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A mechanistic investigation on the electrocatalytic reduction of aliphatic ketones at platinum

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ABSTRACT

In this paper we discuss the mechanism of the electrochemical hydrogenation of aliphatic ketones at platinum electrodes in aqueous acidic electrolytes. Based on the potential dependence of the measured reaction orders and on kinetic considerations, we derive that hydrogen competes with ketones for adsorption sites. Hence, hydrogen underpotential deposition (H-upd) exerts an inhibiting influence on the reduction of ketones and eventually suppresses it.

The variation of the proton concentration has a significant influence on the reaction rate of acetone, but not on the reaction rate of higher aliphatic ketones, from which it is derived that the active species of acetone reduction is the protonated acetone, which forms in solution in a pre-equilibrium. The absence of a proton effect for the hydrogenation of higher aliphatic ketones indicates that in those cases the enol tautomer is adsorbed to the surface.

It is concluded that after reductive adsorption of protonated acetone to the electrode the reduction proceeds in the rate determining step via a proton-coupled electron transfer to the adsorbate. The adsorbate, in which the carbonyl functional group is transformed to an OH-group, is either immediately adsorbed to the surface from solution (acetone, protonated at the carbonyl oxygen) or formed by a surface reaction between the enol (higher aliphatic ketones) and adsorbed hydrogen. The presence of the enol and its reaction with adsorbed hydrogen to the protonated ketone was concluded from Surface-Enhanced Raman spectra. Adsorbed hydrogen is, therefore, necessary to provide the active species of ketone reduction, which is reduced in the rate determining step by the proton-coupled electron transfer. © 2018 The Authors. Published by Elsevier Inc. This is an open access article under the CC BY-NC-ND license

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1. Introduction

Heterogeneously catalyzed hydrogenation of organic compounds is conducted in a variety of industrial processes [1–3]. It ranges from large scale applications such as the hydrogenation of fatty acids in the food industry [4] to small scale applications in the course of vitamin syntheses in the fine chemical and pharmaceutical industry [5]. In these processes usually molecular hydrogen and a substrate molecule react with each other at the surface of a catalyst. In today's economy, hydrogen is produced primarily from steam reforming of fossil fuels which comes along with the emission of CO_2 [6]. However, greenhouse gas emissions have become undesirable for various social and environmental reasons. In order to achieve the goal of decarbonizing the economy also the hydrogenation of organic molecules must proceed via a net zero emission of CO_2 in the future. One way to do so is to produce the hydrogen required for heterogeneous hydrogenation electrochemically (provided the consumed electricity is generated by zeroemission technologies). In such a scenario industrial hydrogenations require both large-scale electrolysis (for the production of hydrogen) and a hydrogenation plant. However, it can be expected that there are cases in which it is more cost effective to hydrogenate organic compounds directly via an electrochemical route as this would eliminate the need for the hydrogenation plant.

Because of the potential importance of electrochemical hydrogenation reactions in a CO_2 neutral economy, we want to learn about the mechanism of the electrocatalytic hydrogenation of organic compounds. In the present article we are studying the mechanism of ketone reduction at platinum electrodes and role of adsorbed hydrogen. We consider such knowledge important for the rational design of electrocatalysts for hydrogenation reactions in general. However, it is difficult to monitor the role of adsorbed hydrogen experimentally in a direct way. Therefore, we rely in this article on kinetic parameters to derive a mechanistic picture of the hydrogenation of aliphatic ketones at polycrystalline platinum electrodes. To this end, we introduce a method to deconvolute the current due to ketone reduction from the current due to

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hydrogen evolution using rotating ring disc electrode (RRDE) voltammetry.

It is often assumed that heterogeneous hydrogenation from the gas phase or from aprotic solvents proceeds via a Langmuir-Hinshelwood mechanism in which adsorbed hydrogen is transferred from the surface to the substrate. Indeed, under these experimental conditions there is little room for other interpretations. However, electrochemical hydrogenation takes place in protic electrolytes, which is often also the case for liquid phase hydrogenation. Under these conditions alternate reaction pathways are conceivable, as was pointed out for liquid phase hydrogenation many years ago [7,8]: specifically, hydrogenation could proceed by proton-coupled electron transfer from the aqueous electrolyte to the substrate molecule. However, a Langmuir-Hinshelwood mechanism for electrochemical hydrogenation is still plausible. since protons can also be adsorbed electrochemically as hydrogen to the surface. Two recent mechanistic studies on the electrochemical hydrogenation of the carbonyl functional group of benzaldehyde also suggest a proton-coupled electron transfer as the rate limiting step [9,10].

Mechanistic knowledge on the electrochemical hydrogenation of aliphatic ketones is still rather limited. It has been shown based on voltammetric data that aliphatic ketones can be reduced electrochemically [11,12]. Hemptinne and Schnuck showed that acetone is reduced to both propane and 2-propanol in an acidic electrolyte [13]. These results are in contrast to work by Bänsch et al. [14] and Zinola et al. [15], who studied the hydrogenation of acetone and butanone, respectively, and who found only the formation of the hydrocarbon by means of differential electrochemical mass spectroscopy (DEMS). However, it is known that the formation of alcohols cannot easily be monitored by means of DEMS as the alcohol does not pass readily into the gas phase. Furthermore, Bänsch et al. and Zinola et al. showed that both ketones adsorb to the platinum surface positive of their reduction potential. A side-on geometry for adsorbed butanone was proposed by Zinola et al. [15]. However, the role of adsorbed hydrogen during ketone reduction has remained elusive. It is interesting in this context that adsorbed H₆-acetone is reduced to D₈-propane, if the electrolyte is changed from H₂O to D₂O [14]. This indicates that the acetone species that resides at the platinum surface constantly exchanges H-atoms at its methyl groups.

