

The Role of Carbonate in Catalytic Oxidations

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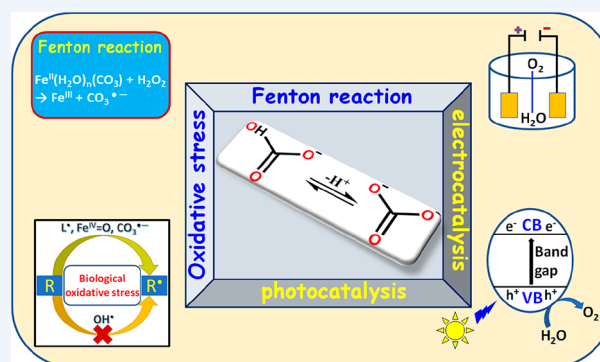
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CONSPECTUS: CO_2 , HCO_3^- , and CO_3^{2-} are present in all aqueous media at $\text{pH} > 4$ if no major effort is made to remove them. Usually the presence of $\text{CO}_2/\text{HCO}_3^-/\text{CO}_3^{2-}$ is either forgotten or considered only as a buffer or proton transfer catalyst. Results obtained in the last decades point out that carbonates are key participants in a variety of oxidation processes. This was first attributed to the formation of carbonate anion radicals via the reaction $\text{OH}^\bullet + \text{CO}_3^{2-} \rightarrow \text{CO}_3^{\bullet-} + \text{OH}^-$. However, recent studies point out that the involvement of carbonates in oxidation processes is more fundamental. Thus, the presence of $\text{HCO}_3^-/\text{CO}_3^{2-}$ changes the mechanisms of Fenton and Fenton-like reactions to yield $\text{CO}_3^{\bullet-}$ directly even at very low $\text{HCO}_3^-/\text{CO}_3^{2-}$ concentrations. $\text{CO}_3^{\bullet-}$ is a considerably weaker oxidizing agent than the hydroxyl radical and therefore a considerably more selective oxidizing agent. This requires reconsideration of the sources of oxidative stress in biological systems and might explain the selective damage induced during oxidative stress. The lower oxidation potential of $\text{CO}_3^{\bullet-}$ probably also explains why not all pollutants are eliminated in many advanced oxidation technologies and requires rethinking of the optimal choice of the technologies applied. The role of percarbonate in Fenton-like processes and in advanced oxidation processes is discussed and has to be re-evaluated. Carbonate as a ligand stabilizes transition metal complexes in uncommon high oxidation states. These high-valent complexes are intermediates in electrochemical water oxidation processes that are of importance in the development of new water splitting technologies. HCO_3^- and CO_3^{2-} are also very good hole scavengers in photochemical processes of semiconductors and may thus become key participants in the development of new processes for solar energy conversion. In this Account, an attempt to correlate these observations with the properties of carbonates is made. Clearly, further studies are essential to fully uncover the potential of $\text{HCO}_3^-/\text{CO}_3^{2-}$ in desired oxidation processes.



KEY REFERENCES

- Burg, A.; Shamir, D.; Shusterman, I.; Kornweitz, H.; Meyerstein, D. The Role of Carbonate as a Catalyst of Fenton-like Reactions in AOP Processes: $\text{CO}_3^{\bullet-}$ as the Active Intermediate. *Chem. Commun.* **2014**, 50, 13096–13099.¹ This study was the first one to point out that carbonate plays a key role in advanced oxidation processes.
- Illés, E.; Mizrahi, A.; Marks, V.; Meyerstein, D. Carbonate-Radical-Anions, and Not Hydroxyl Radicals, Are the Products of the Fenton Reaction in Neutral Solutions Containing Bicarbonate. *Free Radical Biol. Med.* **2019**, 131, 1–6.² This study points out that OH^\bullet radicals are not formed in the Fenton reaction under physiological conditions and therefore calls for a revision of our understanding of oxidative stress.
- Patra, S. G.; Illés, E.; Mizrahi, A.; Meyerstein, D. Cobalt Carbonate as an Electrocatalyst for Water Oxidation. *Chem. - Eur. J.* **2020**, 26, 711–720.³ This study is the most detailed study of the role of carbonate in electrocatalytic water oxidation.

- Mizrahi, A.; Maimon, E.; Cohen, H.; Kornweitz, H.; Zilbermann, I.; Meyerstein, D. Mechanistic Studies on the Role of $[\text{Cu}^{\text{II}}(\text{CO}_3)_n]^{2-2n}$ as a Water Oxidation Catalyst: Carbonate as a Non-Innocent Ligand. *Chem. - Eur. J.* **2018**, 24, 1088–1096.⁴ This study describes the use of pulse radiolysis in the study of the mechanisms of oxidations by $\text{CO}_3^{\bullet-}$ anion radicals.

1. INTRODUCTION

All aerated solutions contain a mixture of $\text{CO}_2/\text{HCO}_3^-/\text{CO}_3^{2-}$, and their speciation depends on the CO_2 solubility under the partial pressure of CO_2 in the air and on the following equilibria:⁵

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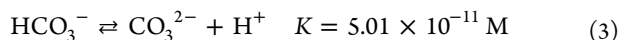
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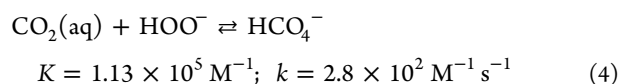
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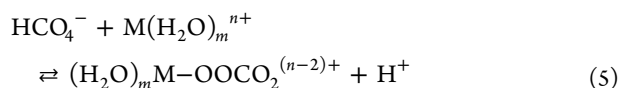
Therefore, one commonly considers the role of $\text{CO}_2/\text{HCO}_3^-/\text{CO}_3^{2-}$ present in solution as a buffer and/or as a proton transfer agent. However, results in recent years have pointed out that the role of $\text{CO}_2/\text{HCO}_3^-/\text{CO}_3^{2-}$ in redox processes is often of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

(a) CO_2 reacts with peroxides via⁶

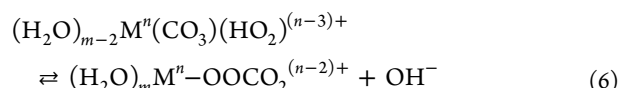
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This reaction is clearly slow in neutral solutions and requires relatively high concentrations of H_2O_2 in order to contribute to redox processes. However, the equilibrium in reaction 4 might shift to the right in the presence of metal cations because of reaction 5:

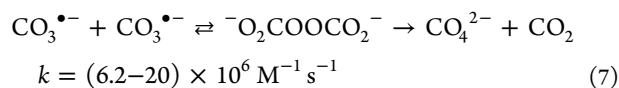


This reaction was shown to be of importance in catalytic oxidations for $\text{M} = \text{Mn}$.^{7,8} Furthermore, reaction 6 was shown to be exothermic and fast, at least for $\text{M} = \text{Co}^{\text{II}}$.¹

