26 Apr 1974

Oxidation Reactions of Unsaturated Hydrocarbons for Fuel Cells

James W. Johnson
Missouri University of Science and Technology

William Joseph James
Missouri University of Science and Technology, wjames@mst.edu

OXIDATION REACTIONS OF UNSATURATED HYDROCARBONS FOR FUEL CELLS

J. W. Johnson   W. J. James   A. K. Agrawal
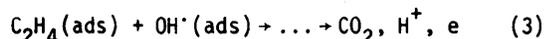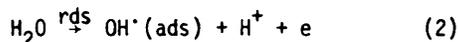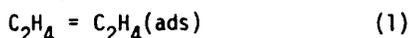
University of Missouri - Rolla   Ohio State University
Rolla, Missouri   65401   Columbus, Ohio 43210

The anodic oxidation of unsaturated hydrocarbons has been the subject of numerous studies, primarily on Pt and Au electrodes at low temperatures, < 100°C. The complete oxidation to CO_2 is usually the predominant reaction with both H_2O and OH^- having been proposed as the oxygen source. Usually a single study consists of a comprehensive investigation of a single compound on a single electrode or a somewhat limited study of several compounds on a single electrode. A diversity of proposed mechanisms has resulted and is illustrated by the following summary.

Alkenes on Pt: Bockris, et al.[1], studied the anodic oxidation of several double-bond hydrocarbons on Pt at 80°C. Included were ethylene, propylene, allene, 1-butene, 2-butene, 1,3-butadiene, and benzene. The predominant product was CO_2 with coulombic efficiencies for its production ranging from 60-90% for butadiene and benzene to 100% for ethylene. The kinetic parameters, quite similar for all the compounds, were: Tafel slope = 2(2.3 RT/F), $\partial \log i/\partial pH$ = 0.39 to 0.45, $\partial \log i/\partial \log P_R$ = -0.11 to -0.20, and E_a^* = 19.7 to 23.0 kcal. It was concluded that all the compounds were oxidized by the same mechanism (shown here for ethylene):

$$C_2H_4 = C_2H_4(ads) \qquad (1)$$

$$H_2O \overset{rds}{\rightarrow} OH \cdot (ads) + H^+ + e \qquad (2)$$

$$C_2H_4(ads) + OH \cdot (ads) \rightarrow \ldots \rightarrow CO_2, H^+, e \qquad (3)$$

The rate equation can be expressed as

$$i = k_2 a_w (1-\theta_T) \exp(\alpha F v/RT) \qquad (4)$$

where v is the potential on the rational scale (vs. the potential of zero charge). Assuming Langmuir-type adsorption, a high surface coverage of the hydrocarbon, and a reported p.z.c.-pH relationship[2], eq. 4 becomes
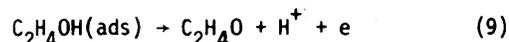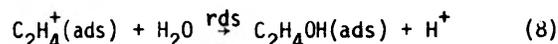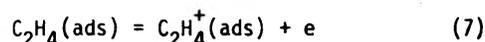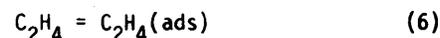
$$i = k' P_R^{-1/n} a_{H^+}^{-0.5} \exp(F V/2RT) \qquad (5)$$

The kinetic parameters of eq. 5 agree quite well with the experimental values.
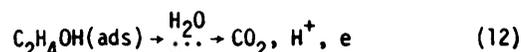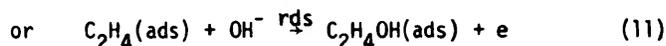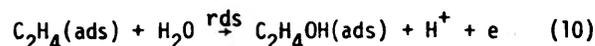
Ethylene on Au: Several studies have been made on the anodic oxidation of ethylene on Au. In studies by Dahms and Bockris[3] and Kuhn, Wroblowa, and Bockris[4],
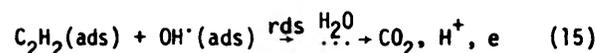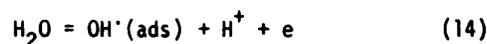
---

the catalytic activities of several noble metals and alloys for ethylene oxidation were investigated. The extent of the studies on Au were thus somewhat limited. Johnson, Lai, and James[5] made a separate study of this reaction on Au at 80°C. In acid solutions, their finding supported those of Dahms and Bockris and their proposal of a carbonium-ion mechanism.

