ABSTRACT: Nitriles are highly important synthetic intermediates with applications in a wide variety of organic reactions including production of pharmaceuticals, fine chemicals, and agricultural chemicals. Thus, developing effective green routes to oxidize amines to nitriles is of great interest. One promising method to achieve the oxidation of primary amines to nitriles is through electrochemical oxidation on NiOOH electrodes. This reaction has long been thought to occur through an indirect mechanism consisting of a series of potential independent hydrogen atom transfer steps to catalytic Ni^{3+} sites in NiOOH, which reduces NiOOH to Ni(OH)_{2}. The role of the applied potential in this mechanism is simply to regenerate NiOOH by oxidizing Ni(OH)_{2}. In this work, we demonstrate that a second, potential-dependent pathway recently found to apply to alcohol and aldehyde oxidation on NiOOH and consisting of potential-dependent hydride transfer to Ni^{4+} sites is the dominant pathway for the oxidation of amines using propylamine and benzylamine as model systems. After qualitatively and quantitatively examining the contributions of indirect and potential-dependent oxidation pathways to amine oxidation on NiOOH, we also examine the effect the amine concentration, solution pH, applied bias, and deuterium substitution have on the two pathways, further clarifying their mechanisms and exploring what factors control their rate. This work provides a comprehensive understanding of the mechanism of primary amine oxidation on NiOOH.

KEYWORDS: amine oxidation, NiOOH, electrochemical dehydrogenation, nitrile, hydride transfer, hydrogen atom transfer

INTRODUCTION

Nitriles are highly important synthetic intermediates with applications in a wide variety of organic reactions including production of pharmaceuticals, fine chemicals, and agricultural chemicals.\textsuperscript{1−3} Traditional methods of preparing nitriles (e.g., ammoxidation, the Sandmeyer reaction, and displacement of halides with cyanide ions), however, suffer from several unattractive features including the use and production of toxic chemicals, harsh reaction conditions, and the generation of significant amounts of chemical waste.\textsuperscript{1−3} As such, there is great interest in developing greener synthetic routes to produce nitriles. One promising alternative is the oxidation of primary amines to nitriles using molecular oxygen and transition metal-based catalysts, notably, ones based on Ru or Cu.\textsuperscript{5,6−8} While these methods are greener than the traditional nitrile synthesis methods and offer several important advantages, there are still challenges that must be overcome, with most methods facing some combination of drawbacks including low turnover numbers, requiring the use of elevated temperatures and O_{2} pressures, or requiring the use of complex ligands and catalysts that can be challenging or expensive to produce.\textsuperscript{5,6−9} Furthermore, side reactivity can be an issue, often stemming from the electrophilic imine intermediate undergoing a nucleophilic attack before it can undergo dehydrogenation to form the nitrile.\textsuperscript{5,6−9}

Another promising method that has been explored is the electrochemical oxidation of primary amines to nitriles.\textsuperscript{10−14} This method shares the benefits of using the transition metal-based catalysts and molecular oxygen in that it eliminates the need for harsh chemicals and stoichiometric oxidizing agents, but it offers additional benefits. First, electrochemical amine oxidation can be performed efficiently at ambient temperatures and pressures without needing O_{2} or a sacrificial oxidant. Second, the electrons gained by the oxidation of amines at the anode are transferred to the cathode and can be used for reduction reactions that produce valuable products such as fuels (e.g., H_{2} by water reduction) or chemicals (e.g., reductive valorization of other organic species), increasing the economic viability. Third, electrochemical oxidation can be driven by...
electricity generated from renewable energy sources and will only become more appealing as an increase in renewable energy sources lowers electricity prices. As such, electrochemical oxidation of primary amines has the potential to be among the greenest methods of producing nitriles.

NiOOH is one of the most promising and practical electrode materials for catalyzing these electrochemical conversions. Previous reports have shown that it can efficiently and selectively convert a variety of primary amines into nitriles under alkaline conditions. As shown in Scheme 1, the oxidation of amines to nitriles bears many similarities to the oxidation of alcohols to carboxylic acids, another class of electrochemical reactions NiOOH is well-known to effectively catalyze. Both processes (alcohol oxidation to carboxylic acid and amine oxidation to nitrile) are 4e⁻ dehydrogenations occurring in two successive 2e⁻ steps, with the first producing an aldehyde/imine and the second then converting that aldehyde/imine into a carboxylic acid/nitrile. One key difference is that before aldehyde oxidation, the aldehyde must first undergo a nucleophilic attack by an OH⁻ ion from the solution to form the 1,1-geminal diol. However, for imine oxidation, the nucleophilic attack by the OH⁻ from the solution must be suppressed as it results in the formation of aldehyde, which can be further oxidized to carboxylic acid.

The electrochemical dehydrogenation of both amines and alcohols on NiOOH has long been understood to proceed through the same general mechanism proposed by Fleischmann et al. (Scheme 2). In this mechanism, NiOOH serves as a chemical oxidizing agent, undergoing a chemical reaction with the amine/alcohol that features a rate-limiting hydrogen atom transfer (HAT) step in which a hydrogen radical from the α-C of the alcohol/amine is transferred to the NiOOH (Scheme 2, step 3). Accordingly, the oxidation of the alcohol/amine through this mechanism is accompanied by the reduction of NiOOH to Ni(OH)₂. The role of electrochemistry is simply to allow the Ni(OH)₂ formed following alcohol/amine oxidation to be reconverted to NiOOH (Scheme 2, step 1). As such, the actual oxidation reaction with the amine is the same as when NiOOH is used as a stoichiometric chemical oxidizing agent, with the potential serving to enable the regeneration of NiOOH and thus its use in a catalytic amount rather than a stoichiometric amount. This regeneration of NiOOH from Ni(OH)₂ is reported to be fast even at low overpotentials relative to the Ni(OH)₂/NiOOH couple. Thus, the overall rate of alcohol/amine oxidation is reported to be dictated by the rate of the chemical HAT step and thus unaffected by the applied potential (so long as the bias is sufficient to ensure fast regeneration for NiOOH). As such, we will refer to this pathway as indirect oxidation.

