996b). These previous accounts focused on DHBQ in organic synthesis. Its pivotal role in cellulose aging and in pulp bleaching chemistry has brought its degradation and “discoloration chemistry” to the fore in recent studies (Hosoya and Rosenau 2013b, c).

Given this fundamental role of DHBQ in yellowing and aging of cellulosics, the chemical behavior of this chromophore during chlorine dioxide bleaching was an important issue for the production of highly bleached and brightness-stable pulps. This study addresses the molecular mechanisms of the degradation of DHBQ by chlorine dioxide based on experimental results and their correlation with computational studies.
**Results and discussion**

Chlorine dioxide as oxidant in pulp bleaching ("D-stage")

Chlorine dioxide—although having some negative environmental repercussions—is still a major bleaching agent in the pulp and paper industries. It is a gas with good solubility and relatively high stability in acidic aqueous media, and thus it is applied this way at a pH around 3. ClO_2 is a strong oxidant for many organic compound classes, such as phenols, aldehydes, unsaturated structures, or amines. There are three typical initial reactions of ClO_2—hydrogen atom abstraction, one-electron transfer, and radical addition reactions to double bonds—which are typically followed by subsequent reactions of ClO_2-derived chlorine species (Leigh et al. 2014; Aguilar et al. 2014; Lehtimaa et al. 2010; Napolitano et al. 2005; Hull et al. 1967). Because of the different reaction modes and many side reactions, its application in synthetic organic chemistry is rather limited, but it is a favored oxidant in pulp bleaching because of its high selectivity: it mainly attacks residual lignin, with its aromatic and quinoid structures, while leaving the carbohydrate structures in cellulose and hemicelluloses largely unchanged. This is one advantage over oxygen-based bleaching chemicals, such as molecular oxygen ("O-stage" bleaching), hydrogen peroxide ("P-stage") or ozone ("Z-stage").

While being reasonably stable in acidic medium, ClO_2 offers a rich disproportionation and symproportionation chemistry in neutral and in particular alkaline aqueous media. Having an unstable oxidation state (+IV) of its central chlorine atom, the compound is a strong oxidant with high reactivity. It is a monoradical, having a doublet ground state. Computations as well as simple VSEPR (valence shell electron pair repulsion) considerations show that the molecule is V-shaped (i.e., it is not linear) with the spin density mainly located at the terminal oxygen atoms and only little at the central chlorine atom. Immediately disproportionating in alkaline medium, the pure substance degrades only slowly in acidic medium, giving rise to many chlorine species in different oxidation states, e.g. chloric acid (V), chlorous acid (III), hypochlorous acid (I), elemental chlorine (0), and chloride (−I). In the presence of redox-active reaction partners those conversions into other oxidation states are much faster, resulting in a very complex redox chemistry. The final, stable products from ClO_2 are hydrochloric acid (HCl) and chloric acid (HClO_3), having oxidation states of −I and +V, respectively. Recording kinetics of reactions involving ClO_2 is not reasonably possible by following ClO_2 itself or one of the chlorine-derived species (Scheme 1).

![Scheme 1](image)

**Scheme 1** Chemical structures of DHBQ (1) and its deprotonated and protonated forms, [DHBQ−2H]^2− and [DHBQ−H]^+−, respectively
because of the complexity of the underlying redox systems and the fast interconversion between the chlorine species. Kinetic studies are therefore reliant on the monitoring of the reaction partner, as was also applied in our case. But even then it is difficult to determine whether a compound was oxidized directly by ClO₂ or rather by one of the secondary oxidants derived from it.

Observations from ClO₂-bleaching of pulps

The preliminary observations, as briefly described in the introduction, led to the general conclusion that oxidative damage to the pulps and metal ion management before/during bleaching were somehow involved in all cases where a poor bleachability in the final D-stage was observed. We thus performed experiments with highly bleached pulps available from previous work (Ahn et al. 2019), which had different degrees of oxidative damage. The pulps contained carbonyl groups (oxidized cellulosic hydroxyl groups) between 13 and 105 μmol/g and had an initial brightness of 88–91% ISO and above. In all bleaching experiments, bidistilled water and high-purity chemicals were used to make sure that any water-associated metal ion effects were at least largely limited, if not fully prevented. An aliquot of the starting pulps was aged under either dry or wet conditions according to standard procedures (ISO 2470-1 2009), which expectedly brought the brightness down to values between 82 and 88% ISO. For two arbitrarily selected aged pulps it was confirmed once more that the discoloration upon aging was mainly due to DHBQ formation, applying the CRI method to isolate the formed DHBQ. The DHBQ contents were between 0.4 and 2.8 ppm, sufficiently high to cause the observed brightness loss. As mentioned, it is known that the formation of DHBQ is a direct result of oxidative damage—to be precise: carbonyl group generation—in cellulosic pulps (Rosenau et al. 2005).

The starting pulps as well as the dry aged and wet aged counterparts were subjected to a simulated D-stage bleaching (pH 3, temperature between 50 and 90 °C). Standard experiments were done at 50 °C, which is somewhat low in comparison to industrial conditions, but slowed the reactions down to time ranges in which they could be conveniently followed. Thus, this temperature seemed to be a good compromise. Upon ClO₂ treatment, the starting pulps showed no significant brightness gain due to the already high starting brightness. For all aged pulps, however, the brightness increase was quite significant, although—at 88–90% ISO—it remained slightly below the initial value (Table 1).

So far, the results had been rather commonplace and fully in line with expectations. However, the addition of Fe(III) cations (3 ppm) to the D-stage medium brought about a surprising twist: while the effect on the starting pulps was zero, the bleachability of all aged pulps was very negatively affected (74–88% ISO), Table 1. For the highly oxidized (C=O content > 62 μmol/g) and aged pulps, the brightness after the ClO₂-treatment was even lower than before! Spontaneously we tried to explain this by the “usual” transition-metal induced radical and degradation reactions, i.e. the often cited “Fenton chemistry”. But firstly, such reactions are typical of alkaline media and peroxide-based systems, but not of the conditions used, which differ greatly from classical Fenton systems. And secondly, the molecular weight of the pulps bleached with and without iron addition did not show any differences at all. This result was inconsistent with the assumption that Fe-based radical chemistry was involved, which surely would have affected cellulose integrity rather negatively. A very simple observation—admittedly purely coincidental—was the key at the time to steer our efforts in a better direction: the effect of iron was almost the same when it was added during the actual bleaching stage. It was now obvious that some iron-containing chromophores, which resulted from DHBQ, had to be the reason for the reduced bleachability, and that the loss of brightness was not caused simply by iron-induced, Fenton-type cellulose degradation. Moreover, these Fe-based chromophores were apparently quite potent (since the iron concentration was very low), formed quite fast (even during washing) and were quite stable on the pulp (because they were not simply washed away). They were formed not only when the metal ion was there during the D-stage, but also when it was present only during the short times of washing with its highly diluted regimes, and they were little affected by an alkaline extraction step.

In the following, the influence of metal ions other than Fe was tested. These results are summarized in Table 2. It was not unexpected that the effect of Cu(II) and Mn(II)—transition metals as well—on
bleachability were the same as that of Fe(II/III); Cu(II) was even slightly more harmful than Fe, Mn(II) somewhat less. However, it was surprising that Zn(II), which is far less redox-active than Fe, Cu and Mn, behaved similarly, and it was even more puzzling that also the main group metals Mg(II) and Ca(II) had a significantly negative effective at higher degrees of oxidative pulp damage. The influence was less than in the cases of transition metals, but still very clear. At 20 times the transition metal concentration (60 ppm), Ca(II) or Mg(II) had an effect similar to Fe, Cu or Mn at a 3 ppm concentration (Table 2). Even very high concentrations of sodium and potassium (200 ppm) decreased the brightness, while Al(III) and ammonium had no negative effect at all (Table 2).

For all cations used, it did not matter with regard to final brightness whether they were already added during the D-stage bleaching or only afterwards in the washing water. There was even a slight tendency for the addition during washing to result in lower brightness, which indicated the fast formation of metal-based chromophores during the relatively short washing times. While the chromophores could be partially dissolved or degraded in the (relatively long) D-stage, the washing was too short (or too ineffective) for such partial removal. The washing was usually performed with neutral bidistilled water (containing the metal salts to supply the respective metal ions). When subsequently an additional alkaline wash (pH 10) was applied, there was no or no significant improvement for the pulps containing Fe, Mn, Cu, Zn, Mg or Ca salts, but some improvement for pulps with Na or K (Table 2), suggesting that the negative effects of the latter two ions were at least partly reversible by alkaline washing.

After D-stage bleaching, DHBQ was not detectable in any of the pulps. The action of chlorine dioxide obviously destroyed the DHBQ generated during accelerated aging, but the pulps now showed a general sensitivity towards metal ions causing poor bleachability—interestingly not limited to transition metal ions. This effect clearly increased with increasing degree of oxidation of the pulps. Since the degree of oxidation also runs parallel to the DHBQ content directly after aging, there was obviously also a correlation between this initial DHBQ content and the subsequent metal ion-induced bleachability problems, but it was impossible at this point to determine whether and how both factors depend on each other.

