The Role of Carbonate in Catalytic Oxidations
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  This study describes the use of pulse radiolysis in the study of the mechanisms of oxidations by CO$_3^{2-}$ anion radicals.

1. INTRODUCTION

All aerated solutions contain a mixture of CO$_2$/HCO$_3^-$/CO$_3^{2-}$, and their speciation depends on the CO$_2$ solubility under the partial pressure of CO$_2$ in the air and on the following equilibria:

\[
\text{CO}_2 + H_2O \rightleftharpoons H_2\text{CO}_3 \\
\end{align}
\]

\[
H_2\text{CO}_3 \rightleftharpoons H^+ + HCO_3^- \\
HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}
\]

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\[ \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \quad K = 1.70 \times 10^{-3} \ \text{M}^{-1} \]  
\[ \text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \quad K = 4.47 \times 10^{-7} \]  
\[ \text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+ \quad K = 5.01 \times 10^{-11} \ \text{M} \]

Therefore, one commonly considers the role of \( \text{CO}_2/\text{HCO}_3^-/\text{CO}_3^{2-} \) present in solution as a buffer and/or as a proton transfer agent. However, results in recent years have pointed out that the role of \( \text{CO}_2/\text{HCO}_3^-/\text{CO}_3^{2-} \) in redox processes is often of major importance. This is due to three different reasons:

(a) \( \text{CO}_2 \) reacts with peroxides via \( \text{CO}_2(\text{aq}) + \text{HOO}^- \rightarrow \text{HCO}_3^- \)

\[ K = 1.13 \times 10^5 \ \text{M}^{-1} \quad ; \quad k = 2.8 \times 10^2 \ \text{M}^{-1} \ \text{s}^{-1} \]  

This reaction is clearly somewhat higher because of reaction 3. These potentials facilitate photocatalytic water oxidation.\(^{11} \)

(b) The redox potential of the \( \text{CO}_3^{+}^-/\text{CO}_3^{2-} \) couple is 1.57 V vs NHE,\(^{9,10} \) and that for the \( \text{CO}_3^{+}^-/\text{H}^+ \)/\( \text{HCO}_3^- \) couple is clearly somewhat higher because of reaction 3. These potentials are considerably lower than those of the \( \text{OH}^+/\text{OH}^- \) and \( \text{OH}^+/\text{H}^+ \)/\( \text{H}_2\text{O} \) couples. Thus, at all pH values \( \text{CO}_3^{+}^- \) has the potential to oxidize water, i.e., it is expected to be involved in oxygen evolution reactions (OERs). Therefore, it is thermodynamically easier to oxidize bicarbonate/carbonate than to oxidize water. Not surprisingly, adsorbed carbonates on semiconductors facilitate photocatalytic water oxidation.\(^{11-14} \)

Therefore, it is also not surprising that \( \text{HCO}_3^- \) and \( \text{CO}_3^{2-} \) catalyze the Fenton reaction, forming \( \text{CO}_3^{+}^- \) and not \( \text{OH}^+ \).\(^{2,15} \)

\( \text{CO}_3^{+}^- \) and \( \text{CO}_3^{2-} \) also act as electrocatalysts for the OER process.\(^{3,4,16-19} \)

In the absence of other substrates, \( \text{CO}_3^{+}^- \) decomposes via\(^{6,20,21} \)

\[ \text{CO}_3^{+}^- + \text{CO}_3^{2-} \rightleftharpoons \text{O}_2\text{CO}_2\text{CO}_2^- \rightleftharpoons \text{CO}_4^{2-} + \text{CO}_2 \]

\[ k = (6.2-20) \times 10^8 \ \text{M}^{-1} \ \text{s}^{-1} \]  

\[ \text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \quad K = 2.86 \times 10^{-4} \ \text{M} \]

The \( \text{CO}_4^{2-} \) anion radical is considerably less reactive than the \( \text{OH}^+ \) radical, and its reactions are more selective.\(^{21} \) The \( \text{CO}_4^{+}^- \) anion radical reacts in most systems via the inner-sphere mechanism.\(^{9,22} \)

The carbonate anion radical is also formed via the following reactions:\(^{23,24} \)

\[ \text{OH}^+ + \text{CO}_3^{2-} \rightarrow \text{CO}_3^{+}^- + \text{OH}^- \]

\[ k = 4.0 \times 10^8 \ \text{M}^{-1} \ \text{s}^{-1} \]  

\[ \text{OH}^+ + \text{HCO}_3^- \rightarrow \text{CO}_3^{+}^- + \text{H}_2\text{O} \]

\[ k = 1.0 \times 10^7 \ \text{M}^{-1} \ \text{s}^{-1} \]  

