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Review

Recent Progress in the Development of Molecular Electrocatalysts for Formate Oxidation

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Abstract

Fuel cells based on renewable synthetic fuels are promising alternatives to fossil fuel combustion for efficient electricity production. Much focus has been placed on hydrogen as a chemical fuel, but being a flammable gas, there are challenges with its safe handling. Formic acid is an attractive liquid fuel for use in direct formic acid or formate fuel cells, and it can in principle be produced from the thermal or electrochemical reduction of carbon dioxide. Over the past ten years, advances have been made in the development of molecular catalysts for the electrochemical oxidation of formate, relevant to direct formic acid or direct formate fuel cells. In this review, we present the current state of the field for molecular catalysts that promote electrochemical formate oxidation. We highlight the activity and mechanism of each system, and comment on future directions in catalyst design.

Keywords

Fuel cells; electrocatalysis; formic acid; formate oxidation; metal hydride; transition metal

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1. Introduction

Since the dawn of the industrial revolution, the production of energy through the combustion of fossil fuels has been a primary means of meeting the energy demands of society and has played a major role in the proliferation of climate change. Renewable energy sources such as solar and wind power will require energy storage in synthetic chemical fuels to overcome the variability of these resources. As our society continues to move toward these more sustainable energy sources, there is a pressing need for practical chemical fuels and for more efficient methods of harvesting usable energy from these fuels. Combustion is an inherently wasteful process since a significant portion of the energy stored in the chemical fuel is lost as heat. Fuel cells offer higher theoretical efficiencies than standard combustion engines and are promising energy harvesters [1, 2]. In a fuel cell, a chemical fuel is directly oxidized at the anode through an electrochemical oxidation process rather than through chemical combustion.

Hydrogen gas has been the subject of much recent interest as a synthetic fuel for use in fuel cells [3-5]. The prospect of generating hydrogen via water electrolysis powered by renewable energy resources is especially attractive, while the reverse reaction in hydrogen fuel cells simply yields water and usable energy. However, the volumetric energy density of hydrogen is drastically lower compared to liquid fuels due to its gaseous nature under ambient conditions [6]. This poses a significant challenge for widespread implementation of a hydrogen-fuel economy. Large investments in infrastructure will be required for safe storage, handling, and transport of highly-pressurized hydrogen gas or liquified hydrogen [7]. With these difficulties in mind, there remains a large desire to explore other possible alternative liquid fuels to be used in fuel cell devices.

Formic acid is a liquid at room temperature and has a higher volumetric energy density than liquid hydrogen, making direct formic acid fuel cells (or direct formate fuel cells under alkaline conditions) an attractive option [7]. In these fuel cells, formic acid is electrochemically oxidized to carbon dioxide at the anode. While formic acid is indeed a carbon-based fuel, the conversion of atmospheric carbon dioxide into formic acid, either through thermal hydrogenation catalysis [8] or electrocatalytic reduction [9, 10], offers the possibility of a carbon neutral cycle for fuel production and energy generation (Figure 1). Catalysts for direct formic acid fuel cells are primarily based on heterogeneous precious metal systems, especially Pt and Pd, and generally exhibit poor rates and selectivity [11-14]. Dehydration of formic acid to generate carbon monoxide is a common issue, quickly leading to poisoning of the catalyst surface. While in recent years, there have been promising advances with heterogeneous systems based on single-atom catalysts or high entropy alloys that show improved activity and stability for formate oxidation [15, 16], homogeneous molecular catalysts can provide new avenues for exploration. In general, heterogenous systems tend to offer greater thermal stability, facile catalyst separation, and easier recyclability. On the other hand, molecularly-defined catalysts can be more selective than ill-defined heterogeneous systems. With homogenous metal catalysts, it is also generally easier to systematically modify the catalyst structure, to characterize the catalytically active species, and to establish structure-active relationships, making these systems more amenable to mechanistic interrogations [17]. While the practicality of homogenous catalysts is limited for fuel cell applications, molecular systems can be immobilized onto an electrode surface, thus combining the benefits of both catalyst classes [18].

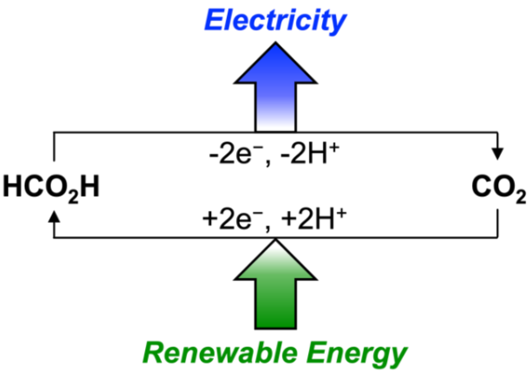

Figure 1 Renewable energy cycle based on formic acid as a synthetic chemical fuel.

