

The Key Role of Solvation in Enhancing Electrochemical Promotion of Brønsted Acid Catalysis

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Cite This: <https://doi.org/10.1021/jacs.6c13986>



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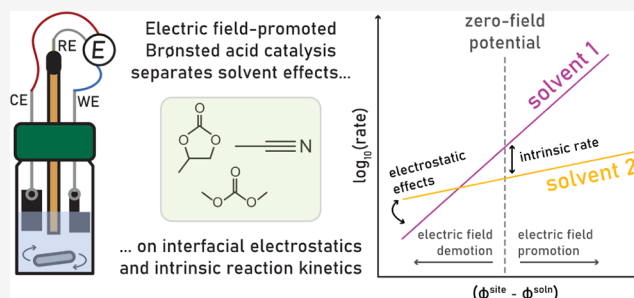


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ABSTRACT: Electrostatic polarization of catalyst-solution interfaces can modulate the rate of liquid-phase heterogeneous Brønsted acid catalysis by up to 5 orders of magnitude. Previous studies in acetonitrile establish that maximal rate-potential scaling emerges only at high ionic strength, indicating that rate promotion is sensitive to the interfacial electrostatic potential profile. Herein, we examine the role of the solvent on the electrolyte strength sensitivity of polarization-induced promotion of Brønsted acid catalysis. Using carbon paper with Brønsted acid functionalities, we measured 1-methylcyclopentanol dehydration rates in dimethyl carbonate, acetonitrile, and propylene carbonate, with electrolyte concentrations ranging from 1 to 600 mM. In acetonitrile and dimethyl carbonate, the alcohol dehydration rate-potential scaling is a function of ionic strength, implying that the proton traverses only a fraction of the electrostatic potential drop to form a surface-bound oxonium intermediate prior to the rate-limiting C–O bond cleavage. In contrast, in more polar propylene carbonate, the rate-potential scaling aligns well with the maximum dependence predicted for a single-charge process and is insensitive to electrolyte concentration down to 1 mM. This behavior is consistent with the proton traversing the entire electrostatic potential drop to form a freely solvated oxonium intermediate outside the electrochemical double layer. These findings highlight that enhanced solvation of protonated intermediates is essential for maximizing electrostatic promotion in Brønsted acid catalysis. Together, the kinetic data show that solvent selection modulates both the intrinsic reaction rate and sensitivity to catalyst potential, emphasizing the importance of understanding interfacial electrostatic effects in thermochemical reaction systems.



INTRODUCTION

Solid acid catalysts are widely used in industrial chemical manufacturing to avoid the separations challenges and waste streams associated with homogeneous acids.^{1–7} However, achieving practical reaction rates on solid acid catalysts can require elevated reaction temperatures for sluggish reactions, increasing energy demand and creating logistical challenges for decarbonization.^{8,9} One alternative way to increase reaction rate without increasing operating temperature is to change the reaction solvent. In liquid-phase Brønsted acid catalysis, solvent environment has been shown to promote or demote reaction rates by orders of magnitude.^{10–14} This modulation has been proposed to result from a number of effects, including stabilization of reactive intermediates and transition states, interactions with the active site, and modification of the reaction mechanism.

However, a factor that is more seldom considered is the effect of the solvent on the electrostatic potential profile at the interface. At any solid–liquid interface, both free ions in solution and molecules with dipoles spontaneously arrange to establish an electrostatic potential gradient across the phase boundary.¹⁵ This gradient in electrostatic potential produces an interfacial

electric field that serves as an orthogonal driving force for interfacial proton transfer, thereby strongly influencing the rate of Brønsted acid catalysis.

Recent studies establish that interfacial polarization can promote liquid-phase alcohol dehydration rates by up to 5 orders of magnitude.^{16,17} Specifically, our groups demonstrated that polarizing a solid Brønsted acid catalyst in a three-electrode electrochemical configuration strongly alters thermochemical Brønsted acid-catalyzed 1-methylcyclopentanol (1MCPol) dehydration, with rates changing by approximately 1 order of magnitude for every 70 mV change in applied electrochemical potential.¹⁶

This rate–potential scaling was attributed to the electrostatic free energy change when a proton traverses some portion of the electrostatic potential drop across the solid–liquid interface,

Received: July 7, 2026

Revised: September 25, 2026

Accepted: September 28, 2026

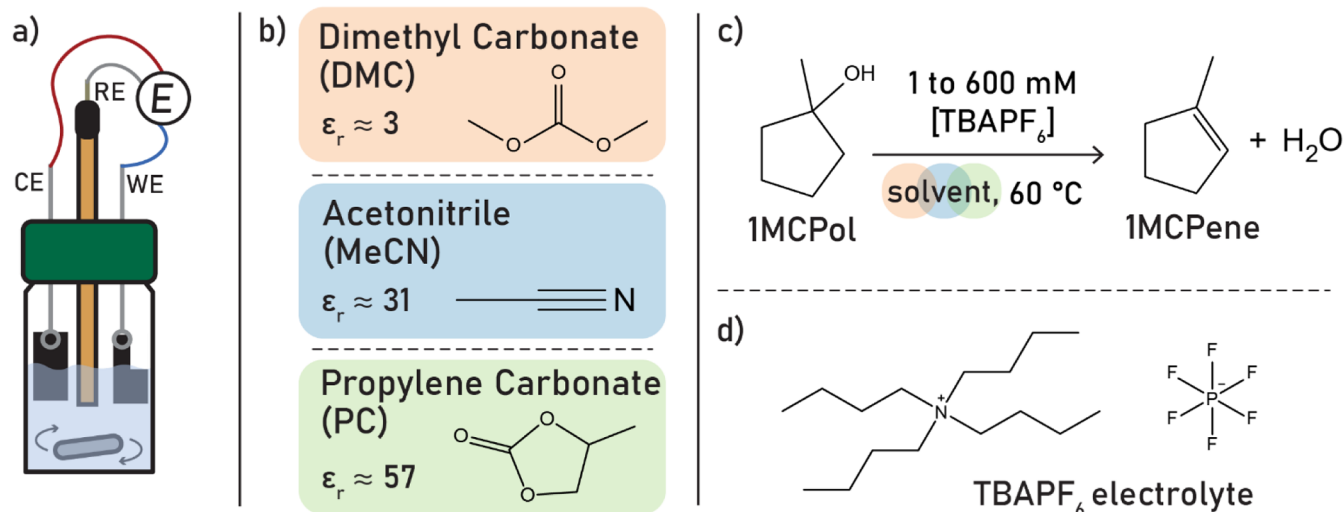


Figure 1. a) Illustration of three-electrode carbon paper batch reactor. The working electrode (WE), counter electrode (CE), and Ag/AgCl reference electrode (RE) are attached to a potentiostat. b) Names, bulk dielectric constants (at 60 °C), and chemical structures of solvents used in this study. c) Reaction conditions for the dehydration of 1-methylcyclopentanol (1MCPol) to 1-methylcyclopentene (1MCPene). d) Structure of tetrabutylammonium hexafluorophosphate (TBAPF_6) electrolyte.

where it forms a pre-equilibrated oxonium intermediate prior to rate-limiting C–O bond cleavage.¹⁷ Accordingly, the magnitude of potential sensitivity was found to depend on electrolyte concentration. Higher ionic strengths compress the electrostatic potential decay length scale and increase the fraction of interfacial potential drop over which the proton traverses, leading to reaction rates that are more strongly dependent on applied potential. This interpretation is dependent on the key assumption that the oxonium intermediate remains bound to the active site, eventually undergoing the rate-limiting C–O cleavage step within the electrochemical double layer at some relatively invariant position away from the active site, called the “reaction plane.” Importantly, to the extent that this reaction plane resides partially within the electrochemical double layer potential decay profile, it serves to attenuate the magnitude of polarization-induced promotion of Brønsted acid catalysis.