Table 2 summarizes the initial bleaching trials with metal ion addition and illustrates the obvious negative effects of some metal ions. From this outcome, it seemed clear to us that conventional D-stage experiments with usual pulps would not allow more detailed explanations and that mechanistic studies with model pulps and model compounds were necessary for a thorough understanding of the underlying chemistry.

Observations from bleaching of DHBQ-enriched pulps

In the next set of experiments, we therefore used the starting pulps (carbonyl group content 28 and 45 µmol/g, initial brightness > 90% ISO, see above) and enriched them with DHBQ. For this purpose, so much of an aqueous solution of DHBQ in distilled water was applied to the pulp that a DHBQ content of 3 ppm or 10 ppm, respectively, was reached after drying. Then the pulp was kneaded for a few minutes. The DHBQ is firmly adsorbed to the cellulose under these conditions and does not adhere to glassware or containers, thus ensuring that the amount of DHBQ transferred to the system with the water really remains in/on the cellulose and that the concentration is as intended within the error limits. For one case it was additionally confirmed that DHBQ was indeed only adsorptively (but not covalently) bound and can therefore be completely re-extracted by alkaline washing (0.1 mM NaOH, pH 10): three parallel extractions gave DHBQ recoveries of 96, 97 and 101%, respectively (UV/Vis determination). The ISO brightness of the DHBQ-enriched pulps was 83% ISO (3 ppm) and 79% ISO (10 ppm).

The pulps enriched with DHBQ were directly subjected to D-stage bleaching followed by washing to neutral pH with distilled water. In all cases, brightness returned nearly to the initial values (90–91% ISO). If

1 The use of pulps with higher oxidation degree was not necessary: high degrees of pre-oxidation were only required in connection with the aging to produce higher DHBQ contents. Since the DHBQ is now supplied externally but not generated “internally”, neither high oxidation degrees nor subsequent aging procedures are needed. If accelerated aging was nevertheless carried out, the brightness deteriorated rapidly and the amount of re-extractable DHBQ decreased drastically, suggesting that DHBQ was converted into other, more potent chromophoric species. Results of this part of the study will be reported later.

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an additional alkaline washing step was subsequently applied, the brightness gained was excellent with 91–92% ISO. It was obvious that the added DHBQ was efficiently destroyed in the D-stage (Table 3). When the DHBQ-enriched and bleached pulps were aged, the brightness was the same as that for the initial pulps, meaning that the two steps of DHBQ-enrichment and removal had no permanent negative effect to the pulp. The ClO₂ system had selectively attacked the additionally provided chromophore without causing any further damage to the cellulose, which would have shown up in additional chromophore formation and brightness decrease after aging. Our attempts at that time to isolate any reaction products of DHBQ from the pulps seemed to have failed. The NMR spectra of concentrated alkaline extracts (D₂O/NaOD) showed no signal in the ¹H domain, and a solitary, highly concentration and matrix dependent singlet (158 ppm) in the ¹³C spectra which—incorrectly, as it turned out later—was assigned to carbonate (see also the peak at 177 ppm in Fig. 1).

As soon as metal ions were involved, the situation changed once again fundamentally. In principle, all results were identical to those obtained with the above oxidized/aged pulps (which were not DHBQ-enriched, but contained DHBQ generated by aging). Thus, it was evident that the brightness-impairing effect of DHBQ—whatever its nature was—was independent of the DHBQ source, i.e. independent of whether DHBQ was generated “naturally” from oxidized functionalities upon accelerated aging or provided “artificially” by spiking the pulp with a DHBQ solution. The addition of 3 ppm of transition metal salt solutions (Fe(II), Cu(II), Mn(II) as the respective sulfates) during the D-step decreased the final brightness after bleaching to values between 72 and 78% ISO. Again, higher concentrations of Ca(II) and Mg(II) (60 ppm) as well as Na(I) and K(I) (300 ppm) had a similar effect, see Table 3. In all cases the point of metal ion addition played no role, i.e., the effect was the same when the metal ions were added during bleaching or thereafter together with the neutral washing solution. An additional alkaline washing step had only a minor effect for all metal ions except Na(I) and K(I), for both of which the brightness significantly improved (Table 3). It was evident that under D-stage conditions the combination of DHBQ (or its reaction/degradation products) and metal ions afforded some chromophores, which were not further degraded and thus decreased the final brightness, and which for most metal ions could not be removed by neutral or alkaline washing (Table 3).

In the case of Na(I) and K(I) being present, when chromophore extraction was possible, we tried to

### Table 1  Bleachability of oxidized and aged (wet or dry) pulps under D-stage conditions: the negative effect of iron during bleaching or washing. All brightness values in %ISO

| Brightness | Carbonyl group contents of starting pulps |
|------------|------------------------------------------|
|            | 13 µmol/ 28 µmol/ 45 µmol/ 62 µmol/ 79 µmol/ 105 µmol/ |
|            | g  g  g  g  g  g |
| Starting brightness | 91 91 90 90 90 88 |
| After wet aging | 88 88 86 84 84 83 |
| After wet aging/D-stage | 90 90 89 89 89 88 |
| After dry aging | 85 85 84 83 83 82 |
| After dry aging/D-stage | 89 89 89 88 88 88 |
| After wet aging/D-stage with 3 ppm Fe³⁺ | 88 85 83 80 78 77 |
| After dry aging/D-stage with 3 ppm Fe³⁺ | 87 85 82 77 76 74 |
| After wet aging/D-stage/washing with 3 ppm Fe³⁺ | 88 86 84 82 76 76 |
| After dry aging/D-stage/washing with 3 ppm Fe³⁺ | 88 85 80 76 74 74 |
| After wet aging/D-stage with 3 ppm Fe³⁺/washing plus alkaline extraction | 88 85 83 82 80 79 |
| After dry aging/D-stage with 3 ppm Fe³⁺/washing plus alkaline extraction | 87 85 82 80 77 77 |
concentrate the extracts, keeping the pH at 10 (to avoid any condensations in the strongly alkaline medium that would form by removal of the water). Again, the $^1$H NMR spectra did not show any signals, although the solution was deeply yellow. This was not surprising, since chromophore mixtures already at very low concentrations—far below the typical NMR-accessible range—might form strongly colored solutions. The $^{13}$C NMR spectra, in turn, provided only the alleged carbonate peak, as described above.2

To confirm the complete oxidation of DHBQ to carbonate in aqueous solution, we used the old and simple—yet quite reliable—acidification test, which was expected to cause some gas generation, and the purging of the formed CO$_2$ into a BaCl$_2$ solution that would turn white from the formation of precipitated BaCO$_3$. However, no gas development was observed during acidification, but a clearly noticeable brightening to light yellow was seen, which remained unchanged even after the acidified solution had been refluxed for some minutes. The initial dark yellow color returned after re-alkalization with NaOH. When the acidified sample was re-measured with NMR, the $^{13}$C NMR spectra surprisingly showed three peaks (at about 92, 141 and 190 ppm) which converged to a single signal at 177 ppm upon re-alkalization (Fig. 1).

Table 2  Bleachability of oxidized and aged pulps under D-stage conditions: the negative effect of transition and main group metal ions. All brightness values in %ISO. Metal ions (concentrations see text) were added either during the D-stage itself (D, see footnote d) or in the neutral washing step after the bleaching stage (W, see footnote e). An optional additional mild alkaline extraction step was performed after the neutral washing (E, see footnote f)

| Metal ions | Fe$^{3+}$ | Fe$^{3+}$/E | Cu$^{2+}$/E | Mg$^{2+}$/E | Ca$^{2+}$/E | Al$^{3+}$/E | Na$^{+}$/E | K$^{+}$/E | NH$_4$+ | NH$_4$+/E |
|------------|----------|------------|------------|------------|------------|-----------|----------|---------|--------|--------|
| 13 (µmol/g) | 86       | 86         | 85         | 90         | 89         | 90        | 90       | 90      | 90     | 90     |
| 28 (µmol/g) | 85       | 85         | 84         | 83         | 89         | 89        | 89       | 89      | 89     | 89     |
| 45 (µmol/g) | 82       | 81         | 79         | 78         | 86         | 87        | 87       | 87      | 87     | 87     |
| 62 (µmol/g) | 76       | 75         | 74         | 71         | 78         | 79        | 79       | 81      | 81     | 81     |
| 79 (µmol/g) | 75       | 71         | 70         | 70         | 75         | 75        | 75       | 80      | 80     | 80     |
| 105 (µmol/g)| 72       | 70         | 70         | 70         | 76         | 76        | 76       | 80      | 80     | 80     |

2 At that time, it seemed unclear to us how any (hydrogen) carbonate could have survived the acidic D-stage conditions and eventually been extracted by alkali, and why the peak appeared so much low-field shifted.
changes in the $^{13}$C resonances pointed to the structure of rhodizonic acid (RhA, 2), see Scheme 2. This was additionally confirmed by comparison and spiking with an authentic sample. Evidently, DHBQ had been converted into rhodizonic acid under the D-stage conditions, and the interaction of the formed RhA with metal ions caused the observed poor bleachability.

