Computational Study of CO₂ Reduction Catalyzed by Iron(I) Complex at Different Spin States: Cooperativity of Hydrogen Bonding and Auxiliary Group Effect

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ABSTRACT: To explore alternative approaches to the CO₂ reduction to formate and provide an insight into the spin state effect on the CO₂ reduction, we theoretically designed a kind of low-valence iron(I) model complex, whose doublet, quartet, and sextet states are denoted as 2Fe(I), 4Fe(I), and 6Fe(I), respectively. This complex is featured with an iron(I) center, which bonds to a 1,2-ethanediamine (en) and a 2-hydroxy-biphenyl group. Reaction mechanisms for the CO₂ reduction to formate catalyzed by this iron(I) model complex were explored using density functional theory (DFT) computations. Studies showed that the univalent iron(I) compound can efficiently fix and activate a CO₂ molecule, whereas its oxidized forms with trivalent iron(III) or bivalent iron(II) cannot activate CO₂. For the iron(I) compound, it was found that the lowest spin state 2Fe(I) is the most favorable for the CO₂ reduction as the reactions barriers involving 2Fe(I), 4Fe(I), and 6Fe(I) are 25.6, 37.2, and 35.9 kcal/mol, respectively. Yet, a photosensitizer-free visible-light-mediated high–low spin shift from 4Fe(I) and 6Fe(I) to 2Fe(I) is likely through the reverse intersystem crossing (RIC) because the 4Fe(I) and 6Fe(I) compounds have strong absorption in the visible-light range. Notably, the synergistic interaction between the hydrogen bonding from the auxiliary hydroxyl group in the 2-hydroxy-biphenyl moiety to CO₂ and an intermediate five-membered ring promotes the proton transfer, leading to the formation of the —COOH moiety from CO₂ and the Fe−O bond. With the addition of H₂, one H₂ molecule is split by the Fe−O bond and thus serves as H atom sources for both the CO₂ reduction and the recovery of the auxiliary hydroxyl group. The present theoretical study provides a novel solution for the challenging CO₂ reduction, which calls for further experimental verifications.

INTRODUCTION

Excessive CO₂ has been released into the atmosphere due to the large-scale fossil fuel consumption. This has generated detrimental environmental consequences and forced us to mitigate the impacts of CO₂ and prepare for potential energy crises. The ideal solution is the cyclic utilization of CO₂, which serves as a cheap, abundant, and nontoxic C1 building block for value-added chemicals. To this end, the CO₂ hydrogenation with 100% atom economy to formic acid and its derivatives is a particularly significant and promising route. In the past two decades, steady progresses have been achieved in exploring diverse routes of homogeneous catalytic hydrogenation of CO₂. However, the majority of reported catalysts are based on noble metals, such as rhodium, ruthenium, and iridium, which do not meet economic sustainability and environmental safety, and further, their uses require very demanding conditions such as high temperature and/or acidic solutions. Consequently, there are growing interests in developing catalytic systems using earth-abundant and non-noble (base) metals. For instances, base-metal catalysts based on iron, cobalt, nickel, copper, and manganese have been employed to catalyze the hydrogenation of CO₂, but their catalytic performances so far are well below those based on precious transition metals. Therefore, it is highly desirable to develop high-efficient and low-cost base-metal catalysts to produce useful chemical feedstock such as formic acid from CO₂ and H₂.

Indeed, the exploration of high-efficient iron-based catalysts is a very active research field since iron is one of the most abundant and cheapest base metals on Earth. The uniqueness of iron lies in its variable oxidation states (I, II, and III) and high- and low-spin states in its complexes. Recent studies showed that the regulation of the oxidation state of catalysts is an important strategy for designing better-performing catalysts for the CO₂ reduction. Complexes with the iron oxidation state II or III have been extensively tested. For instances, the groups of Laurenczy and Beller, Milstein, Gonsalvi, Hazari and Bernskoetter, etc. have developed several well-differentiated iron(II) and iron(III) complexes with improved catalytic performances. Therefore, it is highly desirable to develop high-efficient and low-cost base-metal catalysts to produce useful chemical feedstock such as formic acid from CO₂ and H₂.
defined phosphine iron complexes, which can catalyze the hydrogenation of \( \text{CO}_2 \) to formic acid. The Zhu27 and Renaud28 groups independently reported the hydrogenation of \( \text{CO}_2 \) to formate catalyzed by phosphine-free iron cyclopentadienone (IC) complex under an air- and moisture-tolerant environment. Yang et al. further revealed a self-promoted mechanism of this reaction by performing density functional theory (DFT) computations.29