In order to maximize the effect of interfacial polarization on dehydration reaction rate, it would be preferable for the oxonium intermediate to fully dissociate from the surface. Since the protonation of the alcohol is assumed to be quasi-equilibrated, the relevant electrostatic driving force for this step is given by the difference in electrostatic potential between the proton at the surface and that of the oxonium intermediate as it undergoes the rate-determining step (RDS). Thus, dissociation of the oxonium to form a free-solvated intermediate should yield the strongest possible rate-potential scaling, regardless of electrolyte concentration.

While an appropriately polar solvent could be sufficiently stabilizing to facilitate dissociation of protonated intermediates (and therefore maximize the influence of interfacial polarization on reaction rate), changing the solvent may also change other key reaction variables. The solvent’s size, dielectric constant, and hydrogen bonding capacity, among other factors, serve to alter the double layer structure and the electrostatic potential decay profile.^{18–21} Simultaneously, the solvent influences the intrinsic pK_a of an active site (in the absence of local polarization) and the extent of stabilization of both reactive intermediates and transition states.^{22–24} Consequently, isolating the influence of solvent on the polarization contribution to Brønsted acid catalysis rates is challenging.

We recently showed that the effects of polarization can be deconvoluted from intrinsic changes in reaction rate by analyzing the ionic-strength dependence of rate-potential scaling plots. Specifically, we found that rate-potential scaling plots across various ionic strengths converge at an iso-kinetic potential (IKP), at which the reaction rate is independent of ionic strength.¹⁷ This IKP defines the potential at which the local electrostatic potential drop at the active site vanishes, providing a direct measure of the intrinsic rate of catalysis in the absence of electrostatic driving forces. Importantly, for solvents that enable dissociation of the protonated intermediate from the Brønsted acid catalyst, there should no longer be a singular intersection potential for rates at different electrolyte concentrations (the IKP), since the reaction rate is no longer sensitive to the electrostatic potential profile in the electrochemical double layer.

Herein, we examine the ionic-strength dependence of rate-potential scaling across dimethyl carbonate (DMC), acetonitrile (MeCN), and propylene carbonate (PC) solvents for the Brønsted acid-catalyzed liquid-phase dehydration of 1-methylcyclopentanol (1MCPol) to 1-methylcyclopentene (1MCPene). In all solvents, the dehydration rate scales exponentially with applied catalyst potential. However, in DMC and MeCN, the rate-potential scaling depends on ionic strength gonionic strength, indicative of a bound oxonium intermediate residing within the electrochemical double layer. In these solvents, the apparent transfer coefficients range from 0.26 to 0.69, which we interpret as the proton traversing between about 26 and 69% of the interfacial electrostatic potential drop to form the bound oxonium intermediate. Both solvents return IKPs similar to each other, with an extrapolated approximate 5-fold enhancement in rate in the absence of an electric field in MeCN compared to DMC. However, in PC, no IKP is observed and the rate-potential scalings are in alignment with a unity transfer coefficient (Nernstian scaling) across a range of ionic strengths down to 1 mM, indicating that, in each catalytic cycle, the proton traverses nearly the entire double layer to form an unbound oxonium intermediate. This finding suggests that in polar solvents, such as PC, electrostatic polarization can profoundly affect Brønsted acid catalysis rates, even in the

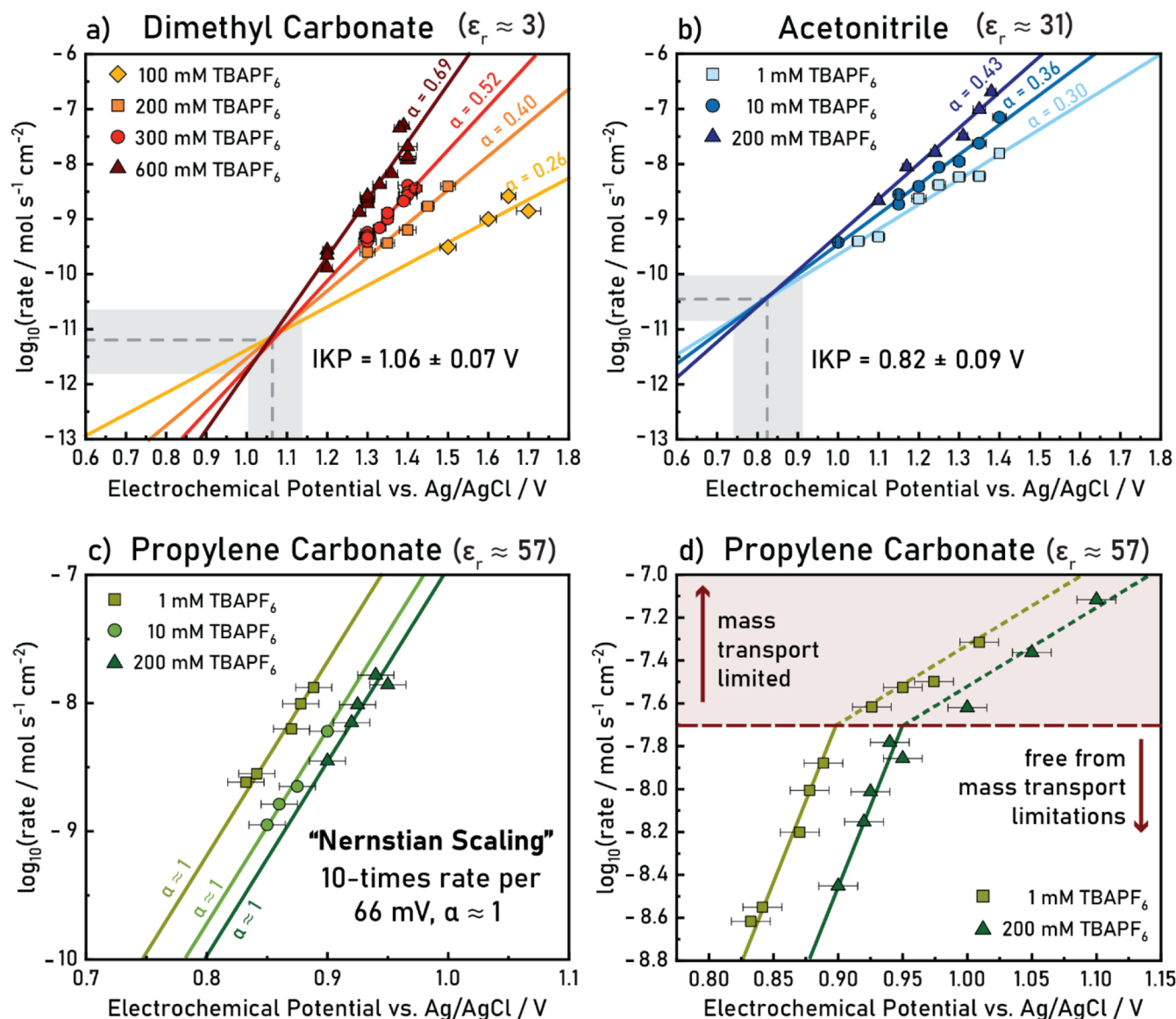


Figure 2. Rate of formation of 1MCPene per carbon paper area for the dehydration of 0.1 M 1MCPol at 60 °C versus carbon paper applied electrochemical potential in a) DMC with 100, 200, 300, and 600 mM of TBAPF₆ electrolyte, along with best fit lines; b) MeCN with 1, 10, and 200 mM TBAPF₆ electrolyte, along with best fit lines; c) PC with 1, 10, and 200 mM of TBAPF₆ electrolyte, plotted with lines representing Nernstian scaling, or 66 mV per decade of rate. d) Emergence of internal mass transport limitations in PC leads to approximately half of the original log₁₀(rate) versus potential slope. These rates were excluded from the calculation of α . Error bars in the x -direction in all plots represent the sum of the standard deviation of applied potential and the standard deviation in drift of the leakless RE compared to a master Ag/AgCl reference electrode in the respective solvent with 100 mM TBAPF₆. Error bars in the y -direction were propagated to the calculation of the IKP and rate at IKP via Monte Carlo simulation (Section S8). α , or the apparent transfer coefficient, is computed from the slope of the line of best fit and is listed for each electrolyte concentration (Section S3.6).

absence of substantial added electrolyte as well as in systems where catalyst potential is not measurable.