The importance of fuel cell technologies for efficient energy production is high, and with the promise of formic acid as a synthetic liquid fuel, research into the development of competent molecular catalysts for the electrochemical oxidation of formate is currently underway. In the past decade, a handful of molecular systems have been reported for this transformation [19-23]. Here, we outline the reported examples of transition metal catalysts for formate oxidation. For each system, we highlight the mechanistic proposals for formate oxidation and relevant thermodynamic analysis to rationalize the observed reactivity. We will also comment on possible future directions for catalyst development in this field.

2. Electrocatalytic Oxidation of Formate

Under basic conditions, the electrochemical oxidation of formate to carbon dioxide is an overall two-electron, one-proton process. Given that the hydride anion formally consists of two electrons and one proton, direct hydride transfer from formate is a logical chemical process toward accessing overall electrochemical formate oxidation. In fact, there are many examples of the *thermal* oxidation of formic acid using molecular dehydrogenation catalysts [24, 25] and molecular transfer hydrogenation catalysts [26] based on transition metals. In general, these thermal catalytic systems involve cleavage of the formate C-H bond and hydride transfer to the metal catalyst, though the exact mechanistic pathway for this step depends on the particular system. Thus, metal-hydride species are a common key intermediate in the thermal catalytic oxidation of formate with molecular catalysts. This trend extends to molecular catalysts capable of mediating the electrocatalytic oxidation of formate, where the systems reported to date may involve a metal-hydride intermediate as a central species in the proposed mechanism for formate oxidation [19-23].

In the following sections, the known examples of electrochemical formate oxidation with molecular systems will be presented. Our discussion is divided into two parts: catalysts based on non-precious, earth-abundant transition metals, and those based on precious, noble transition metals. When available, the overall efficiency and overpotential of these systems will be highlighted for comparisons of their reactivity.

2.1 Molecular Catalysts Based on Non-precious Metals

The first example of a molecular catalyst for the electrocatalytic oxidation of formate was reported in 2011 [19]. Kubiak and co-workers prepared a series of diamagnetic nickel(II) complexes

1-**8** containing two bidentate phosphine ligands (Figure 2a). Importantly, these ligands have a pendent amine group that is not coordinated to the metal center and is available to participate in catalysis as an acid/base site [27]. This class of nickel(II) complexes was previously shown to be highly active electrocatalysts for the electrocatalytic hydrogen evolution reaction (HER), as well as hydrogen oxidation [28, 29]. Both of these reactions involve hydride transfer between H_2 and the nickel(II) center, setting up these complexes for other possible reactivity through similar hydride transfer pathways. Furthermore, previous work had also shown that the thermodynamic hydricity of nickel(II)-hydride complexes in this family is generally greater than the thermodynamic hydricity of the formate anion in acetonitrile [30, 31]. Thus, the authors anticipated that their series of nickel(II) complexes would be capable of formate oxidation by accepting a hydride anion from this substrate and should be thermodynamically competent electrocatalysts for this reaction [32].

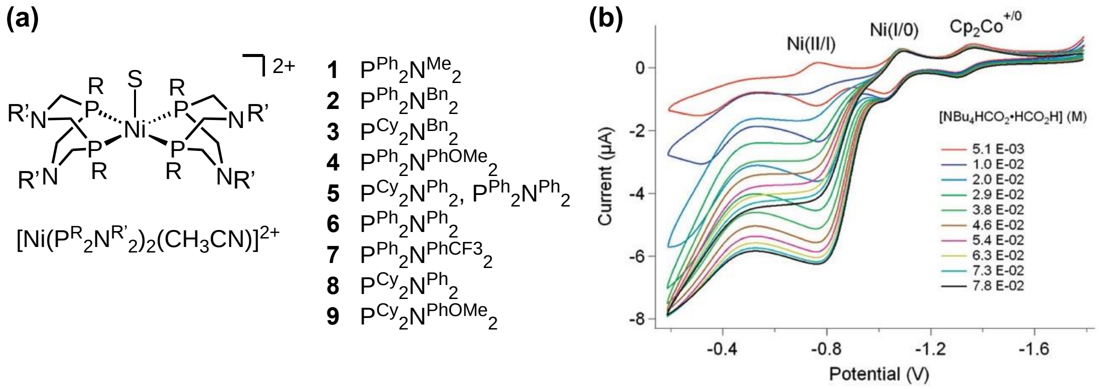

Figure 2 (a) Structure of nickel(II) complexes **1**-**9**. (b) CVs of complex **5** (1.2 mM) with increasing addition of $NBu_4HCO_2{\cdot}HCO_2H$ in benzonitrile. Potential in V vs. $Fc^{+/0}$. Reprinted with permission from ref. [19]. Copyright 2011 American Chemical Society.