Rhodizonic acid is present as 5,6-dihydroxycyclohex-5-ene-1,2,3,4-tetrone (2) in the solid state and in non-aqueous solutions. In acidic and neutral aqueous media, the compound exists as the bis(ketohydrate), namely 2,3,5,6,6-hexahydroxycyclohex-2-ene-1,4-dione (2a), cf. the observed characteristic $^{13}$C resonance of the ketohydrate at about 94 ppm. The compound is often (and wrongly) referred to as rhodizonic acid “dihydrate”, but it is in fact a bis(ketohydrate) and not a coordination compound with water in the hydrate shell. In alkaline medium, RhA forms a symmetric (space group $S_6$) rhodizonate dianion (2b), which in $^{13}$C NMR results in only a single resonance. The dianion is aromatic, which explains both its very high stability and the ease of formation.

Rhodizonic acid forms deeply colored salts with transition metal ions, such as Fe, Cu, Mn, Ag and Pb, which have extremely high extinction coefficients (see Fig. 2). The actual colors are well distinguishable in the low mM and μM range. At the very low concentrations present on the pulp, only a slight discoloration is observed, recognizable as yellowing effect, which was measured as decrease in ISO brightness (see Tables 2, 3). Moreover, the transition metal salts of RhA are almost insoluble, forming a so-called “lacquer” which readily precipitates and sticks tightly to surfaces. A simple color test for the presence of RhA is performed with Pb(II) ions, which give the

### Table 3: Bleachability of DHBQ-enriched pulps (3 or 10 ppm) under D-stage conditions: the negative effect of transition and main group metal ions. All brightness values in %ISO.

| Pulp       | C=O content 28 μmol/g | C=O content 45 μmol/g |
|------------|-----------------------|-----------------------|
| B(0)\(^a\) | 91                    | 90                    |
| DHBQ content | 3 ppm              | 10 ppm               |
| DHBQ\(^b\) | 83                   | 79                   |
| D(0)\(^c\) | 91                   | 91                   |

| Metal ions | D\(^d\) | W\(^e\) | D | W | D | W | D | W |
|------------|--------|--------|---|---|---|---|---|---|
| Fe\(^{2+}\) | 74     | 74     | 68 | 67 | 74 | 73 | 68 | 66 |
| Fe\(^{2+}/E\(^f\) | 72     | 72     | 72 | 72 | 74 | 73 | 65 | 65 |
| Cu\(^{2+}\) | 73     | 72     | 68 | 66 | 72 | 72 | 67 | 66 |
| Cu\(^{2+}/E\(^f\) | 73     | 73     | 72 | 72 | 74 | 73 | 71 | 72 |
| Mn\(^{2+}\) | 77     | 76     | 74 | 74 | 78 | 76 | 73 | 73 |
| Mn\(^{2+}/E\) | 76     | 77     | 77 | 77 | 80 | 77 | 77 | 76 |
| Zn\(^{2+}\) | 86     | 87     | 82 | 82 | 86 | 86 | 82 | 81 |
| Zn\(^{2+}/E\) | 88     | 88     | 86 | 86 | 87 | 87 | 85 | 85 |
| Mg\(^{2+}\) | 89     | 88     | 85 | 85 | 88 | 88 | 84 | 85 |
| Mg\(^{2+}/E\) | 88     | 87     | 85 | 85 | 87 | 88 | 84 | 84 |
| Ca\(^{2+}\) | 86     | 86     | 82 | 81 | 86 | 87 | 75 | 76 |
| Ca\(^{2+}/E\) | 85     | 85     | 81 | 81 | 85 | 86 | 80 | 82 |
| Al\(^{3+}\) | 88     | 89     | 88 | 88 | 89 | 87 | 83 | 82 |
| Al\(^{3+}/E\) | 89     | 89     | 88 | 88 | 89 | 89 | 87 | 88 |
| Na\(^{+}\) | 87     | 87     | 85 | 85 | 86 | 86 | 85 | 85 |
| Na\(^{+/E}\) | 88     | 88     | 86 | 85 | 85 | 86 | 86 | 86 |
| K\(^{+}\) | 86     | 87     | 85 | 85 | 87 | 86 | 85 | 85 |
| K\(^{+/E}\) | 86     | 87     | 86 | 86 | 85 | 85 | 86 | 85 |
| NH\(_4\)\(^{+}\) | 90     | 89     | 87 | 87 | 90 | 88 | 87 | 87 |
| NH\(_4\)\(^{+/E}\) | 90     | 90     | 89 | 89 | 90 | 90 | 89 | 89 |
deeply colored lead salts, the most stable and least soluble of all RhA salts (Chalmers and Telling 1967; Feigl and Suter 1942). Upon addition of Pb$^{2+}$, main group salts of RhA (and also those of Zn$^{2+}$ and ammonium) are converted into the Pb salt, which is accompanied with a significant color change. Therefore, the Pb(II) test works for both RhA itself and its main group salts, which are altogether converted into the black Pb-salt. In our experiments, the Pb(II) test had been clearly positive in all cases where decreased brightness and bleachability was observed, confirming that these effects were always due to rhodizonate salt formation.

In conclusion, the action of ClO$_2$ on DHBQ upon D-stage bleaching produced rhodizonic acid as the primary, stable and detectable product. As a pure substance and in acidic aqueous solution RhA has a yellow color, but with many metal cations it forms deeply colored and hardly soluble salts. This is the reason for the observed loss of brightness, deteriorated bleachability, and the great influence of metal ions. It also explains why the bleachability changes with the transition metal content in the pulp, which shows for instance seasonal or inter-species variations.

Model compound experiments

Monitoring the reaction kinetics

Admittedly, we could not solve the problem how the reaction kinetics of DHBQ and ClO$_2$ could be measured directly under D-stage conditions in a simple and convenient way. The first UV/Vis-based data—which we recorded when we had not yet learned that rhodizonic acid was the main product—had to be discarded because they were inconsistent and inconclusive. In retrospect, it was quite clear that a UV/Vis approach had to fail: the spectra of DHBQ and RhA under acidic conditions are partly overlapping and do not allow isolation of a wavelength for kinetic monitoring (Fig. 3, top) and they overlap additionally with the absorption of ClO$_2$ ($\lambda_{\text{max}}$ at 355 nm). In addition, RhA salts are virtually insoluble and tend to precipitate on the walls and bottom of the cuvette, even at concentrations as low as 1 µM. GC–MS was not an option either: the reaction had to be stopped reliably, and the sample had to be dried and derivatized, which did not work quantitatively for either compound (Hettegger et al. 2019). The rapid
neutralization with excess sodium sulfite solution and subsequent UV/Vis measurement of the resulting alkaline solution at 310 nm worked very well and was the method of choice. An aliquot of the bleaching mixture was taken and immediately mixed with double the volume of concentrated aqueous Na₂SO₃. All oxidants present—ClO₂ and oxidizing Cl-derived species, such as HOCl, HOCl₂ and HOCl₃—are immediately reduced to chloride, and sulfite is oxidized to sulfate in turn. At the same time, the pH is changed to 11–12 in an instant, with both DHBQ and RhA being present as anions, very soluble and readily measurable by UV/Vis spectrometry (Fig. 3, bottom).

The reaction between DHBQ and ClO₂ at pH 3 was generally fast. A tenfold excess of ClO₂ consumed DHBQ completely within 4 min. Very interesting was the fact that the course of the reaction seemed to be strongly dependent on the DHBQ/ClO₂ ratio, see Fig. 4.

Influence of the ratio DHBQ/ClO₂

At a 1:1 molar ratio between DHBQ and chlorine dioxide, a maximum of 82% of the quinone was consumed after 240 s, but some of the starting material was slowly regenerated, so that 54% of the initial concentration was reached again after 32 min and remained constant afterwards (see Fig. 4).

We had just observed a similar kinetic behavior for the reaction of another key chromophore, 5,5-dihydroxy-1,4-naphthoquinone (DHNQ), with ClO₂ (Hosoya et al. 2018). Its degradation kinetics could be explained by the occurrence of an unstable intermediate that was slowly reconverted into the starting material. Due to some parallels in the chemistry of DHNQ and DHBQ, it was logical to search for such a transient species also in the DHBQ case, although UV/Vis had not provided any indication of this. However, ¹H NMR spectroscopy clearly showed the appearance of a new singlet at 6.1 ppm, apart from the expected decrease of DHBQ’s singlet at 5.8 ppm.³ The new signal completely disappeared within 30 min (which was fully consistent with the UV/Vis data) and the intensity of the singlet from the starting material returned to almost half the original intensity, demonstrating slow regeneration of DHBQ. The ¹H NMR kinetics were recorded by a series of measurements with 4 accumulated scans and quantification by simple peak integration.