Compared to the oxidation states II and III, iron (I) complexes are relatively few and have been less investigated, though in the literature they have been employed to catalyze certain reactions without the participation of \( \text{CO}_2 \). For example, there are \( \text{C}−\text{H} \) bond aminations catalyzed by \( \text{Ar}^k\text{Fe}^l \) (\( \text{Ar}^k = 5\)-mesityl-1,9-(2,4,6-\( \text{Ph}_3\text{C}_6\text{H}_2 \))dipyrrin)30 and \( \text{N}_2 \) fixation and activation using nitrogenase or its mimics.31 However, to the best of our knowledge, the \( \text{CO}_2 \) reduction catalyzed by iron(I) compounds is seldom reported and only applied to certain limited systems, for example, electrochemical conversion of \( \text{CO}_2 \) to \( \text{CO} \) catalyzed by iron complexes with an \( \text{N}_2\text{O}_2 \)-type \( \text{N}_2\text{N}′ \)-bis(salicylaldehyde)-1,2-phenylenediamine salophen ligand.32 Thus, it is interesting and valuable to gain a deep insight into the \( \text{CO}_2 \) reduction catalyzed by iron(I) compounds and to expand the applications of inexpensive iron-based catalysts. Regarding the less common iron(I) complexes, additional ligands are often required to stabilize the metal center. In recent years, multiform ligands have been experimentally synthesized and employed to stabilize the central \( \text{Fe}^+ \) ion in several 3d7/3d54s2 high-spin iron(I) complexes, for example, 3,6-di-tert-butyl-1,8-bis((diter-t-butylphosphino)methyl)-carbazole,33 5-mesityl-1,9-(2,4,6-\( \text{Ph}_3\text{C}_6\text{H}_2 \))dipyrrin,30 1,3-dicyclohexylimidazol-2-ylidene (ICy),34 and N-heterocyclic carbenes (NHCs).35

To explore the potential applications of iron(I)-based catalytic systems to the \( \text{CO}_2 \) reduction, here, we theoretically designed a kind of low-valence iron(I) model complex where the iron(I) center binds to an ethanediamine (en) and a 2-hydroxy-biphenyl group. This model system can exist in three spin states, doublet \( ^2\text{Fe}^\text{(I)} \), quartet \( ^4\text{Fe}^\text{(I)} \), and sextet \( ^6\text{Fe}^\text{(I)} \). The selection of 2-hydroxy-biphenyl is based on the reported gold(I) complex with a phosphine-free protonated 2-(2-pyridyl)-phenyl ligand,36 except that we replaced the protonated 2-(2-pyridyl) group with a phenol, which contains a hydroxyl group. The role of ethanediamine is to safeguard the “naked” iron(I) species by improving the stabilities of \( ^2\text{Fe}^\text{(I)} \), \( ^4\text{Fe}^\text{(I)} \), and \( ^6\text{Fe}^\text{(I)} \). In this work, the hydrogenation of \( \text{CO}_2 \) to formate catalyzed by the above-designed low-valence iron(I) catalyst was investigated by performing DFT

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**Figure 1.** Optimized structures of the designed iron(I)-based complex at the spin states \( ^2\text{Fe}^\text{(I)} \), \( ^4\text{Fe}^\text{(I)} \), and \( ^6\text{Fe}^\text{(I)} \). The bond lengths are in Å, and the free energies are in kcal/mol.

**Figure 2.** Simulated UV–vis absorption spectroscopies and the designated d–d transitions in the range of visible light.
calculations, aiming at providing a novel idea of iron-based catalyst design for the CO₂ reduction.

### RESULTS AND DISCUSSION

**Geometries of \(^{2}\text{Fe}(I), \ ^{4}\text{Fe}(I), \text{and} \ ^{6}\text{Fe}(I)\) States with Intramolecular Hydrogen Bonding and Spin Shift among Spin States.** Iron-based complexes with distinctive electronic and coordinative unsaturation usually possess enhanced reactivity in certain reactions and play an important role as either reagents or catalysts.\(^{37,38}\) Our interest here is in iron complexes with the less common iron(I) oxidation state (3d⁷ and 3d⁵4s²), as we intend to gain an insight into their electronic structure characteristics and explore their potential applications in the CO₂ reduction. To achieve these goals, we designed a low-valence iron(I) model complex, where the iron(I) center binds to an ethanediamine (en) and a 2-hydroxy-biphenyl group. Figure 1 depicts the optimized structures of this iron(I)-based complex at the doublet state \(^{2}\text{Fe}(I)\), the quartet state \(^{4}\text{Fe}(I)\), and the sextet state \(^{6}\text{Fe}(I)\). Interestingly, it is found that the ground state of the low-valence iron(I) model complex is the quartet state \(^{4}\text{Fe}(I)\). Although the doublet state \(^{2}\text{Fe}\) and the sextet state \(^{6}\text{Fe}(I)\) have higher energies by 30.3 and 25.7 kcal/mol than \(^{4}\text{Fe}(I)\), their geometric parameters are very close (see Figure 1). The plots of the spin density at the three states revealed the similar localizations of the most spin density (unpaired electrons) around the metal center (see Figure S1 in the Supporting Information).