Taken together, these results demonstrate that the solvation of reaction intermediates in Brønsted acid catalysis is a critical factor in dictating both the magnitude of electrostatic promotional effects and zero-field reactivity—two effects that cannot be separated without a measurable catalyst potential.

RESULTS AND DISCUSSION

Carbon-Paper Batch Reactor to Explore Solvent Effects on the Dehydration of 1MCPol

To isolate the effect of solvent choice on electric field-promoted Brønsted acid catalysis, we employed a conductive catalyst that

could be directly polarized without chemical modification. Commercial Sigracet 39 BB carbon paper met these criteria and required no pretreatment for Brønsted acid catalytic activity. We hypothesize that carboxylic acid or other oxidic acid groups within the microporous carbon layer of Sigracet 39 BB provide Brønsted acid functionality, but the exact structure of the active site remains unknown.

We performed kinetic measurements in a three-electrode batch reactor configuration (Figure 1a), with a flag-shaped carbon paper serving as the working electrode (WE), a rectangular piece of carbon paper as the counter electrode (CE), and a leakless Ag/AgCl reference electrode (RE). We selected three polar aprotic solvents spanning a wide range of

bulk dielectric constants at 60 °C (Figure 1b): DMC (low, $\epsilon_r \approx 3$),²⁵ MeCN (intermediate, $\epsilon_r \approx 31$),²⁸ and PC (high, $\epsilon_r \approx 57$).²⁷ Each solvent was electrochemically stable up to at least 1.2 V vs Ag/AgCl under reaction conditions (Figure S19), and solubilized tetrabutylammonium hexafluorophosphate (TBAPF₆) and 1MCPol well.

We measured initial reaction kinetics in the three solvents for the dehydration of 0.1 M 1MCPol to 1MCPene at 60 °C at varying concentrations of TBAPF₆ (Figure 1c and Figure 1d). DMC required relatively high electrolyte concentrations (100, 200, 300, and 600 mM of TBAPF₆) to achieve measurable product yield (>0.5%) in less than a day (Figure 2a), while faster rates in MeCN enabled a wider range of TBAPF₆ concentrations (1, 10, and 200 mM, Figure 2b).

From the slope of $\log_{10}(\text{rate})$ vs applied electrochemical potential, we extracted a “rate-potential scaling,” describing the potential difference required to alter the reaction rate by 10-fold. From the rate-potential scaling, we compute the apparent transfer coefficient, α , which we define as eq 1,

$$\alpha = \frac{RT}{F} \frac{d \ln(\text{rate of alkene formation/mol s}^{-1} \text{ cm}^{-2})}{dE} \quad (1)$$

where R is the ideal gas constant, T is temperature, F is Faraday's constant, and E is the applied electrochemical potential. We note, in electrochemistry, the transfer coefficient typically takes the same form, except the Faradaic current replaces the thermochemical reaction rate.^{28,29}

For a single positive charge traversing some portion of the double layer, the apparent transfer coefficient should be bounded ($0 \leq \alpha \leq 1$), with $\alpha = 0$ indicating the reaction rate is completely independent of catalyst potential and $\alpha = 1$ indicating the strongest potential dependence possible (Nernstian scaling, 66 mV per decade of rate at 60 °C, Section S3.6).

DMC with a TBAPF₆ concentration of 100 mM exhibited weak potential dependence (250 mV per decade of rate; $\alpha = 0.26 \pm 0.06$); reaction rates faster than those plotted in Figure 2a could only be reached at applied potentials that generated large parasitic currents and required iR compensation beyond what our potentiostat could accurately provide. At higher TBAPF₆ concentrations in DMC, the reaction rate of 1MCPol dehydration became strongly potential dependent, with a 10-fold increase in reaction rate for every 96 mV of applied electrochemical potential at 600 mM TBAPF₆, equivalent to α reaching 0.69 ± 0.04 .

In MeCN, changing the electrolyte concentration from 1 to 200 mM resulted in a moderate increase in the strength of rate-potential scaling from 220 mV per decade to 154 mV per decade (α increases from 0.30 ± 0.01 to 0.43 ± 0.02). We further increased the concentration of electrolyte in MeCN up to 1000 mM TBAPF₆ under iso-potential conditions and saw the reaction rate continuously rise across these electrolyte concentrations (Section S3.5).

Rate data at varying concentrations of TBAPF₆ in both DMC and MeCN exhibited well-defined IKPs. In DMC, we observe an IKP of 1.06 ± 0.07 V, and in MeCN the IKP was 0.82 ± 0.09 V (all electrochemical potentials are reported against Ag/AgCl unless otherwise stated; Section S2.6.2). As shown in prior work from our groups,^{17,30} the IKP corresponds to the applied electrochemical potential at which there is no interfacial electric field formed at the catalyst surface. At their respective IKPs, the extrapolated rate in MeCN is approximately 5-fold faster than in DMC. However, these rates were too slow to verify experimentally.

PC rate-potential data were collected across the same range of electrolyte conditions as MeCN (1, 10, and 200 mM), but showed a strong dependence on potential, regardless of TBAPF₆ concentration (Figure 2c). Due to the narrow electrochemical potential window over which we collected rate data in PC, there is substantial uncertainty in the freely fitted apparent transfer coefficients: $\alpha = 0.87 \pm 0.22$ for 1 mM, 0.94 ± 0.34 for 10 mM, and 0.86 ± 0.27 for 200 mM (Section S8). Rates at lower potentials in PC were experimentally infeasible to measure due to limitations in quantification via ¹H NMR (Section S2.5.5). We also attempted to measure dehydration rates in PC at higher potentials, but for rates higher than about $2 \times 10^{-8} \text{ mol s}^{-1} \text{ cm}^{-2}$ (−7.7 on a $\log_{10}$ scale), we observed a change in rate-potential scaling to approximately half of the original value (Figure 2d). This behavior is consistent with internal diffusional limitations, which may arise at lower rates in PC due to higher viscosity compared to DMC or MeCN (Section S5.2). We did not identify a change in slope indicative of mass transport limitations in DMC or MeCN over the approximately 3 orders of magnitude of rate measured.

Due to the small range of applied electrochemical potentials where it was feasible to measure transport-artifact-free rates in PC, the linear regression of slopes in the PC rate data is highly sensitive to errors in individual data points. Therefore, instead of using exact regression, we plotted rate-potential scaling lines with $\alpha = 1$ (66 mV per decade) for each electrolyte concentration. These theoretical lines visually fit our data well and $\alpha = 1$ is within the propagated uncertainty of all computed apparent transfer coefficients, and no systematic dependence of α on electrolyte concentration is resolved. The PC data are consistent with Nernstian scaling, the maximum expected sensitivity to catalyst potential, across all tested electrolyte concentrations. We note that our rates are slightly enhanced in 1 mM TBAPF₆ electrolyte compared to 10 or 200 mM, which we hypothesize is an indication that our rate measurements are taken below the potential of zero electric field, with precise α values slightly deviating from unity; however, we cannot rule out other effects such as electrolyte site-blocking (Section S3) or inaccuracies in iR compensation methods (Section S2.5.4).

