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Mechanism of Electroreduction of Allyl Alcohol at Platinized Platinum Electrode in Acidic Aqueous Solution

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The electroreduction of allyl alcohol to form propene at the platinized platinum electrode in acidic aqueous solution has been studied using CV plots, IR, ESR, and MS spectra, and a semiempricial MO method (MOPAC7/AM1, PM3). From the determinations of charge-transfer coefficients, reaction orders and apparent activation energy for the given reaction, the detection of the intermediates such as $C_3H_5^+$, $C_3H_5^\bullet$, and $C_3H_5^-$ species, and PM3 calculations of charge distribution and frontier orbital energies of the reaction species C_3H_5OH and $C_3H_5^+$, the authors suggest that in acidic aqueous solution the production of propene via reductive splitting of the C−OH bond situated in the allyl position of allyl alcohol obeys a carbonium ion−carbanion mechanism.

Introduction

In recent years, analysis of the electroreduction products of allyl alcohol (AA) at a platinized platinum electrode in perchloric acid aqueous solutions using MS and IR spectroscopy has been performed by Chen Jian et al.[1] and Pastor et al.,[2] respectively, who point out that in acidic aqueous solution propene and propane are the main products. To elucidate the production of the products, the electroreduction mechanism concerned is suggested by Chen Jian et al.[1] and Horányi and Torkos.[3] According to them, at the electrode surface, propene is formed via the allyl radical $C_3H_5^\bullet$ and propane via catalytic hydrogenation of propene. Nevertheless, they hold different views about how the radical $C_3H_5^\bullet$ and propene can be formed during the electroreduction of AA. Chen Jian et al. assume that the radical $C_3H_5^\bullet$ is formed from the dissociation of the anion radical $C_3H_5OH^{\bullet -}$ and propene from the hydrolytic action of the carbanion $C_3H_5^-$. In contrast, Horányi and Torkos suppose that the radical $C_3H_5^\bullet$ is formed via the carbonium ion $C_3H_5^+$ dissociated from the oxonium ion $C_3H_5OH_2^+$ and propene via a coupled reaction between the radical $C_3H_5^\bullet$ and the atom H. We have studied the electroreduction reaction from AA to propene at the platinized platinum electrode in perchloric acid aqueous solution and put forward a carbonium ion−carbanion mechanism to elucidate the reaction process. It is of wide significance to elucidate the mechanism to produce alkene or alkyne via the electroreduction cleavage of the C−OH bonds situated in allyl or propargyl positions of some unsaturated fatty alcohols, e.g., allyl alcohol, propargyl alcohol, 1,4-butynediol, and 3-hexyne-2,5-diol in acidic aqueous solutions.

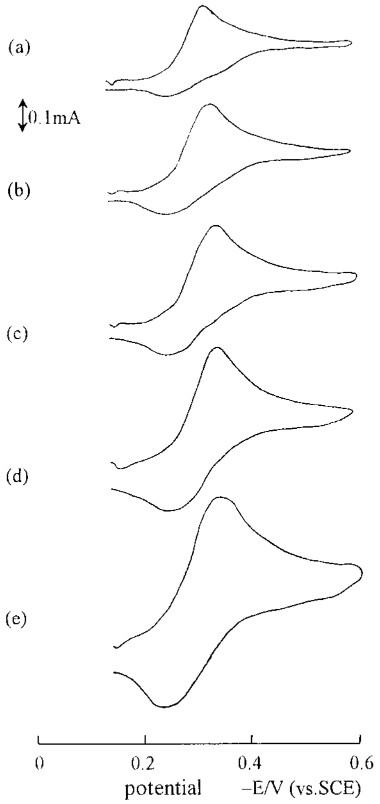

Figure 1. CV plots of electroreduction of AA at variable sweep rates. Test solution: 5.0×10^{-3} mol L^{-1} AA + 0.10 mol L^{-1} $NaClO_4$ + 5.0×10^{-3} mol L^{-1} $HClO_4$ + H_2O. Sweep rates, mV s^{-1}: (a) 26, (b) 39, (c) 52, (d) 78, (e) 157. Platinized platinum electrode (ca. 0.02 cm^2).

Results and Discussion

Characteristics of Electroreduction of AA. The electroreduction of AA in acidic aqueous solution observed in Figure 1 takes place in a less negative potential, −0.35 V (vs SCE, the same below), which is consistent with the values reported by different authors.[1−3] In the electroreduction of organic compounds, it is seldom the

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(1) Chen, J.; Liu, P. F.; Wang, H.; Zha, Q. X. *Acta Chim. Sin.* **1993**, *51,* 150 (Ch.).

(2) Pastor, E.; Wasmus, S.; Iwasita, T.; Arévalo, M. C.; Ganzález, S.; Arvia, A. J. *J. Electroanal. Chem.* **1993**, *353,* 81.

(3) Horányi, G.; Torkos, K. *J. Electroanal. Chem.* **1980**, *111,* 279.

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Table 1. Electrochemical Parameters of Electroreduction of AA

transfer coefficients		reaction orders		apparent activation energy, ΔE_a
α_c	α_a	Z_{AA}	Z_{H^+}	(kJ mol^{-1})
0.49 ± 0.05^a	1.14 ± 0.15^a	0.72 ± 0.07^a	1.13 ± 0.05^a	18.0

[a] Average error in two calculated values.

case that the reduction potential is more positive than the potential, −0.42 V, of evoluting hydrogen in acidic aqueous solution.[4] Its electroreduction occurring with ease was also proved by the fact that the apparent activation energy of the electroreduction of AA obtained from recording reduction current of AA at various temperature was no more than 18.0 kJ mol^{-1} (Table 1).