In biological systems it is formed via the following reactions:\(^{25} \)

\[ \text{NO}^+ + \text{O}_2^{+} \rightarrow \text{O} = \text{N} = \text{O} = \text{O}^- \]

\[ k = (4.3-6.7) \times 10^9 \ \text{M}^{-1} \ \text{s}^{-1} \]  

\[ \text{O} = \text{N} = \text{O} = \text{O}^- + \text{CO}_2 \rightarrow \text{O} = \text{N} = \text{O} = \text{OCO}_2^- \]

\[ k = 3 \times 10^4 \ \text{M}^{-1} \ \text{s}^{-1} \]  

\[ \text{O} = \text{N} = \text{O} = \text{OCO}_2^- \rightarrow 67\% (\text{NO}_3^- + \text{CO}_2/\text{HCO}_3^-) + 33\% (\text{NO}_2^+ + \text{CO}_3^{+}^-) \]  

The \( \text{CO}_3^{+}^- \) thus formed is believed to be one of the sources of oxidative stress induced by superoxide.\(^{26-28} \) \( \text{CO}_3^{+}^- \) is also formed in several enzymatic processes, e.g., in superoxide dismutase.\(^{29} \) The above-mentioned processes are shown graphically in Scheme 1.  

**Scheme 1. Mechanisms for the Formation of \( \text{CO}_3^{+}^- \) and \( \text{HCO}_3^- \) in the Absence of Transition Metal Complexes**

(c) As a strong hard base, carbonate is a very good ligand for high-valent transition metal cations and therefore stabilizes transition metal complexes with higher valence, e.g., \( \text{Mn}^{\text{III}}, \text{Fe}^{\text{IV}, \text{II}, \text{III}}, \text{Co}^{\text{IV}, \text{III}, \text{II}}, \text{Ni}^{\text{IV}, \text{III}}, \text{Cu}^{\text{IV}, \text{III}}, \text{Ru}^{\text{IV}, \text{III}}, \) etc. In these complexes, the carbonate is a noninnocent ligand and is therefore involved in electrocatalytic OER processes and photoelectrocatalytic processes.

In the next sections these processes are discussed separately.
Water oxidation is of major importance in understanding the fundamental mechanism of photosynthesis and in addressing modern-day energy challenges by means of water electrolysis and solar energy conversion via photochemical water splitting. As water oxidation involves the loss of 4e⁻/4H⁺ and the formation of the O–O bond, it has a high activation energy. Thus, the use of a catalyst is indispensable. All catalysts reported contain a transition metal, M. It is commonly accepted that water oxidation proceeds via reactions 14–17 in Scheme 2.

Scheme 2. Outline of Water Oxidation Mechanisms; M Is the Metal, and n Represents the Highest Oxidation State

The formation of a percarbonate complex in the presence of carbonate has been reported (reaction 20).

\[
M^\text{II}(\text{OH})(\text{CO}_3)^\text{ll}_\text{aq} \rightarrow (\text{CO}_3)^\text{ll}_{\text{aq}}M^\text{III}_{\text{aq}}^\text{ll} + \text{OH}^- + \text{H}^+ \tag{20}
\]

It is evident that in reactions 15–17 in Scheme 2, O^2⁻ and OH^- behave as noninnocent ligands, where the reactions proceed via radical pathways to form the O–O bond. A similar radical pathway can be expected when other noninnocent ligands are used.

Carbonate can act as a catalyst/cocatalyst in electrocatalytic water oxidation on the basis of the arguments raised in the Introduction. On the basis of the redox properties of carbonate, the reactions shown in Scheme 3, where M^\text{III} is formed electrochemically, have to be taken into account to describe the participation of bicarbonate/carbonate in electrocatalytic water oxidation processes. In all of these reactions, the formed peroxide is easily further oxidized to form molecular oxygen at lower potentials. The involvement of bicarbonate/carbonate in homogeneous and heterogeneous electrocatalytic water oxidation, including mechanisms involving specific metal ions (e.g., Cu, Co, Ni), are discussed in the following sections.

Scheme 3. Various Plausible Processes Involved during Electrocatalytic Water Oxidation by Metal Carbonates in Aqueous Bicarbonate/Carbonate Solutions

2. ELECTROCATALYTIC WATER OXIDATION BY METAL CARBONATE COMPLEXES

2.1. Homogeneous Electrocatalysis

The first study reporting homogeneous electrocatalytic water oxidation in the presence of CO\text{II}/HCO\text{II}/CO\text{III} was by Chen and Meyer. They showed that Cu^\text{II}(aq) with CO\text{II}/HCO\text{II}/CO\text{III} in the medium acts as an efficient water oxidation catalyst on a variety of working electrodes. The catalytic current increases with [Cu^\text{II}+] with a cathodic shift of the onset potential. The catalytic current depends linearly on [Cu^\text{II}+] in neutral media, while under alkaline conditions it depends on [Cu^\text{II}+]^2.