At a DHBQ/ClO₂ ratio of 2:1 (which could consume only half of the introduced DHBQ at full ClO₂ conversion), the DHBQ content dropped to 53% (i.e. 47% were consumed) and increased to 74% within 30 min, i.e. about half of the initially consumed DHBQ (half of 47%) was regenerated again in this case. The concentration of the intermediate was maximum after 3–4 min and gradually decreased to zero. ¹H NMR showed nicely that the DHBQ peak decreased to about 50% of initial intensity and then regained intensity, while the intermediate’s singlet reached a maximum at about 4 min and then dropped to zero within 30 min.

With DHBQ/ClO₂ ratio of 1:2, the initial consumption of DHBQ was as high as 98%, with 12% DHBQ being regenerated after half an hour. The intermediate was hardly detectable by NMR between reaction times of 3–8 min. At a reagent ratio of 1:3 and above (1:5, 1:10), DHBQ was consumed completely, and none of it was re-formed. In all of these cases, no intermediate was NMR-detectable. Even with such high ClO₂ charges, DHBQ consumption did not accelerate significantly, and was finished quite constantly after 180–200 s reaction time. It was thus concluded that chlorine dioxide must be present in at least a threefold molar excess to consume DHBQ reliably and permanently (without regeneration), see Fig. 4.

If DHBQ was reacted with a 100-fold excess of ClO₂, it can be assumed that the concentration of ClO₂ remained constant during the reaction in a first approximation. The reaction kinetics for the consumption then clearly followed a first (actually: pseudo-first) order. The same applied to the consumption of RhA, even though it was much slower. Due to the complexity of the ClO₂ system it did not seem reasonable to record complete kinetics and derive the activation parameters, as this would only reflect the unknown rate-determining step from a whole lengthy sequence. However, a comparison of the rate constants k—and thus the half-lives $t_{1/2}$—would allow an easy comparison of how fast the two chromophores DHBQ and RhA are degraded. Note that in first-order kinetics, rate constant $k$ and the half-life $t_{1/2}$ are given.

³ Note that these spectra cannot be recorded in D₂O as the solvent as usual because the methine protons of DHBQ undergo H–D exchange. Instead, only little D₂O is added for locking purposes and the spectra are recorded in the original reaction mixture (H₂O) with water signal suppression.
by the equation \( t_{1/2} = \frac{\ln 2}{k} \) and the half-lives are therefore concentration-independent. Under our standard conditions (50 °C, pH 3, hundredfold molar excess of ClO\(_2\)) the degradation of DHBQ was 42 times faster than that of RhA, and 25 times faster at 80 °C with otherwise unchanged parameters. This shows that the degradation of DHBQ under D-stage conditions converts the key chromophore DHBQ into the secondary chromophore rhodizonic acid, which is degraded much slower than DHBQ itself.

The degradation of RhA by ClO\(_2\) caused small gas bubbles adhering to the walls of the reaction vessel. The BaCl\(_2\) test confirmed the gas to be CO\(_2\), which was confirmed by flushing into diluted NaOH and \(^{13}\)C NMR (carbonate peak). NMR of the acidic mother solution provided only one \(^{13}\)C peak, which was identified as oxalic acid based on previous experiments (Hosoya et al. 2018) and by spiking with an authentic sample. The final reaction products of the degradation of RhA (and thus indirectly of DHBQ) were thus oxalic acid (COOH\(_2\)) and CO\(_2\). Determining the ratio between these two final products is meaningless, since oxalic acid is also slowly oxidized to CO\(_2\) by ClO\(_2\), so that the ratio is not a constant and therefore cannot be used to obtain more detailed information on the mechanism.

All these kinetic results suggested the general mechanism shown in Scheme 3. It was evident that DHBQ reacted rapidly with ClO\(_2\) to a labile intermediate (path A) that was slowly converted back to DHBQ (path B) in the absence of additional ClO\(_2\). However, in the presence of excess ClO\(_2\), the intermediate was converted into the stable product, rhodizonic acid (path C). Path B is not just the reversal of path A: it is much slower, and no ClO\(_2\) was regenerated. It was reasonable to assume that path A actually followed a 1:1 stoichiometry and that the small deviations from the exact 1:1 ratio were due to the difficulty of the exact dosing of the oxidant and the many potential side reactions of chlorine dioxide, as well as the minor contribution of the subsequent oxidation (path C), which already started as a parallel reaction before DHBQ was completely converted into the intermediate. Path C—in contrast to path A—is irreversible and has no possibility of leading back to DHBQ. RhA finally becomes oxalic acid and CO\(_2\) in the reaction with excess ClO\(_2\) (path D), which are the stable and colorless end products. At 50 °C path D (degradation of RhA) was 42 times slower than path A (consumption of DHBQ).

**Scheme 2** Chemical structures of rhodizonic acid (RhA) in solid state (2), as bis(ketohydrate) in acidic and neutral aqueous solution (2a) and as aromatic rhodizonate dianion (2b) in alkaline aqueous solution.

**Fig. 2** Color of 1 mM aqueous solutions of rhodizonic acid, and its Na(I), Cu (II), Fe(II) and Pb(II) salts (from left to right). Transition metal salts, in particular that of Pb, have low solubility and tend to precipitate even at very low concentrations, forming “lacquers” on supports, such as pulp or paper. This behavior is used analytically for transition metal ion detection in the form of their rhodizonates.
The initial reaction step

In the case of the ClO$_2$ oxidation of DHNQ we had observed a modest kinetic H/D isotope effect (Hosoya et al. 2018), and therefore we also performed the reaction of DHBQ in D$_2$O instead of H$_2$O. The effect was more drastic than in the case of DHNQ: the reaction rate was more than halved, and complete consumption of DHBQ at a 1:1 ratio of DHBQ/ClO$_2$ was only reached after 8.5 min (instead of 4 min in H$_2$O). This indicated the involvement of an H-R bond cleavage in the rate-determining step, R being the binding partner of the proton. Possible examples for such processes are proton shifts (keto-enol tautomerism), addition reactions, eliminations after protonation of the leaving group (HO$^-$/DO$^-$), or hydrogen atom (H) abstraction reactions, which would all show a kinetic isotope effect. In particular the last alternative seemed likely since the initial reactions of ClO$_2$ are often H abstraction (or transfer of an electron and a proton, formally giving H$^-$), as also observed in the case of DHNQ (Hosoya et al. 2018).

Fig. 3 UV–vis absorbance spectra of DHBQ and RhA. a DHBQ (0.01 mmol/L) in deionized water. b RhA (0.1 mmol/L) in deionized water. c DHBQ (0.01 mmol/L) deprotonated by dissolving in 0.01 mol/L NaOH. d RhA (0.1 mmol/L) deprotonated by dissolving in 0.01 mol/L NaOH. The dashed grey line in c and d at 310 nm indicates the wavelength used for tracing the reaction kinetics. All Spectra were normalized to a maximum absorbance of one arbitrary unit (AU)

Fig. 4 Time course of the degradation of DHBQ by ClO$_2$ in different molar ratios (pH 3, 50 °C), seen by UV/Vis absorbance at 310 nm, after stopping the reaction with conc. aqueous Na$_2$SO$_3$ (see text). UV data are normalized to the starting absorbance at t = 0 s. In the D$_2$O experiment, 85% of H$_2$O was replaced with D$_2$O. Values at t = 30 min are final and do not change with longer reaction times
This H abstraction would also explain the relatively large size of the effect, because in radical H abstraction reactions the D transfer is usually significantly slower than an H transfer, while the difference between the corresponding cations D⁺ and H⁺, as in tautomerisms or hydroxyl group exchange, is smaller. Computations (see below) have shown that the first step in the reaction was indeed an H atom transfer from protonated DHBQ to ClO₂ (see Scheme 3), resulting in a DHBQ radical and chlorous acid HClO₂, which has a Cl(III) oxidation state.

Identification of the intermediate

From the kinetics described above (see “Influence of the ratio DHBQ/ClO₂” section) we knew that the intermediate I showed only one singlet at about 6.1 ppm in ¹H NMR and that it was degraded in the reaction mixture within about 15–30 min (pH 3, 50 °C). This consumption led back to DHBQ if no ClO₂ was present, or to RhA in the presence of excess ClO₂ (see Scheme 3). After generating I under conditions where its concentration was as high as possible (DHBQ/ClO₂ ratio 1:1, 50 °C, 240 s), the reaction mixture was immediately cooled to 0 °C to slow down its further conversion, and a ¹³C NMR spectrum of the reaction mixture was recorded. The spectra yielded four resonances in the aromatic range, three of them from quaternary carbons at 141, 154 and 155 ppm at an intensity ratio of 2:2:1, and one from an aromatic CH (111 ppm). After 30 min, these signals disappeared and only the three ¹³C resonances of the starting material DHBQ were retained.

Trimethylsilylation (TMS) in the NMR tube with an excess of N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) did not significantly shift the peak of the aromatic proton (Δν = + 0.06 ppm), but the compound’s stability was increased. The spectrum showed no changes or losses in signal intensity even after 4 days. The proton integrals indicated the presence of five trimethylsilyloxy resonances, suggesting that intermediate I had five OH groups which reacted with BSTFA to their corresponding TMS-derivatives.