$$C_2H_4 = C_2H_4(ads) \qquad (6)$$

$$C_2H_4(ads) = C_2H_4^+(ads) + e \qquad (7)$$

$$C_2H_4^+(ads) + H_2O \overset{rds}{\rightarrow} C_2H_4OH(ads) + H^+ \qquad (8)$$

$$C_2H_4OH(ads) \rightarrow C_2H_4O + H^+ + e \qquad (9)$$

In weakly acidic and basic solutions, a change in the Tafel slope was noted. It was suggested that this resulted from a change in the reaction mechanism. That suggested was similar to the proposal of Kuhn, Wroblowa, and Bockris.

$$C_2H_4 = C_2H_4(ads) \qquad (6)$$

$$C_2H_4(ads) + H_2O \overset{rds}{\rightarrow} C_2H_4OH(ads) + H^+ + e \qquad (10)$$

$$\text{or} \quad C_2H_4(ads) + OH^- \overset{rds}{\rightarrow} C_2H_4OH(ads) + e \qquad (11)$$

$$C_2H_4OH(ads) \rightarrow \overset{H_2O}{\ldots} \rightarrow CO_2, H^+, e \qquad (12)$$

Acetylene on Pt: The anodic oxidation of acetylene on Pt was studied by Johnson, Wroblowa, and Bockris[6] at 80°C. They found the oxidation to CO_2 to be complete. The kinetic parameters were: Tafel slope = 2.3 RT/F, $\partial \log i/\partial pH$ = 0.8, $\partial i/\partial P_A$ < 0, and E_a = 21.5 to 26 kcal. The suggested reaction mechanism was

$$C_2H_2 = C_2H_2(ads) \qquad (13)$$

$$H_2O = OH \cdot (ads) + H^+ + e \qquad (14)$$

$$C_2H_2(ads) + OH \cdot (ads) \overset{rds}{\rightarrow} \overset{H_2O}{\ldots} \rightarrow CO_2, H^+, e \qquad (15)$$

Acetylene on Au: Johnson, Reed, and James[7] studied the anodic oxidation of acetylene on Au at 80°C. CO_2 production efficiencies varied from 60-80%. A discontinuity found in the Tafel region of the polarization curves in weak acids and bases was interpreted in terms of a change in the reaction mechanism with increasing potential at a given pH. The discontinuity appeared at low c.d.'s in bases and was shifted to higher c.d.'s with decreasing pH. It had disappeared completely in 1N H_2SO_4, apparently shifted outside the Tafel region. The kinetic parameters were: (a) strong acids - Tafel slope = 2(2.3 RT/F), $\partial \log i/\partial pH$ = 0, $\partial i/\partial P_A > 0$, E_a = 19.5 kcal; (b) bases and weak acids (btr)* - Tafel slope =

2(2.3 RT/F), $\partial \log i/\partial pH = 1$, $\partial i/\partial P_A < 0$, $E_a = 19.5$ kcal; and (c) bases and weak acids (atr)* - Tafel slope = 2(2.3 RT/F), $\partial \log i/\partial pH = 1$, $\partial i/\partial P_A > 0$, $E_a = 13$ kcal. The proposed reaction sequences were:

Below the transition region

$$C_2H_2 = C_2H_2(ads) \qquad (16)$$

$$H_2O \xrightarrow{rds} OH \cdot (ads) + H^+ + e \qquad (17)$$

and

$$OH^- \xrightarrow{rds} OH(ads) + e \qquad (18)$$

$$C_2H_2(ads) + OH \cdot (ads) \xrightarrow{H_2O} \ldots \rightarrow CO_2, H^+, e \qquad (19)$$