Since acetone reduction proceeds only at potentials considerably more negative than the potential at which adsorption occurs, it is not clear whether the H/D-exchange proceeds only at a certain potential and requires, more specifically, the presence of adsorbed hydrogen. By comparing Surface-Enhanced Raman spectra obtained in H₂O and D₂O based electrolytes, we will show that the H/D-exchange does not proceed in the double layer region of platinum. Only after a step into the H-upd region, an H/Dexchange is observed. This suggests that adsorbed acetone exchanges hydrogen with the surface. Together with the kinetic data, these results allow us to formulate a detailed new mechanism for the electrocatalytic hydrogenation of aliphatic ketones on platinum electrodes.

2. Experimental

The blank electrolyte was prepared from *MilliQ*-water and $HClO_4$ (EMSURE, *Merck*). For experiments that required constant ionic strength appropriate amounts of NaClO₄ (HPLC-grade, *Sigma-Aldrich*) were added to the electrolyte. Acetone, butanone, 3-pentanone and D₂O were obtained from *Sigma-Aldrich*. Heavy water was distilled prior to use. All solutions were freed from oxygen by purging with argon (6.0, *Linde*). All potentials were measured versus an Ag/AgCl electrode obtained from *Pine Instrument*

and converted to the RHE scale afterwards using the Nernst Equation. Prior to use the reference electrode was calibrated by measuring the open circuit potential versus a reversible hydrogen electrode in an electrolyte the pH of which was adjusted to 1 by adding appropriate amounts of HClO₄. A platinum wire was used as a counter electrode.

RRDE-measurements were conducted with polycrystalline platinum ring and disc electrodes. The rotator and the ring-disc assembly were obtained from *Pine Instruments*. In order to activate the platinum electrodes, both ring and disc electrode were cycled in the potential range between 0.05 V and 1.5 V with a sweep rate of 0.1 V/s until the CV did not change anymore. Hydrogen, evolved at the disc electrode, was detected at the ring electrode, which was set to a potential of 0.4 V. At this potential oxidation of hydrogen is diffusion limited and the presence of acetone does not interfere, as shown in Fig. S1 of the Supporting Information.

Raman spectra were obtained at a roughened gold electrode onto which a thin film of platinum was deposited following a procedure described by Zou and Weaver [16]. In brief: roughening of the gold electrode was achieved by several potential steps between 1.2 V (5 s) and -0.6 V (20 s) vs. Ag/AgCl in a solution of 0.5 M KCl. Platinum was then deposited galvanostatically from a solution of 100 μ M H₂PtCl₆ in 0.35 M Na₂HPO₄ with a current density of 400 μ A/cm² for 40 s. The Raman spectra were collected with a Lab-Ram HR800 (Horiba Jobin Yvon) confocal microscope that was equipped with an HeNe-Laser (632.81 nm). A detailed description of the setup and the methodology is given by Lai et al. [17].

3. Results and discussion

3.1. Kinetics of acetone reduction

Fig. 1 compares the cyclic voltammogram (CV) obtained at a polycrystalline platinum electrode in an acetone containing electrolyte of 0.1 M HClO₄ with the CV obtained in the blank electrolyte. In line with previous results [13,14], a shoulder prior to hydrogen evolution appears in the presence of acetone that indicates its reduction. In order to conduct a kinetic analysis of acetone reduction the currents due to hydrogen evolution and due to the reduction of acetone, which are convoluted in Fig. 1, must be separated. To that end we conducted RRDE-measurements in which we collected a CV at the platinum disc electrode and kept the potential of the ring electrode at 0.4 V. At this potential hydrogen is oxidized, which allows us to quantify the amount of hydrogen evolved at the disc electrode. Therefore, it is possible to employ



Fig. 1. CV at a polycrystalline platinum electrode in an electrolyte of 0.1 M HClO₄ in the absence (black curve) and presence (red curve) of 0.1 M acetone. Sweep rate: 0.01 V/s.

Eq. (1) to separate the currents due to hydrogen evolution and due to acetone reduction.

$$I_{acetone} = I_D - \frac{I_R}{N} \tag{1}$$

In Eq. (1), $I_{acctone}$ is the current due to acetone reduction (*i.e.* the current at the disc electrode corrected for hydrogen evolution), I_D is the current measured at the disc electrode (*i.e.* current due to both acetone reduction and hydrogen evolution), I_R is the current measured at the ring electrode (*i.e.* the current due to hydrogen oxidation at the ring) and N is the collection efficiency. Its value of approximately 0.18 was determined prior to each experiment by evolving hydrogen at the disc electrode and oxidizing it at the ring electrode in the blank electrolyte. Eq. (1) can only be employed if the current due to hydrogen oxidation at the ring electrode are oxidized and are, therefore, detected. In the Supporting Information Fig. S1 and the related discussion shows that hydrogen oxidation is not limited by kinetics but limited by diffusion under the conditions of acetone reduction.