Unlike the reversible electrode reaction of evoluting hydrogen in which its peak potential is independent of sweep rate and the difference between the cathodic and anodic peak potentials is no more than 0.059 V,[4] the electrode reaction in the electroreduction of AA has some irreversible characteristics in which its cathodic (or anodic) peak potential shifts negatively (or positively) with increasing sweep rate and the difference between cathodic and anodic peak potentials is greater than 0.059 V (Figure 1). In addition, considering that there also exists an anodic peak together with a cathodic peak in its CV plot, it may be confirmed that the electrode reaction studied is not a totally irreversible electrode reaction but a partly irreversible or quasireversible electrode reaction.

That the reaction order with respect to H^+ is close to 1 (Table 1), which was found from the cathodic peak currents of AA by changing the pH values in the studied solutions, indicates there is a preceding chemical reaction involving H^+ in the studied solution. In other words, the electroreduction of AA in acidic aqueous solution obeys a CE model rather than an EC model.

The fact that the reaction order with respect to AA is a fraction, 0.72 (Table 1), is a reflection of the difference between the surface and bulk concentrations of AA.[5] That is, the reactant AA or protonated AA during its electroreduction is adsorbed at the electrode surface. It may be further recognized that the reactant AA or protonated AA has a weak adsorption at the electrode surface since a small peak is absent at the back of the cathodic peak at −0.35 V.[6] Therefore, following the above-mentioned preceding chemical step in the bulk solution, there is also an adsorption step involving AA or protonated AA at the electrode/solution interface prior to the charge transfer steps of the partly irreversible electrode reaction.

On the basis of the data $(\alpha_c + \alpha_a) > 1$ and $\alpha_a > \alpha_c$ (Table 1) and Tafel coefficient $2.3RT/(\alpha_c n_a F)$ close to 0.118,[7a] it may be deduced from the Butler−Volmer equation[7b] that the electroreduction of AA is a two-electron reaction involving two one-electron consecutive electrochemical steps in which the first electrochemical step is the rate-determining step (rds, the same below) of the electroreduction of AA.

The broad reduction wave at −0.35 V is surely related to the original electroreduction of the stable reactant AA or protonated AA. Moreover, the final products propene and propane could also be received at the potential as such. It follows that the broad wave should be regarded as two reduction waves merged with each other,[8] which result from the above-mentioned two one-electrom reactions forming the products from the reactant. In addition, the reduction wave at −0.35 V remains unchanged in its wave shape and wave height even though the CV plot was recorded repeatedly in a higher sweep rate. Consequently, the reaction intermediates taking part in the two one-electron reactions are all unstable. Therefore, to elucidate in detail the mechanism of the electroreduction of AA, it is necessary to detect these intermediates using a variety of spectroscopic techniques.

Analysis of Intermediates. Allyl Cation. AA is a molecule with uneven charge distribution, where the atom O has the largest negative charge density (Scheme 1, A) and will easily result in an attack of the electrophilic reagent H^+ and form the oxonium ion $C_3H_5OH_2^+$. In addition, the protonation heat of AA may amount to 766.9 kJ mol^{-1}.[9a,b] As a result, like many alcohols, e.g., ethyl alcohol, in acidic aqueous solution, AA will also partly exist in the form of $C_3H_5OH_2^+$ via the reaction $C_3H_5OH + H^+ = C_3H_5OH_2^+$. However, unlike $C_2H_5OH_2^+$, which is unable to dissociate and form the ethyl cation $C_2H_5^+$, $C_3H_5OH_2^+$ may dissociate and form the allyl cation $C_3H_5^+$, as its dissociation energy was no more than 66.9 kJ mol^{-1}.[9a] Forming $C_3H_5^+$ with ease is due to its an amount of stabilty, which comes from the divergence of its positive charge (Scheme 1, B) resulting from the overlap of its π-orbit electron and empty p-orbit.

A strong nucleophilic reagent, e.g., sodium azide, might be used as a trap-to-trap carbonium ion.[10] The IR spectra of AA in acidic aqueous solutions containing sodium azide (Figure 2) can be explained by means of reaction scheme 2.

reaction scheme 2

a. acidic aqueous solution of ethyl alcohol:

$$C_2H_5OH_2^+ + N_3^- \xrightarrow{SN_2} C_2H_5N_3 + H_2O(aq) \tag{1}$$

b. acidic aqueous solution of AA:

$$\begin{gathered} C_3H_5OH_2^+ \xrightarrow{SN_1} C_3H_5^+ + H_2O(aq) \\ C_3H_5^+ + N_3^- \rightarrow C_3H_5N_3(aq) \end{gathered} \tag{2}$$

c. acidic aqueous solution of AA being electrolyzed:

$$\begin{gathered} C_3H_5OH_2^+ \xrightarrow{SN_1} C_3H_5^+ + H_2O(aq) \\ C_3H_5^+ + N_3^- \rightarrow C_3H_5N_3(aq) \\ C_3H_5^+(aq) + e_M^- \rightarrow C_3H_5{}^{\bullet}{}_{ads} \end{gathered} \tag{3}$$

A weak absorption of ν_{C-N} of the azide $C_2H_5N_3$ at 1325 cm^{-1} is observed on line a, which is attributed to the SN_2 reaction (1) between $C_2H_5OH_2^+$ and N_3^- owing to the

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(4) Breiter, M. *Electrochim. Acta* **1963**, *8*, 925.

(5) *Theoretical Electrochemistry*; Antropov, L., Wu, Z. D., et al., Eds.; translated from English; Higher Education Press: Beijing, 1982; Chapter 20 (Ch.).

(6) Wopschall, R. H.; Shain, I. *Anal. Chem.* **1967**, *39*, 1527.