Extraction of the intermediate (accompanied by unreacted DHBQ as a by-product) with deuterated chloroform (CDCl₃) and immediate NMR measurement resulted in a spectrum of better quality. The stability of the compound in the unpurified extract was approximately as high as in the original reaction mixture (degradation over 30 min). When the extract was quickly dried by passing it over anhydrous MgSO₄, the stability of I in solution increased significantly, so that there was no significant loss even after 24 h. Interestingly, an acidic wash (dil. HCl) had no effect, while an alkaline wash (dil. Na₂CO₃) apparently degraded the compound immediately.

TLC analysis of the chloroform (CDCl₃) extract showed only the starting material under visible light. UV detection yielded a second component, evidently intermediate I, at a lower R̄ value (Fig. 5). The intermediate did not have Vis absorption, but a distinct UV absorption at 254 nm, and it was more polar. Rewetting the TLC spot with alkali (dil. Na₂CO₃) and repeated TLC analysis showed that I was not present any longer and only DHBQ was detectable, confirming the facile reconversion of the former into the latter.

Clear evidence of the nature of intermediate I was provided by DESI-MS analysis (Schedl et al. 2016) both directly from the TLC plate and in a paperspray-MS setup (Wenger et al. 2015; Schedl et al. 2017), identifying intermediate I as pentahydroxybenzene (PHB). The mass data of the compound and its penta(trimethylsilyl) derivative are given in Table 4. The TMS-derivative I-TMS confirmed the five TMS-protected OH groups that had already been assumed from the ¹H NMR experiments. The aromatic CH (C-6) resonates at 6.1 ppm/111 ppm (¹H/¹³C), and the magnetic equivalence of C-1/C-5 and C-2/C-4 explains the observed intensity ratio of 1:2:2:1 for the four carbon resonances. Intermediate I (PHB) is the formal product of water addition to DHBQ. Such a process, however, is hypothetical and just a mnemonic to visualize the chemical interrelation between the two compounds. In reality, aqueous solutions of DHBQ under ambient conditions are largely stable, regardless of pH, and DHBQ obviously does not add water to provide PHB. The observed formation of PHB under D-stage conditions must therefore be caused directly or indirectly through the action of chlorine dioxide.

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4 With regard to nomenclature, note that no atom numbering is required and that C-6 bears the proton.

5 If water is added to one of the two double bonds, a 1,4,5-trihydroxy-cyclohex-1-ene-3,6-dione system would be obtained which was converted by rearomatization to pentahydroxybenzene, involving keto-enol tautomerism of the two quinoid keto groups.
By contrast, the reverse reaction, elimination of water from PHB leading to DHBQ, occurs readily. It proceeds in the minute range under conditions of D-stage bleaching and represents the process responsible for the reformation of DHBQ in the absence of excess ClO\textsubscript{2} (path B in Scheme 3). The process is catalyzed by alkali: when PHB comes in contact with alkaline solutions, e.g. by an alkaline washing step, PHB is instantly degraded to DHBQ.

This reconversion from PHB (I) to DHBQ was vividly demonstrated by TLC. While the spot of PHB (see Fig. 5) was not perceptible under ambient light conditions, it turned slowly into the brown spot of DHBQ within 20–30 min in ambient atmosphere. When the freshly developed TLC plate was exposed to ammonia (alkaline medium), an immediate color change of the spot to red occurred. This is the color of the DHBQ dianion in aqueous medium (sometimes appearing almost black in high concentrations). We assume that the formation of the highly stabilized DHBQ dianion (Scheme 1) is the driving force of the elimination in alkaline medium.

Computational studies of the detailed reaction mechanism

**Initial reaction step: PCET mechanism**

The initial step in the reaction between DHBQ and ClO\textsubscript{2} was evaluated computationally on the DFT(M06-2X)/BS-II level of theory. In this first step, a hydrogen atom is transferred from protonated DHBQ (DHBQ-H\textsuperscript{+}) to chlorine dioxide, forming the radical cation DHBQ\textsuperscript{+} and chlorous acid, HClO\textsubscript{2} (see also Scheme 3), according to a proton-coupled electron transfer (PCET) mechanism (Tishchenko et al. 2008). Figure 6 shows the potential energy curve of this process. ClO\textsubscript{2} accepts a proton from the previously protonated quinone oxygen of DHBQ-H\textsuperscript{+}, followed by an electron transfer (state jump). The DHBQ moiety becomes a radical (DHBQ\textsuperscript{+}) and at the same time ClO\textsubscript{2} (in the doublet (radical) state) is converted into non-radical HClO\textsubscript{2}. The PCET mechanism is slowed down when the reaction is carried out in D\textsubscript{2}O instead of H\textsubscript{2}O, which explains the observed pronounced kinetic isotope (H/D) effect (see Fig. 4).

The reaction of DHBQ with ClO\textsubscript{2} clearly occurs after protonation of DHBQ, i.e. from DHBQ-H\textsuperscript{+}. When comparing DHBQ or DHBQ-H\textsuperscript{+} with regard to the activation energies of the reaction, the value was significantly higher for the PCET starting from non-protonated DHBQ (22.2 vs. 14.4 kcal/mol). This is in line with the experimental observations that, compared to pH 3, the reaction with ClO\textsubscript{2} was about 50 times slower at pH 4.5 and about 940 times slower at pH 6. The formation of protonated DHBQ thus seemed to be a prerequisite for the onset of the entire reaction sequence.

The values of the activation energy ($E_a$) for a PCET reaction are usually slightly overestimated, being about 10% too positive, even at the used advanced level of theory. This is because the computations do not consider resonance interactions between the states 1 and 2 and tunneling of the hydrogen (Tishchenko et al. 2008). The absolute value of the potential energy for the PCET, i.e. 14.4 kcal/mol, should therefore be...
only taken as an estimate. However, the potential energy difference between the SJ for DHBQ-H$^+$ and DHBQ is quite accurate, as errors cancel each other out. A more accurate computational determination of the absolute numbers would have meant considerable additional computation time, but without providing any further information on the mechanism.

**Detailed reaction mechanism**

The reaction mechanism was computationally evaluated on the CCSD(T)/BS-II level of theory, with the detailed mechanism shown in Scheme 4.

The initial PCET reaction is accompanied by the disproportionation of two molecules of formed chlorous acid into the more stable hypochlorous acid HClO and chloric acid HClO$_3$. Considering this disproportionation, the generated radical cation DHBQ$^+$ has a Gibbs energy of $-4.1$ kcal/mol (Scheme 4), thus being sufficiently stable to render the reverse process of the PCET negligible. DHBQ$^+$ is stabilized by extensive resonance.

From the experimental results we knew that pentahydroxybenzene (PHB) would be formed as a metastable intermediate that subsequently can regenerate DHBQ. Therefore, we evaluated the addition of water to DHBQ$^+$ that results in the cation radical of PHB. This species, PHB$^+$, was much more stable than DHBQ$^+$, its Gibbs energy being $-14.0$ kcal/mol relative to DHBQ$^+$ (18.1 kcal/mol relative to DHBQ), see Scheme 4. Also, the activation barrier in the formation of PHB$^+$ from DHBQ$^+$ and water was calculated to be quite small, $\Delta G^\text{Gibbs}$ = 16.0 kcal/mol. While the initial cyclohexanedione water addition product would not provide significant thermodynamic stabilization, the overall process becomes significantly exergonic through immediate rearomatization to the pentahydroxybenzene cation radical PHB$^+$, see also Scheme 5. The stability of PHB$^+$ is due to its high symmetry and the fact that charge and spin can be more easily accommodated (better delocalized and stabilized) in the aromatic system than in the benzoquinoid cation radical DHBQ$^+$.

In the presence of excess ClO$_2$, PHB$^+$ is immediately oxidized to trihydroxy-[1,4]-benzoquinone.
(THBQ) under release of chlorous acid and a proton in a rather exergonic process (−15.2 kcal/mol), see Scheme 4. In the absence of ClO2, PHB$^+$ quite easily disproportionated into PHB (intermediate I) and the corresponding quinone, trihydroxy-[1,4]-benzoquinone, with release of two protons (Scheme 4), as seen by CCSD(T)/BS-II level computations. The fact that the activation barrier for the disproportionation was almost zero indicated that the process would indeed be spontaneous when two molecules of PHB$^+$ “meet” and form a suitable quinhydrone-type transition state. The Gibbs energy of −7.8 kcal/mol indicated that the process itself is slightly exergonic: while intermediate I (PHB) is relatively stable (at least persistent enough to be detected), the second product, THBQ, is rather labile and immediately adds water to form hexahydroxybenzene (HHB), the free activation energy of the latter process being negligibly small (1.4 kcal/mol). The actual driving forces of the disproportionation process are thus the follow-up reactions of PHB and, in particular, THBQ, which lead to thermodynamically very stable compounds.

