

Question:

Let us consider the aqueous phase, heterogeneous catalytic oxidation of benzene (A) into its hydroxylated product, phenol (B). Under practical conditions, some amount of B would undergo further uncontrolled oxidation into other by-products such as (1,4)-hydroquinone (C) and (1,4)-benzoquinone (D) which exist in equilibrium with each other (Scheme 1). Each of these steps are individually known to be first-order elementary reactions. Neglecting adsorption and desorption effect of each product on the catalyst surface:

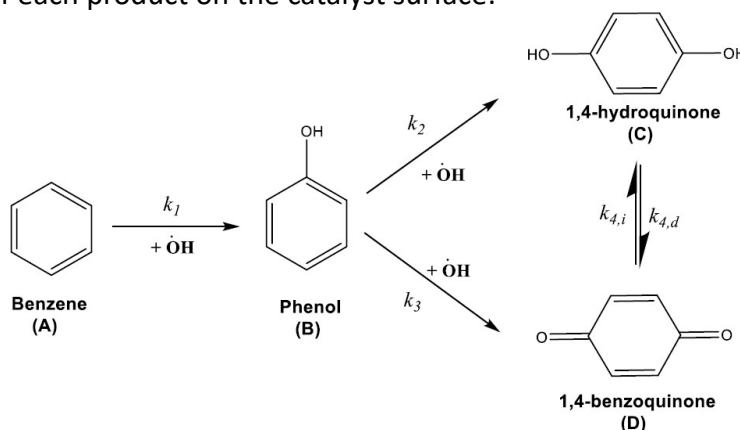


Figure 1: Pathways for oxidation of phenol into hydroxylated products.

Where k_1 , k_2 , k_3 , $k_{4,i}$ and $k_{4,d}$ are rate constants for the oxidation of species A, B, C and D respectively.

1. Set up a species balance for the concentration of the reactant, product, and the by-products.
2. Determine expressions for the temporal variation in concentration of A, B, C and D, assuming initially there are no components in the reactor other than A.
3. In a laboratory experiment, 11.7 mM of benzene and 1 g Pt/MgO catalyst were dissolved in 75 mL acetonitrile and illuminated under sunlight. The concentrations of A, B, C and D were found as given in Table 1. Using these values, determine the rate constants k_1 , k_2 , k_3 , $k_{4,i}$ and $k_{4,d}$.

Time (min)	Reactant con. (mM)	Product con. (μM)		
	Benzene (A)	Benzoquinone (D)	Hydroquinone (C)	Phenol (B)
0	11.700	0.000	0.000	0.000
30	11.574	11.853	22.891	78.994
60	11.456	35.669	46.705	174.546
90	11.341	96.270	53.960	276.537
120	11.224	145.833	68.577	315.064
180	10.993	221.053	84.932	416.034
240	10.767	376.401	96.685	471.018

Table 1: Concentration of benzene and hydroxylated products over time.

Solution:

1.

Species balance:

For A:

$$\frac{dC_A}{dt} = -k_1 C_A$$

For B:

$$\frac{dC_B}{dt} = -(k_2 + k_3)C_B + k_1 C_A$$

For C:

$$\frac{dC_C}{dt} = -k_{4,d}C_C + k_2 C_B + k_{4,i}C_D$$

For D:

$$\frac{dC_D}{dt} = -k_{4,i}C_D + k_3 C_B + k_{4,d}C_C$$

2.

Assumption: $C_A(0) = C_{A0}$, $C_B(0) = C_C(0) = C_D(0) = 0$

Take Laplace transformation of the above species balance equations:

$$\begin{aligned} s\bar{C}_A - C_A(0) &= -k_1 \bar{C}_A \\ s\bar{C}_B - C_B(0) &= -(k_2 + k_3)\bar{C}_B + k_1 \bar{C}_A \\ s\bar{C}_C - C_C(0) &= -k_{4,d}\bar{C}_C + k_2 \bar{C}_B + k_{4,i}\bar{C}_D \\ s\bar{C}_D - C_D(0) &= -k_{4,i}\bar{C}_D + k_3 \bar{C}_B + k_{4,d}\bar{C}_C \end{aligned}$$