Recently, we revealed that for oxidation of alcohols and aldehydes to carboxylic acids on NiOOH, there is a second, potential-dependent (PD) pathway that occurs in addition to the indirect one and that this PD pathway is dominant for alcohol oxidation. Unlike indirect oxidation, which uses Ni³⁺ as the catalytic center and achieves dehydrogenation through HAT, PD oxidation uses Ni⁴⁺ as the catalytic center and achieves dehydrogenation through hydride transfer. This recent finding made us wonder if the oxidation of amines to nitriles on NiOOH truly occurs through indirect oxidation, as has been believed, or if it also occurs partly or dominantly through PD oxidation.

The goal of this study is to interrogate and establish the oxidation mechanisms of amines to nitriles on NiOOH using various electrochemical techniques that can qualitatively and quantitatively analyze the indirect and PD oxidation pathways. We used aliphatic propylamine and aromatic benzylamine as model systems and examined how the structure and concentration of amines, pH, and oxidation potential influence the indirect and PD oxidation processes. By comparing the results obtained from amine oxidation with those from alcohol oxidation, we would expect the addition to nitriles on NiOOH to nitriles on NiOOH truly occurs through indirect oxidation, as has been believed, or if it also occurs partly or dominantly through PD oxidation.

RESULTS AND DISCUSSION

The NiOOH electrodes used in the study were prepared by depositing a thin Ni(OH)₂ film onto a fluorine-doped tin oxide (FTO) substrate. The thickness of the film was optimized to provide as thin a Ni(OH)₂ film as possible while still being able to complete a constant-potential electrolysis in a reasonable amount of time. The use of these thin Ni(OH)₂ electrodes minimizes the heterogeneity among Ni sites and prevents any possible transport-related complications that could arise in the analysis if using thicker films.

Cyclic Voltammetry Analysis

We first examined cyclic voltammograms (CVs) of NiOOH in a pH 13 solution with and without propylamine or benzylamine (Figure 1). If amine oxidation on NiOOH occurs only through indirect oxidation, we would expect the addition
of amines to only enhance the anodic peak associated with the oxidation of Ni(OH)$_2$ to NiOOH. This is because in the indirect mechanism, the amine is not directly oxidized by the applied bias.$^{16,17}$ Instead, it chemically reacts with NiOOH to reform Ni(OH)$_2$, which would then be reoxidized to NiOOH during the cyclic voltammetry scan, enhancing the Ni(OH)$_2$/NiOOH peak. Our results, however, show that there is only a minor enhancement of the Ni(OH)$_2$/NiOOH peak when the amines are present and that instead the Ni(OH)$_2$/NiOOH peak is followed by a separate oxidation peak in the more positive potential region (Figure 1). This cannot be explained by indirect oxidation. Additionally, we note that the second oxidation peak is significantly larger than the enhancement of the Ni(OH)$_2$/NiOOH peak, indicating that it, rather than the indirect process, accounts for the majority of amine oxidation. Furthermore, we note that according to the indirect mechanism, the current for a solution rapidly stirred to minimize mass transport limitation should settle into a potential independent plateau shortly after reaching potentials anodic enough to oxidize Ni(OH)$_2$. In reality, however, CVs we collected in rapidly stirred amine solutions show that the current is highly potential dependent and keeps increasing as the potential is swept to the positive direction without ever settling into a plateau (Figure S1).

For the CVs shown in Figure S1 and for our rate deconvolution analyses discussed below, we chose to use a rapidly stirred solution instead of a rotating disk electrode because this allowed us to use the exact same NiOOH electrode and reaction setup/conditions for all the different types of experiments we performed in this study (cyclic voltammetry, rate deconvolution experiments, and electrolysis). (We define “rapidly stirred” as stirred sufficiently fast such that further changes to the stir speed no longer changed the current density.) Our choice of experimental conditions ensures that the mechanistic findings and analysis performed based on the cyclic voltammetry and rate deconvolution data apply directly to constant potential electrolysis conditions.

While the CVs depicted in Figure 1 deviate significantly from the those expected for indirect oxidation mechanisms, their shape is nearly identical to the shape of those we have previously observed for alcohol oxidation where PD oxidation dominates.$^{20,21}$ This suggests that amine oxidation also occurs predominantly through PD oxidation. The PD oxidation mechanism we proposed for alcohol oxidation is shown in Scheme 3.$^{20,21}$ In this mechanism, Ni$^{4+}$ is the active center (step 1, Scheme 3), which is why PD oxidation is enabled in a more positive potential region than that for indirect oxidation (which uses Ni$^{3+}$). The alcohol is oxidized through a hydride transfer from the alpha position of the organic substrate to a Ni$^{4+}$ site in the catalyst (step 4, Scheme 3), thereby reducing that site back to Ni$^{2+}$. In order to activate the alcohol to hydride transfer, its OH group must also be deprotonated. We believe that for alcohols, this most often occurs as a separate step in solution prior to adsorption (step 2, Scheme 3); however, it is also possible that it occurs either after the alcohol adsorbs or in concert with the hydride transfer. After the hydride transfer, the now reduced Ni site will be electrochemically reoxidized to regenerate Ni$^{4+}$, closing the catalytic cycle (step 5, Scheme 3).

Our proposed PD oxidation mechanism for amines is shown in Scheme 4. It is very similar to that for alcohol oxidation, still featuring a hydride transfer from the alpha position of the adsorbed organic substrate to a Ni$^{4+}$ site in the catalyst. The biggest difference with the mechanism for alcohol oxidation is that because amines are much less acidic than alcohols, the deprotonation that enables the organic species to undergo hydride transfer is unlikely to occur in solution. Instead, the deprotonation is expected to occur after adsorption. This is written in the scheme as a separate step (step 3, Scheme 4) to hydride transfer (step 4, Scheme 4); however, it is also possible

**Scheme 3. Hydride Transfer Mechanism We Have Previously Proposed for the Oxidation of Alcohols to Aldehydes through the PD Oxidation Pathway**

\[
2\text{OH}^- + \text{Ni(OH)}_2^- \rightarrow \text{NiO}_2^- + 2\text{H}_2\text{O}
\]  
(1)

\[
\text{OH}^- + \text{RCH}_2\text{OH} \rightarrow \text{RCH}_2\text{O}^- + \text{H}_2\text{O}
\]  
(2)

\[
\text{RCH}_2\text{O}^- \rightarrow \text{RCH}_2\text{O}^-\text{ads}
\]  
(3)

\[
\text{RCH}_2\text{O}^-\text{ads} + \text{NiO}_2^- \rightarrow \text{RCHO}_{\text{ads}} + \text{Ni(OH)}O^- 
\]  
(4)

\[
\text{Ni(OH)}O^- + \text{HO}^- \rightarrow \text{NiO}_2^- + \text{H}_2\text{O}
\]  
(5)

"The oxidation of aldehydes to carboxylic acids proceeds through the same steps because aldehydes in solution are in equilibrium with their hydrate, a 1,1-geminal diol, which is an alcohol."
that the two occur in a concerted manner. Another notable difference in the mechanism comes after the imine is formed. Unlike with aldehyde oxidation, the imine does not undergo a nucelofephilic attack by \( \text{OH}^- \) before undergoing further oxidation to the imine. Because the imine is highly reactive and its further oxidation is very fast, we did not detect any imine intermediates and could not directly probe its mechanism as we could for aldehyde oxidation. Accordingly, while we expect that imine oxidation proceeds though a similar combination of indirect and PD mechanisms, as does aldehyde oxidation, we could not experimentally confirm this. Accordingly, in Scheme 4 we do not propose specific steps for imine oxidation, instead showing it as an undefined set of fast steps resulting in a nitrile (step 5, Scheme 4).

To summarize, there are several key differences between the indirect pathway laid out in Scheme 2 and the PD one shown in Scheme 4. The two mechanisms feature different key mechanistic steps with PD oxidation involving a hydride transfer (\( \text{H}^+/2e^- \)) and a deprotonation instead of two HATs (\( \text{H}^+/1e^- \)). Additionally, they differ in the primary active site they occur at, with PD oxidation occurring only on \( \text{Ni}^{3+} \), while indirect oxidation can occur on \( \text{Ni}^{3+} \) (and also possibly \( \text{Ni}^{4+} \)). Finally, as is expanded upon below, they differ in the role the potential plays in the mechanism. For indirect oxidation, the potential is important only for generating the oxidized Ni site, while for PD oxidation, the applied bias is critical not only for generating the \( \text{Ni}^{4+} \) sites but also for enabling their reaction with the amine.

Deconvolution of Indirect and PD Oxidation Currents

In order to quantitatively determine the contributions the indirect and PD pathways have toward amine oxidation, we performed a rate deconvolution analysis using the procedure that we developed to study alcohol and aldehyde oxidation on NiOOH.\(^{20}\) Our method for measuring the rate of a potential independent, indirect oxidation pathway involves performing a series of three-step electrochemical procedures. (A corresponding scheme is provided in Figure S2.) The details of this three-step procedure are described in a prior work\(^{20}\) and in the Methods section, so we will provide only a brief overview here. In the first step, we pre-oxidize Ni(OH)\(_2\) to NiOOH by allowing the NiOOH to sit under open circuit conditions for a specified amount of time. As the system is under open-circuit conditions, NiOOH cannot be regenerated during this time, nor will any potential dependent process occur; however, NiOOH can act as a stoichiometric chemical oxidizing agent, oxidizing the amine while being reduced back to Ni(OH)\(_2\). After a specified amount of time has elapsed under open circuit conditions in this second step, we move to the third step, where a reducing potential is applied to rapidly convert the remaining NiOOH back to Ni(OH)\(_2\). The charge passed during this reduction shows how much NiOOH “reactant” remained after undergoing the potential independent chemical oxidation process for the amount of time that the system was under open circuit conditions. By repeating this process for several different open circuit times, a data series can be constructed that shows the disappearance of the NiOOH reactant due to its role as a chemical oxidant as a function of reaction time (i.e., the length of time sitting at the open circuit). Kinetics equations that describe the rate of the indirect process can then be derived from this data series. For all the reactions examined here, at relatively short times at the open circuit, a plot of 1/charge versus time is linear. This means that during the time frame of interest, the indirect process behaves as if it is second-order with respect to charge in the NiOOH film (Table S1), and therefore, its rate can be described according to eq 1, where \( Q_{\text{Ni}} \) is the positive charge stored in the film beyond its Ni(OH)\(_2\) resting state (i.e., the positive charge available for organic oxidation), which will be referred to as the charge stored in the NiOOH film. We note that this does not necessarily mean that the reaction is truly “second-order” with respect to the charge stored in the NiOOH film. Indeed, we suspect that the true rate law is probably more complicated. For our purposes, however, it is not necessary that eq 1 is the true rate law but rather just that it accurately models the disappearance of charge from NiOOH across the time frame of interest. The linearity of the 1/charge versus time plots shows that this is true for all the conditions tested in this work.

\[
\text{Rate}_{\text{ind}} = k_{\text{obs,ind}}Q_{\text{Ni}}^2
\]  

We use \( k_{\text{obs,ind}} \) rather than \( k_{\text{obs}} \) in eq 1 because the solution is rapidly stirred during our rate deconvolution trials, meaning that the concentration of the organic species at our electrode surface is constant over the duration of the experiments and thus is effectively “flooded”. This means that the influence the concentration of the organic species has on the reaction rate will be incorporated into \( k_{\text{obs,ind}} \) according to eq 2, where \( a \) is the reaction order with respect to the organic species.