Therefore, at pH 10.8 a bimolecular mechanism involving the active intermediate was proposed, while at pH 6.7 a single copper site was suggested to be the active species. The redox potential of Cu^\text{III}/II(H\text{H}_2\text{O})_\text{aq} is >2.3 V vs NHE,1 which is obviously shifted cathodically by the strong carbonate ligand. However, the authors did not clarify the involvement of either Cu^\text{III} or Cu^\text{IV} as the active species in the catalytic cycle. Later, a density functional theory (DFT) study at pH 8.3 suggested the possibility of a Cu^\text{IV} complex as the active intermediate.4,40

Pulse radiolysis is a useful tool to study the chemical properties of complexes in unstable oxidation states.42,43 This technique was used to study the properties of [Cu^\text{III}(CO\text{II})_\text{aq}]^3–2n formed by the oxidation of [Cu^\text{II}(CO\text{II})_\text{aq}]^3–2n by CO\text{II}^*-. The results suggested the following oxidation mechanism:4

\[
[Cu^\text{II}(CO\text{II})_{n-1}(CO\text{III}^2-)_\text{aq}]^{2-2n} + CO\text{II}^* \rightarrow (CO\text{II})_{n-1}(CO\text{III}^2-)^\text{aq} + CO\text{II}^* + CO\text{III}^* + H^+ \tag{36}
\]

\[
[Cu^\text{II}(CO\text{II})_{n-1}(CO\text{III}^2-)_\text{aq}]^{3-2n} + CO\text{II}^* \rightarrow (CO\text{III})_{n-1}(CO\text{II}^2-) + CO\text{II}^* + CO\text{III}^* + H^+ \tag{37}
\]

DFT calculations of the NBO charges suggested that significant charge transfer from the CO\text{II}^2- to the central metal ion in Cu^\text{III}(CO\text{II})_n takes place. The Cu^\text{III}(CO\text{II})_n thus formed decomposes in a process that obeys second-order kinetics irrespective of the pH of the medium:4

\[
2Cu^\text{III}(CO\text{II})_{n} \rightarrow 2Cu^\text{II}(CO\text{II})_{n-1} + 2CO\text{II}^2- + C_2O\text{III}_6 \tag{38}
\]

The discrepancy with the electrochemical results in neutral solutions is probably due to the fact that in neutral media the electrocatalytic process proceeds via reactions 30–34 in Scheme 3. This hypothesis cannot be tested by the pulse radiolysis technique.53

The analogous systems containing other divalent first-row transition metal cations in the presence of HCO\text{II}/CO\text{III}^2- are
Aluminum porphyrin complexes also act as an active catalyst for water oxidation in the presence of carbonate at pH 9.0–11.0. The proposed mechanism is a "proton shuttle" mechanism, as shown in Scheme 5.44 However, the possible oxidation of carbonate to percarbonate complex as the key intermediate.45

In the latter, the central cation is clearly not oxidized, and they act as homogeneous water oxidation catalysts in the presence of bicarbonate/carbonate.

(3) A process with very large currents, with a current density of 10.50 mA cm⁻² at [CoII] = 0.50 mM at a peak plateau that starts at >1.2 V vs Ag/AgCl, is due to the formation of CoIV(CO₃)₃⁻/2⁻ redox couple. The CoIV(CO₃)₃⁻/2⁻ complex oxidizes both water and bicarbonate/carbonate. The results suggest that the oxidation proceeds via reaction 20 and reactions 25–28 and 30–33 in Scheme 3. If one assumes, as these equations indicate, that the rate-determining step in this catalytic process involves a two-electron oxidation process, then \( k_{\text{cat}} = 350 \text{s}^{-1} \). During long-time electrolysis at these potentials, a precipitate forms that is a heterogeneous OER catalyst (vide infra).

It should be noted that in order to calculate the redox potential, the simplest structures, \([\text{Co}^{III/IV}(\text{CO}_3)_3]^{3-/2-}\) with octahedral geometries (Figure 1), were considered.

In the examples given above, carbonate was the only ligand lowering the redox potential of the central transition metal cation. However, carbonate can also be a second ligand, where it is the ligand getting oxidized. The following are such systems: NiII(1,4,8,11-tetraazaacyclotetradecane)³⁺, NiII ל₄⁻,¹⁶ CuII(N,N'-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamidate), CuII²⁺⁴⁴ and AlIII(TMPyP) (TMPyP = 5,10,15,20-tetrakis(1-methylpyridin-1-ium-4-yl porphyrinate)).⁴⁵ In the latter, the central cation is clearly not oxidized, and they act as homogeneous water oxidation catalysts in the presence of bicarbonate/carbonate.

In the system containing the NiL₂²⁺ complex, the role of carbonate is due to the lowering of the redox potentials of the NiIII/II and NiIV/III couples and to the reactions shown in Scheme 4. Recently the process of water oxidation by NiL₂²⁺ was reinvestigated, and it was shown that the formation of nickel oxide on the electrode surface is mainly responsible for the catalysis. However, the large catalytic wave in the cyclic voltammogram and the isomerization of the complex were not addressed. Under long-term chronoamperometry, the oxidation of the organic ligand and the formation of nickel oxide and/or nickel carbonate as nanocomposites cannot be ruled out.