Overall, eight electrocatalysts based on the $[Ni(P^R_2N^{R'}_2)(CH_3CN)]^{2+}$ scaffold were reported [19], as well as complex **9** that was investigated in a later article [20]. In the absence of formate, cyclic voltammograms of each complex display two reversible features for the Ni(II/I) and Ni(I/0) redox couples in acetonitrile. Titration of tetra-n-butylammonium formate (as a 1:1 adduct with formic acid) [19] to each solution resulted in a large increase in current near the Ni(II/I) oxidation potential (Figure 2b). From this current increase, the rate of formate oxidation was estimated to range from 1.1 to 15.8 s^{-1}, depending on the phosphine and amine substituents. The electrocatalytic generation of carbon dioxide was confirmed using controlled potential electrolysis experiments with complex **4**: a Faradaic efficiency of 93 ± 5% for CO_2 was obtained at approximately -0.77 V vs. $Fc^{+/0}$ (where $Fc^{+/0}$ is the ferrocenium/ferrocene redox couple). The catalytic potential corresponds to an overpotential of roughly 0.53 V for formate oxidation in acetonitrile, using the values reported by Kubiak and co-workers [33, 34]. Catalytic turnover frequencies were found to be first-order with respect to formate concentration up to approximately 40 equivalents. The authors also examined the reactivity of a related complex with no pendent amine groups, $[Ni(depe)_2(MeCN)]^{2+}$ **10**, which showed no evidence of electrocatalytic current enhancement on the timescale of the cyclic voltammetry experiment [19]. This result highlights the crucial involvement of the pendent amine in achieving fast catalytic turnover for formate oxidation.

The Ni(II/I) and Ni(I/0) potentials of each complex were found to directly correlate with the thermodynamic hydricity and pK_a of the analogous nickel(II)-hydride, which is consistent with general trends for transition metal hydrides [33]. However, the turnover frequency for formate oxidation did not correlate with the hydricity of the nickel(II)-hydride, and surprisingly the least hydridic system (complex **8**) was in fact the slowest catalyst in the series. On the other hand, the rate of formate oxidation shows a reasonable correlation with the pK_a of the pendent amine substituent of each complex. The authors thus proposed the mechanism shown in Figure 3a based on the above results and other spectroscopic and electrochemical experiments [19, 20]. In this proposal, coordination of the formate anion to nickel(II) is followed by abstraction of the formyl hydrogen as a proton by the pendent amine group (a β-deprotonation) with concomitant 2e$^-$ transfer to the nickel(II) center. Subsequent oxidation and deprotonation steps regenerate the starting nickel(II) species. This mechanistic proposal is quite unusual since it does not invoke direct hydride transfer from formate to the metal catalyst.

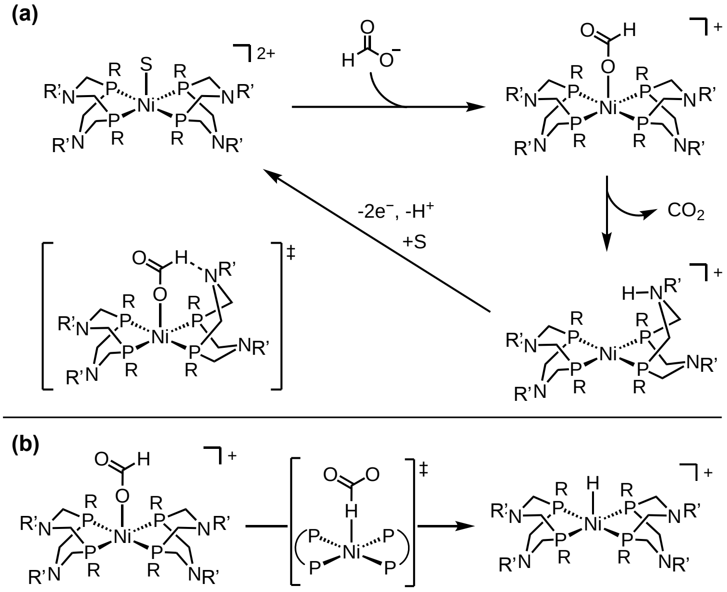

Figure 3 (a) Proposed β-deprotonation mechanism for formate oxidation with $[Ni(P^{R}{}_{2}N^{R'}{}_{2})(CH_3CN)]^{2+}$ complexes [19, 20]. (b) Alternative proposed direct hydride transfer mechanism [21].

The mechanism of formate oxidation with this family of nickel complexes was re-evaluated by Xue and Ahlquist in 2014 [21]. In this report, DFT computational methods were used to predict the energetics of different possible pathways for the key formate oxidation step using complex **1** as the primary representative catalyst. Their calculations were unable to locate a pathway for β-deprotonation of the nickel(II)-formate intermediate by the pendent amine. Instead, direct hydride transfer from formate to the metal was predicted to be accessible with a reasonable transition state barrier under ambient conditions (11.3 kcal/mol, Figure 3b). Thus, the authors conclude that the direct nickel(II)-hydride route is more reasonable than the mechanism originally proposed by Kubiak and co-workers [19-21]. Xue and Ahlquist calculate that the pendent amine assists in the subsequent deprotonation of the nickel(II)-hydride by serving as a proton shuttle to lower the kinetic barrier for this process. Notably, the calculated barrier is much greater for complex **10**, in line with the activity of this complex observed experimentally [19]. Despite the remaining ambiguity of the operative mechanism for formate oxidation, both proposed pathways require the pendent amine group to lower transition state barriers and underscore the critical role of the amines in facilitating the overall electrocatalytic cycle [34].

The above work on nickel(II) complexes remains the only demonstration of electrocatalytic formate oxidation with non-precious metal catalysts. A recent report from our group demonstrates the future potential for molecular cobalt complexes to promote this reaction as well [35]. While thermodynamic hydricity measurements of cobalt complexes are very limited compared to nickel systems [31, 33], cobalt(III)-hydrides are generally not very reactive for hydrogen evolution, suggesting modest hydride donating abilities [4, 36-38]. Thus, we isolated a series of cyclopentadienyl cobalt(III) complexes with diphosphinoamine ligands (Figure 4) [35]. The analogous cobalt(III)-hydride complex was isolable for a cyclohexylphosphine-substituted ligand, while the other ligand systems examined resulted in decomposition. The X-ray crystal structure of complex **11** showed the strained four-membered metallacycle created by the bidentate phosphine ligand and the cobalt center. The rigidity of this coordination environment and the planarity at the nitrogen in this ligand indicate the pendent amine is unlikely to function like the P_2N_2 ligands above. We showed that treatment of complex **11** with tetra-n-butylammonium formate (as a 1:1 adduct with formic acid) at 65°C resulted in generation of the cobalt(III)-hydride complex and carbon dioxide, which we proposed proceeds through a unique pathway of competing equilibria. Given the inaccessibility of the ligand nitrogen in this complex, hydride transfer from formate likely proceeds via a direct hydride transfer mechanism. While electrocatalytic turnover for formate oxidation to carbon dioxide was not demonstrated with complex **11**, a series of individual chemical and electrochemical steps were independently shown that together sum to achieve overall electrochemical formate oxidation (Figure 4): (1) coordination of formate and subsequent hydride transfer to cobalt(III), (2) deprotonation of the cobalt(III)-hydride by the formate anion, and (3) oxidation of cobalt(I) to cobalt(III) at the electrode. Improving the design of cobalt(III) complexes to lower the kinetic barrier for the hydride transfer step should result in competent catalysts for electrochemical formate oxidation. Studies along these lines are currently underway in our group.

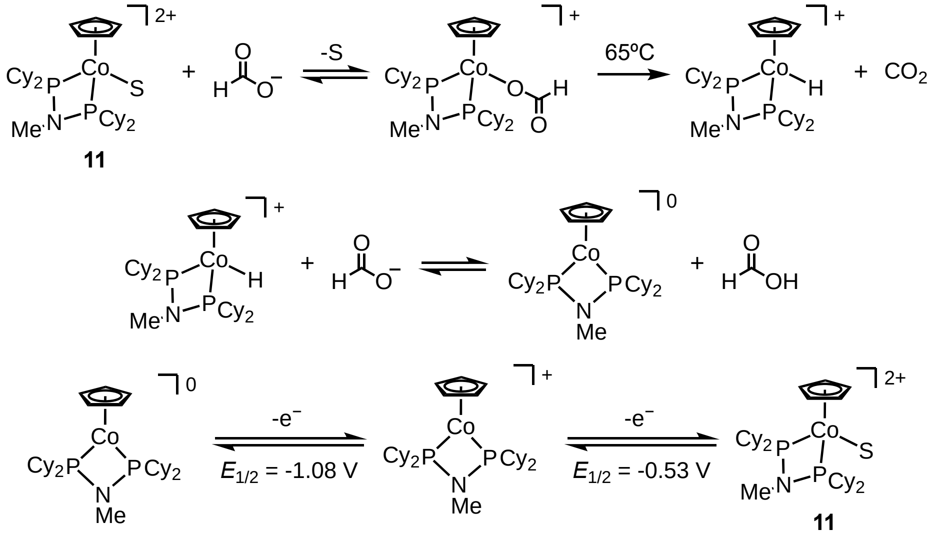

Figure 4 Stoichiometric reactivity observed with cobalt(III) complex **11**, summing to overall electrochemical formate oxidation. Potentials in V vs. $Fc^{+/0}$ [35].