Fig. 2A and B show the current due to acetone reduction for a variety of acid and acetone concentrations as obtained by correcting the measured disc current via Eq. (1). Strikingly, the acetone reduction current shows a maximum in all measurements. The experiment was conducted under quasi steady state and hydrodynamic conditions and, therefore, not limited due to mass transport. This is also illustrated in Fig. S2 showing that the current due to acetone reduction is independent of the rotation speed. Competi-



Fig. 2. Current due to acetone reduction for various concentrations of protons (A) and acetone (B) at a polycrystalline platinum electrode in an RRDE experiment. The currents shown are corrected for hydrogen evolution according to Eq. (1). The electrolyte was 0.3 M HClO₄ with various acetone concentrations (B) or an electrolyte with 0.1 M acetone and various proton concentrations (A). In the latter case the ionic strength was kept at 0.3 M by adding the appropriate amount of NaClO₄. From the data presented in A and B the reaction order in acetone and protons was derived and plotted as a function of potential (C). Scan rate: 0.05 V/s, rotation rate: 1500 rpm. For clarity only negative-going (cathodic) sweeps are shown.

tive adsorption between hydrogen and acetone is the most likely explanation for the peak in Fig. 2A and B. Inhibition by adsorbed hydrogen has been observed before for relatively weakly adsorbing reactants, such as during nitrate reduction and N₂O reduction [18,19]. Oxidation reactions are also well known to become inhibited by competitive adsorption by adsorbed oxygen. Fig. S1 shows how hydrogen oxidation declines at 1.2 V, due to the adsorption of OH and oxygen, respectively, at the platinum surface.

Notwithstanding any effect due to competitive adsorption, in Fig. 2 the current due to acetone reduction depends on the concentration of both acetone and the acid. From these data the reaction order in both protons and in acetone have been determined and plotted as a function of potential in Fig. 2C. With more negative potential, the reaction orders in both acetone and in protons increase in a very similar way. The reaction orders remain fractional over the entire potential range of acetone reduction. In the experiments from which we determine the reaction order, we kept the ionic strength constant by while altering the pH-value, therefore, increasing the cation concentration. It is known that the presence and the nature of the alkali metal cations influences the kinetics of hydrogen evolution [20,21]. The same is true for the pH-value [20,21]. However, in our work we separate current contributions due to hydrogen evolution and acetone reduction. Hence, any kinetic effect on hydrogen evolution does not distort the obtained reaction orders in acetone and protons. A cation effect on acetone reduction was not observed.

Fractional reaction orders can have their origin either in a chemical reaction that precedes the charge transfer or in the involvement of adsorbed species. However, it is hardly possible to construct a case in which a chemical reaction causes the potential dependence of the reaction order that is observed in Fig. 2C. It is more likely that the fractional reaction orders are caused by an intermediate coverage of the active species. We show in the Supporting Information that the increasing reaction order in acetone with more negative potential indicates that the coverage with the active species decreases as the potential decreases. This is not unexpected if competitive adsorption between acetone and hydrogen is considered.

Similar conclusions as for acetone cannot be drawn from the reaction order in protons. That is, the coverage of a platinum electrode with hydrogen is fixed for a given potential on the RHE scale irrespective of the proton concentration. Hence, even if the coverage with hydrogen enters the rate law of acetone reduction, the corresponding reaction order in H⁺ should still be zero (on the RHE scale). The fractional reaction order in hydrogen must, therefore, have a different origin.

As pointed out above the reaction orders in protons and in acetone change in a very similar way. To a first approximation we are going to assume that both reaction orders are coupled. We are going to address later in this paper how we can understand that both reaction orders deviate from one another (as seen in Fig. 2C). We assume that the coupling of the reaction orders in protons and acetone means that the reacting species is not acetone. It rather indicates that the concentration of the species that is actually reduced is proportional to the concentration of both acetone and protons. Hence, we conclude that protonated acetone is the active species of acetone reduction. The pKa-value of protonate acetone in literature varies over a wide range between -1.6 [22] or -7 [23]. In any case the equilibrium concentration of acetone in our electrolyte is guite low. Based on the low equilibrium concentration of protonated benzaldehyde, both Cantu et al. [9] and Song et al. [10], who studied the electrochemical hydrogenation of benzaldheyde, ruled out protonated benzaldehyde is involved in the reduction process. However, a low equilibrium concentration in itself does not render a mechanism based on protonated acetone unlikely. Chemical reactions often proceed via intermediates with low equilibrium concentration: the equilibrium constant for the formation of some carbocations is in the range of 10^{-15} , yet nucleophilic substitution reactions proceed via an S_N1-mechanism [24]. It is important, however, that the equilibrium is maintained throughout the reaction, which requires fast kinetics. Since rate constants of protonation reactions are fast [25], we can assume that the equilibrium concentration of protonated acetone is maintained throughout the reaction.

Since protonation of acetone leaves an electron deficiency at the carbonyl carbon atom [26], it is likely that protonated acetone adsorbs via the carbonyl carbon to the platinum surface negative of the point of zero charge (as shown in Schemes 1 and 2). This is particularly likely, since the carbonyl carbon is the only atom left that is not covalently saturated in protonated acetone. However, after adsorption the acidity of protonate acetone is bound to decrease drastically, since the positive charge is at least partially neutralized by the interaction with the platinum surface. Hence, a low pK_a -value in solution does not necessarily translate into unfavorable thermodynamics of protonate acetone in the adsorbed state.

From the interpretation that the active species is protonated acetone, we can derive two mechanisms of acetone reduction. The first one is shown in Scheme 1 where protonated acetone is formed via Equilibrium 1 in solution and adsorbed via Equilibrium 2 to a free surface site at the platinum electrode. We are going to refer to the adsorbed acetone species in Scheme 1 as "adsorbed protonated acetone" in the following. This is not meant as a statement on the charge of the adsorbed species which might be neutral or partially positive. Parallel to acetone adsorption, hydrogen is adsorbed to the surface via Equilibrium 3. We have argued that there is a competition between the adsorption of hydrogen and acetone. This is accounted for by Equilibrium 4 where hydrogen replaces adsorbed protonated acetone. The actual reduction step takes place in Reaction 5 where adsorbed protonated acetone is reduced via a proton-coupled electron transfer. We will refer to this mechanism as the Competitive-Adsorption mechanism (CAM).

As pointed out in the introduction, the hydrogenation of organic compounds is often assumed to proceed via the a Langmuir-Hinshelwood mechanism in heterogeneous catalysis. Since acetone reduction takes place in the potential region of hydrogen adsorption, this mechanism is also conceivable for the electrochemical reduction of acetone. Such a mechanism is shown in Scheme 2,



Scheme 1. Reaction sequence of the Competitive-Adsorption mechanism (CAM).



Scheme 2. Reaction sequence of the Langmuir-Hinshelwood mechanism (LHM).

which we will refer to as the Langmuir-Hinshelwood mechanism (LHM) of acetone reduction. The first 4 steps of the LHM are the same as those of the CAM: Formation and adsorption of protonated acetone, adsorption of hydrogen at a free surface sites and those that are already occupied by adsorbed protonated acetone. In the actual hydrogenation step (Reaction 6), adsorbed protonated acetone tone reacts with adsorbed hydrogen at the surface.

In order to show that the mechanisms in Scheme 1 and Scheme 2 reproduce the general behavior in Fig. 2 we calculated the reaction rate and the reaction order in protonated acetone, as shown in Fig. 3. The relevant equations are derived in the Supporting Information, where we also provide a broader discussion of the observed behavior. Note that the calculations shown in Fig. 3 are not meant to provide an exact simulation of the curves in Fig. 2. Potential, rates, concentrations etc. do not have a quantitative meaning. Fig. 3 is meant to provide a qualitative picture of how different parameters affect the current and reaction orders. A quantitatively accurate model would require knowledge about rate constants, equilibrium constants and adsorption energies, which are not available to us. Hence, we made generic assumptions for these values, given in the Supporting Information. Furthermore, we have not considered that the equilibrium constant for the adsorption of protonated acetone from solution is potential dependent. Considering that Equilibrium 2 entails a net charge transfer, this appears to be an invalid assumption. However, we will show later in this paper that in a refined model of acetone reduction the potential dependence of the coverage with adsorbed protonated acetone is accounted for by the potential dependence of hydrogen adsorption. Irrespectively, the calculation in Fig. 3 allows us to estimate to what degree a change in potential and in the concentration of protonated acetone in solution affects the reaction order and the reaction rate.

Fig. 3 shows that both the CAM and the LAH predict a bellshaped current-potential curve. Also an increase of the reaction order in protonated acetone with decreasing potential is predicted by both mechanisms. As pointed out above, the concentration of protonated acetone in solution is coupled to the concentrations of protons and acetone. Therefore, the reaction orders in protons and acetone are the same as those in protonated acetone. The reaction order increases from close to 0 in the case of the CAM, or -1 in the case of the LHM, at high concentration of protonated acetone, to 1 for low concentrations. Similarly, the reaction order changes from 0 (CAM) or -1 (LHM) to 1 with increasingly negative



Fig. 3. Kinetic simulation of the reaction rate (A and C) and the reaction order in protonated acetone/protons/acetone (B and D) for the CAM (A and B) and the LHM (C and D) assuming different concentrations of protonated acetone. The relevant equations and the assumed values are provided in the Supporting Information.

potential. The negative reaction order for the LHM is a direct result of the Langmuir-Hinshelwood step.

An interesting outcome of our model are Eqs. (2) and (3): The equations show that the relationship between coverage of protonated acetone and its reaction order (m_{AH}) is quite simple for both the CAM (Eq. (2)) and the LAH (Eq. (3)). Both equations are derived in the Supporting Information.

$$m_{AH}^{CAM} = 1 - \theta_{AH} \tag{2}$$

$$m_{AH}^{LHM} = 1 - 2\theta_{AH} \tag{3}$$

It is clear from these equations why the reaction order behaves as shown in Fig. 3B and D: As pointed out above, competitive adsorption between hydrogen and protonated acetone causes the coverage of the latter to decrease as the coverage with hydrogen increases. Hence, the reaction order increases with decreasing potential. However, assuming Langmuir conditions, the coverage also depends on the concentration of protonated acetone in solution. If the concentration is small also the coverage is small, irrespective whether acetone adsorption competes with hydrogen adsorption or not. In that case the reaction order is close to one at all potentials.

Fig. 3 shows that the LHM predicts a negative reaction order. A prominent and well investigated example for an electrochemical reaction that follows the Langmuir-Hinshelwood mechanism is the oxidation of CO at platinum surfaces, for which negative reaction orders in CO have indeed been observed [27,28]. Notwith-standing this, the potential dependence of the reaction order in acetone and protons observed in Fig. 2 can be explained by both the CAM and the LHM. However, Fig. 3 shows that positive reaction orders are expected for the LHM only if the concentration of the species in solution is not large enough to reach a full coverage. As the concentration increases also the coverage increases and following Eq. (3) the reaction order decreases. Hence, a plot of the logarithm of the current density versus the logarithm of acetone concentration, from which we determined the reaction orders shown in Fig. 2C, would not yield a straight line with a slope of zero

for the LHM. That is, over a concentration range that changes by two orders of magnitude the resulting curve should have a section with a positive and a negative slope. A reaction order of zero is then only observed for a specific concentration. However, this behavior has not been observed and, therefore, the absence of negative reaction orders indicates that it is more likely that the reaction follows the CAM.

