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Deactivation of Co-Schiff Base Catalysts in the Oxidation of *para*-Substituted Lignin Models for the Production of Benzoquinones

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The effect of quinones on the deactivation of four- and five-coordinate Co-Schiff base catalysts used for the oxidation of lignin models is systematically studied. 2,6-Dimethoxy-1,4-benzoquinone does not affect the catalytic activity of any of the studied Co-Schiff base catalysts, but 1,4-benzoquinone and 2-methoxy-1,4-benzoquinone have a strong effect on the catalytic activity. Quinone solubility in the reaction solvent does not correlate with catalyst deactivation, but added pyridine (a basic axial ligand) promotes catalyst deactivation by quinone. The synthesis and characterization of a catalytically inactive Co-Schiff base-quinone complex is presented and preliminary computational analysis of this complex in comparison to a dimeric Co-Schiff base peroxo complex is also discussed. Quinone and the Co-Schiff base redox potentials are found to correlate with catalyst deactivation. Thus, catalysts with a lower redox potential were more susceptible to deactivation, and quinones with a higher redox potential deactivate the catalysts. Based on these results, two mechanisms for deactivation of the catalyst are proposed. The first mechanism describes how the formation a Co-Schiff base-quinone complex prevents formation of the key catalytically active Co-superoxo complex. The second proposed mechanism suggests that quinones inhibit the Co-Schiff base catalyst by scavenging intermediate Co-superoxo radicals.

1. Introduction

Transition-metal catalyzed oxidative depolymerization of lignin is a means to expand a sustainable fuel and chemical industry based on lignocellulosic biomass.[1-6] We have examined the aerobic oxidation of lignin and lignin models catalyzed by Co-Schiff base complexes for the production of *para*-benzoquinones.[7-10] Quinone production from lignin is of interest to biorefining as quinones are an important class of organic molecules that have industrial application in the fabrication of dyes,[11] the manufacture of batteries and organic solar cells,[12-14] and the production of anthraquinone, used in industry as a catalyst for hydrogen peroxide production and as additive to improve alkaline pulping in the pulp and paper industry.[15, 16]

The accepted reaction mechanism for the Co-Schiff base-catalyzed production of quinones is shown in Scheme 1.[17-21] The oxidation of *para*-substituted phenolic lignin models is initiated when a four-coordinate Co-Schiff base catalyst, denoted as $L_4Co(II)$, binds molecular oxygen in the presence of an donor ligand (B) to produce a superoxo radical complex **1**.[22-27] [22-27] Using syringyl alcohol **2** as an example, the superoxo adduct **1** abstracts a phenolic hydrogen from **2** giving phenoxy radical **4** and a hydroperoxo metal complex **3** that breaks down to regenerate the starting catalyst. The reaction of **4** with a second molecule of Co-superoxo radical affords the intermediate peroxy-*para*-quinolato cobalt complex **5** that is isolable under some conditions.[17, 28, 29] Finally, the elimination of a molecule of formaldehyde from **5** generates dimethoxybenzoquinone **6** (DMBQ) and the Co-hydroxy species **7**, which is known to be catalytically active in the oxidation of phenols.[29, 30] The preference for the oxidation reaction at *para*-position is attributed to the bulkiness of Co(salen)-superoxo complexes.[19]

Despite current advances in lignin and lignin model oxidation using Co-Schiff base catalysts, the key issue of catalyst deactivation remains poorly understood.[10, 31-33] Catalyst deactivation is one of the most critical aspects in homogeneous transition metal catalysis.[34] Collectively, multiple pathways are available for catalyst deactivation and include ligand degradation, metal deposition, dimer formation, or reaction with the products, the solvent or the substrate. Each of these processes stops or inhibits the formation of the desired products.[35, 36]

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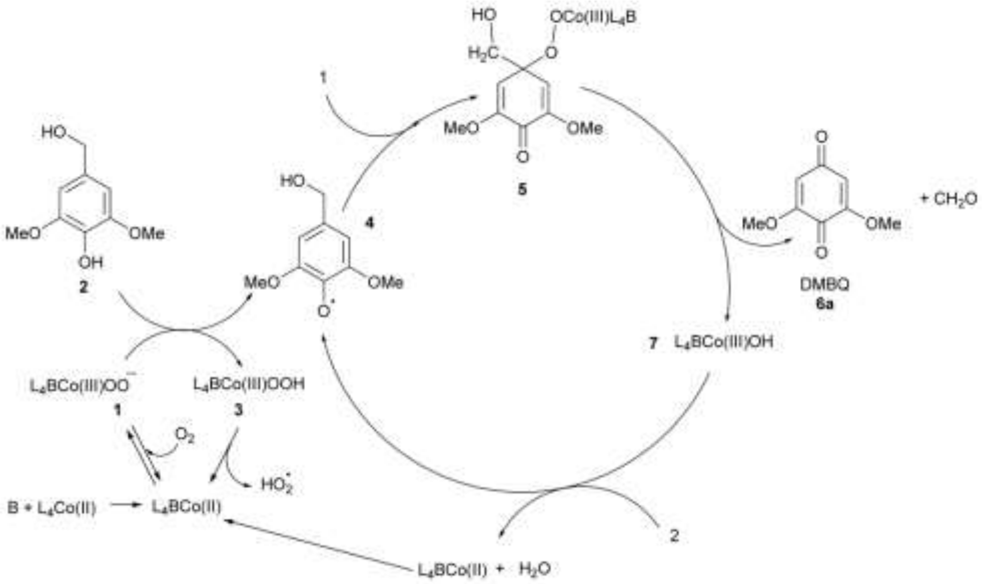


Scheme 1 Oxidation of vanillyl and syringyl alcohol with a 4-coordinate Co-Schiff base catalyst ($L_4Co(II)$) in presence of a base (B).

Loss of catalytic activity in the Co-Schiff base-catalyzed oxidation of syringyl alcohol to DMBQ can occur by the formation of inactive species during the reaction. Co-Schiff base complexes react with either oxygen alone or with oxygen and a substrate of low reactivity to generate an unidentified complex with no catalytic activity.[22] Deactivation of the catalyst due to oxidation of the ligand system of the cobalt complex as well as formation of a dimeric μ-peroxo cobalt complex has been reported in the cobalt-Schiff base catalyzed oxidation of olefins by dioxygen.[37] Formation of Co(salen)-OH has been suggested to reduce the catalytic activity during hydrolytic kinetic resolution of epichlorohydrin, but this species is active in phenol oxidation.[23, 38] Deactivation by reaction of the catalyst was reported in the oxidation of 2,6-di-*tert*-butylphenol to 2,6-di-*tert*-butyl-*para*-benzoquinone. The exact identity of the inhibitor and mechanism of such deactivation was not established, although organic acids were proposed.[17, 23]

Quinones can deactivate some homogeneous transition metal catalysts and enzymes. For example, cobalt catalyzed oxidation of hydrocarbons (*ortho*-xylene and tetralin) was inhibited when 1,2-naphthoquinone formed a complex with the catalyst leading to precipitate formation, color changes, and loss of catalytic activity.[39] Inhibition of Cytochrome P450 enzymes by quinones was also reported.[40] Co-Schiff base catalyst deactivation by quinones, however, has not been reported. Formation of quinone-Co adducts and electron transfer (ET) reactions are known to take place between quinones and Co-Schiff base complexes.[41-46] Quinone-ET reactions are the basis of some catalytic systems, such as the use of quinones as redox shuttles in Pd-catalyzed 1,4-diacetoxylation of cyclohexadiene.[47] ET reactions between quinones and Co-Schiff base complexes, without the formation of adducts, have been studied, but not as a means of catalyst deactivation.[41, 48-50] Formation of adducts between Co-Schiff base complexes and quinones was studied as a way to model reactions in respiration and photosynthesis, but those studies were not related with a loss of catalytic activity.[41, 51, 52]