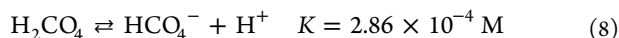


(b) The redox potential of the $\text{CO}_3^{\bullet-}/\text{CO}_3^{2-}$ couple is 1.57 V vs NHE,^{9,10} and that for the $(\text{CO}_3^{\bullet-} + \text{H}^+)/\text{HCO}_3^-$ couple is clearly somewhat higher because of reaction 3. These potentials are considerably lower than those of the $\text{OH}^\bullet/\text{OH}^-$ and $(\text{OH}^\bullet + \text{H}^+)/\text{H}_2\text{O}$ couples. Thus, at all pH values $\text{CO}_3^{\bullet-}$ 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 HCO_3^- and CO_3^{2-} catalyze the Fenton reaction, forming $\text{CO}_3^{\bullet-}$ and not OH^\bullet .^{2,15} HCO_3^- and CO_3^{2-} also act as electrocatalysts for the OER process.^{3,4,16–19} In the absence of other substrates, $\text{CO}_3^{\bullet-}$ decomposes via^{6,20,21}

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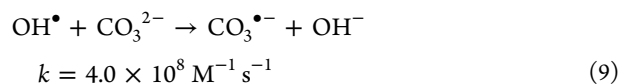


The $\text{CO}_3^{\bullet-}$ anion radical is considerably less reactive than the OH^\bullet radical, and its reactions are more selective.²¹ The $\text{CO}_3^{\bullet-}$

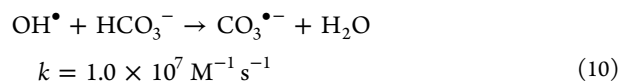
anion radical reacts in most systems via the inner-sphere mechanism.^{9,22}

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

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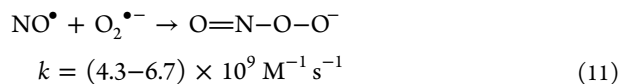


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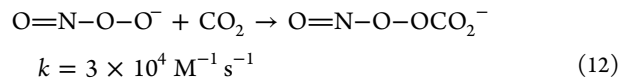


In biological systems it is formed via the following reactions:²⁵

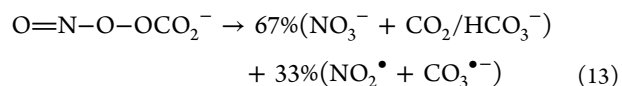
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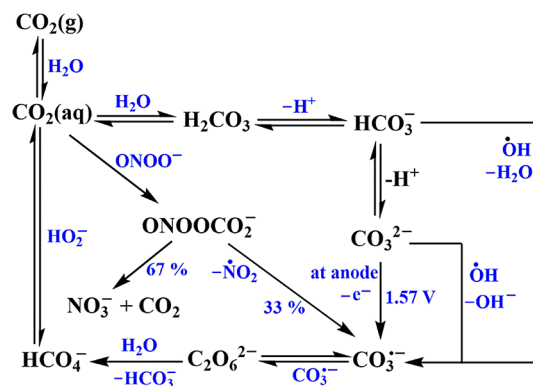


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The $\text{CO}_3^{\bullet-}$ thus formed is believed to be one of the sources of oxidative stress induced by superoxide.^{26–28} $\text{CO}_3^{\bullet-}$ is also formed in several enzymatic processes, e.g., in superoxide dismutase.²⁹ The above-mentioned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

Scheme 1. Mechanisms for the Formation of $\text{CO}_3^{\bullet-}$ and HCO_4^- in the Absence of Transition Metal Complexes



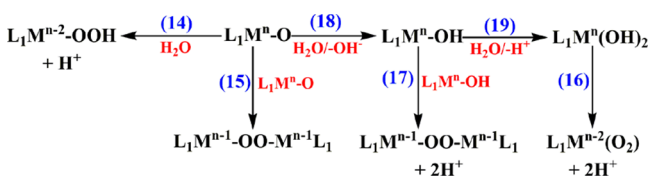
(c) As a strong hard base, carbonate is a very good ligand for high-valent transition metal cations and therefore stabilizes transition metal complexes with higher valence, e.g., Mn^{III} ,³⁰ $\text{Fe}^{\text{IV,III}}$,^{19,31} $\text{Co}^{\text{V/IV,III}}$,³ $\text{Ni}^{\text{IV/III}}$,³² $\text{Cu}^{\text{IV/III}}$,⁴ Ru^{IV} ,³² 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.

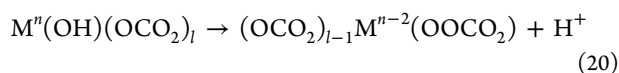
2. ELECTROCATALYTIC WATER OXIDATION BY METAL CARBONATE COMPLEXES

Water oxidation³ is of major importance in understanding the fundamental mechanism of photosynthesis³³ and in addressing modern-day energy challenges by means of water electrolysis^{34,35} and solar energy conversion via photochemical water splitting.^{36–39} 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 2.⁴

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



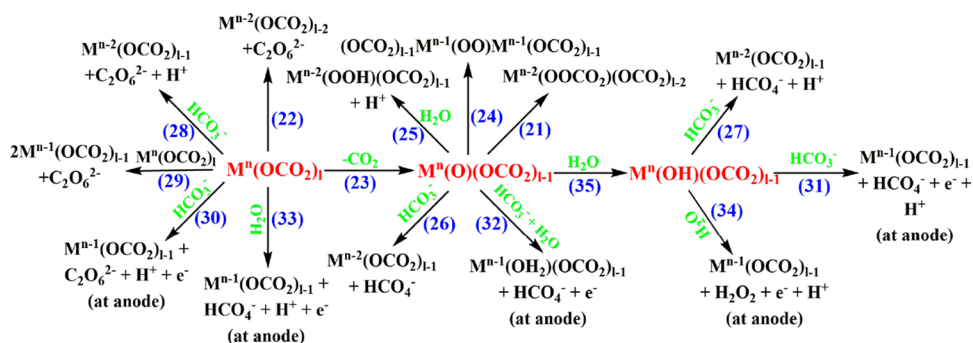
The formation of a percarbonate complex in the presence of carbonate has been reported (reaction 20):⁴⁰



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^n 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.