CuL₃ also acts as an active catalyst for water oxidation in the presence of carbonate at pH 9.0–11.0. The proposed mechanism is a "proton shuttle" mechanism, as shown in Scheme 5.44 However, the possible oxidation of carbonate to HCO₃⁻ and CO₂⁻ was not considered⁴⁴ and cannot be ruled out. Carbonate was also shown to act as a cocatalyst in electrocatalytic water oxidation by an aluminum porphyrin (Al(TMPyP)). This catalytic system forms H₂O₂ as the major product. The suggested mechanism involves the formation of an AlIII-percarbonate complex as the key intermediate.⁴⁵

2.2. Heterogeneous Catalysis

Bicarbonate and carbonate are involved also in heterogeneous electrocatalytic water oxidation processes via precipitates on the anode. Reactions analogous to reactions 20–34 are expected on the electrodes. Here the role of the carbonate is also dual: it lowers the redox potential of the central cation, and it has a lower oxidation potential than OH⁻/H₂O. Processes analogous to reactions 22, 23, 29, and 33 in Scheme 3 require carbonate in the homogeneous medium only to replace the carbonate loss from the precipitate. Processes analogous to reactions 21, 24—27, 31, 32, and 34 in Scheme 3 can also proceed without any carbonate in the precipitate on the electrode:

\[
\text{M}^n(\text{OH})_l + \text{HCO}_3^- \rightarrow \text{M}^{n-2}(\text{OH})_{l-1}(\text{OH})_2 + \text{HCO}_4^- \quad (26')
\]

\[
\text{M}^n(\text{OH})_l + \text{HCO}_3^- \rightarrow \text{M}^{n-2}(\text{OH})_{l-1} + \text{HCO}_4^- + \text{H}^+ \quad (27')
\]

\[
\text{M}^n(\text{OH})_l + \text{HCO}_3^- \rightarrow \text{M}^{n-1}(\text{OH})_{l-1} + \text{HCO}_4^- + \text{H}^+ + e^- \quad \text{(at an anode)} \quad (31')
\]

\[
\text{M}^n(\text{OH})_l + \text{HCO}_3^- \rightarrow \text{M}^{n-1}(\text{OH})_{l-1} + \text{HCO}_4^- + e^- \quad \text{(at an anode)} \quad (32')
\]

An example of the latter type of catalysis is the report that NiII(aq) adsorbed on a SiO₂ sol–gel matrix and mixed with graphite acts as an OER electrocatalyst in solutions containing HCO₃⁻/CO₃²⁻ with a current proportional to [HCO₃⁻/CO₃²⁻].³⁶,⁴⁴ Clearly one cannot rule out that ligand exchange in the sol–gel matrix transforms the NiII(aq) into carbonate

**Figure 1.** Structure of \([\text{Co}^{III/IV}(\text{CO}_3)_3]^-\) obtained at the B3LYP/6-311+G(2d,p) level. Reprinted with permission from ref 3. Copyright 2020 Wiley-VCH.
complexes. In this study it was proposed that the catalytic process involves the formation of CO$_3^{2-}$ radical anions. In the study of homogeneous electrocatalysis of the OER in solutions containing CoII and HCO$_3^{-}$/CO$_3^{2-}$, it was noted that during chronoamperometry a green precipitate of Na$_3[Co-(CO_3)_3]$ is formed. This precipitate on the anode surface serves as an excellent heterogeneous catalyst in the presence of bicarbonate/carbonate. This catalytic process was shown to be in agreement with reactions analogous to reactions 22 and 26 in Scheme 3. DFT calculations suggest that the active species in these process is the CoV(CO$_3$)$_3^{-}$ complex. In an analogous study, a precipitate was formed on an anode by electrolysis of a CO$_2$-saturated solution containing FeII(aq) and HCO$_3^{-}$. The thin film thus formed contained Fe$_{III}$, O$_{II}$, OH$^{-}$, and CO$_3^{2-}$. This film was shown to be a good OER electrocatalyst for which the current increased with [HCO$_3^{-}$/CO$_3^{2-}$]. The detailed mechanism causing the electrocatalytic process was not discussed. Clearly reactions analogous to reactions 22 and 26-34 are probably responsible for the electrocatalytic properties of this precipitate. The observation that the film is stable during electrolysis in carbonate solutions that do not contain FeII ions proves that the mechanism does not involve reduction of the Fe ions in the precipitate to Fe$^{III}$ and dissolution to the aqueous phase.