\[
k_{\text{obs,ind}} = k_{\text{obs}}[\text{organic species}]^a
\]  

By solving eq 1 for when the positive charge stored in the Ni film (\( Q_{\text{Ni}} \)) is equivalent to its steady state value at the constant potential applied during the first step (obtained from the \( y \)-intercept of the 1/charge vs time plots), the current due to the indirect pathway can be obtained. We can then use this to obtain the current for the PD pathway by noting that as long as we have chosen a potential before the onset of water oxidation when generating our pre-oxidized NiOOH film, the total current will be equal to the sum of the indirect and PD partial currents (eq 3).

\[
I_{\text{tot}} = I_{\text{ind}} + I_{\text{PD}}
\]
We note that our rate deconvolution method works only because PD oxidation cannot occur under the open-circuit condition; when the applied potential is removed, PD oxidation stops, and only indirect oxidation continues until all existing Ni\(^{3+}\) (and likely Ni\(^{4+}\)) centers are reduced via HATs from the organic species, which is experimentally observed.\(^{20,21}\) This means that unlike for indirect oxidation where the potential is needed only to (re)generate the oxidized Ni sites, for PD oxidation the potential is critical not only to (re)generate the Ni\(^{3+}\) catalytic centers but also to enable the actual hydride transfer to the Ni\(^{4+}\) centers.

The rate deconvolution results obtained with 10 mM benzylamine and propylamine solutions at a pH of 13 and 1.52 V versus the reversible hydrogen electrode (RHE) are shown in Figure 2. (The 1/charge vs time plots used to obtain these results are shown in Figure S3.) The results confirm that, as was suggested qualitatively by the CVs (Figure 1), for both the aliphatic propylamine and the aromatic benzylamine, the indirect mechanism only accounts for a small fraction of the oxidation current (13% for propylamine and 19% for benzylamine), with the clear majority being due to a PD process. Additionally, we note that the aromatic benzylamine is more reactive for both PD and indirect oxidation than the aliphatic propylamine.

**pH Dependence**

We next considered how pH affects the rate of indirect and PD oxidation by comparing the rate deconvolution analyses obtained at 1.52 V versus RHE in pH 12, 13, and 14 solutions. Before the rate deconvolution analysis, we confirmed that the Faradaic efficiency for amine oxidation to nitrile in all these solutions (Figure S4) is high with no detectable side products, which is an important prerequisite for the rate deconvolution analysis. The fact that no aldehydes and carboxylic acids are detected suggests that once the imine intermediate is formed, further oxidation to the nitrile is rapid. The pH-dependent rate deconvolution results, \(k_{\text{obs,ind}}\) and Ni valence are shown in Figure 3. The CVs and the 1/charge versus time plots used to determine the rate and \(k_{\text{obs,ind}}\) in pH 12, 13, and 14 solutions are provided in Figures S5–S8. These plots can also be used to calculate the steady-state average Ni valence at the potential and amine concentration used for the rate deconvolution trial if the total amount of Ni in the NiOOH film has been quantified (see the Supporting Information for more details).

Figure 3 shows that for both propylamine and benzylamine, the PD current increases considerably as pH increases. This pH dependence can be attributed to two factors. The first is that the Ni(OH)\(_2\)/NiOOH couple follows a non-Nernstian shift as pH changes (Figure S9). As a consequence, even when the same potential is applied versus RHE, under more basic conditions this same potential versus RHE will represent a greater overpotential with respect to the Ni(OH)\(_2\)/NiOOH peak, leading to faster regeneration of higher valent Ni. This improves the kinetics for the PD process as the rate of this pathway is limited in part by the regeneration of Ni\(^{4+}\) sites, as can be seen by noting that the average Ni valence is significantly lower in the presence of amine than in its absence. For example, at 1.52 V versus RHE in a pH 13 solution, the average Ni valence without amine was determined to be +3.68 in our previous study\(^{20}\) while in the presence of 10 mM propylamine it is +3.44, and in the presence of the more reactive benzylamine it is only +3.27. The faster regeneration of Ni\(^{4+}\) sites as pH increases can lead to an increase in the average Ni valence and thus the number of active sites available to support PD oxidation, accounting for an increase in the observed current.

This first factor (faster Ni\(^{4+}\) regeneration) alone, however, cannot explain the effect of pH on the increase in the PD oxidation current for the less reactive propylamine, where the Ni valence is relatively high even at a pH of 12 and does not meaningfully increase as pH does. The results of propylamine oxidation suggests that the effective rate constant for the PD oxidation, \(k_{\text{obs,PD}}\), must include an \([\text{OH}^-]\) term, as shown in eq 4, where \(b\) is the order with respect to \([\text{OH}^-]\). In fact, eq 4 can also explain why propylamine does not show an enhancement in the average Ni valence as pH increases. While a higher pH does enhance the rate of Ni\(^{3+}\) regeneration, it also enhances the rate of consumption of Ni\(^{4+}\) through the PD process. In the case of propylamine, these two effects seem to net out to zero, leading to no change in the average Ni valence, while for benzylamine, the effect on the regeneration step is greater, leading to a higher average Ni valence as pH increases.

\[
k_{\text{obs,PD}} = k_{\text{PD [organic species]}}[\text{OH}^-]^b
\]

The most likely reason \(k_{\text{obs,PD}}\) has a \([\text{OH}^-]\) dependence is because, in addition to the hydride transfer, conversion of a primary amine into a nitrile through the PD process involves removing two protons from the –NH\(_2\) group. The pH dependence suggests that for the PD pathway, at least one of these deprotonation steps affects the rate. Moreover, due to the high reactivity of the imine and the lack of any observed aldehyde product (indicating that the lifetime of any imine formed is quite short), we can conclude that the first deprotonation step (step 3, Scheme 4) is the one much more likely to be rate-affecting. As was mentioned when discussing Scheme 4, this deprotonation is very unlikely to occur in solution and instead is expected to occur after the amine adsorbs, either shortly before hydride transfer or in concert with hydride transfer. In either case, it appears that this deprotonation of the adsorbed amine is critical to activate it toward hydride transfer. This is analogous to the case of PD oxidation involving alcohols, where previous computational results have indicated that hydride transfer to Ni\(^{3+}\) sites is
favorable so long as the alcohol either has already undergone deprotonation to form the alkoxide or does so in concert with the hydride transfer.\textsuperscript{20}