We looked into the electronic excitation properties of the iron(I)-based complex involving \(^{2}\text{Fe}(I)\), \(^{4}\text{Fe}(I)\), and \(^{6}\text{Fe}(I)\), in virtue of simulated UV–vis absorption spectroscopy. As depicted in Figure 2, the maximum absorption is in the range of ultraviolet for all three states. The maximum absorption intensities for \(^{4}\text{Fe}(I)\) and \(^{6}\text{Fe}(I)\) are almost 3 times higher than that for \(^{2}\text{Fe}(I)\). Of particular, in the range of visible light, there is a secondary maximum absorption near 580 nm wavelength for \(^{2}\text{Fe}(I)\) and \(^{4}\text{Fe}(I)\), respectively, and the corresponding absorption intensity for \(^{4}\text{Fe}(I)\) is about 1.5 times higher than that for \(^{2}\text{Fe}(I)\). There is a secondary maximum absorption near 670 nm wavelength for \(^{4}\text{Fe}(I)\), and its absorption intensity is 2 times higher than that for \(^{2}\text{Fe}(I)\). Since \(^{4}\text{Fe}(I)\) and \(^{6}\text{Fe}(I)\) have much stronger excitations through d–d transition than \(^{2}\text{Fe}(I)\), there is a possibility for the photosensitizer-free visible-light-mediated high–low spin shift from the stable quartet or sextet state to the less stable doublet state through reverse intersystem crossing (RISC)\(^{39,40}\) (see Figure 1). Here, it should be mentioned that RISC is usually defined as a process of energy transfer from the excited triplet (high) state back to the singlet (low) state in previous studies.\(^{40}\) In addition, vertical ionization energies (IE) are calculated at the M06/6-311+G(d,p)/def2tzvp level to be 6.43, 6.67, and 4.67 eV for \(^{2}\text{Fe}(I)\), \(^{4}\text{Fe}(I)\), and \(^{6}\text{Fe}(I)\), respectively.

It should be noted that the distance between the hydrogen of the hydroxyl group and the carbon bonding to Fe(I) (H1−C1) is about ~2.2 Å at all \(^{2}\text{Fe}(I)\), \(^{4}\text{Fe}(I)\), and \(^{6}\text{Fe}(I)\) states (marked in Figure 1), which is much shorter than the sum of van der Waals radius between C and H atoms (~2.9 Å). Thus, it is safe to say that there is an intramolecular hydrogen bond O−H⋯C, where the O−H bond (~0.98 Å) is slightly stretched, compared with the value in phenol (0.960 Å) and in 2-hydroxy-biphenyl (0.964 Å). Like normal hydrogen bonds, the stretching vibrations of the O−H bond are red-shifted by 447, 333, and 117 cm⁻¹ for the \(^{2}\text{Fe}(I)\), \(^{4}\text{Fe}(I)\), and \(^{6}\text{Fe}(I)\) states, respectively, with the reference of 2-hydroxy-biphenyl (3816 cm⁻¹). To further validate the formation of the hydrogen bond O−H⋯C, electrostatic potentials (ESPs) near the hydroxyl group and the C atom were examined, as shown in Figure 3. ESP can be used to analyze the sites of electrophilic and nucleophilic attacks based on its negative and positive ESP values, respectively. Sites with minimum ESP were generally prone to electrophilic attack. As depicted in Figure 3, on the one hand, the local minimum ESP values can be observed near the marked C atom region (\(V_{\text{esp}}\)min = −31.1 kcal/mol in \(^{2}\text{Fe}(I)\), −30.4 kcal/mol in \(^{4}\text{Fe}(I)\), and −33.7 kcal/mol in \(^{6}\text{Fe}(I)\)), which can act as a hydrogen-bond receptor. On the other hand, the local maximum ESP values can be observed near the H atom region of the marked hydroxyl group (\(V_{\text{esp}}\)max = 0.9 kcal/mol in \(^{2}\text{Fe}(I)\), 1.9 kcal/mol in \(^{4}\text{Fe}(I)\), and 11.2 kcal/mol in \(^{6}\text{Fe}(I)\)), which can act as a weak hydrogen-bond donor. From the electrostatics point of view, we inferred that the hydrogen bond O−H⋯C was formed between the marked C atom and the H atom of the marked hydroxyl. The formed hydrogen bond was also examined with the quantum chemical topology method (QTAIM). The bond critical points (BCPs) and bond paths were obtained with the program Multiwfn\(^{41,42}\) and are illustrated in Figure 3. Obviously, there are BCPs between the two interacting atoms of the marked C and H atoms, which are connected by the corresponding bond paths. Figure 3 also lists the electron density (\(\rho\)) and Laplacian (\(\nabla^2\rho\)) values at BCPs, which fall into the range of the criteria for the
formation of hydrogen bonds proposed by Lipkowski et al. (0.002−0.04 and 0.02−0.15 au for ρ and Laplacian ∇2ρ).43 These results confirm the existence of hydrogen bonds O−H⋯C at all 2Fe(I), 4Fe(I), and 6Fe(I) states. Besides, color-mapped RDG isosurface graphs and scatter diagrams of RDG versus sign (λ2)ρ for 2Fe(I), 4Fe(I), and 6Fe(I) were also provided in the Supporting Information (see Figure S2 in the Supporting Information). All information concludes that there is a weak hydrogen bond in 2Fe(I) and a moderate hydrogen bond in 4Fe(I) and 6Fe(I).