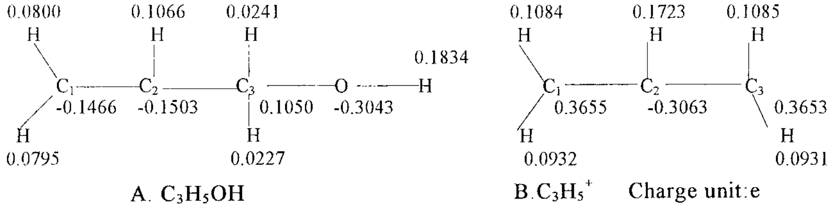
(7) (a) *An Introduction to Electrode Kinetics*; Zha, Q. X., Ed.; Science Press: Beijing, 1976; Chapter 4 (Ch.). (b) Bockris, J. O'M.; Damjanovic, A. D. *J. Electrochem. Soc.* **1972**, *119*, 285.

(8) Plocyn, D. S.; Shain, I. *Anal. Chem.* **1966**, *38*, 370.

(9) (a) Luo, Y.-R.; Holmes, J. L. *J. Phys. Chem.* **1994**, *98*, 303. (b) Moryl, J. E.; Greasy, W. R.; Farrar, J. M. *J. Phys. Chem.* **1983**, *87*, 1954.

(10) Harris, J. M.; Saber, D. J.; Hall R. E.; Schleyer, P. R. *J. Am. Chem. Soc.* **1970**, *92*, 5729.

Scheme 1



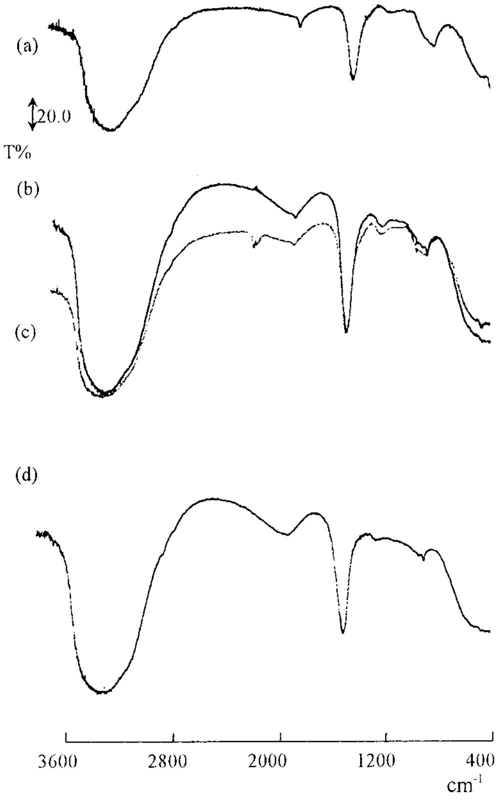


Figure 2. IR spectra of various solutions in the presence of sodium azide: (a) 5.0×10^{-2} mol L^{-1} $HClO_4$ + 7.5×10^{-2} mol L^{-1} NaN_3 + 1:3 C_2H_5OH:H_2O (ratio in volume); (b) 1.5×10^{-2} mol L^{-1} AA + a; (c) 1.5×10^{-2} mol L^{-1} AA + 5.0×10^{-2} mol L^{-1} $HClO_4$ + 12.5×10^{-2} mol L^{-1} NaN_3 + 1:3 C_2H_5OH:H_2O; (d) 1.5×10^{-2} mol L^{-1} AA + a, Controlled potential: −0.40 V, Tme of electrolysis: 30 min.

existence of the solvent ethyl alcohol in the studied solution. A strong absorption of ν_{C-N} at 1350 cm^{-1} on line b is due to the formation of $C_3H_5N_3$ via the SN_1 reaction (2) between $C_3H_5OH_2^+$ and N_3^- rather than the SN_2 reaction in between. This view was supported by the fact that the reaction velocity of the reaction, i.e., $C_3H_5OH_2^+ + N_3^- \rightarrow C_3H_5N_3 + H_2O$, is independent of the concentration of N_3^-* (SN_1 reaction $\nu = k[C_3H_5OH]$; SN_2 reaction $\nu = k'[C_3H_5OH][N_3^-]$) considering that the intensity of ν_{C-N} on line c in comparison with that on line b remains unchanged despite increasing the concentration of sodium azide. Therefore, no doubt, $C_3H_5^+$ can be formed through the dissociation of $C_3H_5OH_2^+$ in AA acidic aqueous solution.

In the acidic aqueous solution of AA being electrolyzed, the intensity of the absorption ν_{C-N} on line d is decreased in comparison with that on line b or c. The difference lies in that the electrode electron can act as "another nucleophilic reagent" along with sodium azide in the bulk solution. Under the circumstances, they will commonly combine with $C_3H_5^+$ via the reactions (3) and thus decrease the concentration of $C_3H_5^+$ and $C_3H_5N_3$ in the bulk solution. That is to say, the allyl cation $C_3H_5^+$ will not only form from the dissociation of the oxonium ion $C_3H_5OH_2^+$ in the bulk solution will but also partcipate in the electroreduction of AA as a reactive intermediate at the electrode/solution interface.

Allyl Radical. A six-line spectrum having triplets-of-doublets pattern is observed in Figure 3 (with the asterisks). Hyperfine coupling constants of the spin adduct concerned, $\alpha_N = 15.50 \times 10^{-4}$ T, $\alpha_{H}{}^{\beta} = 21.60 \times 10^{-4}$ T, were obtained from the six-line spectrum. Obviously, not an oxyl radical but a carbon-centered radical, which was trapped by the spin trap 5,5-dimethyl-1-pyrroline-1-oxide (DMPO), was formed during the electroreduction of AA because $\alpha_{H}{}^{\beta}$ is greater than α_N and additional hyperfine splitting of γ-H is wanting in this spectrum.[11]

In the first place, the hydroxylethyl radical $CH_3\dot{C}HOH$ cannot be formed from the solvent ethyl alcohol through abstracting its hydrogen by electrogenerated atom H at the cathode or electrogenerated radical OH at the anode separated by the cathode. It may be proved by the lack of the six-line pattern in the spectrum of the electrolyzed blank solution without AA. Similarly, the hydroxylallyl radical $CH_2{=}CH\dot{C}HOH$ should not be formed from the reactant AA, which might further be confirmed by the fact that when the trap phenyl *tert*-butyl nitrone (PBN) in lieu of DMPO was used in our previous work[12] the six-line spectrum with a large β-H splitting resulting from the adduct $CH_2{=}CH\dot{C}HOH$ and PBN[13] was not present in the observed spectrum. Obviously, the above-mentioned carbon-centered radical trapped by DMPO does not come from either the solvent C_2H_5OH or the reactant AA. It is surely the carbon-centered radical formed in the process of the electroreduction of AA.

According to Chen Jian[1] and Horányi,[3] the propyl radical $C_3H_7^{\bullet}$ and the allyl radical $C_3H_5^{\bullet}$ were possibly the radicals formed during the electroreduction of AA. However, cis-hydrogenation of the two carbons on the double bond of propene to produce propane occurs almost simultaneously and thus $C_3H_7^{\bullet}$ has a low yield at the electrode surface. In addition, like propane, $C_3H_7^{\bullet}$ has a very small solubility in alcohol−water solutions and thus less possibility to be trapped. On the contrary, $C_3H_5^{\bullet}$, as will be mentioned in reaction scheme 4, forms easily from the discharge of $C_3H_5^+$ at the electrode/solution interface. Additionally, it has a definite solubility in the bulk solution because of the polarization effect of its π-electron. Therefore, in comparison with $C_3H_7^{\bullet}$, $C_3H_5^{\bullet}$ will be a radical to be trapped and detected easily. Its formation might also be proved from the decaying spectra lines in our previous work,[12] which should be ascribed to the

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[11] Janzen, E. G.; Liu, J. I. *J. Magn. Reson.* **1973**, *9*, 510.

[12] Zhang, J. D.; Kuang, Y. F.; Huang, S. K.; Xie, N. X.; Wang, F. Z.; Chen, D. W. *Electrochemistry* **1996**, *3*, 343 (Ch.).

[13] Janzen, E. G.; Lopp, I. G. *J. Magn. Reson.* **1972**, *7*, 107.

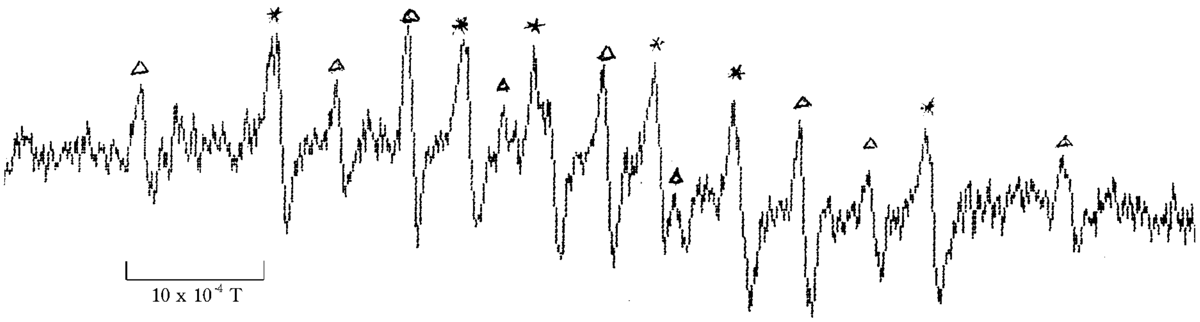
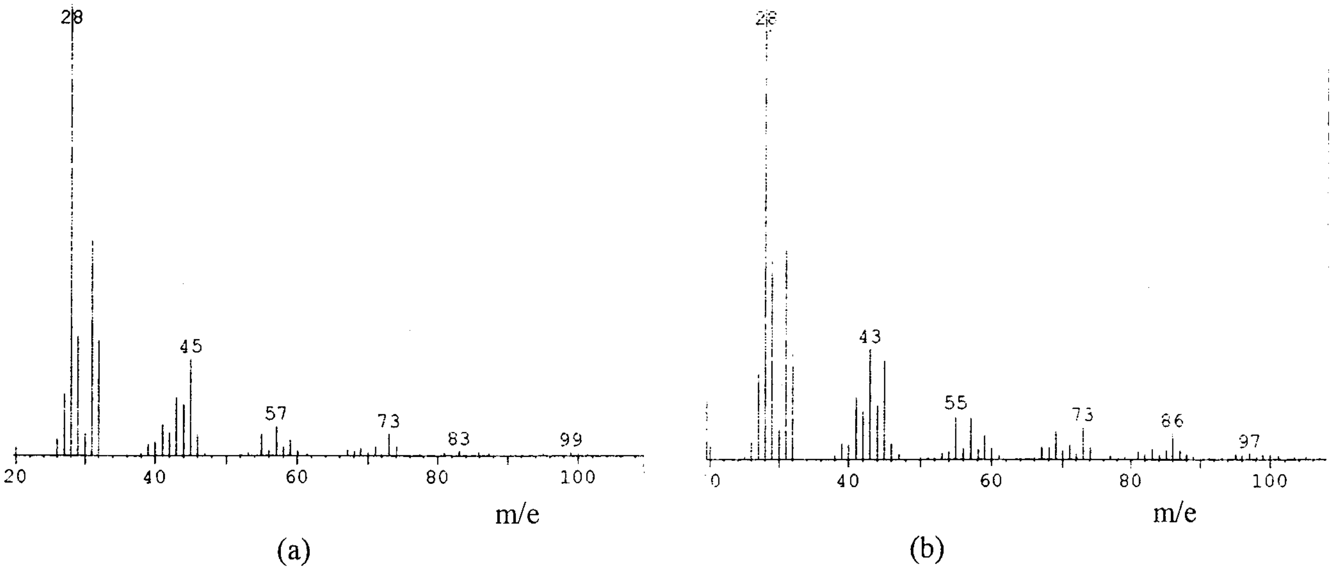


Figure 3. ESR spectrum of product solution during the electroreduction of AA in the presence of DMPO. Test solution: 1.0 × 10^{-2} mol L^{-1} AA + 1.0 × 10^{-2} mol L^{-1} DMPO + 0.1 mol L^{-1} $NaClO_4$ + 5.0 × 10^{-3} mol L^{-1} $HClO_4$ + 1:3 C_2H_5OH:H_2O. Controlled potential: −0.40 V. Time of electrolysis: 10 min.



