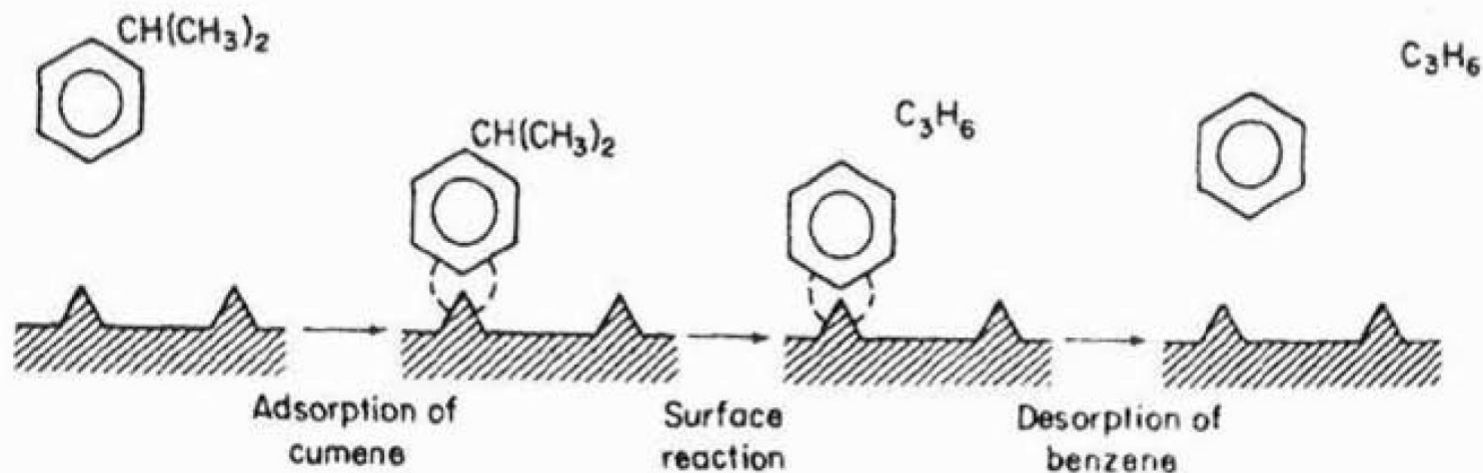


10.3 Synthesizing a Rate Law, Mechanism, and Rate-Limiting Step

We now wish to develop rate laws for catalytic reactions that are not diffusion-limited. In developing the procedure to obtain a mechanism, a rate-limiting step, and a rate law consistent with experimental observation, we shall discuss a particular catalytic reaction, the decomposition of cumene to form benzene and propylene. The overall reaction is



A conceptual model depicting the sequences of steps in this platinum-catalyzed reaction is shown in Figure 10-14. Figure 10-14 is only a schematic representation of the adsorption of cumene; a more realistic model is the formation of a complex of the π orbitals of benzene with the catalytic surface, as shown in Figure 10-15.



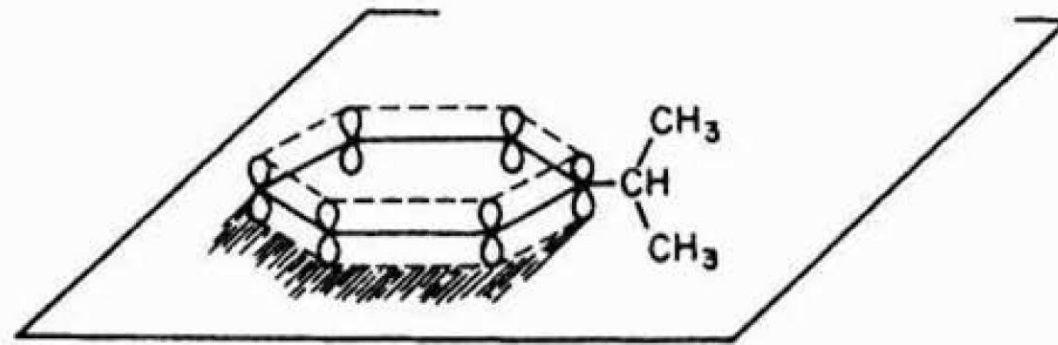


Figure 10-15 π -orbital complex on surface.