The CAM and LHM also predict different Tafel slopes if we assume the hydrogenation step to be rate determining. In Fig. 4 the thick black lines are the plots of the applied potential versus the logarithm of the respective reaction rate. The displayed potential range is sufficiently positive of the peak potential where the Tafel slope becomes infinite. If the hydrogenation steps are assumed to be rate-determining the CAM and the LHM have Tafel slopes of 0.12 V/dec and 0.06 V/dec, respectively. The former Tafel slope is expected for electrochemical reaction in which the electron transfer is rate determining. The Tafel slope of 0.12 V/dec results then from the potential dependence of the rate constant. A Tafel slope of 0.06 V/dec generally is expected when a chemical



Fig. 4. Tafel plot of the simulated reaction rate (thick black lines) and of the experimental data shown in Fig. 2A (color coding as in Fig. 2A).

reaction follows on an electrochemical reaction. Here the Tafel slope of 0.06 V/dec results from potential dependence of the adsorption constant of hydrogen (reaction (3) in Scheme 2). Both Tafel slopes are rationalized in more detail in the Supporting Information.

Aside from the predicted Tafel slopes, Fig. 4 also features the Tafel plots of the curves shown in Fig. 2A. The average slope of the experimental data is 0.127 V/dec and is, therefore, similar to the one expected for the CAM. Hence, the experimental observations discussed so far suggest that the reduction of acetone proceeds via a proton-coupled electron transfer in the rate determining step. However, this mechanism does not explain why the hydrogenation of acetone proceeds strikingly close to the hydrogen adsorption region. Furthermore, based on this mechanism it is not possible to understand why Bänch et al. [12] observed an H/D-exchange of adsorbed acetone in D_2O based electrolyte.

3.2. Refinement of the kinetic model of acetone reduction

Fig. 5 shows SERS-spectra obtained at a polycrystalline platinum electrode in both a H_2O based electrolyte and in a D_2O based electrolyte that contains 0.1 M acetone. At 0.4 V a band at 2914 cm⁻¹ is observed in both electrolytes. When the potential is kept at 0.4 V for 30 min the spectra do not change significantly. However, the spectra change as the potential is stepped to 0.05 V. In the H_2O based electrolyte the band at 2914 cm⁻¹ is still present. However, a second peak appears at 2869 cm⁻¹ that is present at 0.4 V only as a shoulder. In the D_2O based electrolyte a new band appears at 2124 cm⁻¹ along with a shoulder at 2173 cm⁻¹ that can neither be observed at 0.4 V nor in the H_2O based electrolyte. Hence, it can be concluded that the band at 2124 cm⁻¹ is related to the deuterium containing environment.

The symmetrical CH₃-strech vibration of methyl groups has a band around 2900 cm⁻¹ [29], while bands of symmetrical CD₃strech vibration of methyl groups appear around 2150 cm⁻¹ [29]. Hence, the bands at 2914 cm⁻¹ that appear in both electrolytes at 0.4 V can be assigned to the symmetrical CH₃-strech vibration of the methyl group of the acetone. Also the band at 2869 cm⁻¹ that appears after a step to 50 mV can be assigned to a CH₃methyl group. The fact that we observe two distinct methyl groups at 0.05 V indicates that acetone forms two different adsorbates at this potential.



Fig. 5. SERS-spectra obtained in an electrolyte of 0.1 M H_2SO_4 containing 100 mM of acetone. The electrolyte is based on H_2O (left) or D_2O (right). Black: at 0.4 V vs. RHE; Red: at 0.05 V vs. RHE. The signal between 2400 cm⁻¹ and 2600 cm⁻¹ in the right spectra is due to O,D-stretching vibrations of D_2O . Light colors: original data; darker colors: smoothed data.

The band at 2124 cm^{-1} and the shoulder at 2173 cm^{-1} are assigned to the symmetrical stretch vibration of CD₃-methyl groups. The band appears at the expense of the bands at 2914 cm^{-1} and 2869 cm^{-1} , which suggests that the corresponding CH₃-group are transformed in D₂O and at 0.05 V to CD₃-groups. This confirms the interpretation of Bänsch et al. that the H/D-exchange proceeds at the surface [10]. The H/D-exchange can obviously also take place in solution. However, this process is slow on the timescale of the experiment, as otherwise a band at 2124 cm⁻¹ should appear also at 0.4 V in spectra obtained in D₂O-based electrolytes. The observation that the H/D-exchange only proceeds after a step to 0.05 V indicates that it requires the presence of adsorbed hydrogen.