Given the strong rate-potential scaling in PC at 1 mM, we sought to examine the rate in the absence of exogenous electrolyte. Using electrochemical impedance spectroscopy, we measured the resistance of this solution to be about 100,000 Ω , consistent with approximately 0.03 mM of ionic species in solution (Section S7.3). With such high solution resistance, we were unable to accurately measure/control the electrochemical potential upon external polarization; however, we measured the open circuit potential (OCP) as approximately 0.1 V. With rate-potential scaling in PC (nearly) independent of electrolyte concentration between 1 and 200 mM, it follows that at even smaller ionic strengths, dehydration rate would continue to be strongly dependent on catalyst potential. Indeed, at the OCP, we observed no measurable reactivity over 72 h, consistent with 0.1 V being much smaller than the potential of zero field and persistent strong rate-potential scalings in PC at lower ionic strengths.

While our reaction system is largely free of electroactive species, the system is not perfectly polarizable, and some (relatively small) amount of current is required to maintain the applied electrochemical potential. For non-Faradaic reactions undergoing electric field-promoted catalysis, this current represents an inefficiency because it consumes electrical power

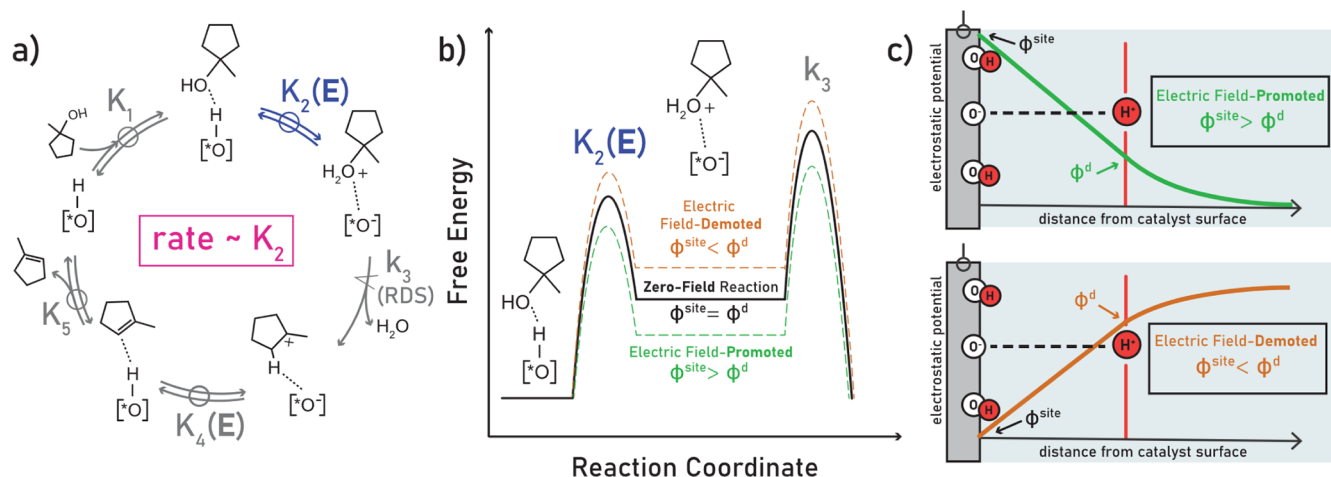


Figure 3. a) Proposed mechanism for the Brønsted acid-catalyzed dehydration of 1MCPol to 1MCPene and water. Interfacial charge transfer in quasi-equilibrated step 2 leads to exponential overall rate dependence on catalyst potential, provided that the most abundant reactive intermediate is not the oxonium. b) Free energy diagram of the protonation of 1MCPol and the subsequent C–O bond cleavage. Polarizing the active site above (green curve) or below (orange curve) the solution electrostatic potential stabilizes or destabilizes charge separation and modulates K_2 without altering the intrinsic barrier for C–O bond cleavage. c) Illustration of the process by which interfacial electric fields promote or demote Brønsted acid-catalyzed reactions. The green and orange curves show the change in electrostatic potential across the solid–liquid interface, with the resulting ϕ^d relative to ϕ_{site} determining if the reaction is electric field-promoted (green) or -demoted (orange).

without contributing to desired chemical turnovers. We previously defined the pseudo-Faradaic efficiency (pFE) as eq 2,

$$\text{pFE} = \frac{\# \text{ molecules of product}}{\# \text{ electrons passed}} \quad (2)$$

where pFEs above 100% indicate the process cannot be purely electrochemical in nature, and higher pFE values are favorable, indicating higher selectivity to the desired product.^{16,17} We note pFE is distinct from Faradaic efficiency, which has a maximum value of 100% and requires a defined electron stoichiometry for the desired electrochemical product and is therefore not applicable to the thermochemical dehydration reaction studied here.

For DMC and MeCN, both reaction rate and Faradaic current increase with increasing ionic strength and applied potential. In DMC, we find that for all ionic strengths tested, increasing applied electrochemical potential increases the pFE, indicating Brønsted acid rates scale more strongly than Faradaic rates in the tested regime (Figure S23). The maximum pFE in DMC was about 350%. In MeCN, the pFE did not have a clear trend with ionic strength or potential, with most values between 500 and 2,500%, meaning, in the regimes tested, Brønsted acid rates and Faradaic rates scale similarly in MeCN (Figure S24).

In PC, at all ionic strengths tested, pFE increased with applied potential. Further, lower concentrations of TBAPF₆ yielded lower Faradaic currents while concurrently increasing dehydration rates, increasing all pFEs measured at 1 mM to above 10,000% (Figure S25). Despite the very high pFE in this high resistance PC solution, it remains unknown how overall energy efficiency changes with electrolyte concentration. Future studies are needed to quantify the trade-off between the electrical efficiency penalty associated with operating in high-resistance solutions and the reduced parasitic charge consumption achieved at lower electrolyte concentrations.

Electrostatic Polarization Impacts the Kinetics of Brønsted Acid Catalysis

The liquid-phase dehydration of tertiary alcohol 1MCPol follows an E1-type mechanism (Figure 3a), as elucidated by

prior studies in MeCN,¹⁶ and we use this mechanism as the working framework across the solvents examined here. Assuming C–O bond cleavage is the RDS, the remaining steps are in quasi-equilibrium, and neglecting possible site blocking by solvent or electrolyte, the overall reaction rate at low conversion can be expressed as eq 3:

$$\frac{\text{reaction rate}}{\text{catalyst area}} = \frac{K_1 K_2 k_3 [1\text{MCPol}] \Gamma}{1 + K_1 [1\text{MCPol}] + K_1 K_2 [1\text{MCPol}]} \quad (3)$$

where Γ is the Brønsted acid site density (sites cm⁻²), and the rate is proportional to K_2 as long as the protonated alcohol remains a minor species (Section S3.1). The rate laws corresponding to alternative elementary steps as the RDS in the E1 mechanism are derived in Section S3.1.1. However, the rate dependence on applied electrochemical potential (Figure 2) and 1MCPol concentration (Section S3.2) are most consistent with C–O bond cleavage remaining the RDS across the solvents examined.

Polarizing a catalyst in the presence of an electrolyte solution induces an electrochemical double layer at the catalyst interface.^{15,28} This double layer creates a decay in electrostatic potential from the catalyst surface to the bulk solution over a varying length scale. Assuming that the proton traverses a distance d through the electrostatic potential gradient, the proton experiences an electrostatic free energy change, described by eq 4:

$$\Delta G_{\text{electrostatic}} = -F(\phi^{\text{site}} - \phi^d) \quad (4)$$

where ϕ^{site} is the electrostatic potential at the active site on the carbon paper, and ϕ^d is the electrostatic potential at the reaction plane, where the oxonium resides prior to the following catalytic steps. We note that it would be kinetically indistinguishable if the proton traversed the potential decay as just a proton, as the oxonium intermediate, or as some combination of the two. The path taken to distance d is also irrelevant; only the electrostatic potential at the position where the oxonium undergoes step k_3 (ϕ^d) is relevant for the computation of $\Delta G_{\text{electrostatic}}$.