The nomenclature in Table 10-3 will be used to denote the various species in this reaction: C = cumene, B = benzene, and P = propylene. The reaction sequence for this decomposition is

TABLE 10-3. STEPS IN A LANGMUIR-HINSHELWOOD KINETIC MECHANISM

$C + S \xrightleftharpoons[k_{-A}]{k_A} C \cdot S$	Adsorption of cumene on the surface	(10)
$C \cdot S \xrightleftharpoons[k_{-S}]{k_S} B \cdot S + P$	Surface reaction to form adsorbed benzene and propylene in the gas phase	(10)
$B \cdot S \xrightleftharpoons[k_{-D}]{k_D} B + S$	Desorption of benzene from surface	(10)

These three steps represent the mechanism for cumene decomposition.

Equations (10-22) through (10-24) represent the mechanism proposed for reaction.

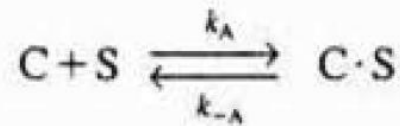
When writing rate laws for these steps, we treat each step as an elementary reaction; the only difference is that the species concentrations in the phase are replaced by their respective partial pressures:

Ideal Gas Law
 $P_C = C_C RT$

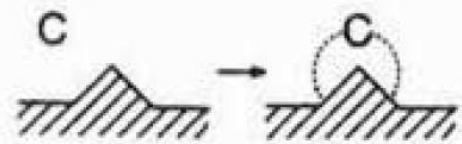


There is no theoretical reason for this replacement of the concentration, with the partial pressure, P_C ; it is just the convention initiated in the 1930s used ever since. Fortunately P_C can be calculated directly from C_C using ideal gas law.

The rate expression for the adsorption of cumene as given in Equation (10-22) is



$$r_{AD} = k_A P_C C_v - k_{-A} C_{C \cdot S}$$



Adsorption: $r_{AD} = k_A \left(P_C C_v - \frac{C_{C \cdot S}}{K_C} \right)$

(10)

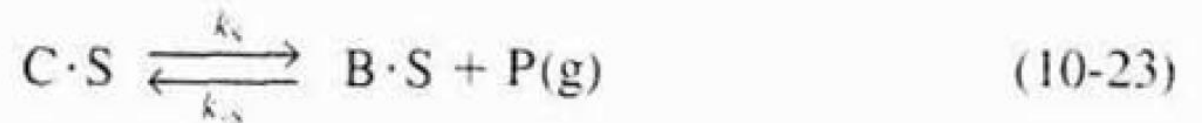
If r_{AD} has units of (mol/g cat·s) and $C_{C\cdot S}$ has units of (mol cumene adsorbed/g cat) typical units of k_A , k_{-A} , and K_C would be

$$[k_A] \equiv (\text{kPa}\cdot\text{s})^{-1} \text{ or } (\text{atm}\cdot\text{h})^{-1}$$

$$[k_{-A}] \equiv \text{h}^{-1} \text{ or } \text{s}^{-1}$$

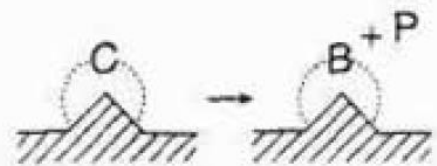
$$[K_C] \equiv \left[\frac{k_A}{k_{-A}} \right] \equiv \text{kPa}^{-1}$$

The rate law for the surface reaction step producing adsorbed benzene and propylene in the gas phase,



is

$$r_S = k_S C_{C\cdot S} - k_{-S} P_P C_{B\cdot S}$$



Surface reaction: $r_S = k_S \left(C_{C\cdot S} - \frac{P_P C_{B\cdot S}}{K_S} \right)$

(10-26)

with the *surface reaction equilibrium constant* being

$$K_S = \frac{k_S}{k_{-S}}$$

Typical units for k_S and K_S are s^{-1} and kPa, respectively.