2.2 Molecular Catalysts Based on Precious Metals

Kang and co-workers reported a reversible iridium(III) electrocatalyst **12** that is capable of both electrochemical carbon dioxide reduction and electrochemical formate oxidation [22]. This catalyst is based on a tridentate PONOP pincer ligand that creates a stable coordination environment at the metal. The authors demonstrated that incremental addition of tetra-n-butylammonium formate (as a 1:1 adduct with formic acid) to a solution of complex **12** in acetonitrile resulted in an increase in oxidative current at -0.15 V vs. NHE (roughly -0.15 V vs. $Fc^{+/0}$) [39], as observed through cyclic voltammetry experiments (Figure 5). Under optimized conditions, the highest turnover frequency for formate oxidation with **12** was calculated to be 4.8 s^{-1}. The increase in oxidative current was first order with respect to both the formate and catalyst concentrations. Interestingly, the rate of carbon dioxide reduction with this same catalyst was significantly faster (67 s^{-1}).

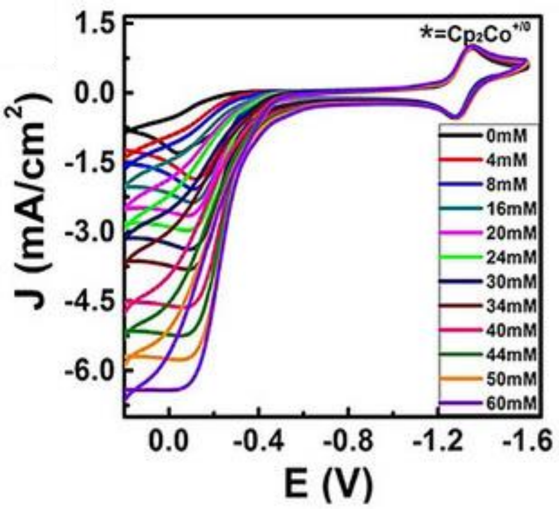

Figure 5 CVs of complex **12** (2 mM) with increasing addition of $NBu_4HCO_2{\cdot}HCO_2H$ in acetonitrile. Potential in V vs. NHE. Reprinted with permission from ref. [22]. Copyright 2019 John Wiley and Sons.

Controlled potential electrolysis of complex **12** with excess formate salt resulted in carbon dioxide as the only product at -0.1 V vs. NHE. The Faradaic efficiency for CO_2 was 87 ± 5 % under these conditions. Impressively, the electrolysis current was stable for more than 35 h, indicating that this catalyst is highly stable over extended reaction times. From their data, the authors propose the electrocatalytic mechanism shown in Figure 6. Starting with the trihydride species **12**, loss of two electrons and one proton through oxidative deprotonation at the electrode yields an Ir(III)-acetonitrile intermediate, which is rapidly displaced by the formate anion. Decarboxylation of the bound formate ligand releases carbon dioxide and regenerate complex **12**. While the mechanism of hydride transfer from formate was not evaluated in this study, a direct hydride transfer pathway is likely given the unfunctionalized nature of the ancillary ligands in this system. Based on the known potential of the cobaltocenium/cobaltocene redox couple versus $Fc^{+/0}$ [39], and the approximate E_{cat} value from Figure 5 [40], the overpotential for formate oxidation is roughly 1.25 V in acetonitrile [33]. A similar but reversed mechanism is proposed for the electrochemical reduction of carbon dioxide with complex **12**, where reduction is the key electrochemical step as opposed to oxidation [22].

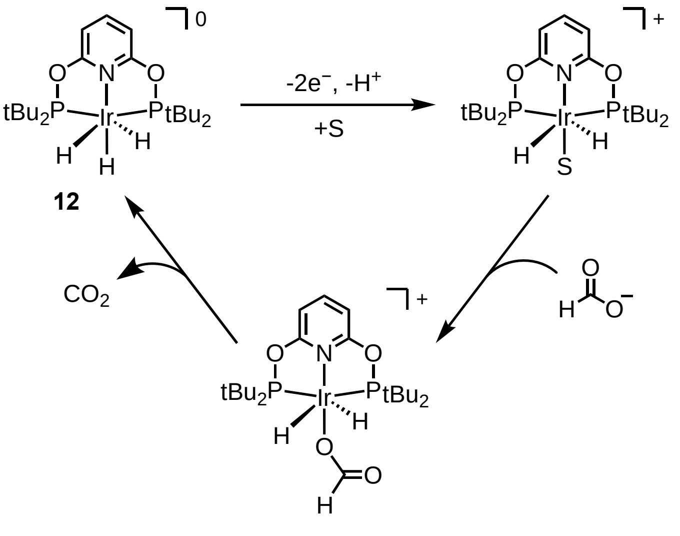

Figure 6 Proposed mechanism for formate oxidation with complex **12** [22].