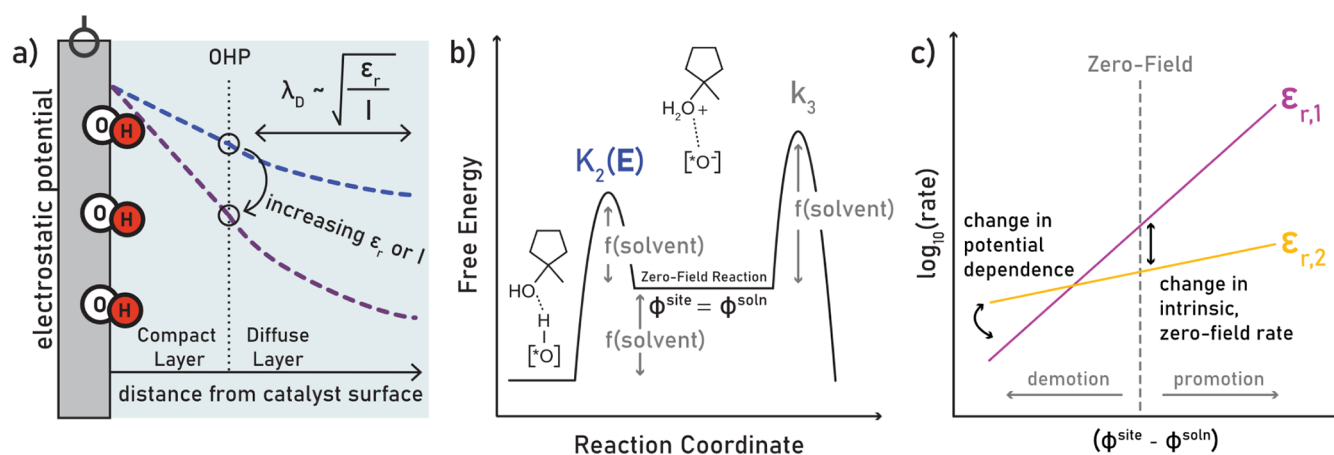


Figure 4. a) Expected relative change in potential decay profile for varying dielectric constants (ϵ_r) and ionic strengths (I). As ϵ_r , or I increase, the electrostatic potential decay partitioning to the compact layer increases. In the diffuse layer, the Debye length (λ_D) governs the decay. Higher I yields steeper decay profiles and higher ϵ_r yields shallower decays. b) Solvent-dependent stabilization of transition states and reactive intermediates changes the free energy landscape, even in the absence of any electric field effects. c) Qualitative graph demonstrating the two major trends in rate-potential scaling expected when the reaction solvent is changed in an electric field-promoted Brønsted acid catalytic system. First, solvent-dependent differences in the interfacial potential decay profile alter the fraction of the total potential drop traversed by the proton and/or oxonium, manifesting as a change in slope. Second, solvent-specific stabilization of transition states modifies the reaction rate in the absence of an electric field appearing as a vertical shift at the electrostatic potential of zero-field (IKP).

It is also important to note that potentiostats experimentally measure the electron electrochemical potential in the carbon paper electrode, $\hat{\mu}_{e^-}^{\text{electrode}}$ (eq 5), not the electrostatic potential, with

$$\hat{\mu}_{e^-}^{\text{electrode}} = \mu_{e^-}^{\text{electrode}} - F\phi^{\text{electrode}} \quad (5)$$

where $\mu_{e^-}^{\text{electrode}}$ is the chemical potential of an electron in the carbon paper. If we assume the carbon paper has a sufficiently high density of electronic states, then $\mu_{e^-}^{\text{electrode}}$ is expected to be constant across the applied potential range.³¹ Therefore, the change in applied electrochemical potential is equivalent to the change in electrostatic potential. If we further assume that the active site resides at the same electrostatic potential as the surface, $\phi^{\text{electrode}} = \phi^{\text{site}}$, then changes in the applied electrochemical potential directly translate to changes in the electrostatic potential of the active site. This assumption is supported by the $\alpha = 1$ scaling observed in PC, but we note that we cannot unequivocally verify that this assumption holds in the other solvents. Importantly, if the Brønsted acid proton were located away from the conductive surface such that the change in electrostatic potential was only a fraction of the change in surface electrostatic potential, the maximum apparent transfer coefficient would be correspondingly less than 1.

The protonation step described by K_2 experiences the electrostatic free energy contribution defined in eq 4, resulting in a potential-dependent equilibrium constant given by eq 6:

$$K_2 = K_2^0 e^{-\Delta G_{\text{electrostatic}}/RT} = K_2^0 e^{F(\phi^{\text{site}} - \phi^d)/RT} \quad (6)$$

where K_2^0 is the equilibrium constant in the absence of a local electric field. This electrostatic (de)stabilization increases (or decreases) the population of the protonated alcohol intermediate, thus modulating the overall rate without modifying the intrinsic barrier for the C–O bond cleavage step (Figure 3b and Figure 3c).

Within the foregoing mechanistic scheme and model, the apparent transfer coefficient, α , reflects the fraction of the interfacial potential drop traversed by the positively charged

moiety during proton transfer, which can be mathematically expressed as eq 7,

$$\alpha = \frac{\phi^{\text{site}} - \phi^d}{\phi^{\text{site}} - \phi^{\text{soln}}} = \frac{\Delta\phi}{\Delta\phi^{\text{max}}} \quad (7)$$

where ϕ^{soln} is the electrostatic potential of the reaction solution, $\Delta\phi$ is the change in potential experienced by the proton (or oxonium), and $\Delta\phi^{\text{max}}$ is the maximum possible change in electrostatic potential across the interface. Within the assumptions above, $\Delta\phi^{\text{max}}$ is equivalent to the difference between the applied electrochemical potential and the IKP, at which the active site is not polarized.

Assuming the shape of the potential decay profile and the reaction plane are largely invariant across the range of applied potentials, α is independent of the applied potential, and the rate expression simplifies to eq 8:

$$\text{rate} \sim K_2 \sim e^{F\alpha(\Delta\phi^{\text{max}})/RT} \sim e^{F\alpha(E - E_{\text{IKP}})/RT} \quad (8)$$

with E_{IKP} as the electrochemical potential where there is no local electric field at the active site. If the proton traverses the entire electrochemical double layer during oxonium formation, $\alpha \rightarrow 1$, corresponding to a rate-potential scaling of 66 mV per decade at 60 °C.

Low to Moderate Dielectric Constant Solvents Lead to Partial Electrostatic Promotion

In the limit that the oxonium intermediate remains bound to the interface, the rate-potential scaling is expected to be strongly dependent on the electrostatic profile in the electrochemical double layer, leading to electrolyte strength dependence in the rate-potential scaling and a corresponding IKP. This phenomenon is observed for DMC and MeCN (Figure 2a and Figure 2b). Notably, rate-potential scaling slopes are far less sensitive to ionic strength in higher dielectric MeCN compared to the lower dielectric DMC. This broad qualitative trend can be understood in the context of the Gouy–Chapman–Stern (GCS) theory of electrochemical double layers.²⁸