Propylene is not adsorbed on the surface. Consequently, its concentration on the surface is zero.

$$C_{P \cdot S} = 0$$

The rate of benzene desorption [see Equation (10-24)] is

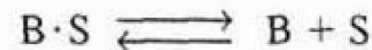
$$r_D = k_D C_{B \cdot S} - k_{-D} P_B C_v \quad (10-27)$$



Desorption: $r_D = k_D \left(C_{B \cdot S} - \frac{P_B C_v}{K_{DB}} \right)$

(10-28)

Typical units of k_D and K_{DB} are s^{-1} and kPa, respectively. By viewing the desorption of benzene,



from right to left, we see that desorption is just the reverse of the adsorption of benzene. Consequently, it is easily shown that the benzene adsorption equilibrium constant K_B is just the reciprocal of the benzene desorption constant K_{DB} :

$$K_B = \frac{1}{K_{DB}}$$

and Equation (10-28) can be written as

$$\text{Desorption: } r_D = k_D (C_{B \cdot S} - K_B P_B C_v) \quad (10-29)$$

Because there is no accumulation of reacting species on the surface the rates of each step in the sequence are all equal:

$$-r'_C = r_{AD} = r_S = r_D \quad (10-30)$$

For the mechanism postulated in the sequence given by Equations (10-22) through (10-24), we wish to determine which step is rate-limiting. We first assume one of the steps to be rate-limiting (rate-controlling) and then formulate the reaction rate law in terms of the partial pressures of the species present. From this expression we can determine the variation of the initial reaction rate with the initial total pressure. If the predicted rate varies with pressure in the same manner as the rate observed experimentally, the implication is that the assumed mechanism and rate-limiting step are correct.

10.3.1 Is the Adsorption of Cumene Rate-Limiting?

To answer this question we shall assume that the adsorption of cumene is indeed rate-limiting, derive the corresponding rate law, and then check to see if it is consistent with experimental observation. By assuming that this (or any other) step is rate-limiting, we are considering that the reaction rate constant of this step (in this case k_A) is small with respect to the specific rates of the other steps (in this case k_S and k_D).¹³ The rate of adsorption is

$$-r'_C = r_{AD} = k_A \left(P_C C_v - \frac{C_{C \cdot S}}{K_C} \right) \quad (10-25)$$

Because we can measure neither C_v or $C_{C \cdot S}$, we must replace these variables in the rate law with measurable quantities for the equation to be meaningful.

For steady-state operation we have

$$-r'_C = r_{AD} = r_S = r_D \quad (10-30)$$

Need to express C_v
and $C_{C \cdot S}$ in terms
of P_C , P_B , and P_P

For adsorption-limited reactions, k_A is small and k_S and k_D are large. Consequently, the ratios r_S/k_S and r_D/k_D are very small (approximately zero), whereas the ratio r_{AD}/k_A is relatively large. That is, the product for the adsorption step $[k_A P_C]$ (s^{-1}) is small with respect to the other rate constants: k_S (s^{-1}) for the surface reaction step and k_D (s^{-1}) for the desorption step.

The surface reaction rate law is

$$r_S = k_S \left(C_{C \cdot S} - \frac{C_{B \cdot S} P_P}{K_S} \right) \quad (10-31)$$

Again, for adsorption-limited reactions the surface specific reaction rate k_S is large by comparison, and we can set

$$\frac{r_S}{k_S} \approx 0 \quad (10-32)$$

and solve Equation (10-31) for $C_{C \cdot S}$:

$$C_{C \cdot S} = \frac{C_{B \cdot S} P_P}{K_S} \quad (10-33)$$

To be able to express $C_{C \cdot S}$ solely in terms of the partial pressures of the species present, we must evaluate $C_{B \cdot S}$. The rate of desorption of benzene is

$$r_D = k_D (C_{B \cdot S} - K_B P_B C_v) \quad (10-29)$$

However, for adsorption-limited reactions, k_D is large by comparison, and we can set

$$\frac{r_D}{k_D} \approx 0 \quad (10-34)$$

and then solve Equation (10-29) for $C_{B \cdot S}$:

$$C_{B \cdot S} = K_B P_B C_v \quad (10-35)$$

After combining Equations (10-33) and (10-35), we have

$$C_{C \cdot S} = K_B \frac{P_B P_P}{K_S} C_v \quad (10-36)$$

Replacing $C_{C \cdot S}$ in the rate equation by Equation (10-36) and then factoring C_v , we obtain

$$r_{AD} = k_A \left(P_C - \frac{K_B P_B P_P}{K_S K_C} \right) C_v = k_A \left(P_C - \frac{P_B P_P}{K_P} \right) C_v \quad (10-37)$$

Observe that by setting $r_{AD} = 0$, the term $(K_S K_C / K_B)$ is simply the overall partial pressure equilibrium constant, K_P , for the reaction

Using
 $\frac{r_S}{k_S} = 0 \approx \frac{r_D}{k_D}$
 to find $C_{B \cdot S}$ and
 $C_{C \cdot S}$ in terms of
 partial pressures



$$\boxed{\frac{K_S K_C}{K_B} = K_P} \quad (10-37)$$

The equilibrium constant can be determined from thermodynamic data and is related to the change in the Gibbs free energy, ΔG° , by the equation (Appendix C)

$$\boxed{RT \ln K = -\Delta G^\circ} \quad (10-38)$$

where R is the ideal gas constant and T is the absolute temperature.

The concentration of vacant sites, C_v , can now be eliminated from Equation (10-37) by utilizing the site balance to give the total concentration of sites, C_t , which is assumed constant:¹⁴

$$\boxed{\text{Total sites} = \text{Vacant sites} + \text{Occupied sites}}$$

Because cumene and benzene are adsorbed on the surface, the concentration occupied sites is $(C_{C \cdot S} + C_{B \cdot S})$, and the total concentration of sites is

Site balance

$$C_t = C_v + C_{C \cdot S} + C_{B \cdot S} \quad (10-$$

Substituting Equations (10-35) and (10-36) into Equation (10-40), we h

$$C_t = C_v + \frac{K_B}{K_S} P_B P_P C_v + K_B P_B C_v$$

Solving for C_v , we have

$$C_v = \frac{C_t}{1 + P_B P_P K_B / K_S + K_B P_B} \quad (10-$$

Combining Equations (10-41) and (10-37), we find that the rate law for catalytic decomposition of cumene, assuming that the adsorption of cumene is the rate-limiting step, is

Cumene reaction
rate law if
adsorption were
the limiting step

$$-r'_C = r_{AD} = \frac{C_t k_A (P_C - P_P P_B / K_P)}{1 + K_B P_P P_B / K_S + K_B P_B} \quad (10-$$

We now wish to sketch a plot of the initial rate as a function of the partial pressure of cumene, P_{C_0} . Initially, no products are present; consequently, $P_P = P_B = 0$. The initial rate is given by

$$-r'_{C_0} = C_t k_A P_{C_0} = k P_{C_0} \quad (10-43)$$

If the cumene decomposition is adsorption rate limited, then the initial rate will be linear with the initial partial pressure of cumene as shown in Figure 10-16.

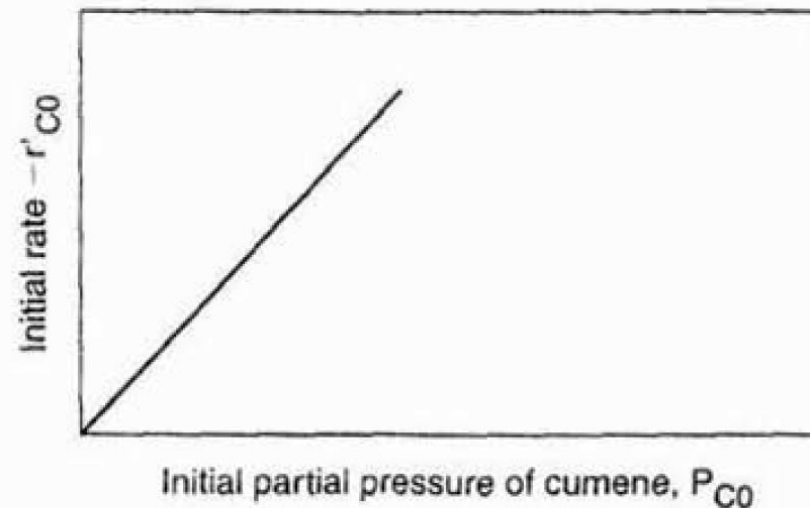


Figure 10-16 Uninhibited adsorption-limited reaction.