(a) (b)

Figure 4. MS spectra of product solutions of electroreduction of AA: (a) 5.0 × 10^{-2} mol L^{-1} AA + 0.1 mol L^{-1} $NaClO_4$ + 2.0 × 10^{-2} mol L^{-1} $HClO_4$ + 1:3 C_2H_5OH:H_2O; (b) a + CO_2(gas). Controlled potential: −0.40 V. Time of electrolysis: ca. 1 h.

formation of the less stable adduct PBN−$C_3H_5^\bullet$ rather than that of the stable adduct PBN−$C_3H_7^\bullet$, as the π-type radical $C_3H_5^\bullet$ is more stable than the σ-type radical $C_3H_7^\bullet$.

It is known that a solvated electron is stable in liquid ammonia and unstable in aqueous solution. The formation of $C_3H_5^\bullet$ is highly improbable through the combination of the solvated electron with $C_3H_5^+$ in the bulk solution. Consequently, the reaction intermediate $C_3H_5^\bullet$ is sure to form at the electrode/solution interface via the electron-transfer reaction $C_3H_5^+(aq) + e_M^- \rightarrow C_3H_5{}^\bullet{}_{ads}$.

Allyl Anion. As compared to Figure 4a, the peaks of the molecular ion $C_3H_5COOH^{\bullet+}$ (m/e = 86) and its fragment $CH_2{=}C(OH)\,(OH^+)$ (m/e = 60) arising from the so-called McLafferty rearrangement are presented in Figure 4b. In addition, the m/e = 41 and m/e = 69 peaks have an increasing height, caused separately by the fragments $CH_2{=}CHCH_2^+$ (M − 45) and $CH_2{=}CHCH_2C{\equiv}O^+$ (M − 17) produced from the fission of the molecular ion. All these characteristic peaks of lower fatty acids indicate 3-butenoic acid, C_3H_5COOH, was formed in the electrolyzed AA test solution agitated with carbon dioxide. Evidently, only the intermediate allyl anion $C_3H_5^-$ may react with CO_2 to form C_3H_5COOH via a nucleophilic addition reaction, i.e., $C_3H_5^- + H_2O + CO_2 \rightarrow C_3H_5COOH + OH^-$. It follows that $C_3H_5^-$ is likely to form during the electroreduction of AA.

The allyl anion $C_3H_5^-$ possesses a greater resonance stabilization than the allyl radical $C_3H_5^\bullet$[14] and thus $C_3H_5^-$ is possibly formed via the combination of $C_3H_5^\bullet$ with an electron. Considering that $C_3H_5^\bullet$ has a great yield at the electrode surface, Fermi electrons at the electrode surface have a higher surface concentration and reaction activity,[7a] and in aqueous solution $C_3H_5^-$ neither forms via the combination of $C_3H_5^\bullet$ with the solvated electron nor exists due to its reaction with H^+ or H_2O to produce propene, it is certain that $C_3H_5^-$ is formed at the electrode surface via the electron-transfer reaction $C_3H_5{}^\bullet{}_{ads} + e_M^- \rightarrow C_3H_5{}^-{}_{ads}$.

Mechanism of Electroreduction of AA. Because in acidic aqueous solution and low concentrations of AA (below 20.0 × 10^{-3} mol L^{-1}) AA exists in the form of a monomeric molecule instead of a polymer[15] and propene is a stable product received from the electroreduction of AA, the overall electroreduction reaction producing propene from AA may be represented as follows:

$$C_3H_5OH(aq) + 2H^+(aq) + 2e_M^- \rightarrow C_3H_6(g) + H_2O(aq) \quad (4)$$

The formation of the allyl radical $C_3H_5^\bullet$ should be presupposed from the production of propene. In fact, it

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[14] Jarjis, H. M.; Khalil, S. M. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1701.

[15] Smith, P.; Wood, P. B. *Can. J. Chem.* **1967**, *45*, 649.

has been detected by ESR spectroscopy (Figure 3). Its detection is an important step to elucidate the mechanism of the electrogeneration of propene from AA. Reaction 4 may be regarded as the combination of the two reaction stages of forming $C_3H_5^{\bullet}$ from AA and producing propene from $C_3H_5^{\bullet}$ on the basis of the formation of the radical $C_3H_5^{\bullet}$. The reaction pathways of the two reaction stages will be discussed separately.

Reactions Forming $C_3H_5^{\bullet}$ from AA (eqs 5−11).

$$\text{reaction: } C_3H_5OH(aq) + H^+(aq) + e_M^- \rightarrow C_3H_5{}^{\bullet}{}_{ads} + H_2O(aq) \quad (5)$$

reaction scheme 3

$$\text{anion radical pathway}^1\text{: } C_3H_5OH(aq) + e_M^- \rightarrow C_3H_5OH^{\bullet-}{}_{ads} \quad (6)$$

$$C_3H_5OH^{\bullet-}{}_{ads} \rightarrow C_3H_5{}^{\bullet}{}_{ads} + OH^-(aq) \quad (7)$$

$$H^+ + OH^- \rightarrow H_2O\,(aq) \quad (8)$$

reaction scheme 4

$$\text{carbonium ion pathway}^3\text{: } C_3H_5OH + H^+ \rightarrow C_3H_5OH_2{}^+(aq) \quad (9)$$

$$C_3H_5OH_2{}^+ \rightarrow C_3H_5{}^+ + H_2O(aq) \quad (10)$$

$$C_3H_5{}^+(aq) + e_M^- \rightarrow C_3H_{5ads} \quad (11)$$

According to Chen Jian[1] and Horányi,[3] two pathways exist to form $C_3H_5^{\bullet}$ from AA. Like $C_3H_5OH_2^+$, $C_3H_5OH^{\bullet-}$ is also an easily dissociated species due to the formation of more stable radical $C_3H_5^{\bullet}$, and thus the degree of the difficulty or ease of combination of the electrode electron with C_3H_5OH or $C_3H_5^+$ will play a main role in determining the pathway for forming $C_3H_5^{\bullet}$. Fukui[16] pointed out that under the given electrode and solvent conditions the reduction potential of any organic compound is linearly related to the energy of the lowest unoccupied orbit. The higher its lowest unoccupied level, the more negative its reduction potential, and thus its electroreduction will be rare. When $C_3H_5OH^{\bullet-}$ is electrogenerated from the AA molecule, an electrode electron will be required to fill into the antibonding orbit of the molecule AA, where its LUMO is 1.05 eV and the energy gap between LUMO and HOMO is 11.36 eV, calculated by PM3. However, the electrogeneration of $C_3H_5^{\bullet}$ from $C_3H_5^+$ will make the electrode electron occupy the nonbonding orbit of $C_3H_5^+$, where its NBMO is −8.28 eV, with the energy gap between NBMO and HOMO 9.66 eV. As compared to the AA molecule, the allyl cation $C_3H_5^+$ obviously has a lower level and energy gap. Therefore, the carbonium ion pathway is surely preferred to the anion radical pathway.

The above-mentioned inference obtained from the quantum-chemical calculation was supported by many experimental facts. First, in the case of forming an anion radical, the reduction potential should have a relatively negative value.[17a,b] However, the electroreduction of AA occurs in a less negative potential −0.35 V, which is consistent with the carbonium ion pathway with a lower unoccupied level. Second, if $C_3H_5OH^{\bullet-}$ was formed, like the electroreduction of some unsaturated aromatic alcohols via anion radicals,[18] *n*-propyl alcohol should be partly received in the final products. However, the yield of *n*-propyl alcohol was negligibly small.[1,2] On the contrary, the formation of the allyl cation $C_3H_5^+$ has been discovered in this work. Finally, if the formation of $C_3H_5^{\bullet}$ from AA could be ascribed to the anion radical pathway, the electroreduction of AA should have an EC model as indicated in reaction scheme 3. In fact, its electroreduction, as mentioned earlier, belongs to a CE model as indicated in reaction scheme 4.

An anion radical is a common intermediate during the electroreduction of organic compounds, indeed. But it is not the case with regard to the electroreduction of AA in acidic aqueous solution. As indicated by Horányi, it "seemed to be an interesting exception to the general rule".[19] The "interesting exception", as mentioned in this work, lies in that the allyl cation $C_3H_5^+$ can be easily formed by means of the reductive splitting of the $C-OH_2^+$ bond situated at the allyl position of the oxonium ion $C_3H_5OH_2^+$ which exists in AA acidic aqueous solution. However, our further work[17c] also indicated that when the electroreduction of AA takes place at the mercury electrode and in nearly neutral aqueous solutions, its electroreduction to produce propene will occur at a more negative potential, e.g., −1.25 V. Under the circumstances, the anion radical pathway forming $C_3H_5^{\bullet}$ from AA must be obeyed.

Reactions Producing Propene from $C_3H_5^{\bullet}$ (eqs 12−18).

$$\text{reaction: } C_3H_5{}^{\bullet}{}_{ads} + H^+(aq) + e_M^- \rightarrow C_3H_6(g) \quad (12)$$

reaction scheme 5

$$\text{coupling pathway}^3\text{: } H^+(aq) + e_M^- \rightarrow H_{ads} \quad (13)$$

$$H_{ads} + C_3H_5{}^{\bullet}{}_{ads} \rightarrow C_3H_6(g) \quad (14)$$

reaction scheme 6

$$\text{carbanion pathway}^1\text{: } C_3H_5{}^{\bullet}{}_{ads} + e_M^- \rightarrow C_3H_5{}^-{}_{ads} \quad (15)$$

$$C_3H_5{}^-{}_{ads} + H^+(aq) \rightarrow C_3H_6(g) \quad (16)$$

or even more correctly, the hydration of $C_3H_5{}^-{}_{ads}$:

$$C_3H_5{}^-{}_{ads} + H_2O(aq) \rightarrow C_3H_6(g) + OH^-(aq) \quad (17)$$

$$H^+ + OH^- \rightarrow H_2O(aq) \quad (18)$$

In organic electroreduction the reaction forming carbanion and the coupled reaction are two kinds of common reactions that produce hydrocarbon products from radical

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[16] Fukui, K.; Morokuma, K.; Kato, H.; Yonezawa, T. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 217.

[17] (a) Huang, S. K.; Chen, D. W.; Huang, S. H. *Acta Chim. Sin.* **1996**, *54*, 783 (Ch.). (b) Piette, L. H.; LuDwig, P.; Adams, R. N. *Anal. Chem.* **1962**, *34*, 916. (c) Huang, S. K.; Zhang, J. D., unpubilished work.

[18] Lund, H.; Doupeux, H.; Michei, M. A.; Mousset, G.; Somonet, J. *Electrochim. Acta* **1974**, *19*, 629.