Above the transition region

$$C_2H_2 = C_2H_2(ads) \qquad (20)$$

$$C_2H_2(ads) + H_2O \xrightarrow{rds} C_2H_2OH(ads) + H^+ + e \qquad (21)$$

and

$$C_2H_2(ads) + OH^- \xrightarrow{rds} C_2H_2OH(ads) + e \qquad (22)$$

$$C_2H_2OH(ads) \xrightarrow{H_2O} \ldots \rightarrow CO_2, H^+, e \qquad (23)$$
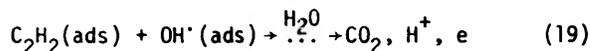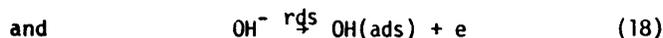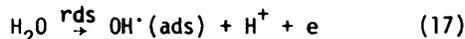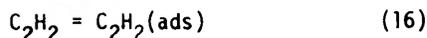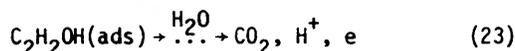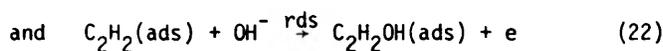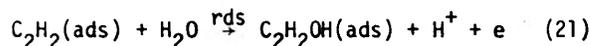
The pH effect was explained by the participation of H_2O in the reaction in acid solutions where the OH^- concentration was not sufficient to sustain the observed currents.

1-Pentyne on Pt and Au: The anodic oxidation of 1-pentyne on Pt and Au electrodes at 70°C was studied by Danielson.[8] On Pt, the kinetic parameters were: Tafel slope = 2.3RT/F; $\partial \log i/\partial pH < 1$ (acid electrolytes), = 1 (basic electrolytes); $\partial i/\partial P_P < 0$, and $E_a = 18$-22 kcal. Polymer formation was evidenced by solution darkening and the presence of small floating particles in acid electrolytes. No evidence of polymerization was visible in basic electrolytes. Coulombic efficiencies for CO_2 production were ~ 70%, independent of pH. No significant changes were noted for decreased partial pressures of 1-pentyne. Small amounts of by-products, formaldehyde in acid electrolytes and ethanol in basic, were detected by gas chromatographic analyses.

On Au, studies could not be made in electrolytes with pH < 10.9 due to the formation of an adherent polymer film on the electrode. The film 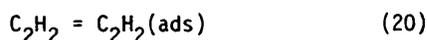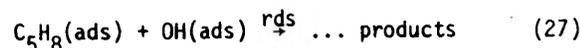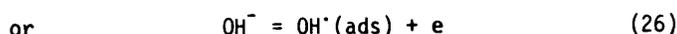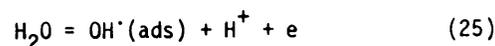was invisible, but its presence was indicated by apparent passivation and an acquired non-wetting characteristic of the electrode after a short period of polarization. There was no visible evidence of polymerization in the electrolyte. In electrolytes with pH > 11.7, the kinetic parameters were: Tafel slope = 2.3 RT/F, $\partial \log i/\partial pH = 2$, $\partial i/\partial P_P < 0$, and $E_a = 22$ kcal. Coulombic efficiencies for CO_2 production were ~ 50%. Ethanol and 1-propanol were identified as by-products.
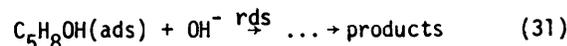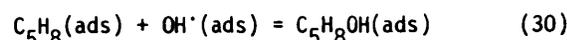
It was possible to correlate the data for 1-pentyne oxidation on Pt and Au with similar reaction sequences. For Pt, the sequence was the same as that proposed previously for acetylene, i.e.,

$$C_5H_8 = C_5H_8(ads) \qquad (24)$$

$$H_2O = OH \cdot (ads) + H^+ + e \qquad (25)$$

or

$$OH^- = OH \cdot (ads) + e \qquad (26)$$

$$C_5H_8(ads) + OH(ads) \xrightarrow{rds} \ldots \text{products} \qquad (27)$$

For Au, an additional step was necessary to account for the pH effect of 2,

$$C_5H_8 = C_5H_8(ads) \qquad (28)$$

$$OH^- = OH \cdot (ads) + e \qquad (29)$$

$$C_5H_8(ads) + OH \cdot (ads) = C_5H_8OH(ads) \qquad (30)$$

$$C_5H_8OH(ads) + OH^- \xrightarrow{rds} \ldots \rightarrow \text{products} \qquad (31)$$

In this latter sequence, the step represented by eq. 29 could also be the equilibrium discharge of water.

1,3-Butadiene on Pt and Au: The anodic oxidation of butadiene on Pt and Au was studied by Agrawal[9] at 70°C. Special precautions were necessary to prevent the butadiene from polymerizing prior to anodic oxidation. The oxidation reaction proceeded without any visible signs of polymerization on Pt in acidic and basic electrolytes and on Au in basic electrolytes. However on Au in acid electrolytes, a polymer formed on the electrode surface that precluded steady-state studies. The coulombic efficiencies for CO_2 production were 85 ± 5% with Pt in acid electrolyte, 92 ± 5% with Pt in basic electrolyte, and 70 ± 10% with Au in basic electrolyte. A trace of a moderately volatile by-product from the oxidation on Pt in acid electrolyte was detected by flame-ionization gas chromatographic analysis. It could not be identified as any of the common oxygen-containing C_1 thru C_4 species.

The majority of the polarization curves for butadiene contains two distinct linear sections with Tafel slopes of ca. 140 and 70 mv in the lower and higher potential regions, respectively. The transition from one section to the other occurred at c.d.'s of about 10^{-4} amp/cm^2 on Pt and 10^{-6} amp/cm^2 on Au. (These are roughly equivalent taking into account a roughness factor of ~ 10^2 for platinized Pt.) The pH effect on current was varied. With Pt at low pH's (0.35 and 1.3), there was almost no effect. At higher pH's, below the transition region, $\partial \log i/\partial pH = 0.5$; above the transition region, $\partial \log i/\partial pH = 1$. With Au in basic electrolytes, $\partial \log i/\partial pH = 1$. Over the pressure range 1 to 10^{-2} atm, the pressure effect ($\partial i/\partial P_B$) with Pt was negative. On Au, it was negative at the higher pressures but became positive as the pressure was reduced below 0.3 atm. Apparent activation energies were about 21-24 kcal, decreasing with increasing potential. No distinct difference was noted between Pt and Au.

A comparison of reaction mechanisms shown above for the oxidation of unsaturated hydrocarbons on Pt and Au shows that none of them completely explain the kinetic parameters observed for butadiene. The primary discrepancies are associated with a seemingly anomalous effect of pH on c.d. and potential. Piersma, et al.[1] resolved this difficulty for ethylene by basing the potential driving force on the rational scale (vs. pzc) rather than the normal hydrogen scale (vs. SHE). The logic of doing this has been recognized and propounded by various investigators, but the characteristics of many reactions and the scope of

the associated studies have not made it necessary. This possibly may have led to the lengthy assortment of mechanisms that have been used to explain individual cases. The desirability and necessity of using potential driving forces based on a null-value applicable to the electrode under consideration become apparent when one sees that compositional changes in the electrolyte (eg. pH) may affect the pzc and reaction rate in an unequal manner.

Potential of Zero Charge: In the studies reported here, the primary variable affecting the pzc is the pH of the electrolyte. Thus, the pH effects, $\partial \log i/\partial pH$ and $\partial V/\partial pH$, will be affected by shifts of the pzc with pH if one considers the potential driving force for reaction to be

$$\nu = V - V_{pzc} \qquad (32)$$

To correlate the experimental results, it is therefore necessary to know the variation of the pzc with pH on both Pt and Au.

On Au, the effect of pH on the pzc has been reported by Andersen, et al.,[10] in the presence of various inorganic anions. In solutions containing non- or slightly adsorbing anions, the relation can be expressed as

$$V_{pzc} = V^{\circ}_{pzc} - \zeta\, pH \qquad (33)$$

where

$$\zeta = 0 \text{ (acidic solutions)} \qquad (34)$$

$$= 2.3\ RT/F \text{ (basic solutions)} \qquad (35)$$

$$V^{\circ}_{pzc} = 0.14\ V$$

On Pt, the effect of pH (2.5-11.2) on the pzc for ClO_4^- solutions has been reported by Bockris, et al.[11] The relationship is the same as shown in eq. 33 with

$$\zeta = 2.3\ RT/F \qquad (36)$$

$$V^{\circ}_{pzc} = 0.56\ V \qquad (37)$$

In solutions of lower pH, the pretreatment of the Pt electrode is apparently an important consideration if there is opportunity for hydrogen to be dissolved in the metal. As the electrodes used in this study were activated prior to use, the results reported by Frumkin, et al.[11] will be used for solutions with pH < 2.5, i.e.,
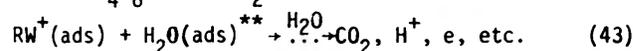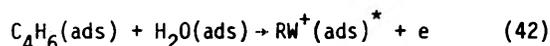
$$\zeta = 0 \text{ to } 0.018 \qquad (38)$$

$$V^{\circ}_{pzc} = ca.\ 0.2\ V \qquad (39)$$

Using these relationships (eqs. 32-39), the kinetic parameters based on the rational potential scale (vs. pzc) for butadiene oxidation were calculated and are shown in Table I. The corresponding values based on the normal hydrogen scale (vs. SHE) are shown for comparison.*