If adsorption were rate-limiting, the data should show $-r'_0$ increasing linearly with P_{C_0} .

Before checking to see if Figure 10-16 is consistent with experimental observation, we shall derive the corresponding rate laws and initial rate plots when the surface reaction is rate-limiting and then when the desorption of benzene is rate-limiting.

10.3.2 Is the Surface Reaction Rate-Limiting?

The rate of surface reaction is

Single-site
mechanism

$$r_s = k_s \left(C_{C \cdot s} - \frac{P_P C_{B \cdot s}}{K_S} \right) \quad (10-26)$$

Since we cannot readily measure the concentrations of the adsorbed species, we must utilize the adsorption and desorption steps to eliminate $C_{C \cdot s}$ and $C_{B \cdot s}$ from this equation.

From the adsorption rate expression in Equation (10-25) and the condition that k_A and k_D are very large by comparison with k_s when surface reaction is controlling (i.e., $r_{AD}/k_A \approx 0$), we obtain a relationship for the surface concentration for adsorbed cumene:

$$C_{C \cdot s} = K_C P_C C_v$$

In a similar manner, the surface concentration of adsorbed benzene can be evaluated from the desorption rate expression [Equation (10-29)] together with the approximation:

$$\text{when } \frac{r_D}{k_D} \approx 0 \quad \text{then } C_{B \cdot s} = K_B P_B C_v$$

Using
 $\frac{r_{AD}}{k_A} \approx 0 \approx \frac{r_D}{k_D}$
to find $C_{B \cdot s}$ and
 $C_{C \cdot s}$ in terms of
partial pressures

Substituting for $C_{B \cdot S}$ and $C_{C \cdot S}$ in Equation (10-26) gives us

$$r_S = k_S \left(P_C K_C - \frac{K_B P_B P_P}{K_S} \right) C_v = k_S K_C \left(P_C - \frac{P_B P_P}{K_P} \right) C_v$$

The only variable left to eliminate is C_v :

Site balance

$$C_t = C_v + C_{B \cdot S} + C_{C \cdot S}$$

Substituting for concentrations of the adsorbed species, $C_{B \cdot S}$, and $C_{C \cdot S}$ yields

$$C_v = \frac{C_t}{1 + K_B P_B + K_C P_C}$$

Cumene rate law
for surface-
reaction-limiting

$$-r'_C = r_S = \frac{\overbrace{k_S C_t K_C}^k (P_C - P_B P_P / K_P)}{1 + P_B K_B + K_C P_C} \quad (10-44)$$

The initial rate is

$$-r'_{C0} = \frac{\overbrace{k_S C_t K_C P_{C0}}^k}{1 + K_C P_{C0}} = \frac{k P_{C0}}{1 + K_C P_{C0}} \quad (10-45)$$

At low partial pressures of cumene

$$1 \gg K_C P_{C0}$$

and we observe that the initial rate will increase linearly with the initial partial pressure of cumene:

$$-r'_{C0} \approx kP_{C0}$$

At high partial pressures

$$K_C P_{C0} \gg 1$$

and Equation (10-45) becomes

$$-r'_{C0} \equiv \frac{kP_{C0}}{K_C P_{C0}} = \frac{k}{K_C}$$

and the rate is independent of the partial pressure of cumene. Figure 10-17 shows the initial rate of reaction, as a function of initial partial pressure of cumene for the case of surface reaction controlling.

If surface reaction were rate-limiting, the data would show this behavior.