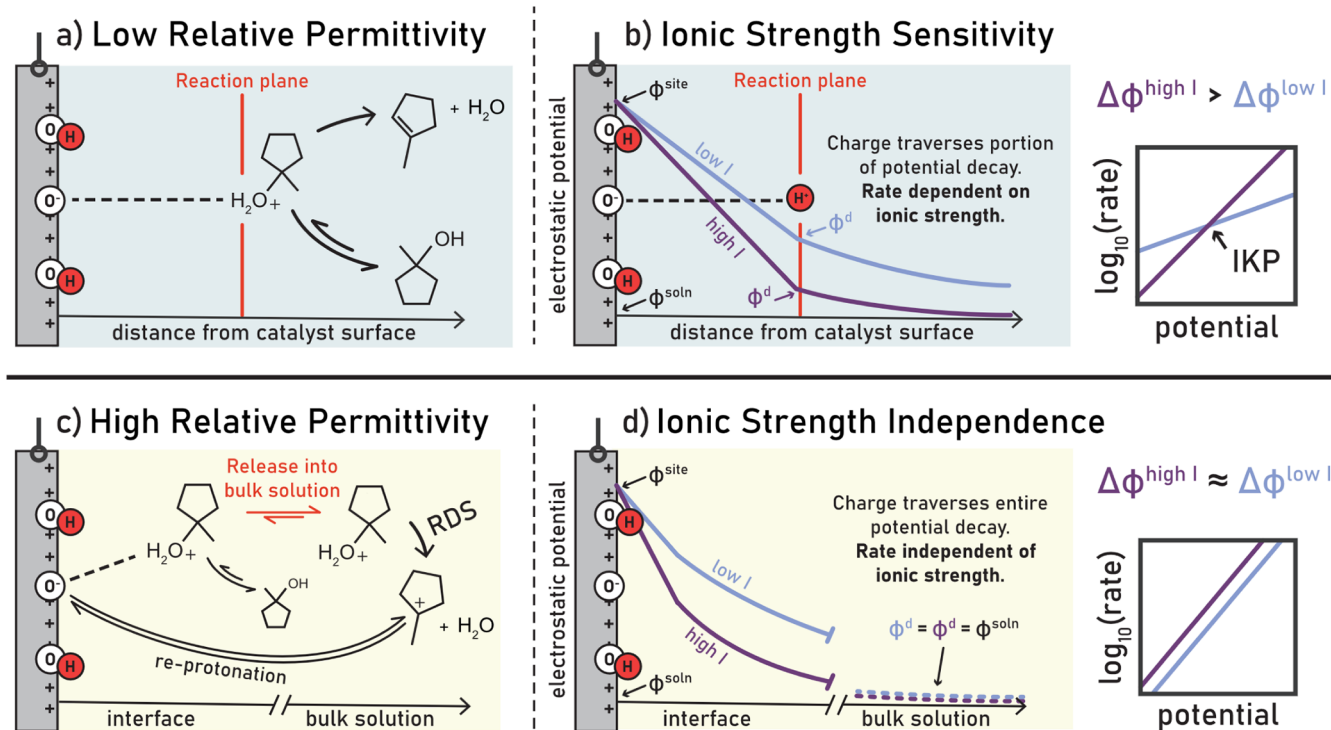


Figure 5. a) Proposed mechanism by which IMCPol undergoes Brønsted acid-catalyzed dehydration in lower dielectric constant solvents. The oxonium intermediate undergoes the RDS at the fixed distance of the “reaction plane” while remaining coordinated to the active site. b) Electrostatic potential decay profiles at lower (blue curve) and higher (purple curve) ionic strengths. Because the higher ionic strength compresses the potential decay, there is a larger change in electrostatic potential between the site (ϕ_{site}) and the reaction plane (ϕ^d) at higher ionic strengths. This yields stronger rate-potential scalings with higher ionic strengths and allows for the identification of an IKP by measuring rate-potential scalings at different ionic strengths. c) Proposed mechanism by which IMCPol undergoes Brønsted acid-catalyzed dehydration in higher dielectric constant solvents. The oxonium intermediate is stable enough to dissociate from the active site and undergoes the RDS beyond the distance over which electrostatic potential decay occurs. d) Electrostatic potential decay profiles at lower (blue curve) and higher (purple curve) ionic strengths. At the distance from the active site where the oxonium intermediate undergoes the RDS, the electrostatic potential of the lower ionic strength (ϕ^d , blue), the higher ionic strength (ϕ^d , purple), and the solution (ϕ^{soln}) are approximately equal. This yields stronger rate-potential scalings, regardless of ionic strength, and kinetically does not allow the determination of the IKP.

In GCS theory, the electrochemical double layer is modeled as a pair of capacitors in series representing the compact and diffuse double layers. The compact double layer hosts a roughly linear electrostatic potential drop between the electrode and the outer Helmholtz plane (OHP), the first layer of nonspecifically adsorbed counter charge. Compact double layer capacitances are formally independent of ionic strength, and local dielectric constants within the compact layer are low, even for high dielectric constant solvents like water.³² In contrast, the diffuse double layer hosts an exponential electrostatic potential decay of any residual potential drop outside the OHP, with the diffuse double layer capacitance scaling with the square root of both the bulk dielectric constant and the ionic strength. Thus, as the bulk dielectric constant and/or ionic strength increases, the diffuse layer capacitance is expected to increase. Since the potential drop across the compact and diffuse layers scales inversely with their capacitance, increasing dielectric constant and/or ionic strength results in a higher fraction of the overall potential drop within the compact layer (Figure 4a). If we assume that the reaction plane of the bound oxonium intermediate is in the vicinity of the OHP, the foregoing expected trends in the partitioning of potential drop between compact and diffuse double layers are in line with the ionic strength dependence of rate-potential scaling in DMC and MeCN and the more muted dependence in the latter. While GCS theory, a mean field model, appears to capture the broad qualitative trends in these two

solvents, we stress that an atomistic model or simulation of the double layer structure that accounts for numerous solvent properties including viscosity, coordination strength, and intermolecular forces would be required to make quantitative predictions of the rate-potential scaling.

For both DMC and MeCN, the extrapolated rate at the IKP provides insight into the intrinsic rate of catalysis, independent of interfacial electrostatic driving forces. Bulk solvent chemical structure and dielectric constant, among other properties, can greatly change the extent to which the reactive intermediates and transition states are stabilized. Specifically, this IKP rate reflects solvent-dependent changes in intrinsic equilibrium constant (K_2^0) and RDS barrier (k_3) (Figure 4b). Kinetically, this solvent-dependent (de)stabilization manifests as a change in the intrinsic, zero-field rate (Figure 4c, vertical shift), such that in the absence of an interfacial electric field ($\phi_{\text{site}} = \phi^d = \phi^{\text{soln}}$), different solvents yield different reaction rates over the same catalyst. By extrapolating reaction rates at the IKP, we can quantitatively isolate the influence of the solvent on intrinsic reaction kinetics from its influence on the electrochemical double layer, which can dramatically modify reaction rates by changing the extent of solid acid polarization (Figure 4c, change in slope).

Figure 5a illustrates how, in lower relative permittivity solvents, including DMC and MeCN, we posit that the oxonium intermediate remains bound to the active site, where it

eventually undergoes the RDS of C–O bond cleavage. Increasing the ionic strength within the same solvent (Figure 5b) increases partitioning of the electrostatic potential drop to the compact layer, resulting in a larger $\Delta\phi$, ultimately increasing α and allowing the extrapolation of the IKP by finding the intersection point of the rate-potential scaling at each ionic strength.

With DMC's low dielectric constant ($\epsilon_r \approx 3$), GCS theory predicts that at low-moderate ionic strengths, only a small fraction of the electrostatic potential drop will occur within the compact layer. As ionic strength in DMC increases, the partitioning of potential decay into the compact layer increases, and the characteristic length scale in the diffuse layer (the Debye length) shortens. Together, these two effects should make DMC rates very sensitive to electrolyte concentration. Indeed, in DMC, α changes from 0.26 to 0.69 when increasing the concentration of TBAPF₆ by only 6-fold from 100 to 600 mM. Further, due to solution-phase ion pairing for low permittivity solvents,³³ we suspect the amount of free [TBA⁺][PF₆[−]] in solution is significantly lower than the nominal amount of electrolyte added (as low as about 10% of the added ionic strength), meaning in DMC, reaction rate may be even more sensitive to ionic concentration than our data initially suggests (Section S7.2).

In MeCN ($\epsilon_r \approx 31$), at low-moderate ionic strengths, a larger fraction of the electrostatic potential drop should occur within the compact layer compared to DMC; however, because the Debye length increases with dielectric constant, the length scale of decay within the diffuse layer is much larger than in DMC. These competing effects yield a weaker dependence of rate-potential scaling on electrolyte concentration, yet still allow the extrapolation of an IKP. In MeCN, a 200-fold increase in TBAPF₆ concentration changes α from 0.30 to 0.43, suggesting the reaction plane lies well within the double layer, but with a rather shallow potential decay at all ionic strengths tested.

High Dielectric Constant Solvents Allow Full Electrostatic Potential Drop Traversal

Unlike in DMC and MeCN, we do not observe an IKP in PC and instead observe (near) Nernstian polarization dependence across the range of electrolyte strengths examined. This can be explained by invoking that the strong solvating power of PC allows for dissociation of the oxonium intermediate from the interface (Figure 5c), with the RDS occurring beyond the length of electrostatic potential decay in the bulk solution. At sufficiently large distances from the interface, the electrostatic potential will decay to that of the bulk solution, irrespective of the ionic strength, yielding no change in rate-potential scaling between ionic strengths (Figure 5d).

For PC, across the 200-fold increase in TBAPF₆ concentration investigated, the rate-potential scaling is not only insensitive to electrolyte strength, but also returns the limiting apparent transfer coefficient of $\alpha = 1$. Indeed, all the rate-potential scalings in PC are within error of the Nernstian value of 66 mV per decade, which is in line with the expectation for a fully dissociated oxonium intermediate as depicted in Figure 5c and d.

It follows that at even lower concentrations of TBAPF₆ (or another ionic species), the proton may still traverse a significant portion of the interfacial electrostatic potential decay. This is in line with the observation of no measurable rate of catalysis at OCP in the absence of added TBAPF₆. While the high resistivity of this medium precluded external polarization to the desired

potential, we measured OCP of the catalyst as 0.1 V, 700 mV lower than the potential region of data collection in Figure 2c. If the observed Nernstian scaling were to hold even in the presence of 0.03 mM adventitious ionic strength, this potential difference would correspond to a rate attenuation of $\sim 10^{10}$ fold, in line with the lack of observed reactivity. As the discussion highlights, catalyst potential is an extremely important parameter in heterogeneous Brønsted acid catalysis, particularly in media that strongly solvates reaction intermediates and, therefore, maximizes rate-potential scaling.

With full proton traversal across the electrochemical double layer at all tested electrolyte concentrations in PC, we are unable to use the rate-potential scalings at different electrolyte concentrations to extract the zero-field potential and corresponding intrinsic rate of Brønsted acid catalysis. However, once the solvent-specific Ag/AgCl reference electrodes were calibrated to a decamethylferrocene/decamethylferrocenium (DmFc/DmFc⁺) couple, the IKPs of DMC and MeCN were within error of each other with an average of 1.01 V vs DmFc/DmFc⁺ (Section S2.6.2). We posit that electrostatic driving forces vanish at a similar potential for PC as for MeCN and DMC. Using this 1.01 V vs DmFc/DmFc⁺ (or 0.9 V vs Ag/AgCl) as an estimated zero-field potential in PC, we extract an intrinsic rate in PC of $\sim 1.0 \times 10^{-8} \text{ mol s}^{-1} \text{ cm}^{-2}$, $\sim 3\text{--}4$ orders of magnitude greater than the corresponding intrinsic rates in MeCN (rate_{MeCN} = $3.4 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$) and DMC ($7.2 \times 10^{-12} \text{ mol s}^{-1} \text{ cm}^{-2}$). These rates align with the trend, $\epsilon_r, \text{DMC} < \epsilon_r, \text{MeCN} < \epsilon_r, \text{PC}$, which we interpret as primarily a result of solvent-dependent stabilization of the transition states or reactive intermediates (Figure 4b).

CONCLUSION

In this work, we quantified the role of solvent in electric field-promoted Brønsted acid catalysis by systematically varying ionic strength and solvent while recording kinetic measurements for the liquid-phase dehydration of 1MCPol. Based on the disparate abilities of different solvent systems to stabilize charge-separated intermediates together with the electrochemical double layer's structural dependence on the bulk dielectric constant, we anticipated two distinct solvent-dependent effects in electric field-promoted Brønsted acid catalysis: first, the intrinsic, zero-field rate varies with solvent, and second, the dependence of rate on applied electrochemical potential varies in magnitude.

Indeed, estimation of the IKP predicts a zero-field rate that increases with solvent dielectric constant, consistent with enhanced stabilization of charge-separated transition states. Further, we found decreasing sensitivity to electrolyte concentration as the dielectric constant increased. In the highest dielectric constant medium, PC, not only was rate-potential scaling independent of ionic strength, but the apparent transfer coefficient returned $\alpha = 1$, maximizing the extent of rate promotion with polarization.

Through the lens of GCS theory, we propose that, in lower permittivity media, the oxonium intermediate remains bound to the active site within the electrochemical double layer, yielding rate-potential scalings that depend on ionic strength. However, for higher permittivity media that are sufficiently stabilizing for dissociation of the oxonium intermediate, we propose the RDS occurs outside of the electrochemical double layer, giving rise to reaction rates that follow Nernstian scaling, even for interfaces with relatively shallow electrostatic potential decay profiles (i.e., [TBAPF₆] = 1 mM).

Ultimately, to best leverage electric-field effects in promoted Brønsted acid catalysis, we should seek to maximize the rate-potential scaling while minimizing unwanted Faradaic processes. Working in low ionic strength but highly polar solutions optimizes both of these targets simultaneously, by suppressing Faradaic processes through high solution resistance, yet still providing strong rate-potential scaling for non-Faradaic Brønsted acid catalytic turnovers. Together, these findings highlight the significant role solvents play in electric field-promoted catalysis and emphasize the importance of understanding electrostatic effects in non-Faradaic catalytic systems, especially those with high polarity solvents.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.6c13986>.

Materials and experimental methods, full characterization and experimental data, supplementary discussions (PDF)

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Notes

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■ ACKNOWLEDGMENTS

Y.R.-L. acknowledges support from the Department of Energy, Office of Basic Energy Sciences, under Award No. DE-SC0016214. Y.S. acknowledges support from Award No. DE-SC0020973. K.G. was supported by the MITEI Energy Scholars Program. B.D. was supported by the National Science Foundation Graduate Research Fellowship Program (GRFP) under Grant No. 2141064. Partial support was provided by the National Science Foundation Graduate Research Fellowship Program under Grant No. 1745302 for K.S.W. and M.T.M. M.D. was supported by the Center for Programmable Energy Catalysis under Award No. DE-SC0023464. Nuclear magnetic resonance spectroscopy was performed at the MIT DCIF using its shared user facilities. We thank Walt Massefski and Sarah Willis for their assistance in developing NMR solvent suppression methods for this work. We thank Emily Wu, Liang Li, Hannah Even, Zachary Westman, Anna Brenner, and Khadiza Rahman for insightful discussions.