While the PD pathway was dominant at all pH values, there was also always a modest indirect component to the current. For propylamine, both the current from indirect oxidation and $k_{\text{obs,ind}}$ remain more or less the same. This is as expected since HAT, which is reportedly the rate-determining step for indirect oxidation, is pH independent. For benzyl amine, however, there is a modest enhancement in the indirect oxidation under more basic conditions, with the current increasing from 0.54 to 0.74 mA/cm$^2$. This occurs despite $k_{\text{obs,ind}}$ remaining constant, meaning that the reactivity of the higher valent Ni sites toward HAT has not changed (which is as expected). The reason for the increased current is because for a highly reactive amine such as benzylamine, the rate of HAT is quite fast, and at 1.52 V.
V versus RHE, HAT is not actually the sole rate-determining step. Instead, the overall rate for the indirect pathway is also partially limited by the regeneration of the catalytic center, which, as discussed above, is faster under more basic conditions due to the non-Nernstian shift of the Ni(OH)2/NiOOH couple as pH changes.

**Concentration Dependence Study**

Next, we examined the effect varying the amine concentration had on the current through both pathways. This was achieved by performing rate deconvolution experiments at 1.52 V versus RHE in pH 13 solutions with propylamine and benzylamine concentrations ranging from 5 to 50 mM. The resulting 1/charge versus time plots are shown in Figures S10 and S11, whereas the deconvoluted current, \( k_{\text{obs,ind}} \), and average Ni valence data are shown in Figure 4.

As can be seen in Figure 4, the PD current for benzylamine oxidation increases as the concentration increases from 5 to 20 mM, after which it plateaus. The reason for this plateau is that oxidation increases as the concentration increases from 5 to 20 PD current is eventually limited by Ni4+ regeneration and the importance of the Ni4+ regeneration step as benzylamine becomes independent of concentration, which appears to occur at 20 mM when the applied potential is 1.52 V versus RHE. (If a more positive potential is used, the plateau would be achieved at a higher concentration.) The increased importance of the Ni4+ regeneration step as benzylamine concentration increases is well-demonstrated by the trend in the average Ni valence. As the concentration of benzyl amine increases, Ni4+ is consumed more rapidly, and the steady-state average Ni valence declines considerably. Thus, further increasing the rate of PD oxidation would require the application of a more positive potential to enhance the rate of Ni4+ regeneration.

For the PD oxidation of propylamine, a gradual increase in current is observed as the concentration increases, and no plateau is reached in the concentration range studied here. This is because propylamine is significantly less reactive than benzylamine, which means that the effective rate constant for the consumption of Ni4+ sites through PD oxidation, \( k_{\text{PD}} \), is significantly lower for propylamine than for benzylamine. As a consequence, at a given amine concentration, the relative importance of the regeneration step for determining the PD oxidation rate will be smaller for propylamine than it is for benzylamine, and the concentration at which PD oxidation becomes concentration independent will be significantly higher for propylamine. The smaller relative importance of the regeneration step for determining the PD oxidation current for propylamine relative to that for benzylamine is well-supported by comparing the changes in average Ni valence as the concentration of the two amines is increased. For propylamine the decrease is gradual, and even at 50 mM the average Ni valence is still +3.2. In contrast, for benzylamine the decline is precipitous with the average Ni valence dropping to only +2.6 at 50 mM benzylamine, which means that only a small portion of the total Ni sites are in the active Ni4+ state at any given moment.

For the indirect pathway, \( k_{\text{obs,ind}} \) which includes an amine concentration term (eq 2), increases along with the concentration for both benzylamine and propylamine. Since it is the amount of adsorbed amine (rather than the solution amine concentration) that matters for the indirect process, this increase in \( k_{\text{obs,ind}} \) as the solution amine concentration increases means that across the concentration range studied here, the active higher valent Ni sites are not fully covered with amines and the coverage of these sites by amines increases along with the concentration. Despite the increase in \( k_{\text{obs,ind}} \), the actual rate for indirect oxidation does not increase along with the concentration. This is because, as shown in eq 1, the rate of indirect oxidation depends not only on \( k_{\text{obs,ind}} \), but also on the positive charge stored in the NiOOH film, and as shown in Figure 3c, the Ni valence decreases as the concentration increases, offsetting the increase in \( k_{\text{obs,ind}} \). In other words, as is the case for PD oxidation, regeneration can also become a key limiting step for indirect oxidation when \( k_{\text{obs,ind}} \) is enhanced by a high amine concentration.

The discussion above does beg the question why, for propylamine, the PD rate increases with concentration while the indirect rate does not. This difference likely stems from the difference in the primary active site of indirect and PD oxidation. PD oxidation must occur at Ni4+ sites, and adsorption on these is likely to be more difficult as it necessitates outcompeting hydroxide and oxygen evolution reaction (OER) intermediates for adsorption on those sites. Conversely, amine adsorption on the Ni3+ sites that are primarily responsible for indirect oxidation does not face this competition with OER intermediates. Consequently, the coverage of the Ni3+ sites with adsorbed propylamine is likely to be higher than that of the Ni4+ sites, meaning that increasing the solution concentration of propylamine would enhance the PD pathway more than the indirect one. The trend in \( k_{\text{obs,ind}} \) as propylamine concentration increases reflects this. While it does increase, this increase is modest (and is much smaller than that for the more reactive benzylamine), indicating that while the coverage of the Ni3+ sites with propylamine does increase along with concentration, this increase is fairly modest.