An analogous study involving nickel carbonate solutions resulted in the formation of an analogous Ni$_{III}$(HCO$_3^{-}$)$_{3-n}$/Ni$_{III}$(CO$_3^{2-}$)$_{n}$$_{3-2n}$ precipitate on the anode that is a good electrocatalyst for water oxidation in solutions containing NiII and HCO$_3^{-}$/CO$_3^{2-}$. However, the precipitate dissolves during electrolysis when no NiII ions are present in solution. This proves that the catalytic step involves the reduction of a NiIV complex into a NiII complex that is soluble, i.e. via reactions analogous to reactions 21, 22, 25, and 26 in Scheme 3. In another study, an amorphic nickel carbonate nanowire array on a nickel foam (NiCO$_3$/NF) anode was prepared. This modified electrode is a very good electrocatalyst for water oxidation in solutions containing only HCO$_3^{-}$/CO$_3^{2-}$. The source of the discrepancy between these two studies might be that the nickel foam supplies the needed nickel to preserve the precipitate. The use of a mixture of salts of iron and nickel in carbonate solutions was also reported to form an oxide precipitate that acts as an efficient catalyst in carbonate media to oxidize water.

Scheme 4. Electrocatalytic Processes Occurring during Electrocatalytic Water Oxidation Using the Ni$_{III}L_2^{2+}$ Complex in HCO$_3^{-}$/CO$_3^{2-}$
To sum up this section, the results suggest that precipitates of transition metal oxides and/or carbonates, where the central cation can be oxidized to a high oxidation state, on anodes serve as good electrocatalysts for water oxidation in solutions containing HCO$_3^-$/CO$_3^{2-}$. The detailed mechanisms of these catalytic processes depend on the properties of the central cation. The advantage of these catalytic processes is that all of the components are stable inorganic species that are not consumed during the catalytic process.

3. PHOTOCATALYSIS

The difference in the oxidation potentials of the CO$_3^{2-}$/CO$_3^{3-}$ and OH$^+$/OH$^-$ (aq) or (OH$^+$ + H$_2$O$^+$)/2H$_2$O couples suggests that the holes formed photochemically in semiconductors will oxidize HCO$_3^-$/CO$_3^{2-}$ faster and in higher yields than the oxidation of water. This was verified computationally in a DFT study of the photocatalysis by GaN (Figure 2). It was found that adsorption of HCO$_3^-$/CO$_3^{2-}$ on the surface of the semiconductor, i.e., a relatively high point of zero charge (the pH at which the net charge of the adsorbent’s surface is zero or positive), is favorable. The products of these oxidations are either CO$_3^{3-}$ or C$_2$O$_6^{2-}$. Indeed, several studies have pointed out that the presence of HCO$_3^-$/CO$_3^{2-}$ in the system catalyzes photochemical water oxidation. Furthermore, it has been shown that photochemical oxidation of SO$_2$ in aqueous media is enhanced by the presence of carbonate. It was proposed that the formation of CO$_3^{3-}$ is involved.

In the previous section, the role of metal carbonate precipitates as efficient heterogeneous electrocatalysts for water oxidation was reviewed. It seemed to be of interest to check whether these precipitates are photoactive, and indeed, preliminary results point out that precipitates of cobalt and nickel carbonate act as photoelectrocatalysts for water and methanol oxidations.

4. PERCARBONATE AS AN OXIDATION AGENT

In principle, percarbonates are involved in two types of processes:

1. An inorganic percarbonate salt, e.g., sodium percarbonate (Na$_2$CO$_4$·1.5H$_2$O$_2$), is used as the oxidizing agent. These percarbonates are used mainly in advanced oxidation processes (AOPs) (vide infra). Their mechanisms of oxidation are suggested to proceed via formation of H$_2$O$_2$ upon dissolution followed by Fenton-like and/or photolytic processes and/or reaction with O$_3$, often involving CO$_3^{3-}$ anion radicals.

2. The percarbonate is formed in situ via the reaction of H$_2$O$_2$ with a transition metal carbonate complex, analogous to reaction 4 followed by 5, or via reactions analogous to reaction 6 or reaction 69 below.

The first peroxocarbonate complex of a transition metal was reported by Hashimoto et al. It was formed via the reaction of a bis(μ-hydroxo)diiron(III) complex with H$_2$O$_2$ and CO$_2$. Oxidative degradation of an organic dye, Orange II, by Mn$^{III}$(TPPS) (TPPS = 5,10,15,20-tetrakis(4-sulfonatophenyl)-21H,23H-porphyrin) in carbonate buffer was proposed to involve the formation of a percarbonate–metal complex that undergoes decomposition to form a Mn$^{IV}$=O species and degrades Orange II via reactions 53–56.
5. ROLE OF BICARBONATE IN FENTON AND FENTON-LIKE REACTIONS

The Fenton reaction, \( \text{Fe}(	ext{H}_2\text{O})_6^{2+} + \text{H}_2\text{O}_2 \), is of major importance. Thus, a search in SciFinder for “Fenton” limited to articles in English for 2019 yielded 2371 results. The major source of this importance is in its role in inducing oxidative stress\(^{61-66}\) and its role in AOPs.\(^{67-70}\) The Fenton reaction and Fenton-like reactions, in which another low-valent metal ion replaces Fe and/or another ligand L replaces \( \text{H}_2\text{O} \) and/or another peroxide replaces \( \text{H}_2\text{O}_2 \), were shown to proceed via a variety of mechanisms.\(^{71}\)

\[
\text{M}^{II}\text{L}_{mn} + \text{H}_2\text{O}_2 \rightleftharpoons \text{L}_{mn-1}\text{M}^{II} = \text{OOH} + \text{H}^+ \quad (63)
\]

where RH is a substrate. The reactions always proceed via the inner-sphere mechanism.