Fixation and Activation of CO2 and Hydrogen-Bond Exchange. By adding a CO2 to the designed iron(I) compound, we performed geometry optimizations to study the fixation and activation of CO2 at all 2Fe(I), 4Fe(I), and 6Fe(I) states. The optimized structures are shown in Figure 4. Significant differences can be observed in the resulting 2Fe-CO2, 4Fe-CO2, and 6Fe-CO2 complexes. In 2Fe-CO2 with the lowest spin state, it is found that the fixation of CO2 on the Fe center occurs through the d−π coordination. Remarkably, the OCO angle bends to 145°, while the C2=O2 bond involved in the interaction with the Fe center is stretched from 1.155 to 1.240 Å and the C2=O3 bond length is 1.203 Å. But in 4Fe-CO2 and 6Fe-CO2 with high spin states, the C2 of CO2 interacts with the Fe center through single coordination. In 4Fe-CO2, the C2=O2 and C2=O3 bond lengths are 1.217 and 1.227 Å, respectively, and the OCO angle bends to 139°.

Similarly, in 6Fe-CO2, the C2=O2 and C2=O3 bond lengths are 1.229 and 1.234 Å, respectively, and the OCO angle is 136°. These data suggest that the process of the CO2 fixation on the Fe center is also the process of the CO2 activation. For comparison, we studied the CO2 fixation on the same designed Fe complex but with a trivalent iron(III) or a bivalent iron(II) and found that the CO2 fixation on the Fe center with either II or III oxidation state is only an adsorption process through van der Waals interactions, and CO2 is thus not activated (see Figure S3 in the Supporting Information).

Interestingly, the CO2 fixation on the iron(I) complex is an exergonic process with decreasing Gibbs free energies of 11.2 and 11.9 kcal/mol, for excited states 2Fe and 6Fe2, respectively, but is an endergonic process with increasing Gibbs free energy of 5.9 kcal/mol for the ground state 4Fe. The fixation of CO2 by the iron(I) complex also influences the intramolecular O−H⋯C hydrogen bonding. Compared with the initial iron(I) complex, C1⋯H1 distance is greatly increased to 2.771 Å in 2Fe-CO2, 2.929 Å in 4Fe-CO2, and 3.352 Å in 6Fe-CO2, as seen in Figure 4. These long distances suggest the disappearance of the original O−H⋯C hydrogen bonds with the addition of CO2. Meanwhile, the distances between O3 and H1 is greatly reduced to 2.172 Å in 2Fe-CO2, 1.759 Å in 4Fe-CO2, and 1.696 Å in 6Fe-CO2, suggesting the formation of a new hydrogen bond O−H⋯O in all complexes. Therefore, along with the CO2 fixation on the Fe center, there is an

Figure 4. Optimized structures (left), ESP maps (middle), and BCP figures (right) of 2Fe-CO2, 4Fe-CO2, and 6Fe-CO2. The bond lengths are in Å. In ESP maps and BCP figures, sky blue dots represent the local minima of EPS and yellow dots denote the maxima of EPS.
interesting shifting of hydrogen bonds from the O–H···C hydrogen bond to the O–H···O hydrogen bond.

In the newly formed hydrogen bond O–H···O3, the stretching vibration of the O–H bond is red-shifted by about 165, 508, and 729 cm$^{-1}$ in the complexes of $^{2}$Fe-CO$_2$, $^{4}$Fe-CO$_2$, and $^{6}$Fe-CO$_2$, respectively, in comparison with the value 3816 cm$^{-1}$ in 2-hydroxy-biphenyl. We also validated the formation of the hydrogen bonds from the electrostatics point of view. The ESPs of $^{2}$Fe-CO$_2$, $^{4}$Fe-CO$_2$, and $^{6}$Fe-CO$_2$ are exhibited in Figure 4 (middle). The local minimum ESP values can be observed near the marked O3 atom region ($V_{\text{min}} = -45.1$, $-49.5$, and $-51.1$ kcal/mol in $^{2}$Fe-CO$_2$, $^{4}$Fe-CO$_2$, and $^{6}$Fe-CO$_2$), which can act as a hydrogen bond receptor. The local maximum ESP values can be found near the H atom region of the marked hydroxyl group ($V_{\text{max}} = 21.6$, 12.7, and 12.6, respectively), which can act as a hydrogen-bond donor. The electrostatic attraction thus drives the formation of the hydrogen bond O–H···C between the marked O3 and H atoms of the marked hydroxyl group. Further, the bond critical points (BCPs) and bond paths depicted in Figure 4 (right) also verified the formed hydrogen bonds. As shown in Figure 4, the BCPs between the two interacting atoms of the marked O3 and H atoms can be identified and connected by the corresponding bond paths. Figure 4 also lists the electron density ($\rho$) and Laplacian ($\nabla^2 \rho$) values for $^{2}$Fe-CO$_2$, which fall in the range of the criteria for the formation of hydrogen bonds (0.002–0.04 and 0.02–0.15 au for $\rho$ and $\nabla^2 \rho$, respectively).
These data confirm the existence of hydrogen bonds O—H⋯O3 in ²Fe-CO₂. In ⁴Fe-CO₂ and ⁶Fe-CO₂, the values of ρ and Laplacian V²ρ are slightly larger than the top limit of the proposed criteria, leading to the speculation that the bonds O—H⋯O3 in ²Fe-CO₂ and ⁴Fe-CO₂ may be strong hydrogen bonds. Color-mapped RDG isosurface graphs and scatter diagrams of RDG versus sign (λ²)ρ for ²Fe, ⁴Fe, and ⁶Fe are shown in Figure S4 in the Supporting Information. In brief, there is a weak hydrogen bond in ²Fe-CO₂ and a strong hydrogen bond in ⁴Fe-CO₂ or ⁶Fe-CO₂. QTAIM analyses also confirmed the destruction of the original hydrogen bond O—H⋯C and the formation of the new O—H⋯O hydrogen bond in both ²Fe-CO₂ and ⁴Fe-CO₂.

Reduction of CO₂ Catalyzed by Iron(I)-Based Complex at the ²Fe(I), ⁴Fe(I), and ⁶Fe(I) Spin States. We continued the study of the reduction of CO₂ catalyzed by the iron(I)-based complex at its doublet, quartet, and sextet spin states, as the CO₂ reduction to formic acid and/or its derivatives has attracted enormous attention due to the potential applications. As presented above, while CO₂ is fixed on the Fe center, which could be in various ²Fe(I), ⁴Fe(I), or ⁶Fe(I) spin states, a hydrogen-bond exchange occurs. Consequently, it is very likely that a conceived cooperation promotes the formation of a –COOH moieties through a proton transfer from CO₂ to CO₂ and the formation of the O1–Fe bond through a hypothesized five-membered ring O1–H1–O3–C2–Fe. The generation of –COOH from CO₂ may be considered as an essential step in the CO₂ reduction to formic acid and its derivatives, and thus the iron(I)-based complex would provide an alternative access to the exploration of the CO₂ reduction.