**Potential Dependence Study**

The results from the concentration dependence study discussed above make it clear that for both the indirect and PD pathways, the rate of regeneration of higher valent Ni sites plays an important role in determining the current. As the regeneration of these Ni sites is a potential dependent process, this means that to have a more complete understanding of how amine oxidation occurs on NiOOH, it is also necessary to understand how these two pathways are affected by changes in the applied potential. (The choice of potentials used in this section may look unusual, but this is because the actual experiments were performed using potentials of 0.55, 0.60, 0.65, and 0.70 V vs Ag/AgCl, while they are reported here vs RHE.)

We found that NiOOH is more catalytic toward amine oxidation than toward water oxidation; even when we apply a potential that can enable water oxidation such as 1.67 V versus RHE (the onset potential for water oxidation is ~1.55 V vs RHE at a pH of 13), the Faradaic efficiency toward amine oxidation remains high (Figure S12). This enabled us to apply our rate deconvolution technique to separate out the contributions of the indirect and PD pathways to the current at higher bias conditions. We did so using 10 mM solutions of propylamine and benzylamine at pH 13 with the applied potential ranging from 1.52 V versus RHE to 1.67 V versus RHE. The resulting 1/charge versus time plots are shown in...
Figures S13 and S14, while the deconvoluted current, \( k_{\text{obs,ind}} \), and average Ni valence data are shown in Figure 5.

As expected, the rate of the PD process increases significantly as the applied potential increases. This is as expected since the applied bias affects not only Ni\(^{4+}\) regeneration but also the rate constant for hydride transfer. The strong enhancement in the rate of PD oxidation also means that, as expected, the proportion of the current occurring through the PD pathway increases along with the potential.

We found that the indirect rate also increased with the applied potential, although the increase was not as significant (Figure 5a). Surprisingly, this increase is primarily caused by an increase in \( k_{\text{obs,ind}} \) (Figure 5b), which should theoretically be potential independent, rather than by an increase in the average Ni valence (Figure 5c). We believe that this is caused by the fact that not all the Ni sites in the NiOOH used in our experiments are perfectly identical. Instead, the local environments of the Ni sites vary and so do their catalytic activities toward amine oxidation. When we consider the steady-state balance of sites that will be oxidized versus reduced at a given applied bias, the least reactive sites toward amine oxidation are the ones most likely to be in the oxidized state (since they would be the slowest to react with the amine and be reduced),

Figure 5. Plots depicting (a) partial current densities for oxidation through the indirect and PD pathways, (b) \( k_{\text{obs,ind}} \), and (c) average steady-state Ni valence at various applied potentials in a rapidly stirred pH 13 solution with a 10 mM concentration of benzylamine (top) and propylamine (bottom).

Figure 6. CVS collected using a Ni(OH)$_2$ WE in pH 13 solutions with 10 mM normal (black) and deuterated (red) solutions of (a) propylamine and (b) benzylamine (scan rate, 10 mV/s).
while the most active sites toward amine oxidation are the most likely to be in the reduced state. Accordingly, when the applied bias is increased (increasing the driving force for Ni oxidation), the accompanying increase in the steady-state average Ni valence is primarily caused by an increased number of these most reactive sites being in the oxidized state rather than in the reduced state. This in turn means that the average reactivity of the oxidized sites toward amine oxidation will be higher (i.e., $k_{\text{obs,ind}}$ will be higher). This occurs not because the higher applied bias has done anything to make any individual site more reactive but rather because applying a higher bias means that the most active sites toward amine oxidation will comprise a greater proportion of the Ni sites in the oxidized state (rather than in the reduced state). This appears to have had a greater relative effect on propylamine than on the more reactive benzylamine, perhaps because benzylamine is sufficiently reactive that even the less active Ni sites are already enough to ensure rapid benzylamine oxidation.

**Kinetic Isotope Effect Experiments**

To gain further insights into what steps are important for determining the rate of PD and indirect oxidation of primary amines, we performed experiments comparing the results of oxidation of normal propylamine and benzylamine with oxidation of propyl-$d_1$-amine and benzyl-$\alpha$-$\alpha$-$d_2$-amine to test whether substituting the hydrogens at the alpha position for deuterium results in a primary kinetic isotope effect (KIE). We did this first by comparing CVs obtained at a pH of 13 with 10 mM solutions of the normal and deuterium-substituted amines. The results are shown in Figure 6 and reveal that for both propylamine and benzylamine, deuterium substitution does anodically shift the peak corresponding to amine oxidation, though the effect on the peak current achieved is minimal. These results qualitatively indicate that there is at least a modest KIE caused by deuterium substitution.

To gain more detailed information into the extent of this KIE and whether it differs for PD and indirect oxidation, we also compared the results of rate deconvolution experiments for normal and deuterium-substituted amines performed with 10 mM solutions at pH 13 and 1.52 V versus RHE. The resulting 1/charge versus time plots are shown in Figure S15, while the comparison of the partial current densities is shown in Figure 7.

These results show that for the indirect process, there is a modest KIE evident for both propylamine ($I_H/I_D = 1.3$) and benzylamine ($I_H/I_D = 1.4$). Notably, these measured KIE values are much lower than the KIE of $\sim 7$ reported by Fleischmann et al. for methanol oxidation. Instead, the more modest values found here are consistent with the other results reported throughout our pH Dependence, Concentration Dependence, and Potential Dependence sections, which highlight that both amine adsorption and regeneration of oxidized Ni sites play a meaningful role in determining the rate of the indirect process. All told, then, our data suggest that rather than being determined solely by the rate of the HAT step, as implied by Fleischmann et al.'s proposed mechanism (Scheme 2), the rate of the indirect process is actually controlled by a more complex interplay between several steps, with the HAT step being but one.