Still, nearly all of the recent articles cite the Fenton reaction as proceeding via the formation of \( \text{OH}^\cdot \). Furthermore, recent results point out that in systems where it is difficult to oxidize the central cation, the central cation is not oxidized in the process, and the reaction proceeds via the following mechanism:\(^{72,73}\)

\[
\text{M}^{II}\text{L}_{mn} + k\text{H}_2\text{O}_2 \rightleftharpoons \text{L}_{mn-1}\text{M}^{II} = \text{O}_2\text{H}^{k-1}(\text{H}_2\text{O}_2) + k\text{L} + (k - 1)\text{H}^+ \quad (65)
\]

\[
\text{L}_{mn-1}\text{M}^{II} = \text{O}_2\text{H}^{k-1}(\text{H}_2\text{O}_2) \rightarrow \text{L}_{mn-1}\text{M}^{II} = \text{O}_2\text{H}^{k-1} = \text{OH}^- + \text{OH}^+ \quad (66)
\]

Reaction 66 indicates that \( \text{H}_2\text{O}_2 \) ligated to a central cation can oxidize another ligand that has no bond with it. DFT calculations verified this for other ligands, including carbonate.\(^{74}\) For the carbonate-containing systems, three cases were studied in detail:

1. The reaction of \( \text{H}_2\text{O}_2 \) with \( \text{Co} = \text{H}_2\text{O}_6^{2+} \) (10–25.0 mM) in the presence of 0–0.6 mM \( \text{H}_2\text{O}_2 \) was studied. Under these conditions, \( [\text{Co} = \text{OH}^{2+}] > [\text{Co} = \text{OH}^{2+}] \). The following reactions were observed:\(^{75}\)

\[
\text{Co}^{II} = \text{H}_2\text{O}_6^{2+} + \text{H}_2\text{O}_2 \rightleftharpoons \text{Co}^{II} = \text{HCO}_3^- = \text{Co}^{II} = \text{HCO}_3^- = \text{H}_2\text{O} + \text{H}^+ \quad (67)
\]

\[
(\text{H}_2\text{O}_2)^{2-} + \text{H}_2\text{O}_2 \rightleftharpoons (\text{H}_2\text{O}_2)^{2-} + \text{H}_2\text{O} + \text{H}_2\text{O}_2 \quad \Delta G^\circ = -12.1 \text{ kcal mol}^{-1} \quad (68)
\]

\[
(\text{Co}^{II} = \text{H}_2\text{O}_6^{2+}) = \text{Co}^{II} = \text{H}_2\text{O}_2 \rightleftharpoons \text{cyclic} = (\text{Co}^{II} = \text{H}_2\text{O}_6^{2+}) \quad \Delta G^\circ = -6.2 \text{ kcal mol}^{-1} \quad (69)
\]

\[
(\text{Co}^{II} = \text{H}_2\text{O}_6^{2+}) = \text{cyclic} = (\text{Co}^{II} = \text{H}_2\text{O}_2) \rightleftharpoons \text{cyclic} = (\text{Co}^{II} = \text{H}_2\text{O}_2) \quad \Delta G^\circ = -14.8 \text{ kcal mol}^{-1} \quad (70)
\]
cyclic-(CO$_4^{2-}$)Co$^{II}$((OOH$^-$)(H$_2$O))$^-$·H$_2$O →
Co$^{II}$((OOH$^*$)((OH$^-$)$_2$)(H$_2$O) + CO$_3^{2-}$ & Δ$G^o = -6.8$

kcal mol$^{-1}$

(71)

These results point out the following: (a) No OH$^*$ radicals are formed. Though a percarbonate ligand is formed as an intermediate in the process, the active oxidizing agent formed is the CO$_3^{2-}$ anion radical. (b) The central Co$^{II}$ cation is not oxidized during the process. The process is analogous to reactions 65 and 66 with $k = 2$. Thus, in AOPs with Co$^{II}$(H$_2$O)$_6^{2+}$ and H$_2$O$_2$, the active species is CO$_3^{2-}$ and not OH* as usually assumed. The mechanism is outlined in Scheme 7.