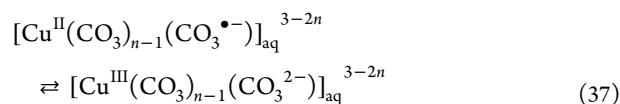
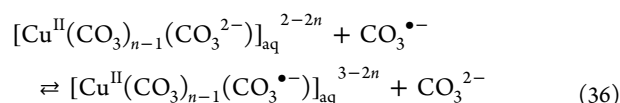
Scheme 3. Various Plausible Processes Involved during Electrocatalytic Water Oxidation by Metal Carbonates in Aqueous Bicarbonate/Carbonate Solutions



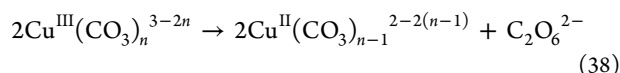
2.1. Homogeneous Electrocatalysis

The first study reporting homogeneous electrocatalytic water oxidation in the presence of $CO_2/HCO_3^-/CO_3^{2-}$ was by Chen and Meyer.¹⁷ They showed that $Cu^{II}(aq)$ with $CO_2/HCO_3^-/CO_3^{2-}$ in the medium acts as an efficient water oxidation catalyst on a variety of working electrodes. The catalytic current increases with $[Cu^{II}]$ with a cathodic shift of the onset potential. The catalytic current depends linearly on $[Cu^{II}]$ in neutral media, while under alkaline conditions it depends on $[Cu^{II}]^2$. 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 $Cu^{III/II}(H_2O)_n$ is >2.3 V vs NHE,⁴¹ which is obviously shifted cathodically by the strong carbonate ligand. However, the authors did not clarify the involvement of either Cu^{III} or Cu^{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^{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 $[Cu^{III}(CO_3)_n]^{3-2n}$ formed by the oxidation of $[Cu^{II}(CO_3)_n]^{2-2n}$ by $CO_3^{\bullet-}$. The results suggested the following oxidation mechanism:⁴



DFT calculations of the NBO charges suggested that significant charge transfer from the CO_3^{2-} to the central metal ion in $Cu^{III}(CO_3)_n^{3-2n}$ takes place. The $Cu^{III}(CO_3)_n^{3-2n}$ thus formed decomposes in a process that obeys second-order kinetics irrespective of the pH of the medium:⁴



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.²³

The analogous systems containing other divalent first-row transition metal cations in the presence of HCO_3^-/CO_3^{2-}

pointed out that Co^{II} in the presence of $>1 \times 10^{-3} \text{ M HCO}_3^- / \text{CO}_3^{2-}$ is an excellent catalyst for electrocatalytic water oxidation.³ During chronoamperometry, a precipitate is formed that serves as a heterogeneous catalyst for the same (vide infra). Electrochemically, three homogeneous processes are observed:

- A relatively small wave is observed at $E_{\text{pa}} \approx 0.71 \text{ V vs Ag/AgCl}$ that is due to the $\text{Co}^{\text{III/II}}$ redox couple, i.e., the carbonate ligands shift the redox potential of the $\text{Co}^{\text{III/II}}$ couple cathodically by ca. 0.9 V.
- A second wave is observed at $E_{\text{pa}} \approx 1.10 \text{ V vs Ag/AgCl}$ that has a considerably larger current (by a factor of >20) than the first peak. This process is attributed to the $\text{Co}^{\text{IV/III}}(\text{CO}_3)_3^{2-/3-}$ redox couple. The observed potential is in good agreement with the results of DFT calculations. The large current is attributed to catalytic oxidation of bicarbonate/carbonate by the Co^{IV} complex to form HCO_4^- via reactions analogous to reactions 26–28 and 31 in Scheme 3.
- A process with very large currents, with a current density of $10.50 \text{ mA}\cdot\text{cm}^{-2}$ at $[\text{Co}^{\text{II}}] = 0.50 \text{ mM}$ at a peak plateau that starts at $>1.2 \text{ V vs Ag/AgCl}$, is due to the formation of $\text{Co}^{\text{V}}(\text{CO}_3)_3^-$, and the observed redox potential is in accord with that calculated using DFT for the $\text{Co}^{\text{V/IV}}(\text{CO}_3)_3^{-/2-}$ couple. The $\text{Co}^{\text{V/IV}}(\text{CO}_3)_3^{-/2-}$ 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, $[\text{Co}^{\text{III/IV/V}}(\text{CO}_3)_3]^{3-/2-/-}$ 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

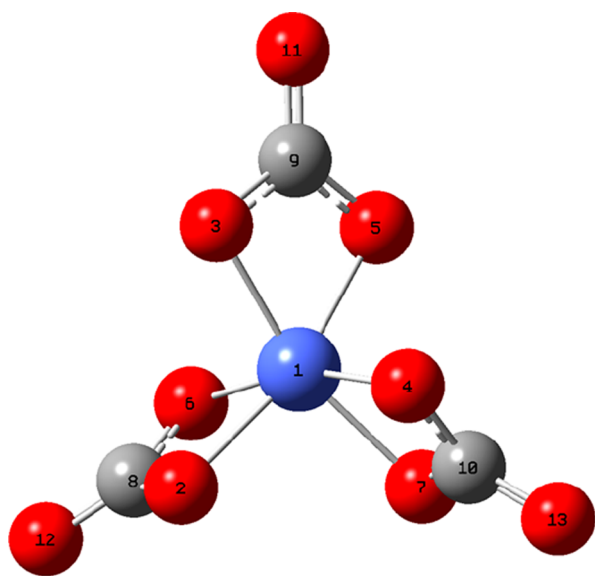


Figure 1. Structure of $[\text{Co}^{\text{V}}(\text{CO}_3)_3]^-$ obtained at the B3LYP/6-311+G(2d,p) level. Reprinted with permission from ref 3. Copyright 2020 Wiley-VCH.

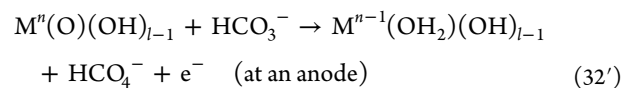
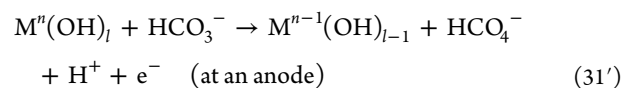
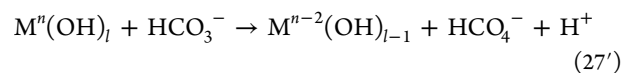
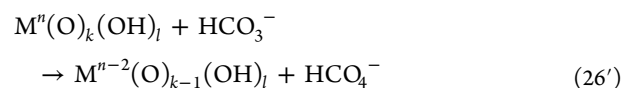
is the ligand getting oxidized. The following are such systems: $\text{Ni}^{\text{II}}(1,4,8,11\text{-tetraazacyclotetradecane})^{2+}$, $\text{Ni}^{\text{II}}\text{L}_2^{2+}$,¹⁶ $\text{Cu}^{\text{II}}(N,N'\text{-bis}(2,6\text{-dimethylphenyl})\text{-}2,6\text{-pyridinedicarboxamidate})$, $\text{Cu}^{\text{II}}\text{L}_3$,⁴⁴ and $\text{Al}^{\text{III}}(\text{TMPyP})$ (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 NiL_2^{2+} complex, the role of carbonate is due to the lowering of the redox potentials of the $\text{Ni}^{\text{III/II}}$ and $\text{Ni}^{\text{IV/III}}$ couples and to the reactions shown in Scheme 4. Recently the process of water oxidation by $\text{Ni}^{\text{II}}\text{L}_2^{2+}$ 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.