Get:

$$\begin{aligned} \bar{C}_A &= \frac{C_{A0}}{s + k_1} \\ \bar{C}_B &= \frac{k_1 C_{A0}}{(s + k_1)(s + k_2 + k_3)} = \frac{\frac{k_1 C_{A0}}{s + k_1}}{s + k_2 + k_3} + \frac{\frac{k_1 C_{A0}}{s + k_2 + k_3}}{s + k_1} \end{aligned}$$

From:

$$\begin{aligned} s\bar{C}_C &= -k_{4,d}\bar{C}_C + k_2 \bar{C}_B + k_{4,i}\bar{C}_D \\ s\bar{C}_D &= -k_{4,i}\bar{C}_D + k_3 \bar{C}_B + k_{4,d}\bar{C}_C \end{aligned}$$

Get:

$$\begin{aligned} \bar{C}_C &= \frac{k_2 k_1 C_{A0} s + (k_2 + k_3) k_{4,i} k_1 C_{A0}}{s(s + k_{4,d} + k_{4,i})(s + k_1)(s + k_2 + k_3)} \\ \bar{C}_D &= \frac{k_3 k_1 C_{A0}}{(s + k_1)(s + k_2 + k_3)(s + k_{4,i})} + \frac{k_{4,d} k_2 k_1 C_{A0} s + k_{4,d}(k_2 + k_3) k_{4,i} k_1 C_{A0}}{s(s + k_{4,d} + k_{4,i})(s + k_1)(s + k_2 + k_3)(s + k_{4,i})} \end{aligned}$$

Take the inverse Laplace transform, get:

$$\begin{aligned} C_A(t) &= C_{A0} e^{-k_1 t} \\ C_B(t) &= \frac{k_1 C_{A0}}{-k_1 + (k_2 + k_3)} (e^{-k_1 t} - e^{-(k_2 + k_3)t}) \end{aligned}$$

For $C_C(t)$, set $k_2 k_1 C_{A0} = A$, $(k_2 + k_3) k_{4,i} k_1 C_{A0} = B$, and the roots of $s(s + k_{4,d} + k_{4,i})(s + k_1)(s + k_2 + k_3)$ to be $r_1 = 0$, $r_2 = -(k_{4,d} + k_{4,i})$, $r_3 = -k_1$, $r_4 = -(k_2 + k_3)$:

$$C_C(t) = \frac{Ar_1 + B}{(r_1 - r_2)(r_1 - r_3)(r_1 - r_4)} e^{r_1 t} + \frac{Ar_2 + B}{(r_2 - r_1)(r_2 - r_3)(r_2 - r_4)} e^{r_2 t} \\ + \frac{Ar_3 + B}{(r_3 - r_1)(r_3 - r_2)(r_3 - r_4)} e^{r_3 t} + \frac{Ar_4 + B}{(r_4 - r_1)(r_4 - r_2)(r_4 - r_3)} e^{r_4 t}$$

For $C_D(t)$, set $k_3 k_1 C_{A0} = C$, $k_{4,d} k_2 k_1 C_{A0} = D$, $k_{4,d} (k_2 + k_3) k_{4,i} k_1 C_{A0} = E$, and the roots of $s(s + k_{4,d} + k_{4,i})(s + k_1)(s + k_2 + k_3)(s + k_{4,i})$ to be $r_1 = 0, r_2 = -(k_{4,d} + k_{4,i}), r_3 = -k_1, r_4 = -(k_2 + k_3), r_5 = -k_{4,i}$:

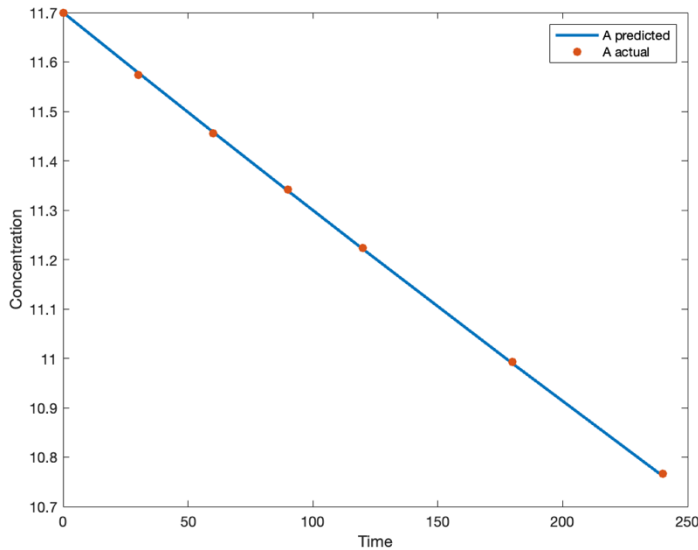
$$C_D(t) = \frac{C((r_4 - r_5)e^{r_3 t} + (r_5 - r_3)e^{r_4 t} + (r_3 - r_4)e^{r_5 t})}{(r_3 - r_4)(r_4 - r_5)(r_5 - r_3)} \\ + \frac{Dr_1 + E}{(r_1 - r_2)(r_1 - r_3)(r_1 - r_4)(r_1 - r_5)} e^{r_1 t} \\ + \frac{Dr_2 + E}{(r_2 - r_1)(r_2 - r_3)(r_2 - r_4)(r_2 - r_5)} e^{r_2 t} \\ + \frac{Dr_3 + E}{(r_3 - r_1)(r_3 - r_2)(r_3 - r_4)(r_3 - r_5)} e^{r_3 t} \\ + \frac{Dr_4 + E}{(r_4 - r_1)(r_4 - r_2)(r_4 - r_3)(r_4 - r_5)} e^{r_4 t} \\ + \frac{Dr_5 + E}{(r_5 - r_1)(r_5 - r_2)(r_5 - r_3)(r_5 - r_4)} e^{r_5 t}$$

3.

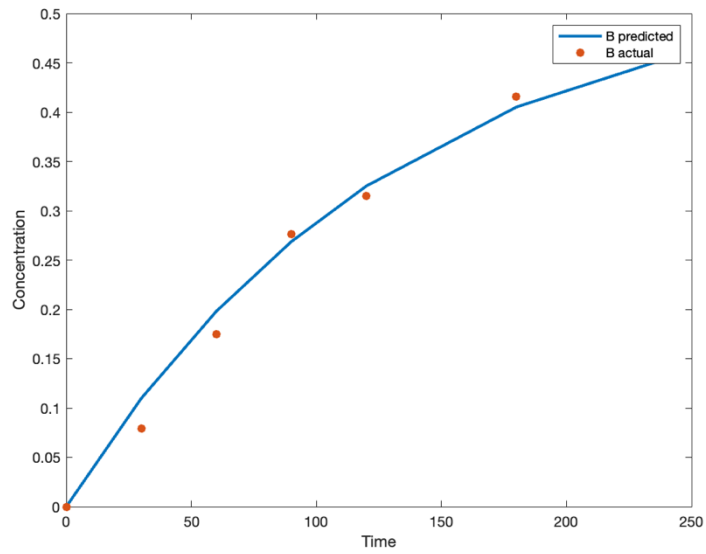
According to the MATLAB results, the values of reaction constants are:

$$k_1 = 3.4821 \times 10^{-4}, k_2 = 0.0069, k_3 = 6.8271 \times 10^{-9}, k_{4,i} = 0.0115, k_{4,d} = 0.066$$

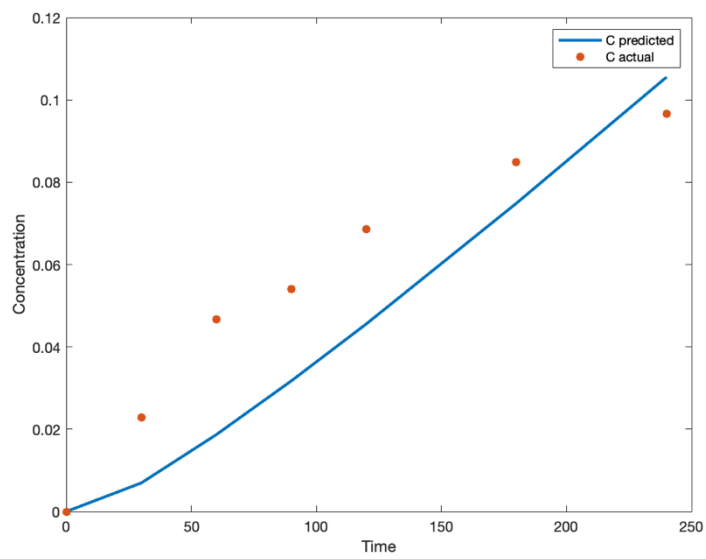
The plot for substance A:



The plot for substance B:



The plot for substance C:



The plot for substance D:

