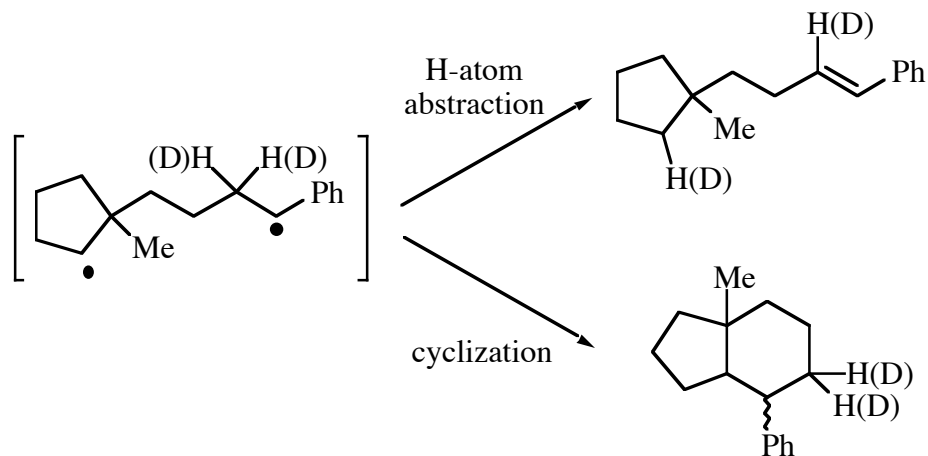## XIII. Parallel 1st-Order Reactions:

A. Observed:

A famous physical organic chemist made the following observation...
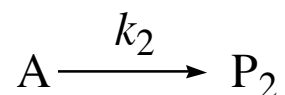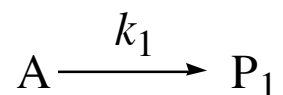

When the rate of formation of the products were monitored independently, it was found that...

$$k_H/k_D = 2.1 \text{ in both cases!!}$$

XIII. Parallel 1st-Order Reactions:

B. <u>Given</u>:

$$A \xrightarrow{k_1} P_1$$

$$A \xrightarrow{k_2} P_2$$

• This case is central to the control of selectivity, but it can be deceptive.

C. <u>Rate Equation</u>:

1. <u>Species A</u>:

$$-d[A]/dt = k_1[A] + k_2[A] = (k_1 + k_2)[A]$$

$$[A] = [A_0] \, e^{-(k_1 + k_2)t}$$

XIII. Parallel 1st-Order Reactions:

2. <u>Species P_1 and P_2</u>:

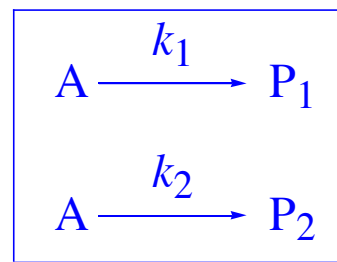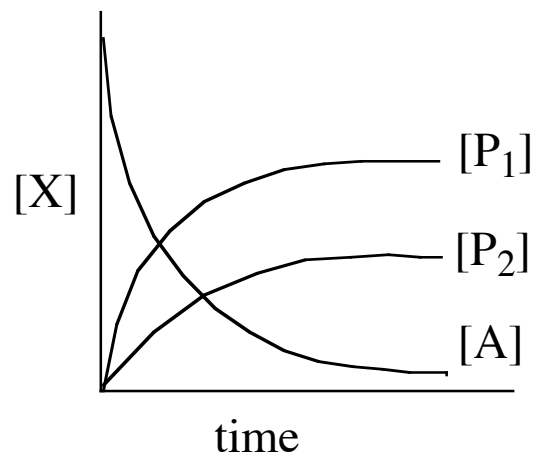$$d[P_1]/dt = k_1[A] = k_1[A_0]e^{-(k_1+k_2)t}$$

Integrate... (CRC #12)

$$[P_1] = \frac{k_1[A_o]}{k_1 + k_2}\left(1 - e^{-(k_1+k_2)t}\right) \qquad\qquad (1)$$

Similarly...

$$[P_2] = \frac{k_2[A_o]}{k_1 + k_2}\left(1 - e^{-(k_1+k_2)t}\right) \qquad\qquad (2)$$

XIII. Parallel 1st-Order Reactions:

D. Graphics:

$$A \xrightarrow{k_1} P_1$$

$$A \xrightarrow{k_2} P_2$$

[X]

[P₁]

[P₂]

[A]

time

1. Starting Material A:

Let...

$$f(x) = ae^{bx}$$

such that...

$$f(x) = [A] \qquad x = t \qquad a = [A_0] \qquad b = -(k_1 + k_2)$$

2. <u>Products P_1 and P_2</u>:

Let...

$$f(x) = a(1 - e^{bx})$$

such that...

$$f(x) = [P_1] \text{ or } [P_2]$$

$$a = k_1[A_0]/(k_1 + k_2)$$

$$(\text{or } k_2[A_0]/(k_1 + k_2))$$

$$b = -(k_1 + k_2)$$

• The values of k_1 and k_2 can be extracted from the values of adjustable parameters <u>a</u> *and* <u>b</u>. However...

XIII. Parallel 1st-Order Reactions:

E. Caveat:

Recall, for a 1st-order reaction...

$$[P] = [A_0] - [A] = [A_0] - [A_0] \, e^{-kt} = [P_\infty](1-e^{-kt})$$

$$f(x) = a(1 - e^{bx})$$

• Therefore, formation of the products in parallel 1st-order reactions follow the same mathematical form as a single 1st-order reaction. *However*, in a parallel reaction, $b = -(k_1 + k_2)$. The difference appears in the pre-exponential term, $\underline{a}$.

• If you monitor the formation of either P_1 or P_2 and analyze the data as a simple first-order reaction, you will get the same rate constant!

• If either k_1 or k_2 has a kinetic isotope effect, the rate of formation of both products will show a kinetic isotope effect. Moreover, formation of $\underline{P}_1$ and $\underline{P}_2$ will exhibit the *same* kinetic isotope effect if treated as a simple (rather than parallel) 1st-order reaction! Mechanistic branch points can be deceptive, and an undetected parallel pathway could be very misleading.

XIII. Parallel 1st-Order Reactions:

$$A \xrightarrow{k_1} P_1$$

$$A \xrightarrow{k_2} P_2$$

F. <u>Selectivity</u>:
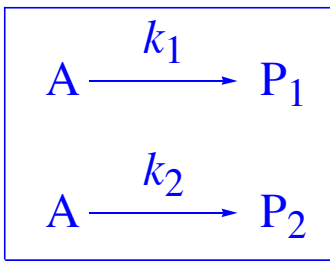
By dividing through the integral
forms of the rate equations (eq (1) and eq (2))...

$$[P_1]/[P_2] = k_1/k_2$$

Alternatively, the integration can be skipped...

$$[P_1]/[P_2] = \frac{d[P_1]/dt}{d[P_2]/dt} = \frac{k_1[A]}{k_2[A]} = \frac{k_1}{k_2}$$