Yang and co-workers recently reported a platinum(II) complex **13** that functions as a bi-directional electrocatalyst for interconverting formate and carbon dioxide at mild overpotentials (Figure 7a) [23]. This reversible reactivity was specifically targeted by the authors: they selected a known metal complex that has a hydride accepting ability (-44.2 kcal/mol) [41, 42] that is almost exactly matched by the hydride donating ability of the formate anion (44 kcal/mol in acetonitrile) [31]. The reaction conditions were also carefully selected by using an amine base ($CH_2(TBD)_2 \cdot HPF_6$, Figure 7a, pK_a = 29.0 in acetonitrile) with a comparable base strength as complex **13** (pK_a of $[HPt(depe)_2]^{2+}$ = 29.7 in acetonitrile) [42]. Their approach enabled access to near-ergoneutral chemical steps with the platinum catalyst for hydride transfer with formate and proton transfer with $CH_2(TBD)_2$ base.

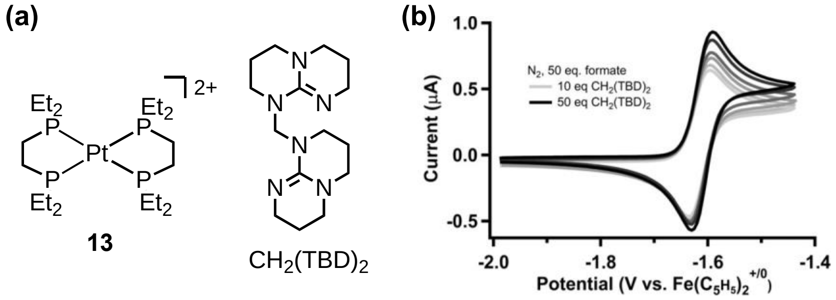

Figure 7 (a) Structure of platinum(II) complex **13** and the $CH_2(TBD)_2$ base. (b) CVs of complex **13** (1.0 mM) and NBu_4HCO_2 (50 mM) with increasing addition of base in acetonitrile. Potential in V vs. $Fc^{+/0}$. Reprinted with permission from ref. [23]. Copyright 2020 John Wiley and Sons.

The cyclic voltammogram of complex **13** in acetonitrile shows a reversible two-electron wave for the Pt(II/0) redox couple. As shown in Figure 7b, there is only a slight difference in the shape of this redox feature in the presence of formate (added as tetra-n-butylammonium formate) with increasing concentrations of base. This behavior is unlike the other catalyst systems discussed thus far and is consistent with a slow turnover frequency for formate oxidation. An upper estimate from this data for the turnover frequency of formate oxidation is given as $< 0.5\ s^{-1}$. The Faradaic efficiency for CO_2 production was 90% based on controlled potential electrolysis studies at -1.4 V vs. $Fc^{+/0}$. This system is stable for at least 4 h and exhibits a minimum turnover number of 2.4.

As shown in Figure 8, formate oxidation with complex **13** is proposed to start with direct hydride transfer to platinum(II), followed by deprotonation of the resulting platinum(II)-hydride intermediate by the exogenous base, and finally oxidation at the electrode to regenerate complex **13**. We note that this proposed mechanism is essentially identical to the pathway observed with cobalt(III) complex **11** shown in Figure 4, except that reoxidation of the reduced platinum center occurs in an overall two-electron step as opposed to separate one-electron features for cobalt [23, 35]. No direct involvement of the phosphine ligand substituents is proposed in the mechanism of the hydride transfer step. As with the iridium(III) complex **12**, these ligands serve to stabilize the metal coordination sphere and tune the thermodynamic properties of the catalyst. Notably, the closely related platinum(II) complex $[Pt(dmpe)_2]^{2+}$ (where dmpe = 1,2-bis(dimethylphosphino)ethane) is an active catalyst for electrochemical CO_2 reduction to formate but not for the reverse formate oxidation [43]. The switch from methyl to ethyl substituents on the phosphine ligands slightly shifts the thermodynamic hydride accepting ability of these two complexes, resulting in different reactivity.