As expected, we indeed located the transition state for the –COOH moiety formation through a proton transfer from O1 to O3 of CO₂ (TSa1 for ²Fe-CO₂, Tsb1 for ⁴Fe-CO₂, and TSc1 for ⁶Fe-CO₂), and the optimized structures are plotted in Figures 5, 6, and 7. In the three transition states, a five-membered O1–H1–O3–C2–Fe ring can be identified, and it results from a proton transfer from the O1 to O3 of CO₂ and the formation of the O1–Fe bond. The cooperativity leads to the formation of a –COOH moiety. In TSa1, the bond distances of O1–H1 and H1–O3 are 1.064 and 1.439 Å, respectively. In TSc1, those are 1.068 and 1.418 Å, respectively. However, in TSc1, the O1–H1 bond is stretched to 1.101 Å, and the H1–O3 bond is shortened to 1.352 Å. These differences indicate that the TSc1 state for ⁶Fe-CO₂ is more favorable to the proton transfer from the O1 to O3 of CO₂ than the TSa1 state for ²Fe-CO₂ and TSc1 state for ⁴Fe-CO₂. The consequence is that, in this step, the former has a barrier of only 0.5 kcal/mol, while the latter have barriers of 9.2 and 1.6 kcal/mol, respectively. The very low energy barrier of TSb1 is likely due to its precursor ⁴Fe-CO₂ with strong hydrogen bonding. In contrast, for TSa1, its precursor ²Fe-CO₂ only has a weak hydrogen bond. Our implication here is that hydrogen bonding may play a role in promoting proton transfers. In the present case, the proton transfer also shortens the distance of the Fe–O1 bond, which is 1.973 Å in Tsa, 2.054 Å in Tsb1, and 2.100 Å in TSc1. For comparison, the values are 2.213 Å in ²Fe-CO₂, 2.117 Å in ⁴Fe-CO₂, and 2.157 Å in ⁶Fe-CO₂.

After the proton transfer transition states, intermediates (²Fe-COOH, ⁴Fe-COOH, and ⁶Fe-COOH) with a –COOH moiety can be obtained with the decreasing standard Gibbs free energy, and the optimized structures are depicted in Figures 5–7, respectively. A significant structural change is the formation of the O1–Fe bond in all intermediates.

To achieve the ultimate goal of generating formic acid, it is necessary for ²Fe-COOH, ⁴Fe-COOH, or ⁶Fe-COOH to form a slightly less stable intermediate ¹IM-H₂, ¹IM-H₂, or ¹IM-H₂, respectively, followed by the splitting of the H–H bond to form the iron hydride complex H²Fe-COOH, H²Fe-COOH, or H²Fe-COOH. The H₂-adsorbed intermediates, the iron hydride complexes, and the H–H bond splitting transition states (TSa2, Tsb2, and TSc2) are depicted in Figures 5–7, respectively. The bond lengths of the adsorbed H₂...
are 0.811, 0.753, and 0.749 Å in IM-H2, 4IM-H2, and 6IM-H2, respectively, which are slightly longer than that of an isolated H2, indicating that the adsorbed H2 is activated in all states. However, the absorption of H2 by 2Fe-COOH, 4Fe-COOH, and 6Fe-COOH are endergonic processes, requiring energy inputs of 5.2, 3.8, and 8.6 kcal/mol, respectively.

In the transition states leading to the H−H bond splitting, the hydrogen atoms are bound by both Fe and O1 atoms of the Fe−O1 bond, which is formed in the H1 proton transfer process, and the H−H distance is stretched to 1.046 in TSa2, 1.022 Å in Tsb2, and 1.023 Å in Tsc2. The O1−H3 distance is 1.251 Å, and the H2−Fe distance is 1.640 Å in Tsa2; the O1−H3 distance is 1.212 Å, and the H2−Fe distance is 1.803 Å in Tsb2; and the O1−H3 distance is 1.215 Å, and the H2−Fe distance is 1.843 Å in Tsc2. Thus, H2 splitting is a combined effort of both Fe and O1 atoms. However, the doublet state is more favorable for the H−H bond splitting than the quartet state and the quartet state, as in this step, their energy barriers are 20.4 versus 34.4 and 27.3 kcal/mol.

Figure 8. Free energy profiles for the CO2 reduction catalyzed by the designed iron(I)-based complex at different states (doublet 2Fe in blue, quartet 4Fe in black, and sextet 6Fe in red).
After undergoing the H–H bond splitting, the auxiliary group OH is recovered and the Fe−H2 bond is forged in the resulting iron hydride complex H4Fe-COOH, H6Fe-COOH, and H8Fe-COOH, respectively. Early study has revealed that the iron hydride complexes exhibit strong reducibility and have been employed in the CO2 reduction.22 In H4Fe-COOH and H6Fe-COOH, the H2 of the Fe−H2 bond is close to neutral, and its NPA charges are only 0.05e and 0.04e, respectively. Differently, in H8Fe-COOH, the NPA charge on the H2 atom is negative (−0.25e). However, the NPA charge indicates that the H2 of the Fe−H2 bond in all three states very likely exhibit strong reducibility. Therefore, the Fe−H2 bonds in H4Fe-COOH, H6Fe-COOH, and H8Fe-COOH would provide a route to the formation of HCOOH through a hydrogen atom transfer from the Fe center to the C2 atom.

The route to the formation of HCOOH can be achieved through the H2-atom-transferred transition states (labeled as TSa3, TSb3, and TSc3 for the doublet, quartet, and sextet states, respectively), which are characterized with a three-membered ring mode, as depicted in Figures 5−7, respectively. In TSa3, the C2−H2 distance is 1.383 Å, while the H2−Fe distance is 1.599 Å, and their intersection angle is 79°; and in TSb3, the C2−H2 and H2−Fe bond distances are 1.743 and 1.565 Å, respectively, and their intersection angle is 74°. Similarly, in TSc3, the C2−H2 and H2−Fe bond distances are 1.504 and 1.774 Å, respectively, and their intersection angle is 77°. We also found that the three-membered ring mode is favorable for the H2 atom transfer, as the energy barriers are only 4.9, 2.8, and 11.9 kcal/mol for TSa3, TSb3, and TSc3, respectively. With the H2 atom transferred, the target product HCOOH attached to the iron(I)-based complex 4Fe, 6Fe, or 8Fe is generated.

Scheme 1 summarizes the complete route of the CO2 reduction catalyzed by the designed iron(I)-based complex at all three spin states, and the energy flow charts for the reaction pathways are plotted in Figure 8. As shown in Figure 8, the absorption and splitting of H2 via transition states TSa2, TSb2, and TSc2 is the rate-determining step in the whole process, with the total free energy barriers of 25.6, 37.2, and 35.9 kcal/mol, respectively. This suggests that the doublet structure of 4Fe(I) is considerably more favorable for the CO2 reduction than the quartet state 4Fe(I) and the sextet state 6Fe(I). The two earlier steps of the proton (H1+) transfer and the H2 atom transfer proceed easily for all 2Fe(I), 4Fe(I), and 6Fe(I) states. It is further revealed that the hydrogen bond O−H···C1 and the five-membered O1−H1−O3−C2−Fe ring exert synergistic effect on the proton (H1+) transfer and that the formation of the three-membered H2C2Fe ring facilitates the H2 atom transfer. It should be reminded that the CO2 fixation by the 4Fe state to form the complex 4Fe-CO2 is an endergonic process with an increasing Gibbs free energy by 5.9 kcal/mol, even though 4Fe(I) is more thermodynamically stable than 2Fe(I) and 6Fe(I). However, the strong absorptivity of 4Fe(I) could lead to a photosensitizer-free visible-light-mediated high−low spin shift to the less stable doublet state 2Fe through reverse intersystem crossing (RISC). In addition, from Scheme 1, an interesting finding is that the formation and break of the Fe−O bond are closely related to the two key steps in the CO2 reduction process. That is to say, the formation of −COOH moiety from CO2 is accompanied by Fe−O1 bond formation, and the splitting of one H2 molecule is accompanied by Fe−O1 bond breaking. Therefore, the rationally designed iron(I)-based complexes 2Fe and 4Fe as well as 6Fe combining visible-light catalytic conditions all can be employed to catalyze the CO2 reduction.

CONCLUSIONS

In this prospect work, we proposed an innovative strategy to explore the CO2 reduction catalyzed by the theoretically designed low-valence iron(I) model complex at various spin states including the doublet state 2Fe(I), the quartet state 4Fe(I), and the sextet state 6Fe(I), where the central iron(I) ion bonds to an ethanediamine (en) and a 2-hydroxy-biphenyl group. Computations revealed notable features in the process of the CO2 reduction. First, CO2 can be facilely captured and activate CO2. Second, the low spin state 2Fe(I) is more favorable for the CO2 reduction than the high spin state 4Fe(I) and 6Fe(I), as the former has a much lower total free energy barrier than the latter. Still, the CO2 reduction process can be initiated from the 4Fe(I) and 6Fe(I) states, as the photosensitizer-free visible-light-mediated high−low spin shift from 4Fe(I) and 6Fe(I) to 2Fe(I) can proceed through the reverse intersystem crossing (RISC). Third, there is a synergistic interaction between a hydrogen bonding and a five-membered ring, which promotes the proton transfer, leading to the formation of the −COOH moiety from CO2. This is the key step for the CO2 reduction to formic acid and/or its derivatives. Fourth, the H−H bond is essentially split by both Fe and O1 atoms of the Fe−O1 bond. The H2 splitting not only recovers the auxiliary hydroxyl group but also serves as the hydrogen atom source. Fifth, the formation of the three-membered H2C2Fe ring facilitates the H2 atom transfer to form the target product HCOOH. Finally, the two key steps (the formation of −COOH moiety from CO2 and the splitting of one H2 molecule) in the CO2 reduction process are closely related to the formation and break of the Fe−O bond in the studied system. The present study provides an alternative approach to the challenging CO2 reduction, and we anticipate that this work can stimulate further theoretical and experimental studies on the catalytic applications of iron(I) complexes in the CO2 reduction.