[19] Horányi, G. *Electrochim. Acta* **1986**, *31*, 1095.

intermediates. Whether one of the two reactions prevails over another or they are of the same importance will depend on the special characteristics of the two reactions under discussion and the given reaction conditions.

As mentioned earlier, the electroreduction of AA at −0.35 V is a two-electron electrode reaction involving two consecutive electrochemical steps, where the first electrochemical step is the rds of the electroreduction of AA. On the one hand, obviously not reaction (13) but reaction (15) is determined to be the consecutive electrochemical step of the first electrochemical step, i.e., the reaction $C_3H_5^+(aq) + e_M^- \rightarrow C_3H_5{}^{\bullet}{}_{ads}$ (11), since the product $C_3H_5^{\bullet}$ of reaction (11) is the reactant of reaction (15). On the other hand, reaction (11) occurs at the electrode/solution interface in which a definite amount of activation potential hill to detach the hydrated shell of $C_3H_5^+(aq)$ needs to be satisfied,[7b] while reaction (15) is a rapid radical quenching reaction at the electrode surface, and hence reaction (11) as compared to reaction (15) will have a slower reaction velocity and is determined to be the rds of the electroreduction of AA when the two electrochemical steps are composed of reactions (11) and (15). Therefore, the second electrochemical step in the electroreduction of AA, which is involved in the reactions producing propene from $C_3H_5^{\bullet}$, is not reaction (13) but reaction (15).

The hydration reaction (17) may also prevail over the coupled reaction (14) due to a lower accumulation of the atom H at the electrode surface when the electroreduction of AA takes places in a less negative potential, e.g. −0.35 V. The above-mentioned view was supported by a higher yield of propene in the final products. The yield of propene may amount to 20−30%[2,3], especially there is an obvious increase in yield from 20 to 29% when the reduction potential of AA was shifted negatively by a small amount from −0.32 to −0.34 V, i.e., from −0.08 to −0.10 V (vs SHE).[19] That much propene is not likely to desorb and evolute at the electrode/solution interface due to the adsorption of propene with the help of its π-electron polarization effect and its catalytic hydrogenation to form propane at the electrode surface. A possible explanation for the greater yield of propene is due to the existence of reaction (17). Unlike propene, partly electrogenerated $C_3H_5{}^-{}_{ads}$, owing to its negative charge, will easily desorb from the cathode surface with the negative charge and enter the interface liquid layer, from where it will rapidly react with H_2O to produce propene, and finally propene will escape from the interface liquid layer in the form of a gas.

Nevertheless, when the electroreduction of AA takes place in at a more negative potential, e.g. −0.40 V, which is close to the hydrogen evolution potential −0.42 V,[4] a large quantity of the atom H will be accumulated at the platinum surface because the recombination of two atoms H is the rds of evoluting hydrogen at platinum.[5] The obvious accumulation of the atom H_{ads} has been proved by the existence of the spin adduct H-DMPO having a nine-line spectrum with a 1:1:2:1:2:1:2:1:1 pattern (Figure 3, peaks denoted Δ) at −0.40 V. A large amount of the atom H_{ads} allowed it to react with the allyl radical $C_3H_5{}^{\bullet}{}_{ads}$ and produce propene. Under the circumstances, the coupled reaction (14) will keep up with the hydration reaction (17), i.e., there is the possibility of two pathways to produce propene.

Mechanism of Electroreduction of AA. The electroredection of AA to produce propene at the platinized platinum electrode in acidic aqueous solution is a complex two-electron electrode reaction. Prior to its electron-transfer reaction, a homogeneous chemical equilibrium related to the formation of the protonated AA, i.e., $C_3H_5OH_2^+$, in the bulk solution and a heterogeneous surface transformation related to the adsorption of AA or $C_3H_5OH_2^+$ at the electrode/solution interface are involved in the process of the electroreduction reaction. Some reaction intermediates, i.e., the allyl cation $C_3H_5^+$, the allyl radical $C_3H_5^{\bullet}$, and the allyl anion $C_3H_5^-$, which are all unstable, are formed during the electroreduction. The overall reaction process may be divided into the two stages of forming $C_3H_5^{\bullet}$ from AA and forming propene from $C_3H_5^{\bullet}$ on the basis of the formation of $C_3H_5^{\bullet}$. Unlike the electroreduction of ordinary organic compounds, the formation of the radical $C_3H_5^{\bullet}$ from AA or $C_3H_5OH_2^+$ is not via the dissociation of the anion radical $C_3H_5OH^{\bullet-}$, which is unable to form in acidic aqueous solution, but via the discharge of the carbonium ion $C_3H_5^+$ dissociated from the oxonium ion $C_3H_5OH_2^+$ and/or the direct discharge of $C_3H_5OH_2^+$ itself because of its easy dissociation. As for the formation of propene from $C_3H_5^{\bullet}$, there are two possibilities, i.e., coupling of $C_3H_5^{\bullet}$ with the atom H and the hydration of the carbanion $C_3H_5^-$, where the latter is the main pathway at the ordinary reduction potential of AA, −0.35 V. The electron-transfer reactions are composed of the two consecutive electrochemical steps, i.e., the step of forming $C_3H_5^{\bullet}$ from $C_3H_5^+$ and/or $C_3H_5OH_2^+$ and the step of forming $C_3H_5^-$ from $C_3H_5^{\bullet}$, wherein the former is the rds of the electroreduction of AA. The overall electrode reaction and a carbonium ion−carbanion mechanism to produce propene from AA may be represented as follows:

$$\text{overall electrode reaction:}\quad C_3H_5OH(aq) + 2H^+(aq) + 2e_M^- \rightarrow C_3H_6(g) + H_2O(aq)$$

$$\text{partial reactions:}\quad C_3H_5OH + H^+ = C_3H_5OH_2^+(aq)$$

$$C_3H_5OH_2^+(aq) = C_3H_5OH_2{}^+{}_{ads}$$

$$C_3H_5OH_2^+ \rightarrow C_3H_5^+ + H_2O(aq) \quad \text{(at Helmholtz layer)}$$