■ REFERENCES

- (1) Liu, F.; Huang, K.; Zheng, A.; Xiao, F.-S.; Dai, S. Hydrophobic Solid Acids and Their Catalytic Applications in Green and Sustainable Chemistry. *ACS Catal.* **2018**, *8* (1), 372–391.
- (2) Clark, J. H.; Macquarrie, D. J. Environmentally Friendly Catalytic Methods. *Chem. Soc. Rev.* **1996**, *25* (5), 303–310.
- (3) Kozhevnikov, I. V. Catalysis by Heteropoly Acids and Multi-component Polyoxometalates in Liquid-Phase Reactions. *Chem. Rev.* **1998**, *98* (1), 171–198.
- (4) Lopez, D.; Goodwin, J.; Bruce, D. Transesterification of triacetin with methanol on Nafion® acid resins. *J. Catal.* **2007**, *245* (2), 381–391.
- (5) Melero, J. A.; van Grieken, R.; Morales, G. Advances in the Synthesis and Catalytic Applications of Organosulfonic-Functionalized Mesoporous Materials. *Chem. Rev.* **2006**, *106* (9), 3790–3812.
- (6) Toda, M.; Takagaki, A.; Okamura, M.; Kondo, J. N.; Hayashi, S.; Domen, K.; Hara, M. Biodiesel made with sugar catalyst. *Nature* **2005**, *438*, 178.
- (7) Corma, A. Inorganic Solid Acids and Their Use in Acid-Catalyzed Hydrocarbon Reactions. *Chem. Rev.* **1995**, *95* (3), 559–614.
- (8) Primo, A.; Garcia, H. Zeolites as catalysts in oil refining. *Chem. Soc. Rev.* **2014**, *43* (22), 7548–7561.
- (9) Wang, G.; Lan, X.-Y.; Xu, C.-M.; Gao, J.-S. Study of Optimal Reaction Conditions and a Modified Residue Catalytic Cracking Process for Maximizing Liquid Products. *Ind. Eng. Chem. Res.* **2009**, *48* (7), 3308–3316.
- (10) Chen, F.; Shetty, M.; Wang, M.; Shi, H.; Liu, Y.; Camaioni, D. M.; Gutiérrez, O. Y.; Lercher, J. A. Differences in Mechanism and Rate of Zeolite-Catalyzed Cyclohexanol Dehydration in Apolar and Aqueous Phase. *ACS Catal.* **2021**, *11* (5), 2879–2888.
- (11) Guo, J.; Chin, Y.-H. C. Rationalizing Solvent Effect in Brønsted Acid-Catalyzed C–O Scission: A Thermodynamically Consistent Framework with Assessable Descriptors. *ACS Catal.* **2025**, *15* (22), 19040–19056.
- (12) Ristanovic, Z.; Kubarev, A. V.; Hofkens, J.; Roefsaers, M. B.; Weckhuysen, B. M. Single Molecule Nanospectroscopy Visualizes Proton-Transfer Processes within a Zeolite Crystal. *J. Am. Chem. Soc.* **2016**, *138* (41), 13586–13596.
- (13) Li, G.; Yi, X.; Huang, L.; Jiang, J.; Yu, Z.; Liu, Z.; Zheng, A. Solvent Effect Inside the Nanocage of Zeolite Catalysts: A Combined Solid-State NMR Approach and Multiscale Simulation. *J. Phys. Chem. C* **2017**, *121* (31), 16921–16931.

- (14) Haw, J. F.; Xu, T.; Nicholas, J. B.; Goguen, P. W. Solvent-assisted proton transfer in catalysis by zeolite solid acids. *Nature* **1997**, 389 (6653), 832–835.
- (15) Bockris, J. O. M.; Reddy, A. K. N.; Gamboa-Aldeco, M. *Modern Electrochemistry*; 2nd ed., Kluwer Academic/Plenum; 2000.
- (16) Westendorff, K. S.; Hulse, M. J.; Wesley, T. S.; Roman-Leshkov, Y.; Surendranath, Y. Electrically driven proton transfer promotes Brønsted acid catalysis by orders of magnitude. *Science* **2024**, 383 (6684), 757–763.
- (17) Dinakar, B.; Westendorff, K. S.; Torres, J. F.; Dakhchoune, M.; Groenhout, K.; Ewell, N.; Surendranath, Y.; Dinca, M.; Roman-Leshkov, Y. Elucidating Electric Field-Induced Rate Promotion of Brønsted Acid-Catalyzed Alcohol Dehydration. *J. Am. Chem. Soc.* **2025**, 147 (31), 27599–27610.
- (18) Wu, Y. C.; Ye, J.; Jiang, G.; Ni, K.; Shu, N.; Taberna, P. L.; Zhu, Y.; Simon, P. Electrochemical Characterization of Single Layer Graphene/Electrolyte Interface: Effect of Solvent on the Interfacial Capacitance. *Angew. Chem., Int. Ed.* **2021**, 60 (24), 13317–13322.
- (19) Kim, I.-T.; Egashira, M.; Yoshimoto, N.; Morita, M. Effects of electrolytic composition on the electric double-layer capacitance at smooth-surface carbon electrodes in organic media. *Electrochim. Acta* **2010**, 55 (22), 6632–6638.
- (20) Schott, C. M.; Schneider, P. M.; Song, K. T.; Yu, H.; Gotz, R.; Haimel, F.; Gubanov, E.; Zhou, J.; Schmidt, T. O.; Zhang, Q.; Alexandrov, V.; Bandarenka, A. S. How to Assess and Predict Electrical Double Layer Properties. Implications for Electrocatalysis. *Chem. Rev.* **2024**, 124 (22), 12391–12462.
- (21) Hou, Y.; Aoki, K. J.; Chen, J.; Nishiumi, T. Solvent Variables Controlling Electric Double Layer Capacitance at the Metal–Solution Interface. *J. Phys. Chem. C* **2014**, 118 (19), 10153–10158.
- (22) Rossini, E.; Netz, R. R.; Knapp, E. W. Computing pK_a Values in Different Solvents by Electrostatic Transformation. *J. Chem. Theory Comput.* **2016**, 12 (7), 3360–3369.
- (23) Zheng, J. W.; Al Ibrahim, E.; Kaljurand, I.; Leito, I.; Green, W. H., pK_a prediction in non-aqueous solvents. *J. Comput. Chem.* **2025**, 46 (1), No. e27517.
- (24) Schenck, G.; Baj, K.; Iggo, J. A.; Wallace, M. Efficient pK_a Determination in a Nonaqueous Solvent Using Chemical Shift Imaging. *Anal. Chem.* **2022**, 94 (23), 8115–8119.
- (25) Rivas, M. A.; Pereira, S. M.; Banerji, N.; Iglesias, T. P. Permittivity and density of binary systems of {dimethyl or diethyl carbonate} + n-dodecane from T = (288.15 to 328.15) K. *J. Chem. Thermodyn.* **2004**, 36 (3), 183–191.
- (26) Gagliardi, L. G.; Castells, C. B.; Rafols, C.; Roses, M.; Bosch, E. Static Dielectric Constants of Acetonitrile/Water Mixtures at Different Temperatures and Debye-Huckel A and a₀B Parameters for Activity Coefficients. *J. Chem. Eng. Data* **2007**, 52 (3), 1103–1107.
- (27) Ding, M. S. Electrolytic Conductivity and Glass Transition Temperatures as Functions of Salt Content, Solvent Composition, or Temperature for LiBF₄ in Propylene Carbonate + Diethyl Carbonate. *J. Chem. Eng. Data* **2004**, 49 (4), 1102–1109.
- (28) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley & Sons, Inc, 1980.
- (29) Guidelli, R.; Compton, R. G.; Feliu, J. M.; Gileadi, E.; Lipkowsky, J.; Schmickler, W.; Trasatti, S. Defining the transfer coefficient in electrochemistry: An assessment (IUPAC Technical Report). *Pure Appl. Chem.* **2014**, 86 (2), 245–258.
- (30) Jackson, M. N.; Pegis, M. L.; Surendranath, Y. Graphite-Conjugated Acids Reveal a Molecular Framework for Proton-Coupled Electron Transfer at Electrode Surfaces. *ACS Cent. Sci.* **2019**, 5 (5), 831–841.
- (31) Fuller, T. F.; Harb, J. N. *Electrochemical Engineering*; Wiley, 2018.
- (32) Sridharan, A.; Satyamurthy, P. V. Potential-distance relationships of clay-water systems considering the Stern theory. *Clay Clay Miner.* **1996**, 44 (4), 479–484.
- (33) Bjerrum, N.; Danske Vidensk Selskab, K. Investigations on the Activity of Ions. *Mater. Fys. Medd* **1926**, 7 (9), 1–38.