The disproportionation eventually regenerates one molecule of starting material DHBQ from two originally consumed molecules (Schemes 3, 4), i.e., half of the spent DHBQ is regenerated (once again: this only applies if there is no excess ClO2 present). This mechanism fully corresponded with the reaction kinetics observed in the model compound experiments. At 82% initial consumption for a 1:1 molar ratio of DHBQ and ClO2, 59% of DHBQ should theoretically be present after some time (18% not consumed from the start, plus 82/2 = 41% regenerated DHBQ), while 54% were found experimentally. At a 2:1 molar ratio of DHBQ and ClO2, with 47% initial DHBQ consumption, the experimental amount of DHBQ after the reaction was 74%, which was very close to the theoretical amount of 77% (53% not consumed, plus 47/2 = 23.5% regenerated DHBQ).

In acidic medium, PHB (intermediate I) is reconverted into DHBQ by the release of water. This reaction corresponds to path B in Scheme 3. DHBQ is 6.2 kcal/mol more stable than I based on the calculated Gibbs energy. Under the same conditions, THBQ adds water to form HHB in a clearly exergonic process (−28.7 kcal/mol). The activation barriers of these conversions are likely to be quite low, because these processes consist of keto-enol interconversions as the elementary steps, which generally proceed easily at room temperature.

Hexahydroxybenzene (HHB, C$_6$(OH)$_6$) is finally oxidized by ClO2 to the stable RhA, requiring four equivalents of the oxidant. As described above for the initial reaction of DHBQ with ClO2, the formation of

![Fig. 6](image-url) Potential energy curve of the DHBQ-H$^+$–ClO2 complex (left) and, for reasons of comparison, the DHBQ–ClO2 complex (right), calculated at the DFT(M06-2X)/BS-I level of theory. The intersection of the two curves indicates the state jump (SJ). The potential energies relate to that of the starting complex, bond lengths are given in Å.
metastable chlorous acid $\text{HClO}_2$ and its immediate disproportionation into the stable $\text{HClO}_3$ and $\text{HOCl}$ represent the driving force of the overall process. The redox series from hexahydroxybenzene to cyclohexanehexaone ($\text{CO}_6$), has been intensively studied and recently reviewed (Hettegger et al. 2016)—the oxidation chemistry of HHB was therefore already known, and was not further computationally studied in detail. In short, it is known that HHB, independent of the type of oxidant, generally forms two oxidation products: the metastable tetrahydroxy-[1,4]-benzoquinone as a result of a 2-electron oxidation process and the

stable rhodizonic acid (RhA) through 4-electron oxidation. Tetrahydroxy-[1,4]-benzoquinone disproportionates into HHB and RhA when no excess oxidant is available, but is normally immediately further oxidized into RhA. RhA is the most stable species along the redox series from HHB to CHH. As such, it is not surprising that this and no other compound has been found as the reaction product of DHBQ.

The degradation and oxidation chemistry of RhA is not yet fully understood. Cyclohexanehexaone, ($\text{CO}_6$), is the formal 2-electron oxidation product of RhA—

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**Scheme 4** Mechanism of the reaction between DHBQ and ClO$_2$ (cf. Scheme 3) from computations at the CCSD(T)/BS-II level of theory. Energies are given in kcal/mol, free energies [$\Delta G = \Delta H - T \times \Delta S$] are based on a temperature of 50 °C (323.15 K). The activation barriers for the water addition reactions were evaluated separately at the DFT(M06-2X) level (see Scheme 5).
and the formal 6-electron oxidation product of hexahydroxybenzene HBB. It is a compound that is unstable both as a neat substance and in aqueous solution, which undergoes ring contraction with CO-loss and degradation to oxalic acid, carbon dioxide CO₂, and carbon suboxide C₃O₂ according to mechanisms not yet completely clarified. In the present case of DHBQ reacting with ClO₂, oxalic acid and carbon dioxide were the final stable products of DHBQ/RhA oxidation and degradation (see Schemes 3, 4).

**Water addition and water elimination reactions involved**

Scheme 5 computationally compares the reactions involving water addition and water elimination between the tetrasubstituted (DHBQ, DHBQ⁺⁺), pentasubstituted (PHB, PHB⁺⁺) and hexasubstituted (HHB, HHB⁺⁺, RhA) benzoid systems. An addition of water increases the number of substituents (–OH, =O) at the six-membered core by one, and an elimination decreases it by one. Instead of the CCSD(T)/BS-II method, the MP4(SDQ)/BS-III method was employed for these conversions since in these ionic reactions the MP4(SDQ) calculations with larger basis sets (BS-III) are more reliable than the CCSD(T) method with smaller basis sets (BS-II). It is noteworthy that water addition from the tetrasubstituted to the pentasubstituted system requires conversion into the cation radicals beforehand (DHBQ⁺⁺ to PHB⁺⁺): it does not occur with the neutral molecules (DHBQ to PHB). At the same time, addition of water from the pentasubstituted to the hexasubstituted neutral molecules (THBQ to HHB) proceeds readily and is thermodynamically favored. The situation is reversed for water elimination: from the pentasubstituted (PHB) back to the tetrasubstituted structure (DHBQ) elimination is favored for the neutral molecules, while it does not occur from the hexa- to the pentasubstituted system (HHB to THBQ).

A comparison of the relative stabilities between the cation radicals PHB⁺⁺ and DHBQ⁺⁺ and the nonradical parent molecules PHB and DHBQ based on the Gibbs energies is another way to explain the observed reactivity. PHB⁺⁺ is 14.0 kcal/mol more stable than DHBQ⁺⁺ based on Gibbs energy (Scheme 4), while for the neutral PHB (I)/DHBQ couple the situation is the opposite, with DHBQ being 6.2 kcal/mol more favored than the corresponding water adduct PHB (Scheme 5). This explains why the neutral DHBQ does not add water, while the cation radical DHBQ⁺⁺ does so readily, and also why PHB (intermediate I) eliminates water to re-form DHBQ, but not PHB⁺⁺ to give DHBQ⁺⁺. The non-paired electron in the

**Scheme 5** Mechanism of the reaction between DHBQ and ClO₂ (cf. Scheme 3) from computations at the DFT(M06-2X)/BS-III level of theory. Energies are given in kcal/mol, free energies \[ ΔG = ΔH – T \times ΔS \] are based on a temperature of 50 °C (323.15 K). The activation barriers for the water addition reactions were evaluated separately with six explicit solvent (water) molecules taken into consideration.
aromatic PHB$^+$ is more delocalized and hence more stabilized than that in the benzoquinoid DHBQ$^+$. The inversion of reactivity while going from the non-radical species to the cation radicals seems to be one of the essential driving forces for the reaction cycle consisting of paths A and B (Scheme 3). For the two pairs THBQ/HHB (neutral) and THBQ$^+$/HHB$^+$ (cation radicals) the situation is opposite. HHB is by 28.7 kcal/mol more favored than the starting THBQ, meaning that water addition is quite largely favored. In the case of corresponding cation radicals HHB$^+$ is 19.3 kcal/mol less stable than THBQ$^+$ (Scheme 5). The THBQ$^+$ cation radical would not undergo water addition, rather HHB$^+$ would eliminate water.

In simple terms, to get from the tetrasubstituted benzoquinoid system DHBQ to the pentasubstituted system (PHB), the reaction proceeds via the cation radicals (from DHBQ$^+$ to PHB$^+$), not via the neutral compounds, but when going from the pentasubstituted (THBQ) to the hexasubstituted system (HHB) the reaction proceeds via the neutral compounds, not via radical species.

**Conclusions**

In this study, we examined the molecular mechanisms of the degradation of the cellulotic key chromophore DHBQ (1) by the oxidant ClO$_2$, i.e., under conditions of an industrial D bleaching stage. The approach used a combination of experimental and computational methods, employing both pulp experiments and model compound work. The reactions in the overall system are rather complex. They can be grouped into four reaction paths. Pathway A describes the formation of the intermediate pentahydroxybenzene (PHB, 1) which is usually further oxidized into rhodizonic acid (RhA, 2) in the presence of excess ClO$_2$ (path C). If the amount of ClO$_2$ is limiting, the intermediate PHB can react back to DHBQ (path B). The pathways A and B together effect a 50% "recycling" of DHBQ, but this recycling happens only if no excess ClO$_2$ is present. Generally, no recycling occurs and path C is the active one. RhA (2) was usually the main reaction product as its further degradation into CO$_2$ and oxalic acid (path D) is much slower than its production from DHBQ.

The entire reaction sequence begins with a proton-coupled electron transfer (PCET), effectively a hydrogen atom transfer, from protonated DHBQ to ClO$_2$. The resulting radical cation DHBQ$^+$ adds water to give a pentahydroxybenzene cation PHB$^+$, which is further oxidized by ClO$_2$ to trihydroxybenzoquinone (THBQ), according to path A. If no ClO$_2$ is available, PHB$^+$ readily disproportionates into pentahydroxybenzene (PHB, intermediate I) and trihydroxybenzoquinone. PHB is stable enough to be detected. It eliminates water to give DHBQ, causing a “50% regeneration” of the starting material DHBQ (path B). THBQ immediately adds water, resulting in hexahydroxybenzene (HHB), which is oxidized to RhA (2) by excess ClO$_2$ (cf. Schemes 3, 4).

RhA is the most stable product in the whole redox series from hexahydroxybenzene to cyclohexane-hexaoxane (Hettegger et al. 2016) and the primary stable product of DHBQ upon D-stage bleaching. Figure 7 shows the two substances DHBQ and RhA as solids in their pure forms. RhA is itself a chromophore, but even more important is the fact that it forms deeply colored salts not only with transition metal cations, but also with main group metal cations (cf. Figure 2). This salt formation comes to bear when the pH value is increased, e.g. during washing or neutralization. The formation of deeply colored rhodizonate salts also explains the reduced bleachability, which has sometimes been observed in bleaching practice, and which was simulated in the above pulp experiments. Although RhA can be degraded by ClO$_2$ into CO$_2$ and oxalic acid, this reaction is rather slow: 42 times slower at 50 °C than the analogous reaction of DHBQ.

The reactions of DHBQ with ClO$_2$ are therefore also noteworthy from a practical point of view: the chromophore DHBQ is converted into an even more potent and stable chromophore, rhodizonic acid and its salts, respectively. The effects of brightness loss and impaired bleachability are particularly prominent in the presence of transition metal ions, many of which form rhodizonate salts of pronounced deep colors and solutions with extremely high extinction coefficients. Iron, copper, and manganese ions are especially important in the pulp bleaching context.

A high ratio between ClO$_2$ and DHBQ is essential to avoid, on the one hand, the “recycling” of DHBQ, and on the other hand, more importantly, to degrade the RhA formed. The removal of RhA should be achieved as completely and quickly as possible. Under industrial conditions the net amount of ClO$_2$ provided is sufficient, but limited mixing might cause local
deficiencies and concentrations that are too low for quantitative degradation. Another precaution to assure high bleaching efficiency is a sufficiently low pH: pH $\leq 4.5$ must be avoided. The initial step of the DHBQ reaction with ClO$_2$ requires DHBQ protonation, which does not proceed above this threshold value. At the same time, pH values above 4.5 promote the precipitation of rhodizonate salts and thus lead to a decrease in bleachability.

It is a lesser known, but intriguing fact, that rhodizonic acid has been used for over a century in criminalistics for detecting gunshot residues on hands and clothing by determining lead traces as their corresponding rhodizonate complex (Werner et al. 2019). This method is extremely sensitive. We are currently attempting to further evolve this approach into an easy screening tool for the presence of RhA and its salts in pulps and for a possible quantitation of a “RhA value”.

**Experimental**

**General**

Commercial chemicals from Sigma-Aldrich (Schnell-dorf, Germany) were of the highest grade available and were used without further purification. Distilled water was used for all aqueous solutions.

For NMR analysis, a Bruker Avance II 400 instrument ($^1$H resonance at 400.13 MHz, $^{13}$C resonance at 100.61 MHz) with a 5 mm broadband probe head (BBFO) equipped with z-gradient with standard Bruker pulse programs and temperature unit were used. $^1$H NMR data were collected with 32 k complex data points and apodized with a Gaussian window function (lb = −0.3 Hz, gb = 0.3 Hz) prior to Fourier transformation. $^{13}$C-jmod spectra with WALTZ16 $^1$H decoupling were acquired using 64 k data points. Signal-to-noise enhancement was achieved by multiplication of the FID with an exponential window function (lb = 1 Hz). Bruker TopSpin 3.5 (3.0) was used for the acquisition and processing of the NMR data. Chemical shifts are given in ppm, referenced to residual solvent signals (7.26 ppm for $^1$H, 77.0 ppm for $^{13}$C in case of CDCl$_3$).

An Agilent 6560 QTOF mass spectrometer equipped with an Agilent G1607A dual Jetstream coaxial ESI interface was used, injection volume: 5 µL, sheath gas temperature: 150 °C, sheath gas flow rate: 12 L/min, nebulizer gas pressure: 20 psi, MS capillary voltage: 4 kV, nozzle voltage: 2 kV, fragmentor: 275 V, scanning mass range: 50–1700 m/z with a TOF acquisition rate of 2.8 spectra/s.

For paperspray MS, the paper tips (isosceles triangle, a = 10 mm) were cut and connected to 4 kV capillary voltage. Whatman filter paper No 1 (Wagner & Munz GmbH, Vienna, Austria) was used as the model sample matrix. The aqueous sample solution was used as a spray solvent. After applying 30 µL of the spray solvent onto the paper surface, mass spectra were recorded in positive or negative ion mode with a Thermo LTQ-MS (LTQ XL™ Linear Ion Trap Mass Spectrometer, Thermo Fisher Scientific, Waltham, Massachusetts, USA) equipped with an ESI ion source. Injection volume: 5 µL. Where applicable, a splitter with the ratio of 1:2 was used to divert the flow for better ESI spray quality. MS settings: Spray
voltage: 6 kV, sheath gas pressure: 5 psi, auxiliary
gas: 2 a.u., transfer capillary temperature: 275 °C,
scan range: m/z 300 to 1000. In case of tandem-MS
investigations, an isolation width of ± 0.5 m/z was
selected. Thermo Fisher Scientific Xcalibur software
(Thermo Xcalibur 2.2 SP1 build 48) was used for
operating the MS instrument.

Preparation of chlorine dioxide solutions

A 30 wt% aqueous sulfuric acid solution (7.5 mL)
was added dropwise to 17.5 mL of an aqueous sodium
chlorite solution (300 g/L) in a 100 mL multi-necked
flask at an addition rate of 0.5 mL/min at room
temperature under a nitrogen gas flow through
the reaction solution. The gaseous chlorine dioxide pro-
duced was introduced with the nitrogen flow into
100 mL of deionized water in another flask pre-cooled
at 0 °C along. After sulfuric acid addition was
complete, the reaction solution was allowed to remain
under nitrogen flushing for another 30 min at room
temperature, to give 100 mL of a yellow-colored
aqueous solution of chlorine dioxide in the second
flask.

The current concentration of chlorine dioxide in the
solution was determined by titration. To 1.0 mL of the
chlorine dioxide solution, 2.0 mL of a 30 wt% aque-
ous sulfuric acid solution and 2.0 mL of a 10 wt%
aqueous potassium iodide solution were added. The
color of the resulting solution turned to dark brown
(oxidation of iodide to elemental iodine). The iodine
produced was titrated with a 0.1 M sodium thiosulfate
solution against starch as an indicator. The concen-
tration according to the above procedure ranged
between 50 and 60 mmol/L. The chlorine dioxide
solution was diluted with deionized water whenever
necessary (UV/Vis measurements).

UV/Vis measurements

All measurements were performed on a Lambda 35
UV/VIS Spectrometer (PerkinElmer®, Waltham, MA,
U.S.A.) controlled by the UV WinLab software
(version: 6.0.3).

A 50 µM solution of DHBQ (50 mL) in water at pH
3 (set by sulfuriic acid or 0.01 M phosphate buffer) was
prepared in a stirred 100 mL Erlenmeyer flask and
heated to 50 °C. Freshly prepared aqueous chlorine
dioxide solution (concentration recently determined)
was added in amounts corresponding to target DHBQ/
ClO2 molar ratios, the volumes being usually between
15 and 50 mL. After certain reaction times, a 0.5 mL
aliquot of the reaction mixture was taken and intro-
duced in a stirred UV cuvette containing 1 mL of
concentrated aqueous sodium sulfite solution in 0.1 M
aqueous NaOH. The concentration of DHBQ and
rhodizonate was determined by UV/Vis measurements
from calibration curves recorded with the pure
substances and its mixtures (molar ratios 100/1, 50/1
10/1, 5/1, 2/1, 1/1, 1/2, 1/5, 1/10, 1/50, 1/100) in neat
0.1 M aqueous NaOH.

Starting celluloses

Two cellulose samples (industrial pulps) were used:
(1) a bleached beech sulfate pulp (kappa number 0.22,
brightness 91.2% ISO, viscosity [cuen] 565 mL/g,
pentosan 0.93%, DCM extract 0.18%, ash 0.05%,
bleaching sequence E-O-Z-P), and (2) a bleached
Eucalyptus pre-hydrolysis kraft pulp (kappa number
0.37, brightness 90.9% ISO, viscosity [cuen]
530 mL/g, pentosan 1.73%, DCM extract 0.13%, ash
0.05%, bleaching sequence D 0-EOP-D). The samples
were thoroughly washed with HPLC-grade acetone (to
remove extractives) and then with distilled water,
followed by air-drying. Initial brightness of the dry
samples was 94% ISO.

General procedure for the determination
of carbonyls in pulp by heterogeneous
fluorescence labeling (CCOA method)

The detailed procedure is given in Röhrling et al.
(2002a, b) and Potthast et al. (2003). The GPC system
is in detail discussed in Potthast et al. (2015). In short,
a stock solution of the CCOA label was prepared by
dissolving the fluorescence label (62.50 mg) in 50 mL
of 20 mM zinc acetate buffer (pH 4.0). Wet pulp
(corresponding to 20–25 mg of dry pulp) was sus-
pended in the acetate buffer containing the dissolved
labelling compound (4 mL). The suspension was
agitated in a water bath for 7 days at 40 °C. The pulp
was isolated by filtration, then activated and dissolved
in 2 mL of DMAc/LiCl (9%, m/V) overnight at room
temperature. Then, the samples of the solution were
diluted with DMAc, filtered through 0.45 µm syringe
filters, and analyzed by GPC. Calibration of the system
was done with the pure CCOA label and by means of
reference pulps, as described previously. For the determination of the overall carbonyl content, the carbonyl peak area was normalized with regard to the injected mass.