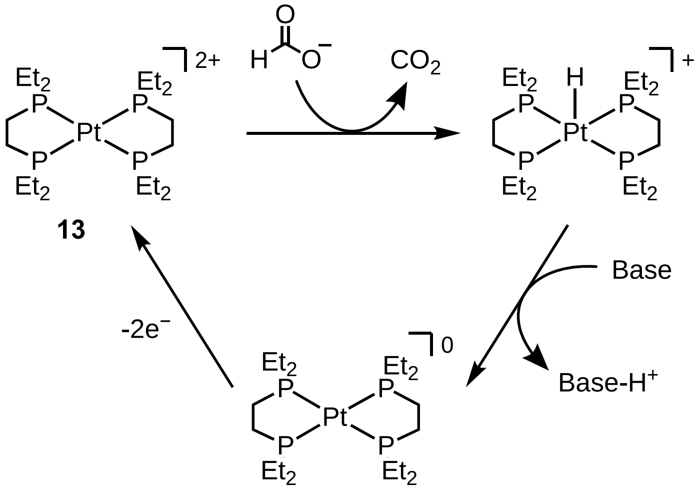

Figure 8 Proposed mechanism for formate oxidation with complex **13** and $CH_2(TBD)_2$ base [23].

3. Discussion

The past decade has seen the first examples of molecular catalysts for the electrochemical oxidation of formate. Three families of catalysts have been reported thus far, based on nickel(II), iridium(III), or platinum(II) [19-23]. The reported turnover frequency and catalytic operating potential for each system is summarized in Table 1, where complex **4** is given as the representative example of the nickel(II) class [19]. The fastest rate of formate oxidation was achieved with one of the nickel(II) P_2N_2 catalysts, complex **1**, for which the catalytic turnover frequency is 15.8 s^{-1} in benzonitrile. Other variations of the phosphine and amine substituents in this family resulted in lower rates of catalysis, and an approximate correlation between the rate and basicity of the pendent amine was observed. The iridium(III) and platinum(II) catalysts (complex **12** and **13**, respectively) also exhibit slower rates [22, 23]. While there is some uncertainty regarding the mechanism of formate oxidation with the nickel family of catalysts, it is generally considered that the decarboxylation step to release carbon dioxide is rate-limiting with all systems. Ligand design will likely play a major role in the development of faster catalysts for formate oxidation. Direct hydride transfer appears to be a viable pathway for decarboxylation, but cooperation from the outer coordination sphere of the catalyst or assistance from exogeneous additives may be needed to decrease the transition state barrier for this process, or alternative lower energy pathways for hydride transfer may be required, such as an indirect β-hydride deprotonation route [44]. There are several examples in the literature demonstrating the crucial role of pendent functional groups for promoting more rapid electrocatalysis in other small molecule transformations, such as CO_2 reduction, H_2 reduction or oxidation, and N_2 reduction [45-49]. An additional factor to consider is the accessibility and positioning of the pendent group within the ligand scaffold. The functional group must be able to orient in such a way to interact favorably with the metal center and formate to facilitate hydride transfer.

Table 1 Summary of molecular electrocatalysts for formate oxidation.

Complex	TOF (s^{-1})	Potential (V vs $Fc^{+/0}$) [a]	Overpotential (V) [b]	FE_{CO2} (%) [c]
4 [19]	8.7	-0.87	0.53	93 ± 5
12 [22]	4.8	-0.15	1.25	87 ± 5
13 [23]	< 0.5	-1.63	0.01	90

[a] Catalytic potential estimated as $E_{cat/2}$. [b] Overpotential = $E_{cat/2} - E^{\circ}(CO_2/HCO_2^{-})$, where $E^{\circ}(CO_2/HCO_2^{-}) = (-0.77 - 0.030pK_a)$ V vs. $Fc^{+/0}$. [c] FE_{CO2} = Faradaic efficiency for carbon dioxide.

The thermodynamic favorability of hydride transfer between formate and the metal catalyst is critical for promoting formate oxidation instead of carbon dioxide reduction, or for accessing reversible reactivity. The hydricity of metal hydride complexes, as well as their pK_a, generally trends with the redox potentials of the parent complex [33]. These correlations are valuable in that the relationships between the energetic requirements for chemical hydride and proton transfer steps and the electrochemical properties of the catalyst are easily seen. The catalytic operating potential also determines the energetic efficiency of the system in terms of overpotential, where this value is given by the difference between the catalytic potential and the thermodynamic potential for the formate/carbon dioxide couple. It is important to remember that this standard potential is proton dependent and thus shifts based on the basicity of the reaction solution. In acetonitrile, this potential is $(-0.77 - 0.030pK_a) = -1.30$ V vs. $Fc^{+/0}$ when 1:1 formate:formic acid is used as a basic buffer [33]. These conditions were used for the nickel and iridium catalysts. The use of stronger bases will shift this value to more negative potentials. A stronger amine base was employed for formate oxidation with the platinum(II) complex **13**, and thus the thermodynamic potential for the formate/carbon dioxide couple is estimated to be -1.64 V vs. $Fc^{+/0}$ [33]. Despite the requirement of more basic conditions, complex **13** exhibits the lowest overpotential for formate oxidation in this data set, which is attributed to careful balancing of the reaction thermodynamics to attain near-ergoneutral reactivity.