---

*Note that Tafel slopes ($\partial V/\partial \log i$) and pressure effects ($\partial i/\partial P_B$) are not altered by changing from the normal hydrogen to the rational scale.

Butadiene Mechanism: As mentioned above, none of the various mechanisms proposed previously for the anodic oxidation of unsaturated hydrocarbons were consistent with the kinetic parameters observed for butadiene on both Pt and Au. Similar difficulties were encountered in finding another sequence applicable for both Au and Pt anodes when the rate expression employed potential driving forces based on the normal hydrogen scale. It was possible to resolve these however with the reaction scheme shown below (eqs. 40-43) in conjunction with potential driving forces based on the pzc. This scheme is similar to that used by Piersma, et al.,[1] except that it incorporates water adsorption as a separate step. The sequence is

$$H_2O = H_2O(ads) \qquad (40)$$

$$C_4H_6 = C_4H_6(ads) \qquad (41)$$

$$C_4H_6(ads) + H_2O(ads) \rightarrow RW^+(ads)^* + e \qquad (42)$$

$$RW^+(ads) + H_2O(ads)^{**} \rightarrow \ldots \xrightarrow{H_2O} CO_2,\ H^+,\ e,\ etc. \qquad (43)$$

The inclusion of the adsorption of butadiene (in some manner) in the reaction sequence (eq. 41) is apparent from both this and other work. The adsorption of water (eq. 40) and its competition with the organic molecules for active surface sites have been discussed by Bockris.[12] The formulation of the remainder of the mechanism (eqs. 42, 43) results from correlating the butadiene data. It will be seen later that this mechanism is also applicable to the anodic oxidation of several other hydrocarbons.

The correlation of the data necessitates some assumptions regarding the mode of adsorption of the reactants butadiene and water on the anode. The initial assumption, which was found to be satisfactory, was the simplest model, Langmuir-type adsorption. This assumption is generally valid only as a limiting condition for either high or low coverages but has been successfully used for the adsorption of several hydrocarbons. Cairns et al.[17], for example, found that propane adsorption on Pt obeyed the Langmuir adsorption rate expression for coverages 0-0.95. This apparently occurred while three different reaction intermediates (ranging from dehydrogenated to partially oxidized propane fragments) were also (proposed as being) present on the electrode surface.

An examination of Table I (both parts a and b) shows that the reaction sequence must yield Tafel slopes of 2(2.3RT/F) and 2.3 RT/F. With Langmuir-type adsorption, these slopes (2.3 RT/αF and 2.3 RT/F) are normally associated with rate determining steps that are the first electron transfer and a chemical reaction following the first electron transfer, respectively. With the usual assumption that $\alpha = 0.5$, these types of reactions are thus fixed as the rds's for the anodic oxidation of

---

*RW^+ represents a combined butadiene-water specie that has lost an electron.

**This reacting specie could also be $H_2O(sol)$. The data from this study do not allow such a distinction to be made in this step.

butadiene. If the reaction sequence is to be consistent with the pH effect (Table I b)*, then water discharge (eq. 2) cannot be the first electron transfer step. This would lead to first order H^+ concentration dependencies when the Tafel slope is lowered to 2.3 RT/F, as would also the removal of a hydrogen atom from the butadiene. These considerations lead one to such a sequence as shown in eqs. 40-43. The negative butadiene pressure effect, indicating a high coverage of butadiene and/or the involvement of another unrelated species prior to or during the rds, suggests that $H_2O(ads)$ be included in eq. 42.