The KIE observed for the PD pathway is also quite small. For propylamine, there is a modest KIE observed for the PD pathway ($I_H/I_D = 1.3$), while for benzylamine, the KIE is negligible. As was the case for the indirect pathway, the data discussed above indicate that amine adsorption and regeneration of Ni$^{4+}$ play an important role in determining the rate of PD oxidation, which explains the small/negligible effects observed here. Furthermore, as was mentioned in the pH Dependence section, the fairly strong effect of pH on the rate of the PD process indicates that the deprotonation step that accompanies hydride transfer likely has an important effect on the rate. When paired with the modest/negligible KIE observed here, this suggests that (at least in pH 13 solutions) this deprotonation step might play a greater role in controlling the rate than does the hydride transfer step, particularly for benzylamine, which shows the greater pH dependence and a negligible KIE for PD oxidation.

**CONCLUSIONS**

The present work offers a comprehensive look at the mechanism for the oxidation of primary amines to nitriles on NiOOH electrocatalysts. It demonstrates that, as is the case for alcohol and aldehyde oxidation on NiOOH, primary amine oxidation occurs through two concurrent mechanisms, indirect oxidation and PD oxidation. In fact, as is the case for alcohol oxidation, amine oxidation on NiOOH occurs predominantly through the PD pathway. We also investigated how the rates of PD and indirect oxidation are influenced by a variety of factors including pH, concentration, applied potential, and deuterium substitution. The results reveal that for both pathways, the rate is determined by a complex interplay between several steps including adsorption of the amines, the hydrogen atom/hydride transfer step, regeneration of higher valent Ni sites, and (for PD oxidation) deprotonation of the amine. The kinetics cannot be reduced to a single controlling step for either pathway, and indeed, the relative impact of each of the steps mentioned varies with changes to the solution conditions, applied potential, and the nature of the amine being oxidized. There are, however, a few general statements that can be made. Across the concentration range examined in this work (5 to 50 mM), the coverage of the active sites with adsorbed amine is not complete and can be increased by increasing the amine concentration in solution. Moreover, for all the conditions examined here, the average Ni valence is substantially lower in the presence of the amines than when no amine is present and decreases further if the amine concentration increases. This effect is more pronounced when a more reactive amine is used.

![Figure 7. Component of the current due to indirect (red) and PD (blue) oxidation of pH 13 solutions with 10 mM concentrations of normal and deuterated benzylamine or propylamine at 1.52 V vs RHE.](https://doi.org/10.1021/jacsau.2c00150)
This demonstrates that the kinetics for Ni(OH)₂ oxidation are not sufficient to keep all the Ni sites fully oxidized in the presence of the amine solution and means that the regeneration of oxidized Ni sites plays an important role in determining the rate of amine oxidation through both pathways. Accordingly, properly understanding the effect each reaction condition (pH, potential, amine reactivity, and concentration) has on the consumption and regeneration of higher valent Ni sites is critical to accurately interpret results and for being able to predict what effect varying these conditions will have.

Overall, this work provides a comprehensive examination of the mechanism of primary amine oxidation on NiOOH. Moreover, the strong similarity between the results found here for amine oxidation and the results we have previously reported for alcohol and aldehyde oxidation indicate that this mechanistic framework provides a good foundation to understand a much broader set of dehydrogenation reactions on MOOH electrocatalysts.

## METHODS

### Materials

The chemicals employed were all acquired from commercial sources and used without further purification: benzylamine (99%, Sigma-Aldrich), propylamine (≥99%, Sigma-Aldrich), n-propyl-d₆-amine (CDN isotopes, 99.4%-d₆), benzyl-tart-d₂ alcohol (CDN isotopes, 99.4%-d₂), potassium hydroxide (≥85%, Sigma-Aldrich), Ni(NO₃)₂·6H₂O (99%, Acros), KNO₃ (99%, Alfa Aesar), KClO₄ (≥99%, Sigma-Aldrich), and boric acid (≥99.5%, Sigma-Aldrich). All solutions were prepared using deionized water (Barnstead E-Pure water purification system, resistivity > 18 MΩ cm).

### Ni(OH)₂ Electrode Preparation

Ni(OH)₂ films were prepared using an established technique in which nitrate is electrochemically reduced. This produces hydroxide and increases the local pH at the WE, causing Ni(OH)₂ to precipitate out and form a Ni(OH)₂ film. This process was controlled using an SP-200 potentiostat/EIS (BioLogic Science Instrument) and carried out using a three-electrode setup in a single-compartment glass cell. The WE was FTO, the counter electrode (CE) was Pt, and the reference electrode (RE) was Ag/AgCl (4 M KCl). To prepare the FTO WE, larger FTO plates were cut into 2.5 cm × 1 cm strips, after which Cu tape was affixed to the top to provide electrical contact, and the FTO was masked with electroplating tape (3M Company) with a 0.5 cm² hole punched in it to ensure that a well-defined conductive surface area was exposed. The Pt CE was prepared by sputter-coating a 20 nm Ti adhesion layer, followed by sputter-coating 100 nm of Pt onto clean glass slides. The Ni(OH)₂ films were deposited by Galvanostatically maintaining a current of ~0.25 mA/cm² for 45 s in an aqueous plating solution consisting of 10 mM Ni(NO₃)₂·6H₂O and 30 mM KNO₃. The resulting Ni(OH)₂ films were rinsed with >18 MΩ cm water and then dried in an air stream.

### Electrochemical Experiments

Cyclic voltammetry and electrolysis were performed using a three-electrode setup in a sealed glass cell. For cyclic voltammetry, the cell was undivided, while for electrolysis, the cell used had a glass frit separating the WE and CE compartments. Ni(OH)₂ films were used as the WE, Ag/AgCl as the RE, and Pt mesh as the CE. Cyclic voltammetry was performed starting from an open circuit potential, and the potential was swept at a scan rate of 10 mV/s in the positive direction first. For all cyclic voltammetry runs, the potential was cycled at least twice, and the curves shown are from the second cycle. For the stirred cyclic voltammetry runs, the solution was rapidly stirred using a magnetic stirring bar throughout the time the potential was being scanned.

Electrolysis was performed at a constant potential in a rapidly stirred amine solution until the stoichiometric charge required for 25% (pH 13 and 14) or 12.5% (pH 12) conversion of the initial amine to nitrite had been passed. The lower charge passed was used for the least reactive case (pH 12) to allow for more rapid completion of the electrolysis. In all cases, we chose to pass only part of the charge required for full conversion to ensure that the results would accurately reflect the selectivities and Faradaic efficiencies of the rate deconvolution experiments as these were conducted with amine concentrations equal to the concentrations at the beginning of the electrolysis. The pH of all solutions used for our electrochemical experiments was adjusted using KOH. For the cyclic voltammetry and rate deconvolution experiments, the pH 12 solutions could be used unbuffered as the minimal amount of charge passed meant that the pH drift would not be an issue even without a buffer. In these cases, 90 mM KClO₄ was added to the pH 12 solutions as the supporting electrolyte to ensure that they had sufficient solution conductivity. When used for electrolysis, the pH 12 solutions were instead buffered using 0.5 M borate.

### Product Analysis

The electrolysis products were quantified via H NMR spectroscopy using a Bruker AVANCE III 400 MHz NMR spectrometer. Samples were prepared by adding 0.450 mL of the electrolysis solution and 0.050 mL of D₂O to an NMR tube and shaking vigorously. The analyses were conducted with a relaxation delay of 30 s, and a WATERGATE method was used with excitation sculpting to remove the background signal from the water solvent. Product quantification was performed by comparing the integrations of the product peaks of the post electrolysis solutions to those of standards of known concentrations.

### Rate Deconvolution Procedure

A detailed explanation of our three-step rate deconvolution procedure can be found in our previous work; however, a brief overview and description is outlined here. The process was performed using a rapidly stirred 30 mL amine solution in a single-cell glass sealed cell with a three-electrode setup. A thin Ni(OH)₂ film deposited using the methods described above was used as the WE, Ag/AgCl as the RE, and Pt mesh as the CE. Before being used for the rate deconvolution experiments, each Ni(OH)₂ film was tested using cyclic voltammetry [two cycles with switching potentials of 1 V vs Ag/AgCl and 0 V vs Ag/AgCl (pH 12), 0.9 V vs Ag/AgCl and 0 vs Ag/AgCl (pH 13), or 0.8 V vs Ag/AgCl and 0 V vs Ag/AgCl (pH 14)] to confirm that the Ni(OH)₂/NiOOH peak and water oxidation behavior of each film was consistent.

In the first step of the three-step procedure, a fixed potential was applied to the WE in a rapidly stirred solution long enough for the current to reach a steady-state value (typical 30 s), where “rapidly stirred” was defined as stirred sufficiently fast such that further changes to the stirring speed no longer charged the current density. This converts the film into the steady-state condition it would be in during a potentiostatic electrolysis at the applied potential. During this step, both the indirect and PD oxidation pathways are active. For the second step, the potential is no longer applied, leaving the film to sit in the stirred solution under open-circuit conditions. During this time, neither the PD pathway nor reoxidation of Ni(OH)₂ can occur (since both require applied bias); however, the indirect pathway, which proceeds through a chemical (rather than electrochemical) HAT step, still occurs. This reduces a portion of the higher valent Ni sites generated during the first step back to Ni(OH)₂. During the third step, the higher valent Ni sites that still remain after step 2 are rapidly reduced back to Ni(OH)₂, by sweeping the potential from the open circuit potential to 0 V versus Ag/AgCl at a scan rate of 1 V/s and then holding the potential at 0 V for 20 s. The magnitude of the charge passed during this third, reductive step corresponds to the amount of charge that was still stored in the film after a portion of it was used in step 2 to oxidize the amine through the indirect pathway. By repeating the whole three-step process with different times for stirring under open circuit conditions in step 2, we could construct plots showing the disappearance of charge from the film as a function
of time under open circuit conditions. This was used to generate kinetics equations and determine the rate of charge loss from the NiOOH film at 0 s under open circuit conditions, which corresponds to the rate of the indirect pathway under electrolysis conditions at the potential applied in step 1. We note that for our method to work, there should be no pathway to consume the positive charge stored in NiOOH during step 2 other than the indirect oxidation of the organic species. It is well-known that NiOOH under open circuit conditions gradually reduces to Ni(OH)₂; however, the discharge kinetics of NiOOH in the absence of amines are considerably slower than those for indirect oxidation when NiOOH is in the presence of amines. Therefore, for the time scales used in this study (≤ 2 s), the charge lost in the absence of amines is negligible relative to the charge lost in the presence of even propyldiamine, which is the least reactive amine tested here (Figure S16).

When conducting the rate deconvolution trials for a given amine and condition, each data point in the 1/charge versus time plots was obtained by averaging the results from four separate measurements obtained with four different Ni(OH)₂ films. During these trials, each Ni(OH)₂ film was replaced after being used to measure data for four different times under open circuit conditions. Additionally, whenever the Ni(OH)₂ film was replaced, the amine solution was replaced with a fresh solution. Finally, we note that in order to obtain precise analysis results, it is important to properly account for any variation of the number of active Ni sites from film to film for all films used in our study. Similarly, it is important to monitor and account for any change in the number of active sites when repeatedly using the Ni(OH)₂ film for our analysis. To achieve this goal, we developed a rigorous measurement and calibration procedure to ensure that any difference in the amount of positive charge stored in NiOOH is solely due to the indirect oxidation of the organic species by NiOOH. This process is explained in detail in the Supporting Information under the “Mathematical calibration of measured charge stored in NiOOH” section.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/jacsau.2c00150.

Additional methods, CVs, 1/Q−t plots, and Faradaic efficiencies (PDF)

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Notes
The authors declare no competing financial interest.

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