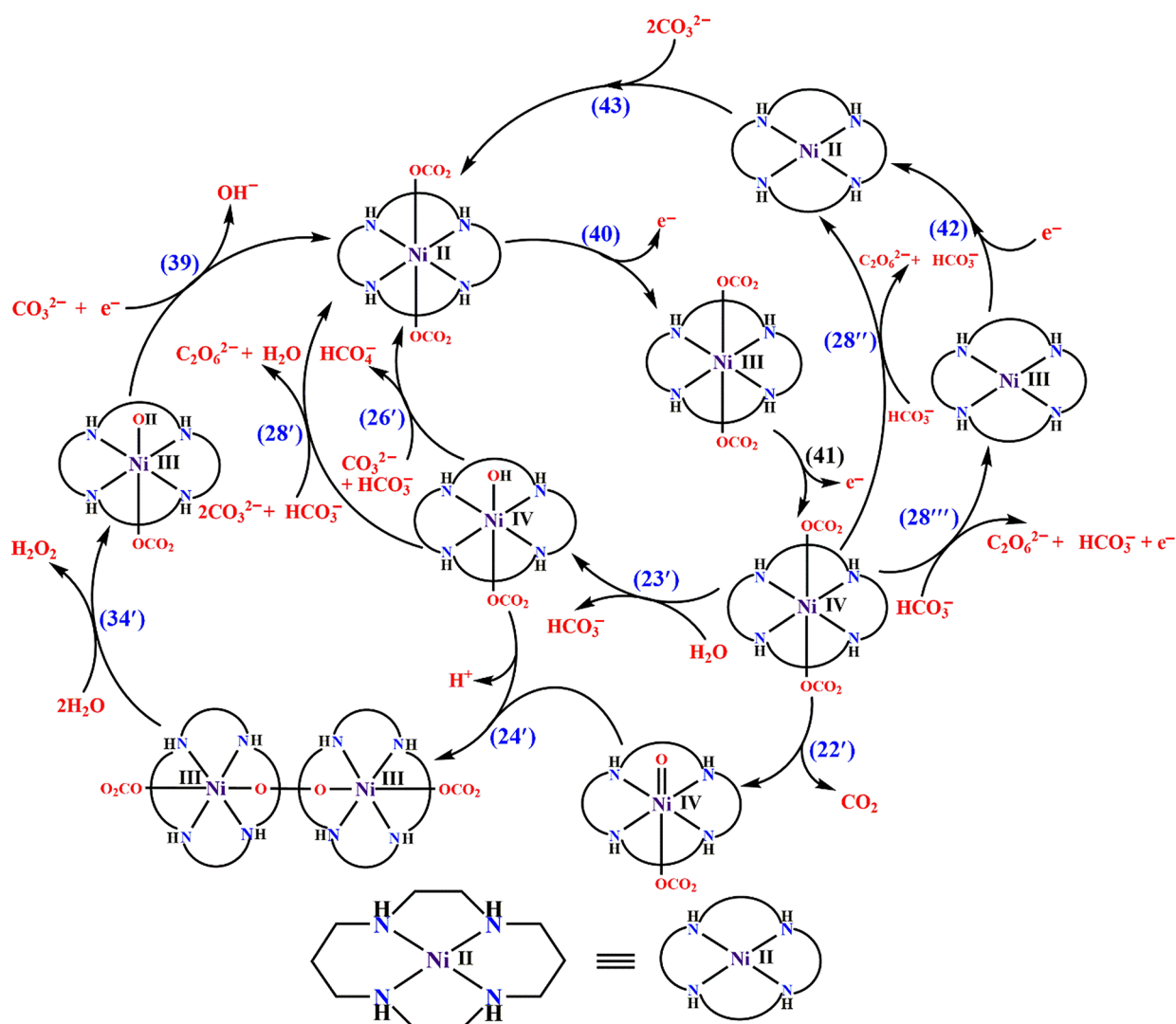
CuL_3 also acts as an active catalyst for water oxidation in the presence of carbonate at pH 9.0–11.0. The proposed mechanism is a “proton shuttle” mechanism, as shown in Scheme 5.⁴⁴ However, the possible oxidation of carbonate to HCO_4^- and $\text{C}_2\text{O}_6^{2-}$ was not considered⁴⁴ and cannot be ruled out. Carbonate was also shown to act as a cocatalyst in electrocatalytic water oxidation by an aluminum porphyrin ($\text{Al}(\text{TMPyP})$).⁴⁵ This catalytic system forms H_2O_2 as the major product. The suggested mechanism involves the formation of an Al^{III} –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 $\text{OH}^-/\text{H}_2\text{O}$. 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:



An example of the latter type of catalysis is the report that $\text{Ni}^{\text{II}}(\text{aq})$ adsorbed on a SiO_2 sol–gel matrix and mixed with graphite acts as an OER electrocatalyst in solutions containing $\text{HCO}_3^-/\text{CO}_3^{2-}$ with a current proportional to $[\text{HCO}_3^-/\text{CO}_3^{2-}]$.^{46,47} Clearly one cannot rule out that ligand exchange in the sol–gel matrix transforms the $\text{Ni}^{\text{II}}(\text{aq})$ into carbonate

Scheme 4. Electrocatalytic Processes Occurring during Electrocatalytic Water Oxidation Using the Ni^{II}L₂²⁺ Complex in HCO₃⁻/CO₃²⁻

complexes. In this study it was proposed that the catalytic process involves the formation of CO₃^{•-} radical anions.⁴⁶