Oxidized pulps

The preparation of cellulosic pulps with increased contents of functional groups has been described in detail before, and the procedures described there have been followed throughout (Siller et al. 2015; Ahn et al. 2019). In short, sodium hypochlorite (HOCl) oxidation was performed with 2 g of dry pulp in total. To improve accessibility, the pulp was suspended in water and shortly disintegrated. The excess of water was removed by vacuum filtration and the wet pulp transferred into a 2 L beaker to suspend it in sodium acetate buffer (1 L, 1 M, adjustment of pH with glacial acetic acid to pH 6.5). The suspension of pulp in the buffer was continuously stirred with a magnetic stirrer. Next, different volumes (between 1 and 120 mL) of HOCl (active chlorine 10–13%, Sigma Aldrich, Schnelldorf, Germany) were added to effect the oxidation. The oxidation was stopped after 45 min by addition of ethanol and was followed by thoroughly washing with water.

For periodate oxidation, different volumes (between 1 and 150 mL) of 0.2 M aqueous sodium metaperiodate (NaIO₄) solutions were added to the cellulose sample (2 g suspended in 100 mL of distilled water). The suspension was stirred at room temperature for 30 min, filtered, and then resuspended in 100 mL of distilled water. A total of 5 mL glycol was added, and the stirring was continued for 1 h. The pulp was separated by filtration and washed thoroughly on a Büchner funnel.

Accelerated aging of pulps

Handsheets were prepared from 2 g of pulp suspended in distilled water (500 mL) on a Büchner funnel, followed by pressing. In some experiments, the pH of water was modified using either sulfuric acid (1 mM) or sodium hydroxide (1 mM). The handsheets were dried at 92 °C for 5 min. Brightness was measured before and after aging according to ISO 2470 (2009), following the remission of UV/Vis light at 457 nm. Aging was carried out continuously under dry conditions following the TAPPI method UM 200 (105 °C, 20% rel. humidity, 4 h), and under humid conditions according to Paptac E.4P (100 °C, 100% rel. humidity, 1 h). The progress was continuously followed by UV/Vis (brightness reversion) measurements to record the kinetics of chromophore formation.

Bleaching of model pulps

Chlorine dioxide bleaching (1% ClO₂, 50 °C if not otherwise stated, 1 h) was run in double-sealed plastic bags in water baths. The impregnate pulps (50 g) were mixed with water and ClO₂ solution to 10% stock consistency and the suspension was kneaded before incubation of the sealed bags in the water bath. In some cases, the added water contained certain amounts of metal ions (3 ppm for transition metal ions and up to 200 ppm for main group metal ions, see main text). After bleaching, a pulp aliquot (5 g) was taken for handsheet production, washed with distilled water or with water containing certain amounts of metal ions (3 ppm for transition metal ions and up to 200 ppm for main group metal ions, see main text). The pulp was then disintegrated with water to 1% stock consistency and filtered directly or after setting the pH of the suspension to pH 6 by addition of 10 mM NaOH. The mixtures were filtered through a Büchner funnel and the remainder dried to obtain the handsheets.

Bleaching of DHBQ-enriched pulps

An aliquot of a saturated solution of DHBQ in distilled water containing 150 μg or 500 μg of DHBQ was mixed with 100 mL of water and added to the dry pulp, so that a content of 3 and 10 ppm, respectively, was set. The pulp was kneaded for about 5 min, in some cases distilled water was added to facilitate intimate mixing. A pulp aliquot of 5 g was taken and the ISO brightness determined, affording 81% ISO (3 ppm DHBQ added) and 75% ISO (10 ppm DHBQ added). The remaining pulp was used for the ClO₂ bleaching experiments as given above.

Degradation of DHBQ by chlorine dioxide

In a 500 mL round-bottom flask, freshly prepared chlorine dioxide solution (concentration recently determined) was added at once to 100 mL of an aqueous DHBQ solution (pH 3, set by sulfuric acid or
0.1 M phosphate buffer), and the mixture was stirred at 50°C in the dark. Reaction temperatures were varied for kinetic measurements as described in the main text. The amount of chlorine dioxide solution was set in a way that a target DHBQ/ClO2 molar ratio was reached. At certain time intervals, 5 mL aliquots were taken and extracted twice with 1 mL of CDCl3. The two extracts were combined and analyzed by NMR either directly or after filtration through a pipette (5 cm path) filled with solid anhydrous MgSO4. Care was taken that the time between taking the aliquot and NMR analysis was less than 30 s (45 s when filtered). The filtered extract was also used for GC/MS analysis. In some cases, a drop of N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) was added prior to NMR and GC/MS runs.

After a reaction time of 2 h, a 50 mL aliquot was analyzed for CO2 according to standard procedures (precipitation as BaCO3). The remaining solution was extracted and analyzed (GC/MS, NMR) for remaining organic compounds according to a procedure previously optimized for carboxylic acid and hydroxyacids in complex matrices (Liftinger et al. 2015).

1,2,4,5,8-Pentahydroxybenzene (PHB, intermediate I)

1H NMR (CDCl3): δ 6.12 (s, 1H), 7.20 ppm (s, br, OH). 13C NMR (CDCl3): δ 112.2 (CH), 144.8 (d.i., C-1, C-5), 146.5 (d.i., C-2, C-4), 154.1 ppm (C-3). Analysis as per-trimethylsilyl derivative: 1H NMR (CDCl3): δ 0.18 (s, 9H, 1 × SiMe3), 0.21 (s, 18H, 2 × SiMe3), 0.25 (s, 18H, 2 × SiMe3), 6.08 ppm (s, 1H). MS data given in Table 4.

2,3,5-Trihydroxy-[1,4]-benzoquinone (THB)

1H NMR (CDCl3): δ 5.94 (s, 1H), 9.8 ppm (s, br, 3H, OH). 13C NMR (CD3OD): δ 108.3 (C-6), 142.4 (C-2), 148.8 (C-3), 152.0 (C-5), 180.4 (C-1), 182.9 ppm (C-4).

Final stable degradation products

Measurement in D2O/NaOD, pD = 10, assignment confirmed by spiking with authentic samples. 13C NMR: δ 144.3 (br, carbonate), 162.0 ppm (oxalate).

Computations

The GAUSSIAN 09 program package was used for all calculations (Frisch et al. 2016). The geometry optimization was carried out at the DFT(M06-2X) level of theory (Zhao and Truhlar 2008). The 6-31G(d) basis sets were employed for H, C, O and Cl, where a diffuse function was added to each of O and a p-polarization function was added to H (these basis sets being named BS-I). It was ascertained that each equilibrium geometry exhibited no imaginary frequency and each transition state exhibited one imaginary frequency. Enthalpy, entropy, and Gibbs energy changes were evaluated at 323.15 K (50°C). Zero-point energy, thermal energy, and entropy change were evaluated at the DFT(M06-2X)/BS-I level. For the water molecule, experimental entropy of water at 298.15 K and 1 atm (16.7 cal/mol K) was employed for the estimation of Gibbs energy.

For single point calculations, either CCSD(T), MP4(SDQ), or DFT(M06-2X) method was employed. The CCDS(T) and MP4(SDQ) methods were mainly employed for the radical and ionic species, respectively. In the CCSD(T) calculations for radicals, restricted open-shell wave functions (ROHF functions) were selected as the reference wave functions, as the unrestricted wave functions (UHF functions) were significantly spin-contaminated. For large species, such as DHNQ-ClO2 complexes, we employed the DFT(M06-2X) method. In the single point calculations at the CCSD(T) and the DFT(M06-2X) levels, 6-311G(d) basis sets (BS-II) were employed for H, C, O and Cl, where a diffuse function was added to each of O and Cl and a p-polarization function was added to H. For the MP4(SDQ) calculations, we employed other basis sets: the aug-cc-pVTZ basis sets were used for O and Cl and the cc-pVTZ basis sets were selected for C and H, where f-type and d-type functions were omitted from the heavy atoms and hydrogen, respectively, to reduce computational costs (BS-III).

In all calculations, the solvation energy in water was evaluated according to the PCM method. For the determination of the cavity size in the PCM calculations, the UFF parameters and the united atom topological model optimized at the HF/6-31G(d) level of theory were used for geometry optimization and energy evaluation, respectively.
Acknowledgments Open access funding provided by University of Natural Resources and Life Sciences Vienna (BOKU). We performed quantum chemical calculations at the Fukui Institute for Fundamental Chemistry at Kyoto University, Japan, and the Vienna Scientific Cluster (VSC) computer center, which we thank for access. The financial support of the Austrian Research Promotion Agency (FFG), project “Chromophores-II”, is gratefully acknowledged.

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