The kinetic parameters for Pt anodes (btr) in solutions pH = 0.35-12.5 are $\partial \nu / \partial \log i = 2(2.3\ RT/F)$, $\partial \nu / \partial pH = 0$, $\partial \log i / \partial pH = 0$, and $\partial i / \partial P_B < 0$. These would be consistent with the reaction sequence shown by eqs. 40-42 with eq. 42 as the rds. Considering reactions shown in eqs. 40 and 41 to be in quasi-equilibrium gives:

$$\theta_W = K_W a_W (1-\theta_T) \tag{44}$$

$$\theta_B = K_B P_B (1-\theta_T)^n \tag{45}$$

Substituting these in an expression for the current density from eq. 42 gives:

$$i = nFk_{42}\ \theta_B\ \theta_W\ \exp(\alpha F\nu/RT) \tag{46}$$

$$= nFk' a_W P_B (1-\theta_T)^{n+1} \exp(\alpha F\nu/RT) \tag{47}$$

In correlating the butadiene partial pressure data, the parameters for eq. 18 which gave the best fit were n = 4, $K_B = 10^7$ atm^{-1} in 1 N H_2SO_4 and n = 8, $K_B = 10^5$ in 1 N KOH.

For Pt anodes (atr) in solution pH = 0.35 to 12.5, the parameters are $\partial \nu / \partial \log i = 2.3\ RT/F$, $\partial \nu / \partial pH = 0$, $\partial \log i / \partial pH = 0$, and $\partial i / \partial P_B < 0$. These fit the sequence of eqs. 40-43 with eq. 43, a chemical combination step, as the rds. This can be visualized as occurring when the increased potential has increased the rate of eq. 42 sufficiently so that the rds is shifted to another step in the sequence. Considering eq. 42 now to also be in quasi-equilibrium gives:

$$\theta_{RW^+} = K_{42} \theta_B \theta_W \exp(F\nu/RT) \tag{48}$$

The current density expression from eq. 43 is now

$$i = nFk_{43}\ \theta_{RW^+}\ a_W$$

$$= nFk' a_W^2\ P_B (1-\theta_T)^{n+1} \exp(F\nu/RT) \tag{49}$$

The same values of n and K_B as mentioned above correlated the partial pressure data. The variation of n for acidic and basic solutions found here was also found earlier in studies with C_2H_2 and C_2H_4.[1,6]

For Au anodes in solutions pH 9.9 - 12.5, the parameters are $\partial \nu / \partial \log i = 2.3\ RT/F$, $\partial \nu / \partial pH = 0$, $\partial \log i / \partial pH = 0$, and $\partial i / \partial P_B$ changes from negative to positive values as P_B is decreased from 1 to 0.01 atm. The same reaction sequence (eqs. 40-43) as used

---

*The difficulty in obtaining a sequence consistent with the pH effect based on the NHS was alluded to earlier.

for Pt (atr) can also be used here. Values of n = 4 and $K_B = 50$ were found to correlate the partial pressure observations on Au. This lower value of K_B is consistent with the lesser ability of Au to adsorb hydrocarbons as compared to Pt.[5,7]

Applicability of the Postulated Butadiene Mechanism to Other Hydrocarbons

1. Acetylene on Pt: The proposed mechanism (eqs. 13-15) gives the current density expression

$$i = k'\ \theta_A (1-\theta_T)\ a_{H^+}^{-1} \exp(FV/RT) \tag{50}$$

With Langmuir-type adsorption, n = 4 and $K_A = 10^4 - 10^6$, and assuming $\theta_T \sim \theta_A$, favorable agreement was found with the experimental partial pressures. These results are the same as for butadiene oxidation on Pt(atr) and thus fit the reaction sequence of eqs. 40-43 with eq. 43 as the rds when the rational potential scale is used.

2. Acetylene on Au: The mechanism proposed for the more acidic electrolytes and btr gives

$$i = nF(k_{17}\ a_W + k_{18}a_{OH^-})(1-\theta_T)\exp(\alpha FV/RT) \tag{51}$$

The proposed mechanism above the transition gives

$$i = nF(k_{21}\ a_W + k_{22}a_{OH^-})\theta_A \exp(\alpha FV/RT) \tag{52}$$

These equations correlated the experimental data with the assumption of Langmuir-type adsorption, $\theta_T \sim \theta_A$, and n = 4, $K_A = 10^4$ in acid solutions and n = 8, $K_A = 2.5$ in base.