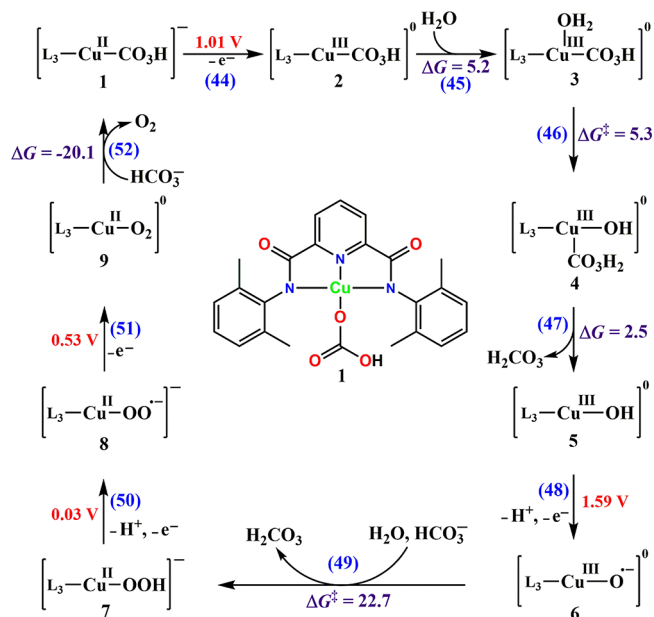
In the study of homogeneous electrocatalysis of the OER in solutions containing Co^{II} and HCO₃⁻/CO₃²⁻, it was noted that during chronoamperometry a green precipitate of Na₃[Co(CO₃)₃] is formed.³ This precipitate on the anode surface serves as an excellent heterogeneous catalyst in the presence of bicarbonate/carbonate. This catalytic process was shown to be in agreement with reactions analogous to reactions 22 and 26–34 in Scheme 3. DFT calculations suggest that the active species in these process is the Co^V(CO₃)₃⁻ complex.³

In an analogous study,¹⁸ a precipitate was formed on an anode by electrolysis of a CO₂-saturated solution containing Fe^{II}(aq) and HCO₃⁻. The thin film thus formed contained Fe^{III}, O₂²⁻, OH⁻, and CO₃²⁻. This film was shown to be a good OER electrocatalyst for which the current increased with [HCO₃⁻/CO₃²⁻].¹⁸ 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 Fe^{II} ions proves that the mechanism does not

involve reduction of the Fe ions in the precipitate to Fe^{II} and dissolution to the aqueous phase.

An analogous study involving nickel carbonate solutions⁴⁸ resulted in the formation of an analogous Ni^{III}(HCO₃⁻)_n³⁻ⁿ/Ni^{III}(CO₃²⁻)_n³⁻²ⁿ precipitate on the anode that is a good electrocatalyst for water oxidation in solutions containing Ni^{II} and HCO₃⁻/CO₃²⁻. However, the precipitate dissolves during electrolysis when no Ni^{II} ions are present in solution. This proves that the catalytic step involves the reduction of a Ni^{IV} complex into a Ni^{II} complex that is soluble, i.e. via reactions analogous to reactions 21, 22, 25, and 26–28 in Scheme 3. In another study,⁴⁹ an amorphous nickel carbonate nanowire array on a nickel foam (NiCO₃/NF) anode was prepared. This modified electrode is a very good electrocatalyst for water oxidation in solutions containing only HCO₃⁻/CO₃²⁻.⁴⁹ 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.¹⁹

Scheme 5. Structure of the Complex $\text{Cu}^{\text{II}}(\text{N,N}'\text{-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamidate})$ ($\text{Cu}^{\text{II}}\text{L}_3$) and its Electrocatalytic Role in Water Oxidation in the Presence of Bicarbonate^a



^aReprinted from ref 44. Copyright 2017 American Chemical Society.

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 $\text{HCO}_3^-/\text{CO}_3^{2-}$. 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 $\text{CO}_3^{\bullet-}/\text{CO}_3^{2-}$ and $\text{OH}^{\bullet}/\text{OH}^-(\text{aq})$ or $(\text{OH}^{\bullet} + \text{H}_3\text{O}^+)/2\text{H}_2\text{O}$ couples suggests that the holes formed photochemically in semiconductors will oxidize $\text{HCO}_3^-/\text{CO}_3^{2-}$ 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).¹³ The condition for this is that adsorption of $\text{HCO}_3^-/\text{CO}_3^{2-}$ 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 $\text{CO}_3^{\bullet-}$ or $\text{C}_2\text{O}_6^{2-}$. Indeed, several studies have pointed out that the presence of $\text{HCO}_3^-/\text{CO}_3^{2-}$ in the system catalyzes photochemical water oxidation.^{14,50,51} Furthermore, it has been shown that photochemical oxidation of SO_2 in aqueous media is enhanced by the presence of carbonate.¹¹ It was proposed that the formation of $\text{CO}_3^{\bullet-}$ 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 results³² point out that precipitates of cobalt and nickel carbonate act as photoelectrocatalysts for water and methanol oxidations.

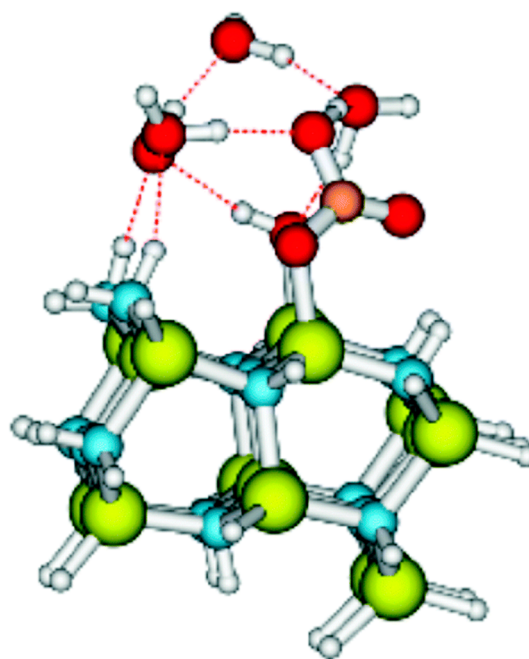


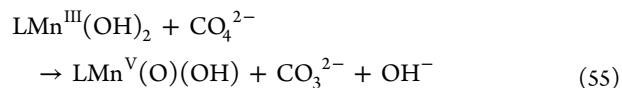
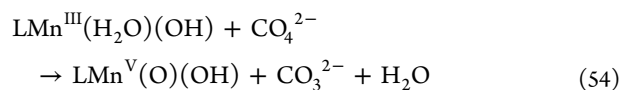
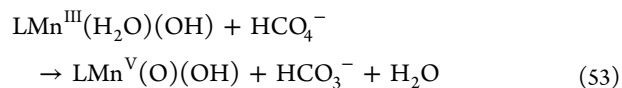
Figure 2. Structure of carbonated GaN. Ga, yellow; C, brown; H, white; O, red; N, blue. Reprinted with permission from ref 13. Copyright 2016 The PCCP Owner Societies.