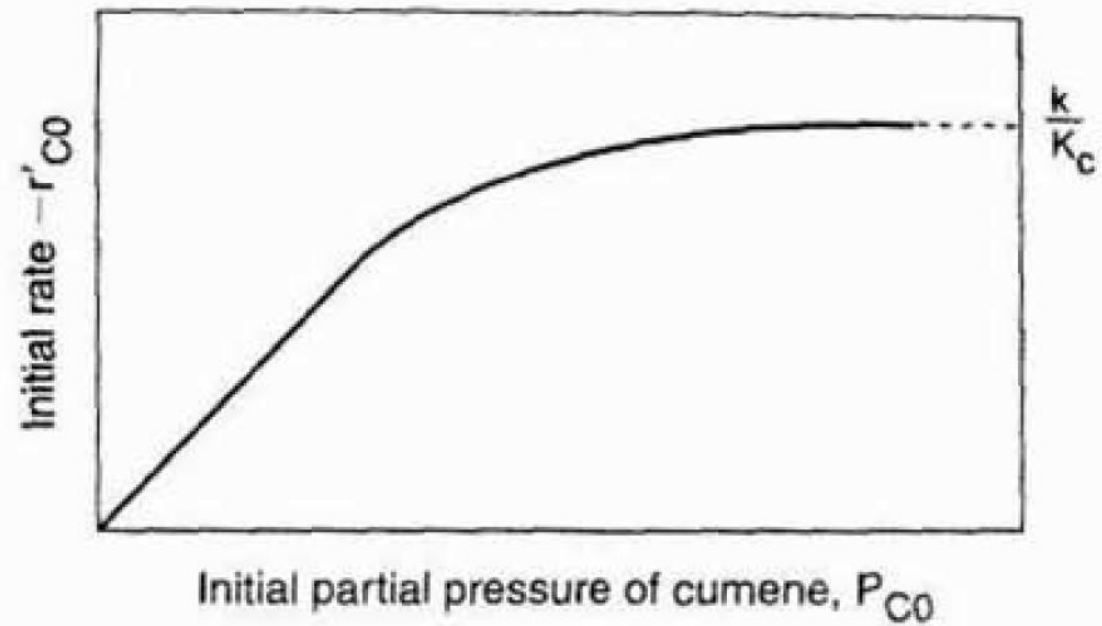


Figure 10-17 Surface-reaction-limited.

10.3.3 Is the Desorption of Benzene Rate-Limiting?

The rate expression for the desorption of benzene is

$$r_D = k_D (C_{B \cdot S} - K_B P_B C_v) \quad (10-29)$$

For desorption-limited reactions, both k_{AD} and k_S are very large compared with k_D , which is small.

From the rate expression for surface reaction, Equation (10-26), we set

$$\frac{r_S}{k_S} \approx 0$$

to obtain

$$C_{B \cdot S} = K_S \left(\frac{C_{C \cdot S}}{P_P} \right) \quad (10-46)$$

Similarly, for the adsorption step, Equation (10-25), we set

$$\frac{r_{AD}}{k_A} \approx 0$$

to obtain

$$C_{C \cdot S} = K_C P_C C_v$$

then substitute for $C_{C \cdot S}$ in Equation (10-46):

$$C_{B \cdot S} = \frac{K_C K_S P_C C_v}{P_P} \quad (10-47)$$

Combining Equations (10-28) and (10-47) gives us

$$r_D = k_D K_C K_S \left(\frac{P_C}{P_P} - \frac{P_B}{K_P} \right) C_v \quad (10-48)$$

where K_C is the cumene adsorption constant, K_S is the surface reaction equilibrium constant, and K_P is the gas-phase equilibrium constant for the reaction. To obtain an expression for C_v , we again perform a site balance:

$$\text{Site balance: } C_t = C_{C \cdot S} + C_{B \cdot S} + C_v$$

After substituting for the respective surface concentrations, we solve the site balance for C_v :

$$C_v = \frac{C_t}{1 + K_C K_S P_C / P_P + K_C P_C} \quad (10-49)$$

Replacing C_v in Equation (10-48) by Equation (10-49) and multiplying the numerator and denominator by P_p , we obtain the rate expression for desorption control:

Cumene decomposition rate law if desorption were limiting

$$-r'_C = r_D = \frac{k_D C_i K_S K_C (P_C - P_B P_P / K_P)}{P_P + P_C K_C K_S + K_C P_P P_C} \quad (10-49)$$

If desorption controls, the initial rate is independent of partial pressure of cumene.

To determine the dependence of the initial rate on partial pressure of cumene, we again set $P_p = P_B = 0$; and the rate law reduces to

$$-r'_{C0} = k_D C_i$$

with the corresponding plot of $-r'_{C0}$ shown in Figure 10-18. If desorption is controlling, we would see that the initial rate would be independent of the partial pressure of cumene.