For the electrolytes of low pH, the kinetic parameters are the same as for butadiene oxidation on Pt (btr). In these solutions, the effect of pH on the pzc is approximately the same ($\zeta \approx 0$) for both Pt and Au. Thus, a reaction sequence as shown in eqs. 40-42 with eq. 42 as the rds can be used to correlate the data and gives the c.d. expression (on the rational scale) shown in eq. 47. Also note that if eq. 51 is transformed to the rational scale using eqs. 32-34 (and remembering that a_{OH^-} is very small in acid solutions), an equation similar in form to eq. 47 results.

In the remainder of the electrolytes, the effects of potential and pH on the current were similar, both above and below the transition region. If one uses the butadiene mechanism for these cases (including Langmuir-type adsorption), the Tafel slopes again determine the sequence in eqs. 40-42 with eq. 42 as the rds. For this sequence, though, on Au and in basic solutions, the pH effect $\partial \log i / \partial pH = 0.5$ (on the NHS) is predicted rather than unity as reported. An examination of the data from Reed's study shows that the experimental effects were 0.75(btr) and 0.85(atr) and were interpreted as being unity. These values might also as reasonably be interpreted as 0.5, which would give agreement between Reed's results and the butadiene mechanism.

3. Alkenes on Pt: The proposed mechanism gives the expression:

$$i = k_2 (1-\theta_T)\ a_W \exp(\alpha F\nu/RT) \tag{53}$$

(As mentioned previously, potentials based on the rational scale were used in the c.d. equation to explain the observed pH effect.) For Langmuir adsorption conditions and $\theta_R > 0.9$, $(1-\theta_T)$ is proportional to P_R, thus allowing the pressure effect to be correlated. The parameters reported for the alkenes are the same as found in this study for butadiene on Pt(btr) (see Table I) and therefore are also consistent with the reaction sequence shown by eqs. 40-42 with eq. 42 as the rds.

It might be noted at this point that if one looked only at the data for the oxidation of butadiene on Pt from this study, the water discharge mechanism (eqs. 1-3) gives a sufficient correlation. The sequence shown by eqs. 40-43 results when one attempts to expand the correlation to the data for Au using a common sequence.

4. **Ethylene on Au:** The proposed mechanisms give the rate equations:

In acid solutions

$$i = nFk_8 K_7 a_w \theta_E \exp(FV/RT) \qquad (54)$$

In basic solutions

$$i = nF(k_{10} a_w + k_{11} a_{OH^-}) \theta_E \exp(\alpha FV/RT) \quad (55)$$

The ethylene partial pressure effects were correlated using the Langmuir isotherm with $K_E = 1$ and $n = 4$ and 8 for acidic and basic media, respectively.

Again, the butadiene mechanism, eqs. 40-43 with eq. 43 the rds, will fit the case for the acidic electrolytes. Note that here the shift of the pzc on Au is zero (eq. 34). A low adsorption equilibrium constant (K_B in eq. 45) such as reported above gives the observed positive pressure effect.

In the basic electrolytes, the reaction sequence eq. 40-42 with eq. 42 as the rds gives the correct parameters with the possible exception of the pH effect. As with acetylene on Au, $\partial \log i/\partial pH = 0.5$ is predicted while a value of ca. unity was reported. Again a re-examination of the data[5] shows that an empirical value of 0.75 was interpreted as unity. If one should opt to interpret the observed value as 0.5, then all the parameters in basic electrolytes would also agree.

5. **1-Pentyne on Pt and Au:** The proposed mechanisms give the following rate equations:
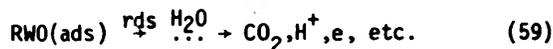
For Pt

$$i = nFk_{27}(K_{25}a_w/a_{H^+} + K_{26}a_{OH^-})(1-\theta_T)\theta_p\exp(FV/RT) \ (56)$$

For Au

$$i = nFk_{31} K_{30}K_{29} a_{OH^-}^2 (1-\theta_T)\theta_p \exp(FV/RT) \qquad (57)$$

The reaction on Pt is the same as for butadiene oxidation on Pt(atr) and thus fit the reaction sequence of eqs. 40-43 with eq. 43 as the rds. The same sequence for Au would also be applicable with the additional chemical equilibria preceding the rds.

$$RW^+(ads) + H_2O(ads) = RWOH(ads) + H^+ \qquad (58)$$

$$RWO(ads) \xrightarrow{rds} \overset{H_2O}{\ldots} \to CO_2, H^+, e, \text{ etc.} \qquad (59)$$

The ability of the butadiene mechanism to correlate data for other unsaturated hydrocarbons on both Pt and Au as illustrated above lends added credibility to its validity. It also gives further evidence that potentials referred to the null value of the electrode under consideration are the appropriate ones to use in formulating kinetic expressions.