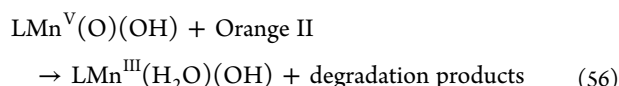
4. PERCARBONATE AS AN OXIDATION AGENT

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

1. An inorganic percarbonate salt, e.g., sodium percarbonate ($\text{Na}_2\text{CO}_4 \cdot 1.5\text{H}_2\text{O}_2$), 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_2O_2 upon dissolution followed by Fenton-like and/or photolytic processes and/or reaction with O_3 , often involving $\text{CO}_3^{\bullet-}$ anion radicals.^{52–55}
2. The percarbonate is formed in situ via the reaction of H_2O_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.

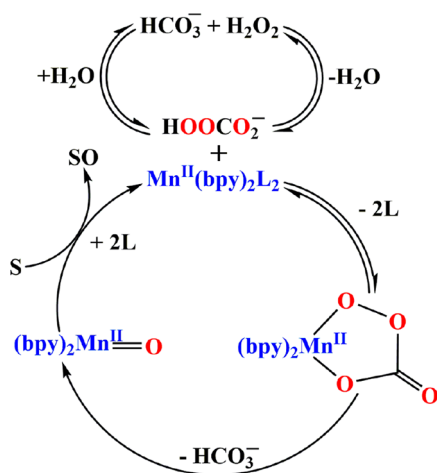
The first peroxocarbonate complex of a transition metal was reported by Hashimoto et al.⁵⁶ It was formed via the reaction of a bis(μ -hydroxo)diiron(III) complex with H_2O_2 and CO_2 . Oxidative degradation of an organic dye, Orange II, by $\text{Mn}^{\text{III}}(\text{TPPS})$ (TPPS = 5,10,15,20-tetrakis(4-sulfonatophenyl)-21H,23H-porphyrin) in carbonate buffer was proposed to involve the formation of a percarbonate–metal complex that undergoes decomposition to form a $\text{Mn}^{\text{IV}}=\text{O}$ species and degrades Orange II via reactions 53–56:⁸





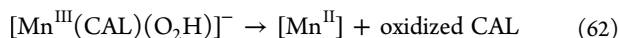
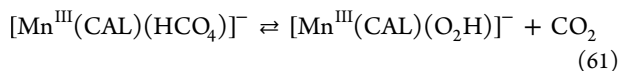
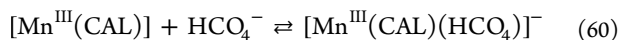
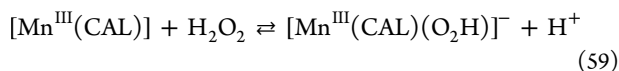
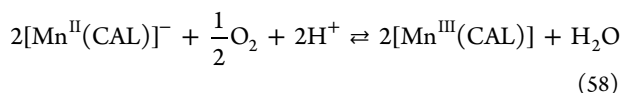
Catalytic oxidation of azo dyes by $[\text{Mn}^{\text{II}}(\text{bpy})_2\text{Cl}_2]$ and $[\text{Mn}_2^{\text{III/IV}}(\mu\text{-O})_2(\text{bpy})_4](\text{ClO}_4)_3$ also involves a similar mechanism.⁵⁷ As reactions 53–55 probably do not involve an oxygen atom transfer, it is reasonable to propose that intermediates in which the percarbonate is ligated to the central Mn^{III} are formed (Scheme 6).

Scheme 6. Proposed Mechanism for the Degradation of Substrate (S) by the Complex $\text{Mn}(\text{bpy})_2\text{L}_2$ (L = Water or Carbonate) Formed from $\text{Mn}(\text{bpy})_2\text{Cl}_2$ or $[\text{Mn}_2^{\text{III/IV}}(\mu\text{-O})_2(\text{bpy})_4](\text{ClO}_4)_3$



^aReprinted with permission from ref 57. Copyright 2010 Royal Society of Chemistry.

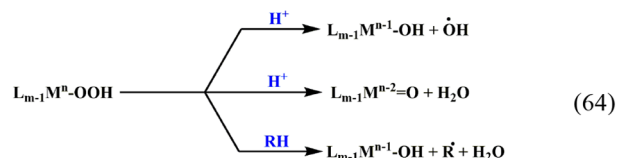
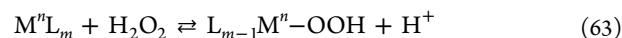
Oxidation of calmagite (H_3CAL) dye in aqueous solution using H_2O_2 at pH 7.5–9.0 is accelerated considerably in the presence of HCO_3^- .⁵⁸ The proposed mechanism involves the following steps:



It should be pointed out that $[\text{Mn}^{\text{III}}(\text{CAL})(\text{HCO}_4)]^-$ might also decompose to form a Mn^{IV} complex and $\text{CO}_3^{\bullet-}$ anion radical. The degradation of various dyes using $\text{Mn}/\text{H}_2\text{O}_2/\text{HCO}_3^-$ has been reported.⁷ It was shown that under visible light percarbonate catalyzes the degradation of rhodamine B in the presence of FeOCl .⁵⁹ Oxidations of primary alcohols to carbonyl compounds using catalytic amounts of percarbonate and dichromate were also reported.⁶⁰

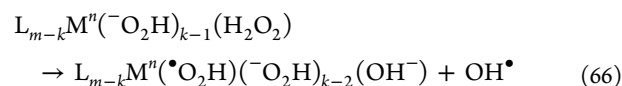
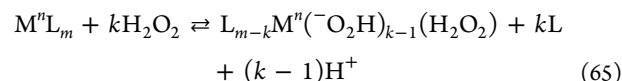
5. ROLE OF BICARBONATE IN FENTON AND FENTON-LIKE REACTIONS

The Fenton reaction, $\text{Fe}(\text{H}_2\text{O})_6^{2+} + \text{H}_2\text{O}_2$, 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 H_2O and/or another peroxide replaces H_2O_2 , were shown to proceed via a variety of mechanisms:⁷¹