Scheme 3 shows the mechanism of H/D-exchange derived from the above observations. Since protonation occurs at the carbonyl oxygen, an electron deficiency is left at the carbonyl carbon [26]. It is, therefore, likely that adsorbed protonated acetone binds to the surface via the carbonyl carbon similar to the mode shown on the left side of Scheme 3. Any H/D-exchange mechanism requires the methyl group of acetone to lose a proton at some point. However, when adsorbed protonated acetone loses a proton at its methyl groups the resulting species is the enol-tautomer of acetone as shown in the center of Scheme 3. An H/D-exchange proceeds when adsorbed acetone continuously switches between the adsorbed enol-tautomer and the adsorbed protonated form of acetone via Equilibrium 7. As shown by the SERS-spectra in Fig. 5 this process appears to require the presence of adsorbed hydrogen. Hence, the cleavage of the C,H-bond in adsorbed protonated acetone proceeds homolytically and results in the formation of adsorbed hydrogen. Depending on the applied potential, hydrogen will desorb in order to achieve its corresponding equilibrium coverage. At 0.4 V the hydrogen coverage of the platinum electrode is very low. Hence, at this potential the overall equilibrium, the net reaction of Equilibrium 3 and 7, lies almost entirely on the side of the enol. Based on this consideration we can assign the band at 2914 cm⁻¹ to the symmetrical CH₃-strech vibration of the methyl group of the enol. Once a potential is applied at which hydrogen adsorbs, the equilibrium of Scheme 3 is shifted in favor of adsorbed protonated acetone. Hence, we can assign the band that appears at 2869 cm^{-1} to the symmetrical CH₃-strech vibration of the two methyl groups of adsorbed protonated acetone. This explains the roughly twofold increase in signal intensity for the symmetrical CH₃-strech vibration, after a step to 0.05 V has been performed.

Scheme 4 shows the two pathways by which the enol can form on the platinum surface at 0.4 V. The enol can form in solution via the Equilibria 1 and 8 and adsorb as a neutral species to the surface via Equilibrium 9. Alternatively protonated acetone adsorbs via Equilibrium 2 from solution and forms subsequently the enol via Equilibria 7 and 3. The important point of Scheme 4 is that either route of acetone adsorption proceeds without the net transfer of charge. Although the adsorption of protonated acetone requires initially the transfer of an electron to the adsorbate, its transformation to the enol and the subsequent desorption of a proton means that the electron is finally transferred back to the electrode. The SERS-spectra in Fig. 5 show that acetone is adsorbed to the platinum surface already at 0.4 V. However, if acetone adsorbed as protonated acetone via a net charge transfer this should appear in the CV as a reductive current at potentials larger 0.4 V. However, since adsorbed acetone is present as enol at this potential, this explains why no reductive adsorption of acetone is observed in Fig. 1.

The two pathways described in Scheme 4 by which acetone can form adsorbed enol also mean that there are two pathways to form protonated acetone at the surface. Scheme 5 shows both pathways and how they affect the mechanism of acetone reduction. In Scheme 5A protonated acetone adsorbs immediately from solution via



Scheme 3. Proposed mechanism of the H/D-exchange. By means of an homolytic cleavage of the C,H-bond the enol-tautomer and adsorbed hydrogen forms from adsorbed protonated acetone via Equilibrium 7. In a second step hydrogen desorbs via Equilibrium 3 in order to achieve its equilibrium coverage at the given applied potential.



Scheme 4. Two pathways illustrating how the enol adsorbate can form at 0.4 V on the platinum surface. Blue: The enol is formed in solution (Equilibrium 8) and adsorbed as a neutral species to the platinum surface (Equilibrium 9). Red: After formation (Equilibrium 1) and adsorption of protonated acetone from solution (Equilibrium 2) the enol is formed via Equilibrium 7 at the surface. The desorption of hydrogen via Equilibrium 3 causes acetone to reside at the surface almost entirely as the enol at 0.4 V.

Equilibrium 2 following its formation in solution via Equilibrium 1. Acetone reduction takes place in the potential region of hydrogen adsorption and, due to a large hydrogen coverage at this potential, Equilibrium 7 is shifted in favor of protonated acetone. However, as shown in Scheme 5B adsorbed protonated acetone can also form on the surface via Equilibrium 7 after formation of the enol in solution via Equilibria 1 and 8 and in its subsequent adsorption via Equilibrium 9. In either case protonated acetone is reduced in Reaction 5 by a proton-coupled electron transfer.

It is important to realize that the two mechanisms shown in Scheme 5 predict different reaction orders in protons. In the mechanism of Scheme 5A protonated acetone in solution is in direct equilibrium with adsorbed protonated acetone. The concentration of protonated acetone in solution is defined by the concentration of acetone and protons. Hence, also the overall achievable coverage with adsorbed protonated acetone is dependent on the proton concentration and a corresponding reaction order in protons is expected. In the mechanism of Scheme 5B Equilibrium 2 does not take place. This can be the case when the formation of adsorbed protonated acetone via Equilibrium 7 is faster than its adsorption from solution and when the desorption of adsorbed protonated acetone is slower than its consumption via Reaction 5. When the reaction follows the pathway in Scheme 5B the coverage with adsorbed protonated acetone is defined by the concentration of the enol in solution. The concentration of the latter does not depend on the proton concentration and, therefore, a reaction order in protons of zero would be expected.

It was pointed out above that it is striking that acetone reduction proceeds in the potential region of hydrogen adsorption. However, the CAM derived in the first part of the paper should not depend on the presence of adsorbed hydrogen. The mechanisms presented in Scheme 5 explain why even a proton-coupled electron transfer requires the presence of adsorbed hydrogen. When acetone reduction proceeds via the mechanism in Scheme 5A, adsorbed hydrogen is required to shift Equilibrium 7 to the left side. That is, the presence of adsorbed hydrogen keeps adsorbed protonated acetone from forming the enol. When acetone reduction proceeds via the mechanism in Scheme 5B, adsorbed hydrogen is necessary to transform the enol adsorbed via Equilibrium 9 to adsorbed protonated acetone. In both mechanisms of Scheme 5 adsorbed hydrogen is important for acetone reduction: In the mechanism of Scheme 5B adsorbed hydrogen is actively involved in the formation of adsorbed protonated acetone, while its role is reduced to a passive one in the mechanism of Scheme 5A.

In both mechanisms of Scheme 5 we assume that the actual reduction step proceeds via a proton-coupled electron transfer to adsorbed protonated acetone. The amount of acetone that resides as adsorbed protonated acetone at the surface, relative to the amount that is present as the enol-tautomer, depends on the hydrogen coverage. Hence, the coverage with adsorbed protonated acetone becomes potential dependent via the proton coverage. It is, therefore, not obvious that the reduction of acetone via the mechanisms in Scheme 5A and 5B has the experimentally observed Tafel slope of 120 mV/dec, which requires a full coverage of adsorbed protonated acetone. This is the case when already a small coverage with hydrogen shifts Equilibrium 7 in favor of adsorbed protonated acetone.

One might argue that both mechanisms in Scheme 5 ignore that also the enol could be reduced by a proton-coupled electron transfer and that such a mechanism is better suited to explain a Tafel slope of 120 mV/dec. Such a reaction step is taken into account in the mechanism of Scheme 6 which was derived from the mechanism in Scheme 5B by introducing Reaction 10 in which the enol is reduced via a proton-coupled electron transfer. However, also adsorbed protonated acetone formed via Reaction 10 is in equilibrium with the adsorbed enol-tautomer. Hence, if adsorbed protonated acetone was formed via Reaction 10 its coverage would still be dictated by the hydrogen coverage, in the equilibrium due to Reaction 7 applies. In any case, if Reaction 10 was of importance the H/D-exchange should not require the presence of adsorbed hydrogen. As this is not the case, we conclude that Reaction 10 should not play a significant role for the reduction of acetone.

In Scheme 5 and 6, net charge transfer occurs in step 5 and during hydrogen adsorption. That is, the surface reaction in step 7 leaves a free surface site at which reductive hydrogen adsorption can occur again.



Scheme 5. Two pathways by which acetone reduction can proceed. A: protonated acetone forms in solution via Equilibrium 1 and adsorbs via Equilibrium 2 to the surface. Due to the presence of adsorbed hydrogen Equilibrium 7 is shifted to the left side and reduction can proceed via Reaction 5. B: The enol is formed in solution via the Equilibria 1 and 8. It is then adsorbed to the surface via Equilibrium 9. In the presence of adsorbed hydrogen the enol is transformed to adsorbed protonated acetone and reduced via Reaction 5. Both mechanisms differ in the expected reaction order in protons. For the mechanism in A the same reaction order in protons is expected when the reaction proceeds via the mechanism in B.



Scheme 6. Mechanism considering the enol as the active species of acetone reduction. The mechanism is derived from the mechanism in Scheme 5B by introduction of Reaction 10. Protonated acetone is formed from the enol by a proton-coupled electron transfer. However, protonated acetone generated in this way is also in equilibrium with the enol and its surface concentration is still dictated by the hydrogen coverage.

3.3. Electrochemical reduction of higher aliphatic ketones

To investigate if the hydrogenation of higher aliphatic ketones such as butanone and pentanone yield the same results as for acetone reduction, Fig. 6 shows the results of measurements following the same experimental procedure as for acetone reduction.

The hydrogenation of higher aliphatic ketones is similar to that of acetone in as far as the reaction shows a current maximum despite forced convection. Furthermore, the reaction takes place in a similar potential range and the reaction rate has a positive reaction order in ketone concentration. However, if the carbon skeleton of acetone increases by only one atom, the acid concentration loses its significant effect on the reaction rate. The slight deviations at potentials smaller 0.06 V for different acid concentrations shown in Fig. 6A and D are probably an artifact due to inaccuracies in the correction for hydrogen evolution. Hence, adsorbed protonated butanone or pentanone do not appear to be the reactive species in this case.

The zero reaction order in protons means that neither the concentration nor the coverage of the reacting species depends on the concentration of protons. This is the case for the enol-tautomer of butanone and pentanone, which can react via the pathway shown in Scheme 5B. However, also the concentration of the ketotautomer is obviously independent of proton concentration. Hence, it is conceivable that butanone and pentanone react via a different mechanism in which the keto-tautomer is the reactive species.

To understand how a methyl group added in β -position could exert an effect on the reactivity of the carbonyl functional group, we consider that the methyl group in β -position has an influence on the stability of the enol-tautomer: The equilibrium concentration of the enol-tautomer of butanone and pentanone is nearly one order of magnitude larger than that of acetone [30]. Hence, it is plausible that an additional methyl group in β -position favors the mechanism in Scheme 5B as compared to the mechanism in Scheme 5A.

4. Summary and conclusion

In this paper, we have formulated a detailed mechanistic model for the electrocatalytic reduction of aliphatic ketones (acetone, butanone, propanone) based on kinetic measurements and in situ Raman spectroscopy. The increasing reaction order in acetone with more negative potential indicates that the electrochemical reduction of acetone involves adsorbed acetone species. This has been corroborated by SERS spectra, which show that acetone is already adsorbed at 0.4 V. The reaction rate of acetone reduction has a maximum in the potential region of hydrogen adsorption indicating that competitive adsorption between the reactive species and hydrogen suppresses acetone reduction at more negative potentials. The reaction orders in both acetone and protons increase with decreasing potential. Our simulations of the reaction rate and the reaction orders show based on a Competitive-Adsorption mechanism and a Langmuir-Hinshelwood mechanism are able to reproduce the experimental observations. However, a surface reaction between adsorbed hydrogen and adsorbed protonated acetone (Langmuir-Hinshelwood mechanism) would predict a negative reaction order under certain conditions, which is not observed. Furthermore, the observed Tafel slope of approximately 0.120 mV/dec is easier to explain by a rate-determining step that proceeds through a proton-coupled electron transfer.