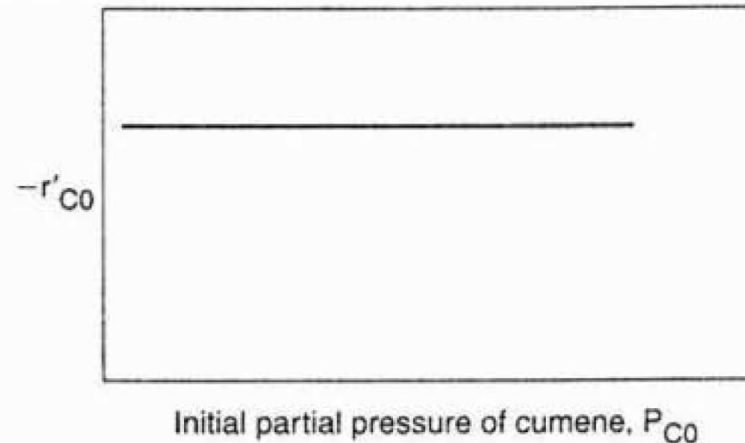
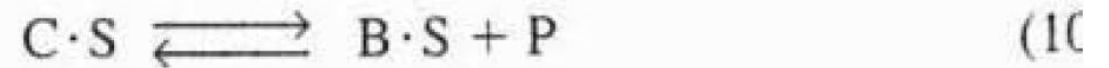


Figure 10-18 Desorption-limited reaction.

10.3.4 Summary of the Cumene Decomposition

Cumene decomposition is surface-reaction-limited

The experimental observations of $-r'_{C_0}$ as a function of P_{C_0} are shown in Figure 10-19. From the plot in Figure 10-19, we can clearly see that neither adsorption nor desorption is rate-limiting. For the reaction and mechanism given by



the rate law derived by assuming that the surface reaction is rate-limiting agrees with the data.

The rate law for the case of no inerts adsorbing on the surface is

$$\boxed{-r'_C = \frac{k(P_C - P_B P_P / K_P)}{1 + K_B P_B + K_C P_C}} \quad (10)$$

Surface limited reaction mechanism is consistent with experimental data.

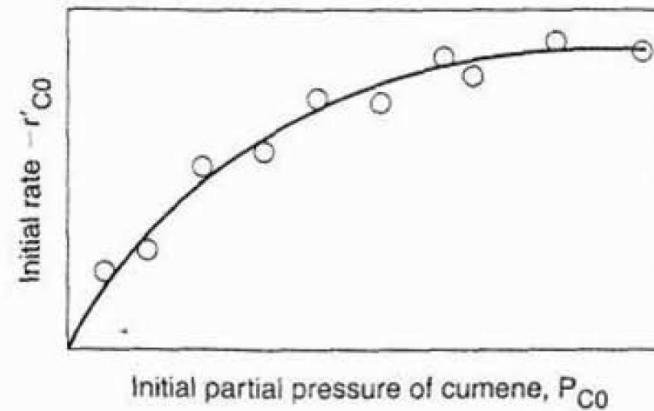


Figure 10-19 Actual initial rate as a function of partial pressure of cumene.

The forward cumene decomposition reaction is a single-site mechanism involving only adsorbed cumene while the reverse reaction of propylene in the gas phase reacting with adsorbed benzene is an Eley-Rideal mechanism.

If we were to have an adsorbing inert in the feed, the inert would not participate in the reaction but would occupy sites on the catalyst surface:



Our site balance is now

$$C_t = C_v + C_{C \cdot S} + C_{B \cdot S} + C_{I \cdot S} \tag{10-51}$$

Because the adsorption of the inert is at equilibrium, the concentration of sites occupied by the inert is

$$C_{I \cdot S} = K_I P_I C_v \tag{10-52}$$

Substituting for the inert sites in the site balance, the rate law for surface reaction control when an adsorbing inert is present is

$$-r'_C = \frac{k(P_C - P_B P_P / K_p)}{1 + K_C P_C + K_B P_B + K_I P_I} \tag{10-53}$$

Adsorbing inerts