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

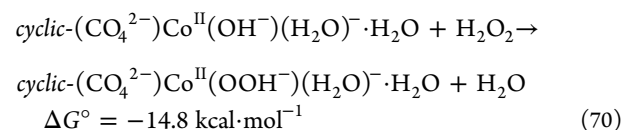
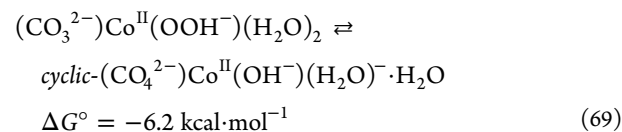
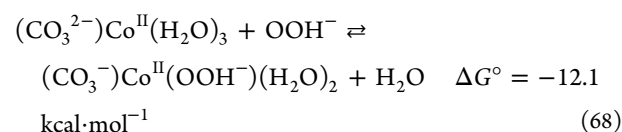
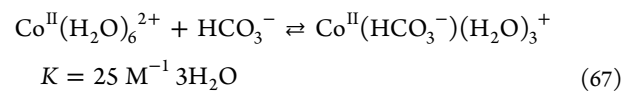
Still, nearly all of the recent articles cite the Fenton reaction as proceeding via the formation of OH^\bullet . Furthermore, recent results point out that in systems where it is difficult to oxidize the central cation, the central cation is not oxidized in the process, and the reaction proceeds via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

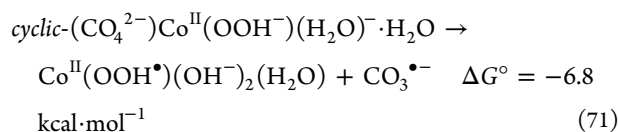


Reaction 66 indicates that H_2O_2 ligated to a central cation can oxidize another ligand that has no bond with it. DFT calculations verified this for other ligands, including carbonate.⁷⁴

For the carbonate-containing systems, three cases were studied in detail:

(I) The reaction of H_2O_2 with $\text{Co}(\text{H}_2\text{O})_6^{2+}$ (10–25.0 mM) in the presence of 0–0.6 mM HCO_3^- was studied. Under these conditions, $[\text{Co}^{\text{II}}(\text{H}_2\text{O})_6^{2+}] > [\text{Co}^{\text{II}}(\text{H}_2\text{O})_5(\text{HCO}_3)^+]$. The following reactions were observed:¹

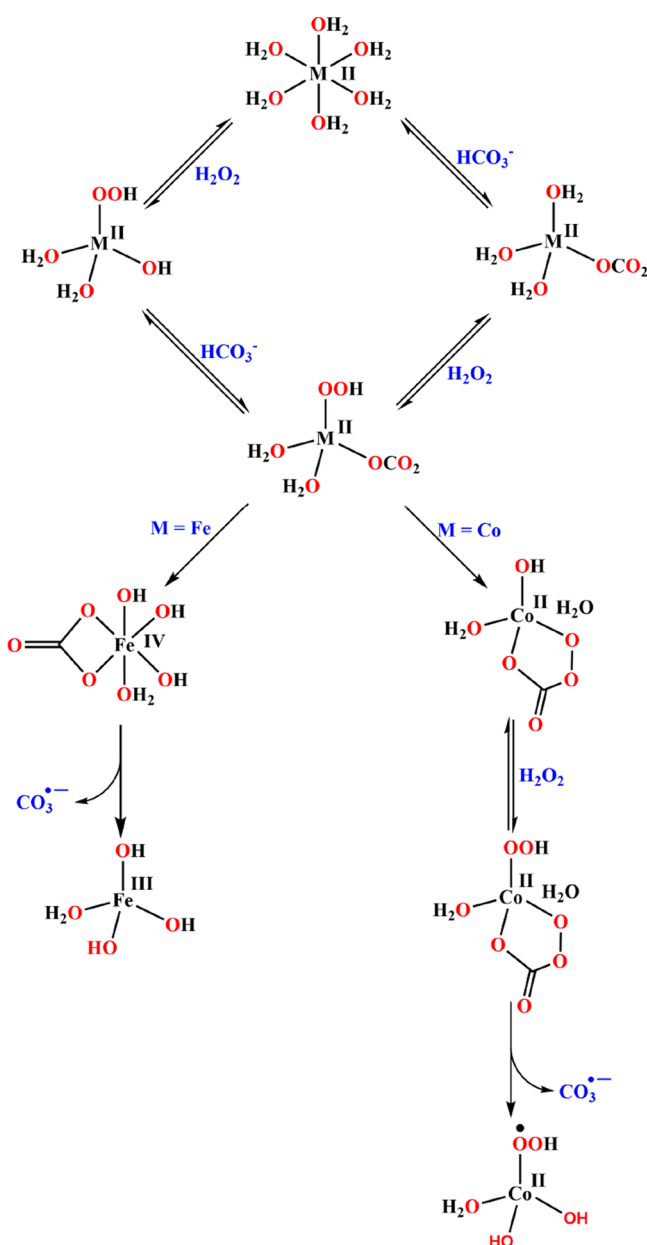




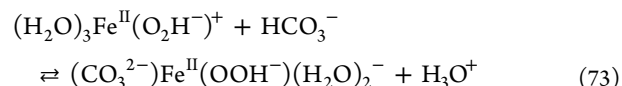
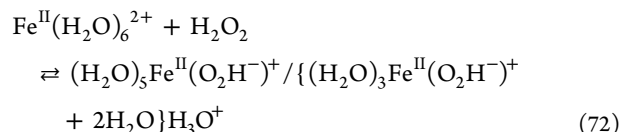
These results point out the following: (a) No OH^\bullet radicals are formed. Though a percarbonate ligand is formed as an intermediate in the process, the active oxidizing agent formed is the $\text{CO}_3^{\bullet-}$ anion radical. (b) The central Co^{II} cation is not oxidized during the process. The process is analogous to reactions 65 and 66 with $k = 2$. Thus, in AOPs with $\text{Co}^{\text{II}}(\text{H}_2\text{O})_6^{2+}$ and H_2O_2 , the active species is $\text{CO}_3^{\bullet-}$ and not OH^\bullet as usually assumed.⁷⁵ The mechanism is outlined in Scheme 7.