Given that our ongoing work in Co-Schiff base-catalyzed oxidation of lignin and lignin models led to the formation of quinones as primary products, we decided to examine whether these products could also serve to deactivate the Co catalyst. In this paper, we report a series of experiments that evaluate the effect of different quinones on the deactivation of Co-Schiff base catalysts and the conditions that originate this deactivation. Also, we report electrochemical characterization of some quinones and Co-Schiff base catalysts, as well as the synthesis and characterization of Co-Schiff base-quinone complexes. We discuss two different mechanisms of deactivation for the Co-Schiff base catalyst in the oxidation of phenols. The study of the conditions that lead to deactivation of the Co-Schiff base complexes will allow the design of a new generation of catalysts for the oxidation of lignin models that can be resilient towards the deactivation by quinones and expand the sustainable chemical industry based on lignocellulosic biomass.[22]

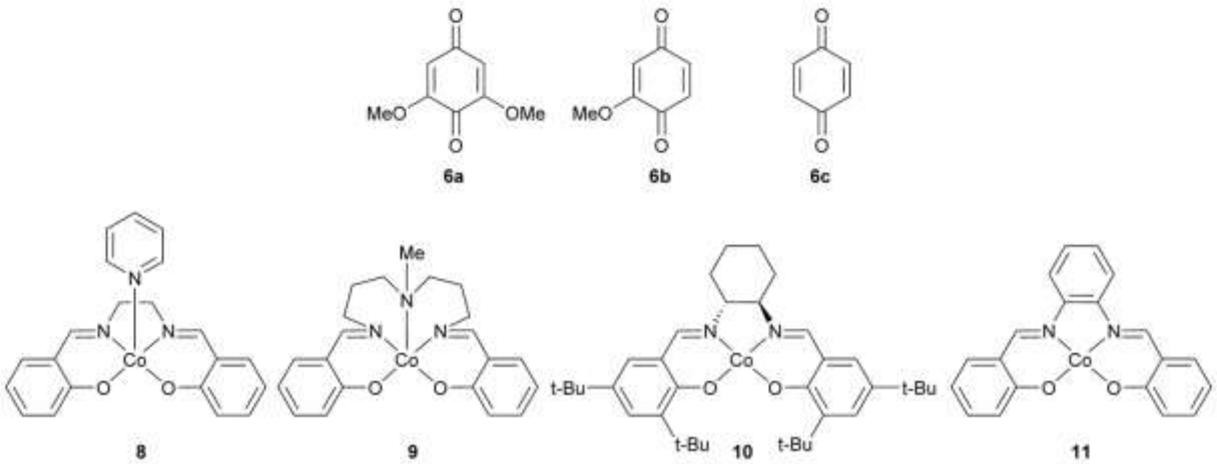


Figure 1 Co-Schiff base catalysts and quinones used in the experimental study.

2. Results and discussion

2.1. Deactivation of Cobalt-Schiff base catalysts in the oxidation of syringyl alcohol 2.

We compared the effect of three quinones (DMBQ **6a**), 2-methoxy-1,4-benzoquinone (MMBQ, **6b**), and 1,4-benzoquinone (1,4-BQ, **6c**) on the deactivation of cobalt-Schiff base catalysts. These quinones represent the products that might be observed in the oxidation of different lignin sources (e. g., hardwood, softwood or herbaceous feedstocks, respectively). Three Co-Schiff base catalysts, 5-coordinate (pyridine)[*N*,*N*′-bis(salicylidene)ethylenediamino]cobalt(II) (Co(II)(Salen)/py, **8**), [*N*,*N*′-bis[(salicylidenamino)ethyl]amine]cobalt(II) (Co(II)(*N*-Me Salpr, **9**), and 4-coordinate *N*,*N*′-bis[(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamino]cobalt(II) (Co(II)(Salen*), **10**) (Figure 1) were studied. Each quinone and the Co-Schiff base catalyst were incubated in methanol for 48h, and the quinone-catalyst mixtures were tested for their ability to oxidize **2** and produce **6a** (Table 1). The conversion of **2** and the yield of **6a** were determined by HPLC

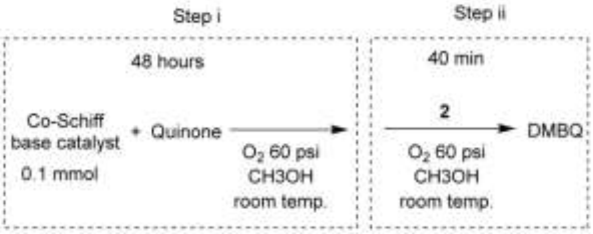
Catalyst **8** gave both the highest yield of DMBQ and conversion of **2** when no quinone was added to the oxidation reaction (Table 1, entry 1). Quinone **6a** did not affect the yield of DMBQ and the conversion of **2** by using catalyst **8** (Table 1, entry 2). But when this catalyst was exposed to quinones **6b** and **6c** the DMBQ yield was drastically reduced to 44 and 29 %, respectively, and the conversion of **2** dropped to 51 and 34%, respectively (Table 1, entries 3 and 4).

In the absence of quinone, catalyst **9** also gave a high conversion of **2**, but the yield of DMBQ was lower than catalyst **8** (Table 1, entry 5). Exposing catalyst **9** to both quinones **6b** and **6c** reduced the conversion of **2** and the DMBQ yield (Table 1, entries 7 and 8), although the extent of reduction was lower than for **8**. Finally, when catalyst **9** was incubated with **6a**, no significant effect on the conversion of **2** and DMBQ yield was observed. (Table 1, entries 6).

Unlike the five-coordinate catalysts **8** and **9**, the 4-coordinate Co-Schiff base **10** was not affected by any of the studied quinones. In all the cases that this catalyst was used, the lignin model was oxidized to DMBQ in high yield regardless of the quinone added, although the DMBQ yield was lower (Table 1, entries 9-12).

Since the oxidation of **2** generally affords DMBQ **6a** as a precipitate, we decided to evaluate the effect of quinone solubility on the deactivation of the Co-Schiff base catalyst. The solubility of quinones **6a**, **6b** and **6c** in MeOH is 12.9, 17.6, and 73.9 mg/ml, respectively (see SI for details). Comparing the conversion of **2** and the DMBQ yield (Table 1) with the quinone solubilities, we conclude that there is not a direct correlation (Figure 2). Whereas the solubility of quinones **6a** and **6b** in methanol is quite similar, their effect on the deactivation of catalyst **8** and **9** is very different (Table 1, entries 2 and 3, and 6 and 7, respectively). Similarly, quinones **6b** and **6c** produce a noticeable loss in the catalytic activity of complexes **8** and **9** (Table 1, entry 3 and 4, and 7 and 8, respectively), despite their significant difference in solubility. Finally, for catalyst **10**, differences in quinone solubility do not have any effect on the catalyst's activity.

Table 1 Oxidation of **2** with Co-Schiff base catalysts **8**, **9** and **10** in presence of quinones **6a**-**c**.



Entry	Co-Schiff base catalyst	Quinone added	2 Conversion (%)[a]	6a Yield (%)[a]
1	**8**	None	100	99 (1.6)
2	**8**	**6a**	100	99 (1.0)
3	**8**	**6b**	51 (1.6)	44 (1.7)
4	**8**	**6c**	34 (4.5)	29 (4.8)
5	**9**	None	100	88 (0.9)
6	**9**	**6a**	100	84 (0.3)
7	**9**	**6b**	81 (5.0)	59 (0.2)
8	**9**	**6c**	59 (3.6)	38 (2.1)
9	**10**	None	100 (0.7)	72 (0.7)
10	**10**	**6a**	99 (0.3)	74 (7.1)
11	**10**	**6b**	99 (0.7)	73 (0.5)
12	**10**	**6c**	99 (0.5)	75 (5.4)

[a] Average of three replicate runs. Values in parentheses are standard deviation

2.2. Effect of the quinone incubation time and concentration on the deactivation of Co-Schiff base catalysts.

The effect of incubation time of quinones **6b** and **6c** with catalyst **8** was evaluated. For quinone **6b**, after 48h of incubation time, the oxidation of **2** yielded 44% DMBQ, whereas, with no incubation time (i. e., all components were mixed at once), the average yield was significantly higher (64%) (See Table S2 for details). On the other hand, quinone **6c** gave a statistically equivalent yield reduction for the oxidation of **2** with either no incubation or after 48 hours of incubation (33 and 30% yield, respectively; see SI for statistical analysis). The difference between the reactivity of quinones **6b** and **6c** suggests that the deactivation of catalyst **8** occurs very quickly with quinone **6c**.