A drawback of the initially derived kinetic model is that it neglects that the adsorption of protonated acetone should be potential dependent. This is justified in retrospect by the introduction of the surface equilibrium between the enol-tautomer of acetone and adsorbed hydrogen on the one side and adsorbed



Fig. 6. Current due to reduction of butanone (A and B) and pentanone (D and E) for various concentrations of protons (A and D) and ketone (B and E), respectively, at a polycrystalline platinum electrode in an RRDE experiment. The currents have been corrected for hydrogen evolution according to Eq. (1). The electrolyte was 0.3 M $HClO_4$ with various acetone concentrations (B and E) or an electrolyte with 0.1 M acetone and various proton concentrations (A and D). In the latter case the ionic strength was kept at 0.3 M by adding the appropriate amount of NaClO₄. From the data presented in A, B, C and D the reaction orders in ketone and in protons were derived and plotted as a function of potential (C and F). Scan rate: 0.05 V/s, rotation rate: 1500 rpm. For clarity only negative-going (cathodic) sweeps are shown.

protonated acetone on the other side. That is, acetone is already adsorbed as the enol and, therefore, as a neutral species at potentials around 0.4 V. It is only transformed to adsorbed protonated acetone as hydrogen adsorbs. The potential dependence of the coverage with adsorbed protonated acetone is, therefore, accounted for by the potential dependence of the hydrogen coverage. The existence of the described surface reaction was derived from SERS spectra, which showed that an H/D-exchange in D₂O based electrolyte only proceeds at potentials where hydrogen is adsorbed to the surface.

In the course of ketone reduction, adsorbed hydrogen has two functions in our mechanism. In the sense of a Competitive-Adsorption mechanism, adsorbed hydrogen makes surface sites inaccessible for ketones and hinders, therefore, the electrochemical reduction of aliphatic ketones. The inhibiting effect of adsorbed hydrogen dominates already 0.08 V negative of the onset potential. Hence, the current due to the reduction of ketones follows a bell shape in the CV. Despite forced convection ketone reduction never enters mass transport limitation.

However, adsorbed protonated ketone, the active species of ketone reduction can only be present at the surface when hydrogen is adsorbed as well. That is, either the ketone adsorbs as the enoltautomer and reacts at the surface with adsorbed hydrogen or it adsorbs immediately from solution as protonated ketone. In the latter case adsorbed hydrogen shifts the equilibrium between protonated ketone and the enol-tautomer in favor of the former. Hence, the presence of adsorbed hydrogen keeps adsorbed protonated acetone from forming a species that is inactive for reduction. In addition to its inhibiting effect the presence of adsorbed hydrogen is a necessary precondition for ketone reduction. The absence of adsorbed hydrogen at 380 mV (the equilibrium potential of acetone reduction) is probably also the reason why the reduction of acetone only commences in the H_{upd} region at relatively large overpotentials.

From the insensitivity of the reduction of butanone and pentanone on the proton concentration, we derive that both are adsorbed to the surface via the enol-tautomer, and are subsequently transformed to the hydrogenated ketone via a surface reaction with adsorbed hydrogen. It is interesting to note that increasing the carbon skeleton by only one C-atom in butanone makes protonation of the carbonyl functional group unnecessary. We assign this to a better stabilization of the C,C-double bond of the enol-tautomer by substitution with an additional methyl group, which results in an equilibrium concentration of the enol that is nearly one order of magnitude larger than that of acetone.

The proton effect observed for the reduction of acetone indicates that protonated acetone adsorbs immediately to the surface. However, if acetone reduction proceeded exclusively by this route, an exact match of the reaction orders in acetone and protons would be expected. This is not the case: at low overpotentials (potentials higher than 0.1 V), we observe a smaller reaction order in protons compared to the reaction order in acetone (c. f. Fig. 2C). Once the potential is reduced below 0.1 V, the reaction order in protons increases with a steeper slope than the reaction order in acetone. The observed mismatch between reaction order in proton and acetone suggests that the mechanism of acetone reduction shifts from an enol-based mechanism at low overpotentials to a mechanism in which protonated acetone is adsorbed immediately from solution.

The current density for the reduction of aliphatic ketones is rather low at platinum electrodes. Strategies to increase the current density will have to deal with the ambivalent function of adsorbed hydrogen, because increasing the overpotential causes hydrogen adsorption to become more favorable. Hence, larger overpotentials inhibit rather than promote ketone reduction, at least in the potential window studied in this paper. However, if adsorbed hydrogen is required to shift the surface equilibrium between protonated ketone and enol in favor of the hydrogenated ketone, no reduction will take place unless hydrogen is adsorbed. That also means that the electrochemical ketone reduction is likely to proceed very close or in parallel to hydrogen evolution at any catalyst material.

However, a rational catalyst designed based on the above mechanism of aliphatic ketone reduction could provide individual adsorption sites for hydrogen and ketone. Exploitation of the bifunctonal mechanism would eliminate competition between hydrogen adsorption and ketone adsorption.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2018.11.019.

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