REFERENCES

(1) H. Wroblowa, B. J. Piersma, and J. O'M. Bockris, J. Electroanal. Chem., 6, 401 (1963): J. O'M. Bockris, H. Wroblowa, E. Gileadi and B. J. Piersma, Trans. Faraday Soc., 61, 2531 (1965). B. J. Piersma, Ph.D. Thesis, University of Pennsylvania (1965).

(2) E. Gileadi, S. D. Argade and J. O'M. Bockris, J. Phys. Chem., 71, 2044 (1966).

(3) H. Dahms and J. O'M. Bockris, J. Electrochem. Soc., 111, 6 (1964).

(4) A. T. Kuhn, H. Wroblowa, and J. O'M. Bockris, Trans. Faraday Soc., 63, 1458 (1967).

(5) J. W. Johnson, S. C. Lai and W. J. James, Electrochim Acta, 15, 1511 (1970).

(6) J. W. Johnson, H. Wroblowa and J. O'M. Bockris, J. Electrochem. Soc., 111, 863 (1964).

(7) J. W. Johnson, J. L. Reed and W. J. James, J. Electrochem. Soc., 114, 573 (1967).

(8) M. J. Danielson, Ph.D. Thesis, Univ. of Missouri-Rolla, 1970.

(9) A. K. Agrawal, Ph.D. Thesis, Univ. of Missouri-Rolla, 1970.

(10) D. D. Bode, Jr., T. N. Andersen and H. Eyring, J. Phys. Chem., 71, 2044 (1967).

(11) O. A. Petrii, A. N. Frumkin and Yu G. Kotlov, Elektrokhimiya URSS, 5, 476 (1969). R.Kh. Burshtein, A. G. Pshenickhnikov and L. A. Schevchenko, Elektrokhimiya URSS, 5, 332 (1969).

(12) J. O'M. Bockris and D. A. J. Swinkels, J. Electrochem. Soc., 111, 736 (1964); J. O'M. Bockris, M. Green and D. A. J. Swinkels, J. Electrochem. Soc., 111, 743 (1964); E. Gileadi, B. T. Rubin and J. O'M. Bockris, J. Phys. Chem., 69, 3335 (1965).

(13) E. J. Cairns, A. M. Breitenstein, and A. J. Scarpellino, J. Electrochem. Soc., 115, 569 (1968).

TABLE I

Summary of Kinetic Parameters for the Anodic Oxidation of Butadiene at 70°C with Potentials based on (a) the Normal Hydrogen Scale and (b) the Rational Scale

Electrode	Electrolyte	(a) Normal Hydrogen Scale (vs. SHE)			
		$\partial V/\partial \log i$	$\partial V/\partial pH$	$\partial \log i/\partial pH$	$\partial i/\partial P_B$
Pt (btr)	strong acids	2(2.3RT/F)	0	0	<0
Pt (atr)	strong acids	2.3RT/F	0	0	<0
Pt (btr)	bases and weak acids	2(2.3RT/F)	-2.3RT/F	0.5	<0
Pt (atr)	bases and weak acids	2.3RT/F	-2.3RT/F	1	<0
Au	bases	2.3RT/F	-2.3RT/F	1	<0 [*] >0 [**]

Electrode	Electrolyte	(b) Rational Scale (vs. pzc)			
		$\partial v/\partial \log i$	$\partial v/\partial pH$	$\partial \log i/\partial pH$	$\partial i/\partial P_B$
Pt (btr)	strong acids	2(2.3 RT/F)	0	0	<0
Pt (atr)	strong acids	2.3RT/F	0	0	<0
Pt (btr)	bases and weak acids	2(2.3RT/F)	0	0	<0
Pt (atr)	bases and weak acid	2.3RT/F	0	0	<0
Au	bases	2.3RT/F	0	0	<0 [*] >0 [**]

[*]P_B = 0.1 to 1 atm

[**]P_B = 0.01 to 0.1 atm