Exercise 3:

The reaction investigated by A. Peloso is

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{CHO} \rightarrow \text{Et}+\text{Ad}
\]  

(1)

The proposed mechanism is:

\[
r = \frac{k_1 [E^*] - (k_2 A^* D^*) / K_{DH}}{[E^*] + K_{DH} P_{DH} + K_{DH} P_{DH}^2} \]

(2)

To formulate a mechanism the following clues can be gained from inspection of the proposed expression:

1) \(P_{DH}\) is raised to the 1st power, so the adsorption and desorption of DH is equilibrated (it is not dissociative adsorption).
2) The denominator is raised to the 2nd power, so surface sites are involved in the RDS.

The following mechanism is proposed:

1) \(E^* \rightarrow E\)
2) \(E^* \rightarrow A^* + D^*\)
3) \(A^* \rightarrow A + \)

\(DH^* \rightarrow DH + \)

The following analysis is used to derive the expression in equation (2).

\[
K_{E} = \frac{[E^*]}{[E][^*]} \quad K_{A} = \frac{[A^*]}{[A][^*]} \quad K_{DH} = \frac{[DH^*]}{[DH][^*]}
\]

(3)

From the RDS,

\[
r = \frac{k_1 [E^*][^*] - k_2 A^* [DH^*]}{[^*]^2}
\]

(4)

The site balance is

\[
[^*] = [^*] + [E^*] + [A^*] + [DH^*]
\]

(5)

After substituting equation (3) into equation (5),

\[
E^* + \rightarrow D^* + A^*
\]

5.4
\[ [\ast] = 1 + K_{\ast 1}[Et] + K_{\ast 2}[Ad] + K_{\ast 3}[DH] \]  

After substituting equation (6) into equation (4), with the assistance of equation (3), the proposed rate expression can be derived. Note that the constants are all lumped into \( k \) and \( K_{\ast} \). In addition, the assumption that \( K_{\ast 3}[DH] \ll 1 \) is needed in order to arrive at the proposed rate expression.
Exercise 5:

The overall reaction is

\[ IP + DO = At + W \quad (1) \]

The proposed rate expression is of the form,

\[ r = \frac{K[IP][DO]^\frac{1}{2}}{(1 + K_1[IP] + K_2[W])(1 + K_3[DO]^\frac{1}{2})} \quad (2) \]

We shall assume that At cannot adsorb on the surface of the catalyst and that the rate of surface reaction between adsorbed IP and adsorbed oxygen is the rate determining step. Since there are two terms in the denominator, there must be two types of surface sites. Therefore, the RDS is proposed to be the following step:

\[ IP^{*1} + O^{*2} \xrightarrow{\text{RDS}} At + W^{*1} + O_2 \quad (3) \]

where \( *_1 \) and \( *_2 \) represent two different types of active sites. Since DO is raised to the \( \frac{1}{2} \) power, DO adsorption/desorption is dissociative.
\[ DO + 2 \cdot 2 \rightarrow 2O_{2} \]

Therefore a reaction mechanism that is consistent with the rate expression is the following:

\[ IP + \cdot \rightarrow IP \cdot \]

\[ DO + 2 \cdot \rightarrow 2O_{2} \quad (4) \]

\[ IP \cdot + O_{2} \rightarrow Al + W \cdot + \cdot \]

\[ W \cdot \rightarrow W + \cdot \]

The following analysis is used to derive the rate expression from the proposed mechanism.

Since the surface reaction step is the RDS, all other steps must be equilibrated. Therefore,

\[ K_{1} = \frac{[IP \cdot]}{[IP][\cdot]} \quad K_{2} = \frac{[O_{2}]}{[\cdot][DO]} \quad K_{3} = \frac{[W \cdot]}{[W][\cdot]} \quad (5) \]

The site balance for site type 1 is

\[ \cdot_{1} = \cdot_{1} + [IP \cdot] + [W \cdot] \quad (6) \]

while the site balance for site type 2 is

\[ \cdot_{2} = \cdot_{2} + [O_{2}] \quad (7) \]

After substituting equation (5) into equation (6), the site balance on site type 1 becomes

\[ \cdot_{1} = \cdot_{1} + K_{1}[IP][\cdot] + K_{3}[W][\cdot] \quad (8) \]

Therefore,

\[ \cdot_{1} = \frac{\cdot_{1}}{1 + K_{1}[IP] + K_{3}[W]} \quad (9) \]

After substituting equation (5) into equation (7), the site balance on site type 2 becomes
\[ [\mathbf{*}^1] = [\mathbf{*}] + K_{1}^{1/2} [\mathbf{*}][DO]^{1/2} \quad (10) \]

Therefore,
\[ [\mathbf{*}^1] = \frac{[\mathbf{*}]}{1 + K_{1}^{1/2} [DO]^{1/2}} \quad (11) \]

The rate of the reaction is the rate of the RDS, therefore,
\[ r = k[IP][\mathbf{*}][DO] \quad (12) \]

After substituting equations (5), (9) and (11) into equation (12),
\[ r = \frac{k(K_{[IP]}[\mathbf{*}^{1}][K_{1}^{1/2}][\mathbf{*}][DO]^{1/2})}{(1 + K_{[IP]} + K_{[W]})(1 + K_{1}^{1/2}[DO]^{1/2})} \quad (13) \]

The rate expression in equation (2) is obtained by grouping all of the constants.