(II) The Fenton reaction at pH 7.4 in solutions containing 2.0×10^{-5} M $\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6^{2+}$, 0–3.0 mM HCO_3^- , and 0–0.8 mM

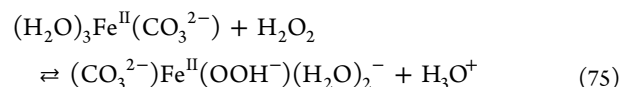
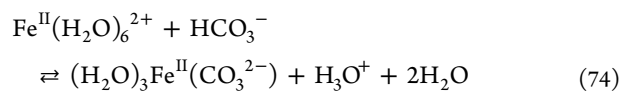
Scheme 7. Proposed Mechanisms of the Fenton Reaction for $\text{M}(\text{H}_2\text{O})_6^{2+}$ ($\text{M} = \text{Fe}, \text{Co}$) in H_2O



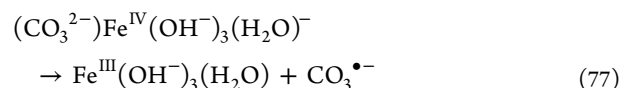
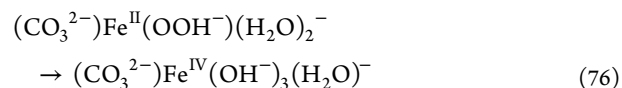
H_2O_2 was studied. Under these conditions, $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_3(\text{HCO}_3^-)]^+$ constitutes less than 3% of the $\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6^{2+}$. However, the observed rate constants increase dramatically with $[\text{HCO}_3^-]$. The following reactions were observed:



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

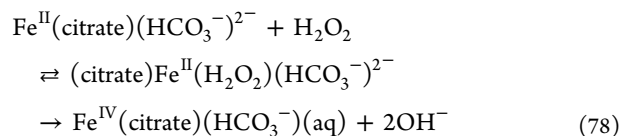


The mechanism is shown in Scheme 7. In the Fe Fenton reaction, metal ion oxidation occurs, whereas in the Co Fenton-like reaction, the metal oxidation state does not change. One more difference is that for Co a cyclic percarbonate complex is formed, but this does not occur in the case of Fe. The $(\text{CO}_3^{2-})\text{Fe}^{\text{II}}(\text{OOH}^-)(\text{H}_2\t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

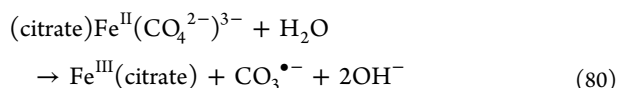
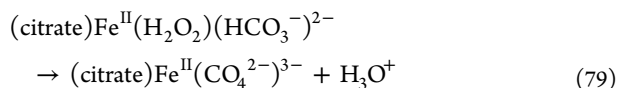


Thus, also in this system, the reactive oxygen species (ROS) formed under physiological conditions (i.e., in the presence of ~ 1.0 mM HCO_3^-) is not the OH^\bullet radical as commonly assumed.

(III) The results concerning the Fenton reaction in the presence of HCO_3^- suggest that under physiological conditions, the Fenton reaction yields $\text{CO}_3^{\bullet-}$ and not OH^\bullet radicals as commonly assumed, and this is of major importance. However, since in biological media Fe^{II} ions are not present as $\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6^{2+}$ but appear in the mobile pool mainly as $\text{Fe}^{\text{II}}(\text{citrate})$, the Fenton reaction was studied¹⁵ in solutions containing 2.0×10^{-5} M $\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6^{2+}$, 0–2.0 mM sodium citrate, 0–8.0 mM NaHCO_3 , and 0–0.39 mM H_2O_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



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



where $(\text{citrate})\text{Fe}^{\text{II}}(\text{H}_2\text{O}_2)(\text{HCO}_3^-)^{2-}$ 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 $\text{CO}_3^{\bullet-}$

As stated in the Introduction, $\text{CO}_3^{\bullet-}$ is formed biologically via the reaction of peroxonitrite with CO_2 (reactions 11–13).⁷⁶ The formation of NO_2^{\bullet} and $\text{CO}_3^{\bullet-}$ is believed to be the main mechanism via which $\text{O}_2^{\bullet-}$ causes oxidative stress.^{77,78} $\text{CO}_3^{\bullet-}$ is also formed enzymatically by the enzymes superoxide dismutase (Cu,Zn-SOD, SOD-1)⁷⁹ and xanthine oxidase.⁸⁰

The $\text{CO}_3^{\bullet-}$ 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 $\text{HCO}_3^-/\text{CO}_3^{2-}$ that is always present in water,^{75,92–96} and sometimes by the addition of $\text{HCO}_3^-/\text{CO}_3^{2-}$ 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^{\bullet} 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 $\text{Fe}^{\text{IV}}(\text{aq})$ and not OH^{\bullet} 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 $\text{Fe}^{\text{IV}}(\text{aq})$ with $\text{CO}_3^{\bullet-}$ 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 $\text{HCO}_3^-/\text{CO}_3^{2-}$ 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 $\text{CO}_3^{\bullet-}/\text{CO}_3^{2-}$ and $(\text{CO}_3^{\bullet-} + \text{H}^+)/\text{HCO}_3^-$ couples is considerably lower than that of the $\text{OH}^{\bullet}/\text{OH}^-$ and $(\text{OH}^{\bullet} + \text{H}^+)/\text{H}_2\text{O}$ couples. Therefore, HCO_3^- and CO_3^{2-} act as cocatalysts in water oxidation and are involved in Fenton-like processes.
3. Percarbonate, as a bidentate ligand, is easily formed in the presence of transition metal cations with fast ligand exchange properties, $\text{HCO}_3^-/\text{CO}_3^{2-}$, and peroxides.

The results obtained thus far point out that the presence of $\text{HCO}_3^-/\text{CO}_3^{2-}$ 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 $\text{HCO}_3^-/\text{CO}_3^{2-}$ 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 $\text{HCO}_3^-/\text{CO}_3^{2-}$ in catalytic oxidations of specific substrates performed electrochemically, photochemically, and photo-electrochemically. Also, the role of $\text{HCO}_3^-/\text{CO}_3^{2-}$ in Fenton-like processes using other peroxides (e.g., $\text{S}_2\text{O}_8^{2-}$, HSO_5^- , 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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Notes

The authors declare no competing financial interest.

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Amir Mizrahi received his Ph.D. in chemistry from Ben-Gurion University under the supervision of Prof. Dan Meyerstein and Prof. Israel Zilbermann. Since 2013 he has been employed by NRCN as a senior research scientist in the Inorganic Chemistry Department. His main field of interest is the redox chemistry of transition metals in aqueous/organic solutions, with an emphasis on full characterization of their reaction mechanisms and various reaction intermediates studied by spectroscopic, kinetic, and electrochemical techniques.

Dan Meyerstein studied chemistry at The Hebrew University of Jerusalem, earning his M.Sc. in 1961 and his Ph.D. in 1965. After a postdoctoral fellowship at Argonne National Laboratory in the USA, he joined Ben-Gurion University in 1968 and was promoted to Professor in 1978. He has served as the President of the Israel Chemical Society in 1988–1991, deputy rector of Ben-Gurion University in 1990–1994, and President of Ariel University in 1995–2012. He is now Professor of Inorganic Chemistry at Ariel University and Professor Emeritus at Ben-Gurion University. His research interests include reaction mechanisms, catalysis, radical processes, radiation chemistry, electrochemistry, and nanochemistry.

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