To evaluate the effect of the concentration of quinones **6b** and **6c** on the deactivation of catalyst **8** (Figure 3), we estimated the quinone amounts that halve of the DMBQ yield (the IC50) by using a 4-parameter logistic model (see SI).[53] The concentration-inhibition fitted models are shown as the continuous line in Figure 3a and 3b. According to these models, quinone **6c** inhibits catalyst **8** with an IC50 value of 1.4 mol/mol of catalyst, whereas the IC50 value for **6b** is 2.3 mol/mol of catalyst. This result shows that both quinones have a significant concentration-dependent deactivation effect on the catalytic activity of Co(salen)py **8** even without any incubation time, with this effect being higher for quinone **6c**.

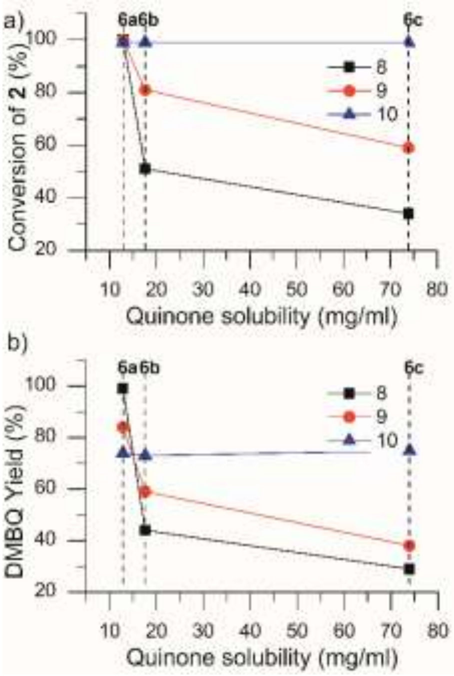


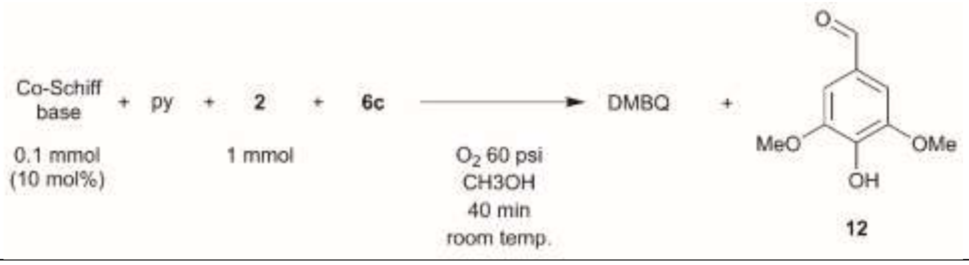
Figure 2 Conversion of **2** (a) and DMBQ yield (b) as a function of the solubility of quinones for different Co-Schiff base catalyst.

2.3. Effect of axial ligands on the inhibition of 4-coordinate Co-Schiff base catalysts.

Motivated by the results of Table 1, the effect of axial ligands on the inhibition of Co-Schiff base activity was evaluated. The oxidation of **2** using 4-coordinate Co(II)(salen) produced DMBQ and syringaldehyde **12** (Table 2, entry 1). When no axial ligand coordinates Co(II)(salen), the addition of **6c** does not affect its catalytic activity (Table 2, entry 2). The catalytic activity of 4-coordinate catalyst **10** is also affected by the presence of axial ligands. Although the conversion of **2** and the DMBQ yield is enhanced when pyridine is added to the reaction (Table 2, entry 3), the addition of this axial ligand simultaneously makes this Co-Schiff base catalyst susceptible to the catalytic inhibition by the quinone **6c** (Table 2, entry 4).

To further confirm the effect of the axial ligands in the deactivation of the catalyst, we evaluated the effect of adding pyridine to (Co(II)(salophen), **11**, a complex that has been reported as a catalyst for the aerobic oxidation of hydroquinone.[54, 55] We found that **11** gave a high conversion of **2**, yielding DMBQ and **12** in modest yields (Table 2, entry 5). When pyridine is added to the reaction, the conversion of **2** and the yield of DMBQ reach the maximum values (Table 2, entry 6), but when pyridine and quinone **6c** are present, only a very small amount of the lignin model is converted to DMBQ (Table 2, entry 7). This result confirms that the conversion of **2** to the corresponding quinone by 4-coordinate Co-complexes is strongly promoted by an axial base, but the catalyst/base complex is also subject to significant deactivation in the presence of certain quinones.

Table 2 Effect of axial ligand base on the deactivation of Co-Schiff base catalyst.



Entry	Co-Schiff base	py (mol %)	6c (mol %)	2 Conversion (%)[a]	DMBQ Yield (%)[a]	12 Yield (%)[a]
1	Co(II)(salen)	0	0	94	29	26
2	Co(II)(salen)	0	40	95	32	31
3	**10**	100	0	100	92	0
4	**10**	100	40	11	7	0
5	**11**	0	0	98	29	36
6	**11**	100	0	98	100	0
7	**11**	100	40	6	4	0

[a] Average of three replicate runs.

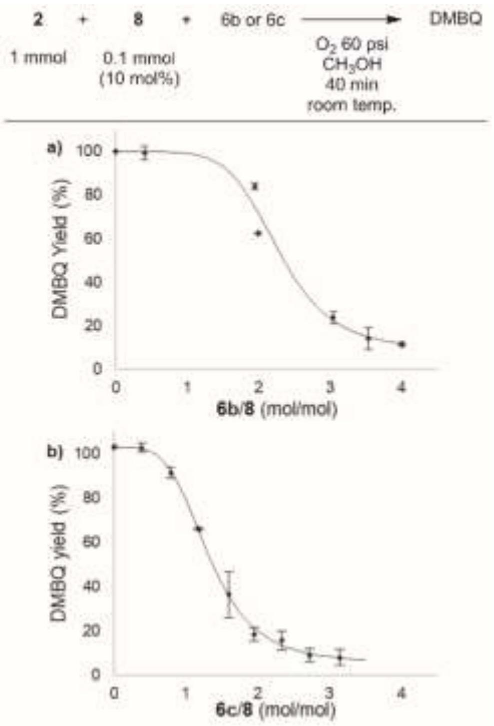


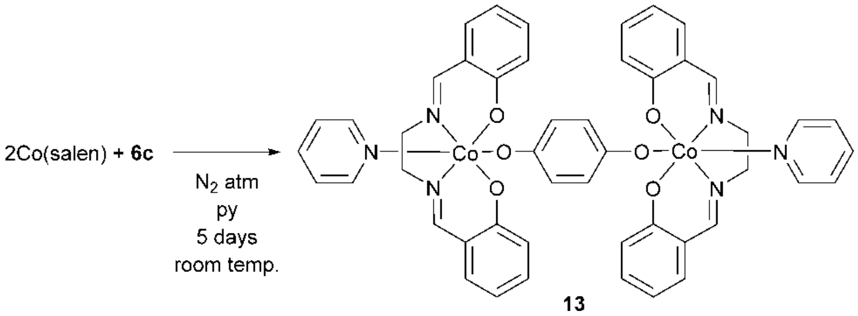
Figure 3. Concentration-effect of **6c** (a) and **6b** (b) on the oxidation of 2 by using catalyst **8**.

2.4. Synthesis, characterization and computational study of Co-Schiff base-quinone complexes.

We studied the synthesis of the complex $[Co(III)(salen)py]_2Q^{2-}$ (**13**), formed by the reaction between Co(II)(salen)py and quinone **6c**, to understand whether formation of adducts between Co-Schiff base catalysts and quinones was a possible route for catalyst inhibition and electron transfer. Dinuclear adducts of Co-Schiff base complexes and *para*-quinones have been characterized as binuclear complexes bridged by a hydroquinone dianion ligand (Q^{2-}) and have been used to understand the magnetic and electronic properties of quinones as redox-active ligands (Scheme 2; see SI).[41, 43, 51, 56-59]

Infrared spectroscopy was used to study the structure of the coordinated hydroquinone ligand in complex **13**.[60] As shown in Figure 4, the IR spectrum of **13** resembles that of the parent Co(II)(salen). No characteristic signals for the original C=O group of the quinone (1700-1560 cm^{-1}) are observed in **13**, which indicates that the quinone was reduced.[51],[61, 62] The imine C=N vibrations (1605 cm^{-1}) shift slightly (~10 cm^{-1}) to lower energies.

While we were able to synthesize complex **13**, attempts to synthesize and isolate analogous complexes between **6b** and **8**, or between **6b** and **6c** and catalysts **9** and **10** were unsuccessful. Based on these results, we carried out DFT analysis to model complex **13** and compare it to the complex expected from the reaction of Co(II)(salen*)py and quinone **6c**. We analyzed the results of our computational modelling using the distance between the salen ligands as criteria for likelihood of formation of the dimers (Figure 5). For the $[Co(II)(salen)py]_2$-Q^{2-} (**13**) dimer, the conformational analysis indicates that the minimal distance between the hydrogens of the salen ligands (5.681 Å), is higher than the Van der Waals radii between them (2.4 Å), so that steric factors do not inhibit formation of the complex.



Scheme 2 Synthesis of Co-Schiff base-quinone complexes.

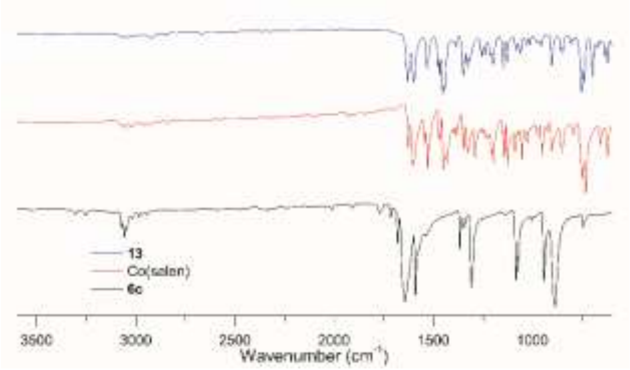


Figure 5. IR spectra of **6c**, **13**, and Co(II)(salen).

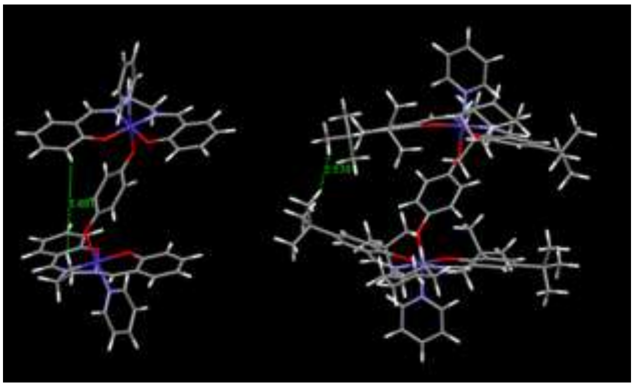


Figure 4. Low energy conformation of dimeric complexes of $[Co(III)(salen)py]_2$-Q^{2-} (left) and $[Co(III)(salen^*)py]_2$-Q^{2-} (right).

For the $[Co(II)(salen^*)py]_2$/quinone dimer, the salen* ligands are significantly closer, but the minimal distance between the hydrogens of the *tert*-butyl group of the salen* ligands, 2.530 Å, is still higher than the Van der Waals radii of the two H atoms, so the steric factor does not conclusively rule out the formation of the dimeric complex. Even though the computational analysis suggests that this last conformer is theoretically possible, we were not able to synthesize it, so a more detailed study should be done to try to isolate it.

2.5. Electrochemical studies of Co-Schiff base catalysts and quinones.

Different authors have pointed out the importance of the redox properties of quinones and Co-Schiff base complexes and the reactions that occur between them (i. e., ET reaction or adduct formation).[41, 48, 51] Therefore, we conducted a series of electrochemical experiments to evaluate the values of anodic, cathodic and halfwave potentials (E_{pa}, E_{pc} and $E_{1/2}$, respectively), and peak-to-peak separation (ΔE) of *para*-quinones **6a**, **6b** and **6c**, and Co-Schiff base catalysts **8**, **9** and **10** (Table 3). Based on their ΔE, all the studied Co-Schiff base catalysts and quinones exhibit quasi-reversible redox behavior ($\Delta E > 59.2$ mV).

There is an association between the one-electron redox potential of the Co(II)/Co(III)-Schiff base couple and its catalytic activity (the lower the potential, the higher the catalytic activity).[24, 63] Our results support this relation. Catalyst **8**, with a $E_{1/2}$ of -0.25 V, shows the maximum DMBQ yield (Table 1, entry 1), whereas catalyst **9** and **10**, with more positive halfwave potentials, have a lower DMBQ yield (Table 1, entries 5 and 9, respectively). It has been reported that the redox potential of Co complexes show a linear correlation with the logarithm of the equilibrium constants for the formation of the corresponding dioxygen complexes.[64-66] The formation of the superoxo radical complex **1** is accompanied by the transfer of electron density from the cobalt center to the half-filled π-antibonding orbitals of the oxygen.[67] Therefore, the oxygen-carrying ability of a Co-Schiff base catalyst depends on its ease of oxidation (more negative potential).[66, 68] Although steric factors are also important, a lower redox potential enhances the Co-Schiff catalytic activity in the oxidation of phenols towards quinones.[24, 63]

Table 3 Electrochemical data for Co-Schiff base catalyst oxidation and quinones reduction in protic solvent.[a]

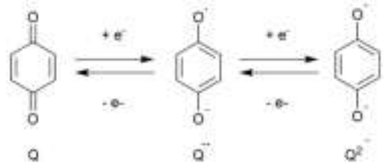
Compound	E_{cp} (V)	E_{ap} (V)	ΔE (V)	$E_{1/2}$ (V)
8	-0.32	-0.18	0.14	-0.25
9	-0.13	0.15	0.27	0.01
10	0.08	0.15	0.07	0.11
6a	-0.35	-0.27	0.08	-0.31
6b	-0.28	-0.19	0.08	-0.24
6c	-0.20	-0.12	0.08	-0.16

[a] Potentials vs Ag/AgCl. See SI for experimental details.

We also found a relation between the Co-Schiff base catalyst's redox potential and their susceptibility to deactivation. Catalysts **8** and **9,** which exhibit lower redox potentials, were most strongly affected by quinones **6b** and **6c** (Table 1). In contrast, catalyst **10**, with a higher redox potential, was not deactivated by the quinones. It can be concluded that a lower redox potential makes the Co-Schiff base catalysts more oxidizable by quinones.