All reported examples of electrochemical formate oxidation thus far have been studied in organic solvent: acetonitrile or benzonitrile. The positive effects of water addition on the rate of catalysis have been demonstrated for the electrochemical reduction of carbon dioxide with various systems

[10]. Similar positive effects are anticipated for electrochemical formate oxidation. An iridium complex, closely related to complex **12**, has been reported for electrocatalytic carbon dioxide reduction to formate in water, thanks to the addition of a pendent tetraalkylammonium charged group that provides water solubility to the complex [50]. Such an approach may also be successful with formate oxidation catalysts. Note that the thermodynamic hydricity of formate and metal-hydride complexes will shift in water compared to acetonitrile, and the range of hydricity values narrows with increasing solvent polarity [31, 51]. Additionally, the hydricity changes for formate and transition metal hydride complexes are not identical due to different degrees of stabilization from solvation and hydrogen bonding with water. These factors should be considered when approaching catalyst design in organic versus aqueous solvent to ensure formate oxidation remains the favorable direction for hydride transfer.

Considering the known thermodynamic hydricity of formate in acetonitrile (44 kcal/mol), we can expect many other transition metal complexes [31] or organic hydride acceptors [52, 53] to have the energetic driving force to facilitate formate oxidation [33]. At the same time, optimization of the thermodynamic requirements for hydride transfer does not guarantee sufficient turnover frequencies, as is the case with platinum complex **13** as well as with our cobalt system **11** that can slowly oxidize formate at elevated temperatures [35]. Catalysts that are highly active for the thermal dehydrogenation of formic acid may provide a promising starting point for electrocatalyst design [24]. For example, Waymouth and co-workers recently showed that an iron dehydrogenation catalyst can promote the electrochemical oxidation of isopropanol to acetone [54]. Given that this system can also convert formic acid to carbon dioxide and hydrogen [55], an electrocatalytic scheme for formate oxidation is likely accessible as well. Further optimization to improve catalyst stability while accessing fast hydride transfer should be the subject of future investigations.

4. Conclusions

The development of new molecular catalysts capable of the electrochemical oxidation of formate is an important emerging field in fuel cell research. In the past several years, key initial examples of this reactivity have been reported, based on both precious and non-precious transition metal systems. The highest turnover frequencies for formate oxidation have been achieved with a family of nickel(II) complexes containing pendent basic sites. While the exact role of these amines remains unclear, these results indicate that these pendent functional groups are critical for facilitating electrocatalytic turnover. Given the large body of work that demonstrates the impressive ability of pendent amines or related basic ligand sites for lowering the kinetic barriers in other electrocatalytic transformations, future work on electrocatalytic formate oxidation should focus on incorporating appropriately positioned pendent functional groups into the outer coordination sphere of the metal catalyst. In terms of energy efficiency, the lowest overpotential for electrocatalytic formate oxidation has been achieved with a platinum(II) complex by carefully considering the reaction free energies of the key chemical steps: hydride transfer and proton transfer. Near-ergoneutral reactivity was observed but with low turnover frequency. Combining both thermodynamic and kinetic considerations will offer many new opportunities for catalyst design and will need to be considered in future research. Studies should also evaluate the effects of electrocatalyst immobilization onto electrode surfaces in terms of catalyst activity and stability toward the development of more practical systems for direct formic acid fuel cells.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Competing Interests

The authors have declared that no competing interests exist.

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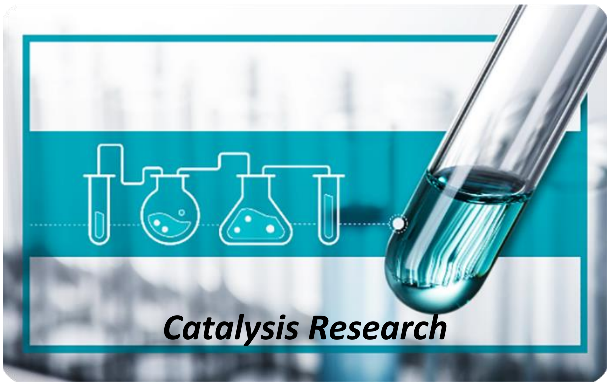

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