Computational Details

All DFT calculations in this work were performed using the Gaussian16 software package44 with the Minnesota density functional (M06)45−47 and the empirical dispersion correction D3 developed by Grimme et al.48,49 and the combination of the Def2TZVP basis set for Fe atom and the augmented correlation consistent basis set 6-311+G(d,p) for all nonmetal atoms.50 In previous reports, Yang et al. performed a density functional theory calculation with the M06 functional to study Knöcker’s iron cyclcopentadienone complex.51 Lefevre et al. established that the Def2TZVP basis set for Fe atom combining with D3(BJ) classical dispersion correction leads to a correct qualitative prediction of the ground spin state of a benchmark of iron(I).52 All geometries of reactants, transition states (TSs), and products were fully optimized without constraints and with the analytic gradients and Berny algorithms using the GEDIIS method. The convergence criteria for electronic structure calculations were set to the default values in Gaussian16. Vibrational frequency calculations at the same level were performed to confirm stationary
points as minima (zero imaginary frequency) or transition states (one imaginary frequency). In several cases, where the TSs could not be easily confirmed by the animation of their vibrations, intrinsic reaction coordinate (IRC)\textsuperscript{52,53} calculations were performed to establish the connection of each TS to its corresponding reactant and product. In the derivation of Gibbs free energies, the temperature for the reactions is set at 298 K and the pressure is at 1 atm unless specified. The energy barriers of key transition states at different pressure are provided in Tables S1 in the Supporting Information (SI). The entropy change and the enthalpy change are evaluated and provided in Table S2. To examine the geometries derived with the M06 functional, we performed computations of the \textsuperscript{2}Fe(I), \textsuperscript{4}Fe(I), and \textsuperscript{6}Fe(I) structures with other density functionals including B3LYP, PBE0, and Wb97XD, and found that the optimized geometric parameters with the M06 functional are consistent with those with other density functional (see Tables S3 in the Supporting Information (SI)). It should be mentioned that coupled cluster theory at the CCSD(T) level, multiconfigurational perturbation theory (CASPT2, NEVPT2), and multireference configuration interaction at the MRCISD+Q level are great benchmarking quantum chemistry methods for spin-state energetics of iron complexes,\textsuperscript{51,54–56} which can check errors of the DFT approach. However, it may be too costly to perform the calculation of the present whole reaction route. Partial atomic charges and vertical ionization energies (IE) were calculated with the natural population analysis (NPA)\textsuperscript{59–61} at the same M06-2X-D3/6-311+G(d,p)//Def2TZVP theoretical level. In addition, electrostatic potential (ESP)\textsuperscript{61} and AIM analysis data were calculated using Multiwfn\textsuperscript{41,62} and drawn with VMD.\textsuperscript{62}

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04758.

Key geometric parameters of \textsuperscript{2}Fe, \textsuperscript{4}Fe, and \textsuperscript{6}Fe complexes at various density functionals;

| Complex | Energy Barrier | 
|---------|----------------|
| \textsuperscript{2}Fe(I) | 0.12 eV | 
| \textsuperscript{4}Fe(I) | 0.83 eV | 
| \textsuperscript{6}Fe(I) | 0.98 eV | 

Comparison of the energy barriers of key transition states at different pressures; entropy change and enthalpy change for the CO\textsubscript{2} reduction catalyzed by the designed iron(1)-based complex at the different states; scatter graphs of Fe(I) and Fe-CO\textsubscript{2} complexes with the doublet, quartet, and sextet spin states and the color graphs of the RDG isosurface; and optimized geometries of the designed Fe complex with trivalent iron(III) and bivalent iron(II) binding CO\textsubscript{2} and atomic coordinates of intermediates and key transition states (PDF).

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### Notes

The authors declare no competing financial interest.

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