We found that the reduction potential of quinones **6a**, **6b** and **6c** is a linear function of the number of electron-donating methoxy substituents (Figure 6a).[69] The OMe groups decrease the redox potential of the quinone by increasing the electron density.[70-73] The more positive the reduction potential, the more easily the quinone is reduced.[74] This explains why quinones **6b** and **6c** have a higher effect on the deactivation of Co-Schiff base catalysts (See Section 3). Finally, the peak-to-peak potentials Δ*E* of the three quinones are the same, indicating that they share a common ET process at the conditions evaluated.

The effect of the solvent on quinone electrochemical behavior was also studied. In a neutral aprotic solvent, such as acetonitrile, two successive one-electron reductions of *para*-benzoquinones lead to the formation of the paramagnetic semiquinone anion radical $Q^{\bullet-}$ and the diamagnetic quinone dianion Q^{2-} (equation 1) that are characterized by two separate redox waves in a voltammogram (Figure 6b, red line).[70, 72, 75]



(1)

We found that in methanol the electrochemical reduction of *para*-benzoquinones occurs reversibly as a single-step, two-electron transfer process (Figure 6b, black line). Similar results have been also reported for different kind of quinones, including quinones **6a** and **6c**, in other alcohols and aqueous systems at neutral pH.[76-80] It has been proposed that this process is possible because the radical anion and the dianion are stabilized by hydrogen bonding with the solvent.[81-83]

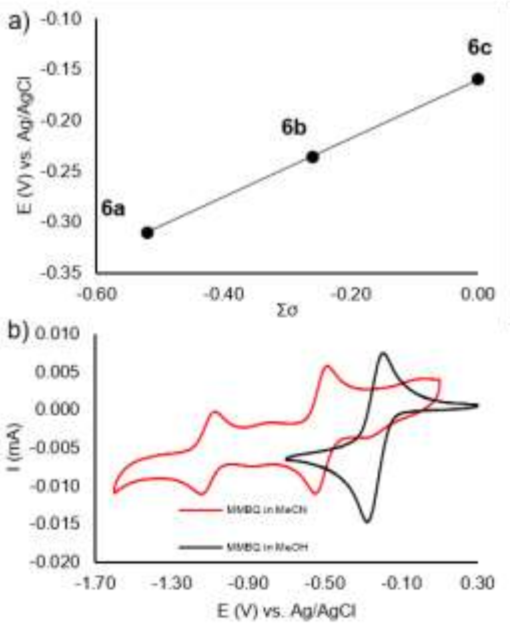
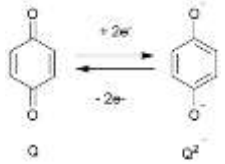


Figure 6. Plot of the $E_{1/2}$ reduction potentials as function of the sum of the Hammett constants for the OMe group. b) Cyclic voltammograms of MMBQ (0.01 M in MeCN and MeOH).

Although both peaks shift to more positive potentials, the peak associated with the reduction of $Q^{\bullet-}$ to Q^{2-} shifts more than the Q to $Q^{\bullet-}$ reduction peak, creating an overlapping of the two redox peaks that are seen as one single $Q \leftrightarrow Q^{2-}$ redox wave (equation 2).[84]

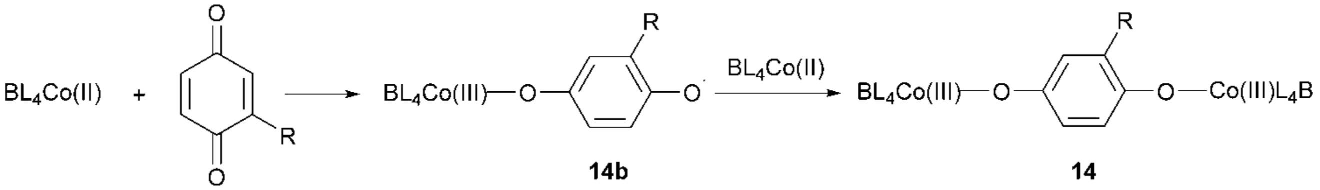


(2)

2.6. Mechanistic proposal for Co-Schiff base catalyst deactivation

Based on the experimental results described above and the literature reviewed, we propose two different mechanisms to explain the observed quinone deactivation of the Co-Schiff base catalysts reported in Tables 1 and 2.

2.6.1. Deactivation by the formation of Co-Schiff base-quinone complexes. The first proposed mechanism results from the formation of the 2:1 adducts, leading to the oxidation of the cobalt catalyst (Scheme 3). According to this mechanism, the cobalt complex $L_4BCo(II)$ would react with a quinone by forming a reduced complex **14b**, that quickly reacts with a second $L_4BCo(II)$ molecule to generate **14.** A similar mechanism has been proposed for the formation of dinuclear complexes of *para*-benzoquinones and $Co(CN)_5^{3-}$.[52, 85, 86]



Scheme 3. Proposed mechanism for the formation of binuclear Co-Schiff base complexes with hydroquinone dianion ligand.

According to this mechanism, the loss of the catalytic activity of **8** would be appreciable if a competitive reaction for the formation of catalytically active cobalt superoxo radical **1** and **14b** took place. This seems to be the case when evaluating the effect of the quinone concentration on the deactivation of Co-Schiff base catalysts (Figure 3a and 3b): when the concentration of the quinone in the solution increased, the oxidation of the phenolic substrate decreased

It has been proposed that the similarities between the 2:1 Co-oxygen and the Co-quinone adducts formation are substantial.[41] When the unpaired electron of the square planar tetradentate d^7 Co(II)(salen) complex is located in the d_{xy} orbital, where it is not available for approaching oxygen molecule, the formation of Co-O_2 complexes is unfavorable.[87] We argue that this is also true for four-coordinate Co-Schiff base catalysts and quinones **6d** and **6c**. In absence of a suitable axial base, the unpaired electron of the catalysts like **10**, **11** and Co(II)(salen) are not available to form a complex with any surrounding quinone. Although methanol can act as a weak axial ligand that helps those four-coordinated Co-Schiff base catalysts to bind oxygen,[54, 88-90] our results suggest that this effect is not enough to make the four-coordinate complexes to bind quinones (Table 1 and 2).

In contrast, when a donor ligand B like pyridine is added to the reaction medium (or when an N axial base is already present like in catalyst **9**) it pulls the cobalt out of the salen ligand plane and donates two more electrons that shift the d_{z^2} orbital from nonbonding with a pair of electrons to antibonding with a single electron.[91, 92] This makes the Co-Schiff-py base complex more reactive towards oxygen.[17, 33, 68, 93, 94] We believe that this process also makes the complexes Co(II)(salen)py (**8**), Co(II)(salen*)py, and (salophen)py Co(*N*-Me salpr) more reactive towards some quinones. Therefore, the formation of a σ-bonding between the oxygen of the quinone and the cobalt center of the five-coordinated complex **8** and **9** would be responsible for the formation of the Co-Schiff-quinone complexes (**13**).

Finally, it has been reported that the formation and the stability of complexes between metal-Schiff bases and quinones are related with their redox potentials. For instance, whereas the dinuclear complex of tetramethyl-1,4-benzoquinone (duroquinone) and Fe(salen) decomposes in contact with air, tetrachloro-1,4-benzoquinone (para-chloranil), which has a higher redox potential, was more stable and did not decompose.[41] Similarly, ortho-quinones with higher redox potential were reported to react more easily with metal-Schiff base complexes than quinones with lower potential values.[51] According to this, the high halfwave potentials values of **6c** and **6d** (Table 3) would explain why they readily deactivate **8**, whereas quinone **6b**, with a lower redox potential, does not deactivate the catalyst.

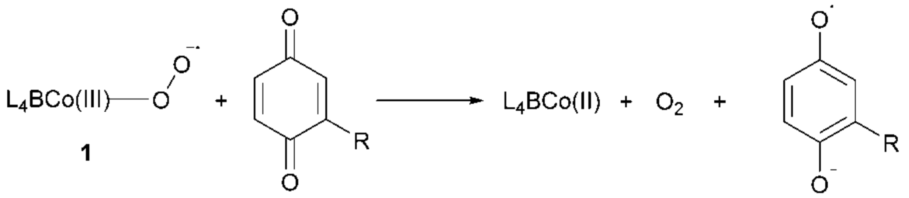
2.6.2. Scavenging of Co-Schiff base-superoxo complexes by quinones.

The second proposed deactivation mechanism is based on an ET reaction between the quinones and the Co-superoxo radical without the formation of Co-quinone complexes. This mechanism is based on the capacity of the superoxide anion radical $O_2^{\bullet -}$ to act as both a reducing and oxidizing agent depending on the redox potential of the substrate with which it reacts.[95-98] When superoxide anion reacts with a quinone, the corresponding semiquinone anion and oxygen are produced (equation 3).[99]

$$O_2^{\bullet -} + Q \rightleftharpoons O_2 + Q^{\bullet -} \qquad (3)$$

This capacity of quinones to scavenge superoxide anion radicals has been observed.[100-108] Joshi and Gangabhagirathi reported the scavenging of superoxide radical and hydroxyethyl radical by 5-hydroxy-2-methyl-1,4-naphthoquinone with the formation of semiquinone radicals.[109] Reaction of 1,4-benzoquinone with α-hydroxyalkyl radicals occurred only by electron transfer.[100] Finally, Petillo and Hultin reported the use of Coenzyme Q_{10} as a free radical scavenger against a lipid-soluble free radical generator, 2,2'-azobis(2,4-dimethylvaleronitrile).[104]

Although there are few examples of reactions between a quinone and a superoxide anion coordinated to a metal,[42] the chemistry of metal-superoxo anion radicals has been compared with the superoxide anions.[68, 110-113] Thus, in this deactivation mechanism, we argue that the reaction of quinones with the



Scheme 4. Proposed mechanism for quenching of the superoxo anion by quinone.

Co-superoxo anions $L_4BCo(III)\text{-}O_2^{\bullet -}$ would quench the oxygenated catalytically active species (Scheme 4).

The one-electron transfer reaction that occurs between Co-superoxo radical like **1** and the quinones in Scheme 4 would depend on the redox potential of the species involved. As mentioned earlier, the more negative the redox potential of the quinones, the more difficult it is to reduce them.[74] According to this, the low $E_{1/2}$ value of **6a** becomes a barrier for any successful electron transfer reaction from the Co-superoxo complex to the quinones. In contrast, quinones **6b** and especially **6c**, with a more positive redox potential, endow thermodynamic favorability of reduction by the Co-superoxo radicals.

It is important to notice that according to equation 3, the semiquinone can be oxidized to regenerate the quinone and superoxide in a one-electron transfer reaction.[114-116] The redox potential of the quinone controls the equilibrium of the reaction between its corresponding semiquinone and dioxygen to form the superoxide anion.[74] The lower the reduction potential, the higher the rate constant for the formation of superoxide from the reaction of the $SQ^{\bullet -}$ with dioxygen. Therefore, semiquinone from **6b** would be a better reducing agent than semiquinone from **6c**. Reported rate constants k for the reaction of Q•- with dioxygen to form superoxide of 5×10^4 $M^{-1}\cdot s^{-1}$ for 1,4-benzosemiquinone and 1.5×10^6 $M^{-1}\cdot s^{-1}$ for 2-methoxy-1,4-benzosemiquinone support this trend.[74, 117]

The synthesis of complex **13** from Co(salen) and quinone **6c** in pyridine shows quinones will complex to Co-Schiff base complexes, supporting the first proposed mechanism. However, the fact that we were unable to synthesize similar catalyst-quinone complexes for the other cobalt complexes suggests that the second mechanism is also possible. The scavenging of superoxide radicals by quinones, which have been used as antioxidants, accounts for the second alternative mechanism.

4. Conclusions

Catalyst deactivation has been always a concern in the use of Co-Schiff base catalysts for the oxidation of lignin models. Here, we have demonstrated that some quinones can deactivate the five-coordinate Co-Schiff base catalysts used in the oxidation of lignin models. This result is important for the oxidative depolymerization of lignin using Co-Schiff base catalysts because five-coordinate catalysts are generally more selective for the production of quinones. Even catalysts with sterically bulky ligands such as Co(salen*) are susceptible to deactivation by quinones. This must be considered when designing new Co-Schiff base catalysts for the oxidation of lignin in the production of quinones.

Traditionally, methanol has been used as a solvent in the oxidation of lignin models by using Co-Schiff base catalyst. The idea is that quinones with low solubility in this solvent (in particular, **6a**) precipitate from the solvent, making them easy to separate. However, we have shown that the hydrogen bonding with methanol increases the redox potential of the quinones, making them more reactive toward the five-coordinate Co-Schiff base catalyst.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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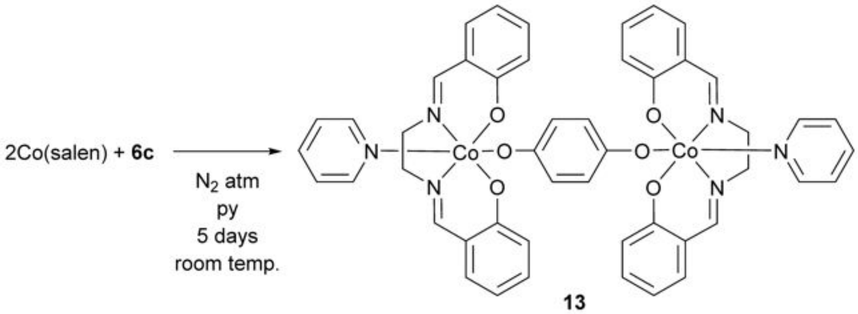
References

1. M. D. Karkas, B. S. Matsuura, T. M. Monos, G. Magallanes and C. R. J. Stephenson, *Org. Biomol. Chem.*, 2016, **14**, 1853-1914.
2. G. Labat and B. Meunier, *J. Org. Chem.*, 1989, **54**, 5008-5011.
3. C. Canevali, M. Orlandi, L. Pardi, B. Rindone, R. Scotti, J. Sipila and F. Morazzoni, *J. Chem. Soc., Dalton Trans.*, 2002, 3007-3014.
4. V. Sippola, O. Krause and T. Vuorinen, *J. Wood Chem. Technol.*, 2004, **24**, 323-340.
5. R. S. Drago, B. B. Corden and C. W. Barnes, *J. Am. Chem. Soc.*, 1986, **108**, 2453-2454.
6. K. Kervinen, H. Korpi, J. G. Mesu, F. Soulimani, T. Repo, B. Rieger, M. Leskelä and B. M. Weckhuysen, *Eur. J. Inorg. Chem.*, 2005, **2005**, 2591-2599.
7. L. T. Servedio, S. Foister, J. J. Bozell and T. A. Zawodzinski, *ECS Meeting Abstracts*, 2014, **MA2014-01**, 581.
8. D. Cedeno and J. J. Bozell, *Tetrahedron Lett.*, 2012, **53**, 2380-2383.
9. B. Biannic and J. J. Bozell, *Org. Lett.*, 2013, **15**, 2730-2733.
10. B. Biannic, J. J. Bozell and T. Elder, *Green Chem.*, 2014, **16**, 3635-3642.
11. M. G. Weaver and T. R. R. Pettus, in *Comprehensive Organic Synthesis*, eds. P. Knochel and G. A. Molander, Elsevier, Netherlands, 2014, ch. 15, pp. 373-410.
12. E. J. Son, J. H. Kim, K. Kim and C. B. Park, *J. Mater. Chem. A*, 2016, **4**, 11179-11202.
13. K. Lin, Q. Chen, M. R. Gerhardt, L. Tong, S. B. Kim, L. Eisenach, A. W. Valle, D. Hardee, R. G. Gordon, M. J. Aziz and M. P. Marshak, *Science*, 2015, **349**, 1529-1532.
14. B. Huskinson, M. P. Marshak, C. Suh, S. Er, M. R. Gerhardt, C. J. Galvin, X. Chen, A. Aspuru-Guzik, R. G. Gordon and M. J. Aziz, *Nature*, 2014, **505**, 195-198.
15. D. R. Dimmel, J. J. Bozell, D. von Oepen and M. Savidakis, in *Chemical Modification, Properties, and Usage of Lignin*, ed. T. Hu, Springer, United States, 2002, ch. 11, pp. 199-219.
16. G. Goor, J. Glenneberg and S. Jacobi, in *Ullmann's Encyclopedia of Industrial Chemistry*, John Wiley & Sons, Germany, 2007, pp. 393-427.
17. A. Zombeck, R. S. Drago, B. B. Corden and J. H. Gaul, *J. Am. Chem. Soc.*, 1981, **103**, 7580-7585.
18. G. T. Musie, M. Wei, B. Subramaniam and D. H. Busch, *Inorg. Chem.*, 2001, **40**, 3336-3341.
19. O. A. Kholdeeva and O. V. Zalomaeva, *Coord. Chem. Rev.*, 2016, **306**, 302-330.
20. A. Nishinaga, K. Nishizawa, H. Tomita and T. Matsuura, *J. Am. Chem. Soc.*, 1977, **99**, 1287-1288.
21. A. Nishinaga, T. Shimizu, Y. Toyoda, T. Matsuura and K. Hirotsu, *J. Org. Chem.*, 1982, **47**, 2278-2285.
22. J. J. Bozell, B. R. Hames and D. R. Dimmel, *J. Org. Chem.*, 1995, **60**, 2398-2404.
23. M. Yamada, K. Araki and S. Shiraishi, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2687-2690.
24. A. Pui and J.-P. Mahy, *Polyhedron*, 2007, **26**, 3143-3152.
25. X. Y. Wang, R. J. Motekaitis and A. E. Martell, *Inorg. Chem.*, 1984, **23**, 271-275.
26. Y. Deng and D. H. Busch, *Inorg. Chem.*, 1995, **34**, 6380-6386.
27. Z. Deng, G. R. Dieckmann and S. H. Langer, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1123-1128.
28. M. Frostin-Rio, D. Pujol, C. Bied-Charreton, M. Perree-Fauvet and A. Gaudemer, *J. Chem. Soc., Perkin Trans. 1*, 1984, 1971-1979.
29. A. Nishinaga, H. Tomita, K. Nishizawa, T. Matsuura, S. Ooi and K. Hirotsu, *J. Chem. Soc., Dalton Trans.*, 1981, 1504-1514.
30. M. Yano, K. Maruyama, T. Mashino and A. Nishinaga, *Tetrahedron Lett.*, 1995, **36**, 5785-5788.
31. R. E. Key and J. J. Bozell, *ACS Sustainable Chem. Eng.*, 2016, **4**, 5123−5135.
32. C. N. Njiojob, J. L. Rhinehart, J. J. Bozell and B. K. Long, *J. Org. Chem.*, 2015, **80**, 1771-1780.
33. T. Elder, J. J. Bozell and D. Cedeno, *Phys. Chem. Chem. Phys.*, 2013, **15**, 7328-7337.
34. R. H. Crabtree, *Chem. Rev.*, 2015, **115**, 127-150.
35. G. Rothenberg, *Catalysis: Concepts and Green Applications*, Wiley-VCH, Germany, 2008.
36. P. van Leeuwen, *Appl. Catal., A- Gen*, 2001, **212**, 61-81.
37. D. E. Hamilton, R. S. Drago and A. Zombeck, *J. Am. Chem. Soc.*, 1987, **109**, 374-379.
38. S. Jain, X. Zheng, C. W. Jones, M. Weck and R. J. Davis, *Inorg. Chem.*, 2007, **46**, 8887-8896.
39. N. G. Digurov, V. I. Zakharova and A. I. Kamneva, *Pet. Chem. U.S.S.R.*, 1966, **6**, 189-194.
40. J. Sridhar, J. Liu, M. Foroozesh and C. L. Klein Stevens, *Chem. Res. Toxicol.*, 2012, **25**, 357-365.
41. C. Floriani, G. Fachinetti and F. Calderazzo, *J. Chem. Soc., Dalton Trans.*, 1973, 765-769.
42. A. Nishinaga, H. Tomita and T. Matsuura, *Tetrahedron Lett.*, 1980, **21**, 4853-4854.
43. J. P. M. Tuchagues and D. N. Hendrickson, *Inorg. Chem.*, 1983, **22**, 2545-2552.
44. J. A. Reingold, S. Uk Son, S. Bok Kim, C. A. Dullaghan, M. Oh, P. C. Frake, G. B. Carpenter and D. A. Sweigart, *J. Chem. Soc., Dalton Trans.*, 2006, 2385-2398.
45. M. C. Depew and J. K. Wan, in *The Quinonoid Compounds*, eds. S. Patai and Z. Rappoport, John Wiley & Sons, Great Britain, 1988, ch. 16, pp. 963-1018.
46. W. Kaim, *Coord. Chem. Rev.*, 1987, **76**, 187-235.
47. A. E. Wendlandt and S. S. Stahl, *Angew. Chem. Int. Ed.*, 2015, **54**, 14638-14658.
48. F. Hartl and A. Vlček, *Inorg. Chim. Acta*, 1986, **118**, 57-63.
49. J. Piera and J.-E. Bäckvall, *Angew. Chem. Int. Ed.*, 2008, **47**, 3506-3523.
50. C. E. Castro, G. M. Hathaway and R. Havlin, *J. Am. Chem. Soc.*, 1977, **99**, 8032-8039.
51. S. L. Kessel, R. M. Emberson, P. G. Debrunner and D. N. Hendrickson, *Inorg. Chem.*, 1980, **19**, 1170-1178.
52. A. A. Vlcek and J. Hanzlik, *Inorg. Chem.*, 1967, **6**, 2053-2059.
53. J. L. Sebaugh, *Pharm. Stat.*, 2011, **10**, 128-134.
54. C. W. Anson, S. Ghosh, S. Hammes-Schiffer and S. S. Stahl, *J. Am. Chem. Soc.*, 2016, **138**, 4186-4193.
55. D. Chen and A. E. Martell, *Inorg. Chem.*, 1987, **26**, 1026-1030.
56. C. G. Pierpont and C. W. Lange, *Prog. Inorg. Chem.*, 2007, **41**, 331-442.
57. C. G. Pierpont and J. K. Kelly, in *The Chemistry of Metal Phenolates*, ed. J. Zabicky, John Wiley & Sons, United States, 2014, ch. 11, pp. 669-698.
58. C. G. Pierpont, L. C. Francesconi and D. N. Hendrickson, *Inorg. Chem.*, 1977, **16**, 2367-2376.