(II) The Fenton reaction at pH 7.4 in solutions containing 2.0 × 10$^{-5}$ M Fe$^{II}$(H$_2$O)$_6^{2+}$, 0–3.0 mM HCO$_3^{-}$, and 0–0.8 mM H$_2$O$_2$ was studied. Under these conditions, [Fe$^{II}$(H$_2$O)$_6^{2+}$(HCO$_3^{-}$)]$^{3+}$ constitutes less than 3% of the Fe$^{II}$(H$_2$O)$_6^{2+}$. However, the observed rate constants increase dramatically with [HCO$_3^{-}$]. The following reactions were observed:

Fe$^{II}$(H$_2$O)$_6^{2+}$ + HCO$_3^{-}$
→ (H$_2$O)$_3$Fe$^{II}$((OOH$^-$))(H$_2$O)$_3^{2+}$ + 2H$_2$O

(72)

This reaction sequence is the major one for [HCO$_3^{-}$] < 1.0 mM. For [HCO$_3^{-}$] > 1.0 mM, reactions 74 and 75 lead to the formation of (CO$_3^{2-}$)Fe$^{II}$((OOH$^-$))(H$_2$O)$_2^{2-}$, i.e., the same intermediate formed in reaction 73:

Fe$^{II}$(H$_2$O)$_6^{2+}$ + HCO$_3^{-}$
→ (H$_2$O)$_3$Fe$^{II}$((CO$_3^{2-}$)) + H$_2$O$_2$

(74)

The mechanism is shown in Scheme 7. In the Fe Fenton reaction, metal ion oxidation occurs, whereas in the Co Fenton-like reaction, the metal oxidation state does not change. One more difference is that for Co a cyclic percarbonate complex is formed, but this does not occur in the case of Fe. The (CO$_3^{2-}$)Fe$^{II}$((OOH$^-$))(H$_2$O)$_2^{2-}$ thus formed decomposes via the following reactions:

(CO$_3^{2-}$)Fe$^{II}$((OOH$^-$))(H$_2$O)$_2^{2-}$ → CO$_3^{2-}$Fe$^{IV}$((OH$^-$))(H$_2$O)$_2^{3-}$

(76)

Thus, also in this system, the reactive oxygen species (ROS) formed under physiological conditions (i.e., in the presence of ∼1.0 mM HCO$_3^{-}$) is not the OH$^*$ radical as commonly assumed.

(III) The results concerning the Fenton reaction in the presence of HCO$_3^{-}$ suggest that under physiological conditions, the Fenton reaction yields CO$_3^{2-}$ and not OH$^*$ radicals as commonly assumed, and this is of major importance. However, since in biological media Fe$^{II}$ ions are not present as Fe$^{II}$(H$_2$O)$_6^{2+}$ but appear in the mobile pool mainly as Fe$^{II}$(citrate), the Fenton reaction was studied$^{15}$ in solutions containing 2.0 × 10$^{-5}$ M Fe$^{II}$(H$_2$O)$_6^{2+}$, 0–2.0 mM sodium citrate, 0–8.0 mM NaHCO$_3$, and 0–0.39 mM H$_2$O$_2$. It was shown that the kinetics of the process and the composition of the final products in the presence of dimethyl sulfoxide depend dramatically on the concentration of HCO$_3^{-}$. The following mechanism was proposed$^{15}$:

Fe$^{II}$(citrate)(HCO$_3^{-}$)$_3^{2-}$ + H$_2$O$_2$
→ (citrate)Fe$^{II}$((H$_2$O)$_3$)(HCO$_3^{-}$)$_3^{2-}$

→ Fe$^{IV}$(citrate)(HCO$_3^{-}$)(aq) + 2OH$^-$

(78)
The mechanism of decomposition of $\text{Fe}^{III}(\text{citrate})(\text{HCO}_3^-)$ was not clarified. It can decompose via the formation of $\text{CO}_4^{2-}$ or via oxidation of the citrate ligand. Alternatively, the mechanism might involve reactions 79 and 80,

$$\text{(citrate)}\text{Fe}^{II}_3\left(\text{H}_2\text{O}_2\right)(\text{HCO}_3^-)^{2-}$$
$$\rightarrow \text{(citrate)}\text{Fe}^{II}_3\left(\text{CO}_4^{2-}\right)^{3-} + \text{H}_2\text{O}^+ \quad (79)$$

$$\text{(citrate)}\text{Fe}^{II}_3\left(\text{CO}_4^{2-}\right)^{3-} + \text{H}_2\text{O}$$
$$\rightarrow \text{Fe}^{III}_3\text{(citrate)} + \text{CO}_3^{2-} + 2\text{OH}^- \quad (80)$$

where $(\text{citrate})\text{Fe}^{III}_3\left(\text{H}_2\text{O}_2\right)(\text{HCO}_3^-)^{2-}$ is formed in a reaction analogous to reaction 76. It was suggested that this mechanism fits the results better.

The results of these three studies of the mechanisms of Fenton and Fenton-like reactions point out that the role of bicarbonate present in biological systems and in wastewater cannot be overlooked. This conclusion was recently verified. 28

6. OTHER BIOLOGICAL SOURCES OF CO$_3^{2-}$

As stated in the Introduction, CO$_3^{2-}$ is formed biologically via the reaction of peroxonitrite with CO$_2$ (reactions 11–13).76 The formation of NO$_3^-$ and CO$_3^{2-}$ is believed to be the main mechanism via which O$_2$ causes oxidative stress. 77,78 CO$_3^{2-}$ is also formed enzymatically by the enzymes superoxide dismutase (Cu,Zn-SOD, SOD-1)79 and xanthine oxidase.80

The CO$_3^{2-}$ anion radicals formed in biological systems can oxidize nucleobases 26–28,77,81,82 and proteins 83,84 and peroxidize low-density lipoprotein.85

7. ADVANCED OXIDATION PROCESSES/TECHNOLOGIES

The treatment of polluted water and soil is of major importance. Many organic pollutants are treated by advanced oxidation processes/technologies.86 There is still no optimal treatment for pollutants, and a variety of technologies have been studied. These include chemical oxidation by peroxides, Fenton and Fenton-like processes (including photo-Fenton and electrochemical Fenton), ozone, photochemical processes (including solar light using TiO$_2$ as a photocatalyst), electrochemical processes, microwave processes, ultrasonic processes, ionizing radiation, hydrodynamic cavitation, and various combinations of these techniques.86 Carbonate is involved in these processes via the addition of percarbonate as an oxidizing agent,52,55,87–91 the involvement of the HCO$_3^-$/CO$_3^{2-}$ that is always present in water,75,92–96 and sometimes by the addition of HCO$_3^-$/CO$_3^{2-}$ to the system.97

The role of the added percarbonate is clear. However, the role of the bicarbonate/carbonate present in the solution is more complicated. For many systems it has been proposed that bicarbonate/carbonate reacts with the OH$^-$ radical initially formed, thus decreasing the reactivity of the oxidizing species formed but increasing its lifetime and its selectivity in the choice of substrates.52,94,95 On the other hand, for some systems involving Fenton and photochemical reactions, at least the carbonate is involved in the ROS formation and therefore increases the pollutant decomposition yield.75 It should be pointed out that the Fenton reaction in neutral solutions in the absence of bicarbonate/carbonate forms Fe$^{IV}(aq)$ and not OH$^-$ radicals.98 This is commonly not addressed in publications on the Fenton reaction discussed in AOPs. Thus, in these systems the presence of bicarbonate/carbonate exchanges Fe$^{IV}(aq)$ with CO$_3^{2-}$ as discussed above.

8. CONCLUSIONS AND PERSPECTIVES

CO$_2$, HCO$_3^-$, and CO$_3^{2-}$ are present in all aquatic media at pH > 4 if no effort to remove them is made. Usually one considers their role only as buffers and/or proton transfer agents. The recent results discussed in this Account point out the important role of HCO$_3^-$/CO$_3^{2-}$ in a variety of catalytic oxidation processes in aqueous media. This role is due to the following properties of carbonates:

1. Carbonate is a strong hard ligand that stabilizes transition metal complexes in high oxidation states. These complexes are key intermediates in electrochemical water oxidation processes.

2. The redox potential of the CO$_3^{2-}$/CO$_3^{2-}$ and (CO$_3^{2-}$ + H$^+$)/HCO$_3^-$ couples is considerably lower than that of the OH$^-$/OH$^-$ and (OH$^-$/H$^+$/H$_2$O) couples. Therefore, HCO$_3^-$ and CO$_3^{2-}$ act as cocatalysts in water oxidation and are involved in Fenton-like processes.

3. Peroxocarbonate, as a bidentate ligand, is easily formed in the presence of transition metal cations with fast ligand exchange properties, HCO$_3^-$/CO$_3^{2-}$, and peroxides.

The results obtained thus far point out that the presence of HCO$_3^-$/CO$_3^{2-}$ dramatically changes the mechanisms of the Fenton and Fenton-like reactions. These findings require reassessment of the major sources of oxidative stress in biological systems and of the role of carbonate anion radicals in oxidative stress. Furthermore, the results point out the activity of HCO$_3^-$/CO$_3^{2-}$ as catalysts/cocatalysts for water oxidation electrochemically and photochemically. This is of importance in developing technologies for efficient water splitting processes.

Extremely little has been done to date on the application of HCO$_3^-$/CO$_3^{2-}$ in catalytic oxidations of specific substrates performed electrochemically, photochemically, and photoelectrochemically. Also, the role of HCO$_3^-$/CO$_3^{2-}$ in Fenton-like processes using other peroxides (e.g., S$_2$O$_5^{2-}$, HSO$_4^-$, and ROOH, where R is an aliphatic residue) has not been studied. These studies might be of importance in the development of new advanced oxidation technologies.

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