$$C_3H_5^+(aq) + e_M^- \xrightarrow{\text{rds}} C_3H_5{}^{\bullet}{}_{ads}$$

$$\text{and/or}\quad C_3H_5OH_2{}^+{}_{ads} + e_M^- \xrightarrow{\text{rds}} C_3H_5{}^{\bullet}{}_{ads} + H_2O(aq)$$

$$C_3H_5{}^{\bullet}{}_{ads} + e_M^- \rightarrow C_3H_5{}^-{}_{ads}$$

$$C_3H_5{}^-{}_{ads} + H_2O(aq) \rightarrow C_3H_6(g) + OH^-(aq)$$

$$H^+ + OH^- \rightarrow H_2O(aq)$$

Experimental Section

Electrochemical Measurement. The electrochemical measurement of the electroreduction of AA was performed using cyclic voltammetric (CV) plots or the electrolysis at a controlled potential, −0.40 V. The electrolytic cell is an H-cell whose cathode and anode were separated by a sintered glass disk, where a special platinized platinum wire (apparent area ca. 0.02 cm^2 in CV plot or 2 cm^2 under the electrolysis of a controlled potential), a platinum film with a large area, and a SCE served as the working, counter, and reference electrode, respectivly. Cleaning and activation treatments of the working electrode at −0.60 V were carried out successively prior to recording data. Of all the electrochemical measurement the background currents without AA were subtracted.

The cathodic and anodic transfer coefficients α_c and α_a of the electroreduction of AA were found separately from the correlations[20] between peak potentials and the square roots of sweep rates and/or peak potentials and the logarithms of peak currents obtained in Figure 1. The reaction orders Z_{AA} of AA and $Z_H{}^+$ of the ion H^+ in the electroreduction reaction of AA were found separately from the correlations between the logarithms of cathodic peak currents of AA and the logarithms of the concentrations of AA and H^+ in the studied solutions, where the cathodic peak currents were measured from the CV plots (plots omitted) at the sweep rate 4.0×10^{-2} V s^{-1} in the studied solutions separately containing $0-6 \times 10^{-3}$ mol L^{-1} AA and 5.0×10^{-3} mol L^{-1} perchloric acid and containing 5.0×10^{-3} mol L^{-1} AA and 2×10^{-4} to2×10^{-2} mol L^{-1} perchloric acid. To find the apparent activation energy ΔE_a of the electroreduction of AA, the electrolysis of AA in the studied solution containing 1.0×10^{-2} mol L^{-1} AA, 0.1 mol L^{-1} sodium perchlorate, and 5.0×10^{-3} mol L^{-1} perchloric acid was carried out at −0.40 V and the reduction currents at 15−60 °C were determined; then ΔE_a was calculated according to the Arrhenius formula.

Spectrum Determination. IR Spectra. A drop of various AA test solutions containing sodium azide, either unelectrolyzed or electrolyzed, was dropped onto a compressed KBr disk, and IR spectra were recorded to detect the allyl cation $C_3H_5{}^+$ in the test solutions (Figure 2).

ESR Spectrum. The AA test solution in the presence of DMPO was electrolyzed under −0.40 V (ex-situ method). After 10 min, the electrolyzed test solution was sucked into a quartz sampling tube, and immediately the tube was inserted into a microwave cavity and the ESR spectrum was recorded (Figure 3) to detect the allyl radical $C_3H_5{}^\bullet$ formed during the electroreduction of AA.

MS Spectra. First, two kinds of AA test solutions, agitated separately with nitrogen and carbon dioxide, were electrolyzed at −0.40 V until only the background currents appeared. Second, the electrolyzed test solutions were drawn from the electrolytic cell and extracted with ethyl ether to eliminate the perchloric acid contained, and finally, the extracted solutions served as an MS analysis to detect the allyl anion $C_3H_5{}^-$ formed during the electroreduction of AA by comparing the two MS spectral lines (Figure 4). To increase the sensitivity of detecting $C_3H_5{}^-$, a direct sampling was adopted. The vaporization of the sample solutions was performed by the programmed temperature rise from 20 to 100 °C at the rate of 80° min^{-1}. The spectra were recorded at the vaporization temperature ca. 60 °C (ca. 0.5 min).

For the purpose of improving the detectable sensitivities for the reaction intermediates $C_3H_5{}^+$, $C_3H_5{}^\bullet$, and $C_3H_5{}^-$ entering into the bulk solutions from the Helmholtz layer and/or the electrode surface, some measures were applied, e.g., the electrolysis at −0.40 V was performed, which is slightly more negative than the potential of the electroreduction of AA −0.35 V, a given volume of the solvent ethyl alcohol was added to the test solution, and the ratio of the apparent area of the working electrode to the volume of the catholyte was enlarged.

Quantum-Chemical Calculation. The charge distribution and frontier orbital energies of the reaction species C_3H_5OH and $C_3H_5{}^+$ were calculated by means of a semiempirical MO method (MOPAC7/AM1, PM3).

Reagents. AA was purified by distillation, the reagents $NaClO_4$, NaN_3 and C_2H_5OH, purchased in China, were of analytical quality, the solvent C_2H_5OH used in ESR spectrum was pretreated by electrolysis, and DMPO was an Aldrich product.

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Supporting Information Available: The CV plots of the electroreduction of AA for different concentrations, that for different pH values and that at the mercury electrode and in nearly neutral aqueous solution, and the charge and spin densities of $C_3H_5OH^{\bullet -}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] *Electrochemical Methods, Fundamentals and Applications*; Bard, A. J., Faulkner, L. R., Eds.; John Wiley & Son. Inc.: New York, 1980; Chapter 6.