59. S. L. Kessel and D. N. Hendrickson, *Inorg. Chem.*, 1978, **17**, 2630-2636.
60. M. W. Lynch, M. Valentine and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1982, **104**, 6982-6989.
61. J. D. Cyran, J. M. Nite and A. T. Krummel, *J. Phys. Chem. B*, 2015, **119**, 8917-8925.
62. A. Y. Girgis, Y. S. Sohn and A. L. Balch, *Inorg. Chem.*, 1975, **14**, 2327-2331.
63. A. Pui, C. Policar and J.-P. Mahy, *Inorg. Chim. Acta*, 2007, **360**, 2139-2144.
64. M. J. Carter, D. P. Rillema and F. Basolo, *J. Am. Chem. Soc.*, 1974, **96**, 392-400.
65. W. R. Harris, G. L. McLendon, A. E. Martell, R. C. Bess and M. Mason, *Inorg. Chem.*, 1980, **19**, 21-26.
66. P. Zanello, R. Cini, A. Cinquantini and P. L. Orioli, *J. Chem. Soc., Dalton Trans.*, 1983, 2159-2166.
67. C. L. Bailey and R. S. Drago, *Coord. Chem. Rev.*, 1987, **79**, 321-332.
68. R. D. Jones, D. A. Summerville and F. Basolo, *Chem. Rev.*, 1979, **79**, 139-179.
69. C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165-195.
70. M. T. Huynh, C. W. Anson, A. C. Cavell, S. S. Stahl and S. Hammes-Schiffer, *J. Am. Chem. Soc.*, 2016, **138**, 15903-15910.
71. C. Frontana, Á. Vázquez-Mayagoitia, J. Garza, R. Vargas and I. González, *J. Phys. Chem. A*, 2006, **110**, 9411-9419.
72. J. Q. Chambers, in *The Quinonoid Compounds*, John Wiley & Sons, Great Britain, 1988, ch. 12, pp. 719-757.
73. C. S. Coates, J. Ziegler, K. Manz, J. Good, B. Kang, S. Milikisiyants, R. Chatterjee, S. Hao, J. H. Golbeck and K. V. Lakshmi, *J. Phys. Chem. B*, 2013, **117**, 7210-7220.
74. Y. Song and G. R. Buettner, *Free Radical Biol. Med.*, 2010, **49**, 919-962.
75. Y. Wang, E. I. Rogers, S. R. Belding and R. G. Compton, *J. Electroanal. Chem.*, 2010, **648**, 134-142.
76. P. A. Staley, E. M. Lopez, L. A. Clare and D. K. Smith, *J. Phys. Chem. C*, 2015, **119**, 20319-20327.
77. N. Gupta and H. Linschitz, *J. Am. Chem. Soc.*, 1997, **119**, 6384-6391.
78. P. S. Guin, S. Das and P. C. Mandal, *Int. J. Electrochem.*, 2011, **2011**, 22.
79. C. Costentin, M. Robert and J.-M. Savéant, *Chem. Rev.*, 2010, **110**, PR1-PR40.
80. R. S. Kim and T. D. Chung, *Bull. Korean Chem. Soc.*, 2014, **35**, 3143-3155.
81. M. Quan, D. Sanchez, M. F. Wasylkiw and D. K. Smith, *J. Am. Chem. Soc.*, 2007, **129**, 12847-12856.
82. G. Armendáriz-Vidales, E. Martínez-González, H. J. Cuevas-Fernández, D. O. Fernández-Campos, R. C. Burgos-Castillo and C. Frontana, *Electrochim. Acta*, 2013, **110**, 628-633.
83. C. Liehn, M. Bouvet and R. Meunier-Prest, *ChemElectroChem*, 2014, **1**, 2116-2123.
84. Y. Hui, E. L. K. Chng, C. Y. L. Chng, H. L. Poh and R. D. Webster, *J. Am. Chem. Soc.*, 2009, **131**, 1523-1534.
85. J. Hanzlík and A. A. Vlček, *Inorg. Chim. Acta*, 1974, **8**, 247-251.
86. J. Fiala and A. A. Vlček, *Inorg. Chim. Acta*, 1980, **42**, 85-94.
87. G. Henrici-Olivé and S. Olivé, *Angew. Chem. Int. Ed.*, 1974, **13**, 29-38.
88. E. Bolzacchini, C. Canevali, F. Morazzoni, M. Orlandi, B. Rindone and R. Scotti, *J. Chem. Soc., Dalton Trans.*, 1997, 4695-4700.
89. B. Rajagopalan, H. Cai, D. H. Busch and B. Subramaniam, *Catal. Lett.*, 2008, **123**, 46-50.
90. R. E. Key, T. Elder and J. J. Bozell, *Tetrahedron*, 2019, **75**, 3118-3127.
91. A. W. Rudie and P. W. Hart, *Tappi J.*, 2014, **13**, 13-20.
92. A. Ceulemans, M. Dendooven and L. G. Vanquickenborne, *Inorg. Chem.*, 1985, **24**, 1159-1165.
93. R. S. Drago and B. B. Corden, *Acc. Chem. Res.*, 1980, **13**, 353-360.
94. T. D. Smith and J. R. Pilbrow, *Coord. Chem. Rev.*, 1981, **39**, 295-383.
95. T. Ozawa and A. Hanaki, *Chem. Pharm. Bull. (Tokyo)*, 1983, **31**, 2535-2539.
96. A. Brunmark and E. Cadenas, *Free Radical Biol. Med.*, 1989, **7**, 435-477.
97. I. B. Afanas'ev, L. G. Korkina, T. B. Suslova and S. K. Soodaeva, *Arch. Biochem. Biophys.*, 1990, **281**, 245-250.
98. A. E. Martell and D. T. Sawyer, *Oxygen complexes and oxygen activation by transition metals*, Plenum Press, United States, 1988.
99. M. Hayyan, M. A. Hashim and I. M. AlNashef, *Chem. Rev.*, 2016, **116**, 3029-3085.
100. A. Maroz and O. Brede, *Radiat. Phys. Chem.*, 2003, **67**, 275-278.
101. X. Ding, K. Zhao and L. Zhang, *Environ. Sci. Technol.*, 2014, **48**, 5823-5831.
102. H. Liu, H. Li, J. Lu, S. Zeng, M. Wang, N. Luo, S. Xu and F. Wang, *ACS Catal.*, 2018, **8**, 4761-4771.
103. N. El-Najjar, H. Gali-Muhtasib, R. A. Ketola, P. Vuorela, A. Urtti and H. Vuorela, *Phytochem. Rev.*, 2011, **10**, 353.
104. D. Petillo and H. O. Hultin, *J. Food Biochem.*, 2008, **32**, 173-181.
105. J. Luo, H. Yu, H. Wang, H. Wang and F. Peng, *Chem. Eng. J.*, 2014, **240**, 434-442.
106. R. Joshi, *ChemistrySelect*, 2016, **1**, 1084-1091.
107. H. C. Sutton and D. F. Sangster, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 695-711.
108. R. Joshi, T. K. Ghanty and T. Mukherjee, *J. Mol. Struct.*, 2009, **928**, 46-53.
109. R. Joshi and R. Gangabhagirathi, *J. Radioanal. Nucl. Chem.*, 2015, **303**, 919-924.
110. M.-T. Maurette, E. Oliveros, P. P. Infelta, K. Ramsteiner and A. M. Braun, *Helv. Chim. Acta*, 1983, **66**, 722-733.
111. B. S. Tovrog, D. J. Kitko and R. S. Drago, *J. Am. Chem. Soc.*, 1976, **98**, 5144-5153.
112. R. S. Drago, *Stud. Surf. Sci. Catal.*, 1991, **66**, 83-91.
113. R. A. Sheldon, in *The Activation of Dioxygen and Homogeneous Catalytic Oxidation*, eds. D. H. R. Barton, A. E. Martell and D. T. Sawyer, Springer, United States, 1993, ch. 2, pp. 9-30.
114. R. I. Samoilova, A. R. Crofts and S. A. Dikanov, *J. Phys. Chem. A*, 2011, **115**, 11589-11593.
115. L. Valgimigli, R. Amorati, M. G. Fumo, G. A. DiLabio, G. F. Pedulli, K. U. Ingold and D. A. Pratt, *J. Org. Chem.*, 2008, **73**, 1830-1841.
116. A. W. Rutherford, A. Osyczka and F. Rappaport, *FEBS Lett.*, 2012, **586**, 603-616.
117. X. Yuan, J. A. Davis and P. S. Nico, *Environ. Sci. Technol.*, 2016, **50**, 1731-1740.



13

Those features which enhance the reactivity of Co-Schiff base oxidation catalysts can also contribute to their demise.